Non-Kekulé Polynuclear Aromatics

Submitted in accordance with the
requirements for the degree of

Doctor of Philosophy

by

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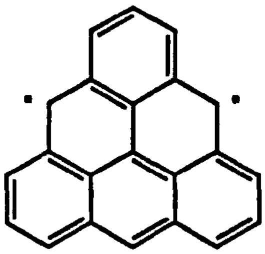
The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to work of others .

Abstract

This thesis is concerned with a previously uninvestigated group of π-biradicals , the non-Kekulé polynuclear aromatics .



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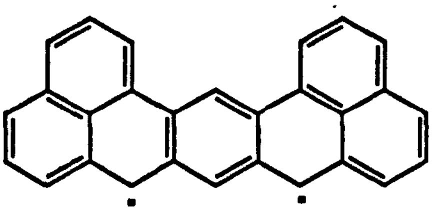

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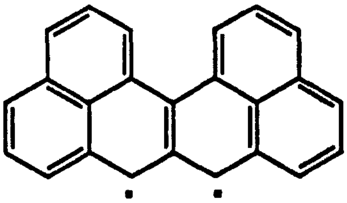

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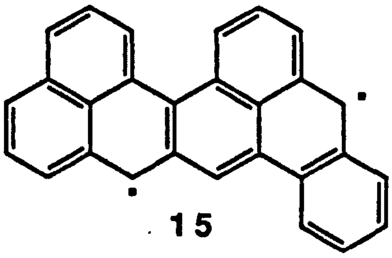

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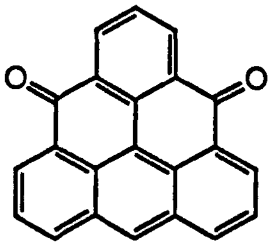
After a brief discussion on the nature of π-biradicals and their classification in general , Chapter 1 summarises previous attempts to synthesise the non-Kekulé polynuclear aromatics **3** , **9** , **10** and **15** .

Chapter 2 outlines the general strategy we pursued for generating the non-Kekulé polynuclear aromatics **3** , **9** , **10** and **15** from their diketone precursors , the quinones **16** - **19** , based on known phenalenone chemistry .



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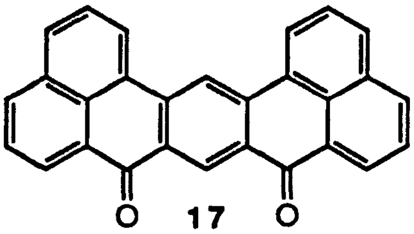

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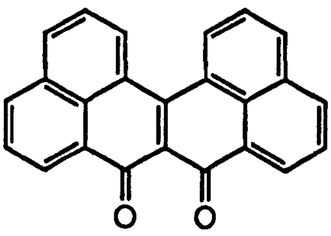

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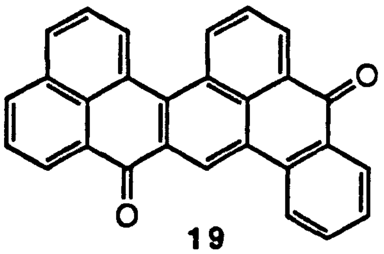

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The synthesis of the biradical precursors is discussed . Although the synthetic methods were based on " known " chemistry , the use of modern analytical techniques showed that reactions previously thought to give single products in fact gave mixtures of products and / or isomers . A great deal of development of the synthetic methods was required before the synthesis of the non-Kekulé polynuclear aromatic precursors , the quinones **16 - 19** , could be undertaken . Chapter 3 describes the various attempts to observe non-Kekulé polynuclear aromatics by ESR and UV / Vis. spectroscopy . What is believed to be the first spectroscopic observation of a non-Kekulé polynuclear aromatic , derived from12-potassoxy-4,8-dioxo-4H,8H-dibenzo[1,2,3-cd,-1,2,3-mn]pyrene , is described .

Chapter 4 describes the projected use of non-Kekulé polynuclear aromatics in making molecular magnets and the necessary work in determining the redox potentials of the biradical precursors by cyclic voltammetry . It concludes that , at least for the non-Kekulé polynuclear aromatic precursors we have made , the reduction potentials are too highly negative to make them viable components of molecular magnets , but points to possible solutions to the problem .

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List of Schemes

In the following table " Schemes " refers to all numbered diagrams in which synthetic reaction pathways are outlined .

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Chapter One

Chapter Two

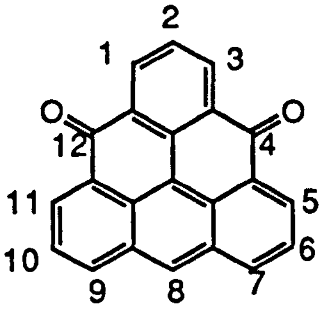
List of Abbreviations

A	Acceptor
Å	Angstrom
AcOH	Acetic acid (glacial)
Ac_2O	Acetic anhydride
$AlCl_3$	Aluminium trichloride
BuLi	Butyl lithium
Bz	Benzene
c.	Concentrated
C	Celsius
$CDCl_3$	Deutero chloroform
CH_2Cl_2	Dichloromethane
$C\ Cl_4$	Carbon tetrachloride
cm	Centimetre
Cu	Copper
D	Donor or zero-field splitting parameter
DDQ	Dichlorodicyanoquinone
DMeFe	Decamethylferrocenium
DMF	N,N-dimethylformamide
DMSO	Dimethylsulphoxide
D_2O	Deuterium oxide
D_2SO_4	Sulphuric acid -d2
E	Extinction coefficient
$E_{1/2}$	Half-wave redox potential
ESR	Electron spin resonance
EtOH	Ethanol
Et_3N	Triethylamine
Et_2O	Diethyl ether
G	Gauss
g	Gram
H	Magnetic field strength
HCl	Hydrochloric acid

HF	Hydrofluoric acid
HI	Hydroiodic acid
HgO	Mercuric oxide
HNO_3	Nitric acid
H_2SO_4	Sulphuric acid
Hz	Hertz
i	current (amperes)
IPA	Iso-propanol
IR	Infra red
J	Proton nmr splitting constant
K	Kelvin
K_2CO_3	Potassium carbonate
$KMnO_4$	Potassium permanganate
KOH	Potassium hydroxide
$LiAlH_4$	Lithium aluminium hydride
MeOH	Methanol
MHz	Megahertz
M.O.	Molecular orbital
mV	Millivolts
Mg	Magnesium
Na	Sodium
Na_2CO_3	Sodium carbonate
NaOH	Sodium hydroxide
NaCl	Sodium chloride
NaOD	Sodium deuteroxide
NaI	Sodium iodide
NBMO	Non bonding molecular orbital
NBSA	Nitrobenzene sulphonic acid
NH_3	Ammonia
nm	Nanometres
P	Phosphorous
P_2O_5	Phosphorous pentoxide
PCl_5	Phosphorous pentachloride

py	Pyridine
PhLi	Phenyl lithium
PhMgBr	Phenyl magnesium bromide
$SOCl_2$	Thionyl chloride
SOMO	Singly occupied molecular orbital
TCNE	Tetracyanoethylene
THF	Tetrahyrofuran
TME	Tetramethyleneethane
TMEDA	Tetramethylethylenediamine
TMM	Tetramethylenemethane
TsOH	Toluenesulphonic acid
UV	Ultra violet
V	Volts
Vis.	Visible
Zn	Zinc
$ZnCl_2$	Zinc chloride

Non-Kekulé Aromatic Diketone Percursors - Numbering Scheme



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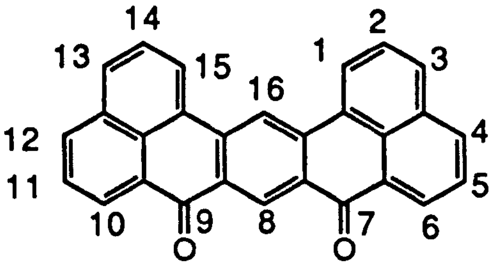

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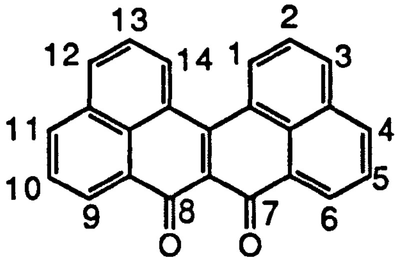

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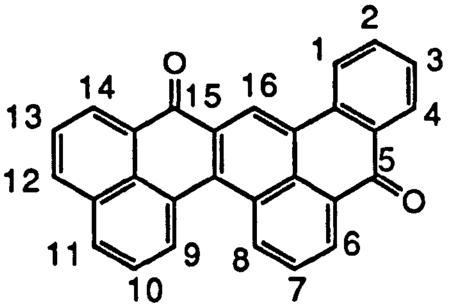

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I would like to thank my supervisor , Dr. Richard J. Bushby , for his guidance , enthusiasm and , above all , patience throughout this project . I must also thank the many members of the Organic Department here at the University of Leeds who offered their help and encouragement along the way .

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Special thanks must go to Ian Kersey for his sterling efforts in proof reading this thesis - for the expert in this field look no furthur (*sic* .)

I've got to thank my Mother , Father and big Sister - Margaret , Arthur and Yvonne Allinson - for just being there when required and not asking too many awkward questions .

Over the last three years many others have contributed to my emotional and spiritual well being and did a great job picking me up , dusting me down and pushing me off when things were bad . The following list is bound not to be comprehensive and for those who feel slighted for lack of a mention , I can only humbly apologise . Therefore thanks , hugs and kisses go to the following :-

Simon Guile , Andrew Knaggs and Christopher Lock for the interesting discussions in both laboratory and " The Oak " - not forgetting Joan Guile who stopped us (them ?) talking shop and taking ourselves too seriously ; I raise my glass (of Tetley's or Guinness ?) to 'Fats' , 'Funk' and 'Shorts' - Paul Bradley , Philip

Hansbro and David Urwin who , along with Nicola Averey , Shahida Ali , Ruth Frankish , Brian Murgatroyd , Tony Ross , John Armstrong , Darren Crichton and the many others from L.U.U.M.C.C. , the lab. and elsewhere , enlivened my evenings no end ; to Dr. Christopher Snowden and to Avril Crossley , the 'Grays' and the 'Whitneys' for their kindnesses one hot Canadian summer and one very , very cold winter !

And , finally , one very special thank you goes to Emma-Kate Crossley . Though in the end she was ' ma belle dame sans merci ' , it is Emma that I must thank for renewing my zest and appetite for life , expanding my horizons (if not my waistline) and nurturing both me and my dreams . For the good times , and the bad , the past and the future , it is to Emma that this thesis is dedicated .

Held , motionless , on my journey
by the magic eyes and light
caressing touch of a dancer .
Orbiting , tantalisingly , out of reach
she weaves her subtle patterns .
And tho' I long'd to break the
gossamer threads of her restraint
to taste the unleashed passions ,
I bound my foolish mind - and
stayed my ardent hand . With
trusting heart and soul I waited :
perchance for perihelion and the
invitation to join the dance .

Chapter One

Synthetic Approaches to Non-Kekulé Polynuclear Aromatics

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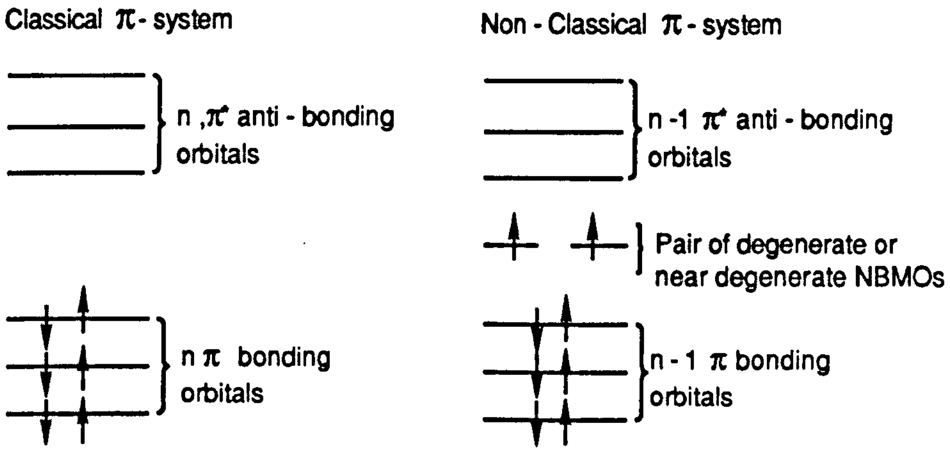
1.1 Introduction

1.1.1 Definition of a Biradical

Put simply , a biradical is a molecule which contains two unpaired electrons [1] . In M.O. terms , a biradical has two partially occupied molecular orbitals when in its lowest energy or ground state . These orbitals are of equivalent or near-equivalent energy ie. they are degenerate or near-degenerate . For a carbon biradical these orbitals lie at , or near , the non-bonding energy level and so are known as Non-Bonding Molecular Orbitals (NBMOs) or , given that each orbital contains only one electron , as Singly Occupied Molecular Orbitals (SOMOs) . Biradicals exist as ' triplets ' when the spins of the unpaired electrons are parallel , or as ' singlets ' when the spins are anti-parallel .

One important group of biradicals are the π-biradicals (also known as the Non-Classical non-Kekulé π -Systems) , of which the principle subject of this thesis , the Non-Kekulé Aromatic Compounds , are a part . The electrons of Classical π - systems , such as 1,3-butadiene , are paired up in a number of π - bonding orbitals , n , mirrored by n , π* antibonding orbitals (Figure 1.1) . However , the two unpaired electrons of the non-classical π - systems are found in a pair of degenerate or near-degenerate π - orbitals - hence the name π-biradicals .

Figure 1.1

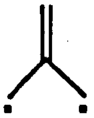


The π-biradicals are a diverse group of molecules and there are not only several ways of classifying them but also a number of rules for predicting their ground state . These classifications and rules are detailed below :

a . The 1 , n classification .

In this , the simplest classification , the biradicals are classified by counting the number of atoms between each unpaired electron .

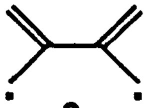
Trimethylene
methane TMM



1

a 1,3 biradical

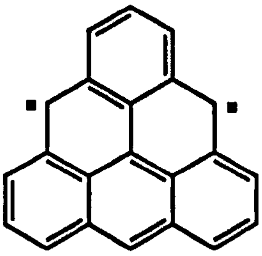
Tetramethylene
ethane TME



2

a 1,4 biradical

However this can be a cumbersome method of classification . For example , triangulene **3** can be classified as either a 1,3 or a 1,5 or a 1,7 biradical .



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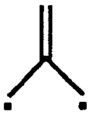
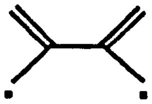
b . Structural classification

The main structural types of π - biradicals are :

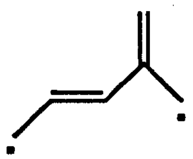
(i) Non - Classical Polyenes . These are aliphatic unsaturated systems of general formula C_nH_{n+2} for which no classical Kekulé structure can be drawn .



1
TMM



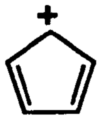
2
TME



4
Vinyl - TMM

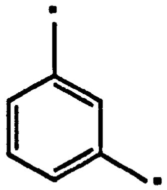
(ii) The Anti-Aromatics . Planar cyclic systems containing 4n π electrons .

cyclobutadiene
5



cyclopentadienyl cation
6

(iii) The Quinodimethanes , Naphthadimethanes and related structures .



1,3 - quinodimethane
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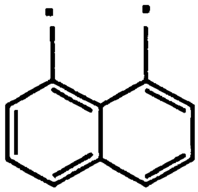
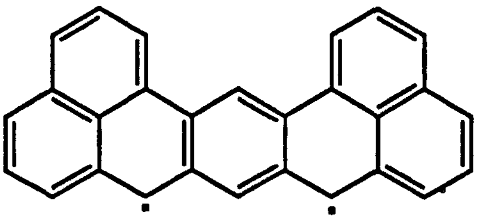
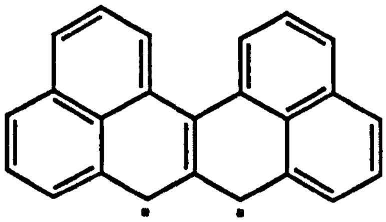


1,8 - naphthoquinodimethane
8

(iv) The Non-Kekulé Aromatics [2] . Cyclic , planar polynuclear aromatic systems for which no classical Kekule structure can be drawn .



Dibenzpentacene
9



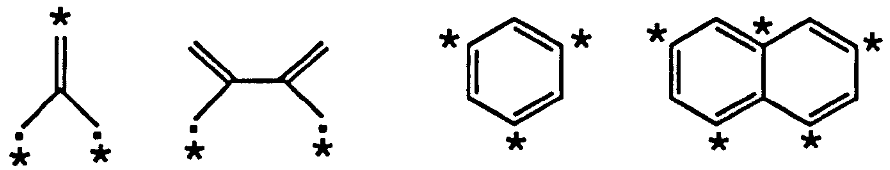
Dibenznaphthacene
10

c. Classification of the spin state of biradicals based on the Hückel Molecular Orbital calculations of Longuet-Higgins.

Longuet-Higgins [3] made predictions , based on the Linear Combination of Atomic Orbitals (LCAO) molecular orbital theory , about the electronic structures of a range of hydrocarbons . He restricted his attention to planar , unsaturated hydrocarbons where there was 100% sp^2 hybridisation of the carbon atoms . The hydrocarbons were classified as either alternant or non-alternant by drawing the chemical structure with alternating " starred " and " unstarred " atoms . If a structure contains like symbols on adjacent carbons the molecule was deemed non-alternant , and *vice versa* . It can be seen (Figure 1.2) that molecules such as TMM **1**, TME **2** , benzene **11** and naphthalene **12** are alternant , whereas fulvene **13** and azulene **14** are non-alternant .

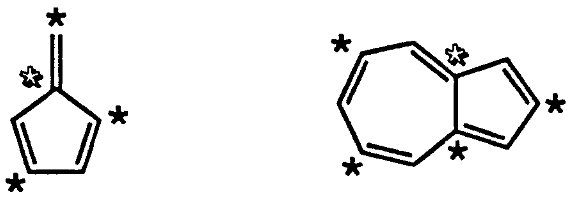
Figure 1.2

Alternant



1 **2** **11** **12**

Non - Alternant



13 **14**

In the general case , an alternant hydrocarbon will have a Kekule structure if , and only if ,

$$N = 2T$$

where N is the number of carbon atoms in the molecule and T is the maximum number of double bonds .

ie.	Benzene **11**	N = 6	T = 3	N = 2T	Kekulé structure
	TMM **1**	N = 4	T = 1	N = 2T+2	Non-Kekulé structure
	Triangulene **3**	N = 22	T = 10	"	" "
	Dibenzpentacene **10**	N = 28	T = 13	"	" "
	Dibenznaphthacene **9**	N = 24	T = 11	"	" "
	Tribenztetracene **15**	N = 28	T = 13	"	" "

When Hund's rule is applied to molecular systems molecular orbital theory suggests that there will be just one electron in each molecular orbital of zero energy and if there are two such electrons their spins will be parallel and hence the biradical would exist in the triplet state . The minimum number of unpaired electrons , K_{min} in the ground state of an alternant hydrocarbon (and also the number of NBMOs with zero energy) is given by the formula

$$K_{min} = N - 2T$$

From this it is predicted that TMM is a triplet [4] and also that m-quinodimethane is a triplet [5] .

This thesis is concerned primarily with the four non-Kekule polynuclear aromatics **3** , **9** , **10** , **15** shown drawn in the " starred " / " unstarred " system in Figure 1.3 . It can be seen that all four are alternant and all have $K_{min} = 2$ and it is predicted , using this classification , that they should exist with the triplet as the ground state .

d . Ovchinikov classification .

Ovchinikov [6] used the " starred " / " unstarred " system of Longuet - Higgins to devise a rule for predicting the ground state spin state of alternant hydrocarbons . This rule is governed by the general formula

$$S = 0.5 [n^* - n]$$

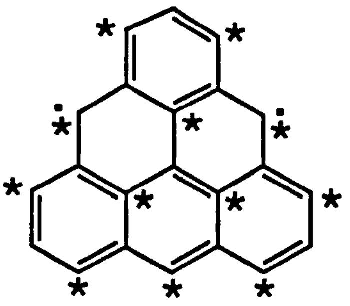
where n^* is the number of " starred " atoms and n the number of " unstarred " atoms . Given that the multiplicity of the spin state of a biradical is given by

$$M = 2S + 1$$

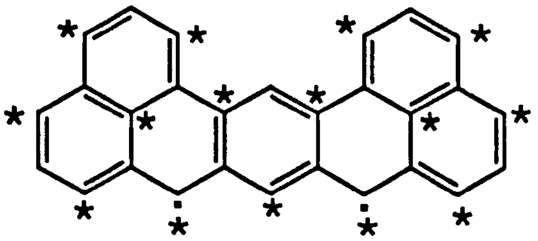
then Ovchinikov's theory predicts that :

TME **2**	$S = 0.5 (3 - 3) = 0$	$M = 1$	a singlet
TMM **1**	$S = 0.5 (3 - 1) = 1$	$M = 3$	a triplet
Triangulene **3**	$S = 0.5 (12 - 10) = 1$	$M = 3$	"
Dibenzpentacene **9**	$S = 0.5 (15 - 13) = 1$	$M = 3$	"
Dibenznaphthacene **10**	$S = 0.5 (13 - 11) = 1$	$M = 3$	"
Tribenznaphthacene **15**	$S = 0.5 (15 - 13) = 1$	$M = 3$	"

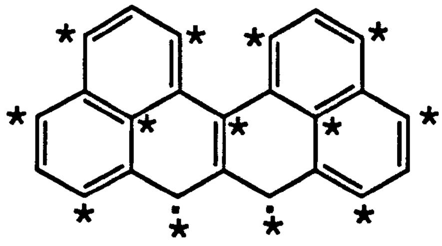
Figure 1.3



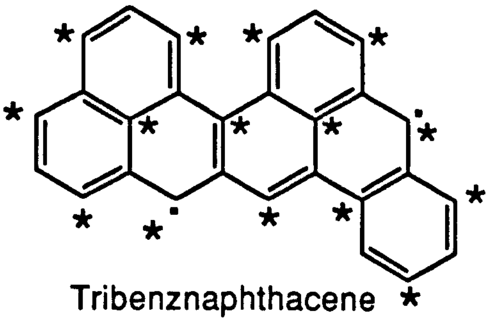
Triangulene
3
$N = 22$
$T = 10$
$K_{min} = 2$



Dibenzpentacene
9
$N = 28$
$T = 13$
$K_{min} = 2$



Dibenznaphthacene
10
$N = 24$
$T = 11$
$K_{min} = 2$



Tribenznaphthacene
15
$N = 28$
$T = 13$
$K_{min} = 2$

e. Borden - Davidson classification

Borden and Davidson [7] classified π - biradicals into two types according to whether or not the NBMOs have atoms in common . If the NBMOs have no atoms in common ie. each molecular orbital is confined to a particular set of atoms , then the system is termed disjoint . In such disjoint systems there is no possibility of the simultaneous occupation of the same atom by both unpaired electrons . Therefore electron - electron repulsion is minimised , as is the energy difference between the singlet and triplet states and therefore it is not possible to predict in which of the two spin states the molecule will exist .

Examples of disjoint systems

2

5

Where the NBMOs of the system have atoms in common the system is termed non - disjoint , the wave functions of the NBMOs contain high energy terms corresponding to electron - electron repulsion and the energy of the triplet state falls well below that of the singlet . In general , non - disjoint biradicals should have a triplet ground state .

Examples of non - disjoint systems

1

7

The symmetry adapted Hückel NBMOs of compounds **3** , **9** , **10** , **15** are illustrated in Figure 1.4 . In all four cases both molecular orbitals have atoms in common . The systems are therefore non - disjoint and therefore the ground state is predicted to be a triplet .

Borden and Davidson also made use of the " starred " / " unstarred " system to predict the multiplicity of alternant hydrocarbon radicals . They point out that where **$n^* = n$** the NBMOs are confinable , the system disjoint and the ground state species either a triplet or a singlet . They go on to predict that where **$n^* = n + 2$** the system should be non - disjoint and the ground state species a triplet .

Using this simple system and with reference to Figure 1.3 , it can be seen that for hydrocarbons **3** , **9** , **10** , **15** the equation $n^* = n + 2$ holds true and that , once more , a triplet ground state is predicted for these molecules .

1.2 Synthetic Approaches to Non - Kekulé Aromatic Systems

1.2.1 Introduction

As was mentioned earlier , this thesis is primarily concerned with the four non - Kekulé aromatic hydrocarbons **3** , **9** , **10** and **15** . Although often mentioned in relation to theoretical work on the nature of non - benzenoid aromaticity [8] , synthetically this very interesting group of π - biradicals has been almost totally ignored since the failure of pioneering work by Clar in the 1950's . Although unable to isolate the biradicals he did report the synthesis of the related quinones **16** - **19** [2,9] .

Murata has also prepared the dications **21a** , **23a** , **21b** - **23b** by treatment of the tetrahydro derivatives **27** and **29** , and the diketones **16** ,

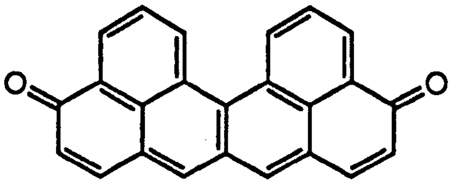


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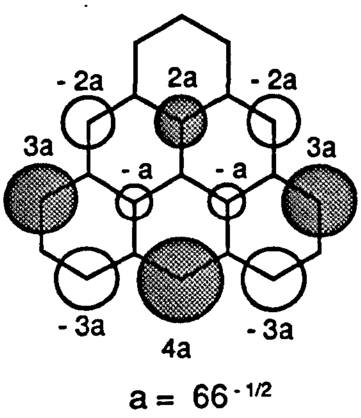
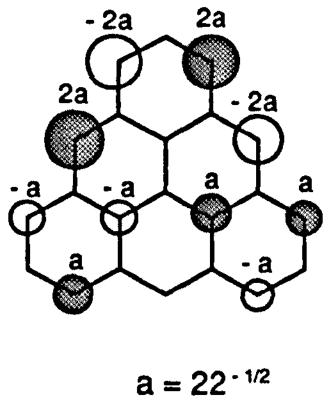
Figure 1. 4 Illustration of the non - disjoint nature of the Hückel NBMOs of non-Kekulé aromatics **3 , 9 , 10 , 15 .**





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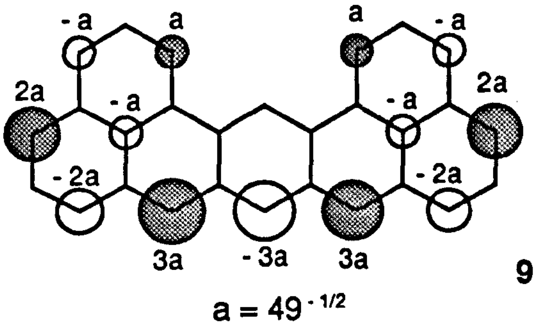

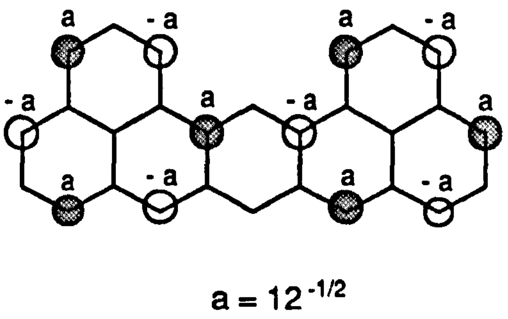

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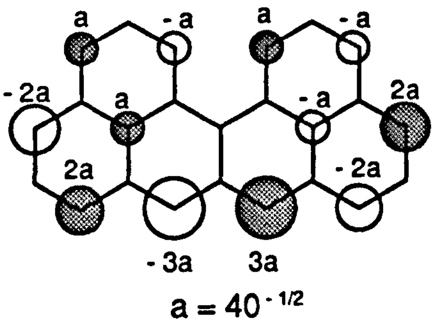

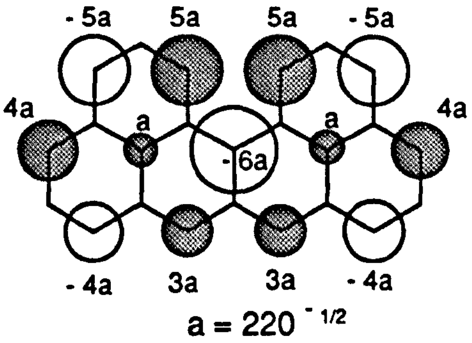

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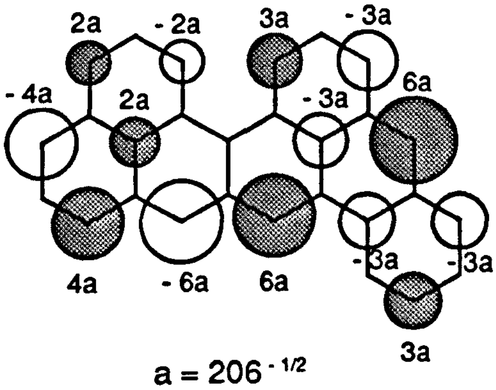

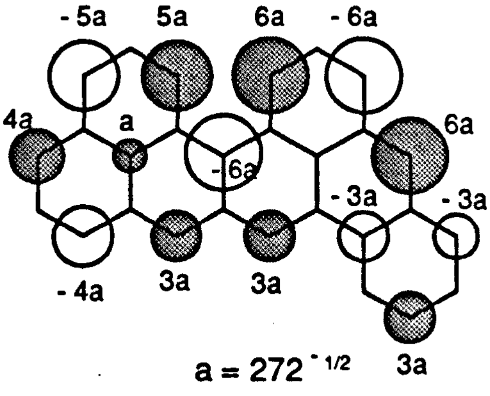

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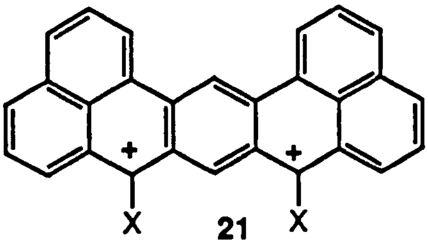
Figure 1.5



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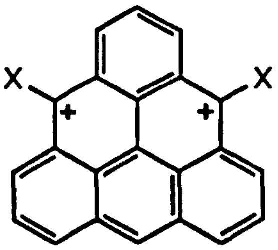

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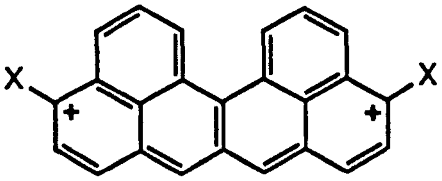
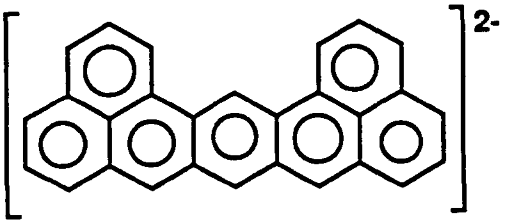


23

21a , 22a , 23a X = H
21a , 22a , 23a X = OD



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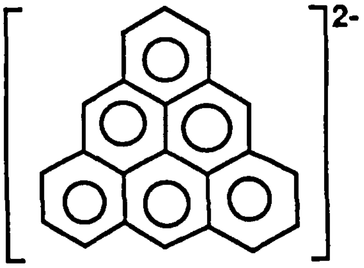

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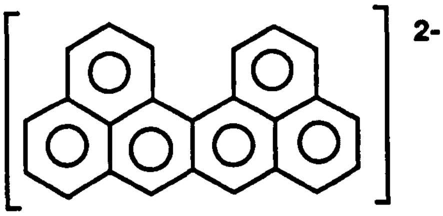

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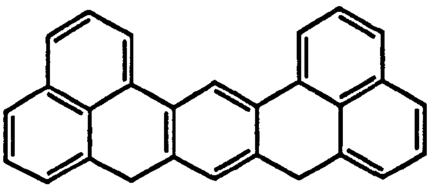

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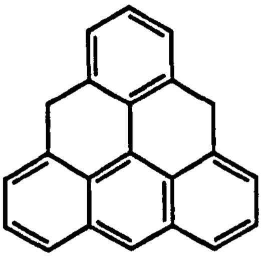

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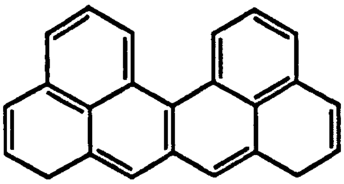

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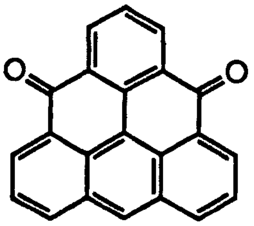

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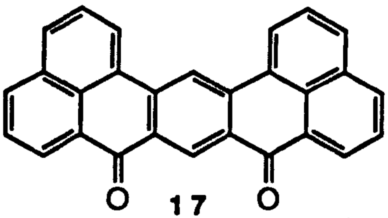

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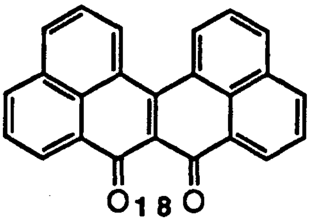

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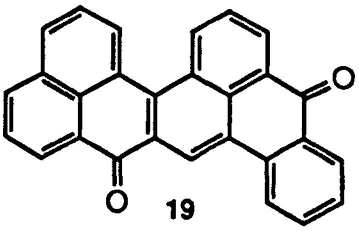


19

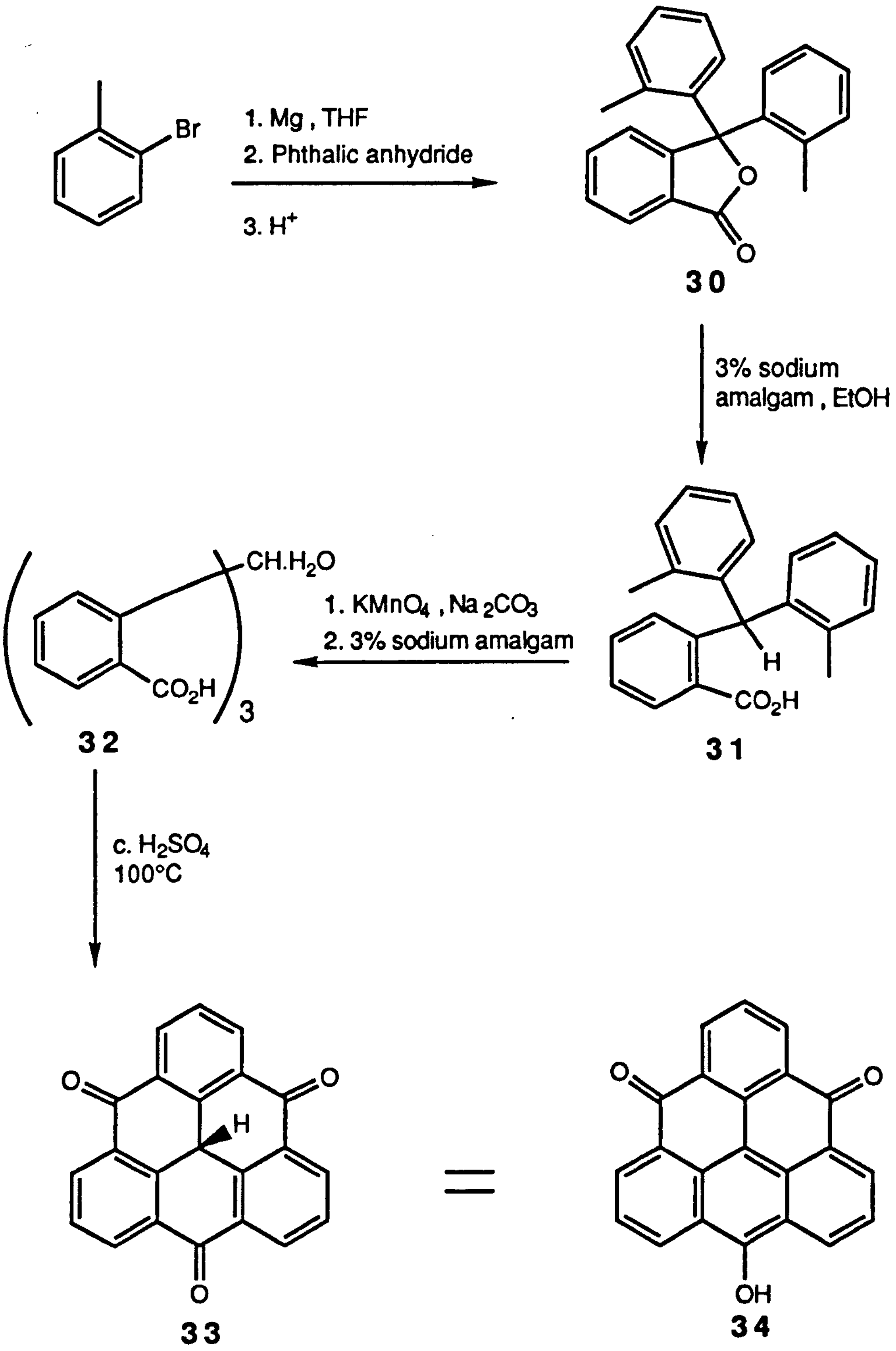
17 and **20** with sulphuric acid - d_2 . The dianions **24** - **26** were prepared by treating compounds **27** - **29** with butyl lithium (Figure 1.5) .

Although Clar attempted to observe the absorption spectra of the biradicals by dehydrogenation of their tetrahydro derivatives , he was unable to do so , reporting instead almost complete polymerisation in all cases . Indeed no observations of these π - biradicals have been reported .

1.2.2 Synthetic Approaches to Triangulene and its derivatives

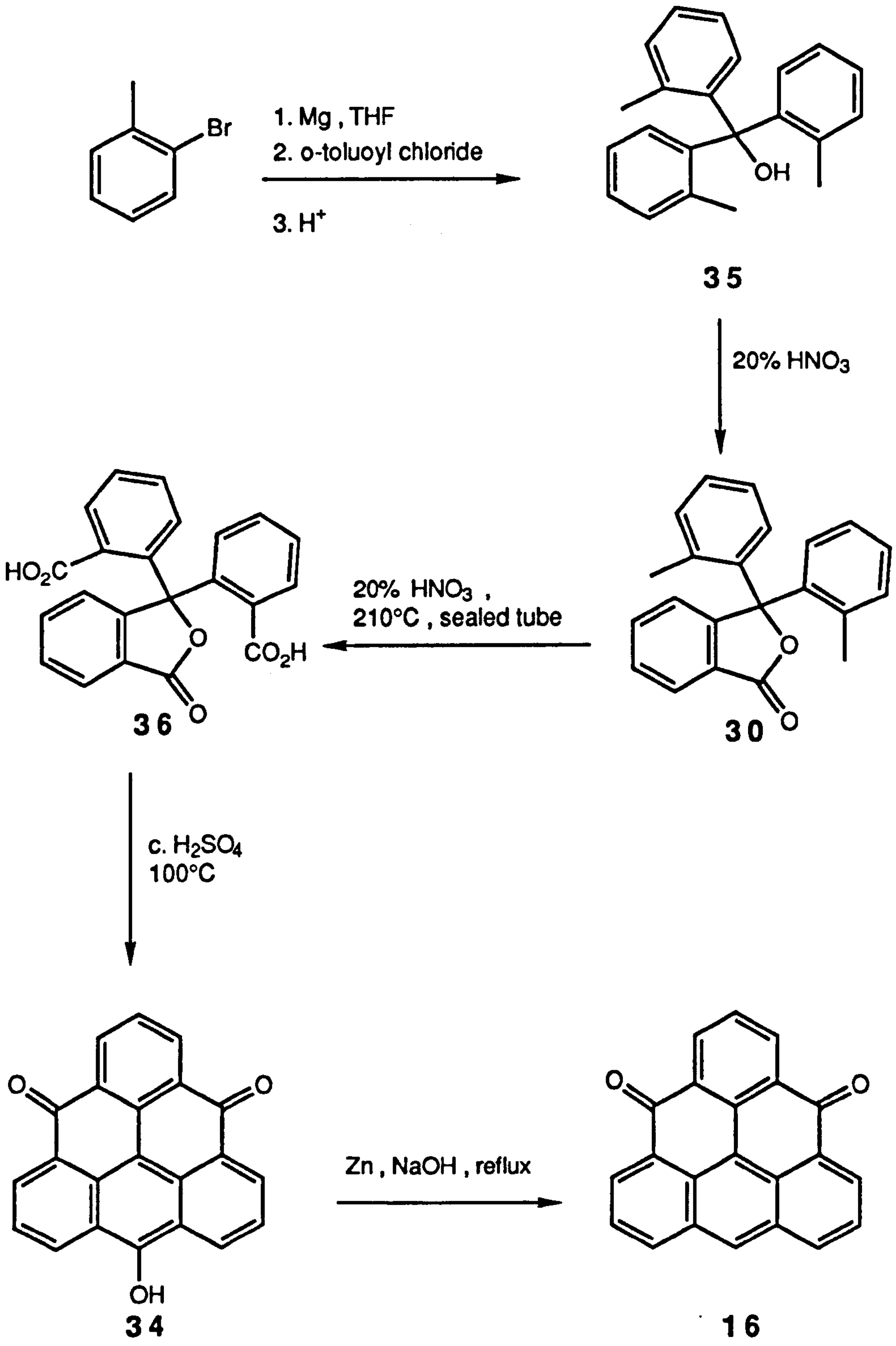
Weiss and Korczyn [11] were the first to report the synthesis of a compound containing the 22-carbon array so recognisable as the triangulene skeleton . They prepared 3,3-di-o-tolylphthalide **30** by the Grignard reaction of o-tolylmagnesium bromide with phthalic anhydride (Scheme 1.1). Reductive ring opening with 3% sodium amalgam was followed by oxidation of the o-tolyl methyl groups with potassium permanganate to give the triacid **32** . Treatment of **32** with sulphuric acid gave a blue compound assigned the structure **33** by Weiss and Korczyn . It is , however , more probable that under such acidic reaction conditions , the compound isolated was in fact the tautomeric hydroxytriangulenequinone **34** resulting from protonation of one of the oxygen functions followed by aromatisation . Indeed , a few years later Clar [12] synthesised this compound and reported that it had identical properties to the compound prepared by Weiss and Korczyn .

Scheme 1.1



Clar[12] reacted o-tolyllithium with o-toluoyl chloride to give the tri-o-tolylcarbinol **35** (Scheme 1.2) . Oxidation with nitric acid at atmospheric pressure gave the phthalide **30** , whilst further oxidation at high temperature and pressure gave the diacid **36** .Cyclisation was once more

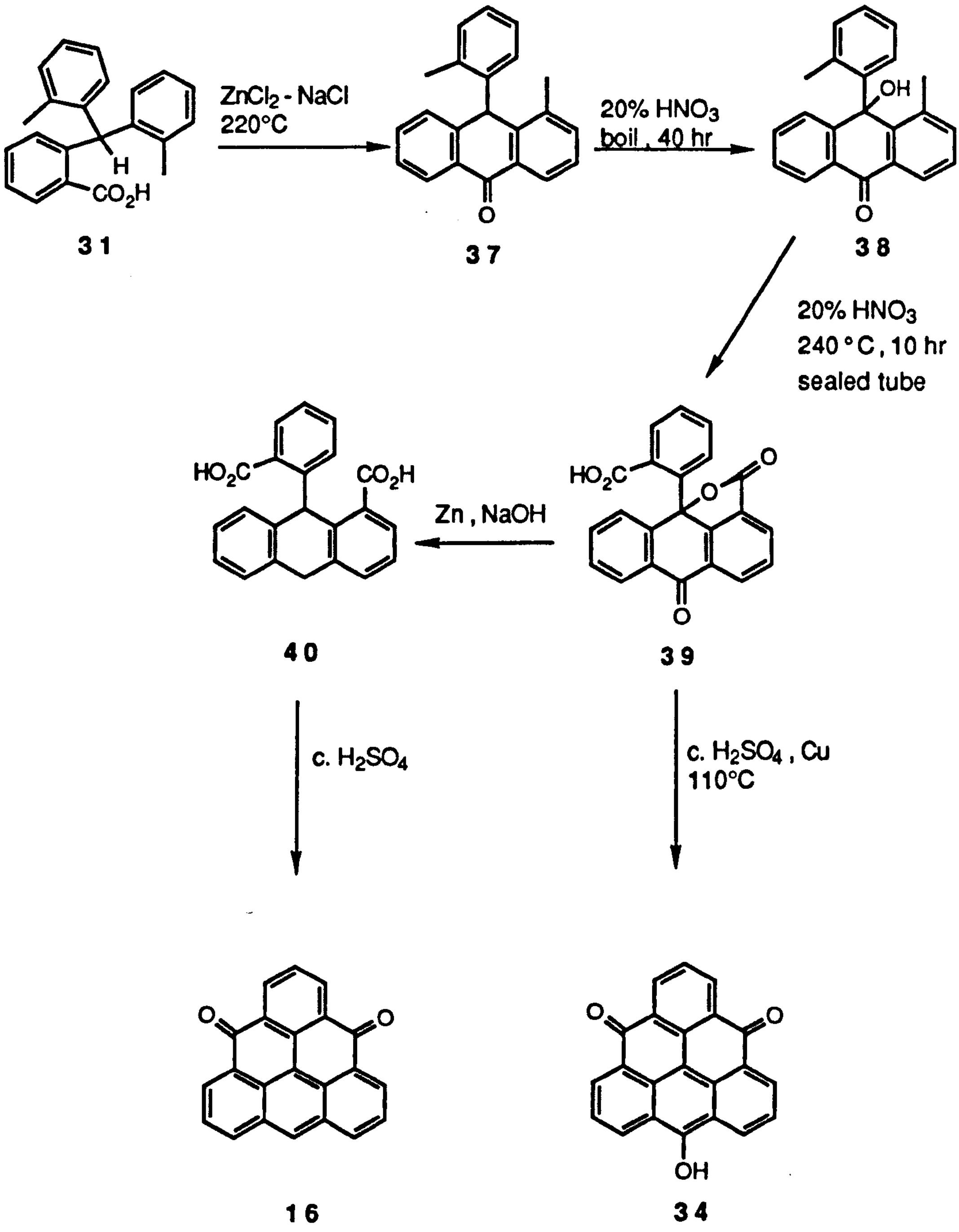
Scheme 1.2



carried out using sulphuric acid to give compound **34**. Having prepared the hydroxytriangulenequinone **34** Clar reduced the phénolic hydroxyl function to yield the red triangulenequinone **16**, albeit in poor yield.

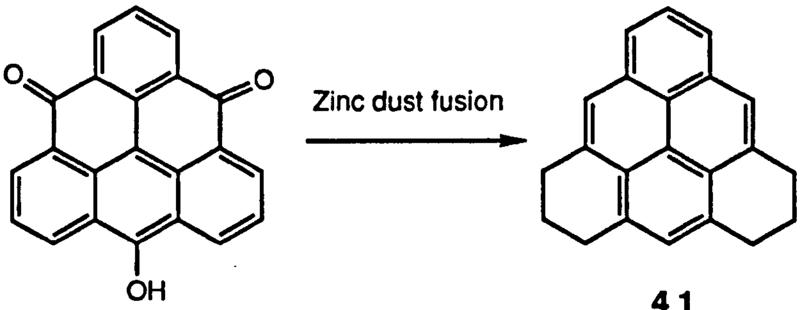
A longer route to the diketone **16** was also pioneered by Clar beginning with the intra-molecular Friedel-Craft's cyclisation of the acid **31** to give the substituted anthrone **37** (Scheme 1.3). Oxidation with nitric acid gave the 9-hydroxy derivative **38** which was further oxidised to the carboxylic acid-lactone **39** by nitric acid at elevated temperatures and

Scheme 1.3



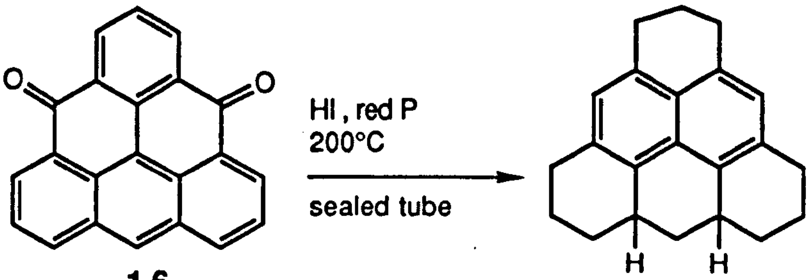
pressures . Clar converted the acid **39** to hydroxytriangulenequinone **34** with sulphuric acid - copper powder . Reduction of the acid **39** with zinc dust in refluxing sodium hydroxide solution gave the dihydroanthracene **40** which was cyclised using sulphuric acid to give triangulenequinone **16** .

Clar attempted to observe triangulene by a variety of reductive methods. When phenol **34** was subjected to Clar's zinc dust fusion procedure[15] a colourless compound was obtained . By comparison with the absorption spectrum of 2,3-methylenepyrene Clar inferred that this product was hexahydrotriangulene **41** . When compound **41** was dehydrogenated by sublimation over a palladium charcoal catalyst , complete adsorbtion onto the catalyst was observed and there was no sublimate indicating , according to Clar , that almost instantaneous polymerisation had occurred .



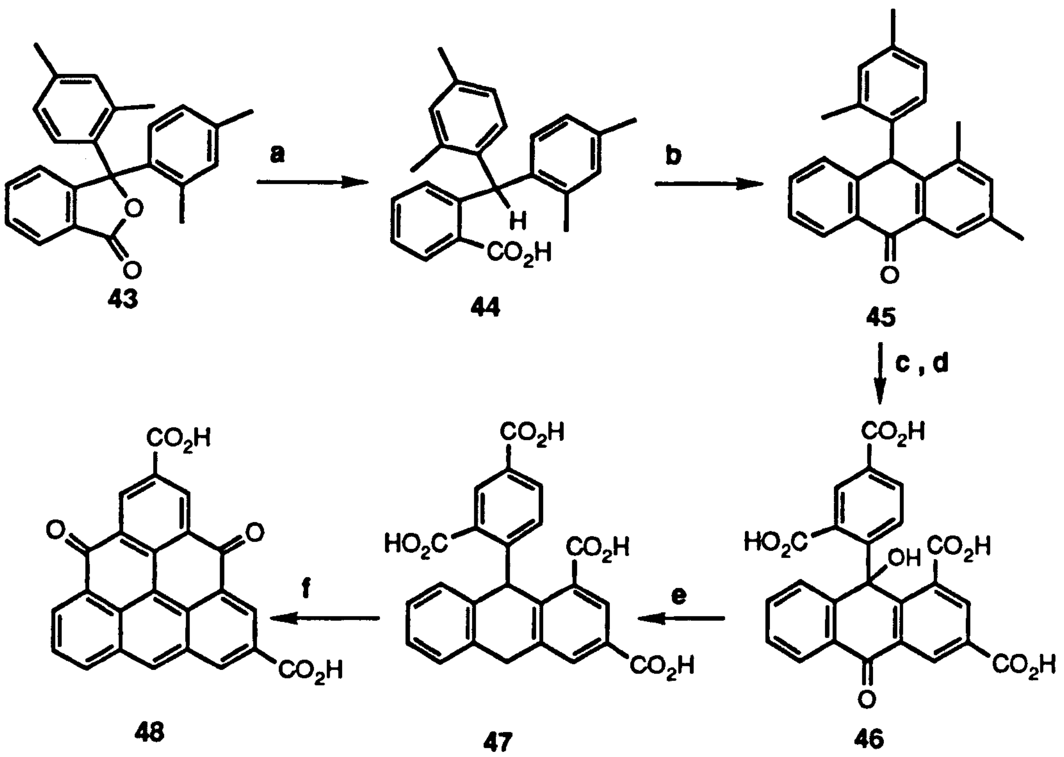
34 **41**

A further attempt to observe the absorption spectrum of the parent diradical **3** was made through the reductive dehydrogenation of the dodecahydrotriangulene **42** , prepared by reduction of **16** with hydroiodic acid and red phosphorous at elevated temperature and pressure . When **42** was melted with palladium charcoal , followed by heating to 250°C , high vacuum sublimation resulted only in the return of a small amount of **42** .

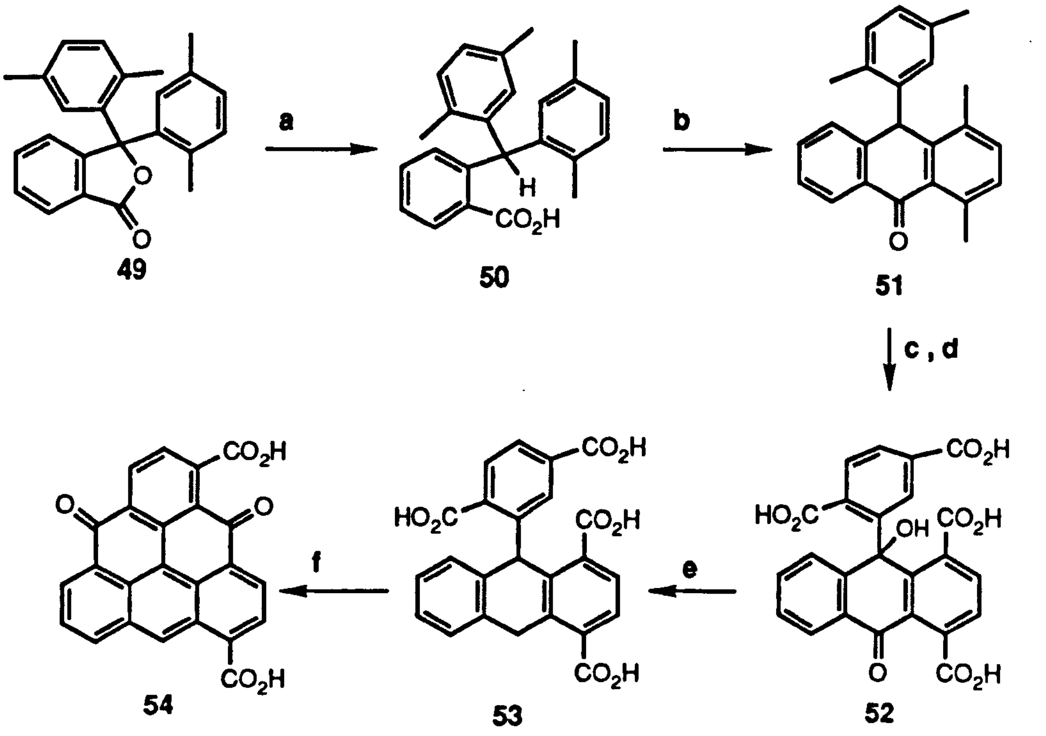


16 **42**

Scheme 1.4

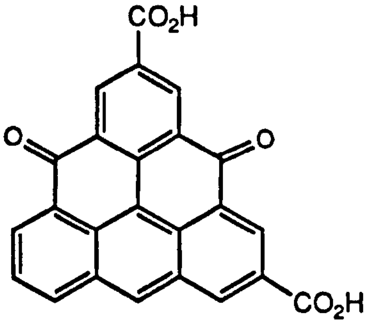


a Zn , KOH , EtOH , reflux
b NaCl , ZnCl , 220°C
c 20% HNO_3 , boil , 40 hr
d $KMnO_4$, NaOH
e Zn , NaOH
f c. H_2SO_4



These results led Clar to conclude that triangulene must exist as a biradical given that complete polymerisation was observed under conditions where " even the most reactive hydrocarbons , like hexatriene or 1,2-benzhexacene , can be prepared " [12].

Clar [14] reported that the two triangulenequinone derivatives **48** and **54** could be prepared from 3,3-di-m-xylylphthalide **43** and 3,3-di-p-xylyl phthalide **49** by the same ' longer ' route described for **16** earlier (Scheme 1.4) . Clar claimed that these two dicarboxylic acids could be converted into the diketone **16** by decarboxylation with copper powder at elevated



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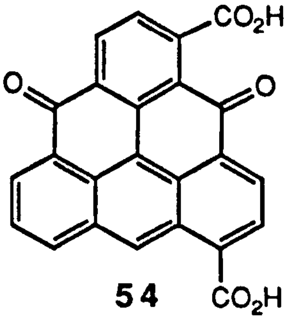
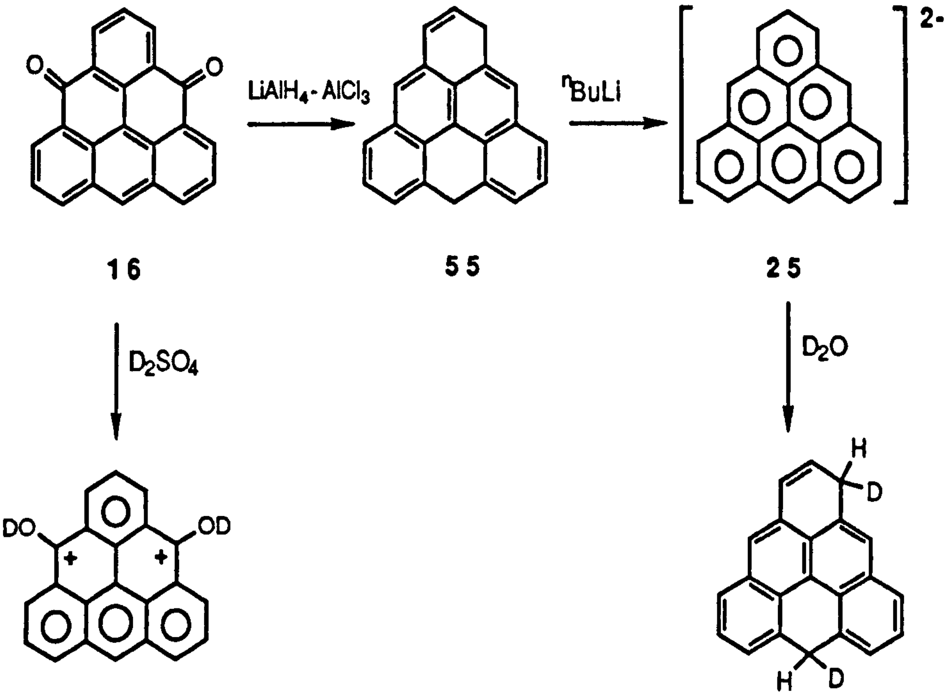


54

Scheme 1.5



16 **55** **25** **22** **56**

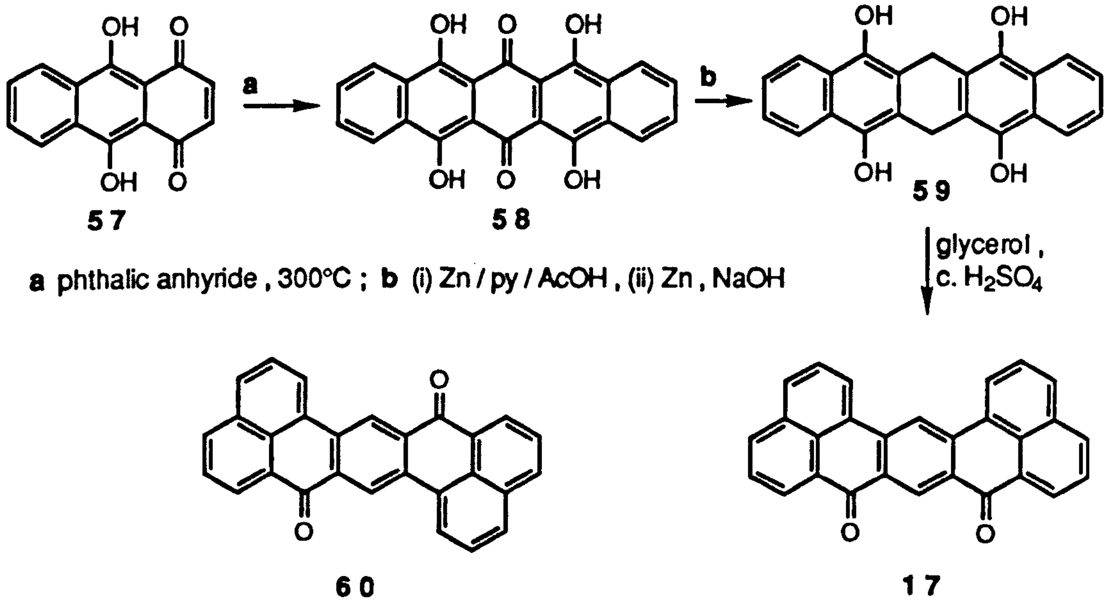
temperature ; and the tetrahyrotriangulene **42** by reduction with hydroiodic acid and red phosphorous followed by decarboxylation with soda lime .

Murata [10b] prepared triangulenequinone **16** via Clar's procedures . He was able to reduce the diketone**16** to the tetrahydro derivative **55** with lithium aluminium hydride - aluminium chloride complex in ether . The methylene protons were observed by proton nmr spectroscopy and their positions confirmed by comparison with the spectra of the deuterated derivative **56** , formed when the dianion **25** was quenched with deuterium oxide . Murata was unable to form the parent dication but did prepare the dication **22** by treating the quinone **17** with sulphuric acid-d2 (Scheme 1.5).

1.2.3 Synthetic Approaches to Dibenzpentacene and its derivatives

The first reported synthesis of dibenzpentacenequinone **17** was that of Clar [2,14] in the 1950's . He condensed leucochinizarin **57** and phthalic anhydride to give the pentacene derivative **58** , which was then subjected to a Skraup condensation with glycerol and sulphuric acid . Clar claimed to isolate the cis-bis-angular compound **17** as the sole product , but it does seem unlikely that none of the trans-bis-angular product **60** was formed in this particular Skraup reaction , given that there are no steric hinderances to promote regiospecificity .

Scheme 1.6

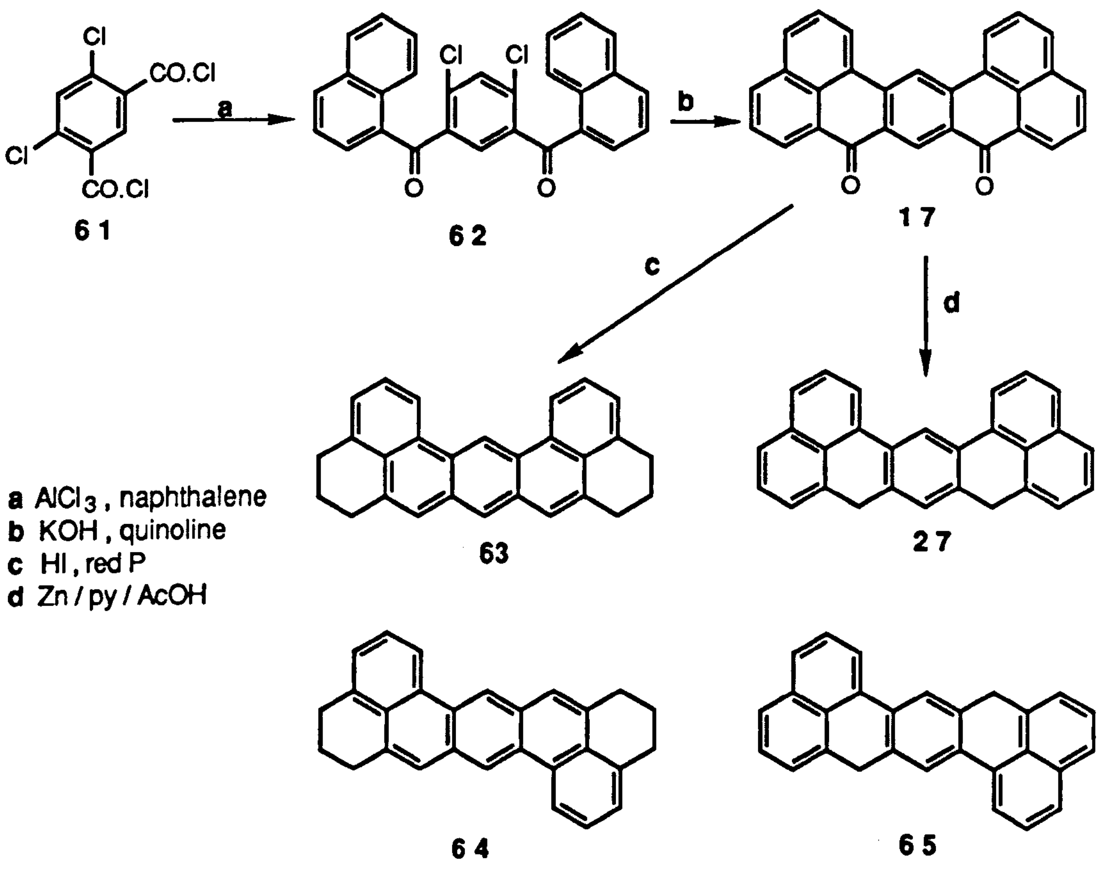


a phthalic anhydride , 300°C ; **b** (i) Zn / py / AcOH , (ii) Zn , NaOH

However Clar subsequently synthesised the diketone **17** by a less ambiguous route. The double Friedel-Craft's condensation of the iso-phthaloyl chloride **61** with naphthalene gave compound **62** in which the basic dibenzpentacene skeleton had been assembled ready for final ring closure (Scheme 1.7) . The intramolecular cylisation was achieved in a mixture of boiling quinoline and potassium hydroxide although yields never exceeded 10% .

Reduction of diketone **17** with hydroiodic acid and red phosphorous gave a hexahydro compound assigned the structure **63** because of the similarity of its absorption spectrum to that of the centrosymmetric isomer **64**. As with compound **40** when this compound was dehydrogenated with palladium-charcoal dehydrogenation and polymerisation took place simultaneously .

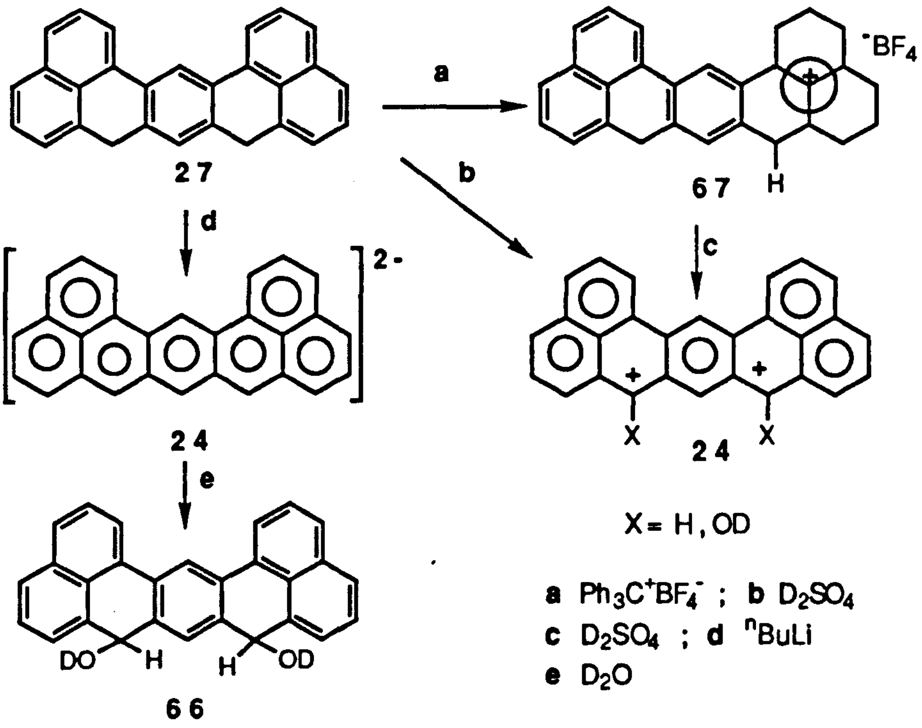
Sheme 1.7



Reduction of the diketone **17** with pyridine , zinc and acetic acid gave a tetrahydro derivative , again assigned the structure **27** by Clar by comparison with the absorbtion spectrum of the centrosymmetric isomer **65** . However Murata [10d] prepared the tetrahydropentacene **27** via Clar's procedures and , with the benefit of modern analytical and spectroscopic techniques , reported that the physical and spectral properties of compound **27** are quite distinct from those reported by Clar . Murata suggested that Clar's compound should be assigned to one of the possible isomers having methylene group(s) at different position(s) .

Clar attempted to dehydrogenate his putative **27** with chloranil in benzene but to no avail . Dehydrogenation with palladium-charcoal again gave polymerisation products . Murata prepared the deuterated derivative **66** by quenching the dianion **24** with deuterium oxide (Scheme 1.8) . Reaction of **27** with two equivalents of trityl tetrafluoroborate resulted in a black solid which Murata believed to be the monocation **67** .

Scheme 1.8

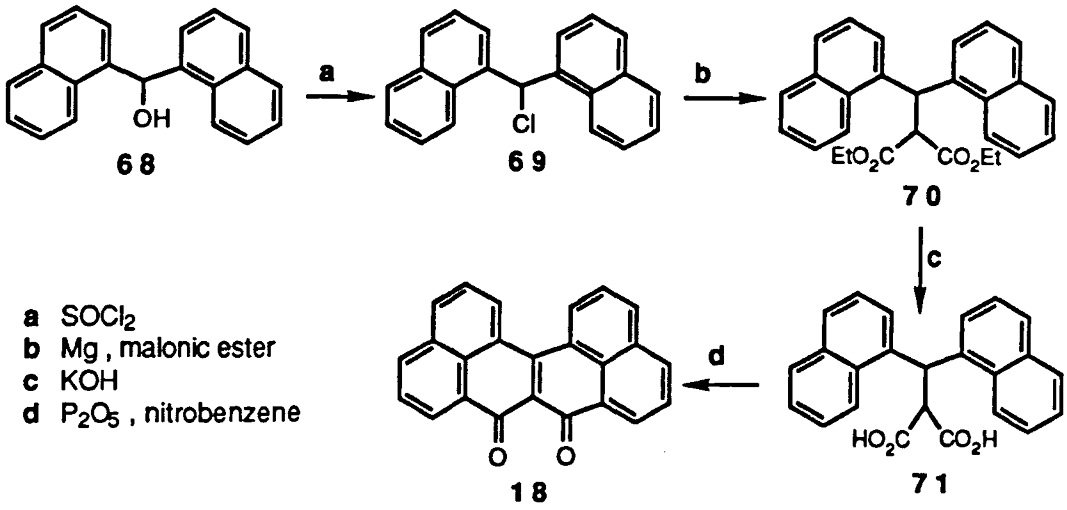


X= H,OD

a $Ph_3C^+BF_4^-$; **b** D_2SO_4
c D_2SO_4 ; **d** ${}^nBuLi$
e D_2O

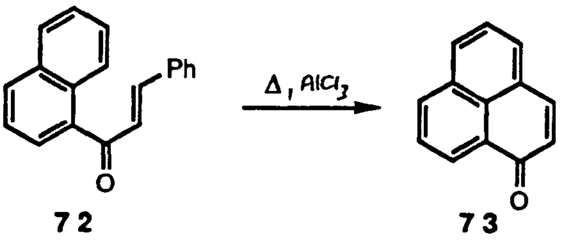
1.2.4 Synthetic Approaches to Dibenznaphthacene and its derivatives

Scheme 1.9

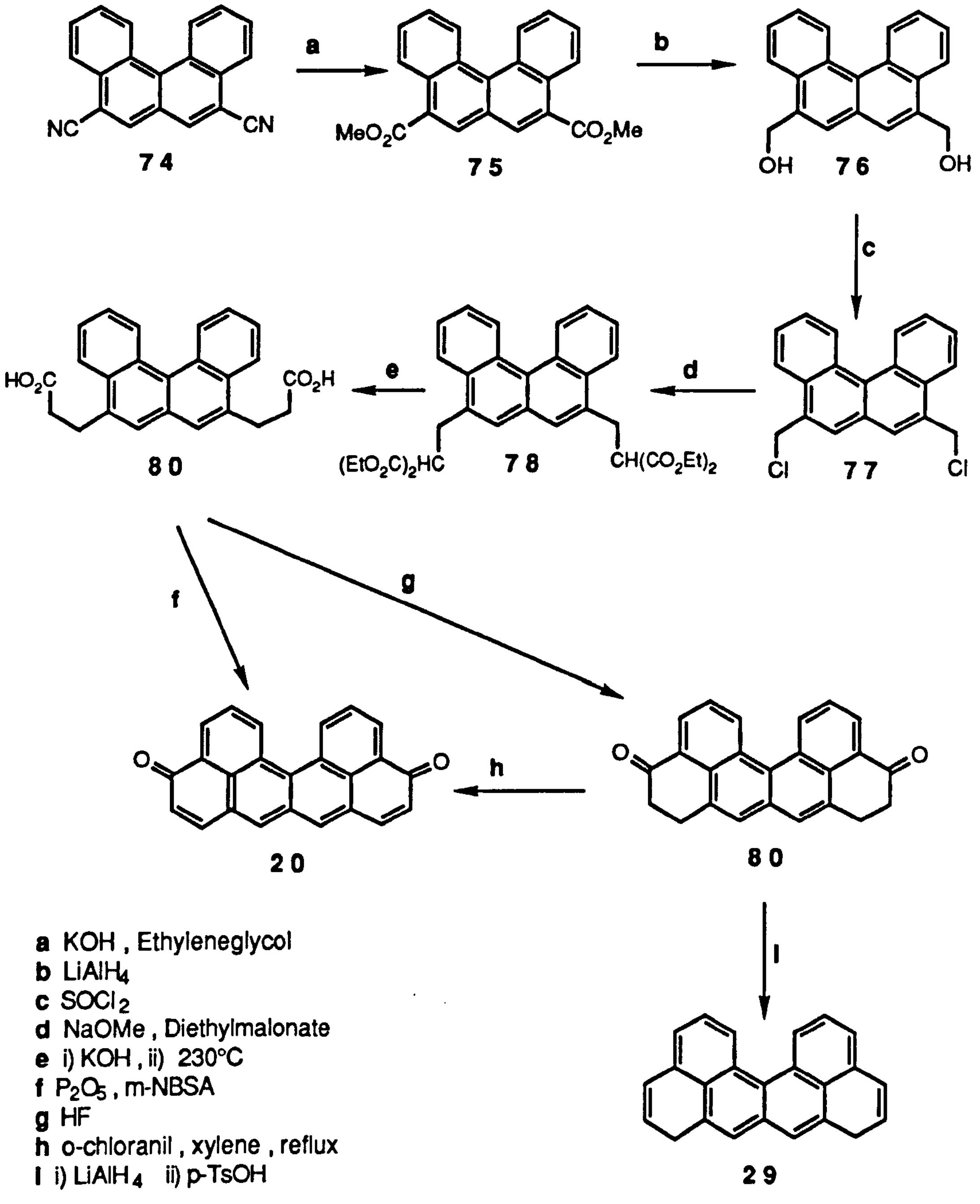


a $SOCl_2$
b Mg , malonic ester
c KOH
d P_2O_5 , nitrobenzene

The synthesis of the quinone **18** was first reported by Clar [2] . He converted the dinaphthyl carbinol **68**[16] to the chloride **69** , which was then condensed with magnesiomalonic ester to give the dinaphthyl malonic ester **70**[17]. Cleavage of the ester groups with alcoholic potassium hydroxide gave the diacid **71** . Intramolecular cyclisation was achieved under Friedel-Craft's conditions with phosphorous pentoxide in nitrobenzene (Scheme 1.9) . Clar observed that the diacid **71** tended to split into naphthalene and phenalenone **73** with other reagents . However Shotter [18] disputed Clar's assertion of partial splitting , preferring instead to invoke a combination of decarboxylation and cyclic - acylation at the *peri* position accompanied by elimination of an aromatic residue . This reaction is similar to that observed with 1 - cinnamoylnaphthalene **72** .[19]



Scheme 1.10

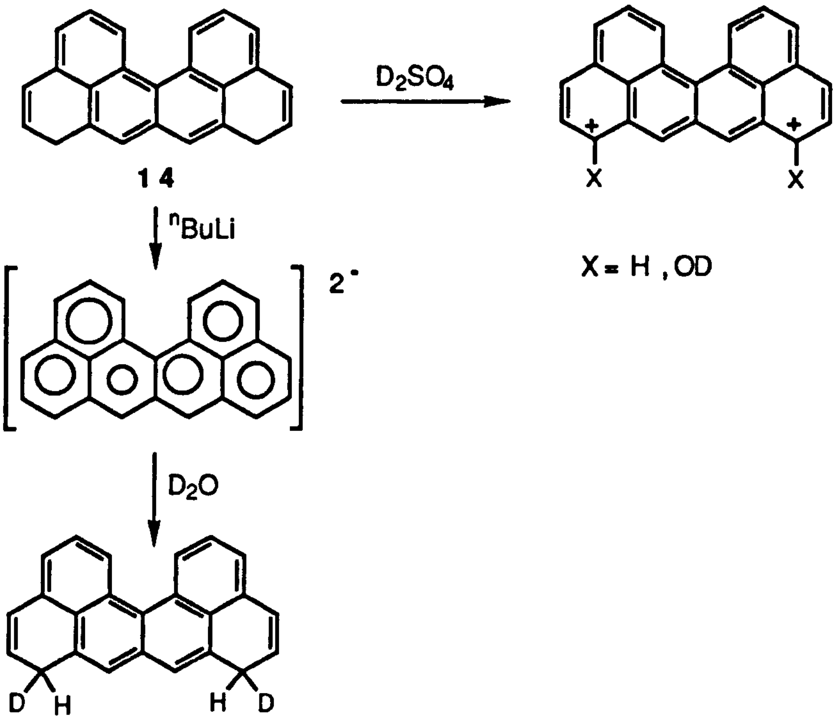


a KOH , Ethyleneglycol
b $LiAlH_4$
c $SOCl_2$
d NaOMe , Diethylmalonate
e i) KOH , ii) 230°C
f P_2O_5 , m-NBSA
g HF
h o-chloranil , xylene , reflux
i i) $LiAlH_4$ ii) p-TsOH

The synthesis of the isomeric dibenznaphthacenequinone **20** was reported by Murata[10], and was prepared from benzo[c]phenanthrene-5,8-dicarbonitrile **74**[10] (Scheme 1.10) . Basic hydrolysis of the dinitrile compound **74** was followed by treatment with diazomethane to give the ester **75** . The ester **75** was reduced to the diol **76** with lithium aluminium hydride and then converted to the chloride **77** with thionyl chloride . Treatment with sodium methoxide - diethyl malonate followed by basic hydrolysis of the ester functions gave the diacid **79** . Murata reported cyclisation by two methods ; polyphosphoric acid and sodium m-nitrobenzene sulphonate gave the diketone **20** , while anhydrous hydrogen fluoride gave the octahydro derivative **80** . Dehydration of the diol derived from the reaction of compound **80** with lithium aluminium hydride , was achieved with a catalytic amount of p-toluene sulphonic acid . Reductive dehydration of compound **80** with o-chloranil gave the diketone **20** .

Murata and co-workers were able to prepare the diketone **20** and the tetrahydro derivative **29** in sufficient quantities to prepare the dianion **26** and the dications **23a** and **23b** in the same manner as discussed earlier (Scheme 1.11) , but Clar was unable to prepare compound **18** in sufficient quantities to allow him to undertake any further experimental work .

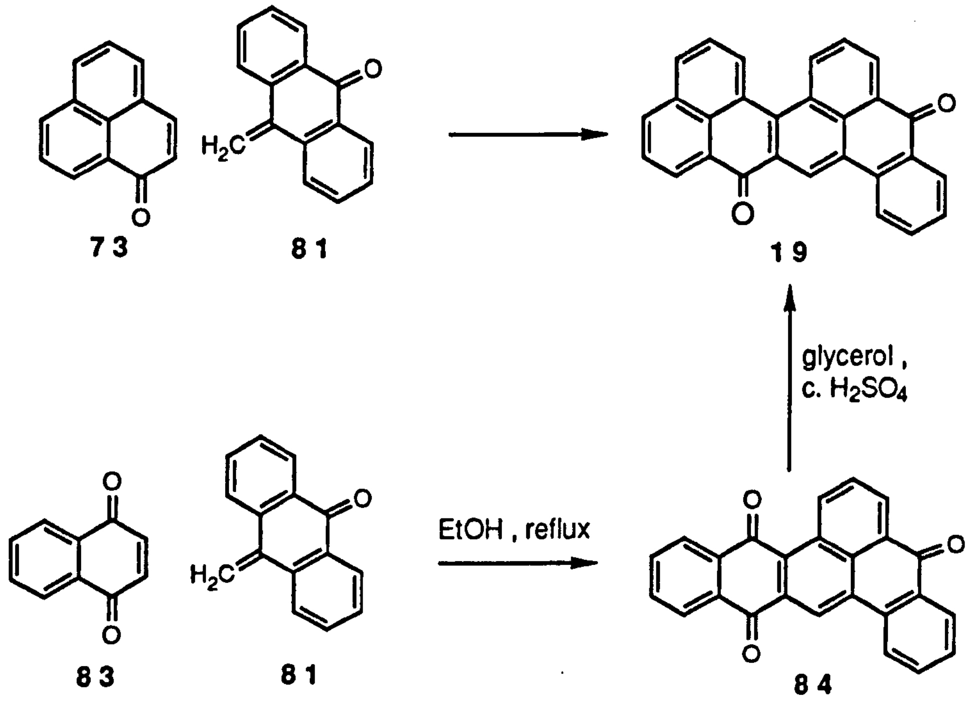
Scheme 1.11



1.2.5 Synthetic Approaches to tribenznaphthacene and its derivatives

Once again Clar[21] was the first to report the synthesis of the tribenznaphthacenequinone **19** in the early 1950's (Scheme 1.12) . Although he originally assigned structure **82** to the condensation product of phenalenone **73** and 10-methyleneanthrone **81** , he later revised this opinion when work by both himself[22] and Vollmann[23] suggested that he had , in fact , isolated the diketone **19** . Vollmann was investigating the Scholl reaction and reported two syntheses of diketone **19** and one of the quinone **82** . This allowed the direct comparison of the physical properties of the two compounds and thus validated Clar's revised opinion . Vollmann condensed 1,4-naphthoquinone **83** with methyleneanthrone **81** to give the dibenznaphthacenequinone **84** . This latter product was treated to a Skraup condensation with glycerol in sulphuric acid to give mainly the desired **19** but with a little of the isomeric compound **82** .

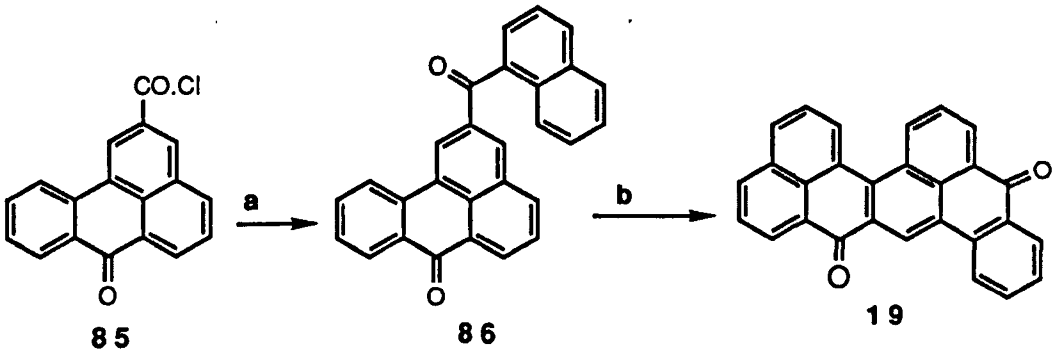
Scheme 1.12



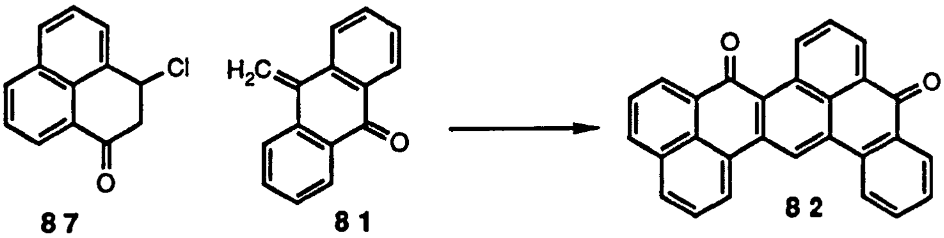
Vollmann had also condensed the acid chloride **85** [24] with naphthalene to give the α-naphthoylbenzanthrone **86** . Cyclisation under Scholl conditions gave the quinone **19** .

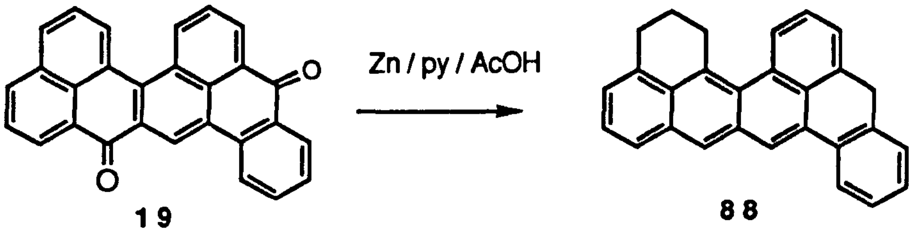
Vollmann confirmed the structure of **82** by condensing the chloro-compound **87** with methyleneanthrone **81** to give the trans-angular product .

Clar reduced the quinone **19** with zinc , pyridine and acetic acid to give the octahydro derivative **88** . Again Clar reported that dehydrogenation gave polymerisation .



a $AlCl_3$, naphthalene ; **b** $AlCl_3$ - NaCl , 140°C





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Chapter Two

Synthetic Approaches to Non-Kekulé Polynuclear Aromatic Precursors

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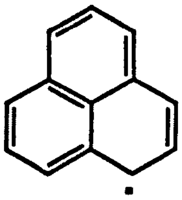
2.1 Introduction



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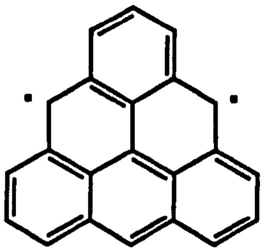

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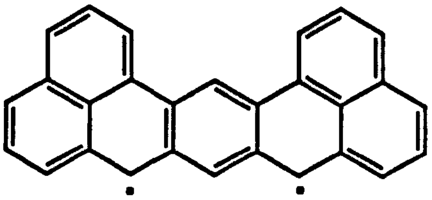

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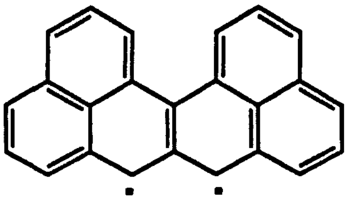

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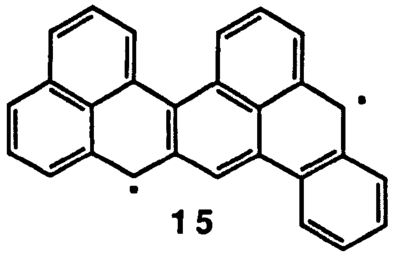

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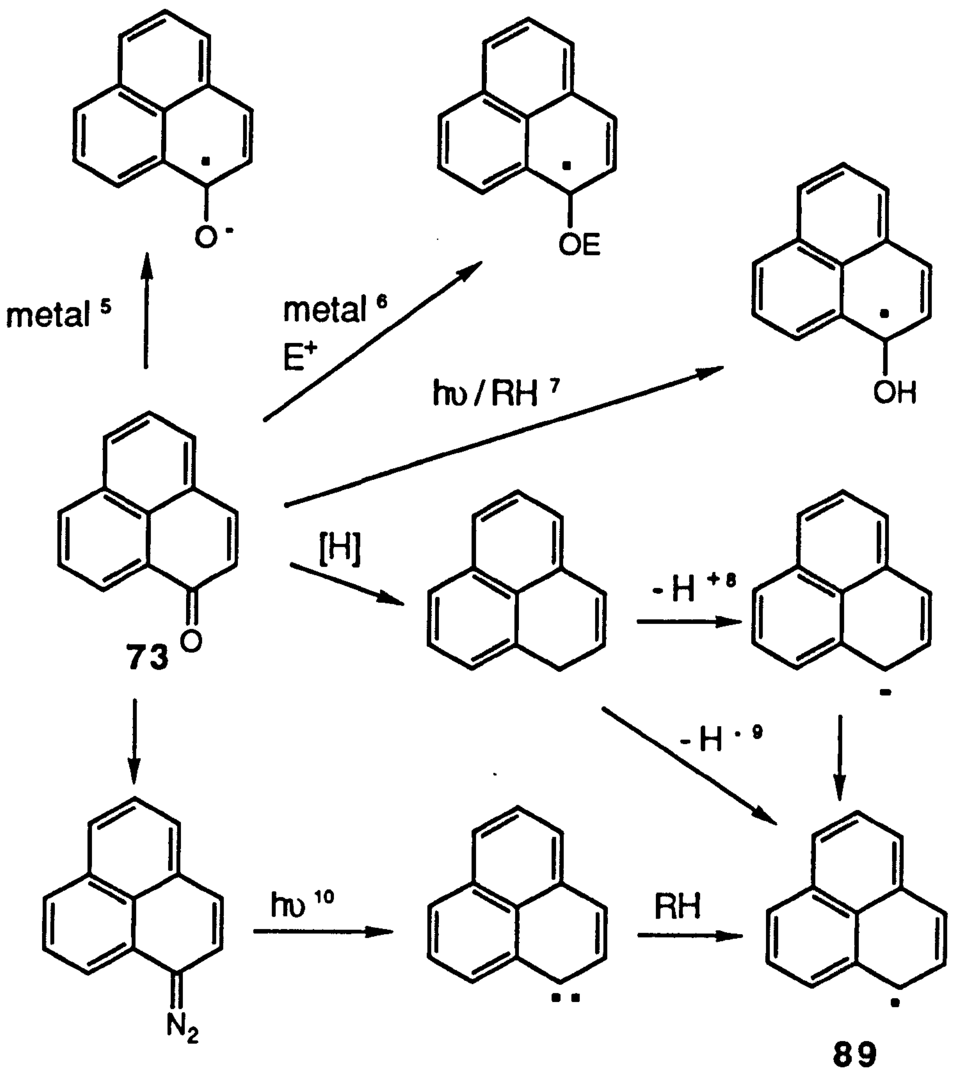
It can be seen from the structure of the phenalenyl radical **89** that the four non-Kekulé polynuclear aromatics **3** , **9** , **10** and **15** may be regarded as expanded versions or " dimers " of this system [1,4,43] . The possibility exists that if one could prepare these π-biradicals they may well have many properties in common with compound **89** [2] ; stability in the absence of oxidising agents being not the least important (the phenalenyl radical is reported as being almost indefinitely stable in such conditions [3]).

Many methods [5-10] have been developed for converting phenalenone **73** into the phenalenyl radical **89** , or derivatives thereof , as Figure 2.1 illustrates . Therefore there is , in principle , a wide range of methods for converting the quinones **16** - **19** into biradicals. For example , triangulene-quinone may be reduced with lithium aluminium hydride - aluminium chloride complex to the tetrahydrotriangulene **28** [8] and then by analogy to phenalenone chemistry , be converted to the triangulene biradical by hydrogen abstraction [9] (Scheme 2.1) ; or the biradical **90** prepared by metal

Figure 2.1



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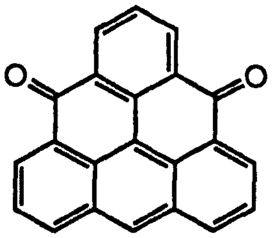
89

reduction in the presence of an electrophile [6].

It can thus be seen that the quinones **16 -19** provide a route to non-Kekulé polynuclear aromatic chemistry and as such they became key intermediates in our synthetic plan . However , although the phenalenone chemistry illustrated in Figure 2.1 and Clar's reported syntheses of the relevant diketones seemed to offer a good route to our desired non-Kekule polynuclear aromatics , as we progressed with the experimental work many disadvantages to this strategy emerged : namely, some of the reported compounds proved to be rather intractable mixtures or isomers of the desired molecules and also these diketones proved to combine the worst



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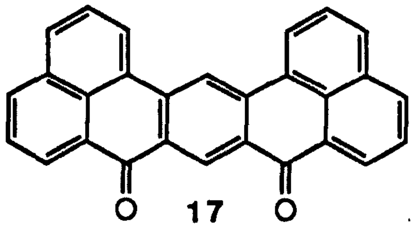

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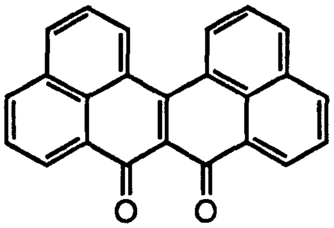

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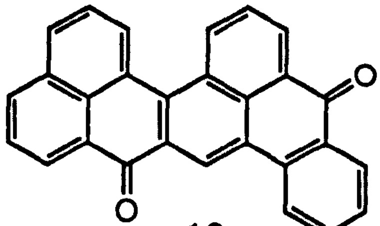

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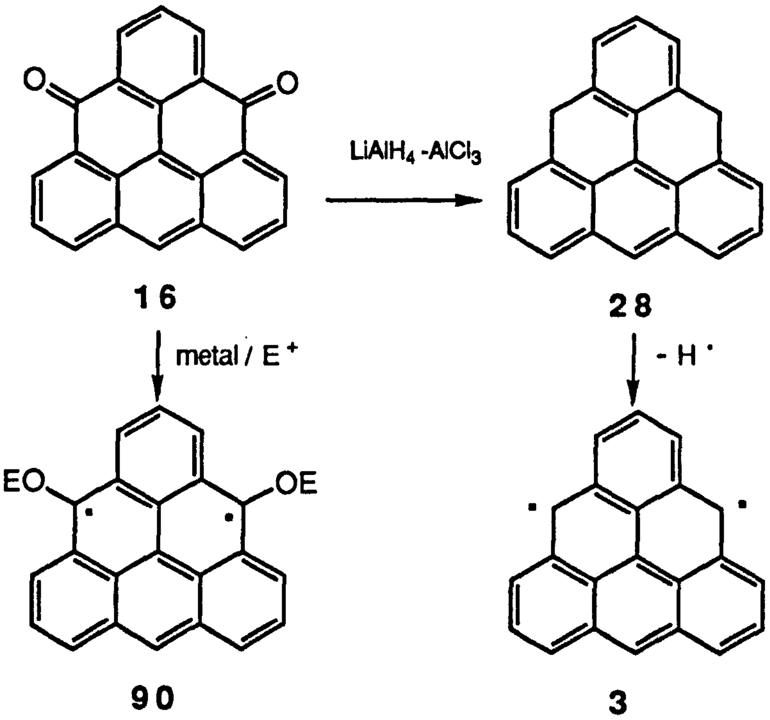
Scheme 2.1



properties of polynuclear aromatics (poor solubility in organic solvents making recrystallisation or chromatographic purification difficult) and of phenalenones (sensitivity to a wide range of reagents , acids and possibly light) . These factors made it difficult to obtain reasonable quantities of pure materials .

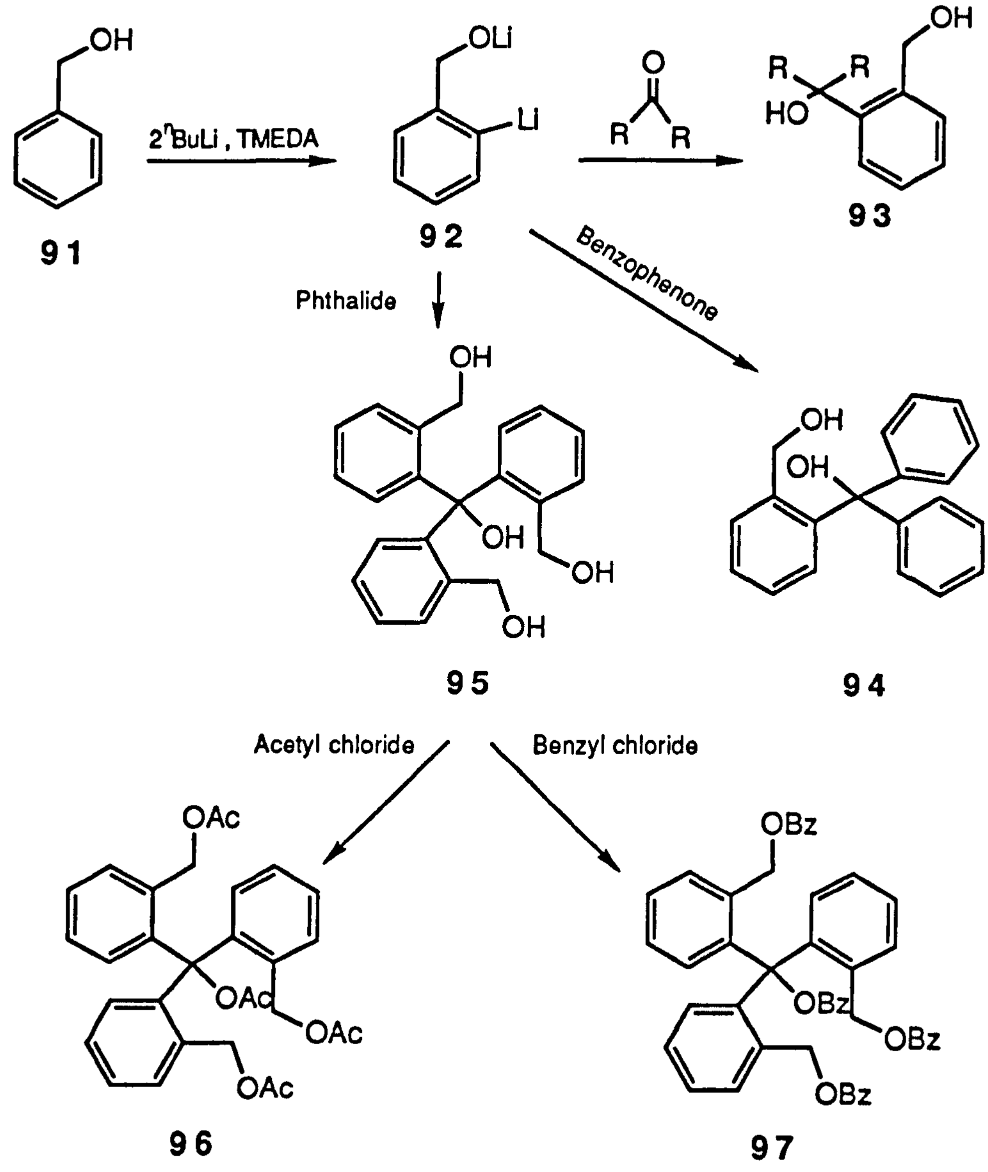
2.2 Synthetic Approaches to Non-Kekulé Polynuclear Aromatic Precursors

2.2.1 Synthetic Approaches to Triangulenequinone and derivatives.

Although Clar [15] provided what on the surface appeared to be a relatively straightforward route to triangulenequinone **16** , upon further reading of his experimental details several potentially awkward oxidations of aromatic methyl groups came to light . However , more recent work by Seebach [11] , House [12] , Yamamoto [13] , and Corrin [14] offered the prospect of preparing the triangulene skeleton in a more highly oxidised state ; or direct manner .

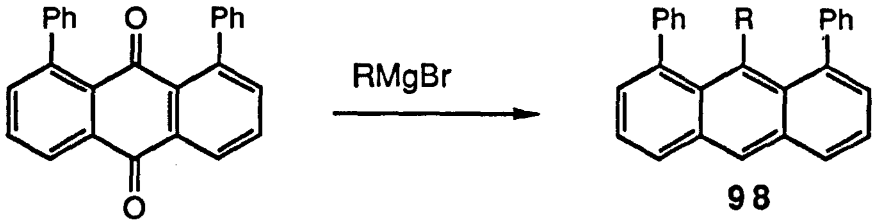
Seebach [11] reported a novel method of preparing ortho-substituted benzyl alcohols (Scheme 2.2) . Double deprotonation of benzyl alcohol **91** (or other phenylcarbinols) by excess n-butyl lithium / tetramethylethylene diamine (TMEDA) gave the lithium ortho-lithio alkoxide **92** . This highly reactive reagent undergoes alkylations , reacts with heteroelectrophiles , and , more interestingly , with carbonyl compounds to give substituted benzyl alcohols of the type **93** and **94** . It was our intention to modify Seebach's procedures by reacting two equivalents of lithio reagent **92** with the carbonyl group of phthalide to prepare the carbinol **95** . Unfortunately we were unable to isolate the desired compound but instead obtained a mixture of inseparable compounds . The proton nmr spectrum of the reaction mixture suggested that these molecules were hydrofurans formed by intramolecular dehydration processes. However , we did manage to trap the tetraol **95** with acetyl chloride and benzyl chloride to

Scheme 2.2



give the highly acid sensitive esters **96** and **97** respectively (identified by proton and carbon nmr spectroscopy) . In addition to the handling problems yields of these esters were very poor and so it was decided to discontinue this line of investigation .

Both House [12] and Yamamoto [13] had reported the preparation of substituted anthracenes and anthrones of the type **98** - **100** via Grignard reactions . Accordingly we prepared the magnesium bromide of compound **101** and reacted it with anthrone under the reported conditions . We were



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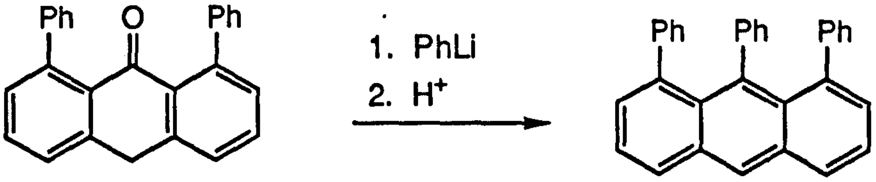

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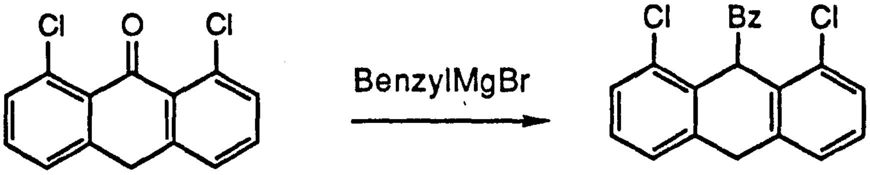

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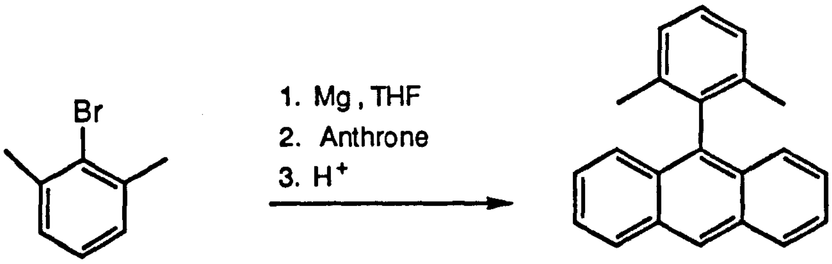

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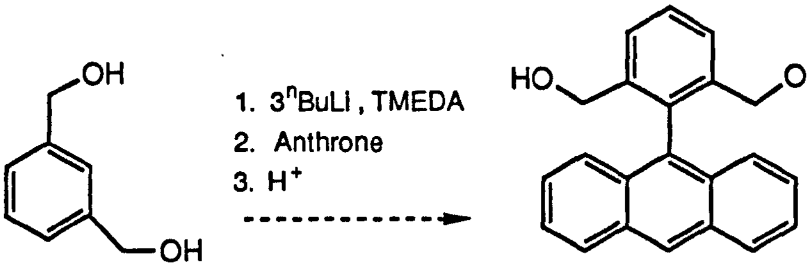
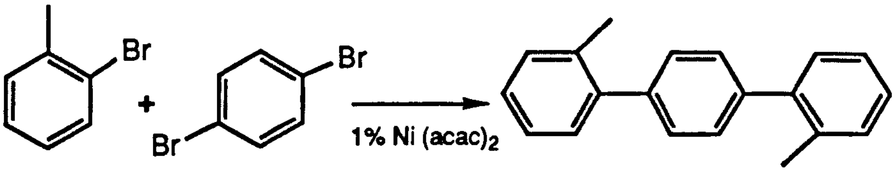


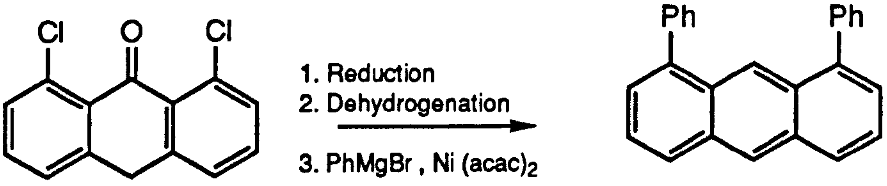
103

104

able to isolate the anthracene **102** but in such poor yields that this was not considered a viable route to the triangulene skeleton . A variation of this theme saw the tri-lithiation of benzyl alcohol **103** under Seebach's conditions but after treatment with anthrone we were never able to isolate any of the desired anthracene derivative **104** .

Corrin [14] reported the nickel diacetoacetate catalysed coupling of aromatic bromides , more particularly ortho substituted aromatic bromides . House [12a] extended these procedures to prepare phenyl substituted anthracenes of type **105** . Since 2-bromo-m-xylene and 9-bromoanthracene are commercially available this again appeared to offer a route to the hydrocarbon **102** and the basic triangulene skeleton . However when the reaction was carried out , under both Corrin's and House's conditions , where there was any evidence of coupling the yields were very poor , generally less than 1% !





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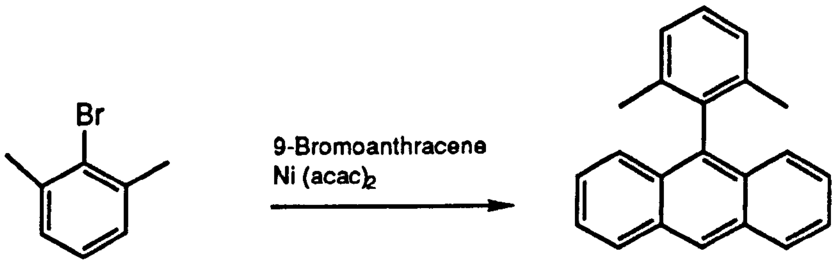
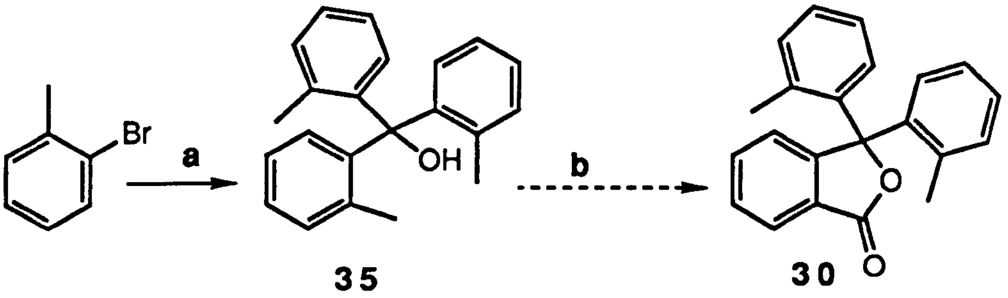


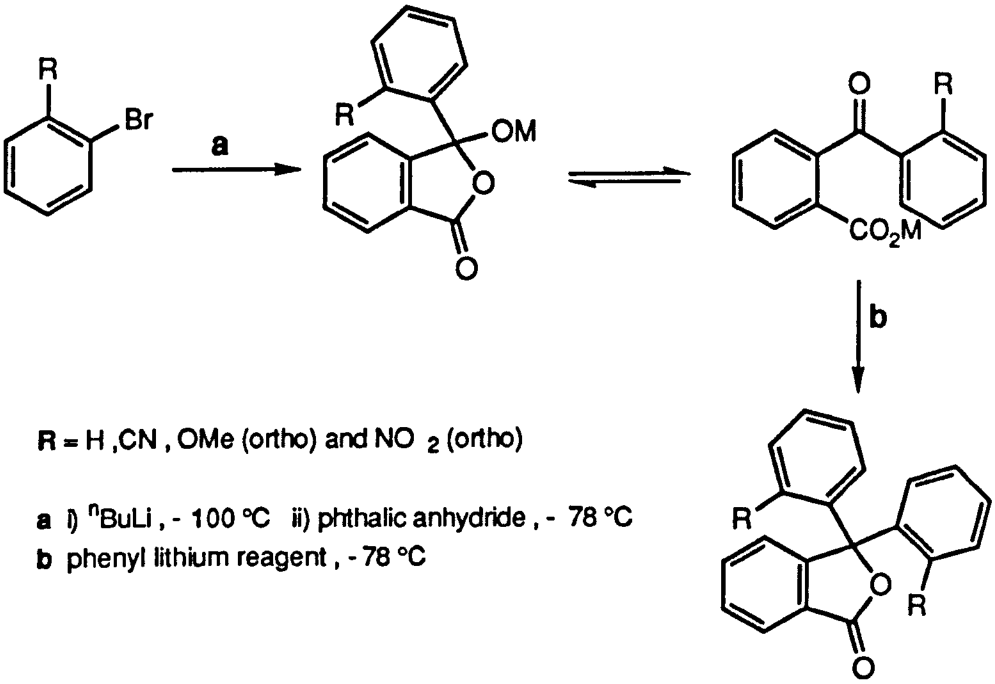
101 **102**

Given the failure of the aforementioned attempts to produce a viable alternative synthesis of triangulene precursors , we turned our attention to Clar's procedures [15] . He began his synthesis by preparing the tri-o-tolyl carbinol **35** and so accordingly we treated o-tolylbromide with lithium metal and then o-toluoyl chloride to obtain the carbinol **35** . Our compound , despite satisying spectral and analytical criteria , had different properties from those reported by Clar and , more importantly , could not be converted to the phthalide **30** by the nitric acid oxidation procedure claimed by Clar .



a i) Li , Et $_2$O ii) o-toluoyl chloride ; **b** 20% HNO_3 , boil , 10 hr

Unable to continue with Clar's synthesis we turned to alternative methods of forming 3,3-disubstituted phthalides . Parham [16] reported the reaction of aryl lithium reagents with phthalic anhydride to give benzoyl benzoic acids and phthalides .

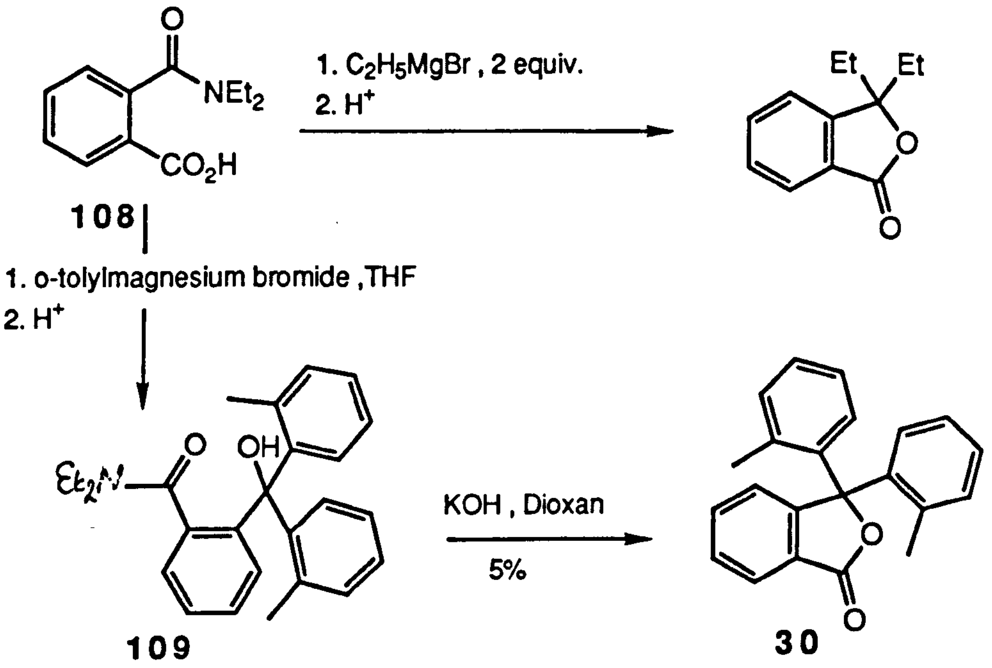


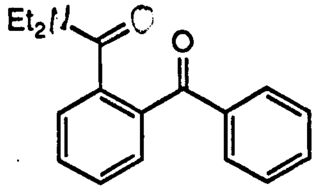
R = H ,CN , OMe (ortho) and NO $_2$ (ortho)

a i) ^{n}BuLi , - 100 °C ii) phthalic anhydride , - 78 °C
b phenyl lithium reagent , - 78 °C

When Parham added one equivalent of phthalic anhyride to one equivalent of phenyl lithium at -78°C he claimed to be able to isolate diphenylphthalide in 78% yield (based on phenyl lithium). In our hands we were unable to repeat Parham's results , which is unfortunate since this route offered the prospect of obtaining phthalides functionalised at the ortho position of the substituent rings in a higher oxidation state than methyl groups .

Maxim [17] reported the preparation of various di-substituted phthalides of the type we were interested in from the action of organomagnesium compounds on the mono diethylamine ester of phthalic acid **108** . The ester was prepared by reacting phthalic anhyride with diethylamine . When we treated this amide with o-tolylmagnesium bromide the reaction product was the unstable compound **109** . We were able to hydrolyse this carbinol to the desired phthalide **30** , albeit in very poor yields . The major product from the Grignard reaction was the mono-o-tolyl derivative **110** which we discovered reacted very sluggishly with the Grignard reagent and was obviously the limiting factor in the reaction .





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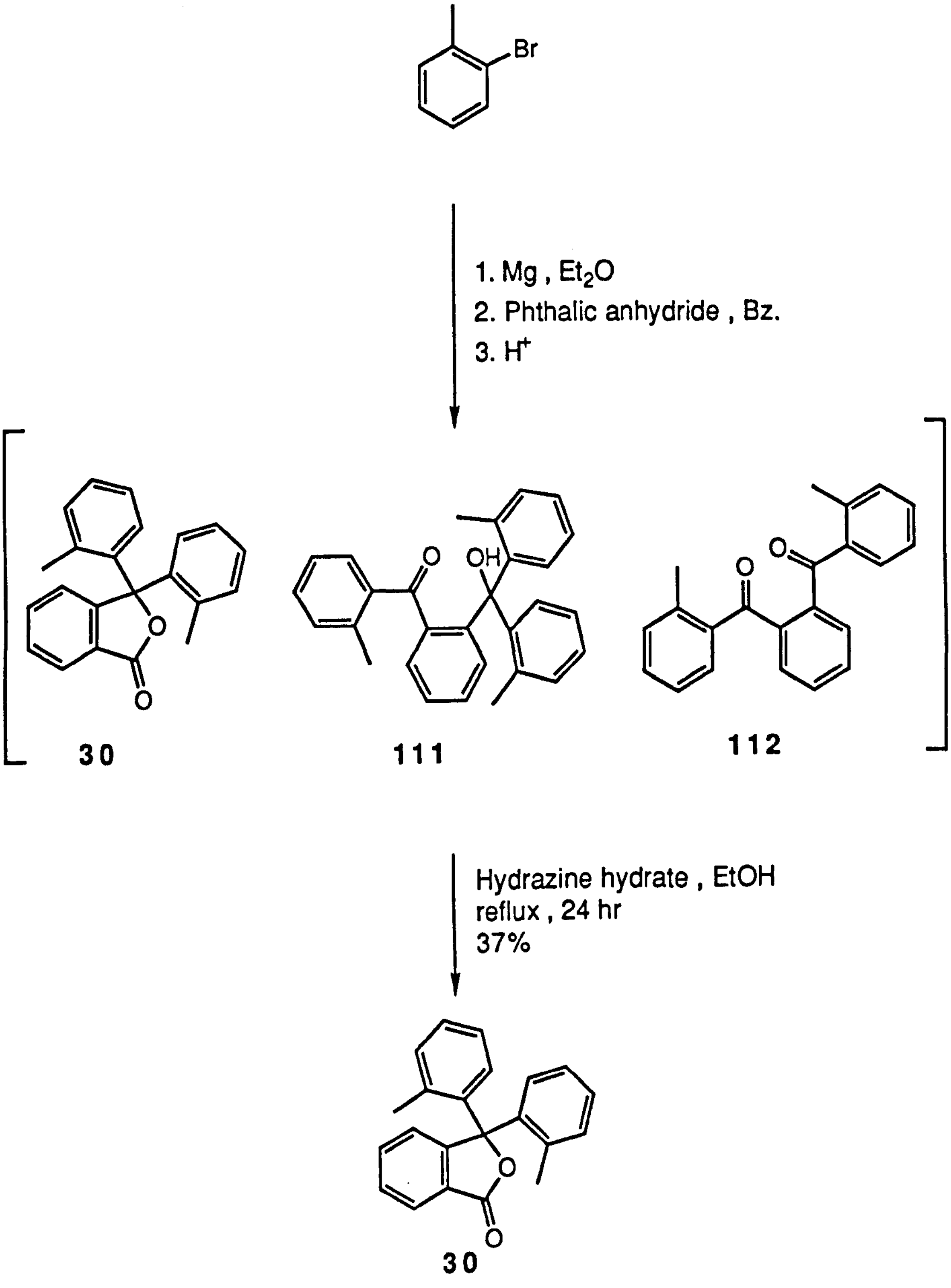
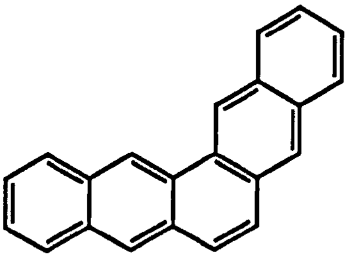
Scheme 2.3



Weiss and Korczyn [18] reported a synthesis of di-o-tolylphthalide **30** in the 1920's based on the Grignard reaction of o-tolylmagnesium bromide with phthalic anhydride . Clar [15] had reported that the major product from the reaction was 1,2-di-o-toluoylbenzene and so this had not appeared a promising route to our target molecule . However when we undertook the reaction we discovered that rather than 1,2-di-o-toluoylbenzene being the major product we obtained an approximately equal mixture of three compounds - the desired phthalide **30** , the carbinol **111** and the aforementioned di-o-toluoylbenzene **112** (Scheme 2.3) . These compounds were essentially co-polar and could not be separated by crystallisation . They could , with difficulty , be separated by column chromatography . This method of purification was suitable only when the reaction was performed on a small scale (less than 1 g) but another method was required for the large scale reactions required to provide a feedstock for the remainder of the synthesis . Ironically it was Clar [15b] who provided the answer . Although not using the method himself to make the phthalide **30** , preferring instead the oxidation route previously mentioned , he had in fact separated this fairly intractable mixture when synthesisng the pentaphene **113** . It turned out that the di-o-toluoylbenzene could be converted to the 1,4-di-o-tolylphthalazine **114** by treating with hydrazine hydrate in ethanol and that under these conditions it is possible to crystallise the phthalide preferentially from the mixture .



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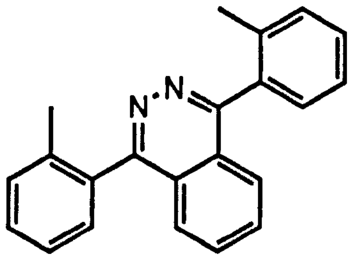
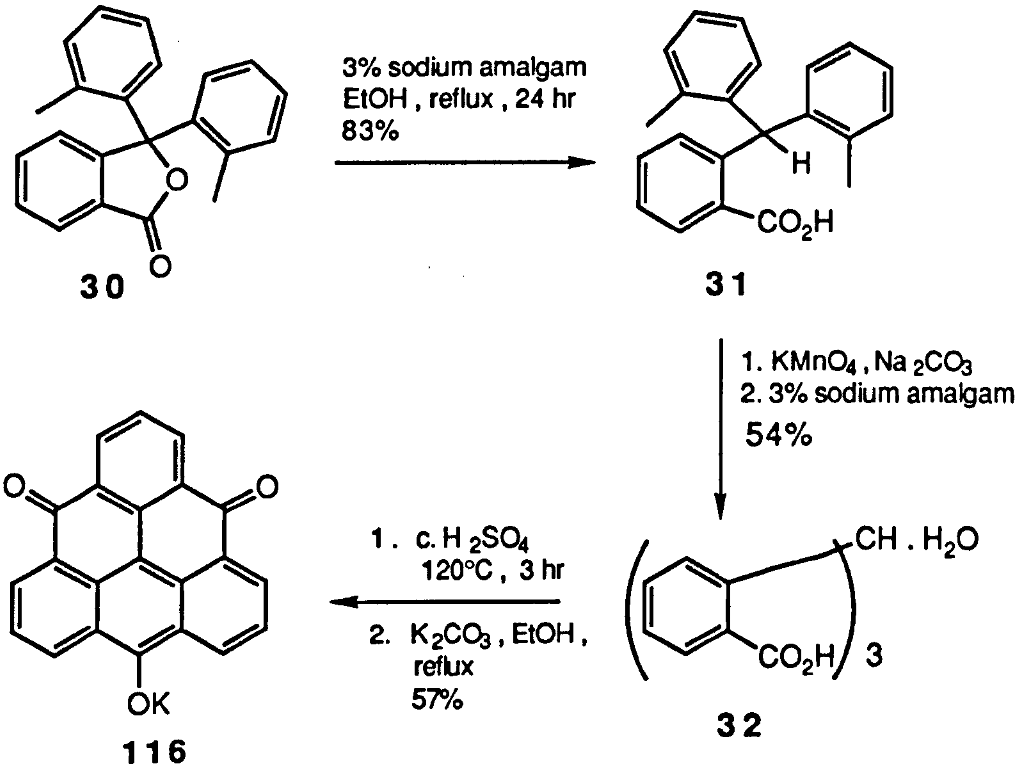


114

The opening of the phthalide lactone ring was trivial . Phthalide **30** was refluxed for twenty four hours with 3% sodium amalgam to give the mono-carboxylic acid **31** (Scheme 2.4) . The methyl groups were oxidised with alkaline potassium permanganate solution . The crude triacid **32** was treated with 3% sodium amalgam to reduce any phthalide that may have been formed during the oxidation . The triple intramolecular Friedel-Craft's cyclisation was achieved by treating the triacid with concentrated sulphuric acid at 110°C . The infra red spectrum of the crude hydroxytriangulenequinone **34** had two strong carbonyl absorbances , one at 1810 cm^{-1} and one at 1710 cm^{-1} . The absorbance at 1810 cm^{-1} was consistent with the presence of a partially cyclised lactone impurity and suggested that cyclisation occurs by a stepwise mechanism , with aromatisation of the ring system not occurring until after two of the rings have been formed . The hydroxytriangulenequinone **34** and the lactone impurity were found to be insoluble in organic solvents , including methanol , dimethylformamide and dimethyl sulphoxide , and so it was not possible to obtain an nmr spectrum of the mixture .

Scheme 2.4



The lactone impurity was removed by refluxing the mixture with potassium carbonate in ethanol . The desired triangulene derivative was

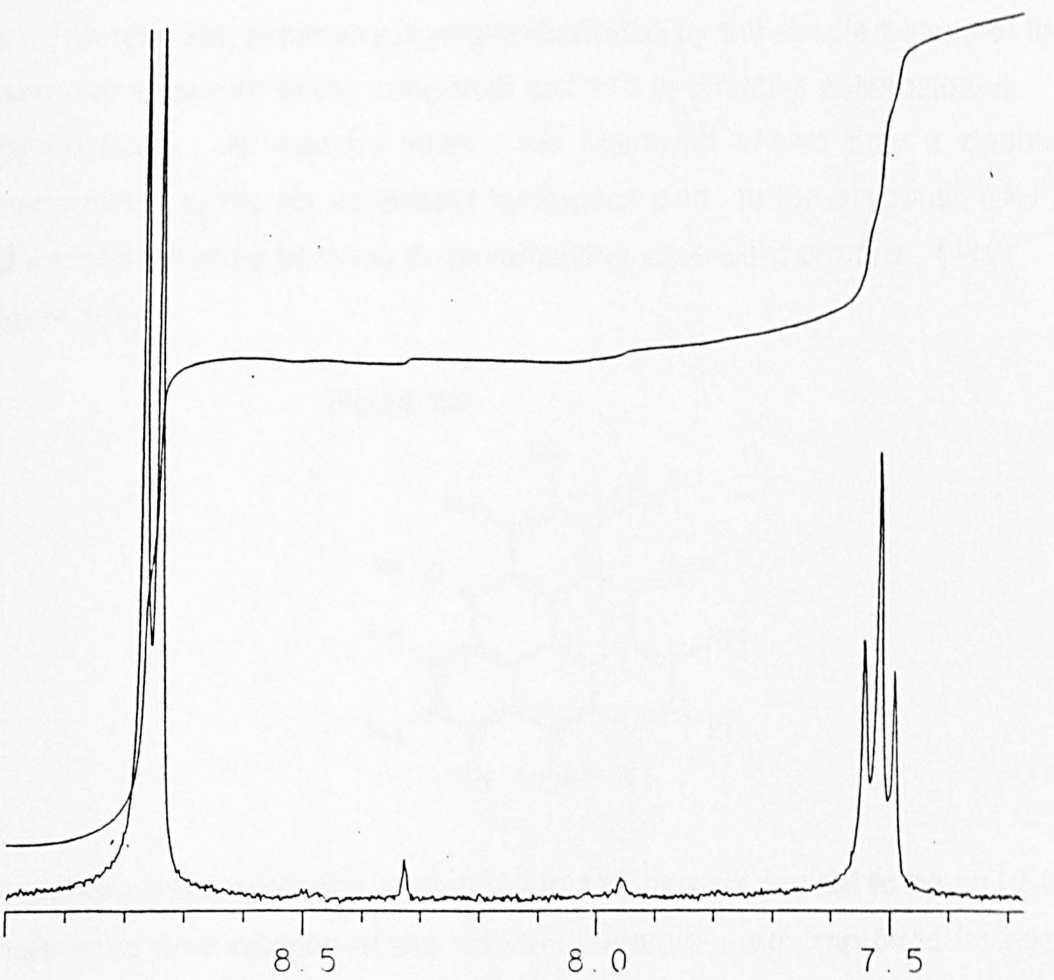
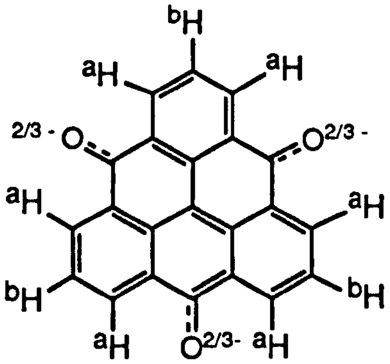


Figure 2.2 300 MHz proton nmr spectrum of potassoxytriangulenequinone **116**

isolated as the potassium salt **116** by filtration from aqueous ethanol ; the potassium salt of the impurity is soluble in this medium whereas the salt **116** is not . The potassium salt **116** itself is not soluble in non-polar organic solvents and has only a limited solubility in more polar solvents . Indeed the best sovent found to date has been dimethyl sulphoxide in which the potassium salt **116** has a solubility of 1mg per ml .

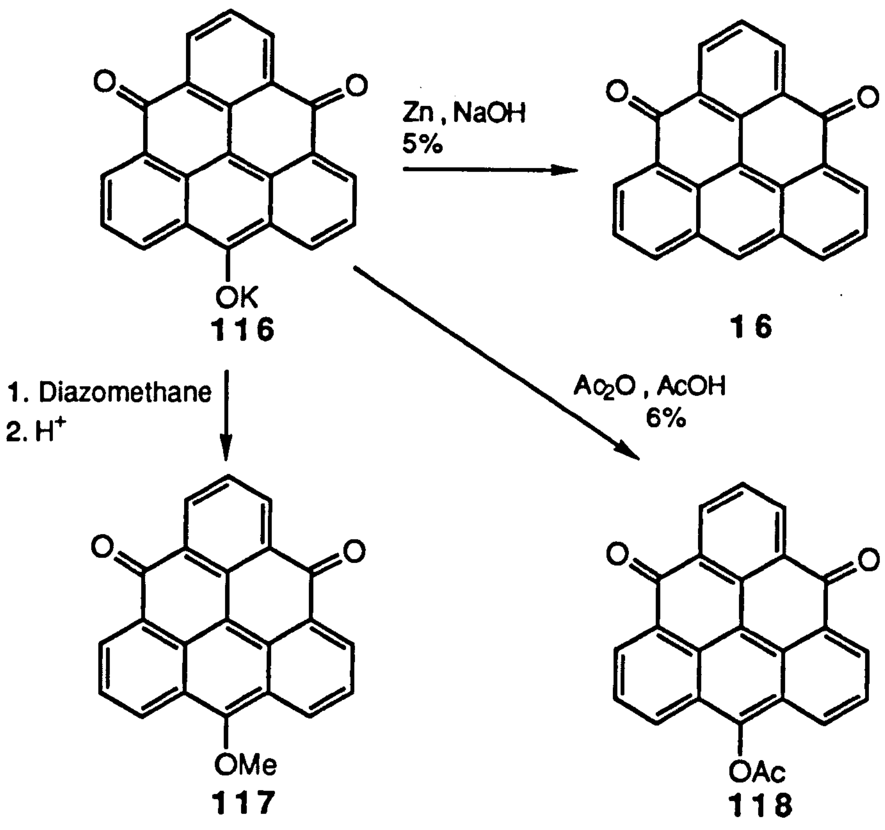
Although illustrated as having formally one phenolic hydroxyl function and two keto functions , it appears that in solution all three oxo - functions are equivalent , and the phenolic anionic charge is delocalised through the ring . The resulting symmetry is amply illustrated by the simple beauty of the proton nmr spectrum of the potassium salt **116** in dimethyl sulphoxide-d_6 (Figure 2.2) . As can be seen , the spectrum shows only a doublet corresponding to the six equivalent hydrogens *peri* to the oxygens , (^{a}H) and a triplet resulting from the three remaining equivalent protons , (^{b}H) (Figure 2.3) .

Figure 2.3



Although the synthesis of compound **116** had not proved to be as trivial as expected from reading of the relevant literature , with improved isolation procedures for the 3,3-di-o-tolylphthalide and the potassoxytriangulenequinone it was possible to prepare the aforementioned quinone in multi-gram quantities , pure and without need for chromatography or recrystallisation at any stage .

Potassoxytriangulenequinone **116** was reduced to triangulenequinone **16** using Clar's zinc - sodium hydroxide reduction [15a] . However the yields , at 5% , were very poor. The methoxy and acetoxy derivatives **117** and **118**



were obtained by reaction of the potassium salt with diazomethane and acetic anhydride respectively . Once again the yields were very poor . The apparent lack of reactivity towards these reagents may be explained by invoking the delocalisation referred to earlier. Since none of the oxygen positions ever carries the full anionic charge when the compound **116** is in solution the system is a very poor nucleophile . It is also worth noting that the yields of the methyl ether and acetyl ester were not helped by the apparent readiness of these esters to hydolyse in acidic , basic or neutral aprotic conditions . This tendency was especially , and most frustratingly , apparent when trying to purify the compounds by column chromatography or preparative thin layer chromatography , where the cherry red bands of the esters would be seen to deposit a blue compound behind them as they were eluted . The blue compound was assumed to be the parent hydroxytriangulenequinone **34** .

Because of the lack of reactivity of the potassium salt , we were unable to prepare sufficient quantities of any of these three compounds to enable any further synthetic work . However we were able to obtain 300 MHz proton nmr spectra for the compounds ; that of triangulenequinone **16** is shown in

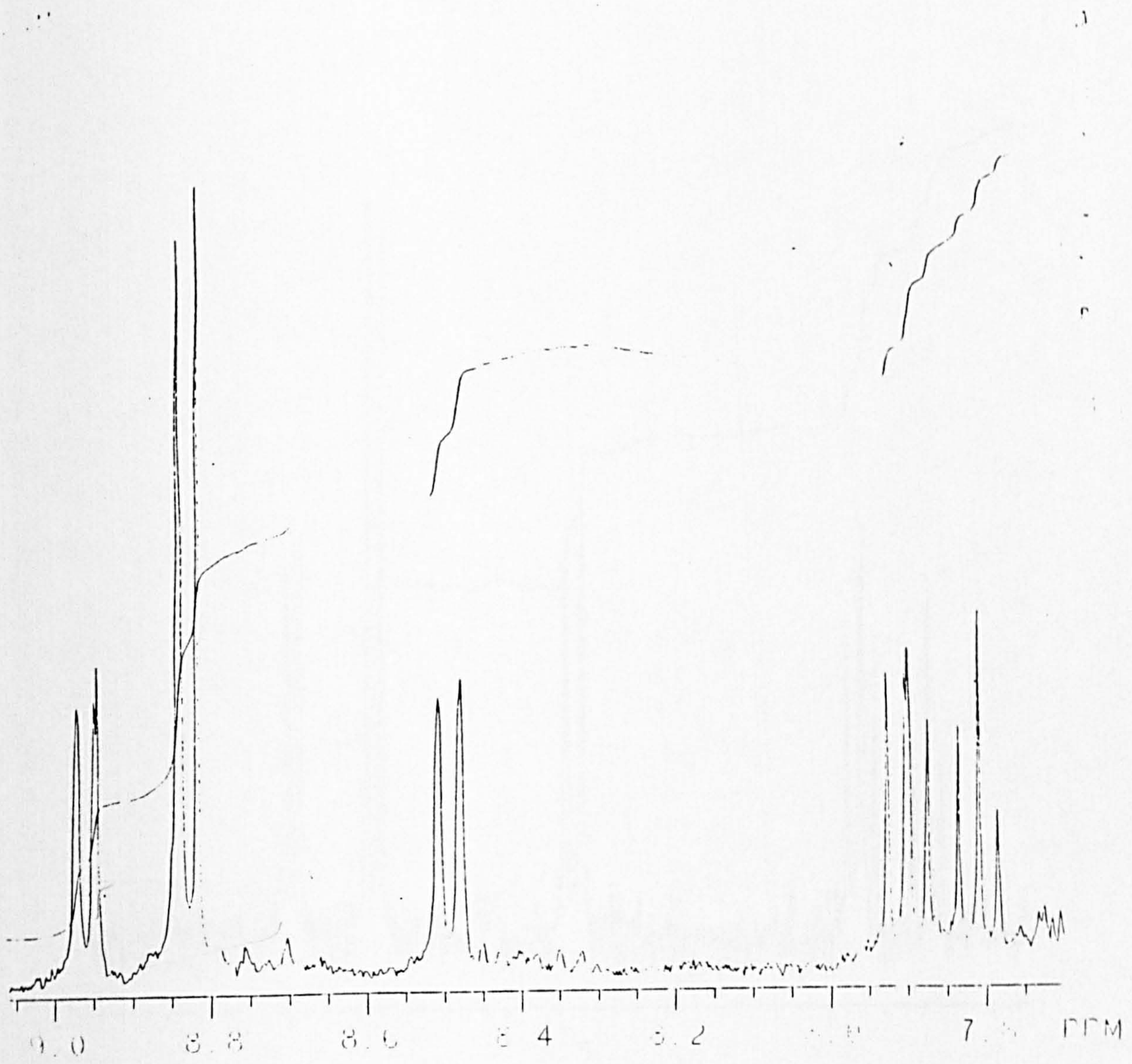


Figure 2.4 300 MHz proton nmr spectrum of triangulenequinone **16**

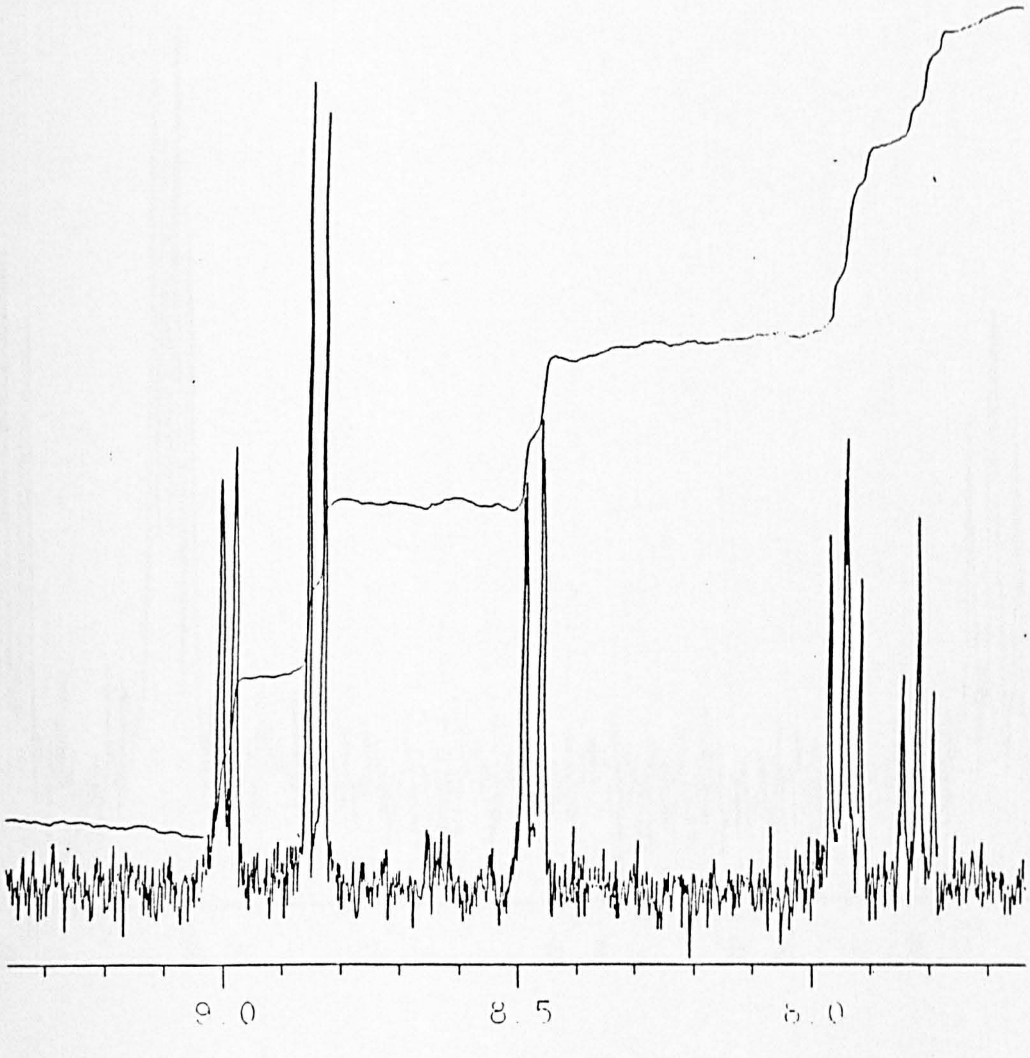


Figure 2.5a 300 MHz proton nmr spectrum of methoxytriangulenequinone **117** (aromatic region only)

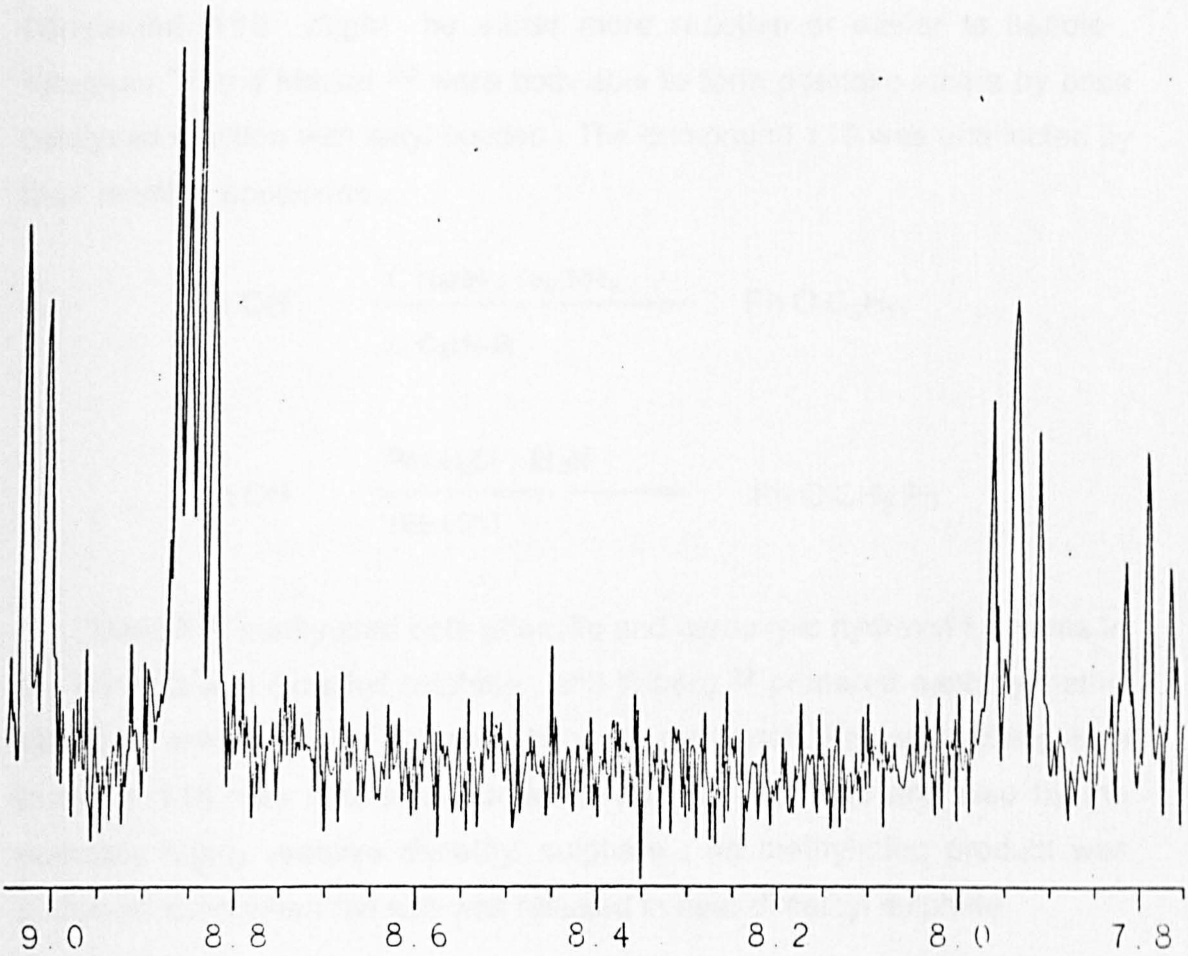


Figure 2.5b 300 MHz proton nmr spectrum of acetoxytriangulenequinone **118** (aromatic region only)

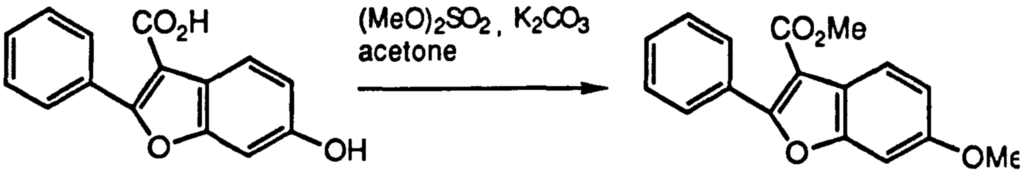
Figure 2.4 , and the aromatic regions of the methoxy and acetoxy derivatives may be compared with that of compound **16** by referring to Figure 2.5 .

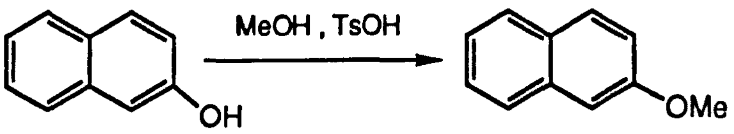
The lack of reactivity of the potassium salt **116** was a particular problem when it came to derivatisation . The hope was that derivatives of compound **116** might be either more reactive or easier to handle . Vaughan [19] and Merker [20] were both able to form phenolic ethers by base catalysed reaction with alkyl halides . The compound **116** was unaffected by their reaction conditions .

$$\mathrm{Ph\,OH} \xrightarrow[\text{2. } \mathrm{C_5H_{11}Br}]{\text{1. } \mathrm{NaNH_2\,/\,liq.\,NH_3}} \mathrm{Ph\,O\,C_5H_{11}}$$

$$\mathrm{Ph\,OH} \xrightarrow[\text{150-90°C}]{\mathrm{Ph\,CH_2Cl\ ,\ Et_3N}} \mathrm{Ph\,O\,CH_2\,Ph}$$

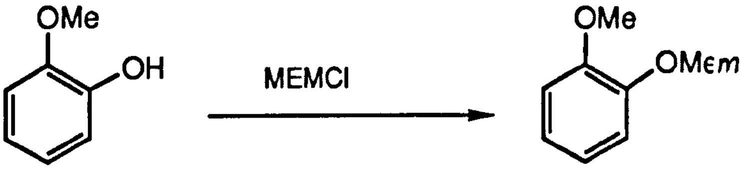
Bickoff [21] methylated both phenolic and carboxylic hydroxyl functions in the one pot with dimethyl sulphate , and Wiberg [22] prepared naphthylmethyl ethers by acid catalysed condensation with methanol . Potassoxytriangulene quinone **116** was unaffected under Wiberg's conditions and also by the normally highly reactive dimethyl sulphate ; no methylation product was observed even when the salt was refluxed in neat dimethyl sulphate .



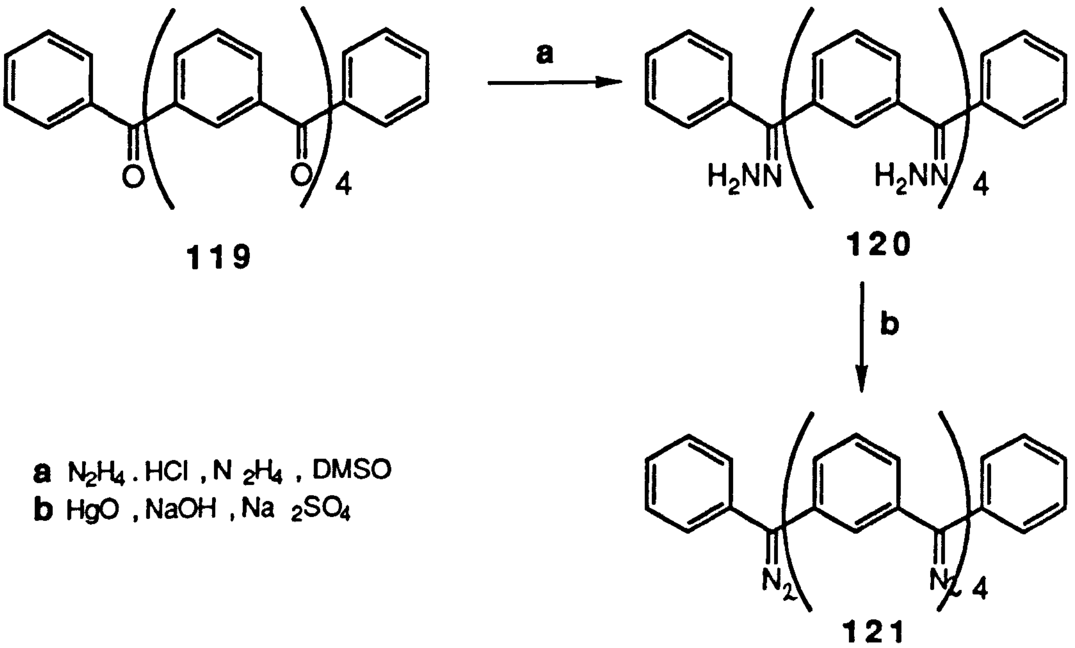


Olah [23] reported the reduction of alcohols to alkanes by the action of iodotrimethylsilane and zinc in a one pot procedure while Corey [24] reported the protection of hydroxyl functions with methoxyethoxymethoxy chloride (MEMCl) . Sadly , we were unable to involve compound **116** in either of these two reactions .

$$ROH \xrightarrow[I_2]{Me_3SiCH_2CHCH_2} R\,O\,SiMe_3 \xrightarrow[2.\ Zn\ ,\ AcOH]{1.\ Me_3SiCl\ ,\ NaI} R\,H$$



As part of their programme for obtaining purely organic magnets Itoh and Iwamura [28] prepared the poyketone **119** . Conversion of this compound to the blood-red penta-kis-diazo compound **121** was achieved by heating the ketone **119** in a solution of hydrazine hydrate and hydrazine in dimethyl sulphoxide followed by treatment with yellow mercuric oxide and sodium sulphate .



119

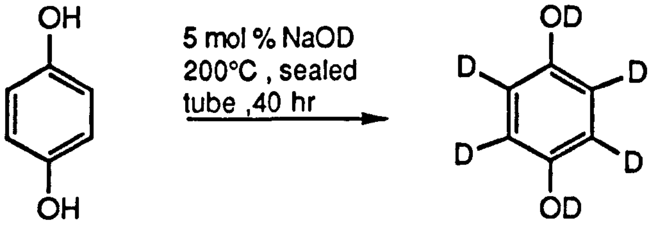
120

121

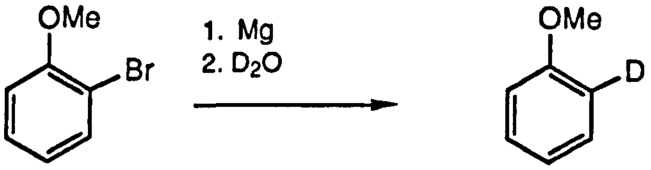
a $N_2H_4 . HCl$, N_2H_4 , DMSO
b HgO , NaOH , Na_2SO_4

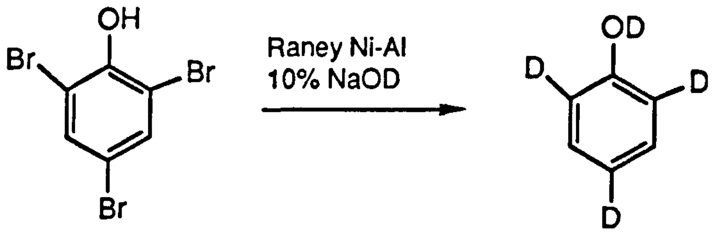
When we subjected the potassium salt **116** to these conditions we observed a dramatic shift to longer wavelength in the absorption spectrum of the reaction mixture . The normally intense blue was replaced by a muddy red , possibly indicative of formation of the diazo derivative . Unfortunately we were unable to isolate any such derivative from the large volumes of dimethyl sulphoxide required to dissolve the starting material .

Potassoxytriangulenequinone **116** was used directly in some ESR studies , as will be discussed in Chapter 3 . Some encouraging results on this front prompted the call for either *per* - deuterated or ring substituted derivatives of **116** . Hallas [25] reported a procedure in which the *per* - deuteration of phenols was achieved by sodium deuteroxide at high temperatures and pressures in a sealed tube . Unfortunately no deuterium incorporation was observed when compound **116** was treated in this manner .

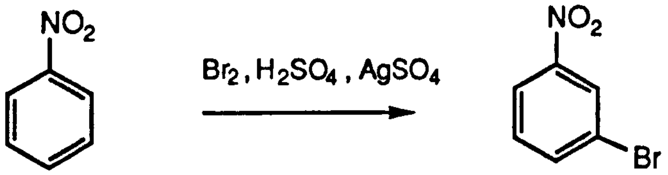


Rowell [26] prepared deuterated aromatic rings by quenching the appropriate aromatic magnesium bromide with deuterium oxide , whilst Tashiro [27] reported the reduction of aromatic halides to the corresponding deuterium compounds with deuterated Raney Nickel .



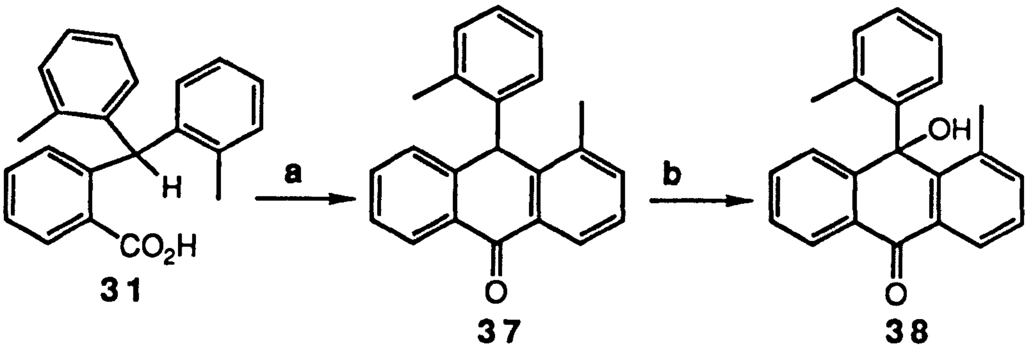


To attempt these reductions required the halogenation of the aromatic ring system of potassium salt **116** . The insolubility of compound **116** in organic solvents ruled out some of the more common methods . However Derbyshire [29] did report aromatic halogenation in the one solvent that potassoxytriangulenequinone will dissolve in - concentrated sulphuric acid ! Derbyshire treated nitrobenzene with bromine in a silver sulphate - sulphuric acid medium but unfortunately we were neither able to either brominate nor chlorinate our ring system under these conditions .



Treatment of compound **116** with potassium carbonate in refluxing deuterium oxide , or with refluxing sodium deuteroxide did not affect the molecule in any way . Proton nmr spectroscopy indicated that there was no proton - deuterium exchange under these conditions , even of the protons *peri* to the oxygens which might have been regarded as 'acidic' . Treatment of the potassium salt with sulphuric acid-d_2 did give some incorporation but never greater than 33 % . Examination of the proton nmr spectra of the products of these reactions indicated that deuteration had been exclusively at the β-positions rather than at the α-positions *peri* to the oxygen functions which were more critical to the ESR experiments .

The intramolecular Friedel-Craft's cyclisation of the acid **31** in a zinc chloride - sodium chloride melt gave the anthrone derivative **37** in good yields . Oxidation of the 9-position with dilute nitric acid gave the hydroxy derivative **38** , again in good yields . Clar oxidised the methyl substituents of anthrone **38** with nitric acid in a sealed tube at elevated temperatures . However we were unwilling to risk such a precarious procedure and , though we tried other oxidation methods , we were unable to find one that produced the desired result .



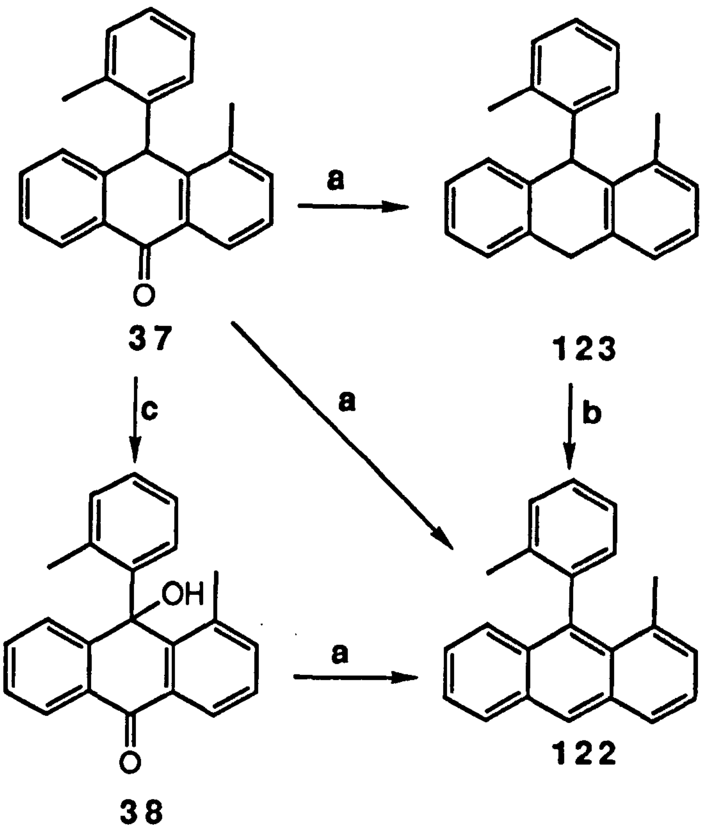
a $ZnCl_2$-NaCl ; **b** 20% HNO_3 , boil , 40 hr

The reduction of anthrones to anthracenes is a well documented procedure[30] and offered the prospect of an alternative route to the quinone **16** and to the tetrahydro derivative **28** . Accordingly the anthrone **37** was treated with lithium aluminium hydride and then refluxed in the presence of p-toluene sulphonic acid . The anthracene **122** was isolated in only 8% yield . The major product was found to be the dihydroanthracene **123** . This latter product could be dehydrogenated with dichlorodicyanoquinone (DDQ) but gave the desired anthracene in only 25% yield .

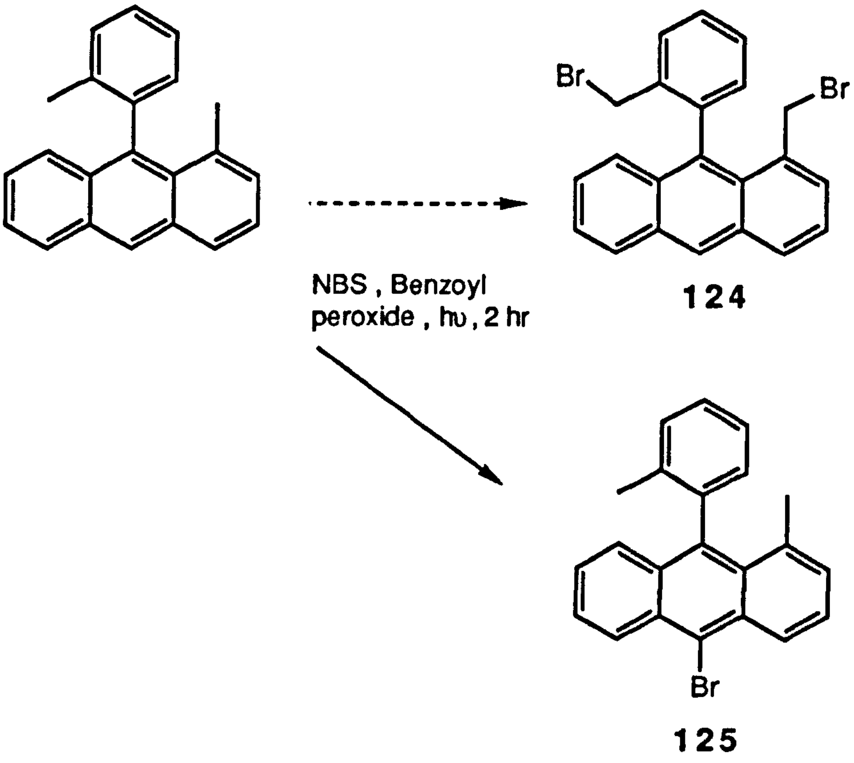
The reduction of the hydroxyanthrone **38** with lithium aluminium hydride afforded a single product , the anthracene **122** in 50% yield . Unfortunately time and experimental constraints prevented the preparation of this anthracene derivative in sufficiently large quantities to allow a thorough investigation of the oxidation of the methyl substituents , and so we were unable to prepare quinone **16** via this route .

It had been hoped that mild benzylic bromination with N-bromosuccinamide and benzoyl peroxide would allow the benzylic bromination of the methyl groups of the anthracene **122** without affecting the active 9-position of the anthracene nucleus , thus affording a route through to tetrahydrotriangulene **28** . When compound **122** was treated with N-bromosuccinamide even this reagent attacked the 9-position first , to give the bromo derivative **125** . Further treatment of **125** with this reagent did not lead to any benzylic bromination products .

Clar[31] patented the syntheses of the two triangulene dicarboxylic acid



a i) LiAlH$_4$, Et$_2$O ; ii) H$^+$; iii) TsOH , Et$_2$O
b DDQ ; **c** 20% HNO$_3$, boil , 40 hr



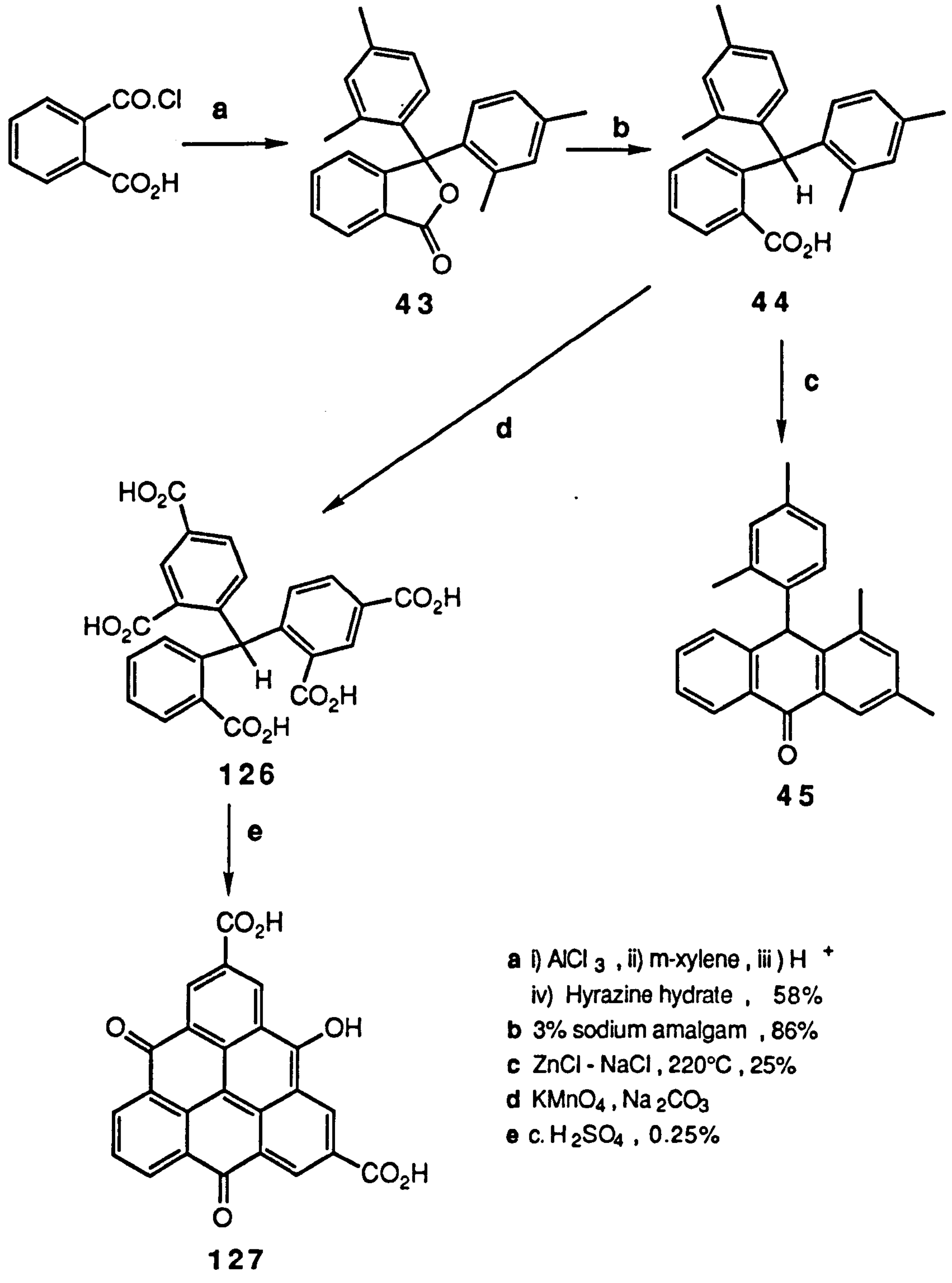
derivatives **48** and **54** in the early 1950's . His interest in these two molecules was as intermediates for mordant wool dyes , a not unusual proposition considering the intense chromaphores exhibited by triangulene quinone based molecules . However our interest focused more sharply on the need for potassoxytriangulenequinone derivatives with less symmetry than the parent **116** (see Chapter 3) . Accordingly an attempt was made to prepare both these dicarboxylic acids .

An equimolar complex of aluminium chloride and *sym* - phthaloyl chloride , prepared by the method of Kyrides [32] , was dissolved in dichloromethane and then added to m-xylene . The product of the reaction , 3,3-di-m-xylylphthalide **43** (Scheme 2.5) was isolated in the same manner as 3,3-di-o-tolylphthalide **30** . The lactone ring was opened using 3% sodium amalgam to give the acid **44** . Intramolecular cyclisation in a zinc chloride - sodium chloride melt gave the anthrone derivative **45** . Clar had reported the oxidation of compound **45** to the tetracarboxylic acid derivative **46** but we were unable to repeat his results . However the carboxylic acid **44** was oxidised in the manner of Weiss and Korczyn [18] to the pent-acid **126** , which in turn was cyclised with sulphuric acid to give the hydroxytriangulene derivative **127** , albeit in poor yields .

The inherent stability of potassoxytriangulene was discussed earlier and explained by invoking delocalisation of the anionic charge around the ring system . In the case of the dicarboxylic acid **127** one can formally involve the carboxylic acid functions in resonance structures , the presence of these functions destabilises the ring system . Indeed compound **127** proved so unstable that what little material we managed to isolate in a pure state decomposed during the attempt to observe its carbon nmr spectrum in dimethyl sulphoxide - d_6 . However we were able to observe the proton nmr spectrum which is illustrated in Figure 2.6 .

A complex of *sym* - phthaloyl chloride and aluminium chloride was added to p-xylene to give the 3,3-di-p-xylylphthalide **49** (Scheme 2.6) . Once again the lactone ring was opened with sodium amalgam to give the acid **50**. The anthrone **51** was prepared in the usual manner from a zinc

Scheme 2.5



a i) $AlCl_3$, ii) m-xylene , iii) H^+
iv) Hyrazine hydrate , 58%
b 3% sodium amalgam , 86%
c ZnCl - NaCl , 220°C , 25%
d $KMnO_4$, Na_2CO_3
e c. H_2SO_4 , 0.25%

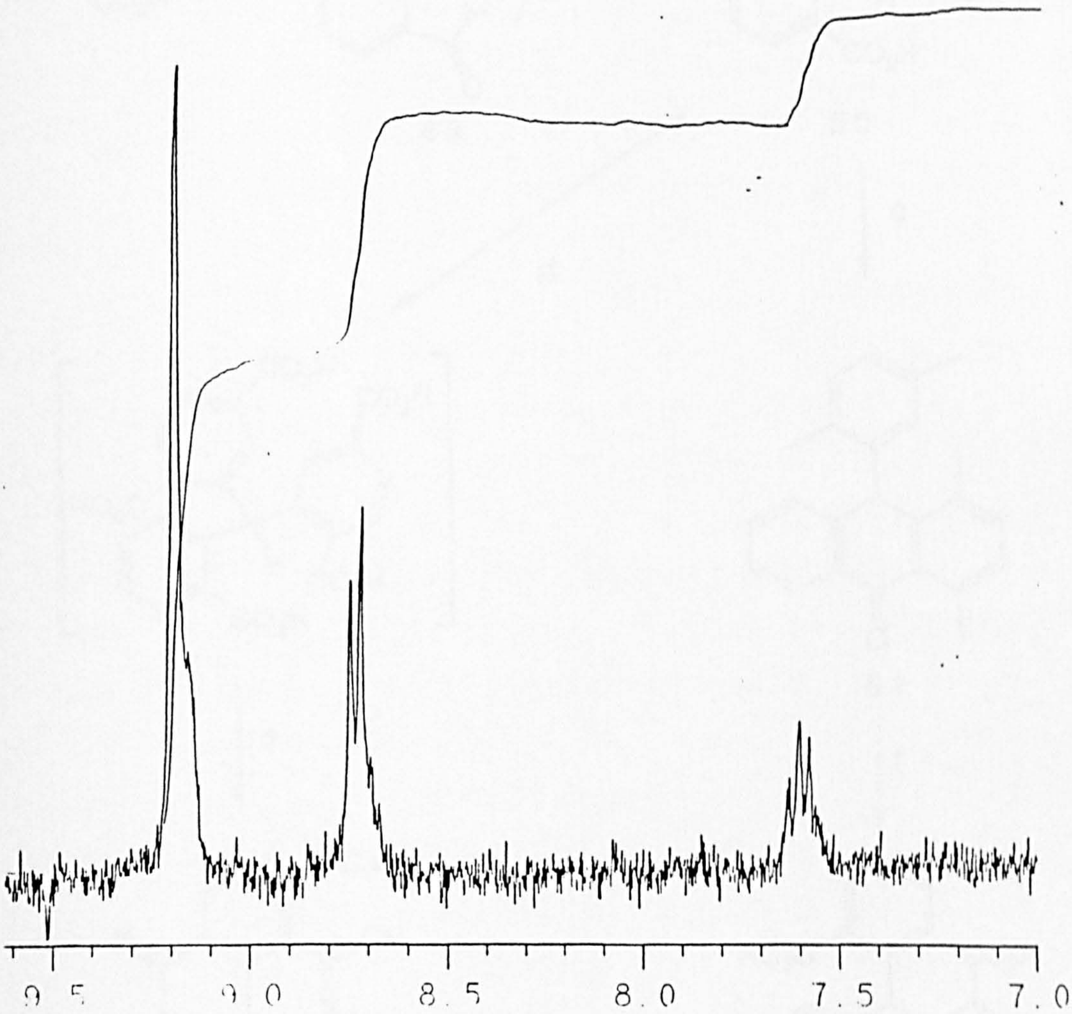
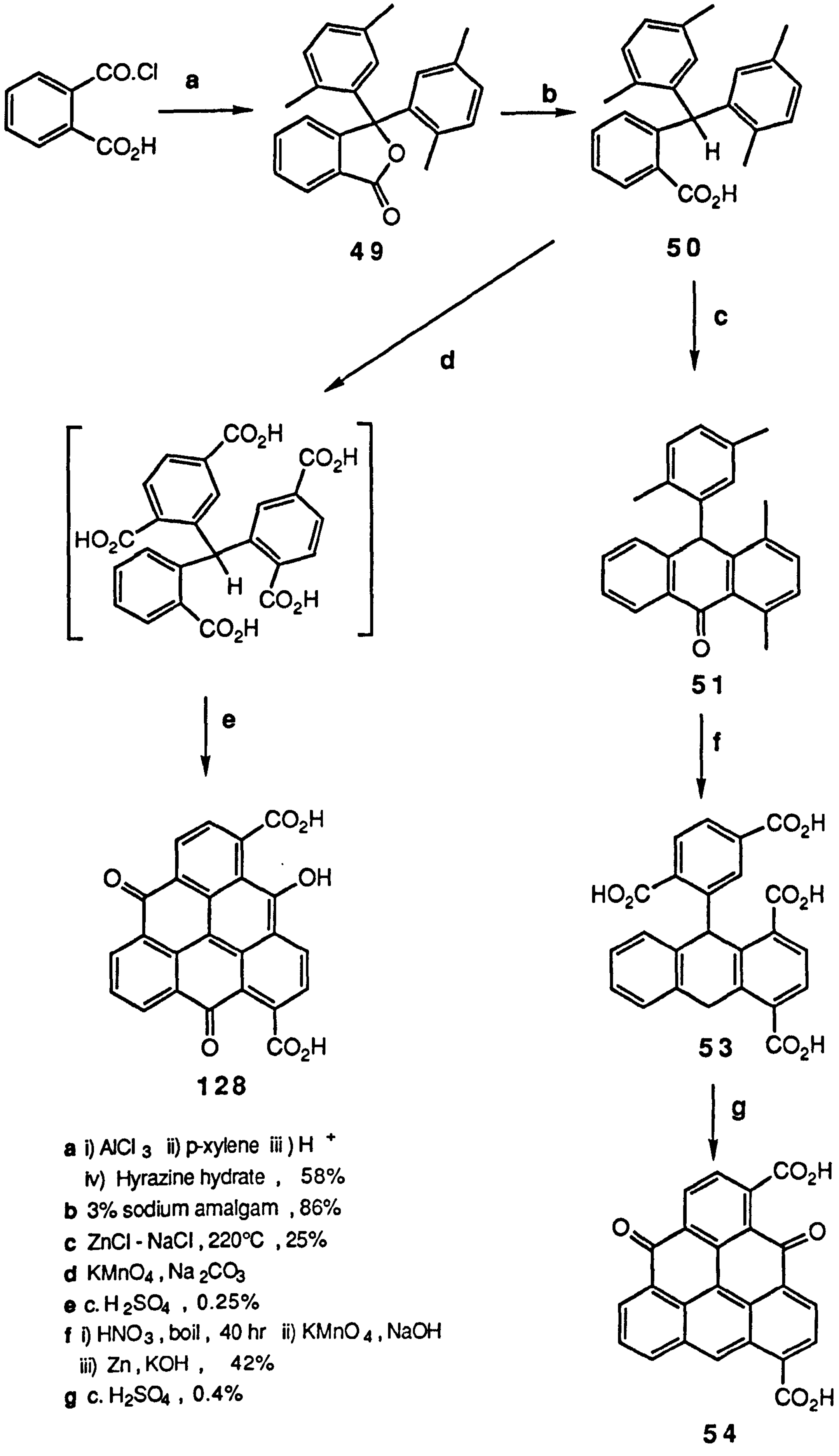


Figure 2.6 300 MHz proton nmr spectrum of the tri-oxo-triangulene-2,6-dicarboxylic acid derivative **127**

Scheme 2.6



a i) $AlCl_3$ ii) p-xylene iii) H^+
iv) Hyrazine hydrate , 58%
b 3% sodium amalgam , 86%
c ZnCl - NaCl , 220°C , 25%
d $KMnO_4$, Na_2CO_3
e c. H_2SO_4 , 0.25%
f i) HNO_3 , boil , 40 hr ii) $KMnO_4$, NaOH
iii) Zn , KOH , 42%
g c. H_2SO_4 , 0.4%

chloride - sodium chloride melt . Oxidation with nitric acid , followed by reduction in a refluxing mixture of zinc and sodium hydroxide gave the tetracarboxylic acid **53** . It is interesting to note the effect the extra two methyl groups in this compound have on the ease of oxidation of the said methyl groups , as it may be recalled that under the same conditions the dimethyl anthrone **37** was oxidised only to the 9-hydroxy derivative **38** . The triangulenequinone dicarboxylic acid derivative **54** was obtained in moderate yields by treatment of the tetra-acid **53** with sulphuric acid and its 300 MHz proton nmr spectrum is shown in Figure 2.7 .

Oxidation of the acid **50** by alkaline potassium permanganate gave a water soluble pent-acid , whose presence was identified by infra red and nmr spectroscopy of the residue remaining after complete evaporation of the aqueous filtrate from the oxidation . This residue was stirred in sulphuric acid whereupon the intense blue colour typical of the hydroxytriangulenequinone cyclisation reactions developed . The dicarboxylic acid **128** was isolated from the reaction mixture as a blue-black solid . As with the parent compound **34** , the acid was contaminated with a partially cyclised lactone impurity . The acid **128** was purified by ion exchange chromatography but yields were poor . Unfortunately we were unable to isolate the compound in sufficient quantities to allow further synthetic work but we were able to record the proton nmr spectrum and this is shown in Figure 2.8 . The compound does not appear to suffer the instability problems associated with the isomeric **127** and was sufficiently soluble as the free acid not to need further derivatisation .

2.2.2 Synthetic Approaches to Dibenzpentacenequinone

The first step in this synthesis was the preparation of 4,6-dichloro-1,3-dimethylbenzene **129** by the method of Claus and Burstert [33] . The desired isomer was isolated from the mixture of chlorinated products by fractional crystallisation . At first glance the oxidation of the aromatic methyl groups appeared trivial but the steam volatility of compound **129** ruled out many of the more common oxidation techniques . Claus and Burstert converted the

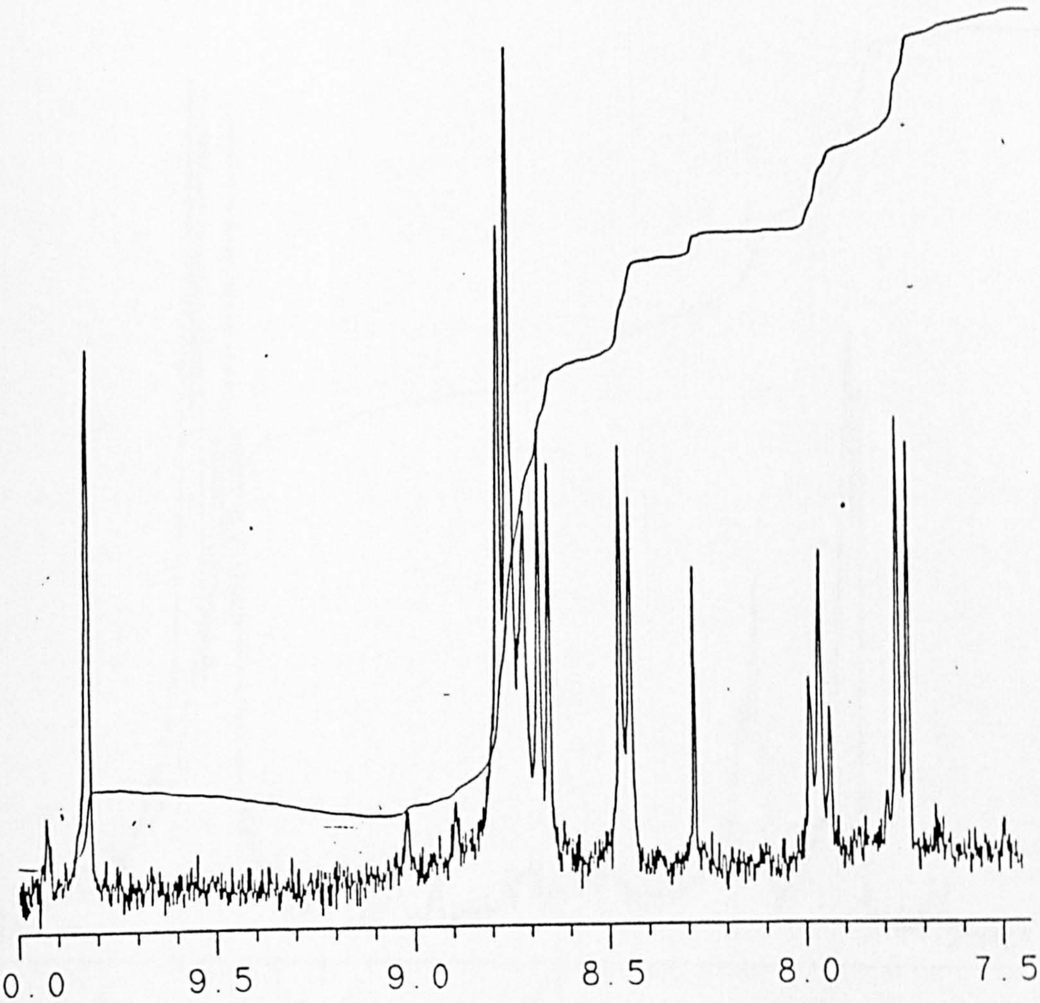


Figure 2.7 300 MHz proton nmr spectrum of the triangulenequinone-3,7-dicarboxylic acid derivative **54**

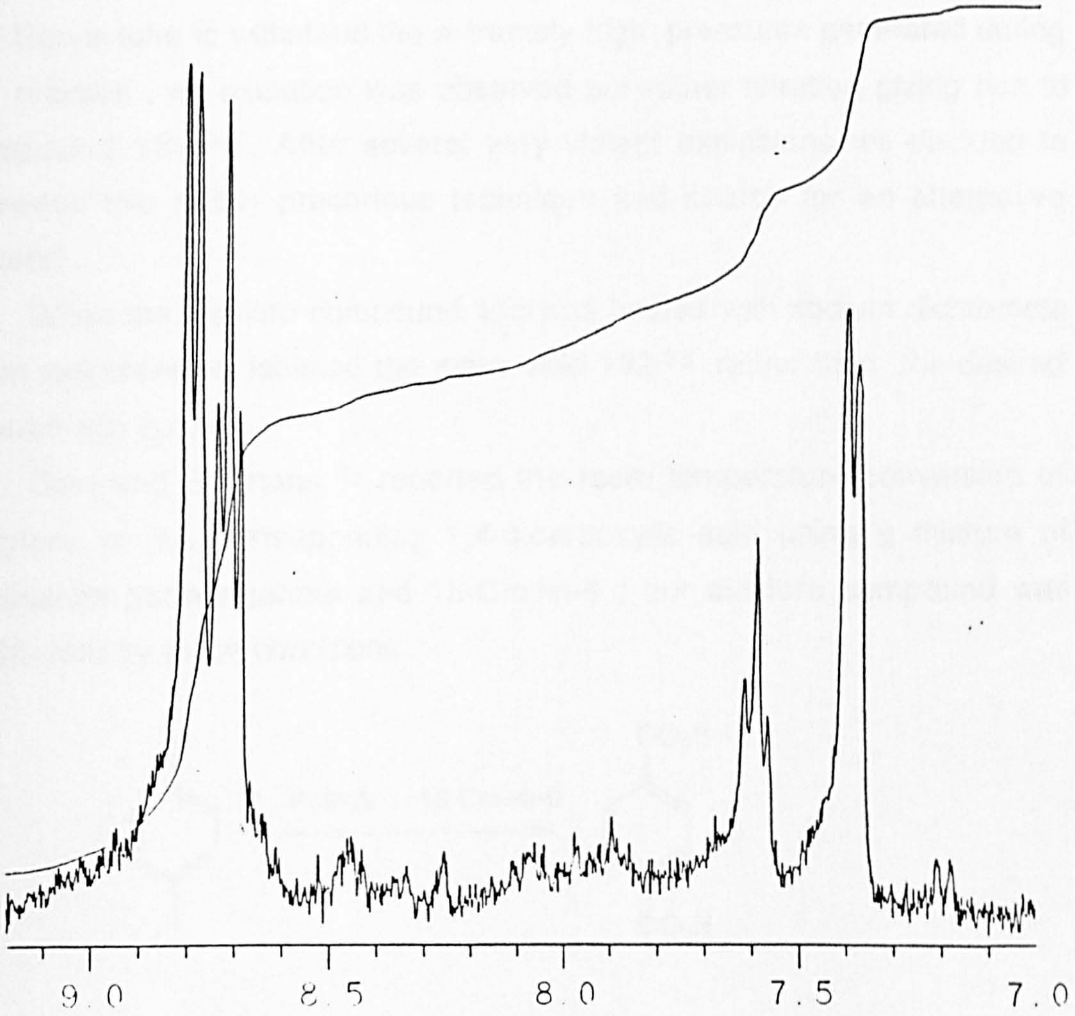
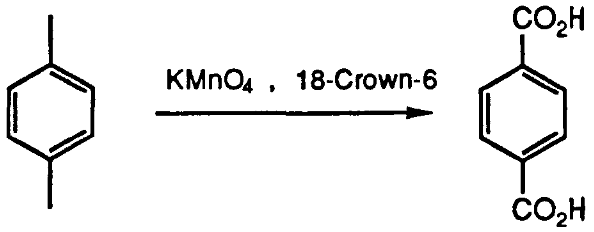


Figure 2.8 300 MHz proton nmr spectrum of the tri-oxo-triangulene-3,7-dicarboxylic acid derivative **128**

dichloro compound to its dicarboxylic acid derivative by heating with nitric acid in a sealed tube at 220°C for 10 hours . When compound **129** was heated with nitric acid under these conditions and we were able to prepare our Carius tube to withstand the extremely high pressures generated during the reaction , no oxidation was observed but rather nitration giving rise to compound **131** [34] . After several very violent explosions we decided to abandon this rather precarious technique and search for an alternative method .

When the dichloro compound 130 was heated with sodium dichromate in an autoclave we isolated the mono acid **132** [33] rather than the desired dicarboxylic acid .

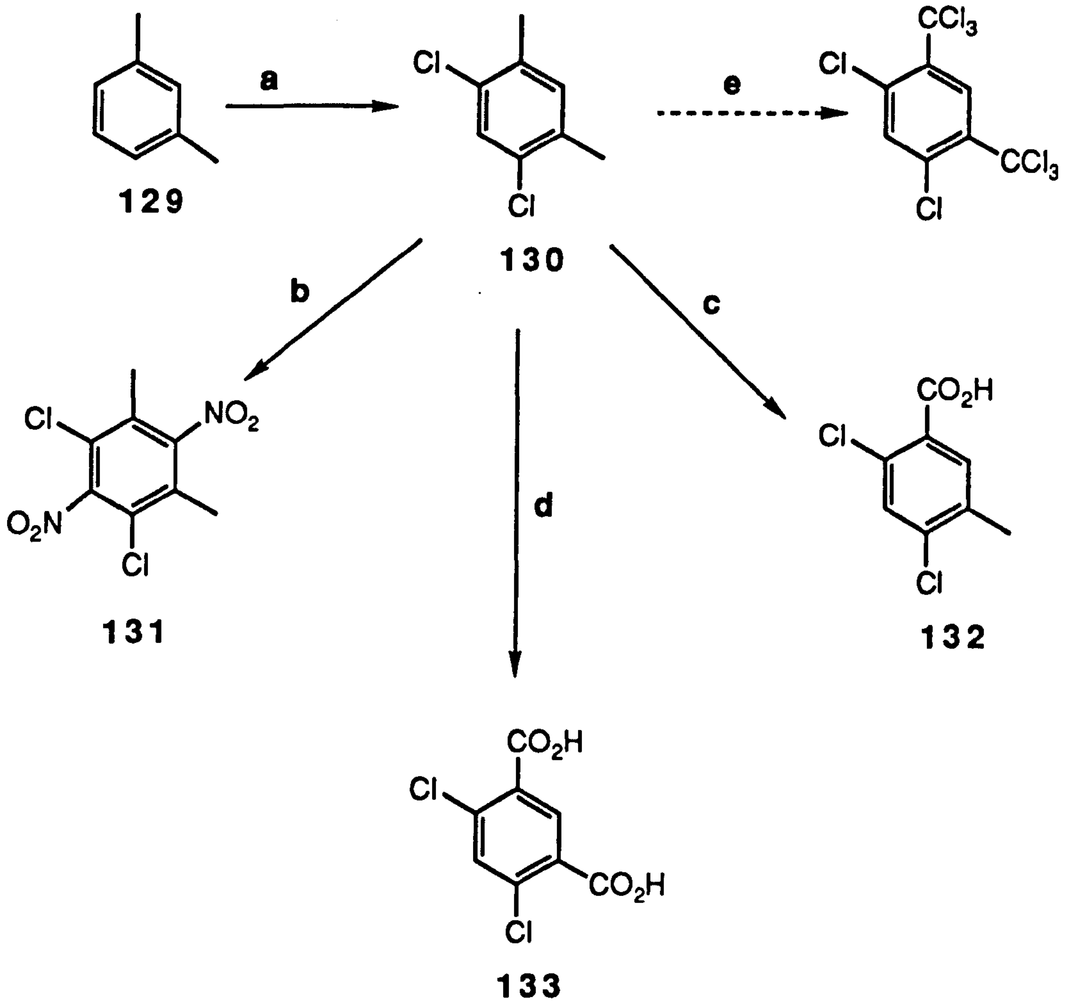
Sam and Simmons [35] reported the room temperature conversion of p-xylene to the corresponding 1,4-dicarboxylic acid using a mixture of potassium permanganate and 18-Crown-6 ; our dichloro compound was unaffected by these conditions .



Benzylic halogenation is also a well documented procedure and there have been a number of reports of the conversion of such ω-halogenated aromatic compounds to the corresponding carboxylic acids [36] . However when our chlorinated m-xylene was subjected to the most popular conditions , chlorine gas in the presence of ultra-violet light , we found that an inseparable mixture of ω-chlorinated products was formed , but unfortunately none of the desired hexa-chloro compound .

The diacid **133** was finally prepared by a variation of the nitric acid oxidation theme first encountered by the author when working in industry in the Research Department of Hickson & Welch Ltd. , and dubbed the "dropping nitric acid " technique by the members of that department . In this technique nitric acid was dropped very slowly and carefully onto a solution

Scheme 2.7



a Cl_2 gas, 0°C, 5 days, 10%
b Nitric acid, 210°C, 3 hr, 14%
c $Na_2Cr_2O_7$, water, 210°C, 18 hr, 7%
d Dropping nitric acid, 50%
e Cl_2 gas, $h\nu$

of compound **130** in nitrobenzene at 160°C for 5 days at which point the oxidation was essentially complete. In nitric acid oxidations there will always be two competing processes ; nitration via electrophilic attack of the nitronium ion or oxidation via the free radical mechanism shown in Figure 2.9 . It has been argued that in the dropping nitric acid process , reaction can only take place at the interface between the landing drop and the stirred solution and that this favours the free radical mechanism because the reaction is time limited , since at that temperature most of the droplet is instantaneously vapourised .

Figure 2.9 Proposed free radical mechanism for oxidations of aromatic methyl groups with nitric acid in the liquid phase [37] .

$$\mathrm{HNO_3} + \mathrm{HNO_2} \rightleftharpoons 2\,\mathrm{\dot{N}O_2} + \mathrm{H_2O}$$

$$\mathrm{\dot{N}O_2} + \mathrm{H^+} \rightleftharpoons \mathrm{HNO_2^{+\bullet}}$$

$$\mathrm{PhCH_3} + \mathrm{HNO_2^{+\bullet}} \longrightarrow \mathrm{Ph\dot{C}H_2} + \mathrm{H_2NO_2^+}$$

$$\mathrm{Ph\dot{C}H_2} + \mathrm{\dot{N}O_2} \longrightarrow \mathrm{PhCH_2ONO}$$

$$\mathrm{PhCH_2ONO} + \mathrm{H_2O} \longrightarrow \mathrm{PhCH_2OH} + \mathrm{HNO_2}$$

$$\mathrm{PhCH_2OH} + \mathrm{HNO_2^{+\bullet}} \longrightarrow \mathrm{Ph\dot{C}HOH} + \mathrm{H_2NO_2^+}$$

$$\mathrm{Ph\dot{C}HOH} + \mathrm{\dot{N}O_2} \longrightarrow \mathrm{PhCH(OH)ONO}$$

$$\mathrm{PhCH(OH)ONO} \longrightarrow \mathrm{PhCHO} + \mathrm{HNO_2}$$

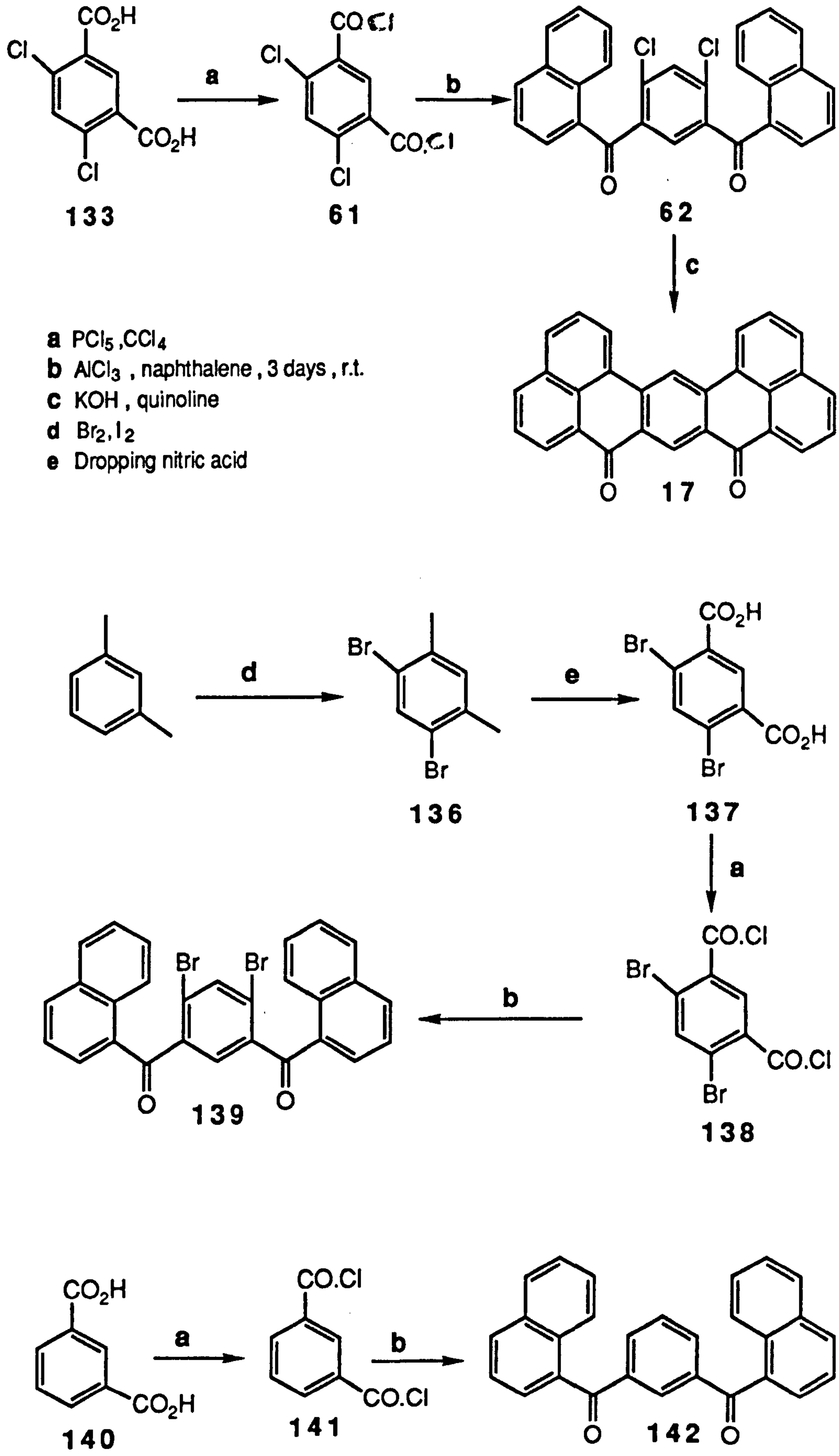
$$\mathrm{PhCHO} + \mathrm{HNO_2^{+\bullet}} \longrightarrow \mathrm{Ph\dot{C}O} + \mathrm{H_2NO_2^+}$$

$$\mathrm{Ph\dot{C}O} + \mathrm{\dot{N}O_2} \longrightarrow \mathrm{PhCO.ONO}$$

$$\mathrm{PhCO.ONO} \longrightarrow \mathrm{PhCO_2H} + \mathrm{HNO_2}$$

The unstable diacid chloride **61** was prepared by reacting the diacid **133** with phosphorous pentachloride and was used without delay in the Friedel-Craft's condensation with naphthalene to form the dichlorodinaphthoyl derivative **62** . We discovered that our dinaphthoyl derivative **62** , although satisfying spectral criteria , did not recrystallise from the solvent system stated by Clar and had a much lower melting point . We were in fact unable to recrystallise the compound and it was used in the cyclisation reactions without further purification . The dibromodinaphthoyl benzene **139** and dinaphthoylbenzene **142** were prepared in a similar

Scheme 2.8



a PCl_5,CCl_4

b $AlCl_3$, naphthalene , 3 days , r.t.

c KOH , quinoline

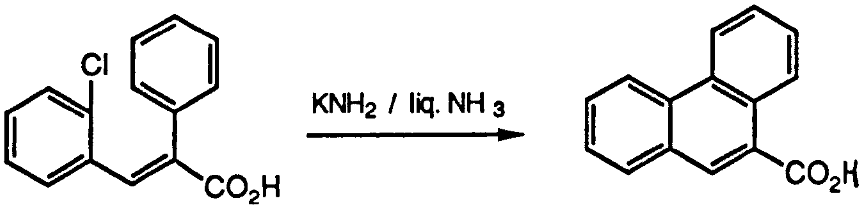
d Br_2,I_2

e Dropping nitric acid

manner from m-xylene and isophthalic acid respectively (Scheme 2.8).

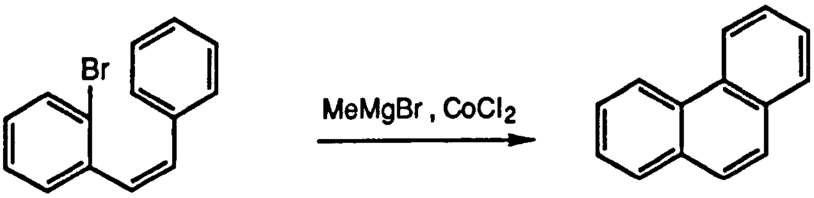
Clar's reported cyclisation of compound **62** [4] was repeated with some diffficulty ; the reaction did not proceed in the manner described by Clar and it was only after much repeated laborious chromatography that we were able to isolate a small amount of the acid and air sensitive diketone **17** .

The poor yields and the laborious procedures involved in the isolation of compound **17** after cyclisation by Clar's method encouraged us to look for alternative cyclisation procedures . Kessar [38] had reported the cyclisation of system **134** using potassium amide in liquid ammonia . Although we treated all three derivatives with potassium amide under Kessar's conditions we were unable to observe any of the desired cyclisation product , either by analytical tlc or nmr spectroscopy .



134

Tiecco [39] and Davies [40] both reported cobalt chloride mediated cyclisations of aromatic bromides such as **135** treated with methyl magnesium bromide . No cyclisation product was observed when our dinaphthoyl derivatives were treated in this manner .



135

Ruzicka [41] reported an improved version of the Scholl reaction in which 1,2-diphenylethane was cyclised by heating in the presence of aluminium chloride . Under these conditions our compounds quickly decomposed to a brown tar of indeterminate composition .

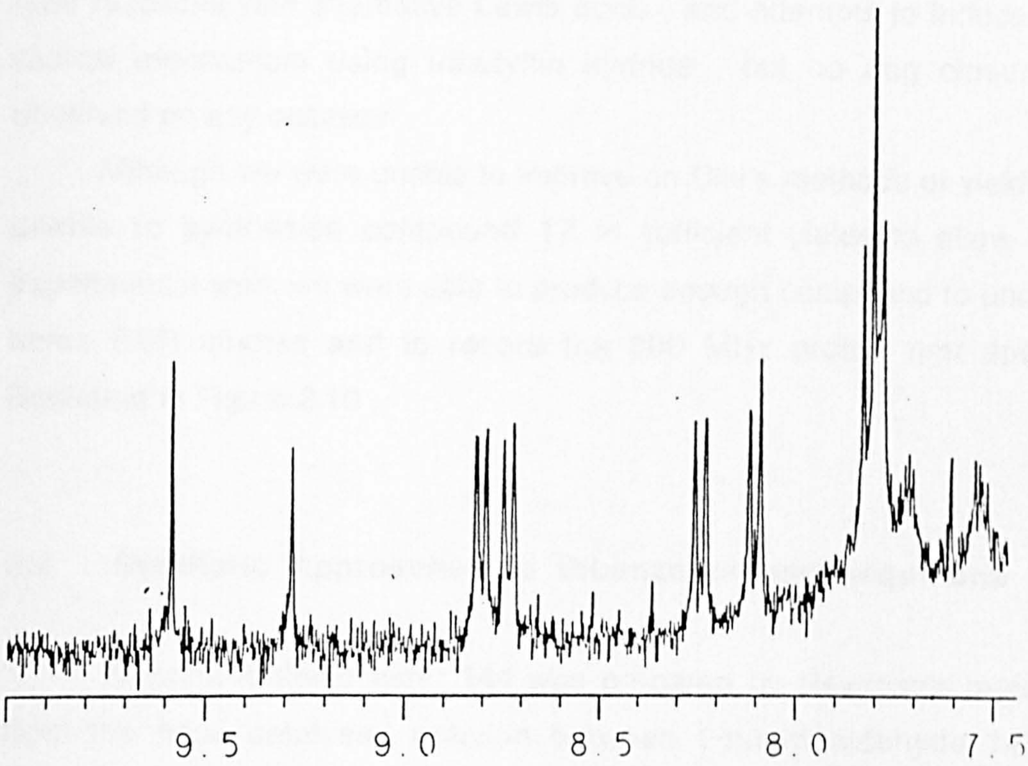
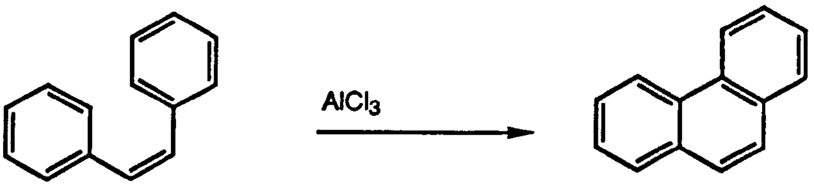


Figure 2.10 300 MHz proton nmr spectrum of dibenzpentacenequinone **17**



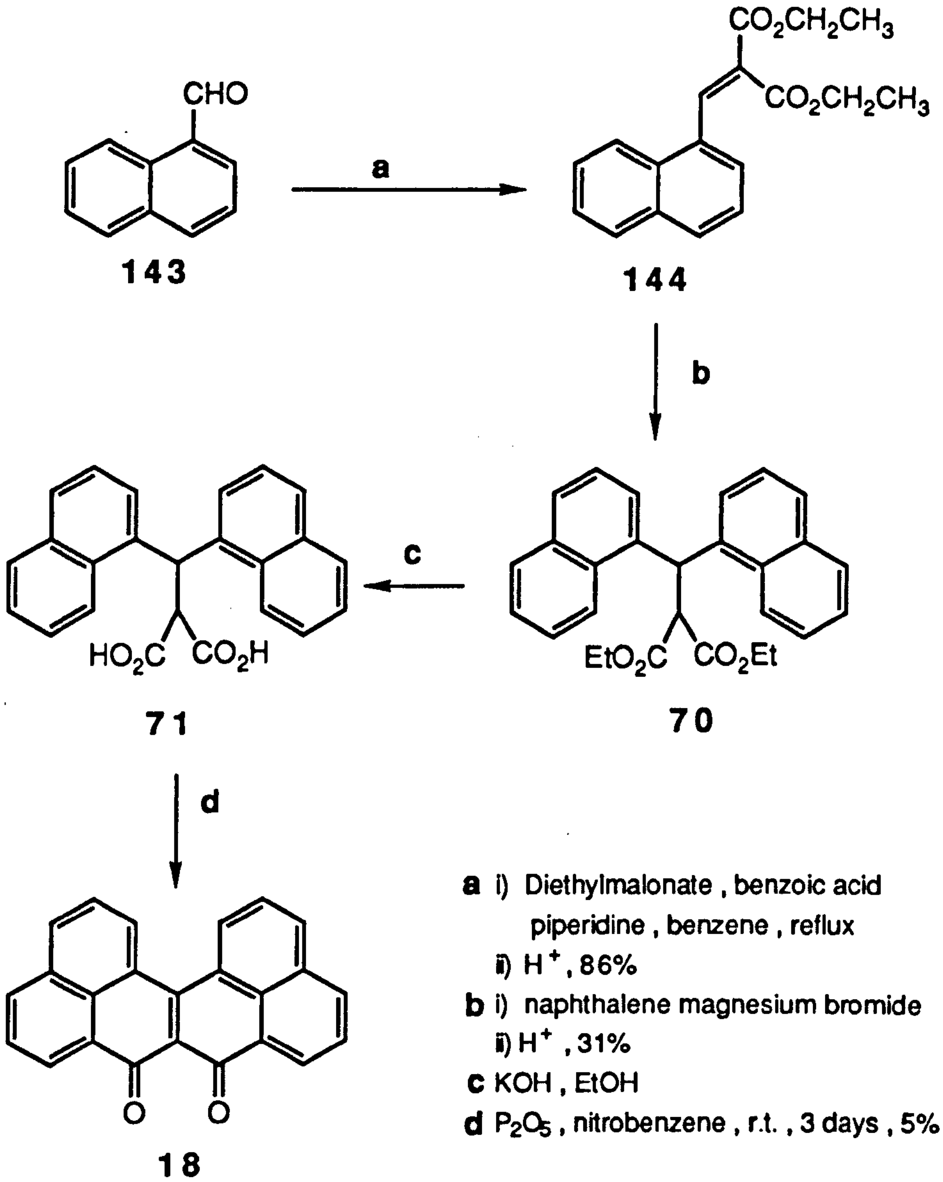
Other attempts at ring closure included photolysis reactions , Scholl type reactions with alternative Lewis acids , and attempts to induce a free radical mechanism using tributyltin hydride , but no ring closure was observed on any occasion .

Although we were unable to improve on Clar's methods or yields , and unable to synthesise compound **17** in sufficient yields to allow further experimental work we were able to produce enough compound to undertake some ESR studies and to record the 300 MHz proton nmr spectrum illustrated in Figure 2.10 .

2.4 Synthetic Approaches to Dibenznaphthacenequinone

Naphthylmalonic ester **144** was prepared by Newman's method [42] from the base catalysed reaction between 1-naphthaldehyde **143** and malonic ester (Scheme 2.9) . The Grignard reaction between compound **144** and1-naphthalene magnesium bromide gave the dinaphthoyl malonic ester **70** in which the basic skeleton of the target molecule can be seen . Hydrolysis of the ester functions gave the diacid **71** . When the diacid **71** was subjected to Clar's cyclisation procedure [4] none of the desired product was isolated . However the diketone **18** could be prepared by stirring a mixture of the diacid **71** with phosphorous pentoxide and nitrobenzene for 3 days at room temperature . After rather laborious work up and column chromatography procedures , we were able to isolate sufficient diketone **18** to undertake some ESR studies and obtain the proton nmr illustrated in Figure 2.11 . Once again we were only able to prepare small quantities of this material .

Scheme 2.9



143 **144** **70** **71** **18**

a i) Diethylmalonate , benzoic acid piperidine , benzene , reflux
ii) H^+ , 86%
b i) naphthalene magnesium bromide
ii) H^+ , 31%
c KOH , EtOH
d P_2O_5 , nitrobenzene , r.t. , 3 days , 5%

2.5 Synthetic Approaches to Tribenznaphthacenequinone

The Diels-Alder reaction between methyleneanthrone **81** and 1,4-naphthoquinone gave the dibenznaphthacenequinone derivative **84** in reasonable yields . This compound was then subjected to a Skraup type reaction with glycerol in sulphuric acid to give a mixture of dibenznaphthacenequinones (contrary to Vollman's assertion that a single substance was produced [43]) . The unwanted transangular compound **82**

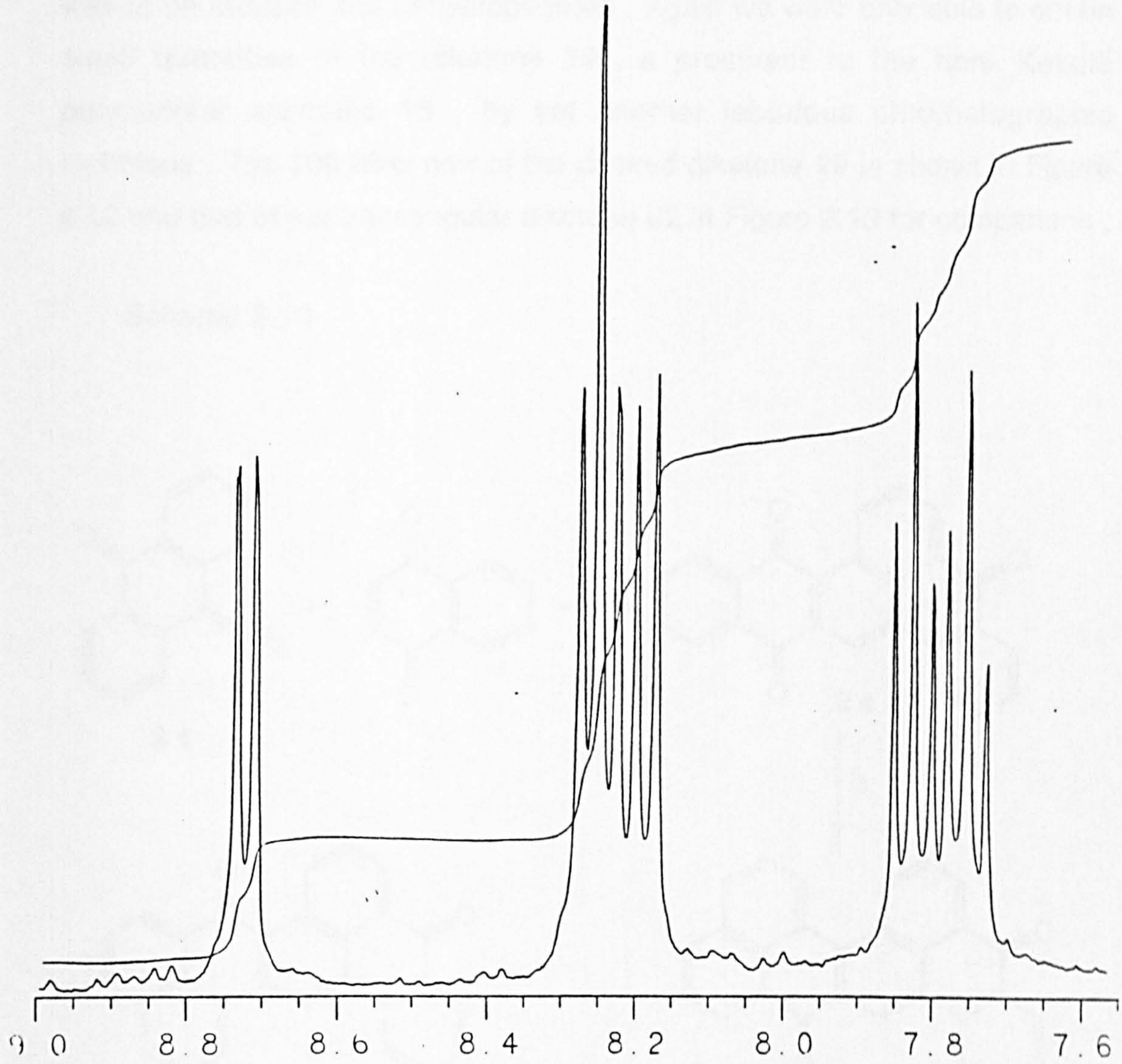
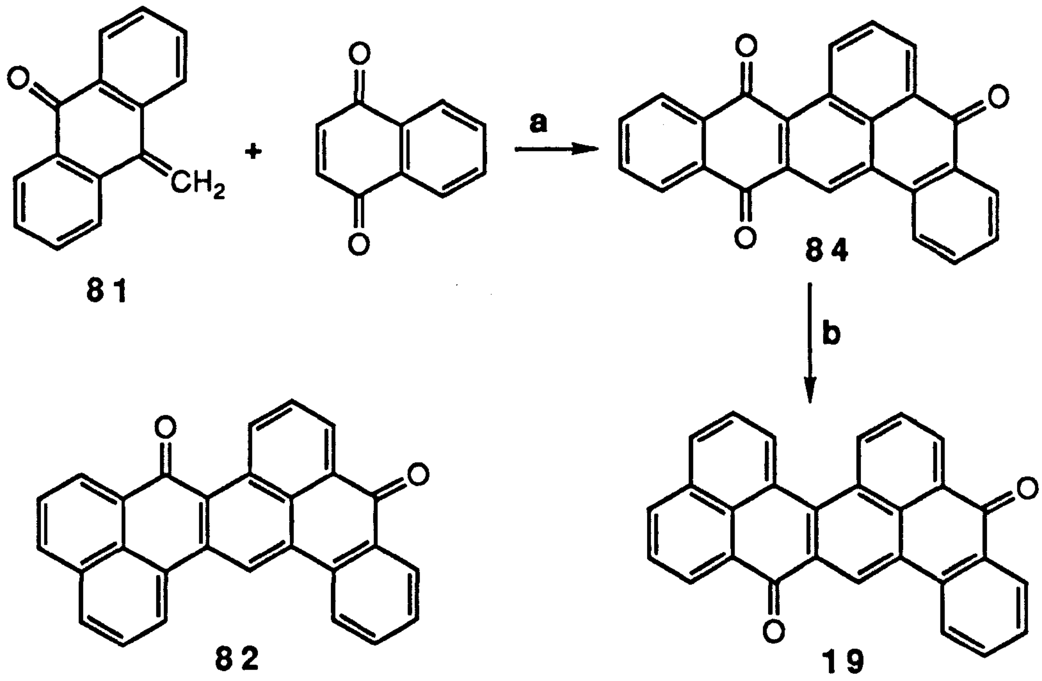


Figure 2.11 300 MHz proton nmr spectrum of dibenznaphthacenequinone **18**

was the major product ; unwanted because Kekulé structures can be drawn if an attempt is made to make the biradical - for example if the compound was to be reduced and dehydrogenated . Again we were only able to obtain small quantities of the diketone **19** , a precursor to the non- Kekulé polynuclear aromatic **15** , by yet another laborious chromatographic technique . The 300 MHz nmr of the desired diketone **19** is shown in Figure 2.12 and that of the transangular diketone **82** in Figure 2.13 for comparison .

Scheme 2.10



a Reflux in EtOH ; **b** glycerol , c. H_2SO_4

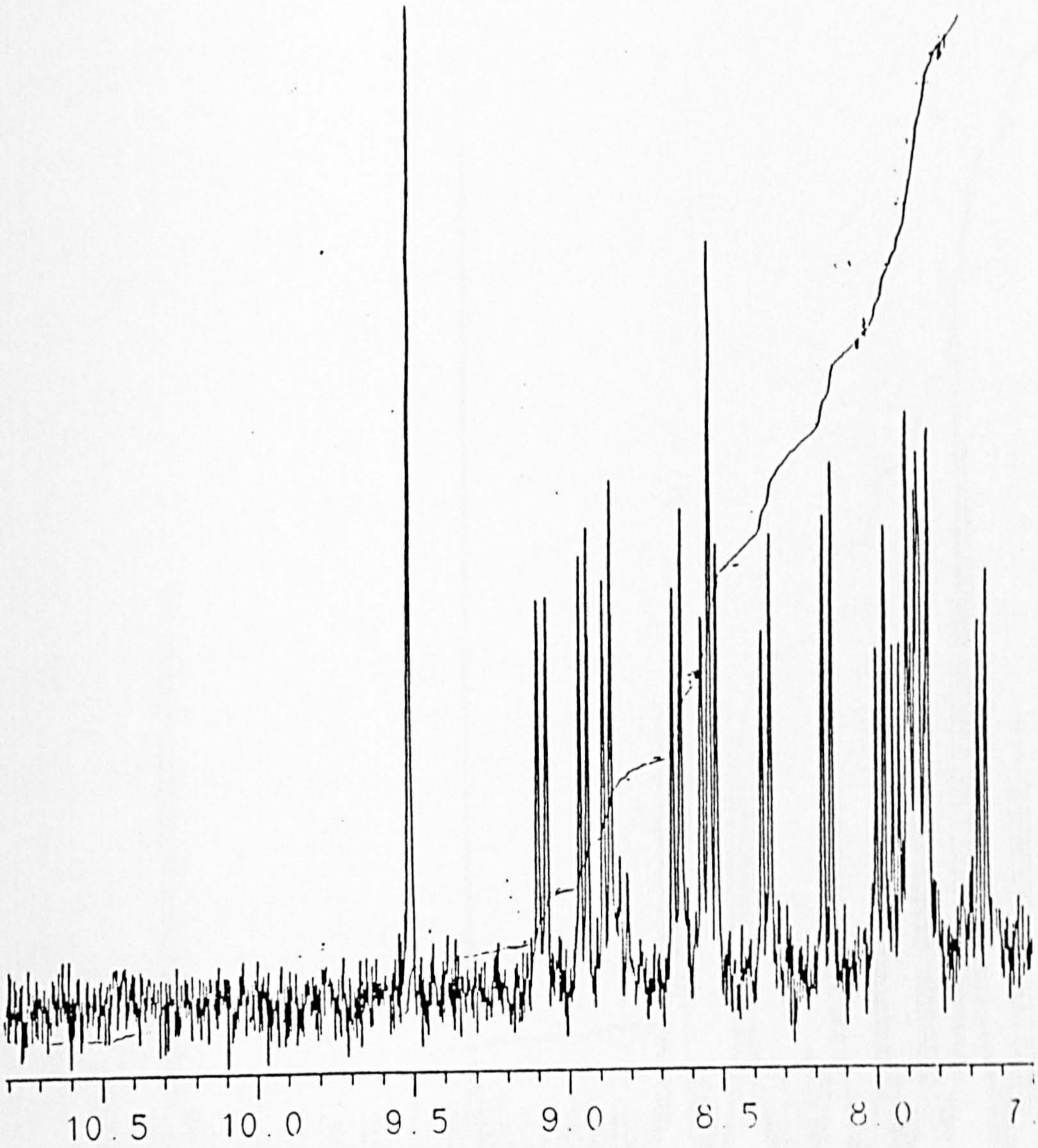


Figure 2.12 300 MHz proton nmr spectrum of tribenznaphthacenequinone **19**

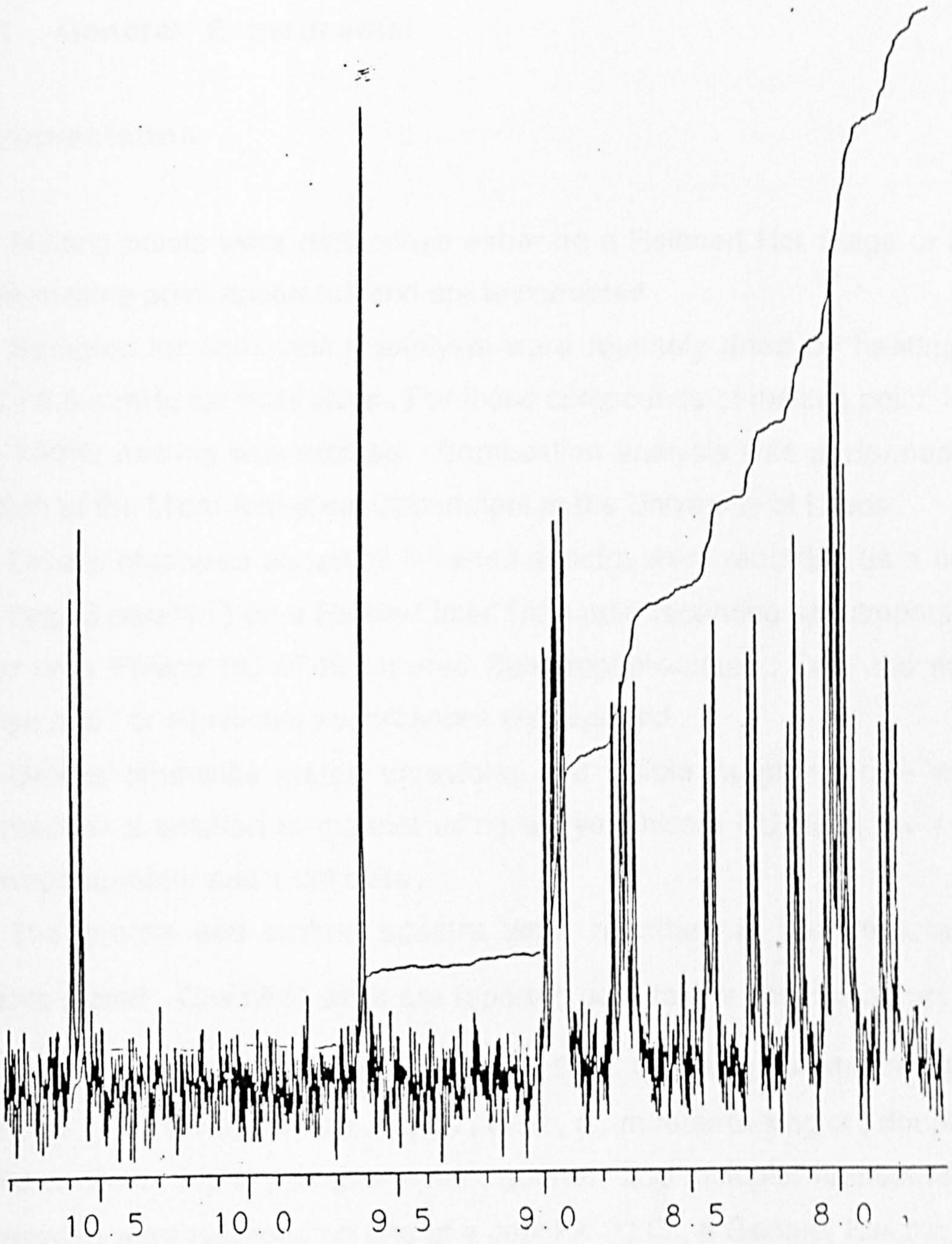


Figure 2.13 300 MHz proton nmr spectrum of tribenznaphthacenequinone 82

2.3 Experimental

2.3.1 General Experimental

Instrumentation

Melting points were determined either on a Reichert Hot Stage or in a Griffin melting point apparatus and are uncorrected .

Samples for combustion analysis were routinely dried by heating at 65°C / 0.5 mmHg for three days . For those compounds of melting point less than 100°C heating was omitted . Combustion analysis was performed by the staff of the Micro Analytical Department at the University of Leeds .

Unless otherwise stated all infra-red spectra were recorded as a nujol mull (liquid paraffin) on a Perkin-Elmer 1420 ratio recording spectrophotometer or a Philips PU 9706 Infrared Spectrophotometer . Only the most intense and / or significant absorbances are reported .

Unless otherwise stated ultraviolet and visible range spectra were recorded as a solution in ethanol using a Pye-Unicam PU 8800 UV / Vis spectrophotometer and 1 cm cells .

The proton and carbon spectra were recorded in the deuterated solvents stated . Chemical shifts are reported as δ values downfield from an internal standard , tetramethylsilane , $\delta = 0.0$. Coupling constants are in hertz (Hz) and the symbols s , d , dd , t , dt , q , m refer to singlet , doublet , double-doublet , triplet , double-triplet , quartet and multiplet respectively . The spectra were recorded on one of a Jeol FX 90 Q , a General Electric QE 300 or a Bruker AM 400 . These instruments operated at 90 , 300 , and 400 MHz respectively for proton nmr spectrometry , and at 22.5 , 75 and 100 MHz for carbon nmr spectrometry .

Low resolution mass spectra were originally recorded on a Kratos MS 25 , with high resolution measurements being taken on a Kratos MS 9 / 50 . Latterly , however , a VG Autospec was used for both types of mass spectrometry and only the assignable fragments are reported .

General Procedures

With the general exception of all oxidation reactions , unless otherwise stated all reactions were conducted under a positive pressure of dry nitrogen. For procedures requiring anhydrous conditions all glassware was oven dried prior to use .

The term " evaporated to dryness " refers to the removal of solvents using a Buchi 461 evaporator at water aspirator pressure followed by evacuation at 0.5 mmHg for 1-3 hours .

Thin layer chromatography (tlc) "on silica " or "on alumina" was performed on ' home-made ' plates prepared by dipping 20 cm x 5 cm glass plates into a homogeneous suspension of Merck Kieselgel 7730 GF 254 or Merck Aluminium oxide PF 254+366 Type E in ethyl acetate . The plates were visualised under UV light (254 nm) and / or by spraying with 50% v/v sulphuric acid and heating .

Column chromatography " on silica " refers to the use of Merck Kieselgel 7731 Type 60 . Column chromatography " on alumina " refers to the use of British Drug Houses' Aluminium oxide active basic , Brockmann Grade 1 . " Ion exchange chromatography " refers to the use of British Drug Houses' Amberlite IGC-50 ion exchange resin in the sodium form . The term " pH 3.42 buffer " refers to an aqueous eluent of pH 3.42 of composition : 500 ml 0.2M sodium citrate solution + 110 ml 1M HCl + 390 ml water + 0.5 ml thiodiglycol per 100 ml .

Solvents were routinely purified according to the procedures described in " Purification of Laboratory Chemicals " , 2nd. Ed. D.D.Perrin , W.L.F. Armarego , B.R.Perrin (Pergamon Press , Oxford) 1980 . Diethyl ether and THF were distilled from sodium benzophenone ketyl where dry solvents were required .

Reagents were purified as required according to the procedures described in ' Perrin & Perrin ' .

The terms " c. HCl " and " aq. HCl " refer to the use of 35% w/w hydrochloric acid and 2M hydrochloric acid respectively .

2.3.2 Experimental Procedures

Tris-(2-methylphenyl)methanol 35 [12]

2-Bromotoluene (100 g , 0.58 mol) was added dropwise over three hours to a vigorously stirred slurry of lithium (8 g , 1.14 mol) in diethyl ether (100 ml) The mixture was stirred for 24 hours at room temperature. A solution of o - toluoylchloride (31.3 g , 0.2 mol) in diethyl ether (100 ml) was added dropwise at such a rate that only a gentle reflux of solvent was observed. The reaction was stirred for 24 hours at room temperature then poured onto aq. HCl (100 ml) . Diethyl ether (100 ml) was added , the organic phase separated , washed with water (2 x 50 ml) , dried ($MgSO_4$) and evaporated to give a pale yellow oil. This oil was dissolved in 40-60°C bp. petroleum ether and refrigerated for two weeks. The resulting mixture was filtered and the filtrate evaporated to dryness to give the title compound as a pale yellow solid , 15.4 g (25 %), m.p. 80 - 90°C (Lit. [12] 105°C) .

(Found C, 87.3 ; H, 7.65 . $C_{22}H_{22}O$ requires : C, 87.4 ; H, 7.3 %)

IR (ν_{max})	3400 , 1600 ,760 cm^{-1}
λ_{max}	200 nm^{-1} ($\varepsilon = 84000\ cm^{-1}\ mol^{-1}\ dm^3$)
δ_H**(90 MHz)** ($CDCl_3$)	7.3-6.6 (12 H , m) , 2.2 (9H ,s , Ar - $C\underline{H}_3$) .
δ_C**(22.5 MHz)** ($CDCl_3$)	143.6 , 137.8 , 132.6 , 129.1 , 127.5 , 125.1 85.9 (Ar_3 -$\underline{C}OH$) , 22.8 (Ar-$\underline{C}H_3$) .

2-[(Diethylamino)carbonyl]benzoic acid 108 [17]

Phthalic anhydride (20 g , 0.135 mol) was added over 2 hours to a solution of diethylamine (19 ml , 14.14 g , 0.18 mol) in benzene (100 ml) cooled to

0 - 5°C in an ice-salt bath. After a further 2 hours at 0-5°C the mixture was filtered. The residue was washed with first benzene then 40 - 60°C bp. petroleum ether and then dissolved in sodium bicarbonate solution , reprecipitated by aq. HCl , filtered and dried to give the title compound as a colourless powder, 22 g (73 %) , m.p. 148°C (Lit. [17] 153°C) .

(Found C, 64.9	; H, 6.85 ; N, 6.25 . $C_{12}H_{15}NO_3$ requires : C, 65.1 ; H, 6.8 ; N, 6.3 %)
IR (ν_{max})	1675 (C=O) , 1560 , 780 , 745 cm^{-1}
λ_{max}	221 , 276 nm^{-1} (ε = 12000 , 1290 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	9.2 (1 H , s , Ar-$CO_2\underline{H}$) , 8.05 (1 H , d d, J = 8.0 , 1.0 Hz) , 7.6 (1 H , dt , J = 8.0 , 1.0 Hz) , 7.45 (1 H , dt , J = 8.0 , 1.0 Hz) , 7.25 (1 H , dd , J = 8.0 , 1.0 Hz) , 3.58 (2 H , q , J = 7.0 Hz , -$C\underline{H}_2CH_3$) , 3.1 (2 H , q , J = 7.0 Hz , -$C\underline{H}_2CH_3$) , 1.25 (3 H , t , J = 7.0 Hz , -$CH_2C\underline{H}_3$) , 1.0 (3 H , t , J = 7.0 Hz , -$CH_2C\underline{H}_3$) .
δ_C(75 MHz) ($CDCl_3$)	171.3 , 169.4 (Ar - carbonyls) , 138.8 , 132.2 , 131.0 , 128.6 , 128.4 , 126.5 , 42.9 (-$\underline{C}H_2$-), 38.8 (-$\underline{C}H_2$-) , 13.43 (-$\underline{C}H_3$) , 12.08 (-$\underline{C}H_3$) .

3,3-Di-o-tolylphthalide 30 - from 2-[(Diethylamino)carbonyl]benzoic acid 108

2 - Bromotoluene (2.0 ml , 2.84 g , 166 mmol) was added dropwise over 1 hour to a vigorously stirred refluxing slurry of magnesium (0.41 g , 170 mmol) in diethyl ether (25 ml) . The reaction was refluxed for a further 4 hours . A solution of tetramethylethylenediamine (1 ml) and 2-[(diethylamino)carbonyl] benzoic acid **108** (1 g , 5 mmol) in diethyl ether (25 ml) was added dropwise over ten minutes to the refluxing solution . After a further 72 hours at reflux the mixture was poured onto aq. HCl (25 ml) , the aqueous phase

extracted with chloroform (5 x 10 ml) and then the combined organic phase was washed with water (2 x 20 ml) , dried ($MgSO_4$) and evaporated to dryness . Column chromatography on silica eluting with dichloromethane gave an air sensitive colourless solid , 0.1 g . This material was stirred for 72 hours in a mixture of potassium hydroxide (0.5 g) , water (1 ml) and dioxan (10 ml) . The solution was neutralised with aq. HCl and then extracted with chloroform (3 x 10 ml). The chloroform extracts were dried ($MgSO_4$) and evaporated to dryness . Column chromatography on silica eluting with 50% v/v 40-60°C bp. petroleum ether gave the title compound as a colourless solid , 60 mg (4.2 %) , m.p. (ethanol) 172-74°C (Lit. [12] 176°C) .

(Found C, 84.1 ; H, 5.8 . $C_{22}H_{18}O_2$ requires : C, 84.15 ; H, 5.7 %)

IR (ν_{max})	1775 (C=O) , 1610 (Ar C=C), 780 , 770, 740 , 710 , 625 cm^{-1}
λ_{max}	204 , 268 nm^{-1} (ε = 29100 , 1790 cm^{-1} mol^{-1} dm^3)
δ_H**(300 MHz)** ($CDCl_3$)	7.95 (1 H , d , J = 9.2 Hz) , 7.70 (1 H , t , J = 9.2 Hz) , 7.57 (1 H , t , J = 9.2 Hz) , 7.40 (1 H , d , J = 9.2 Hz) , 7.34 (2 H , d , J = 7.0 Hz) , 7.28 (2 H , t , J = 7.0 Hz) , 7.08 (2 H , t , J = 7.0 Hz) , 7.02 (2 H d , J = 7.0 Hz) , 2.15 (6H , s , Ar-CH_3) .
δ_C**(75 MHz)** ($CDCl_3$)	169.9 (carbonyl) , 138.7 , 137.1 , 133.8 , 132.8 , 129.20 , 128.5 , 127.1 , 126.4 , 125.6 , 125.1 , 94.0 (C_3) , 21.47 (Ar-CH_3) .

3,3-Di-o-tolylphthalide 30 - from phthalic anhydride [12]

2 - Bromotoluene (140 ml , 199 g , 1.16 mol) was added dropwise to a vigorously stirred refluxing suspension of magnesium (30 g , 1.25 mol) in diethyl ether (600 ml) . The

reaction mixture was refluxed for a further 3 hours at which point the resultant green solution was pumped through PTFE tubing using the blanketing nitrogen pressure on to a solution of phthalic anhydride (70 g , 0.47 mol) in benzene (1000 ml) at such a rate that only a gentle reflux of solvent was observed . The reaction mixture was refluxed for 24 hours and then pumped on to aq. HCl (1000 ml) again at such a rate that only a gentle reflux of solvent was observed . The organic phase was separated, washed with water (3 x 100 ml) , dried ($MgSO_4$) and filtered . The solvent was evaporated to give a viscous orange-red gum * , (160 g) . This gum was dissolved in ethanol (750 ml) and refluxed with hydrazine hydrate (30 ml) for 24 hours . The solution was reduced to approximately 10 % of the original volume and filtered. The residue was washed with ethanol (3 x 50 ml) to give the title compound as a colourless powder , 55 g (37 %) .

* There are three major components to this gum . These may be isolated by column chromatography on silica , eluting with 50% v/v 40-60°C bp. petroleum ether-chloroform , although due to the co-polar nature of the components the procedure is not trivial .

Component 1 : identified by ^1H , ^{13}C nmr and low resolution m/s as 2-(hydroxy-bis(2-methylphenyl)methyl)-2'-methylbenzoylbenzene **111** , m.p. 120°C (Lit. [18] 124-26°C) .

λ_{max} 204 nm^{-1} ($\varepsilon = 44700$ cm^{-1} mol^{-1} dm^3)

δ_H(300 MHz) ($CDCl_3$)	7.83 (2 H , dd , J = 7.9 , 2.0Hz) , 7.75 (3 H , m) , 7.45 (14 H , m) , 7.25 (3 H , dt , J = 7.9 , 2.0 Hz) , 7.15 (2 H , dd , J = 7.9 , 2.0 Hz) , 2.75 (3H , s , Ar-C$\underline{H}_3$) , 2.50 (3H , s , Ar-C$\underline{H}_3$) , 2.3 (3H , s , Ar-C$\underline{H}_3$) , 1.25 (1H , s , Ar$_3$-O$\underline{H}$) .
δ_C(75 MHz) ($CDCl_3$)	198.5 (carbonyl) , 145.2, 141.5 , 140.9 , 139.5 , 137.2 , 136.4 , 135.7 , 131.5 , 131.3 , 130.7 , 130.4 , 129.7 , 129.2 , 127.8 , 127.5 , 127.1 , 125.8 , 125.4 , 125.1 , 124.4 , 122.2 , 119.9 (Ar$_3$ -$\underline{C}$OH) , 21.31 (Ar-$\underline{C}H_3$) , 20.60 (Ar-$\underline{C}H_3$), 19.79 (Ar-$\underline{C}H_3$) .

Note : the observation of three aromatic methyl groups is probably due to hindered rotation within the molecule .

m/z (%)	389 (M$^+$, 50) , 298 (M$^+$ - C_7H_7 , 24) , 119 (C_7H_7 CO$^+$, 100) , 91 (o-tolyl$^+$, 66) .

Component 2 : 3,3-Di-o-tolylphthalide

Component 3 : identified by ^{1}H , ^{13}C nmr and low resolution m/s as 1,2-di-(2'-methylbenzoyl)benzene **112** , m.p. 143-45°C (Lit. [15] 128-31°C) .

λ_{max}	204 , 244 nm^{-1} (ε = 10900 , 7410 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	7.5 (4 H , m) , 7.3 (2 H , dt , J = 7.5 , 1.0 Hz) , 7.2 (4 H , dd , J = 7.5 , 1.0 Hz) , 7.12 (2H , dt , J = 7.5 , 1.0 Hz) , 2.3 (6H , s , Ar-C$\underline{H}_3$) .
δ_C(75 MHz)	198.3 (carbonyl) , 140.8 , 139.4 , 137.1 , 131.4 130.7 , 129.7 , 125.0 , 20.5 (Ar-$\underline{C}H_3$) .
m/z (%)	314 (M$^+$, 87) , 223 (M$^+$ - C_7H_7, 26) , 195 (M$^+$ - C_7H_7, - CO , 100) , 166 (M$^+$ - C_7H_7, - CO , - HCO , 32) , 119 (M$^+$ - 2 x C_7H_7 , CH$^+$, 62) , 105 (M$^+$ - 2 x C_7H_7 , -CO , 13) , 91 (C_7H_7 , 85) .

2"-carboxyphenyl-bis(2'-methylphenyl)methane **31**[18]

Powdered 3% sodium amalgam (240 g) was added to a refluxing solution of 3,3-di-o-tolylphthalide **30** (30 g , 0.095 mol) in ethanol (600 ml) over 4 hours . The mixture was then refluxed for a further 24 hours . The ethanol was distilled from the reaction , the residue boiled with water (6 x 250 ml) and the combined aqueous fractions then acidified to pH 1 with c. HCl . The resulting precipitate was filtered , washed with water and then redissolved in 2M sodium hydroxide , filtered , and reprecipitated with c. HCl . After cooling filtration gave the title compound as a colourless powder , 29 g (90 %) , m.p. (ethanol) 243-45°C (Lit.[18] 243°C) .

(Found C, 83.2 ; H, 6.35 . $C_{22}H_{20}O_2$ requires : C, 83.5 ; H, 6.3 %)

IR (ν_{max})	3450 , 1700 (C=O) , 1610 (Ar C=C) , 1580 , 1080 , 940 , 770 cm $^{-1}$
λ_{max}	202 nm^{-1} ($\varepsilon = 55300$ cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (d^6-DMSO)	7.96 (1 H , dd , J = 8.0 , 1.0 Hz) , 7.33 (1 H , t , J = 7.0 Hz) , 7.26 (1 H , t , J = 7.0 Hz) , 7.08 (3 H , m) , 7.02 (2 H , dd , J = 8.0 , 1.0 Hz) , 6.92 (1 H , s , Ar$_3$C$\underline{H}$) , 6.85 (1 H , d , J = 7.0 Hz ,) , 6.62 (2 H d , J = 8.0 Hz ,) , 2.2 (6 H , s , Ar-C$\underline{H}_3$) .
δ_C(75 MHz) (d^6-DMSO)	168.5 (carbonyl) , 142.1 , 137.0 , 131.4 , 131.2 , 130.3 , 130.1 , 129.0 , 126.1 , 126.0 , 125.5 , 46.1 (Ar$_3\underline{C}$H) , 19.4 (Ar-$\underline{C}$H$_3$) .

Tris-(2-carboxyphenyl)methane 32 [18]

2"-carboxyphenyl-bis(2'-methylphenyl)methane **31** (29 g, 0.092 mol) was added to a solution of sodium carbonate (60 g) in water (2250 ml) and the mixture was boiled until a solution was observed . Nitrogen was then bubbled through the solution and potassium permanganate (90 g , 0.57 mol) added over four hours . After being boiled for a further 24 hours the reaction mixture was reduced to approximately 10% of the original volume. Ethanol (500 ml) was added . When all the purple colour had been discharged the mixture was filtered through a bed of celite and the residue washed with hot ethanol (3 x 250 ml) . The combined filtrates were then refluxed with 3 % sodium amalgam (120 g) for 24 hours . After being decanted from the mercury residues the solution was reduced to approximately 10% of the original volume and acidified to pH 1 with c. HCl , cooled , and filtered to give the title compound as a colourless solid , 18.5 g (54 %) , m.p. 285-90°C (Lit. [18] 303°C) .

(Found C, 68.7 ; H, 4.1 . $C_{22}H_{16}O_6 . 0.5H_2O$ requires : C, 68.6 ; H, 4.15 %) (Lit. [18] gave monohydrate) .

IR (ν_{max})	1700 (C=O) , 1610 (Ar C=C) , 1580 , 1320 , 1280 , 1100 , 760 , 740 cm^{-1}
λ_{max}	204 , 274 nm^{-1} ($\varepsilon = 94000 , 8670$ cm^{-1} mol^{-1} dm^3)
δ_H**(300 MHz)** (d^6-DMSO)	12.5 (3 H , s , -$CO_2\underline{H}$) , 8.11 (1 H , s , Ar_3-C$\underline{H}$) , 7.88 (3 H , d , J = 8.0 Hz) , 7.32 (3 H , t , J = 8.0 Hz) , 7.22 (3 H , t , J = 8.0 Hz) , 6.90 (3H , d , J = 8.0 Hz) .
δ_C**(75 MHz)** (d^6-DMSO)	168.2 (carbonyl) , 145.6 , 131.4 , 131.0 , 130.7 , 130.5 , 125.9 , 46.7 ($Ar_3\underline{C}H$) .

12-Potassoxy-4,8-dioxo-4H,8H-dibenzo-[1,2,3-cd,1,2,3-mn]-pyrene **116**

Tris-(2-carboxyphenyl)methane **32** (30 g , 0.078 mol) was added to sulphuric acid (d = 1.835 , 500 ml) and the mixture heated to 120°C for 2 hours . The resulting blue solution was cooled and added to ice cold water (1500 ml) to give a thick black-blue emulsion . The solids were separated by centrifugation , washed with water (3 x 100 ml) in the centrifuge and then refluxed for 24 hours with potassium carbonate (11 g) in ethanol (500 ml). After cooling , water (500 ml) was added and the resulting suspension filtered . The residue was washed with water (3 x 250 ml) and dried to give the title compound as a blue powder , 20.7 g (57 %) .

(Found C, 73.05 ; H, 3.05 ; K, 10.3 . $C_{22}H_9KO_3$ requires : C, 73.3 ; H, 2.5 ; K, 10.8 %)

IR (ν_{max})	1600 (C=O) , 1560 (Ar C=C) , 1300 , 1200 , 1080 , 1000 , 920 , 770 , 670 cm $^{-1}$
λ_{max} (DMSO)	580 , 640 , 644 , 680 nm^{-1} (ε = 3120 , 3480 , 5160 , 4860 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (d^6-DMSO)	8.74 (6 H , d , J = 7.6 Hz , $C_{1,3,5,7,9,11}$-$\underline{H}$) 7.50 (3 H , t , J = 7.6 Hz , $C_{2,6,10}$-$\underline{H}$) .
δ_C(75 MHz) (d^6-DMSO)	180.5 , 132.8 , 126.9 , 120.2 , 108.8 , 99.9 .

Please Note: The syntheses of compounds 16, 117 and 118 were undertaken before optimisation of the route to 116 : hence the very small scale.

4,8-dioxo-4H,8H,12H-dibenzo-[1,2,3-cd,1,2,3-mn]-pyrene 16[18]

A mixture of 12-Potassoxy-4,8-dioxo-4H,8H-dibenzo-[1,2,3-cd,1,2,3-mn] pyrene **116** (50 mg , 0.14 mmol) and zinc powder (100 mg , 1.5 mmol) in 5% w/w sodium hydroxide solution (20 ml) was refluxed for 24 hours . The mixture was cooled and filtered . Oxygen was bubbled through the filtrate for

15 minutes . Acidification to pH 1 with c. HCl gave a black precipitate which was isolated by centrifugation and dried . Preparative thin layer chromatography on silica eluting with 0.25% v/v methanol-dichloromethane gave the title compound as an air sensitive red solid , 2.5 mg (5.8 %) .

IR (ν_{max})	1720 (C=O) , 1450, 1000 , 690 cm $^{-1}$
λ_{max}	356 , 392 , 332 , 466 , 492 , 526 nm^{-1} (ε = 18500 , 24400 , 17100 ,13100 , 11600 , 12500 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.99 (2 H , d , J = 7.7 Hz , $C_{5,11}$-H) , 8.88 (1 H , s , C_8-H) , 8.86 (2 H , d , J = 7.7 H z , $C_{7,9}$-H) , 8.52 (2 H d , J = 8.0 H z , $C_{1,3}$-H) , 7.92 (2 H , t , J = 7.7 Hz , $C_{6,10}$-H) , 7.82 (1 H , t , J = 8.0 Hz , C_2-H) .

12-Methoxy-4,8-dioxo-4H,8H-dibenzo[1,2,3-cd,1,2,3-mn]-pyrene 117

12-Potassoxy-4,8-dioxo-4H,8H-dibenzo-[1,2,3-cd,1,2,3-mn]-pyrene **116** (37 mg , 0.1 mmol) was stirred with diazomethane solution (approx 3.2 g / 250 ml diethyl ether, 40 ml) for 2 days . The mixture was evaporated to dryness . Column chromatography on silica eluting with 0.25 % v/v methanol-dichloromethane followed by preparative thin layer chromatography on silica of the isolated purple band again eluting with 0.25% v/v methanol-dichlormethane gave the title compound as an air sensitive red solid , 1.5 mg (4.4%) .

IR (ν_{max})	1720 (C=O) , 1640 , 1280, 1260 , 700 cm $^{-1}$
λ_{max} ($CHCl_3$)	390 , 448 , 492 , 516 , 560 nm^{-1} (ε = 11000 , 15400 , 21100 , 22500 , 18300 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	9.00 (2 H , d , J = 6.5 Hz , $C_{1,3}$-H) , 8.84 (2 H , d , J = 7.6 Hz , $C_{5,11}$-H) , 8.82 (2 H , d , J = 7.6 H z , $C_{7,9}$-H) 7.92 (2 H , t , J = 7.6 H z , $C_{8,10}$-H) , 7.80 (1 H , t , J = 6.5Hz , C_2-H) , 4.75 (3H , s , Ar-OCH_3) .

12-Acetoxy-4,8-dioxo-4H,8H-dibenzo-[1,2,3-cd,1,2,3-mn]-pyrene 118

12-Potassoxy-4,8-dioxo-4H,8H-dibenzo-[1,2,3-cd,1,2,3-mn]-pyrene **116** (50 mg , 0.14 mol) was strirred in a mixture of acetic anhydride (10 ml) and sulphuric acid (d = 1.835 , 1 ml) for 3 hours . The mixture was then added to water (20 ml) . The resulting mixture was extracted with dichloromethane (10 x 50 ml) . The red dichloromethane solution was dried ($MgSO_4$) and evaporated to dryness . Column chromatography on silica eluting with 0.25% v/v methanol-dichloromethane followed by preparative thin layer chromatography on silica of the isolated red band gave the title compound as an air sensitive red solid , 3.2 mg (6.3%) .

IR (ν_{max})	1730 (C=O) , 1470, 1300 , 1120 , 720 cm $^{-1}$
λ_{max} ($CHCl_3$)	396 , 436 , 480 , 510 , 540 nm^{-1} (ε = 10500 , 10300 , 13800 , 17600 , 12000 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.98 (2 H , d , J = 7.7 Hz , $C_{1,3}$-$\underline{H}$) , 8.82 (2 H , d , J = 8.0 Hz , $C_{5,11}$-$\underline{H}$) , 8.45 (2 H , d , J = 8.0 H z , $C_{7,9}$-$\underline{H}$) 7.93 (2 H , t , J = 8.0 H z , $C_{6,10}$-$\underline{H}$) , 7.81 (1 H , t , J = 7.7 Hz , C_2-$\underline{H}$) , 2.74 (3 H , s , ArOCO.C$\underline{H}_3$) .

1-Methyl-9-(2'-methylphenyl)-10(9H)anthracenone 37 [31]

A mixture of 2"-carboxyphenyl-bis(2'-methylphenyl)methane **31** (25 g , 0.079 mol) , zinc chloride (12.5 g , 0.08 mol) and sodium chloride (2.5 g , 0.04 mol) was stirred at 220°C for 30 minutes . After cooling to room temperature the grey solids were decomposed first with boiling aq. HCl , then boiling water and finally boiling 2M sodium hydroxide . After being washed with water the residue was recrystallised from glacial acetic acid to give the title compound as colourless needles , 18 g (76%) , m.p. (glacial acetic acid) 186-88°C (Lit. [31] 182°C) .

(Found C, 88.25 ; H, 5.85 . $C_{22}H_{18}O$ requires : C, 88.5 ; H, 6.0 %)

IR (ν_{max})	1650 (C=O) , 1590 (Ar C=C) , 680 , 650 , 610 cm $^{-1}$
λ_{max}	220 , 270 nm^{-1} (ε = 21100 , 12100 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (CDCl$_3$)	8.32 (2 H , d , J = 7.9 Hz) , 7.4 (5 H , m) , 7.13 (1 H , d , J = 7.4 Hz) , 6.99 (1 H , t , J = 7.9 Hz) , 6.95 (1H t , J = 7.4 Hz) , 6.67 (1 H , d , J = 7.4 Hz) , 5.65 (1 H s , bridgehead-CH) , 2.68 (3 H , s , Ar-CH$_3$) , 2.13 (3 H , s , Ar- CH$_3$) .
δ_C(75 MHz) (CDCl$_3$)	185.1 (carbonyl) , 145.4 , 142.7 , 140.4 , 136.7 , 135.5 134.8 , 133.2 , 132.6 , 131.1 , 130.3 , 129.1 , 128.2 , 127.3 , 127.1 , 126.8 , 126.6 , 126.3 , 125.3 , 42.5 (bridgehead-CH), 20.2 (Ar-CH$_3$) , 19.9 (Ar-CH$_3$).

9-Hydroxy-1-methyl-9-(2'-methylphenyl)-10(9H)-anthracenone **38** [31]

A mixture of 1-methyl-(2'-methylphenyl)-10(9H)-anthracenone **37** (5 g) nitrobenzene (2.5 ml) and nitric acid (d = 1.1 , 175 ml) was boiled for 40 hours . The nitrobenzene was removed by steam distillation and the reaction cooled and filtered to give the title compound as a colourless powder , 4.1 g (78%) , m.p. 206°C (Lit.[31] 209°C) .

(Found C, 83.9 ; H, 5.7 . $C_{22}H_{18}O_2$ requires : C, 84.1 ; H, 5.7 %)

IR (ν_{max})	1650 (C=O) , 1600 (Ar C=C) , 1370 , 770 , 740 , 600 cm $^{-1}$
λ_{max}	204 , 220 , 270 nm^{-1} (ε = 40700 , 25400 , 5810 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (CDCl$_3$)	8.44 (1 H , d , J = 7.8 Hz) , 8.13 (2 H , t , J = 8.2 Hz) , 7.46 (1 H , t , J = 7.8 Hz) , 7.35 (5 H , m) , 7.17 (1 H , t , J = 8.2 Hz) , 6.88 (1 H , d , J = 7.3 Hz) , 3.00 (1 H , s , bridgehead-OH) , 2.05 (3 H , s , Ar-CH$_3$) , 1.36 (3 H , s , Ar- CH$_3$) .

δ_C(75 MHz) ($CDCl_3$)	184.0 (carbonyl) , 146.6 , 143.2 , 142.4 , 138.6 , 138.1 , 134.0 , 131.8 , 131.4 , 129.5 , 129.1 , 128.3 , 127.8 , 127.5 , 127.35, 126.2 , 125.5 , 125.4 , 72.5 (bridgehead-$\underline{C}$OH), 21.4 (Ar-$\underline{C}H_3$) , 20.2 (Ar-$\underline{C}H_3$) .

9-(2'-methylphenyl)-1-methylanthracene **122**

A mixture of 1-methyl-9-(2'-methylphenyl)-10(9H)-anthracenone **37** (100 mg , 0.33 mmol) and lithium aluminium hydride (1 g , 3.3 mmol) in diethyl ether was refluxed under nitrogen for 72 hours . The mixture was then poured onto aq. HCl (25 ml) . The aqueous phase was extracted with diethyl ether (5 x 50 ml) . The combined ethereal phases were washed with water (2 x 25 ml) and then refluxed for 24 hours in the presence of p-toluenesulphonic acid (50 mg) . The solution was evaporated to dryness and then column chromatography on silica eluting with 40-60°C bp. petroleum ether gave *9-(2'-methylbenzyl)-1-methylanthracene* **122** as a pale yellow solid , 8 mg (8.5%) , m.p. (40-60°C bp. petroleum ether) 30-35°C .

(Found C, 93.7 ; H, 6.5 . $C_{22}H_{18}$ requires : C, 93.6 ; H, 6.4 %)

IR (ν_{max})	1600 (Ar C=C) , 895 , 870 , 840 cm $^{-1}$
λ_{max}	220 , 250 , 320 , 360 , 380 nm^{-1} (ε = 7980 , 11400 , 690 , 1210 , 1040 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.32 (1 H , s) , 7.83 (1 H , d , J = 8.3 Hz) , 7.78 (1 H , d , J = 8.3 Hz) , 7.2 (8 H , m) , 7.08 (1 H , t , J = 7.5 Hz) , 1.94 (3 H , s , Ar-C$\underline{H}_3$) , 1.82 (3 H , s , Ar- C$\underline{H}_3$) .
δ_C(75 MHz) ($CDCl_3$)	141.7 , 137.7 , 136.0 , 135.5 , 132.7 , 131.3 , 130.9 , 130.7 , 129.4 , 129.3 , 128.9 , 128.2 , 127.9 , 127.8 , 127.7 , 126.6 , 125.4 , 125.2 , 125.0 , 124.6 , 24.6 (Ar-$\underline{C}H_3$) , 20.0 (Ar-$\underline{C}H_3$) .

Further elution of the column with 40-60°C bp. petroleum ether gave the air sensitive *1-methyl-9-(2'-methylphenyl)-9,10-dihyroanthracene* **123** , 80 mg (84%) .

(Found C, 93.0 ; H, 7.0 . $C_{22}H_{20}$ requires : C, 93.0 ; H, 7.0 %)

IR (ν_{max})	1600 (Ar C=C) , 1560 , 950 cm $^{-1}$
λ_{max}	220 , 260 nm^{-1} (ε = 29900 , 4730 cm^{-1} mol^{-1} dm^{3})
δ_H**(300 MHz)** ($CDCl_3$)	7.45 (1 H , m) , 7.23 (3 H , m) , 7.10 (4 H , m) 7.0 (1 H , d , J = 7.4 Hz) , 6.95 (1 H , t , J = 7.4 Hz) , 6.88 (1 H , t , J = 8.8 Hz) , 6.82 (1 H , t , J = 8.8 Hz) , 5.61 (1 H , s , bridgehead-C$\underline{H}$) , 4.44 (1 H , d J = 19.5 Hz , bridgehead-C$\underline{H}$) , 4.0 (1 H , d , J = 19.5 Hz , bridgehead-C$\underline{H}$) , 2.73 (3 H , s , Ar-C$\underline{H}_3$) , 2.17 (3 H , s , Ar- C$\underline{H}_3$) .
δ_C**(75 MHz)** ($CDCl_3$)	143.3 , 139.3 , 138.2 , 136.0 , 135.9 , 134.7 , 134.5 . 130.8 , 128.4 , 128.2 , 128.1 , 127.9 , 126.3 , 126.3 , 126.2 , 126.1 , 125.9 , 125.9 , 44.2 (bridgehead-$\underline{C}$H) , 35.8 (bridgehead-$\underline{C}$H) , 20.7 (Ar-$\underline{C}H_3$) , 19.8 (Ar-$\underline{C}H_3$) .

9-(2'-methylphenyl)-1-methylanthracene 122 - from 1-methyl-9-(2'-methylphenyl)-9,10-dihyroanthracene 123

A solution of 1-methyl-9-(2-methylphenyl)-9,10-dihyroanthracene **123** (80 mg , 0.3 mmol) and dichlorodicyanoquinone (80 mg , 0.35 mmol) in benzene (2 ml) was refluxed for 24 hours and then evaporated to dryness . Column chromatography on silica eluting with 40-60°C bp. petroleum ether gives the title compound , 20 mg (25%) .

9-(2'-methylphenyl)-1-methylanthracene 122 - from 9-Hydroxy-1-methyl-9-(2'-methylphenyl)-10(9H)-anthracenone 38

A mixture of 9-Hydroxy-1-methyl-9-(2'-methylphenyl)-10,(9H)-anthracenone **38** (100 mg , 0.33 mmol) and lithium aluminium hydride (1 g , 3.3 mmol) in diethyl ether was refluxed for 24 hours . The mixture was then poured carefully onto aq. HCl (10 ml) , the aqueous phase extracted with diethyl ether (3 x 10 ml) and then the combined organic phases washed with water (2 x 10 ml) , dried ($MgSO_4$) and evaporated to dryness. Column chromatography on silica eluting with 40-60°C bp. petroleum ether gave the title compound , 45 mg (50 %) . Further elution returned the remainder of the starting material .

Attempted ω-bromination of the methyl groups of 9-(2'-methyl phenyl)-1-methylanthracene 122 using N-Bromosuccinamide .

A mixture of benzoyl peroxide (5 mg) and N-Bromosuccinimide (5 mg) was added to a solution of 9-(2'-methylphenyl)-1-methylanthracene **122** (45 mg , 0.16 mmol) and the reaction stirred under argon for 2 hours then evaporated to dryness . Column chromatography on silica eluting with 40-60°C bp. petroleum ether gave an air sensitive pale yellow oil . This compound on comparison with the ^1H and ^{13}C spectra of **122** was assumed to be the 10-bromo derivative **125** , 40 mg (69 %) .

δ_H(300 MHz) ($CDCl_3$)	8.63 (1 H , d , J = 8.6 Hz) , 8.59 (1 H , d , J = 8.7 Hz) , 7.54 (1 H , dt , J = 8.2 , 1.5 Hz) , 7.40 (2 H , m) ,7.30 (3 H , m ,) , 7.21 (3 H , m) , 1.88 (3 H , s , Ar-C$\underline{H}_3$) , 1.97 (3 H , s , Ar- C$\underline{H}_3$) .
δ_C(75 MHz) ($CDCl_3$)	141.3 , 137.6 , 136.8 , 136.1 , 131.5 , 131.4 , 131.3 , 130.3 , 129.9 , 129.6 , 128.0 , 127.9 , 127.6 , 127.1 , 126.9 , 126.5 , 125.7 , 125.4 , 124.2 , 25.0 (Ar-$\underline{C}H_3$) , 20.1 (Ar-$\underline{C}H_3$) .

The product **125** was redissolved in benzene (2 ml) and a further addition of benzoyl peroxide (5 mg) and NBS (5 mg) made . After a further two hours stirring tlc studies indicated the consumption of compound **125** and the mixture was evaporated to dryness . However upon examination of the ^{1}H nmr spectrum of the reaction mixture no signals indicative of ω - bromination were observed .

2"-carboxyphenyl-bis(2',5'dimethylphenyl)methane 50 [31]

A mixture of *sym* - phthaloyl chloride (64 g , 0.35 mol) and aluminium chloride (64 g , 0.48 mol) was stirred at 100°C for 10 hours . After cooling to room temperature the mixture was dissolved in dichloromethane (250 ml) and then added dropwise to 1,4-dimethylbenzene (213 g , 2.0 mol) at such a rate that only a gentle reflux of solvent was observed . The mixture was then stirred overnight at room temperature before being poured onto aq. HCl (250 ml) . The organic phase was separated and washed with water (2 x 100 ml) before being evaporated to dryness . The residue (120 g) was refluxed for 24 hours in a mixture of ethanol (500 ml) and hydrazine hydrate (20 ml) . The solution was then evaporated to approximately 20% of the original volume and filtered to give a yellow compound , 55 g , which proton nmr studies indicated contained 3,3-di-p-xylylphthalide **49** but which could not be purified in our hands . A portion of this mixture (40 g) was refluxed for 24 hours in ethanol (500 ml) with 3% sodium amalgam (328 g) . The ethanol was then distilled from the reaction , the residue boiled with water (5 x 500 ml) and then the combined aqueous washings acidified to pH 1 by c. HCl . The resulting precipitate was filtered , slurried in dichloromethane (200 ml) , filtered and dried to give the title compound as a grey powder , 30 g (75%) , m.p. (ethanol) 230-33°C (Lit. [31] 233-34°C) .

(Found C, 82.3 ; H, 6.85 . $C_{24}H_{24}O_2$ requires : C, 83.4 ; H, 7.0 %)

IR (ν_{max})	1675 (C=O) , 1590 , 1370, 1300 , 1270 , 1150 , 1070 , 930 , 800 , 740 cm $^{-1}$
λ_{max}	220 , 270 nm^{-1} ($\varepsilon = 39500$, 5160 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (^{d6}-DMSO)	7.82 (1 H , d , J = 7.7 Hz) , 7.43 (2 H d , J = 7.7 Hz) , 7.32 (1 H , t , J = 7.7 H z) , 7.03 (2 H , d , J = 7.7 Hz) , 6.91 (2 H , d , J = 7.7 Hz) , 6.81 (1 H , d , J = 7.7 Hz) , 6.77 (1 H , s , Ar_3-C$\underline{H}$) , 6.34 (2 H , s) , 2.09 (6 H , s , ArC$\underline{H}_3$) , 2.02 (6 H , s , ArC$\underline{H}_3$) .
δ_C(75 MHz) (^{d6}-DMSO)	168.7 (carbonyl) , 143.2 , 141.6 , 134.2 , 133.1 , 131.3 , 131.1 , 130.6 , 130.2 , 130.1 , 129.1 , 126.9 , 126.4 , 45.2 (Ar_3-$\underline{C}$H) , 20.9 (Ar$\underline{C}$H$_3$) , 18.6 (Ar$\underline{C}$H$_3$) .

4-Hydroxy-3,7-dicarboxy-8,12-dioxo-8H,12H-dibenzo-[1,2,3-cd, 1,2,3-mn]-pyrene 128 [31]

A mixture of 2"-carboxyphenyl-bis(2',5'dimethylphenyl)methane **50** (11.4 g 0.033 mol) and sodium carbonate (20 g) in water (750 ml) was boiled until a solution was observed . Nitrogen was bubbled through the solution and potassium permanganate (30 g) was added over 4 hours . The mixture was boiled for a further 24 hours then reduced to approximately 20% of the original volume and filtered through a bed of celite . The residue was washed with hot ethanol (3 x 100 ml) and the combined filtrate refluxed for 24 hours in ethanol (500 ml) with 3% sodium amalgam (40 g) . The ethanolic solution was decanted from the mercury residues , evaporated to approximately 10% of the original volume , acidified to pH 1 with c. HCl and filtered . The residue was dissolved in sulphuric acid (d = 1.835 , 150 ml) and stirred at 120°C for 24 hours . The blue solution was poured onto ice (150 g) and the resulting black-blue suspension centrifuged . The residue was washed with water (3 x 100 ml) in the centrifuge and dried to give a purple-blue solid (4.5 g) . Ion exchange chromatography eluting with pH 3.4 buffer gave the title compound as a blue solid , 55 mg (0.43 %) .

IR (ν_{max})	3400 (C-OH) , 1700 (C=O) , 1650 (C=O) , 1560 , 770 , 720 cm $^{-1}$

λ_{max} (DMSO)	590 , 610 , 648 nm^{-1} ($\varepsilon = 12600$, 12900 , 17100 cm^{-1} mol^{-1} dm^{3})
δ_H(300 MHz) (d^6-DMSO)	8.75 (2 H , d , J = 7.3 Hz , $C_{9,11}$-$\underline{H}$) , 8.72 (1 H , d , J = 7.3 Hz , C_1-$\underline{H}$) , 8.69 (1 H , d , J = 7.3 H z , C_5-$\underline{H}$) 7.60 (1 H , t , J = 7.3 Hz , C_{10}-$\underline{H}$) , 7.40 (2 H , d , J = 7.3 Hz , $C_{2,6}$-$\underline{H}$) .

1,4-dimethyl-9-(2',5'-dimethylphenyl)-9(10H)anthraceneone 51[31]

Prepared from 2"-carboxyphenyl-bis-(2',5'dimethylphenyl)methane **50** using the same general procedure used for the preparation of **37** to yield the title compound as pale grey needles , 11 g (55%) , m.p. (glacial acetic acid) 186-88°C (Lit. [31] 190-99°C) .

(Found C, 88.25 ; H, 6.8 . $C_{24}H_{22}O$ requires : C, 88.3 ; H, 6.7 %)

IR (ν_{max})	1650 (C=O) , 1590 , 1560 , 800 , 740 , 710 cm^{-1}
λ_{max}	218 , 270 nm^{-1} ($\varepsilon = 9840$, 9430 cm^{-1} mol^{-1} dm^{3})
δ_H(300 MHz) ($CDCl_3$)	8.15 (1 H , d , J = 7.2 Hz) , 7.35 (1 H , m) , 7.30 (2 H t , J = 7.2 H z) , 7.14 (2 H , d , J = 7.4 Hz) , 7.0 (1 H , d J = 7.4 Hz) , 6.74 (1 H , d , J = 7.2 Hz) , 6.41 (1 H , s) 5.61 (1 H , s , bridgehead-C$\underline{H}$) , 2.84 (3 H , s , ArC$\underline{H}_3$) 2.67 (3 H , s , ArC$\underline{H}_3$) , 2.13 (3 H , s , ArC$\underline{H}_3$) , 1.96 (3 H , s , ArC$\underline{H}_3$).
δ_C(75 MHz) ($CDCl_3$)	188.0 (carbonyl) , 144.6 , 143.7 , 140.3 , 138.5 , 136.0 , 134.4 , 134.1 , 132.5 , 132.8 , 131.4 , 131.4 , 130.8 , 130.8 , 128.7 , 127.1 , 126.6 , 42.6 (bridgehead-$\underline{C}$H) , 23.5 (Ar$\underline{C}H_3$) , 20.9 (Ar$\underline{C}H_3$) , 19.8 (Ar$\underline{C}H_3$) , 19.8 (Ar$\underline{C}H_3$) .

9-Phenyl-10-dihyroanthracene-1,4,2'5'-tetracarboxylic acid **58** [31]

A mixture of 1,4-dimethyl-9-(2',5'-dimethylphenyl)-9(10H)-anthracenone **51** (0.5 g ,1.53 mmol) , nitrobenzene (0.25 mol) and nitric acid (d = 1.1 , 17.5 ml) was boiled for 48 hours . The nitrobenzene was then steam distilled from the reaction and the mixture filtered .The residue was washed with water and then dissolved in 5% w/w sodium hydroxide solution (20 ml) . The mixture was heated to boiling and potassium permanganate added until the purple colouration was steady to 10 minutes boiling . The reaction was then filtered through a bed of celite , the residue washed with sodium hydroxide solution and the combined alkaline liquors acidified to pH 1 with c. HCl .The resulting solution was evaporated to dryness and the residue dissolved in 15% w/w sodium hydroxide solution (30 ml) . Zinc dust (1 g) was added and the mixture boiled under nitrogen for 24 hours . The reaction was then filtered , the residual zinc washed with water and the combined filtrate acidified to pH 1 with c. HCl . The precipitated solids were filtered and then treated several times by dissolving in base , treating with charcoal , and reprecipitating with acid . This treatment yielded the title compound as a pale yellow powder , 280 mg (42%) , m.p. 340-50°C (dec.) (Lit. [31] 340-45°C).

(Found C, 66.15 ; H, 4.1 . $C_{24}H_{16}O_8$ requires : C, 66.6 ; H, 3.7 %)

IR (ν_{max})	1700 (C=O) , 1570 , 1070 , 920 , 860 , 770 cm $^{-1}$
λ_{max}	226 , 288 nm^{-1} (ε = 48800 , 8260 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (^{d6}-DMSO)	7.86 (3H , m) , 7.67 (2 H , m) , 7.40 (1 H m) , 7.32 (1 H , m) 7.29 (1 H , s ,) , 7.16 (2 H , m) , 4.70 (1 H d , J = 20.3 Hz , bridgehead-CH) , 4.25 (1 H , d , J = 20.3 Hz , bridgehead-CH) .
δ_C(75 MHz) (^{d6}-DMSO)	169.0 , 168.8 , 168.7 , 166.4 (carbonyls) , 145.3 138.9 , 137.9 , 135.3 , 135.1 , 134.6 , 134.1 , 133.1 , 132.0 , 131.1 , 130.9 , 128.8 , 128.7 , 128.6 , 128.3 , 127.6 , 126.8 , 126.8 , 41.8 (bridgehead-CH) , 33.2 (bridgehead-CH) .

3,7-Dicarboxy-4,12-dioxo-4H,8H-dibenzo-[1,2,3-cd,1,2,3-mn]-pyrene 54 [31]

A solution of 9-phenyl-10-dihyro-anthracene-1,4,2'5'-tetracarboxylic acid **53** (1g , 2.3 mmol) and m-nitrobenzoic acid (630 mg , 3,8 mmol) in sulphuric acid (d=1.835 , 10 ml) was stirred at 120°C for 30 minutes . Ice (10 g) was then added and the mixture cooled over one hour to room temperature and filtered . The residue was washed with water then dissolved in o-toluidine (150 ml) to give a blood-red solution. This solution was extracted with 5% w/w sodium hydroxide solution (4 x 50 ml) then washed with water (2 x 50 ml) . The combined aqueous washings were then acidified to pH 1 with c. HCl . The precipitated solids were isolated by centrifugation , washed with water (3 x 100 ml) on the centrifuge and dried to give the title compound as a black-red solid , 224 mg (24.5 %) .

(Found C, 69.95 ; H, 2.7 . $C_{24}H_{10}O_6H_2O$ requires : C, 69.9 ; H, 2.9 %)

IR (ν_{max})	1700 (C=O) , 1630 (C=C) , 1590 , 1530 , 1310 , 1260 1170 cm^{-1}
λ_{max} (DMSO)	440 , 480 , 512 , 552 nm^{-1} (ε = 3940 , 567 , 677 , 614 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (d^6-DMSO)	9.85 (1H , s , $C_8\underline{H}$) , 8.75 (2 H , d , J = 9.0 Hz , $C_{1,5}\underline{H}$) 8.72 (1 H , d , J = 9.0 Hz , $C_2\underline{H}$) , 8.67 (1 H , d , J = 9.0 Hz , $C_6\underline{H}$) , 8.45 (1 H , d , J = 7.9 Hz , $C_{11}\underline{H}$) , 7.95 (1 H , t , J = 7.9 Hz , $C_{10}\underline{H}$) , 7.65 (1 H d , J = 7.9 Hz , $C_9\underline{H}$) .

3,3-Di-(2',4'-dimethylphenyl)phthalide 43 [31]

A mixture of *sym* - phthaloyl chloride (115 g , 0.62 mol) and aluminium chloride (115 g , 0.86 mol) was stirred at 100°C for 10 hours . After cooling to room temperature the mixture was dissolved in dichloromethane (250 ml) and then added dropwise to 1,3-dimethylbenzene (377 g , 3.5 mol) at such a rate that only a gentle reflux of solvent was observed . The mixture was then refluxed overnight before being poured onto 2M hydrochloric acid (250 ml) . The organic phase was separated and washed with water (2 x 100 ml) before being evaporated to dryness . The residue (170 g) was refluxed for 24 hours in a mixture of ethanol (500 ml) and hydrazine hydrate (40 ml) . The solution was then evaporated to approximately 20% of the original volume and filtered to give the title compound as a yellow powder , 126 g (59%) , m.p. (ethanol) 164-66°C (Lit.[31] 167-68°C).

(Found C, 84.2 ; H, 6.45 . $C_{24}H_{22}O_2$ requires : C, 84.2 ; H, 6.4 %)

IR (ν_{max})	1770 (C=O) , 1620 , 1610 (C=C) , 880 , 830 , 800 , 770 , 730 , 700 cm $^{-1}$
λ_{max}	202 , 232 nm^{-1} (ε = 17500 , 6510 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	7.92 (1H , d , J = 7.4 Hz) , 7.65 (1 H , t , J = 7.4 Hz) , 7.52 (1 H , t , J = 7.4 Hz) , 7.35 (1 H , d , J = 7.4 Hz) , 6.97 (2 H , s) , 6.89 (2 H , d , J = 8.3Hz) , 6.85 (2 H , d , J = 8.3 Hz) , 2.09 (6 H , s , Ar-C$\underline{H}_3$) , 2.27 (6 H , s , Ar-C$\underline{H}_3$) .
δ_C(75 MHz) ($CDCl_3$)	170.1 (carbonyl) , 151.6 , 138.1 , 137.0 , 135.9 , 133.7 , 133.6 , 129.0 , 127.1 , 126.4 , 126.1 , 125.5 , 125.0 , 94.1 (Ar$_3\underline{C}$H) , 21.3 (Ar-$\underline{C}$H$_3$) , 20.7 (Ar-$\underline{C}$H$_3$) .

2"-carboxyphenyl-bis(2',4'dimethylphenyl)methane 44 [31]

3% Sodium amalgam (970 g) was added over several hours to a refluxing solution of 3,3-di-(2',4'-dimethylphenyl)phthalide **43** (120 g , 0.35 mol) in ethanol (1500 ml) . Reflux was continued for 24 hours and then the ethanol was distilled from the reaction . The residue was boiled with water (6 x 500 ml) , the combined aqueous liquors acidified to pH 1 with c. HCl , cooled and filtered . The residue was dissolved in 2M sodium hydroxide solution , treated with activated charcoal , filtered and reacidified . Filtration gave the title compound as a colourless powder , 106 g (86%), m.p. (ethanol) 226-28°C (Lit.[31] 235-36°C).

(Found C, 83.8 ; H, 7.2 . $C_{24}H_{24}O_2$ requires : C, 83.8 ; H, 7.0 %)

IR (ν_{max})	1690 (C=O) , 1605 (C=C) , 1580 , 840 , 820 , 800 , 750 , 730 , 670 , 650 cm $^{-1}$
λ_{max} (DMSO)	204 nm^{-1} (ε = 65500 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (d^6-DMSO)	7.82 (1H , dd , J = 8.5 , 1.0 Hz) , 7.36 (1 H , dt , J = 8.5 1.0 Hz) , 7.30 (1 H , t , J = 8.5 Hz) , 6.94 (2 H , s) , 6.81 (2 H , m) , 6.42 (2 H , d , J = 7.8 Hz) , 2.04 (6 H s , Ar-C$\underline{H}_3$) , 2.19 (6 H , s , Ar-C$\underline{H}_3$) .
δ_C(75 MHz) (d^6-DMSO)	168.8 (carbonyl) , 143.6 , 138.9 , 136.0 , 135.0 , 131.2 , 131.1 , 131.0 , 130.5 , 129.8 , 128.5 , 126.2 , 126.19 , 44.6 (Ar$_3\underline{C}$H) , 20.5 (Ar-$\underline{C}H_3$) , 18.9 (Ar-$\underline{C}H_3$) .

1,3-dimethyl-9-(2',4'-dimethylphenyl)-9(10H)-anthracenone 45[31]

Prepared from 64g 2"-carboxyphenyl-bis-(2',4'dimethylphenyl)methane **44** using the same general procedure used to prepare **37** to yield the title compound as pale grey needles , 14.3 g (25%) , m.p. (glacial acetic acid) 164-66°C (Lit.[31] 166-68°C) .

(Found C, 88.25 ; H, 6.7 . $C_{24}H_{22}O$ requires : C, 88.3 ; H, 6.7 %)

IR (ν_{max})	1660 (C=O) , 1610 (C=C) , 880 , 820 , 730 cm $^{-1}$
λ_{max}	221 , 272 nm^{-1} (ε = 25800 , 11400 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.29 (1H , d , J = 7.8 Hz) , 8.11 (1 H , s , Hz) , 7.41 (4 H , m) , 7.17 (1 H , s) , 6.95 (1 H , s) , 6.71 (1 H , d , J = 7.9 Hz) , 6.53 (1 H , d , J = 7.9 Hz) , 5.61 (1 H , s) 2.58 (3 H , s , Ar-C$\underline{H}_3$) , 2.39 (3 H , s , Ar-C$\underline{H}_3$) , 2.17 (3 H , s , Ar-C$\underline{H}_3$) , 2.12 (3 H , s , Ar-C$\underline{H}_3$) .

δ_C(75 MHz) ($CDCl_3$)	185.4 (carbonyl) , 145.8 , 140.2 , 137.7 , 136.6 , 136.5 , 135.8 , 134.5 , 133.0 , 132.4 , 131.7 , 130.5 , 129.0 , 128.2 , 127.4 , 127.3 , 126.7 , 125.3 , 42.0 ($Ar_3\underline{C}H$) , 20.9 ($Ar\text{-}\underline{C}H_3$) , 20.7 ($Ar\text{-}\underline{C}H_3$) , 20.1 ($Ar\text{-}\underline{C}H_3$) , 19.8 ($Ar\text{-}\underline{C}H_3$) .

4-Hydroxy-2,6-dicarboxy-8,12-dioxo-8H,12H-dibenzo-[1,2,3-cd, 1,2,3-mn]-pyrene 127

Prepared from 20g 2"-carboxyphenyl-bis(2',4'dimethylphenyl)methane **44** (40 g 0.12 mol) using the same general procedure used to prepare **116** giving the title compound as a blue black solid , 112 mg (0.25 %) .

IR (ν_{max})	1680 (C=O) , 1630 , 1605 (C=C) , 1550 , 1300 , 1265 720 cm^{-1}
λ_{max} (DMSO)	416 , 580 , 616 , 640 nm^{-1} (ε = 12700 , 11200 , 10600 , 9840 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (d^6-DMSO)	9.19 (4H , s , $C_{1,3,5,7}\underline{H}$) , 8.72 (2 H , d , J = 6.8 Hz , $C_{9,11}\underline{H}$) , 7.58 (1 H , t , J = 6.8 Hz , $C_{10}\underline{H}$) .

9-(2',6'-dimethylphenyl)anthracene 102

A mixture of 2-bromo-1,3-dimethylbenzene (3.8 g , 20.5 mmol) and magnesium (0.5 g , 20.6 mmol) in THF (30 ml) was refluxed for 1 hour . The mixture was then pumped under nitrogen pressure onto a solution of anthrone (2 g , 10.3 mmol) in benzene (25 ml) . The reaction was stirred at room temperature for 24 hours then poured onto aq. HCl , the organic phase separated , washed with water (3 x 25 ml) and evaporated to dryness . Column chromatography on silica eluting with 25% v/v 40-60°C bp. petroleum ether-dichloromethane gave the title compound *9-(2',6-'dimethylphenyl)anthracene* **102** as a colourless solid , 315 mg (10%) , m.p. 134-36°C .

(Found C, 93.3 ; H, 6.4 . $C_{24}H_{18}$ requires : C, 93.6 ; H, 6.4 %)

δ_H(300 MHz) ($CDCl_3$) 8.5 (1H , s) , 8.05 (2 H , d , J = 7.9 Hz ,) , 7.40 (4 H , d J = 8.0 Hz) , 7.32 (3 H , m) , 7.25 (2 H , d , J = 8.0 Hz) , 1.85 (6 H , s , Ar-C$\underline{H}_3$) .

δ_C(22.5 MHz) ($CDCl_3$) 137.6 , 131.5 , 128.5 , 127.6 , 127.3 , 126.1 , 125.7 , 125.6 . 125.1 , 20.0 (Ar-$\underline{C}H_3$) .

m/z (%) 282 (M^+ , 100) , 267 (M^+ - CH_3 , 6.0) , 252 (M^+ - $2CH_3$, 16.6) , 178 (M^+ - C_7H_7 , 3.2) .

4,6-Dichloro-1,3-dimethylbenzene 130 [33]

Chlorine gas was bubbled for 30 hours through a well stirred mixture of 1,3-dimethylbenzene **129** (240.5 g , 2.45 mol) and ferric chloride hexahydrate (18 g , 0.066 mol) kept at 0-5°C by an ice-salt cooling bath until one mole of chlorine had been absorbed by weight . The mixture was washed with aq. HCl (2 x 500 ml) , water (2 x 500 ml) , dried ($CaCl_2$) , filtered and finally distilled under reduced pressure . The fraction boiling between 85-100°C / 0.5 mmHg was collected , refrigerated for three days and filtered to give the title compound as colourless needles , 60 g (10%) , m.p. 70°C (Lit. [33] 68.5°C) .

IR (ν_{max}) 1560 (Ar C=C) , 1100 , 1040 , 960 , 875 , 705 cm^{-1}

λ_{max} 204 nm^{-1} (ε = 20600 cm^{-1} mol^{-1} dm^3)

δ_H(90 MHz) ($CDCl_3$) 7.25 (1 H , s) , 7.0 (1 H , s) , 2.25 (6 H , Ar- C$\underline{H}_3$) .

δ_C(22.5 MHz) ($CDCl_3$) 134.2 , 132.6 , 131.8 , 128.7 , 19.3 (Ar-$\underline{C}H_3$).

Attempted preparation of 4,6-dichlorobenzene-1,3-dicarboxylic acid 133 by nitric acid oxidation - preparation of 4,6-dichloro-2,5-dinitro-1,3-dimethylbenzene 131 [34]

A mixture of 4,6-dichloro-1,3-dimethylbenzene **130** (1g , 5.7 mmol) and nitric acid (d= 1.54 , 17 ml) was heated in a sealed tube at 210°C for 3 hours . The reaction was then cooled and filtered to give the dinitro compound **131** as colourless needles , 0.21 g (14%) , m.p. 185°C (Lit. [34] 223°C) .

(Found C, 36.5 ; H, 2.2 ; Cl, 25.6 ; N, 9.5 . $C_8H_6Cl_2NO_4$ requires : C, 36.25 ; H, 2.28 ; Cl, 26.7 ; N, 10.5 %)

m/z Found M^+ 263.9705 , 265.9668 . $C_8H_6{}^{35}Cl_2NO_4$ requires 263.9705 , $C_8H_6{}^{35}Cl^{37}ClNO_4$ requires 265.9675 .

δ_H(90 MHz) ($CDCl_3$) 2.25 (6 H , Ar- $C\underline{H}_3$) .

Attempted preparation of 4,6-dichlorobenzene-1,3-dicarboxylic acid 133 by autoclave oxidation - preparation of 2,4-dichloro-3-methylbenzoic acid 132 [33]

A mixture of 4,6-dichloro-1,3-dimethylbenzene 130 (8 g , 46 mmol) , sodium dichromate dihydrate (13.5 g) and water (175 ml) was placed in a stainless steel autoclave 'bomb' and heated at 240°C for 18 hours . After cooling and filtering , the filtrate was acidified to pH 1 with aq. HCl and filtered to give the mono carboxylic acid **132** as colourless needles , 0.75 g (7%) , m.p. 178-80°C (Lit. [33] 180°C).

IR (ν_{max}) 1710 (C=O) , 1590 , 1090 cm^{-1}

λ_{max} 240 nm^{-1} ($\varepsilon = 8310$ $cm^{-1}\ mol^{-1}\ dm^3$)

δ_H(400 MHz) ($CDCl_3$)	7.8 (1 H , s) , 7.5 (1 H , s) , 2.4 (6 H , Ar-C$\underline{H}_3$) .
δ_C(100 MHz) ($CDCl_3$)	165.0 (carbonyl) , 136.2 , 133.5 , 132.2 , 129.8 , 129.4 127.9 , 18.0 (Ar-$\underline{C}H_3$) .
m/z (%)	206 (M$^+$, 64) , 204 (M$^+$, 100) , 189 (M$^+$ - OH , 45) , 187 (M$^+$ -OH , 70) , 161 (M$^+$ -OH , -CO , 25) , 159 (M$^+$ -OH , -CO , 39) .

4,6-Dichlorobenzene-1,3-dicarboxylic acid 133 [33]

Nitric acid (d = 1.4 , 25 ml) was added dropwise over 30 hours to a vigorously stirred solution of 4,6-dichloro-1,3-dimethylbenzene **129** (50 g , 0.29 mol) in nitrobenzene (50 ml) at such a rate that the temperature neither fell below 150°C nor rose above 180°C during the addition . The reaction vessel was fitted with a Dean and Stark apparatus to condense any nitrobenzene being carried to atmosphere by the aqueous vapours . The reaction was deemed to be essentially complete when the reaction mixture had assumed the appearance of a very thick emulsion at 160°C . At this point the reaction was cooled to room temperature and carbon tetrachloride (150 ml) was added . Filtration gave the title compound as colourless needles , 24 g (38%) , m.p. (ethanol) 276-78°C (Lit. [33] 280°C).

IR (ν_{max})	1700 (C=O) , 1590 , 1550 , 1310 , 1280 , 1090 cm^{-1}
λ_{max}	221, 244 nm^{-1} (ε = 39400 , 18600 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) (d^6-DMSO)	8.4 (1 H , s) , 7.6 (1 H , s) .
δ_C(22.5 MHz) (d^6-DMSO)	165.0 (carbonyl) , 136.1 , 134.5 , 132.2 , 12.9 (Ar-CH_3) .
m/z (%)	236 (M$^+$, 65) , 234 (M$^+$, 98) , 219 (M$^+$ - OH , 66) , 217 (M$^+$ -OH , 100) , 191 (M$^+$ -OH , -CO , 5) , 189 (M$^+$ -OH , -CO , 7) .

4,6-Dichlorobenzene-1,3-dicarboxylic acid,dichloride 61 [45]

A mixture of 4,6-Dichlorobenzene-1,3-dicarboxylic acid **133** (10 g , 42 mmol) and phosphorous pentachloride (17.7 g , 85 mmol) in carbon tetrachloride (250 ml) was refluxed for 4 hours . The resulting yellow solution was filtered and then evaporated to dryness . The phosphoryl chloride produced during the reaction was removed by heating under high vacuum (0.5 mmHg) . The residue was recrystallised from 40-60°C bp. petroleum ether to give the title as colourless needles , 13.9 g (86%) , m.p. (40-60°C bp petroleum ether) 74-76°C (Lit.[45] 76.5°C) .

IR (ν_{max})	1720 (C=O) , 1540 , 790 cm^{-1}
δ_H(90 MHz) ($CDCl_3$)	8.9 (1 H , s) , 7.7 (1 H , s) .
δ_C(22.5 MHz) ($CDCl_3$)	163.3 (carbonyl) , 140.0 , 137.9 , 134.2 , 131.6 .

4,6-Dichloro-1,3-di([1]-naphthoyl)benzene 62 [4]

A mixture of 4,6-Dichlorobenzene-1,3-dicarboxylic acid,dichloride **61** (2.6 g 9.5 mmol) , aluminium trichloride (7.72 g , 58 mmol) and naphthalene (2.44 g , 19 mmol) in dichloromethane (40 ml) was stirred at room temperature for 5 hours . The mixture was then poured onto aq. HCl (150 ml) . The organic phase was separated , washed with water (2 x 50 ml) , dried ($CaCl_2$) , filtered and evaporated to dryness giving a yellow-orange gum . Column chromatography on silica eluting with 50% v/v 40-60°C bp. petroleum ether-dichloromethane gave the title compound as a yellow powder , 2.8 g (65 %) , m.p. 50°C (Lit.[4] 152°C) .

IR (ν_{max})	1660 (C=O) , 1585 , 1280 , 1230 , 1195 , 1090 , 1070 , 970 , 785 cm^{-1}
λ_{max}	228 , 232 nm^{-1} (ε = 27700 , 20000 cm^{-1} mol^{-1} dm^3)

δ_H(90 MHz) ($CDCl_3$)	8.85 (2 H , d , J = 8.7 Hz) , 7.6 (15 H , m) .
m/z	Found M+ 454.0519 , 456.0491 . $C_{28}H_{16}O_2{}^{35}Cl_2$ requires 454.0527 : $C_{28}H_{16}O_2{}^{35}Cl^{37}Cl$ requires 456.0497 .

7,9-Dioxo-7H,9H-dibenzo-[1,2,3-de,1,2,3-jk]pentacene 17 [4]

A mixture of 4,6-Dichloro-1,3-di([1]-naphthoyl)benzene **62** (4.3 g , 9.5 mmol) and potassium hydroxide (0.85 g) in quinoline (10 ml) was refluxed for 3 hours . The mixture was then poured onto aq. HCl (200 ml) and the precipitated black solids filtered and dried . The title compound was isolated by repeated column chromatography on alumina. The column was eluted first with 40-60°C bp. petroleum ether , then successively with 50% v/v petroleum ether - dichloromethane , 25% v/v petroleum ether - dichloromethane , 10 % v/v petroleum ether - dichloromethane and then dichloromethane until no colour was observed in the eluent . Finally the column was eluted with 0.25% v/v methanol-dichloromethane to give the title compound as an air sensitive yellow solid , 188 mg (5.2%) .

IR (ν_{max}) (CH_2Cl_2)	1740 (C=O) , 1610 (C=C) cm $^{-1}$
λ_{max} (CH_2Cl_2)	224 , 320 , 400 , 423 nm^{-1} (ε = 20800 , 5730 , 5220 , 6620 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	9.59 (1 H , s , C_8-$\underline{H}$) , 9.30 (1 H , s , C_{16}-$\underline{H}$) , 8.82 (2 H d , J = 6.8 Hz , $C_{6,10}$-$\underline{H}$) , 8.75 (2 H , d , J = 6.8 Hz , $C_{1,15}$-$\underline{H}$) , 8.25 (2 H , d , J = 6.8 Hz , $C_{4,12}$-$\underline{H}$) , 8.11 (2 H , d , J = 6.8 Hz , $C_{3,13}$-$\underline{H}$) , 7.80 (4 H , t , J = 6.8 Hz , $C_{2,5,11,14}$-$\underline{H}$) .
δ_C(22.5 MHz) ($CDCl_3$)	173.4(carbonyl) , 139.3 , 135.2 , 131.3 , 130.1 130.1 , 129.7 , 129.1 , 128.8 , 128.4 , 126.7 , 126.5 , 125.8 , 125.7 , 125.1 .

4,6-Dibromo-1,3-dimethylbenzene 136 [46]

Iodine (0.5 g) was added over 30 minutes to a vigorously shaken mixture of 1,3-dimethylbenzene (26 g , 0.245 mol) and bromine (43.4 g, 0.27 mol). The mixture was then shaken for a further 3 hours . 2M sodium hydoxide solution (200 ml) was then added and the reaction shaken for a further 10 minutes . The mixture was then filtered , the residue washed with water and recrystallised from ethanol to give the title compound , 14.5 g (22%) , m.p. 67-69°C (Lit. [46] 69°C) .

(Found C, 36.5 ; H, 3.0 ; Br, 60.35 . $C_8H_8Br_2$ requires : C, 36.4 ; H, 3.0 ; Br, 60.6 %)

IR (ν_{max}) 1050 , 945 , 875 , 720 , 650 cm $^{-1}$

λ_{max} 203 , 219 nm^{-1} (ε = 39600 , 17000 cm^{-1} mol^{-1} dm^3)

δ_H(300 MHz) ($CDCl_3$) 7.6 (1 H , s) , 7.0 (1 H , s) , 2.25 (6 H , s , ArC$\underline{H}_3$) .

δ_C(22.5 MHz) ($CDCl_3$) 136.9 , 135.0 , 132.5 , 122.5 , 22.0 (Ar$\underline{C}H_3$) .

4,6-Dibromobenzene-1,3-dicarboxylic acid 137 [47]

Prepared from 29g 4,6-dibromo-1,3-dimethylbenzene **136** using the same general method used in the preparation of **133** as a colourless powder , 50% , m.p. 248-50°C (Lit [47] 250-54°C) .

IR (ν_{max}) 1700 (C=O) , 1380 , 1060 , 920 , 770 , 720 cm $^{-1}$

λ_{max} 221 , 243 nm^{-1} (ε = 78000 , 36600 cm^{-1} mol^{-1} dm^3)

δ_H(90 MHz) (d^6-DMSO) 8.4 (1 H , s) , 8.05 (1 H , s) .

δ_C(22.5 MHz) (d^6-DMSO)	166.0 (carbonyl) , 139.0 , 133.5 , 131.1 , 124.7 .

4,6-Dibromobenzene-1,3-dicarboxylic acid, dichloride 138 [48]

Prepared from 2.3g 4,6-Dibromobenzene-1,3-dicarboxylic acid **137** using the same general method used to prepare **61** as colourless needles , 87% , m.p. 70-72°C (Lit. [48] 76.5°C) .

IR (ν_{max})	1760 (C=O) ,1570 , 840 cm $^{-1}$
δ_H(90 MHz) ($CDCl_3$)	8.7 (1 H , s) , 8.1 (1 H , s) .
δ_C(22.5 MHz) ($CDCl_3$)	164.1 (carbonyl) , 140.8 , 136.9 , 134.1 , 127.4 .

4,6-Dibromo-1,3-di([1]-naphthoyl)benzene 139

Prepared from 2g 4,6-Dibromobenzene-1,3-dicarboxylic acid, dichloride **138** using the same general method used to prepare **62** to give the title compound *4,6-Dibromo-1,3-di([1]-naphthoyl)benzene* **139** as a pale yellow powder , 19 % , m.p. 68-74°C .

IR (ν_{max})	1675 (C=O) , 1580 , 1280 , 1235 , 780 cm $^{-1}$
λ_{max}	218 , 252 nm^{-1} (ε = 28400 , 16800 cm^{-1} mol^{-1} dm^3)
δ_H(90 MHz) ($CDCl_3$)	8.85 (2 H , d , J = 9.0 Hz) , 7.8 (7 H , m) , 7.6 (8 H , m) .
m/z (%)	544 (M+ , 4) , 155 (naphthoyl+ , 42) , 127 (naphthyl+ 38) , 80 (11 , Br) .

Benzene-1,3-dicarboxylic acid, dichloride 141 [49]

Prepared from 25g benzene-1,3-di-carboxylic acid **140** using the same general procedure used to prepare **61** as colourless needles, 56 %, m.p. 40-42°C (Lit. [49] 43-46°C).

δ_H(90 MHz) ($CDCl_3$)	8.8 (1 H, t, J = 2.5 Hz), 8.45 (2 H, dd, J = 7.7, 2.5 Hz), 7.8 (1 H, t, J = 7.7 Hz).
δ_C(22.5 MHz) ($CDCl_3$)	166.8 (carbonyl), 136.3, 133.7, 133.1, 129.3.

1,3-Di([1]-naphthoyl)benzene 142 [49]

Prepared from 8.8g Benzene-1,3-dicarboxylic acid, dichloride **141** using the same general procedure used to prepare **62** as a pale yellow powder, 26 %, m.p. 170-78°C (Lit [49] 191°C).

IR (ν_{max})	1650 (C=O), 1590, 1300, 1280, 1235, 1195, 1135 780, 750, 720 cm^{-1}
λ_{max}	221 nm^{-1} ($\varepsilon = 37300\ cm^{-1}\ mol^{-1}\ dm^3$)
δ_H(90 MHz) ($CDCl_3$)	8.2 (3 H, m), 7.8 (6 H, m), 7.45 (9 H, m).

[1]-Naphthylmethylenemalonic acid, diethyl ester 144 [42]

A solution of benzoic acid (2.4 g, 20 mmol) and piperidine (3.6 g, 40 mmol) in benzene (8 ml) was added dropwise over 1 hour to a vigorously stirred solution of 1-naphthaldehyde (40 g, 0.26 mol) and diethylmalonate (48 g, 0.30 mol) in benzene (160 ml). The solution was refluxed for a further 3 hours and then poured onto aq. HCl (200 ml). The organic phase was separated, washed with water (2 x 50 ml) and dried ($MgSO_4$). The resulting solution was distilled under reduced pressure to give the title compound as a colourless oil , 66 g (86 %) , bp. 204-06°C / 2.5 mmHg (Lit . [42] 203.5°C / 2 mmHg) .

(Found C , 72.6 ; H, 6.15 . $C_{18}H_{18}O_4$ requires : C, 72.5 ; H, 6.0 %)

IR (ν_{max}) (liquid film)	3000 , 1720 (C=O) ,1640 (Ar C=C) , 1520 , 1480 , 1460 , 1410 , 1380 , 1350 , 1250 , 1080 , 860 , 810 , 790 cm $^{-1}$
λ_{max}	232 , 240 , 310 nm^{-1} (ε = 39100 , 136200 , 95700 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.48 (1 H , s) , 7.89 (1 H , d , J = 7.1 Hz) , 7.84 (1 H , d , J = 7.7 Hz) , 7.59 (1 H , d , J = 7.7 Hz) , 7.5 (3 H , m) , 7.43 (1 H , t , J = 7.7 H z) , 4.39 (2 H , q , J = 7.1 Hz , $-C\underline{H}_2-$) , 4.15 (2 H , q , J = 7.15 Hz , $-C\underline{H}_2-$) , 1.35 (3 H , t , J = 7.15 Hz ,$-C\underline{H}_3$) , 1.04 (3 H , t , J = 7 .1 Hz $-C\underline{H}_3$) .
δ_C(75 MHz) ($CDCl_3$)	165.8 , 163.6 (carbonyls) , 140.8 , 133.0 , 136.0 , 130.5 , 130.2 , 129.0 , 128.4 , 126.6 , 126.1 , 126.1 , 124.9 , 123.7 , 61.4 ($-\underline{C}H_2-$) , 61.1 ($-\underline{C}H_2-$) , 13.9 ($-\underline{C}H_3$) , 13.5 ($-\underline{C}H_3$) .

Di-([1]-naphthyl)methylmalonic acid , diethyl ester 70 [42]

A solution of 1-bromonaphthalene (4.3 g , 20 mmol) in THF (15 ml) was added dropwise over 30 minutes to a vigorously stirred refluxing slurry of magnesium (0.5 g , 20 mmol) in THF (25 ml) . Reflux was continued for a further 3 hours after which point a solution of [1]-Naphthylmethylenemalonic acid , diethyl ester **144** (5.5 g , 18 mmol) in THF (25 ml) was added dropwise over 30 minutes . The solution was refluxed for a further 3 hours and then poured onto aq. HCl (100 ml) . The organic phase was washed with 50 ml portions of water , saturated sodium bicarbonate solution and water again before being dried ($MgSO_4$) . After filtration the solution was evaporated to dryness to give the title compound as a colourless powder , 2.4 g (31 %) , m.p. (ethanol) 108-10°C (Lit [42] 113-14°C) .

(Found C, 78.85 ; H, 6.15 . $C_{28}H_{26}O_4$ requires : C, 78.9 ; H, 6.1 %)

IR (ν_{max})	1770 (C=O) , 1610 (Ar C=C) , 1390 , 1350 , 1290 , 1270 , 1160 , 800 cm^{-1}
λ_{max}	232 , 284 nm^{-1} ($\varepsilon = 86500 , 31000$ cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.42 (2 H , d , J = 7.5 Hz) , 7.85 (2 H , d , J = 7.5 Hz) , 7.75 (2 H , d , J = 7.5 Hz) , 7.5 (8 H , m) , 6.52 (1 H , t J = 12.0 H z , -C$\underline{H}$) , 4.26 (1 H , d , J = 12.0 Hz , -C$\underline{H}$) , 3.9 (4 H , q , J = 7.1 Hz , -C$\underline{H}_2$-) , 0.9 (6 H , t , J = 7.1 Hz ,-C$\underline{H}_3$) .
δ_C(75 MHz) ($CDCl_3$)	167.7 (carbonyl) , 137.4 , 133.7 , 131.2 , 128.5 , 127.4 , 126.1 , 125.3 , 124.9 , 124.6 , 123.2 , 61.1 (-$\underline{C}H_2$-) , 58.3 (-$\underline{C}H$), 40.1 (-$\underline{C}H$), 13.2 (-$\underline{C}H_3$).

Di-([1]-naphthyl)methylmalonic acid 71 [4]

A mixture of di-([1]-naphthyl)methylmalonic acid , diethyl ester **70** (29.1 g , 68 mmol) and potassium hydroxide (112 g) in ethanol (750 ml) was refluxed for 3 hours . The ethanol was then distilled from the reaction vessel and water (250 ml) was added . This too was distilled from the reaction vessel and a second volume of water (250 ml) was added , the pH adjusted to pH 1 with c. HCl , the mixture cooled to room temperature and filtered . The residue was recrystallised from ethanol to give the title compound as colourless needles , 19 g (75 %) , m.p. (ethanol) 190-92 °C (Lit. [4] 196°C) .

(Found C, 78.05 ; H, 5.0 . $C_{24}H_{18}O_4$ requires : C, 78.05 ; H, 4.9 %)

IR (ν_{max})	1710 (C=O) , 1610 (Ar C=C) , 1290 , 1350 , 1290 , 1270 , 1220 , 930 , 795 , 785 cm $^{-1}$
λ_{max}	246 , 280 nm $^{-1}$ (ε = 75100 , 36600 cm $^{-1}$ mol $^{-1}$ dm ^{3})
δ_H(300 MHz) ($CDCl_3$)	7.98 (2 H , d , J = 7.6 Hz) , 7.90 (2 H , d , J = 7.9 Hz) , 7.73 (2 H , d , J = 7.9 Hz) , 7.45 (6 H , m) , 7.33 (2 H , t , J = 7.6 H z) , 6.52 (1 H , d , J = 3.6 Hz , -CH) , 3.57 (1 H , d , J = 3.6 Hz , -CH) .
δ_C(75 MHz) ($CDCl_3$)	173.5 (carbonyl) , 139.3 , 133.5 , 131.1 ,128.8 , 126.8 , 126.6 , 126.1 , 125.2 , 123.3 , 53.4 (-CH) , 42.3 (-CH).

7,8-Dioxo-7H,8H-dibenzo[1,2,3-de,1,2,3-hi]naphthacene 18 [4]

A mixture of di-([1]-naphthyl)methylmalonic diacid **71** (1.9 g , 5.1 mmol) and phosphorous pentoxide (18,5 g) in nitrobenzene (100 ml) was stirred for 3 days at room temperature under argon . Water (100 ml) was added dropwise to the reaction mixture prior to steam distillation of the nitrobenzene . Filtration gave a black residue . The title compound was isolated by repeated column chromatography on alumina . The column was first eluted with 40-60°C bp. petroleum ether and then successively with 50% v/v petroleum ether - dichloromethane , 25% v/v petroleum ether - dichloromethane , 10%v/v petroleum ether - dichloromethane and finally dichloromethane until no colour was seen in the eluent discharge . Elution with 0.25% v/v methanol-dichloromethane gave the title compound as an acid sensitive yellow solid , 90 mg (5%) .

IR (ν_{max}) ($CHCl_3$)	2940 , 1670 (C=O) , 1570 (Ar C=C) , 1370 , 1330 , 1120 , 800 cm $^{-1}$
λ_{max} ($CHCl_3$)	205 , 244 , 362 , 410 nm $^{-1}$ (ε = 27500 , 28600 , 8530 15000 cm $^{-1}$ mol $^{-1}$ dm ^{3})
δ_H(300 MHz) ($CDCl_3$)	8.72 (2 H , d , J = 7.8 Hz , $C_{6,9}$-H) , 8.25 (2 H , d , J = 7.7 Hz , $C_{1,14}$-H) , 8.23 (2 H , d , J = 7.7 Hz , $C_{3,12}$-H) , 8.18 (2 H , d , J = 7.8 Hz , $C_{4,11}$-H) , 7.82 (2 H , t , J = 7.7 H z , $C_{2,13}$-H) , 7.75 (2 H , t , J = 7.8 Hz , $C_{5,10}$-H) .

δ_C(75 MHz) ($CDCl_3$)	181.7 (carbonyl) , 135.4 , 135.3 , 134.4 , 133.3 , 132.3 , 131.3 , 130.3 , 129.9 , 128.3 , 127.6 , 125.9 , 125.4 .

9-methylene-9(10H)anthracenone 81 [43]

Anthrone (5 g , 26 mmol) was added to a boiling solution of sodium hydroxide (5 g) in water (1500 ml) . Boiling was continued until a solution was observed . The pH of the solution was then carefully adjusted to pH 8-9 using sulphuric acid (d=1.835) . The mixture was filtered and formaldehyde solution (40% w/v , 200 ml) added to the filtrate . The mixture was then stood overnight . The title compound was isolated by filtration as a buff-coloured powder , 4.0 g (76 %) , m.p. (benzene) 150°C (Lit [43] 148°C) .

(Found C, 87.2 ; H, 4.75 . $C_{15}H_{10}O$ requires : C, 87.3 ; H, 4.9 %)

IR (ν_{max})	1650 (C=O) ,1600 (Ar C=C) , 1380 , 1180 , 1090 , 920 , 790 , 690 cm^{-1}
λ_{max}	232 , 250 , 270 , 332 , 348 nm^{-1} (ε = 124400 , 50600 51500 , 15000 , 13700 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	8.35 (2 H , d , J = 8.0 Hz) , 8.00 (2 H , d , J = 8.0 , 1.4 Hz) , 7.65 (2 H , t , J = 8.0 , 1.4 Hz) , 7.54 (2 H , t , J = 8.0 H z) , 6.35 (2 H , s -C<u>H</u>$_2$-) .
δ_C(75 MHz) ($CDCl_3$)	136.7 , 136.3 , 132.8 , 130.0 , 128.5 , 127.2 , 127.1 , 123.6 , 115.6 (-<u>C</u>H$_2$-) .

5,9,14-Trioxo-5H,9H,14H-dibenzo[1,2-a,1,2,3-de]naphthacene 84 [43]

A solution of 9-methylene-9(10H)anthracenone **81** (1.0 g , 4.85 mmol) and 1,4-naphthoquinone (1.6 g , 30 mmol) in ethanol (10 ml) was refluxed for

24 hours under argon .The reaction mixture was then cooled and filtered to give the title compound as orange needles , 0.99 g (57 %) .

(Found C, 82.6 ; H, 3.2 . $C_{25}H_{12}O_3$ requires : C, 83.3 ; H, 3.3 %)

IR (ν_{max})	1670 (C=O) ,1590 (Ar C=C) , 1310 , 1280 , 780 , 720 cm $^{-1}$
λ_{max}	208 , 236 , 288 , 420 nm^{-1} (ε = 61100 , 49600 , 43800 , 13800 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	10.09 (1 H , d , J = 8.7 Hz) , 9.34 (1 H , s) , 8.87 (1 H d , J = 7.6 Hz) , 8.57 (1 H , d , J = 8.4 Hz) , 8.50 (1 H , d , J = 8.4 Hz) , 8.33 (2 H , m) , 8.02 (1 H , t , J = 8.4 Hz) , 7.87 (3 H , m) , 7.65 (1 H , t ,J = 7.6) .

5,15-Dioxo-5H,15H-tribenzo[1,2-a,1,2,3-de,1,2,3-hi]naphthacene 19 [43]

A vigorously stirred mixture of 5,9,14-trioxo-5H,9H,14H-dibenzo[1,2-a,1,2,3-de]naphthacene **84** (1 g , 2.77 mmol) , copper powder (1 g) , water (2 ml) and sulphuric acid (d = 1.835 , 19 ml) was heated at 90°C for 15 minutes . Glycerol (1.3 ml , 1.64 g , 178 mmol) was then added and the mixture stirred at 125°C for 30 minutes . The reaction was then cooled and water (15 ml) added . The resulting suspension was filtered and the residue dried. Column chromatography on silica eluting with benzene-chloroform gave the title compound as an orange solid , 10% .

λ_{max} (CH_2Cl_2)	206 , 224 , 304 , 400 , 450 , 470 (ε = 36400 , 36600 , 30200 , 9900 , 16300 , 15200 cm^{-1} mol^{-1} dm^3)
δ_H(300 MHz) ($CDCl_3$)	9.5 (1 H , s , C_{16}-$\underline{H}$) , 9.1 (1 H , d , J = 8.3 Hz , C_{14}-$\underline{H}$) , 8.9 (1 H , d , J = 6.7 Hz , C_4-$\underline{H}$) , 8.8 (1 H , d , J = 6.7 Hz , C_6-$\underline{H}$) , 8.6 (1 H , d , J = 8.3 Hz , C_{12}-$\underline{H}$) , 8.5 (2 H

t , J = 6.7 Hz , $C_{2,3}$-$\underline{H}$) , 8.4 (1 H , d , J = 6.7 Hz , C_{8}-$\underline{H}$) 8.1 (1 H , d , J = 6.7 Hz , C_{1}-$\underline{H}$) , 8.0 (1 H , t , J = 8.3 Hz , C_{13}-$\underline{H}$) , 7.8 (3 H , m , $C_{7,10,11}$-$\underline{H}$) , 7.5 (1 H , d , J = 8.3 Hz , C_{9}-$\underline{H}$) .

Further elution of the column gave the transangular diketone 5,9-Dioxo-5H,9H-tribenzo[1,2-a,1,2,3-de,1,2,3-mn]naphthacene **82** [43] as a pale yellow solid .

λ_{max} (CH_2Cl_2)	232 , 250 , 292 , 364 , 420 (ε = 12100 , 15600 , 10300 , 9500 , 12500 cm^{-1} mol^{-1} dm^{3})
δ_H(300 MHz)	10.5 (1 H , d , J = 8.1 Hz , C_{10}-$\underline{H}$) , 9.1 (1 H , s , C_{16}-$\underline{H}$) 8.9 (3 H , m , $C_{4,8,1}$-$\underline{H}$) , 8.7 (1 H , d , J = 8.1 Hz , C_{6}-$\underline{H}$) , 8.6 (1 H , d , J = 8.1 Hz , C_{12}-$\underline{H}$) , 8.4 (1H d , J = 7.0 Hz , C_{15}-$\underline{H}$) , 8.3 (1 H , d , J = 7.0 Hz , C_{13}-$\underline{H}$) 8.2 (1 H , t , J = 8.1 Hz , C_{3}-$\underline{H}$) , 8.0 (3 H , m , $C_{2,7,11}$-$\underline{H}$) , 7.5 (1 H , t , J = 7.0 Hz , C_{14}-$\underline{H}$) .

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Chapter Three

Electron Spin Resonance Studies

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3.1 Introduction to Electron Spin Resonance Spectroscopy .

It is the aim of this next section to introduce some of the fundamentals of electron spin resonance (ESR) spectroscopy in a qualitative , non-mathematical manner [1] . In doing so , much of the emphasis will be placed on those aspects of theory which relate directly to the ESR spectra discussed later in the chapter ; beginning first with the fundamentals of ESR spectroscopy as related to mono-radicals or radical anions , and later branching out to discuss the situation regarding triplet biradicals .

An electron has an intrinsic angular momentum called spin . The electron may have two spin states ; $M_s = +1/2$ (spin up) or $M_s = -1/2$ (spin down) . In the absence of an external magnetic field the two spin states have the same energy . When a magnetic field is applied it may interact with the magnetic moment of the electron . In such a case the two spin states cease to be degenerate . This is known as the Zeeman effect and the energy levels as Zeeman levels . The energy level of spin state $M_s = -1/2$ is lowered and that of $M_s = +1/2$ raised . The energy gap arising between the spin states is proportional to the intensity of the applied field , H . Transitions from one Zeeman level to the other , in which an electron is said to flip its spin state , occur when the system is exposed to microwave radiation with the resonance frequency υ (Figure 3.1) . This resonance frequency is also proportional to the intensity of the applied field .

In ESR spectroscopy the signal is recorded as the first derivative of the intensity , A , of the absorption of the microwave radiation at the resonance frequency with respect to the field strength , H .

A well resolved ESR spectrum may consist of more than one hundred lines . This complexity is known as the hyperfine structure and is caused by the interaction of the unpaired electron and magnetic nuclei in the radical . The most common elements in organic hydrocarbon radicals are hydrogen , carbon , oxygen and nitrogen . The most common isotopes of carbon and oxygen , ^{12}C and ^{16}O , have spin quantum number $I = 0$ and so , being diamagnetic , do not interact with the electron . As there are no nitrogen

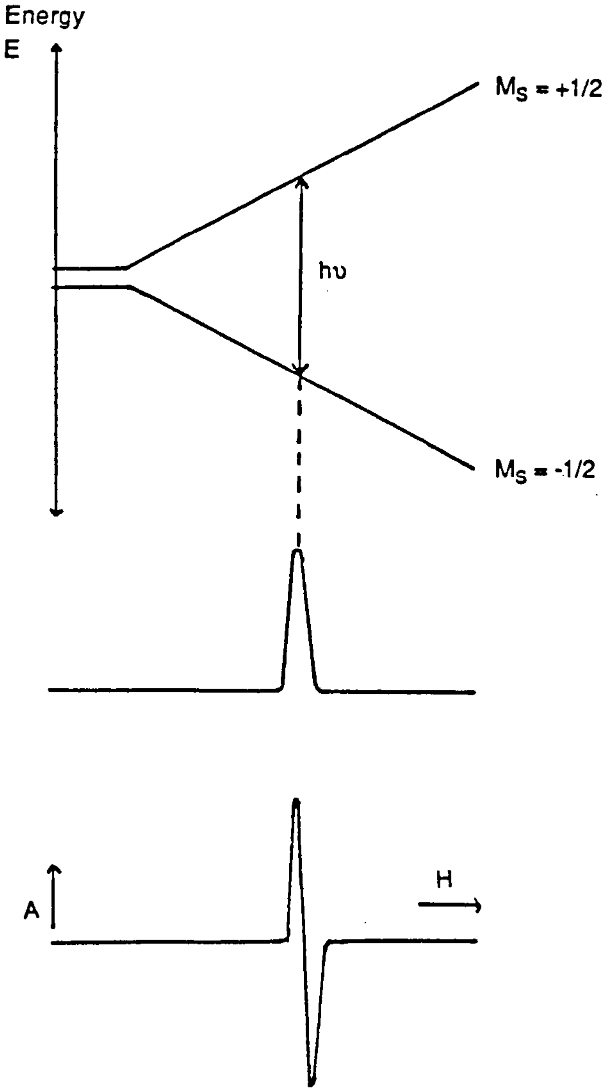


Figure 3.1

Top : Splitting of the spin levels of an electron in an applied magnetic field of intensity, H.

Middle : ESR signal obtained at constant frequency υ and variable field strength, H.

Bottom : 1st derivative of the absorption intensity, A, as a function of field strength, H.

moieties in the compounds we have studied , we shall limit the scope of the discussion of hyperfine structure to the case of the interaction of a free electron with a proton nucleus (Figure 3.2) . The proton has a spin quantum number I = 1/2 . This results in the energy levels of the spin states M_s = +1/2 and -1/2 each being split into two sub-levels corresponding to the two quantum states of the proton , M_I = +1/2 and -1/2 . For the M_s = +1/2 spin state of the electron the sub-level with M_I = +1/2 lies above the unperturbed energy level , while that of M_I = -1/2 lies below . For M_s = -1/2 the reverse is true .

The high field selection rule states that only those transitions which occur between spin states of the same quantum number M_I , are allowed ie. $\Delta M_S = \pm 1$ and $\Delta M_I = 0$. Consequently two hyperfine lines are detected in the spectrum resulting from the interaction of an electron with a proton .

When an electron interacts with two equivalent proton nuclei the hyperfine structure illustrated in Figure 3.3 originates from the degeneracy of certain spin configurations of the equivalent nuclei , greatly reducing the number lines in the resulting spectrum . In general where there are n equivalent nuclei of spin quantum number I , this gives rise to (2nI + 1) equidistant hyperfine lines in the ESR spectrum . In the case of protons , where I = 1/2 , the ESR spectrum will contain (n + 1) lines .

Diagrams similar to Figure 3.3 can be drawn up for radicals containing inequivalent proton nuclei by splitting the energy levels in succession according to the interactions with the nuclei in question . In such cases the hyperfine structure produced by nucleus A is in turn split by the hyperfine structure produced by nucleus B , and so on . It is worth noting at this point that the equivalence , or otherwise , of the proton nuclei of a hydrocarbon radical depends solely on the spin density of the free electron at each nucleus . Predictions of the hyperfine coupling constant can be made from Hückel molecular orbital calculations of the aforementioned spin density .

ESR spectroscopy is a technique used to study unpaired electrons . For a biradical only the triplet state may be observed and we shall now turn our attention to the theory behind the spectra produced in such cases .

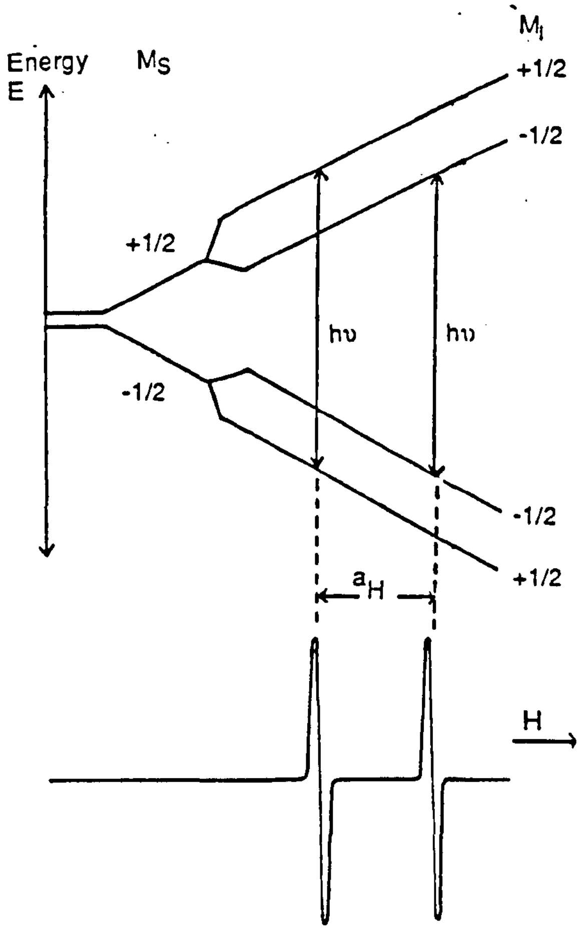


Figure 3.2 : Splitting of an ESR signal by the hyperfine interaction between the unpaired electron and a proton . ^{a}H denotes the coupling constant for the interaction (Gauss) .

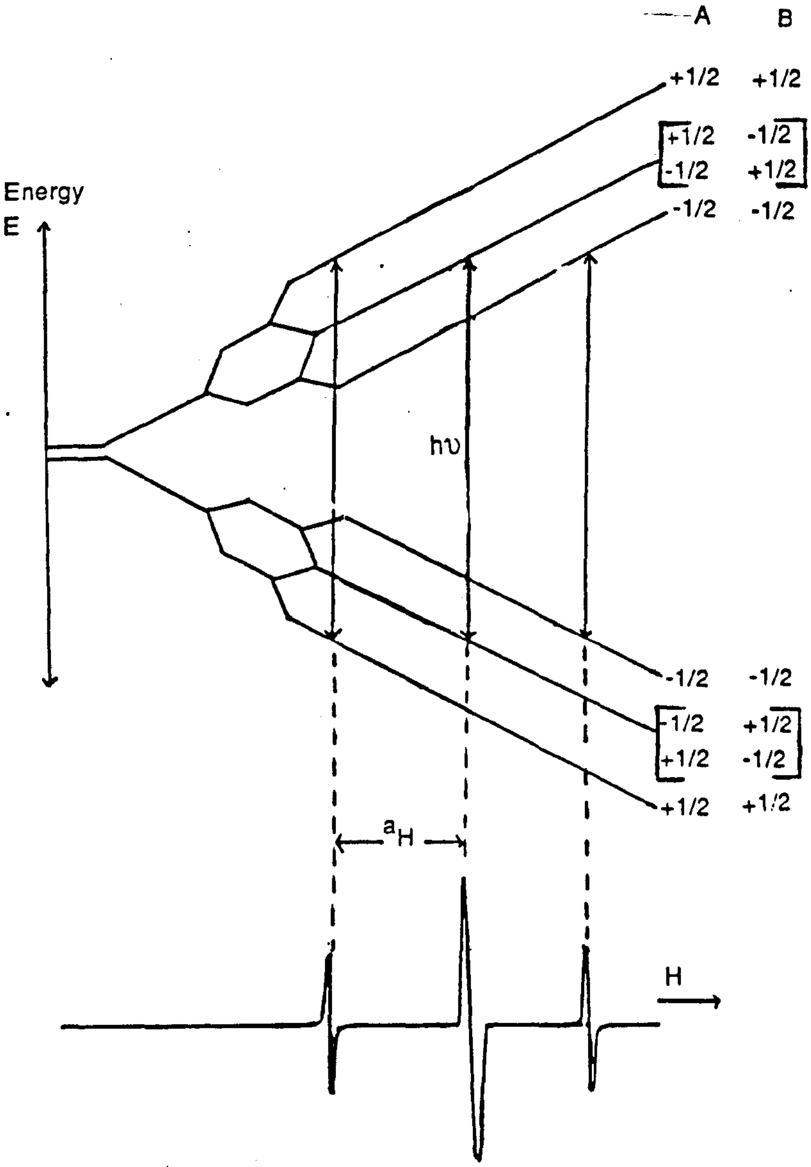


Figure 3.3 : Splitting of an ESR signal by the hyperfine interaction between the unpaired electron and two equivalent protons A and B .

When a molecule contains two unpaired electrons in the triplet state their magnetic properties resemble those of paramagnetic ions of spin quantum number S = 1 . The degeneracy of the ground state energy levels is removed giving rise to three distinct energy levels in the absence of an external field . This is known as ' zero-field splitting ' . This case is illustrated in Figure 3.4 which shows the energy levels and transitions for a triplet molecule as a function of magnetic field strength , H . The $\Delta M_s = \pm 1$ transitions allowed by the high field selection rule give rise to a doublet and the splitting (2D) differs widely according to the orientation of the molecule relative to the field . One consequence of this is that the high field selection rules no longer strictly apply and that there is now a finite probability of observing the " forbidden " $\Delta M_s = \pm 2$ transition . This transition occurs at approximately the half-field position and is therefore known as the half-field line . In an ESR spectrum the intensity of the half-field line is often some tens of times weaker than the two intense lines of the major splitting arising from the dipole-dipole interactions of the electrons . The magnitude of this latter splitting is inversely proportional to the cube of the separation of the unpaired electrons ie. $2D \propto 1/r^3$, and may be several hundreds of Gauss wide .

The ESR spectrum of a triplet ground state biradical cannot normally be observed in solution because the triplet's very short relaxation times give rise to very broad lines . The spectra are therefore normally observed in frozen " glassy " media . The spectrum observed in a frozen matrix is a little more complex than that shown in Figure 3.4 . The splitting between the signals ($\Delta\upsilon$) varies with the angle θ by which the molecule is tilt ed with respect to a parallel orientation to the field in accordance with the formula ,

$$\Delta\upsilon = 2D\ (3/2 \cos^2 \theta - 1/2)$$

where D is the zero field splitting parameter .

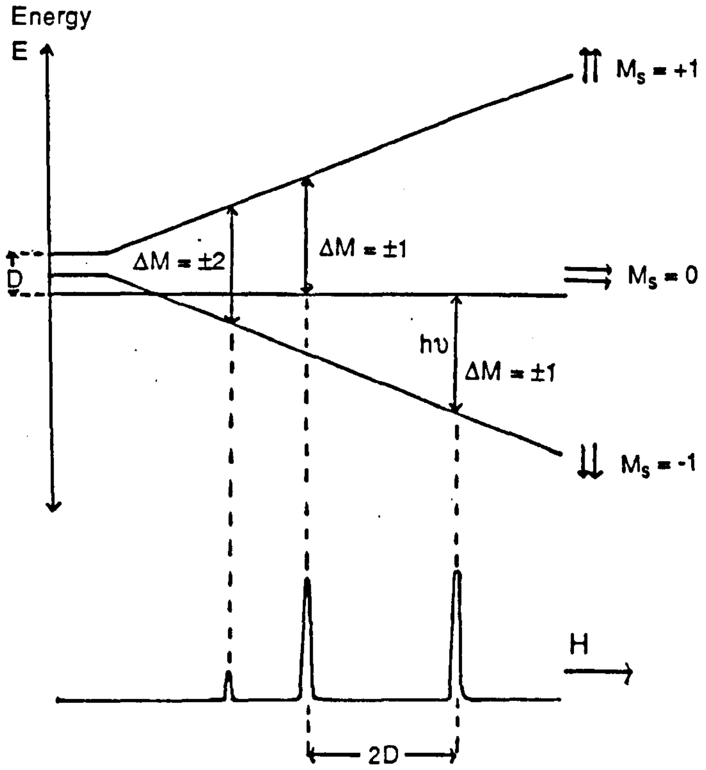


Figure 3.4 : Energy levels and transitions as a function of magnetic field strength , H , for a triplet state molecule .

The signal intensity at each angle θ is dependent on the probability of finding the molecule at that angle . The combination of the orientation dependency of both the signal intensity and dipolar splitting gives the signal line shape illustrated in Figure 3.5 when solved for all values of θ [point z represents the least probable orientation vector aligned with the applied field , H , and xy represents the most probable perpendicular orientations] . The $\Delta M_s = \pm 2$ transition is unaffected by the orientation of the triplet molecule and therefore gives the same signal as before . This line shape is known as a pake curve and is characteristic of triplet molecules . When the first order differential of signal intensity with respect to field strength H is computed , the spectrum is seen to consist of four lines resulting from the dipole-dipole interactions plus the half-field line , as illustrated in Figure 3.6 .

So far we have been considering the unpaired electrons of a triplet as point charges . For π-biradicals account must be taken of the mean separation between the regions of electron density in the π-orbitals . This actually results in there being four regions of electron density , rather than two , but does not affect the overall shape of the pake curve and resulting spectrum .

There is one further complicating factor . For molecules with less than C_{3V} symmetry the angular distribution of the molecules in the frozen matrix must be characterised relative to two angles . This gives an extra $\Delta M_s = \pm 1$ transition related to another zero field splitting parameter E , which may be regarded as a measure of the symmetry of the system being studied . The pake curve under such circumstances is illustrated in Figure 3.8 .

In reality , the structure in the spectra illustrated in Figures 3.6 and 3.8 would be severely broadened due to spin coupling between the unpaired electrons and proton nuclei . This broadening would be greatly reduced if the diyl was generated from a fully deuterated precursor , given that the spin quantum number of deuterium I = 1 and so the deuterium interacts much less strongly with the free electrons .

Figure 3.5

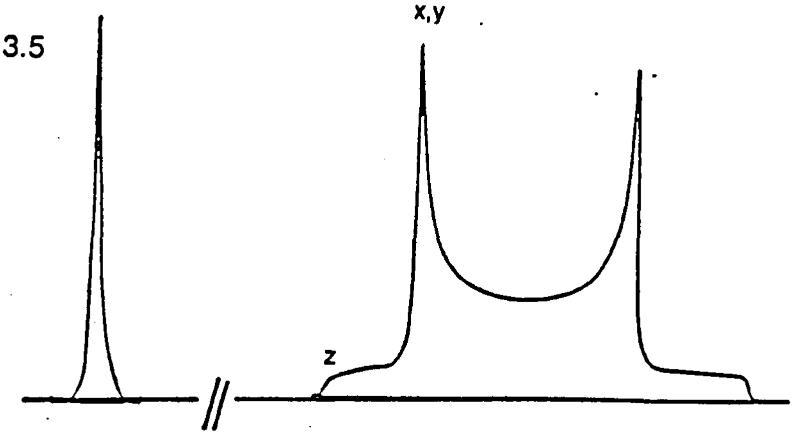
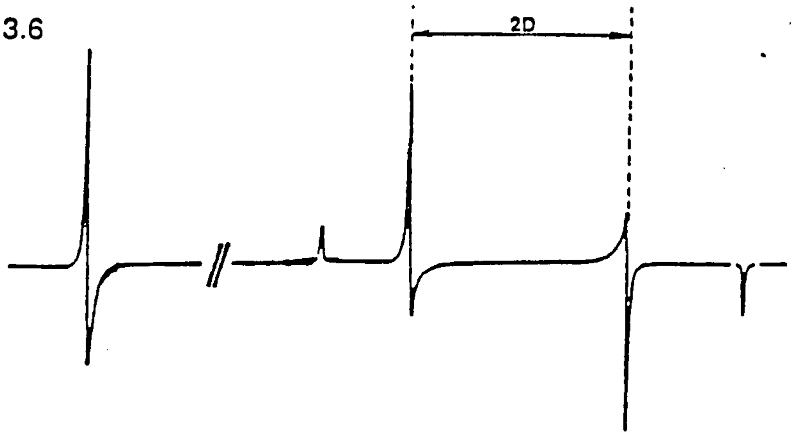


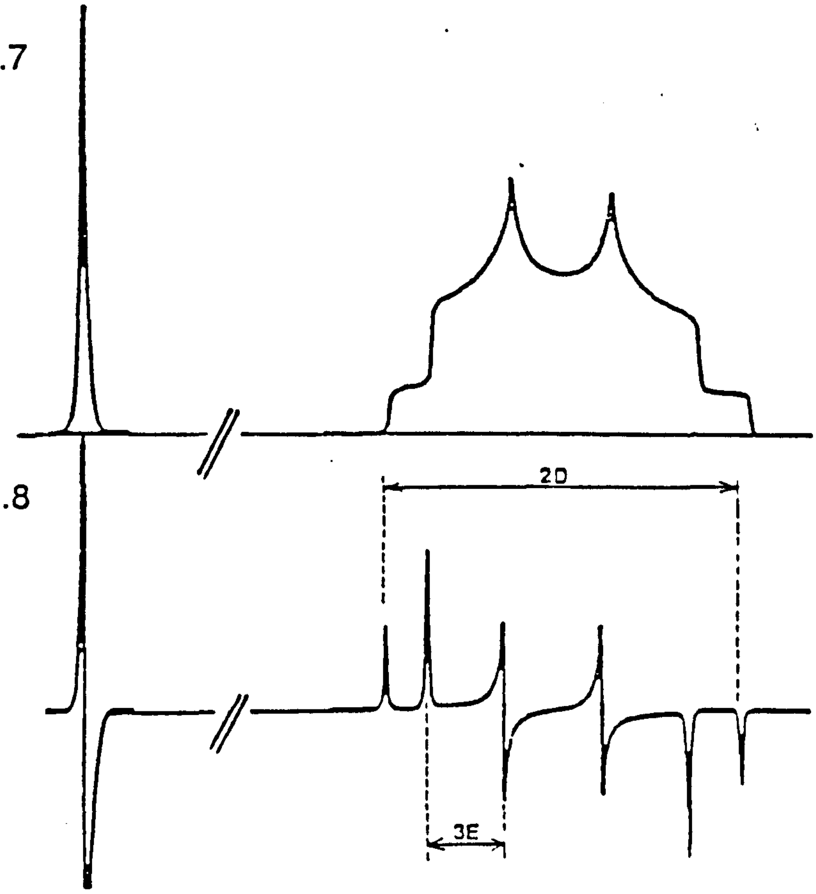
Figure 3.6



Figures 3.5 (top) and 3.6 (bottom) show the theoretical absorption and first derivative spectra for randomly orientated triplet molecules where $E = 0$.

Figure 3.7

Figure 3.8



Figures 3.7 (top) and 3.8 (bottom) show the theoretical absorption and first derivative spectra for randomly orientated triplet molecules where $E \neq 0$.

3.2 Electron Spin Resonance Techniques

The ESR spectra discussed later in this Chapter were observed on either a Bruker ER 200 spectrometer fitted with a Bruker ER 4111 VT-S variable temperature unit or a Varian E-6 spectrometer fitted with a Bruker 4111 VT variable temperature unit .

Figure 3.9 illustrates the basic features of these spectrometers . The sample was accomodated in a resonance cavity placed in the centre of the homogeneous field region between the two poles of the magnet . Energy was supplied to the sample through a wave guide from the source , a klystron valve , as microwave radiation in the X-band ($\upsilon = 3$ cm) . Interposed between the klystron and the wave guide was an attenuator to regulate the power input , and a ferrite insulator to protect the klystron from reflected radiation . The radiation reached the detector via a T-shaped bridge . The sensitivity of the detector was raised by throwing the bridge slightly out of equilibrium . The noise which then appeared was the background noise of the signal . The signal to noise ratio was improved by modulating the magnetic field with a 100 kHz component . The modulated signal which appeared was recorded as the first derivative of intensity with respect to field strength .

Figure 3.10 illustrates the two types of ESR sample tubes used in this research . Those of Type A were used solely in the attempts to generate radicals photochemically and were basically narrow ESR grade silica- glass tubes attached to a pyrex bulb . Type B tubes were a little more complicated but essentially the apparatus split into two halves ; a narrow ESR grade silica-glass tube separated by a coarse glass sinter from the ' reaction vessel ' . The sinter was present to prevent insoluble materials , especially metals , from reaching the ESR tube when the solution under investigation was tipped across from the reaction vessel . Both types of tube could be attached to a high vacuum line and sealed under vacuum across the constriction . The UV / Vis. spectroscopic studies employed a cell similar in design to the Type B ESR tubes but in which a rectangular cross section

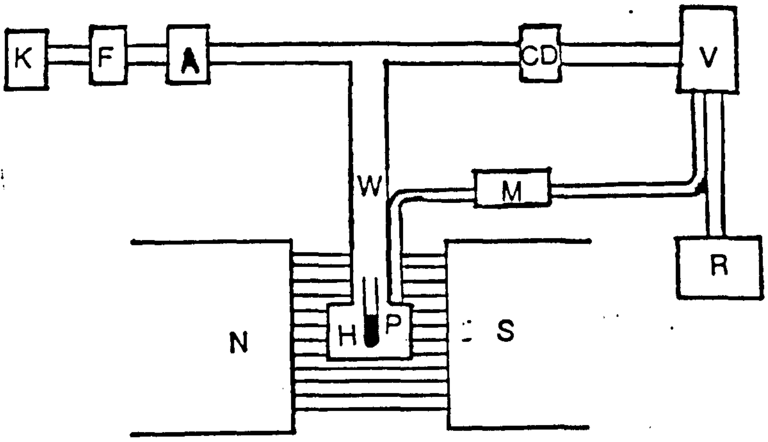


Figure 3.9 : Basic structure of an ESR spectrometer.
N and S = poles of the electromagnet ; H = resonant cavity ; P = sample ; W = wave-guide ; K = klystron ; F = ferrite insulator ; A = attenuator ; CD = crystal detector ; V = amplifier ; R = recorder ; M = modulator.

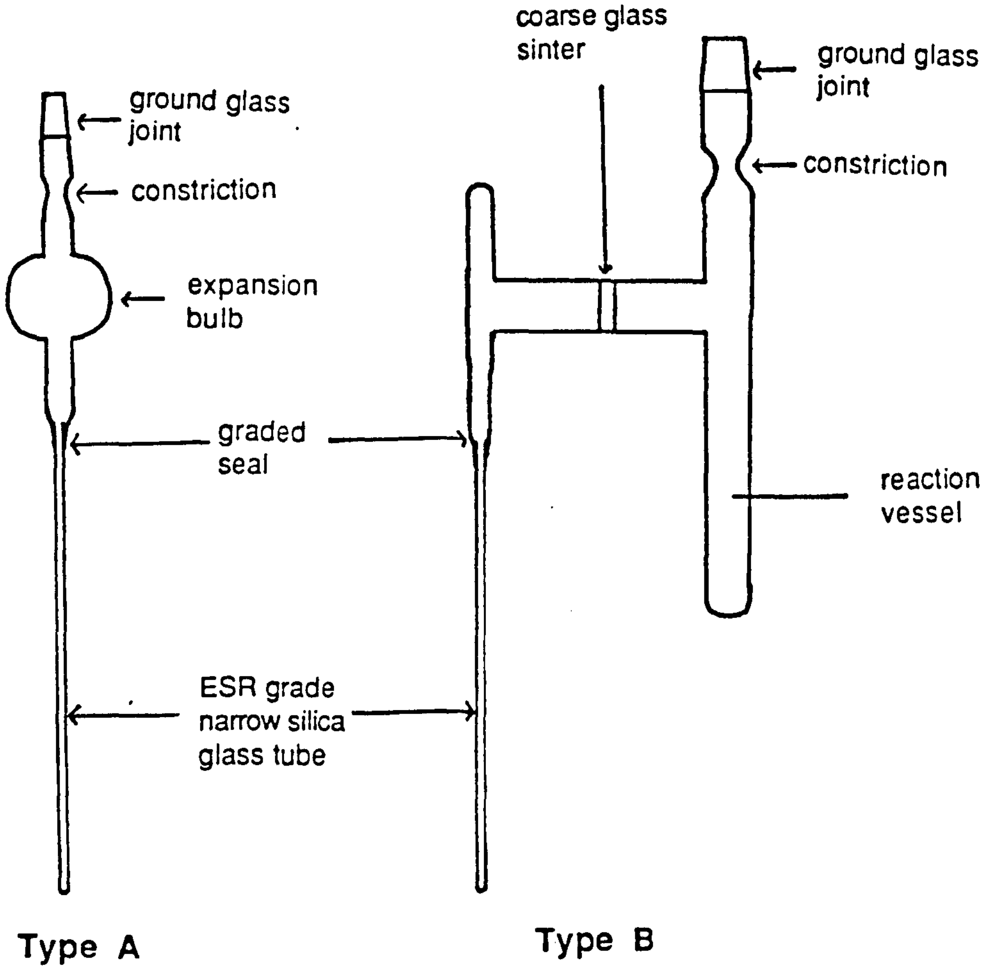


Figure 3.10 : Illustration of the two types of ESR tubes used in our research.

pyrex cell replaced the ESR tube .

Broadening of the spectrum and loss of observable hyperfine splitting caused by dipole-dipole interaction and spin exchange may be observed in concentrated solutions . The dipole-dipole interaction becomes stronger as the distance between the unpaired electrons decreases ie. as the solution is concentrated . Spin exchange , in which two unpaired electrons belonging to neighbouring radicals swap molecules is clearly enhanced with increasing concentration . This effect broadens the spectrum leading to loss of observable hyperfine splitting by reducing the lifetime of a spin state .

In general the concentration of the solutions made up for ESR testing was approximately 0·5 mg of compound dissolved per millilitre of solvent . Obviously in Type A ESR tubes the design did not allow for dilution of the sample once the tube had been sealed . However when radicals were observed in Type B tubes it was possible to dilute solutions by distillation of solvent from the ' reaction vessel ' to the ESR tube , thus diminishing the above described line broadening effects .

When making up ESR samples it was essential to exclude oxygen from the system . Thus after solutions were made up , the ESR tubes were attached to a dedicated high vacuum system operating at 10^{-5} - 10^{-4} mmHg and subjected to multiple freeze-pump-thaw cycles to remove the dissolved oxygen . In these cycles the sample was frozen in liquid nitrogen , the head space of the cell evacuated , the link to the vacuum line closed and the sample allowed to thaw . In doing so any dissolved gases bubbled from solution and filled the head space . After many such cycles the sample was essentially oxygen free . For Type A tubes the samples expanded into the bulbs on thawing , relieving the pressure from the delicate walls of the silica-glass ESR tubes .

The two principle solvents used in these studies were tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) . THF was distilled from sodium benzophenone ketyl directly onto the sample from a THF source attached to the vacuum line , whilst DMF was purified according to the procedures described in Perrin and Perrin [3] , passed through alumina and stored over 4Å molecular sieves .

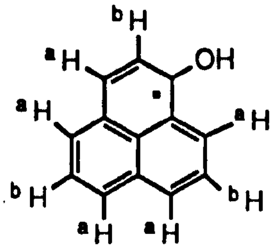
3.3 The Photochemical Route to Non-Kekulé Polynuclear Aromatics .

In the following discussions all photochemical experiments were irradiated at ambient temperatures with an Engelhard-Hanovia Medium Pressure Mercury Vapour Lamp emitting ulta-violet radiation at >310 nm.

3.3.1 The Photolysis of Perinaphthenone

The photolysis of perinaphthenone (phenalenone **73**) was first reported by Rabold [4] in 1965 . He suggested that the hyperfine splitting observable in his first low resolution spectra was due to a set of five equivalent protons at the 3, 4 , 6 , 7 , 9 , or ^{a}H , positions giving rise to a splitting of 6.25 G (Figure 3.11) being split by another set of three equivalent protons , at the 2 , 4 and 8 , or ^{b}H , positions giving rise to a splitting of 2.0 G . However his later , higher resolution spectra suggested that there were small differences among the a and b hyperfine splitting constants.

Figure 3.11



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Our own work has confirmed Rabold's later opinions . We photolysed perinaphthenone in methyl-THF and DMF , recording the spectra at room temperature , Figures 3.12 and 3.13 . The spectra observed in methyl-THF were of much higher resolution than Rabold's and it was possible to see how the slight differences in hyperfine splitting among the a and b protons caused the simple 6 / 4 line spectrum observed in DMF to break down into a more subtly complex pattern . The line broadening observed in the DMF spectra was thought to be a concentration effect . As was mentioned earlier ,

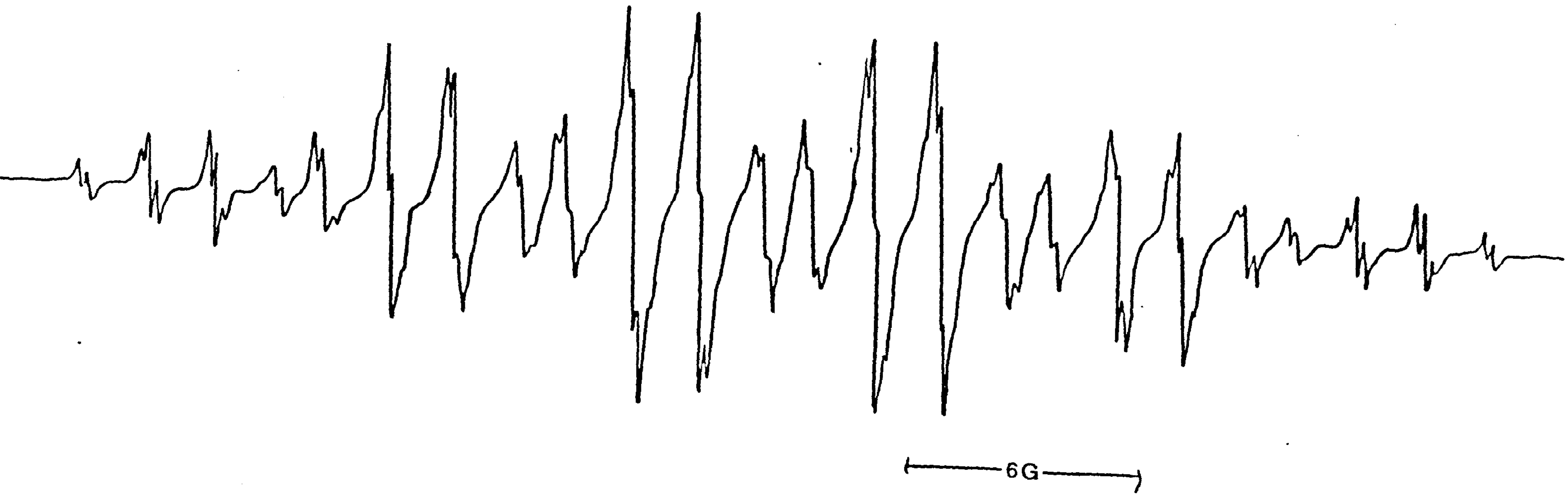
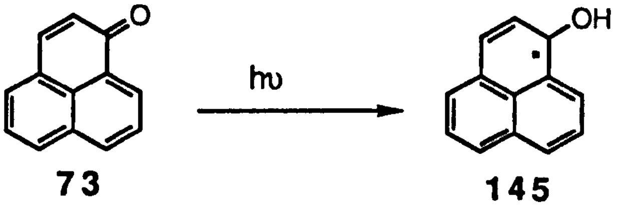


Figure 3.12 : ESR spectrum of the perinaphthenone radical anion after 12 hours photolysis , observed in methyl-THF solution at ambient temperature .

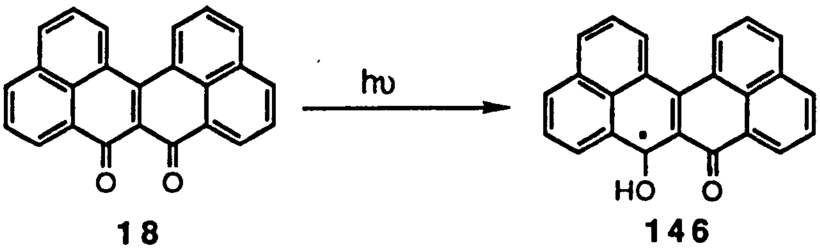
Figure 3.13 : ESR spectrum of the perinaphthenone radical anion after 12 hours photolysis , observed in DMF solution at ambient temperature .

many of the compounds we wished to investigate were insoluble in the common organic solvents traditionally used as ESR solvents, such as THF or methyl-THF . The appearance of the perinaphthenyl radical spectra , albeit broadened but with no other obvious effect from the solvent , vindicated the use of DMF as a rather unusual ESR solvent for radical ion work .



3.3.2 Photolysis of Dibenznaphthacenequinone

The room temperature ESR spectrum obtained from a solution of dibenznaphthacenequinone **18** after photolysis for 12 hours is shown in Figure 3.14 . The spectrum has over 40 peaks with possibly more hidden beneath the broad hyperfine structure . This effect is probably caused by the concentration of the solution . In theory this system is one which could give rise to 2^{12} lines . The complicated nature of the hyperfine structure meant it was not possible to interpret the spectrum . However , the spectrum was thought to be that of the radical **146** . The spectrum broadens to a single peak when cooled to 100K with no evidence of the pake or half-field line so typical of a triplet biradical .



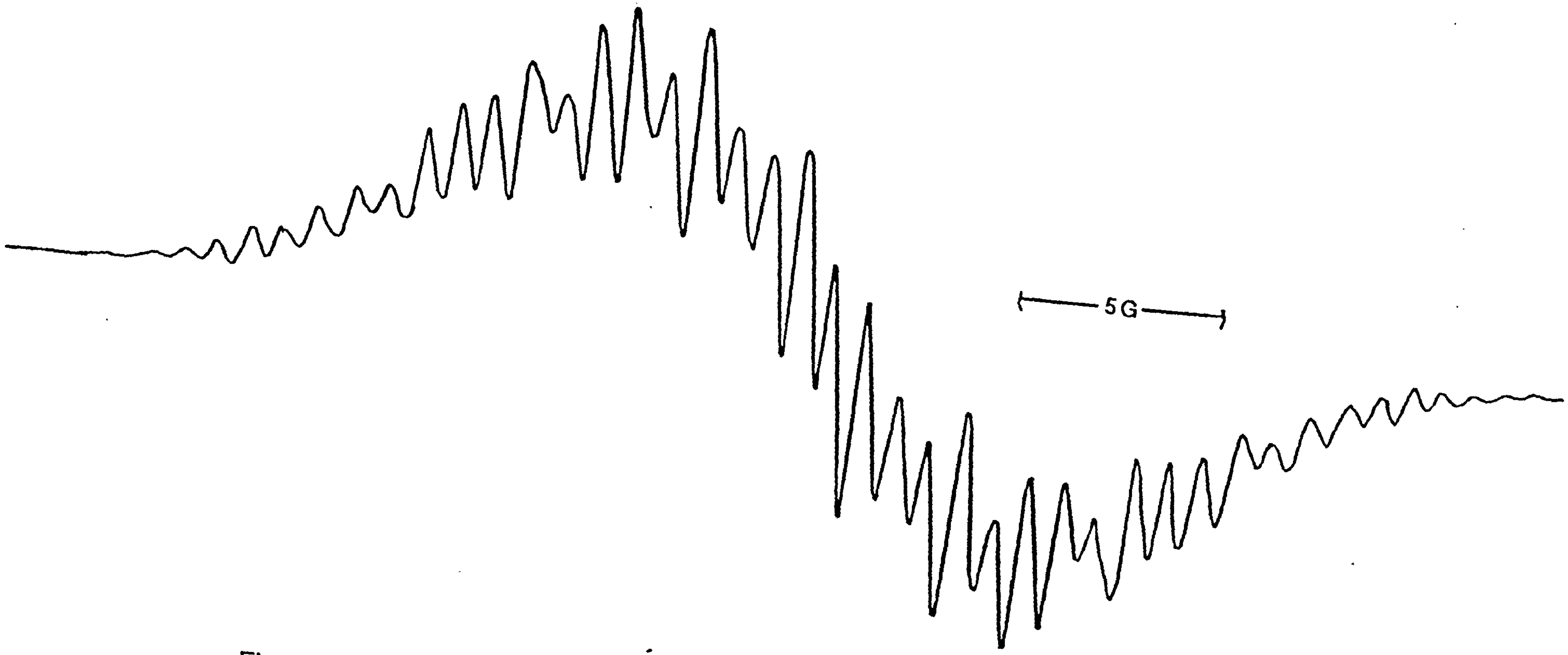


Figure 3.14 : ESR spectrum of the dibenznaphthacenequinone radical anion after 12 hours photolysis , observed in THF solution at ambient temperature .

3.3.3 Summary of Photolysis Experiments

Compound	Solvent	ESR observed after 72 hours irradiation	
		298K	100K
73	IPA	Mono-radical spectrum	Single peak
"	Me-THF	"	"
18	THF	Mono-radical spectrum	Single broad line
"	IPA	No Spectrum	No spectrum
"	glycerol	"	"
"	MeOH	"	"
17	THF	Very weak , broad single peak	No spectrum
16	THF	Very weak , broad single peak	No spectrum
116	DMF	Very weak , broad single peak	Very weak single line
128	DMF	Very weak , broad single peak	No spectrum
54	DMF	Very weak , broad single peak	Very weak single line

The above compounds were all prepared and photolysed in the same manner as dibenznaphthacenequinone **18** . All samples were checked for ESR signals after every six hours photolysis . It is interesting to note the stability of the dibenzpentacenequinone **17** and the triangulenequinone **16** under conditions in which both perinaphthenone **73** and dibenznaphthacenequinone **18** gave rise to radical spectra after only six hours . It is not known why no spectrum was observed when compound **18** was photolysed in Methyl-THF , iso-propanol (IPA) and methanol (MeOH) .

3.4 The Reduction Route to Non-Kekulé Polynuclear Aromatics

In 1972 Woischnik [5] reported the generation of the perinaphthyl radical **145** by alkali metal reduction of the ketone group . He observed an ESR spectrum very similar to that of Rabold . It was our aim to use this principle of metal reduction to sequentially reduce both ketone groups in our molecules **16 - 19** to produce diradical dianions . We were able to investigate the metal reductions of the ketones **16 - 18** but time and equipment constraints prevented us investigating the reduction of compound **19** .

The general experimental procedure was as follows : the compound and metal were loaded into the reaction vessel of a Type B ESR tube . Solvent was added and the sample degassed . After sealing , the samples were placed in a Kerry Ultrasonics Ltd . Type PUL 55 ultra-sound bath operating at 50 Hz and subjected to ultra-sound for twelve hours in order to break up the organic compound and also to break down any oxide coating the metal surface . The samples were then allowed to stand at room temperature and periodically observed for signs of an ESR signal . If a signal was detected at room temperature , the sample was cooled to 100K and the shape of the signal at this temperature observed . If no signal was observed at room temperature the samples were still cooled to 100K to see if any signals were observed at that temperature .

3.4.1 The Reduction of Dibenznaphthacenequinone

The ESR spectrum observed at room temperature when compound **18** was treated with potassium metal in THF is shown in Figure 3.15 . In principle this system could give rise to 3^6 lines . The complicated nature of the spectrum defied complete analysis . Nevertheless it was believed to be that of the radical species **146** . Similar results were obtained from reactions of the quinone **18** with lithium metal , calcium metal or lithium metal and trimethylsilylchloride .

A change in colour was observed during these experiments ; the original yellow solution gradually being replaced by a deep red . Therefore

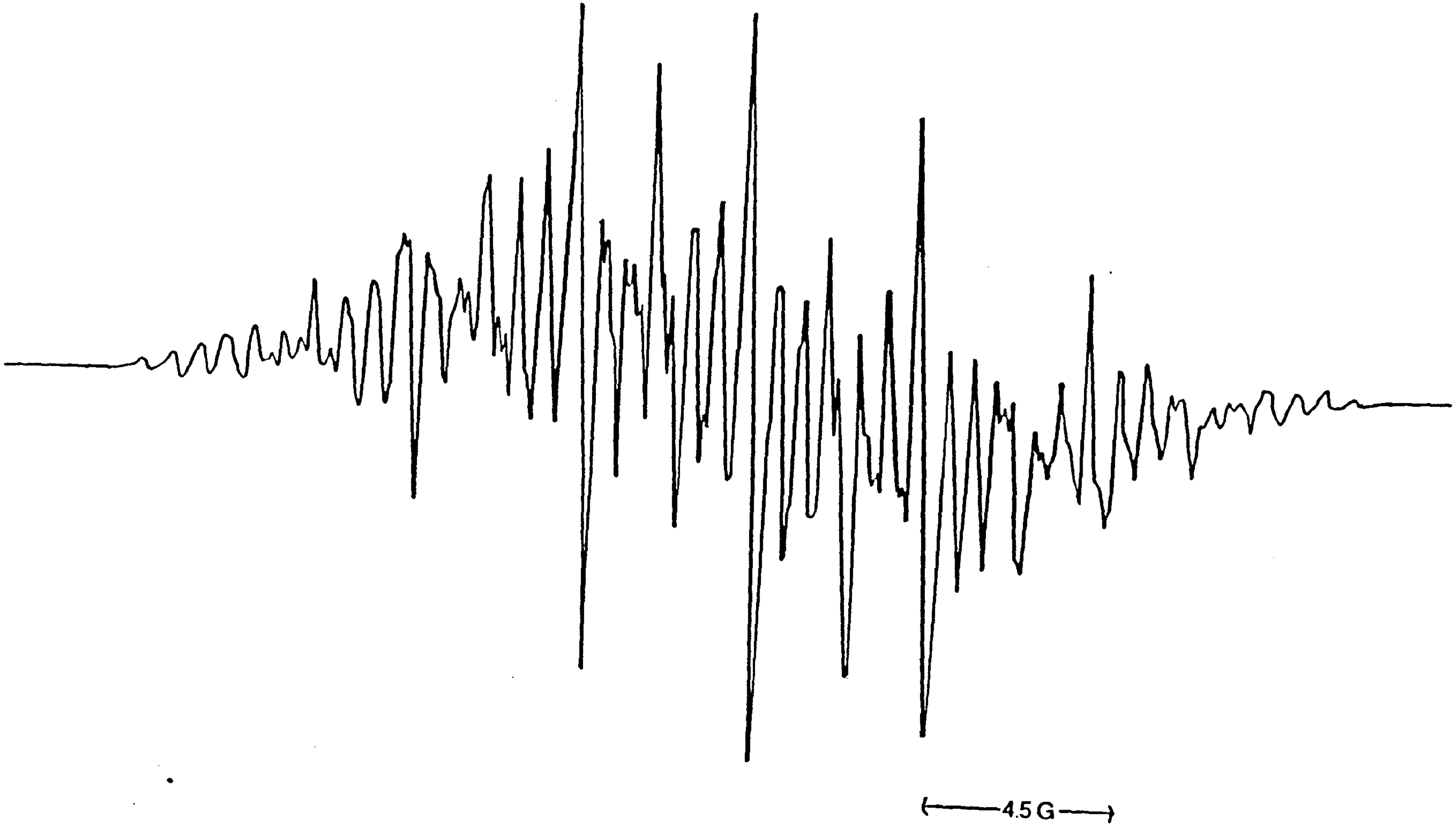


Figure 3.15 : ESR spectrum of the dibenznaphthacenequinone radical anion produced by reduction with potassium metal , observed in THF solution at ambient temperature .

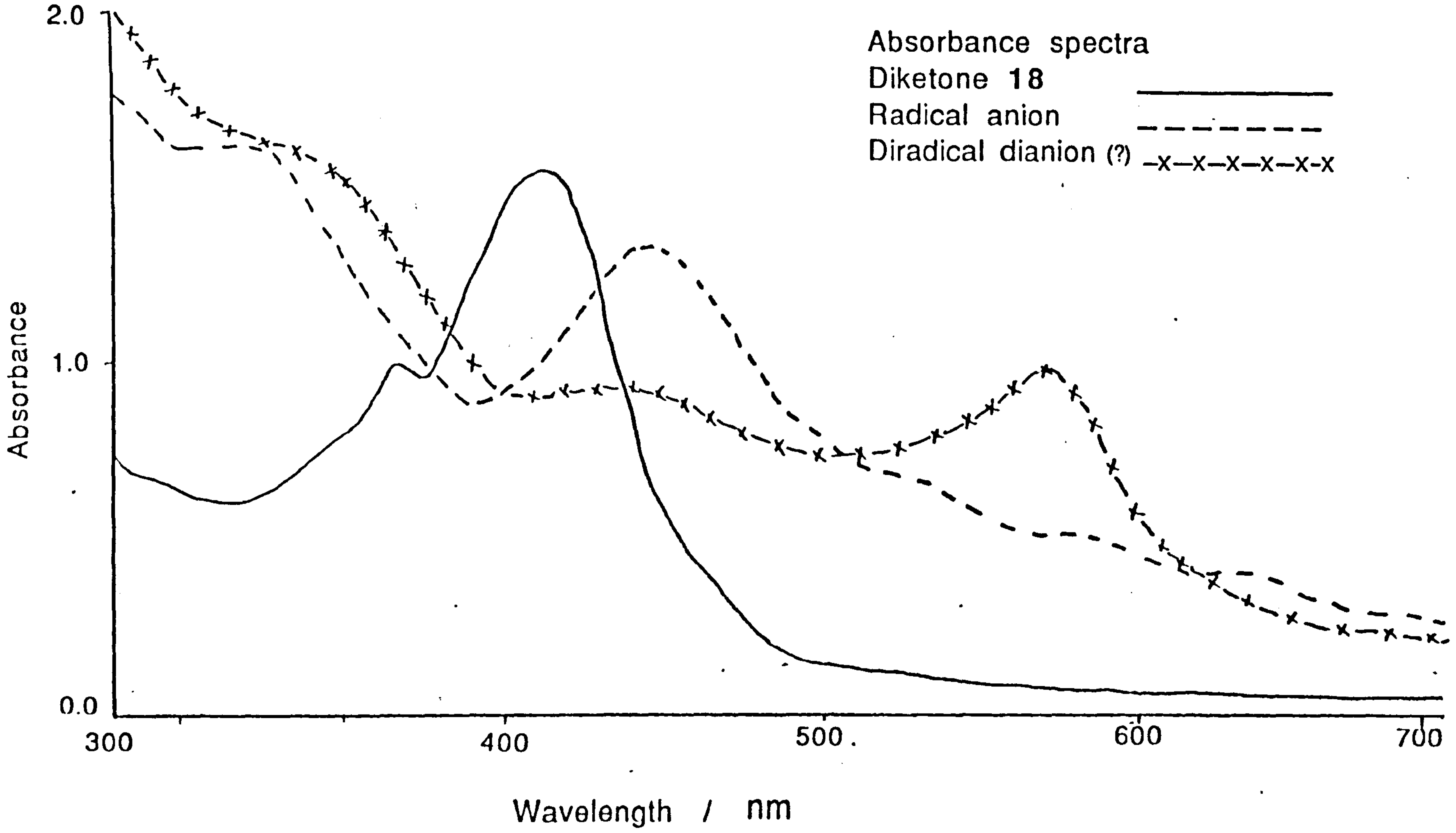
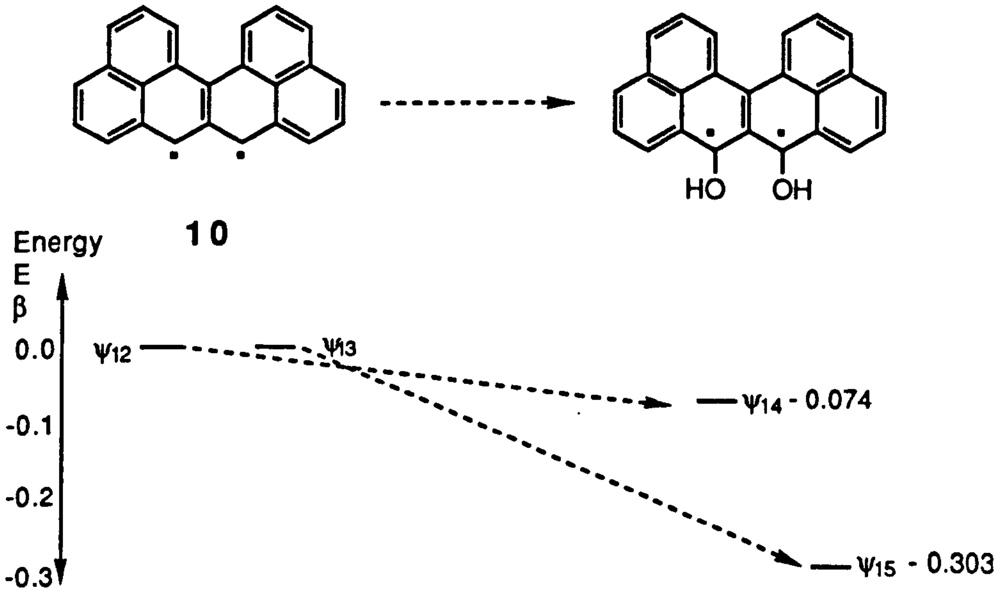


Figure 3.16 : UV / Vis. absorbance spectra observed when a solution of dibenznaphthacenequinone in THF was treated with lithium metal .

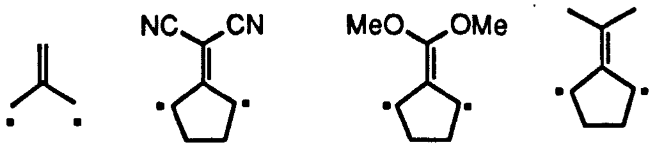
the reduction reactions were followed by observing the change in the absorbance spectra over a period of days . Figure 3.16 illustrates the case where the reaction of the diketone **18** with lithium metal was followed by UV / Vis. spectroscopy . It can be seen that the major absorbance at approximately 415 nm' was shifted to longer wavelengths , first to 445 nm^{-1} an absorbance believed to be due to the monoradical anion , then to 570 nm^{-1} , an absorbance believed to be due to a diradical dianion species . However at 100K only a single peak was observed . No spectra typical of triplet species were observed .

It is possible that the diradical dianion may exist as two independant monoradicals in much the same way as do some triphenylmethane derivatives [1(b)] but given the delocalised nature of the π-system this seems unlikely . What is more probable is that the lifting of the degeneracy of the NBMOs relative to the parent hydrocarbon caused by the oxygen-substituents allows a sufficiently large energy gap to appear between the two orbitals to allow the two unpaired electrons to overcome the electron-electron repulsive forces and find it energetically most favourable to pair up in a single orbital . It thus seems likely that the diradical has a singlet ground state . This situation is illustrated in Figure 3.17 . Since ESR is a technique for observing unpaired electrons , we cannot observe the singlet state diradical dianion .

Figure 3.17



It can be seen from Figure 3.17 that the two oxygen-functions lower the degeneracy of the NBMOs from zero β to -0.074 and -0.303 β , a separation of approximately 0.23 β . However , it is not unusual for triplet molecules to have splittings of this size . Whether or not the second electron pairs up in the lower energy orbital or a triplet is obtained depends on the balance between this energy gap (favouring the singlet) and the electron-electron exchange interaction (favouring the triplet) . In general non-disjoint π-biradicals have large exchange interactions and hence triplet ground states . Berson [6] has studied the molecules illustrated below . The splitting of the NBMOs ranges from 0 - 0.3 β and yet the biradicals still have triplet ground states . It is thus all the more surprising that it appears that the dibenznaphthacenequinone diradical species exists as a singlet , given that its degeneracy splitting is well within the range of those shown below and that the system is non-disjoint .



NBMOs Energy , β	ψ_3 0.000	ψ_6 −0.556	ψ_3 −0.500	ψ_3 −0.818
	ψ_2 0.000	ψ_5 −0.500	ψ_2 −0.390	ψ_2 −0.500
Δβ	0.000	0.056	0.110	0.318

3.4.2 The Reduction of Dibenzpentacenequinone

The diketone **17** was treated with lithium metal , potassium metal and sodium-potassium amalgam in THF in the same manner described earlier . The spectrum observed from the reduction with sodium-potassium amalgam is shown in Figure 3.18 (similar spectra were obtained in the other cases) . Again the colour change from yellow to blood red was monitored by observing the shift in absorbance to longer wavelength during the reduction

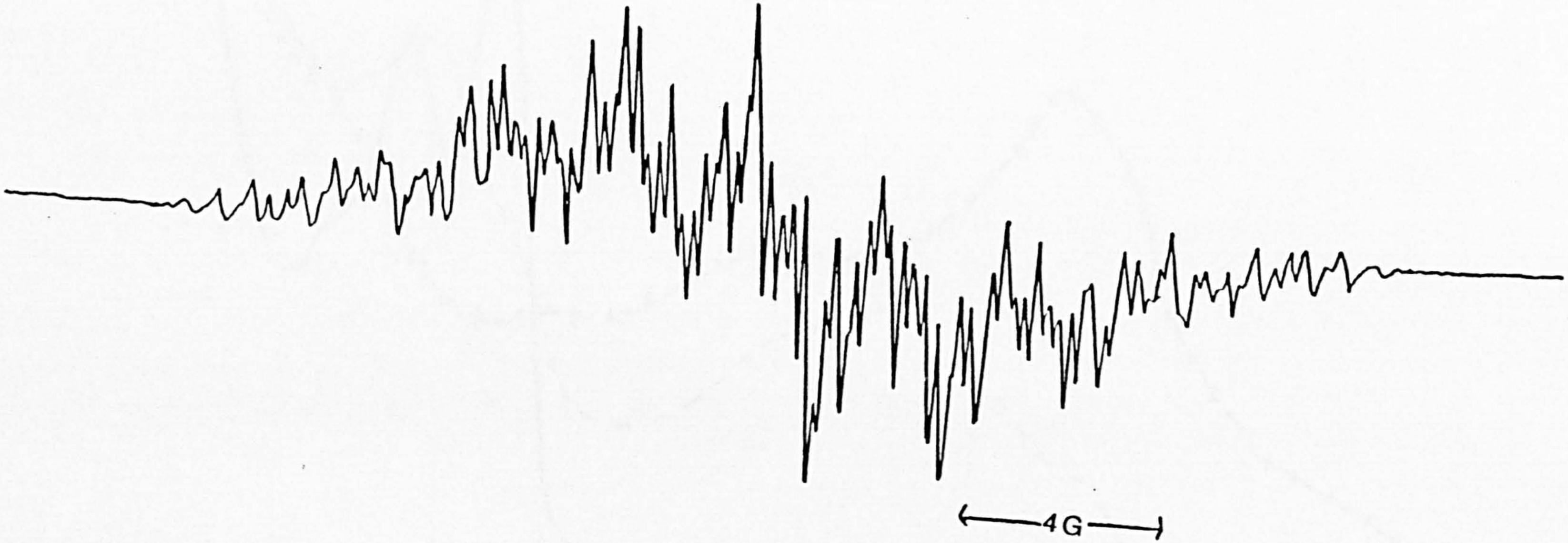


Figure 3.18 : ESR spectrum of the dibenzpentacenequinone radical anion produced by reduction with sodium-potassium amalgam , observed in THF solution at ambient temperature .

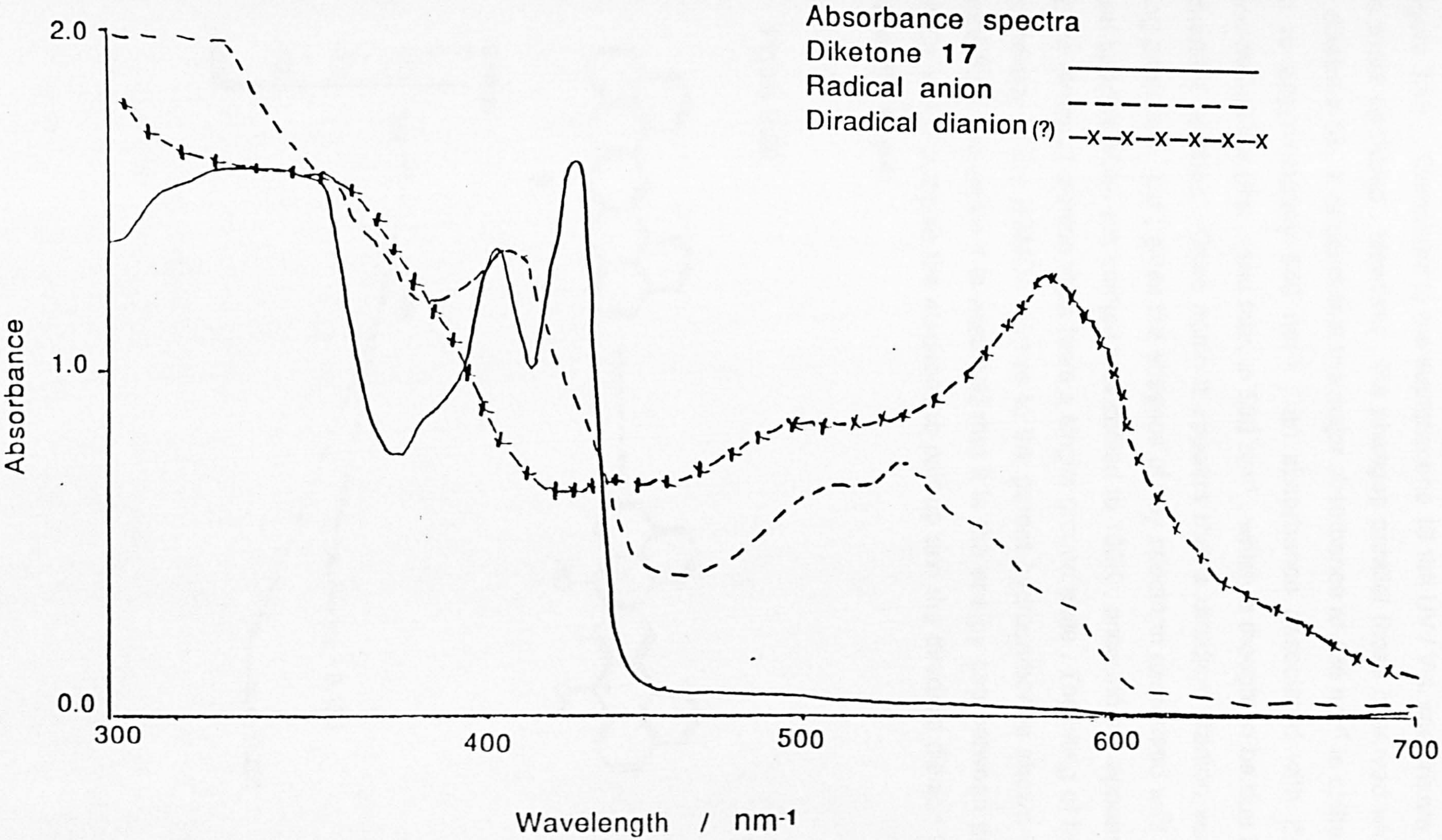
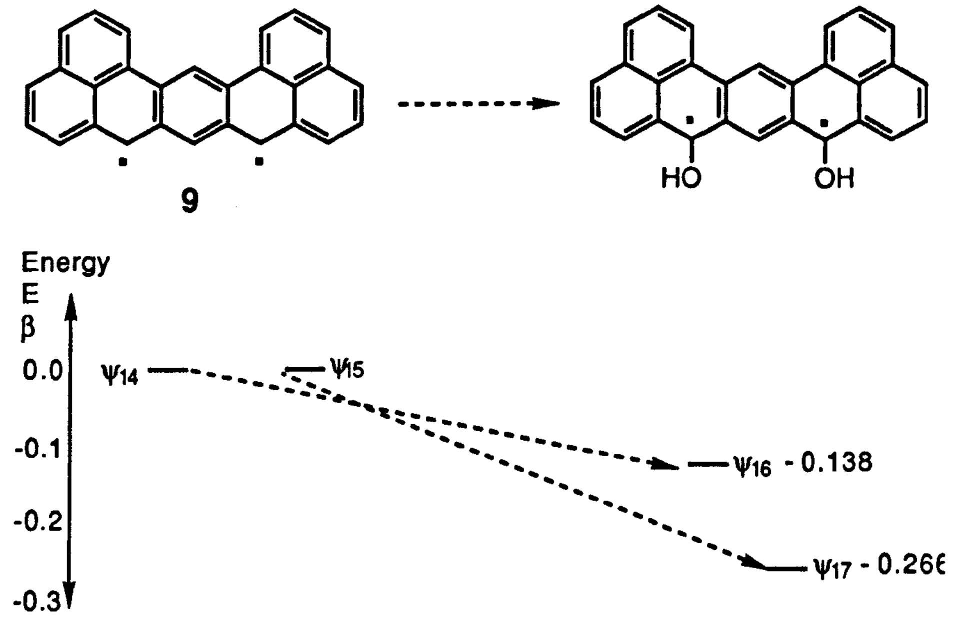


Figure 3.19 : UV / Vis. absorbance spectra observed when a solution of dibenzpentacenequinone in THF was treated with lithium metal .

(Figure 3.19) . Compared to the naphthacene **18** the UV / Vis. spectra are a little more confused . However , the changes parallel those observed with the diketone **18** . It appears that the major absorbance at 435 nm^{-1} is shifted first to approximately 540 nm^{-1} , an absorbance associated with the mono-radical species , and then to 580 nm^{-1} , which is thought to be due to a diradical species . Once again it appears that a diradical dianion was being produced , but , given the absence of any spectrum associated with a triplet species when the sample was cooled to 100K , once more it appears that the diradical dianion must have a singlet ground state . The lifting of the degeneracy of the NBMOs relative to the parent hydrocarbon is shown in Figure 3.20 and again it is assumed that it is the energy gap between the NBMOs which compels the electrons to pair up and the diradical dianion to exist as the singlet .

Figure 3.20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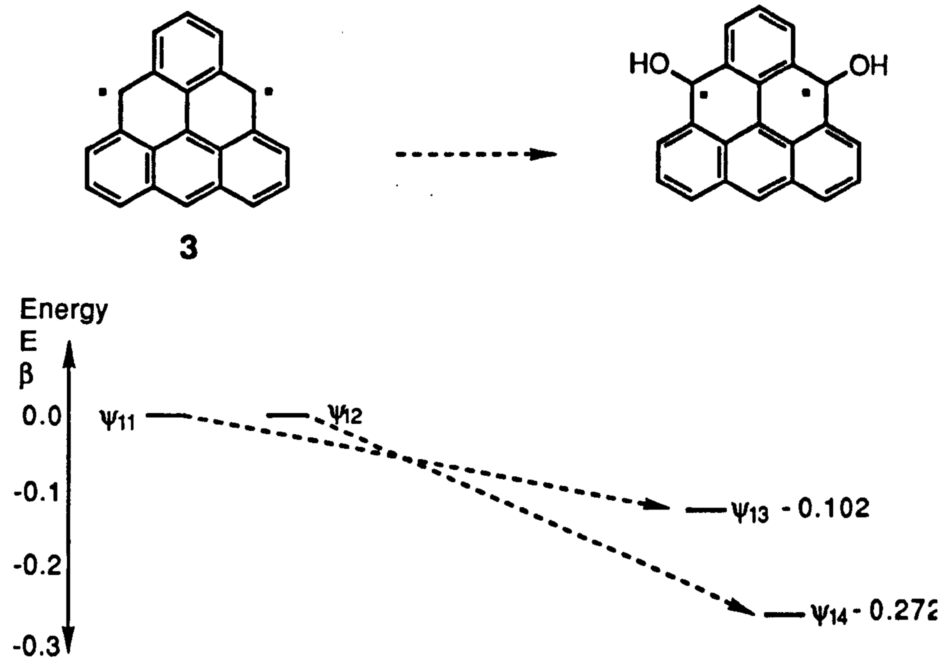
3.4.3 The Reduction of Triangulenequinone

Triangulenequinone **16** was treated with potassium metal in THF and the resulting spectrum is shown in Figure 3.21 . Again a colour change was observed , this time from a pale pink to a ruby red . Although the absorbance spectra were ambiguous , the lifting of the degeneracy of the NBMOs relative to the parent hydrocarbon must force the two electrons of the diradical to overcome their mutual repulsion and pair up in one orbital .

Figure 3.22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However , at least in this case the spectrum of the radical anion is sufficiently simple to allow analysis . The spectrum of the radical anion is shown in Figure 3.21 and results from the combination of the hyperfine splittings resulting from the interaction of the electron with , respectively , one proton ^{a}H giving rise to a splitting of 7.0 G , the four equivalent protons ^{b}H giving rise to a further splitting of 4.5 G and finally the two equivalent protons ^{c}H giving rise to a splitting 0.9 G . This analysis matches the electron densities obtained from molecular orbital calculations .

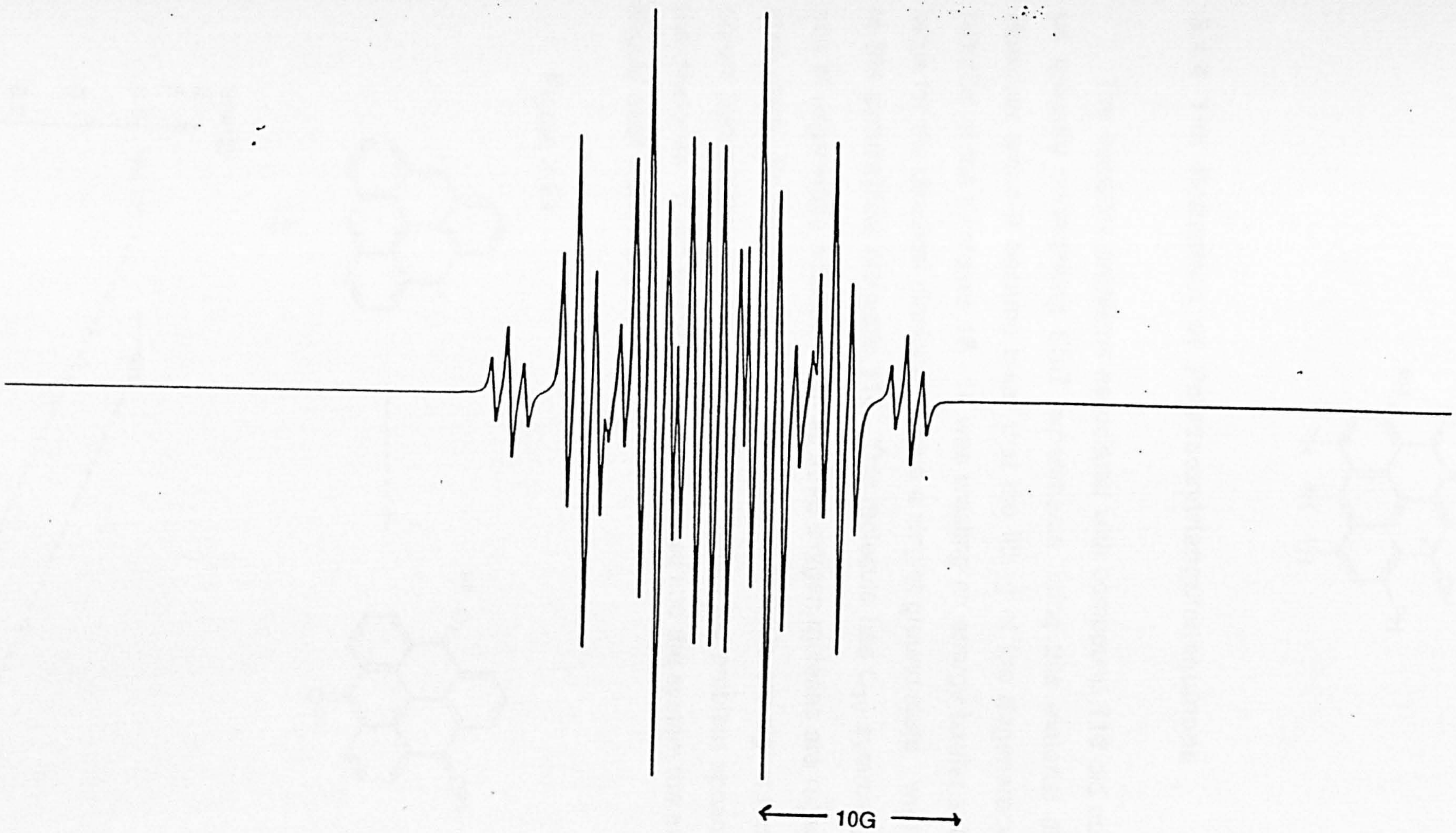
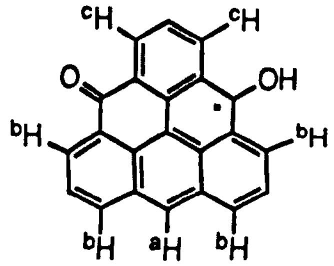


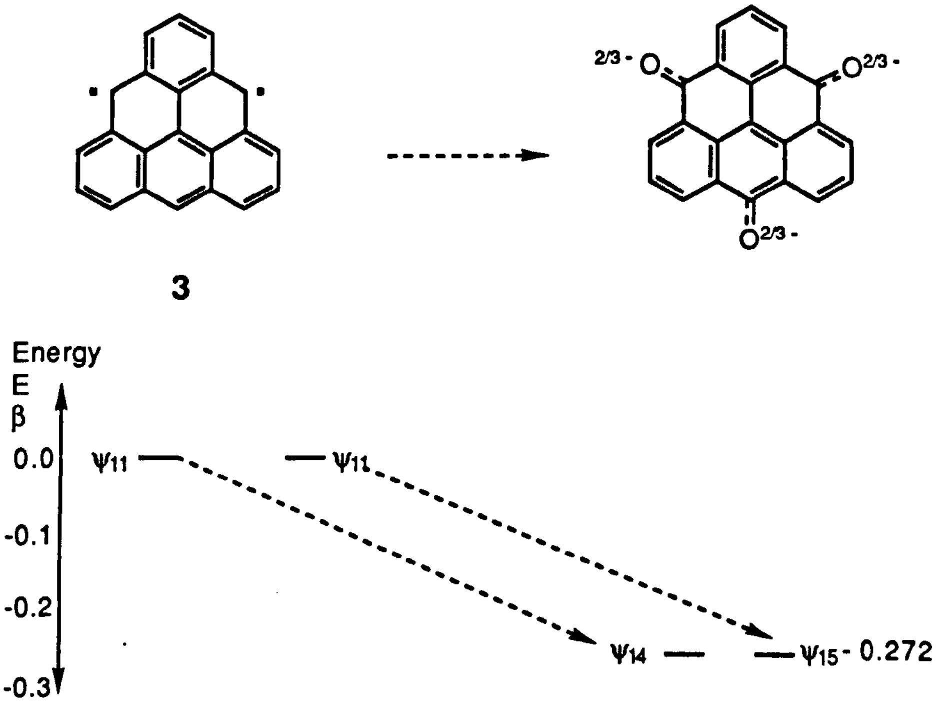
Figure 3. 21 : ESR spectrum of the triangulenequinone radical anion produced by reduction with potassium metal , observed in THF solution at ambient temperature .



3.4.4 The Reduction of Potassoxytriangulenequinone

The solubility problems associated with compound **116** did not incline us towards undertaking ESR experiments using this material directly . However when it became clear that the lifting of the degeneracy of the NBMOs of the diketones **16 - 18** was creating an energy barrier sufficiently large for the diradical dianions to have a singlet ground state , we returned to the symmetrical molecule **116** . This molecule has C_{3v} symmetry and a pair of degenerate NBMOs when all three oxygen moieties are regarded as equivalent . So although the energies of these NBMOs are higher than in the parent hydrocarbon their degeneracy overcomes the problem apparent with the diketones - if two electrons can be inserted into the system the molecule should exist in the triplet state .

Figure 3.23



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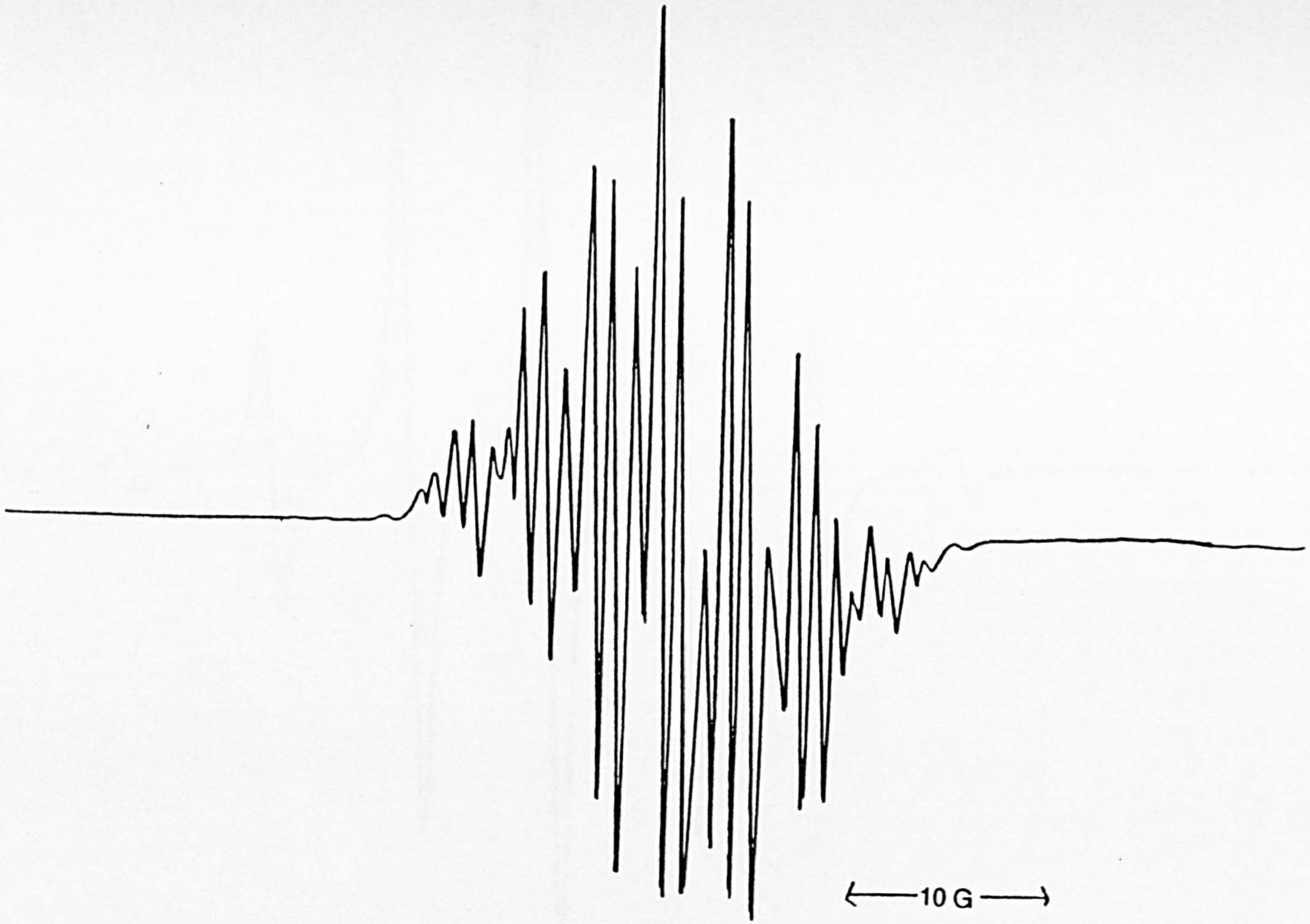


Figure 3.24 : ESR spectrum of the potassoxytriangulenequinone radical anion produced by reduction with calcium metal in the presence of t-butyldiphenylsilyl chloride , observed in DMF solution at ambient temperature .

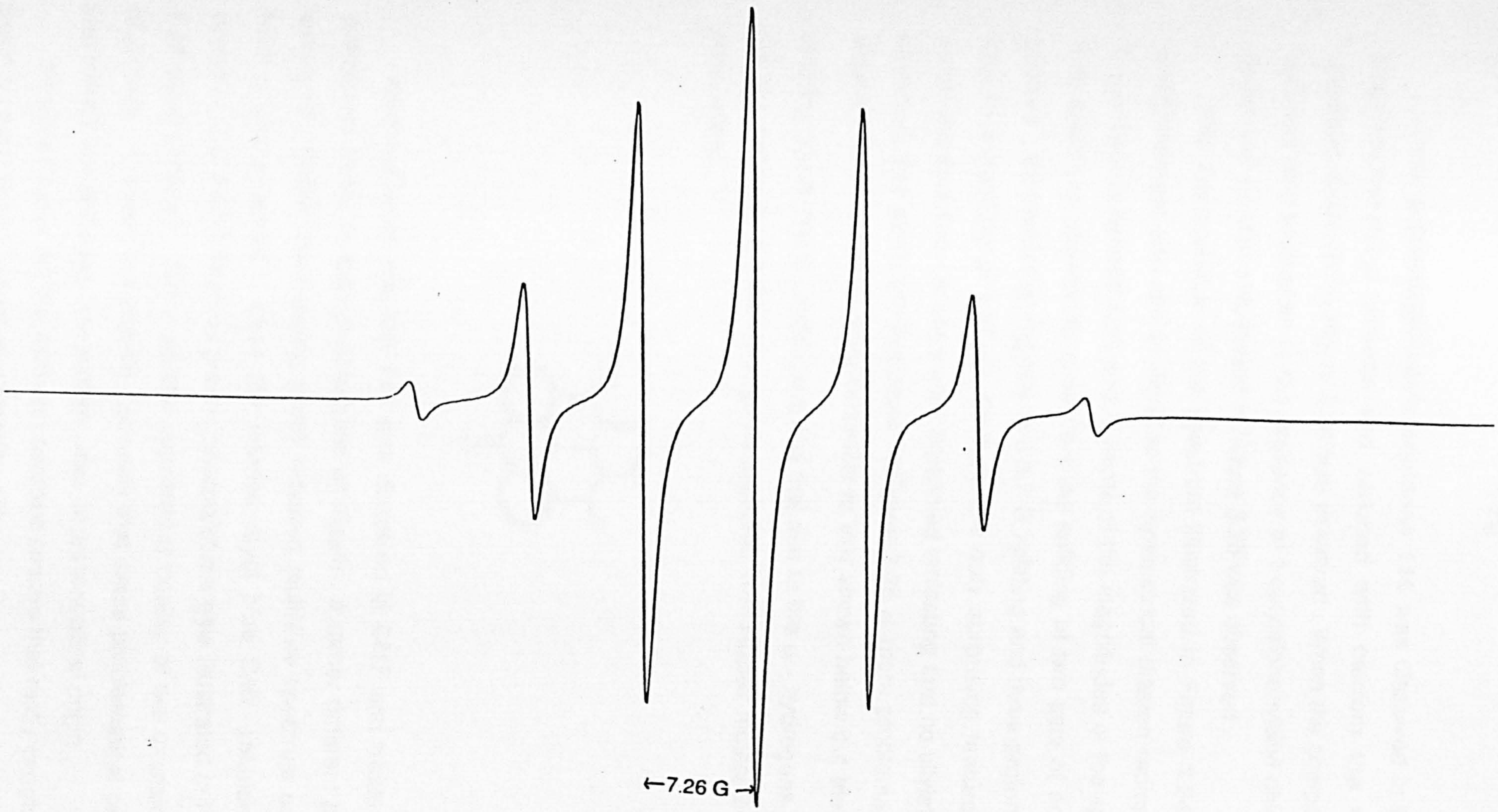
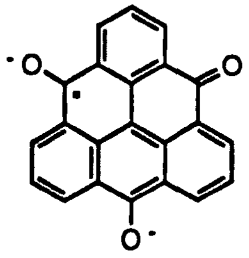


Figure 3.25 : ESR spectrum of the potassoxytriangulenequinone radical dianion produced by reduction with potassium metal in the presence of t-butyldiphenylsilyl chloride , observed in DMF solution at ambient temperature .

When potassoxytriangulenequinone **116** was dissolved in DMF with t-butyldiphenylsilyl chloride and reduced with calcium the multi-line spectrum illustrated in Figure 3.24 was observed . When the compound was reduced with potassium in the presence of t-butyldiphenylsilyl chloride the seven line spectrum illustrated in Figure 3.25 was observed .

The interpretation of the spectrum illustrated in Figure 3.24 is fairly straightforward and can be fitted to the symmetrical dianion radical shown below both in general form and in terms of the magnitudes of the splitting . The spectrum appears to arise from the splitting of two sets of equivalent protons ; six protons giving rise to a 3.7 G splitting and three protons giving rise to a splitting of 1.25 G. Perhaps the only surprising feature is that three-fold symmetry is apparently preserved indicating that no silylation has occurred. The spectrum illustrated in Figure 3.25 is more problematical . It appears to arise from a species similar to that shown below but there is no splitting due to the β - hydrogens and that due to the α - hydrogens *peri* to the oxo-functions is twice as large as expected from Huckel molecular orbital calculations .



However when the salt **116** was dissolved in DMF and treated with potassium metal or sodium-potassium amalgam , a rather different picture emerged . Rather than seeing a well resolved multi-line spectrum derived from a mono-radical , when the intense royal blue DMF solution had changed to a murky Thames green , spectra of the type illustrated in Figure 3.26 were obtained . These spectra appeared to consist of two overlaid sets of signals ; a seven line pattern , possibly that same problematical pattern just mentioned and a five line pattern , also of problematical origin .

However it was not the room temperature spectra that really caught our attention but those observed when the the solutions were frozen at 100K .

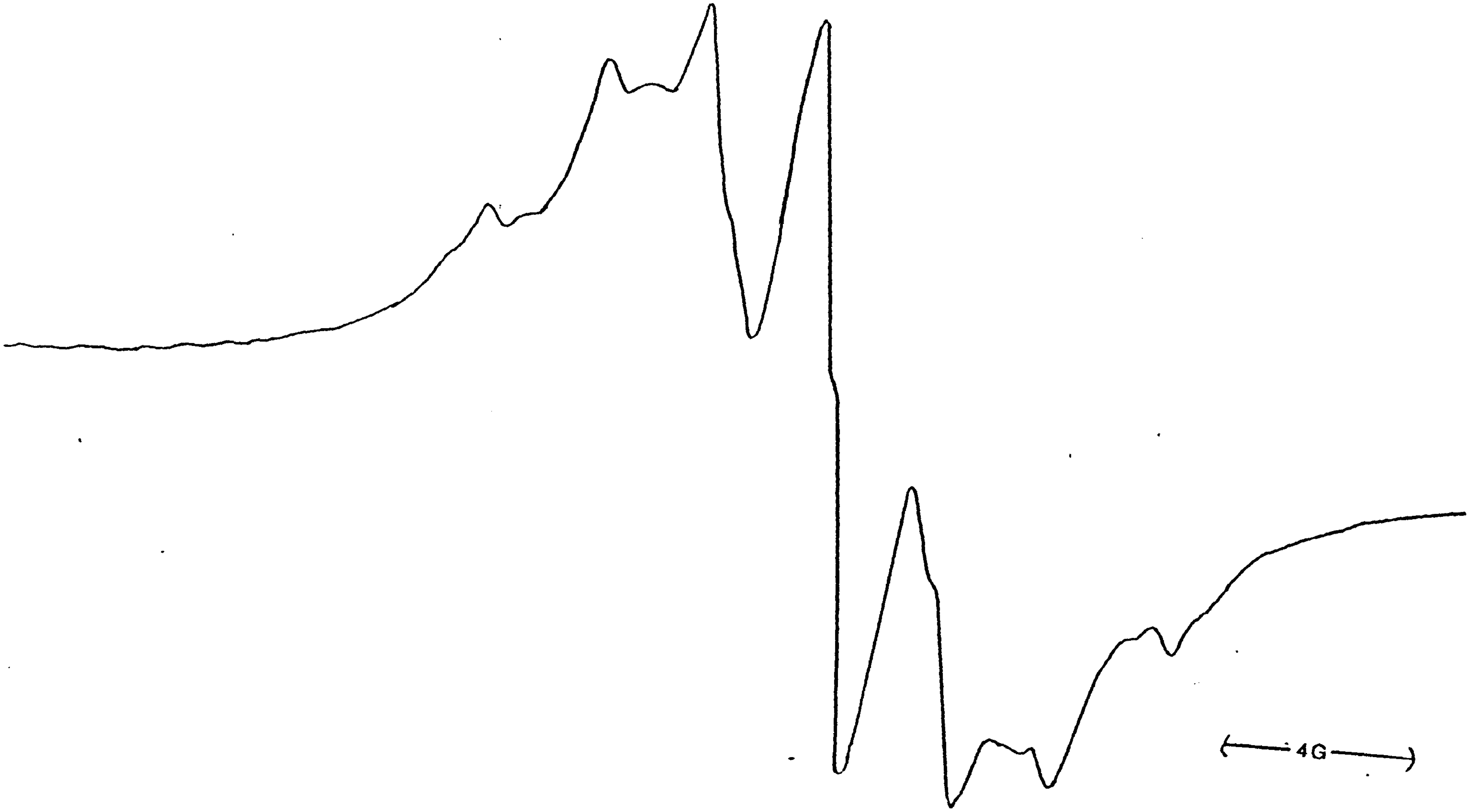


Figure 3.26 : ESR spectrum observed at ambient temperature when potassoxytriangulenequinone was treated with potassium metal in DMF .

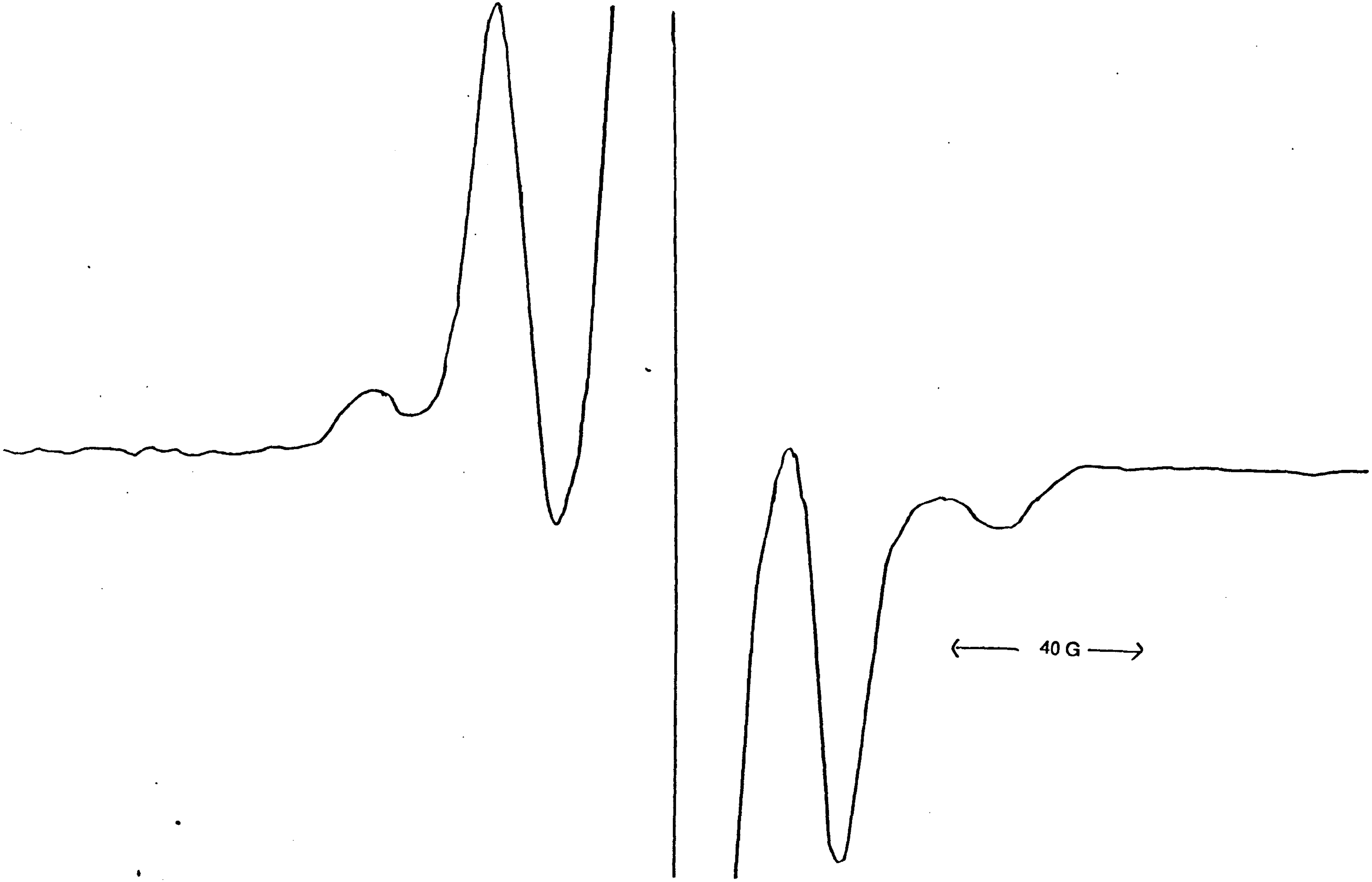


Figure 3.27 : ESR spectrum observed at 100K when potassoxytriangulene quinone was treated with potassium metal in DMF .

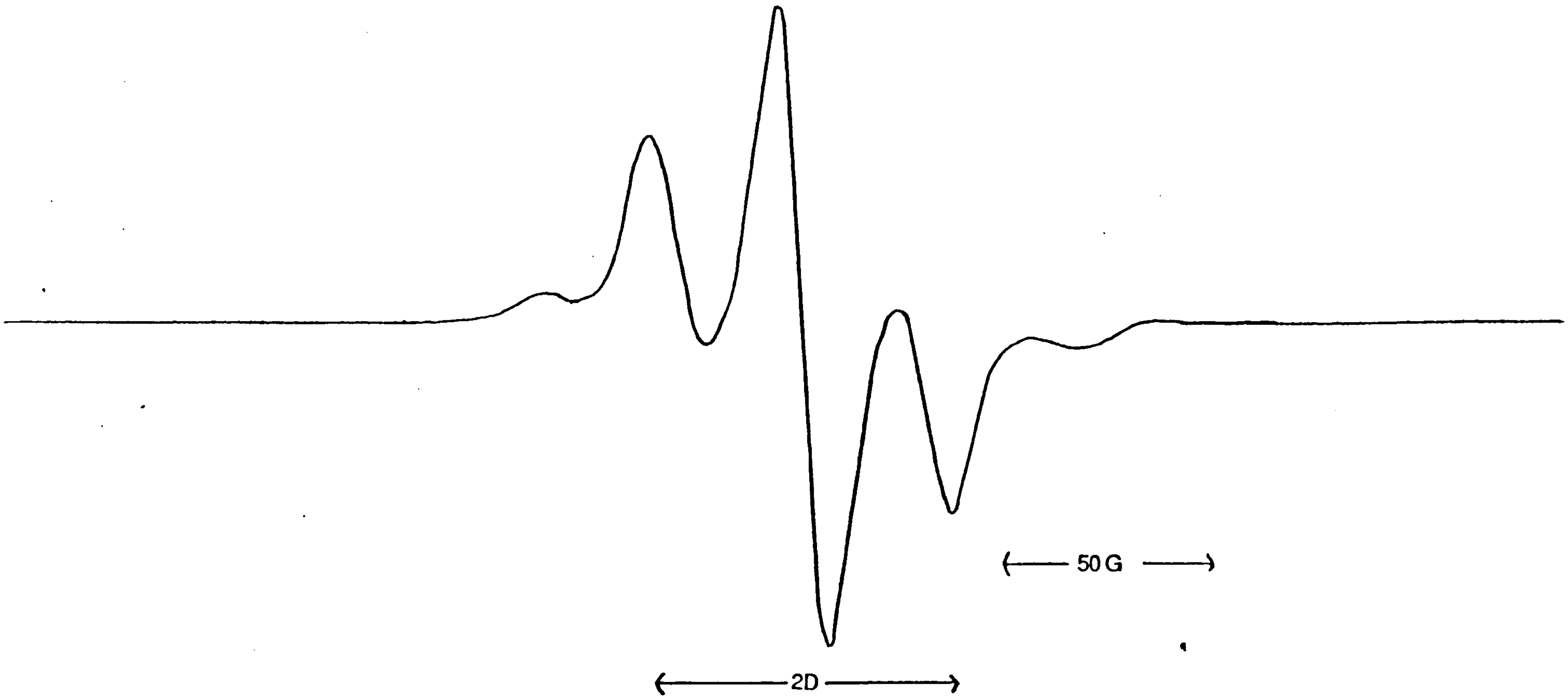


Figure 3.28 : ESR spectrum observed at 100K when potassoxytriangulene quinone was treated with sodium-potassium amalgam in DMF .

The spectrum illustrated in Figure 3.26 broadened to a singlet and a new much wider spectrum appeared . The spectra obtained are illustrated in Figures 3.27 and 3.28 and are almost exactly the shape anticipated for a triplet species with C_{3V} symmetry .

Unfortunately we were unable to observe an absorption at half-field which would have been proof positive of the triplet species . However this is not too surprising given the potential separation of the electrons in this system . The intensity of the half-field line is inversely proportional to r^6 , where r is the separation between the electrons . Other workers have experienced difficulty in observing the half field line for triplet molecules with small zero field splitting parameters [7] . These ' forbidden ' absorptions may therefore be difficult to observe with our X-band instruments operating in the 3 cm region [7].

Berson [8] suggested that there is a reasonably good correlation between the experimentally observed zero field splitting parameter of a triplet biradical , D_{expt} , and that obtained from HMO theory calculations , D_{calc} , of the order ,

$$D_{calc} = 2 \times D_{expt}$$

This relationship is illustrated in Figure 3.29 for a range of biradicals (the data points used in this graph are given in Figure 3.30) . The calculations were done by the point charge method of McWeeney [9] using a computer programme written by Dr. R.J. Bushby and assume all carbon-carbon bond lengths are 1.395Å , carbon-oxygen bond lengths are 1.43Å and that each π-orbital is represented by a pair of points 0.68Å above and below the molecular plane . The slope of the line of the graph in Figure 3.29 represents a computer generated ' best fit ' for all the data points .

The symmetrised NBMOs for triangulene are illustrated in Figure 3.31 along with those for the tri-oxo derivative . We have calculated the zero field splitting parameter for the tri-oxo compound to be in the range D_{calc} = 0.015 - 0.016 cm^{-1} . From our spectra we found D_{expt} = 75 Gauss , or approximately

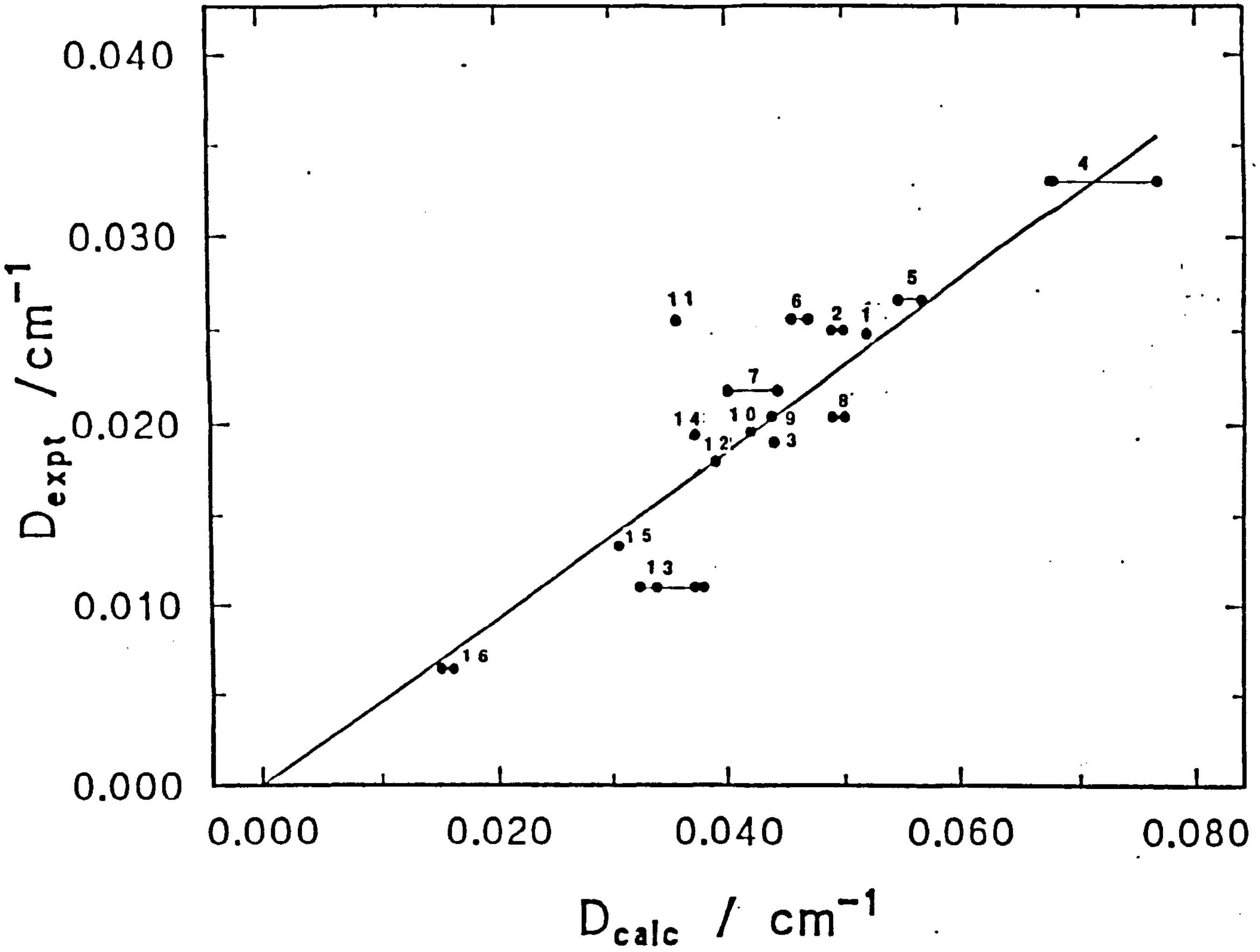


Figure 3.29 : Graph of D_{expt} vs. D_{calc} for a range of triplet biradicals

Figure 3.30 : The triplet biradicals featured in the graph displayed in Figure 3.29 [7,9,11]

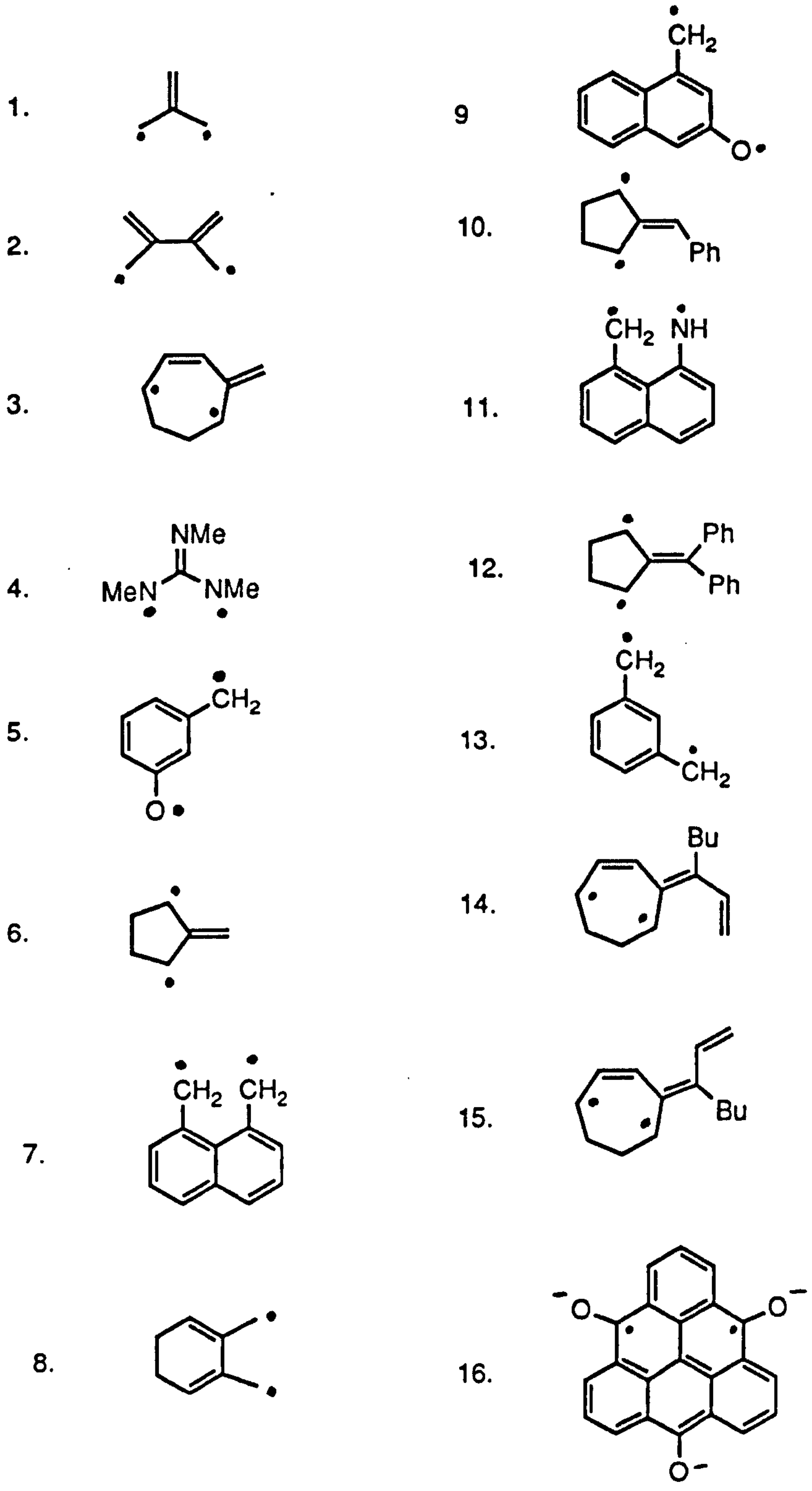
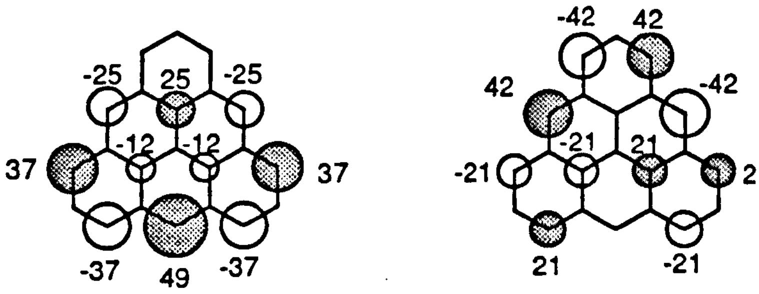


Figure 3.31 : Symmetrised HMOs for Triangulene and its tri-oxy derivative . Coefficients x 10^2 .



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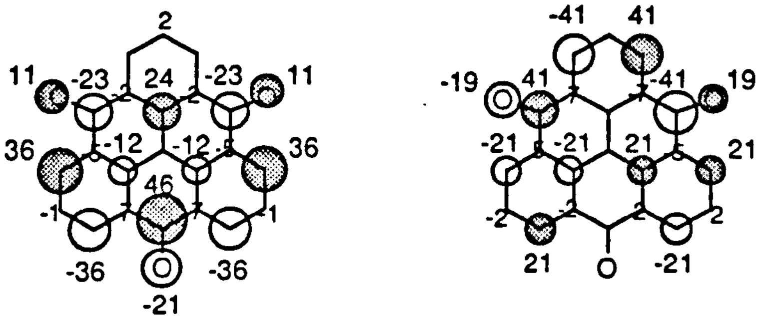
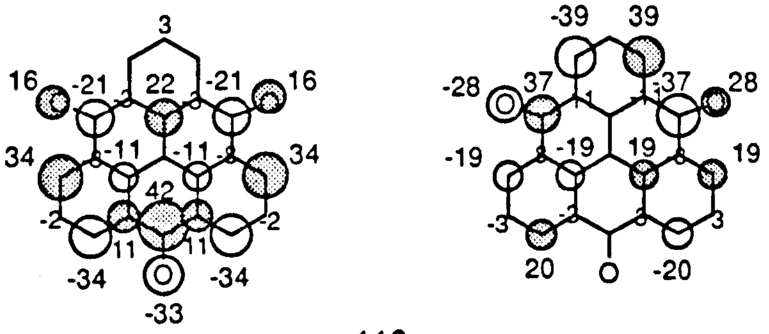
$D_{calc} = 0.0167$
$E_{calc} = 0.0000$



116

$D_{calc} = 0.0150$
$E_{calc} = 0.0000$
$h_o = 2.0$



116

$D_{calc} = 0.0160$
$E_{calc} = 0.0000$
$h_o = 1.0$

0.0068 cm^{-1} . Using Berson's approximation it may be seen D_{calc} that is a little over 2 D_{expt} (approximately 14% too large) but within experimental error . It may also be seen how closely the D_{expt} / D_{calc} points lie to the best fit line of the graph in Figure 3.29 .

It was mentioned earlier that the sharpness of the observed ESR spectra of a triplet species can be improved by per-deuteration of the molecule . Unfortunately we have so far been unable to prepare a deuterated derivative . The other route we have taken is to try to reduce the symmetry of the system without lifting the degeneracy of the NBMOs to such an extent that the singlet state is favoured over the triplet . The aim is to observe a spectrum similar to that described in Figure 3.8 . Unfortunately to date we have been unable to observe any spectra when the dicarboxylic acids **54** and **128** were treated in the same manner as the potassium salt **116** .

We believe that the evidence that we have observed a triplet species from the reduction of potassoxytriangulenequinone with potassium , or sodium-potassium amalgam , is more than circumstantial and enough to obtain judgement in our favour . For our part , though we believe we have seen the triplet species , the Scottish Judgement of " Not Proven " holds until we can observe the half-field line or an asymmetric triplet spectrum .

3.4.5 Summary of attempts to generate Non-Kekule Polynuclear Aromatic by Alkali Metal Reduction .

Compound	Solvent	Metal	Spectrum Observed	
			298K	100K
18	THF	K	radical anion	broad singlet
"	"	Li	"	"
"	"	Li + i	"	"

Compound	Solvent	Metal	Spectrum Observed	
			298K	100K
18	THF	Ca	radical anion	broad singlet
17	THF	K	"	"
"	"	Li	"	"
"	"	Na/K	"	"
16	THF	K	radical anion	broad singlet
116	THF	K	Very weak , very broad singlet	broad singlet
"	"	Li	"	"
"	"	Na / K	"	"
"	"	Ca	"	"
"	"	Li + i	"	"
"	"	K + i	"	"
"	DMF	Ca + i	radical anion	"
"	"	K + i	radical dianion (?)	"
"	"	K	overlaid 5 + 7 line spectrum	triplet spectrum and broad singlet
"	"	Na/K	"	"
"	HMPA	K	structured but very broad *	broad singlet
"	DMF	Cs	No spectrum *	No spectrum
54	"	K	No spectrum	No spectrum

Compound	Solvent	Metal	Spectrum Observed	
			298K	100K
54	"	K + i	No spectrum	No spectrum
128	"	K	"	"
"	"	K + i	"	"

i = t-buytldiphenylsilyl chloride

* The general procedure for observing an ESR spectrum required the solvent solution to be separated from solid material . This was done by passing the solution through the glass sinter . Once the ESR , or lack of , was observed , the solvent was passed back through the sinter and the metal reduction allowed to proceed . In this case it was possible to pass the solution through the sinter only once , the sinter becoming blocked in the process , therefore ending the experiment .

3.5 References

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Chapter Four

Non-Kekulé Polynuclear Aromatics and Organic Magnets

Contents

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4.1 Introduction

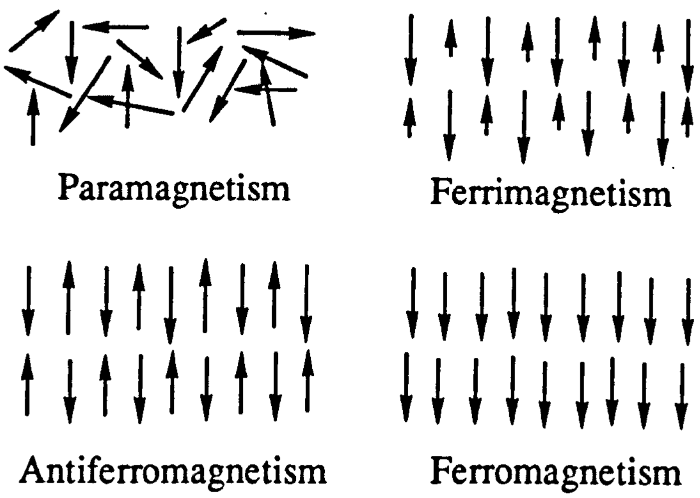
Ever since the observation that iron was attracted to lodestone (or magnetite , an iron oxide of formula Fe_3O_4) magnets have been a source of fascination to mankind . Almost two thousand years ago the Chinese took advantage of this property when they invented the compass . Today magnets are ubiquitous - from the highly magnetic ferro- and ferri- magnetic materials used in recording media (eg. Fe_2O_3 , CrO_2 and Fe_3O_4) , to the small bar magnet that keeps the cupboard door closed , to the powerful electromagnets that lie at the heart of the sophisticated analytical equipment used in our own research , namely the electron spin resonance spectrometer , and the nuclear magnetic resonance spectrometer .

The demand for new and better magnets has led to an international search for organic or molecular magnets . Even though it is unlikely that such magnets would ever wholly replace traditional types , organic magnets are desirable because they may have magnetic properties associated with light weight , solubility in organic solvents and optical activation , any of which could make them useful in the development of novel electronic devices [1-3] .

All materials are magnetic . The number of magnetic behaviours that can be observed in a solid is large , but for solids with unpaired electrons there are four main classes , namely paramagnetism , antiferro- and ferromagnetism , and ferrimagnetism [4] .

The type of magnetic behaviour shown by these solids depends on how the electrons in the material interact with each other . This situation is illustrated in Figure 4.1 . In most materials the electrons are orientated in a random manner relative to each other . These materials are paramagnetic and have no net magnetic moment . However there are classes of material in which there is co-operative behaviour between the spins . This gives rise to spontaneous magnetisation below a critical temperature where the spin-spin interactions are stronger than the thermal energies which cause the electrons to become randomly ordered . This temperature is called the Curie temperature (T_C) for ferromagnets and the Néel temperature (T_N) for ferrimagnets .

Figure 4.1



For a magnetic material to find widespread applications its Curie or Neel temperature must be well above ambient temperature ; most commonly above 400K .

In ferromagnets the magnitudes of the individual spins may be identical or different but the spins always align parallel to each other to give a net bulk magnetic moment . In both antiferromagnets and ferrimagnets the spins align anti-parallel to each other . When the individual magnetic moments are different there is a net magnetic moment and the material is termed ferrimagnetic . If the individual magnetic moments are identical , then the moments cancel out , there is no overall magnetic moment and the material is antiferromagnetic .

Attempts have been made to prepare molecular magnets by designing systems with either bulk ferro- or ferri- magnetism by having parallel or anti-parallel spin alignment . An approach to inorganic molecular magnets has been followed by Kahn [5] who has developed a group of ' bimetallic chain ' compounds where metal ions are linked by organic ligands . The two metals each possess a magnetic moment but they are of different magnitudes and in the crystalline solid the chains align in such a manner that the material exhibits ferrimagnetic properties .

Gatteschi [3] has prepared nitroxide chain complexes similar in principle to Kahn's bimetallic chains except that in this case the nitroxide ligand itself carries spin and it is the ferrrimagnetic coupling between the spin on the ligand and that on the metal ion which is important .

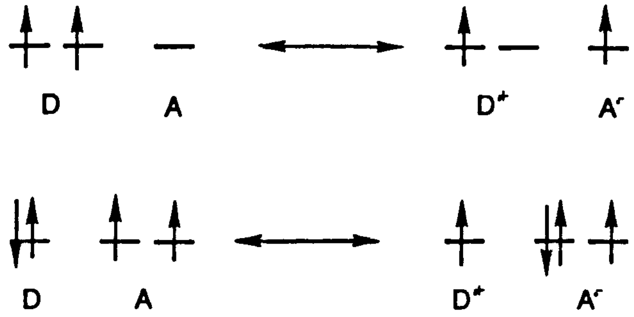
Several groups have tried to prepare purely organic molecular magnets but to date no bulk ferromagnet has been prepared . There have been reports of a small amount of ferromagnetism in polymers based on 1,3,5-triaminobenzene [6] or nitroxide radicals [7] and a few other systems . However , reproducibility of physical or chemical characteristics has been a major problem . Another stategy has been developed by Itoh and Iwamura [8] who have attempted to prepare polymers of linked meta-substituted benzene rings in which bridging methylene groups carry pairs of electrons aligned ferromagnetically . They have so far managed to prove that the spins on individual polymer molecules align but have been unable to produce a solid in which the spins on different molecules align ferrromagnetically .

One system with ferromagnetic ordering is the charge transfer complex decamethylferrocenium tetracyanoethanide **148** which has a Curie temperature of 4.8K . This system , designed by Miller and Epstein [1,2,9] , is an organometallic material based on the theoretical model proposed by McConnell in 1963 [10] which also underpinned our own strategy for achieving ferromagnetic coupling using non-Kekulé polynuclear aromatics . It is to this charge transfer complex model for organic magnets that we will now turn .

4.2 The McConnell Charge Transfer Complex Model for Organic Magnets .

In the early 1960s McConnell [10] observed that ionic molecular crystals were built up from the positive ions of a donor molecule , D , and the negative ions of an acceptor molecule , A , and that many such crystals formed a linear alternating sequence $\ldots D^+A^-D^+A^-\ldots$ in which , although the crystals were paramagnetic , there had obviously been transfer of charge from donor to acceptor molecules . McConnell postulated that if such a crystal could be formed from a donor molecule whose neutral ground state were a triplet , then one would expect back charge transfer to lead to ferromagnetic coupling of the spins on adjacent molecules . The same effect could be achieved if the acceptor had a triplet ground state instead . These mechanisms are illustrated in Figure 4.2 .

Figure 4.2

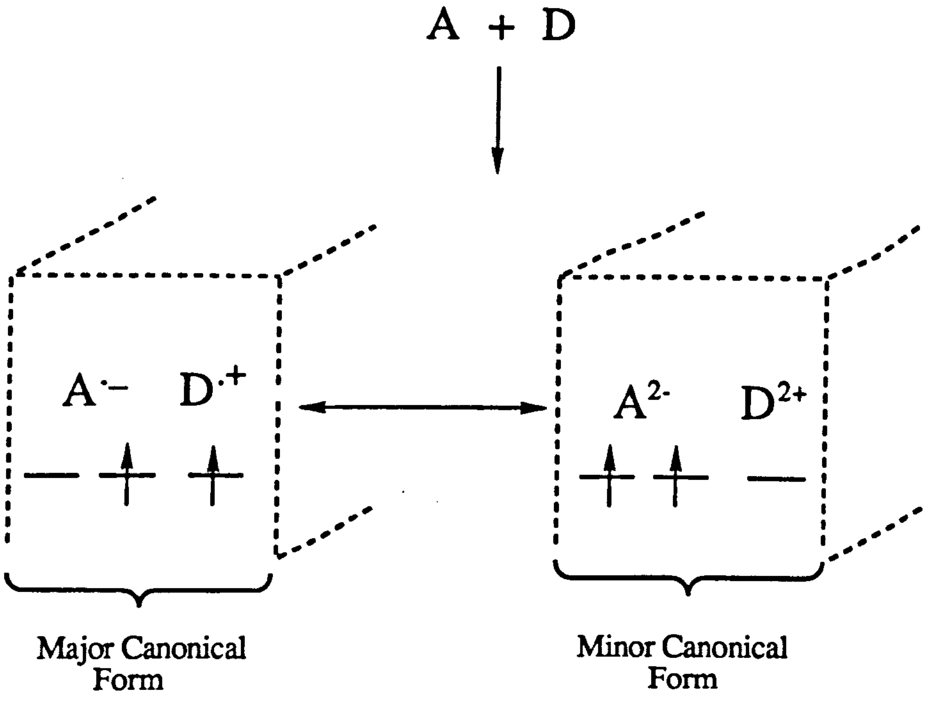


The criteria for such " M^cConnell type " charge transfer complexes have since been refined . In order to achieve ferromagnetic ordering of a charge transfer system one must arrange for the formation of a complex of the type $A^{\cdot-}D^{\cdot+}$, where $A^{\cdot-}$ is the radical anion of the acceptor molecule , and $D^{\cdot+}$ is the radical cation of the donor ; that the complex crystallises as $[A^{\cdot-}D^{\cdot+}]_n$ rather than discrete stacks of the individual radical ions ; and finally that there is a significant admixture of an excited state in which one or other of the constituents (A , D , A^{2-} , D^{2+}). has a triplet ground state . These points are illustrated in Figure 4.3 for the case where A^{2-} has a triplet ground state .

It is worth emphasising the last point - that even though the triplet ground state component may only be present as the minor canonical form , selection rules prevents the inversion of spin when the electron is transferred from the donor to the acceptor and so the major canonical form must also have its spins aligned parallel .

Decamethylferrocenium tetracyanoethanide { $Fe^{III}[C_5(CH_3)_5]_2\}^{\cdot+}$ $[TCNE]^{\cdot-}$, **148** or $[DMeFe]^{\cdot+}[TCNE]^{\cdot-}$, was prepared by Miller and Epstein by reacting decamethylferrocene with tetracyanoethylene in acetonitrile . Each molecule is made up of a pair of radical ions , with one unpaired electron residing on the iron nucleus of the $[DMeFe]^{\cdot+}$ ion and the other delocalised throughout the $[TCNE]^{\cdot-}$ ion .

Figure 4.3 : Ferromagnetic coupling in charge -transfer complexes of the type ($A^{\cdot -}$ $D^{\cdot +}$)$_n$ where A^{2-} is a triplet.



Miller and Epstein [1,2,9] proposed that the bulk solid could have two chain alignments in which the $[TCNE]^{\cdot -}$ ion is sandwiched between the ferrocenium ions . Each chain may be either next to an identical one , in which case positive ions are adjacent to positive ions and negative ions adjacent to negative ions ; or the chain is next to one that is shifted by one unit so that positive ions are adjacent to negative ions . These two cases are illustrated in Figure 4.4 . With either of the two chain alignments the unpaired electrons may co-operate in three dimensions , a feature essential for bulk magnetism . Miller and Epstein propose that in their compound electron transfer is between the e_{2g} orbitals of DMeFe and the π^* anti-bonding orbital of TCNE , as illustrated in Figure 4.5 . This is not , however , the only coupling that can occur . It is possible to envisage ferromagnetic coupling between pairs of $[DMeFe]^{\cdot +}$ ions and antiferromagnetic coupling between pairs of $[TCNE]^{\cdot -}$ ions .

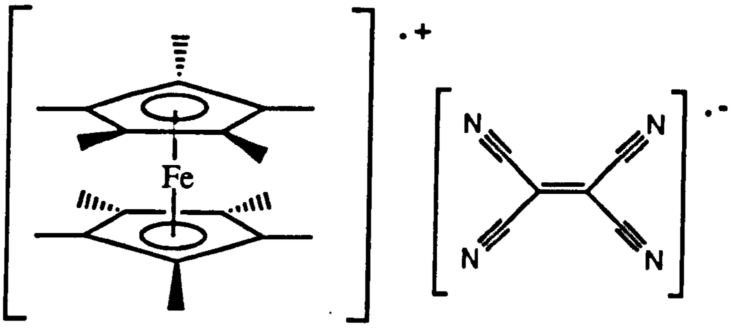


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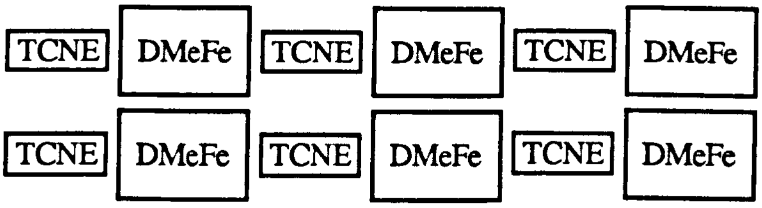
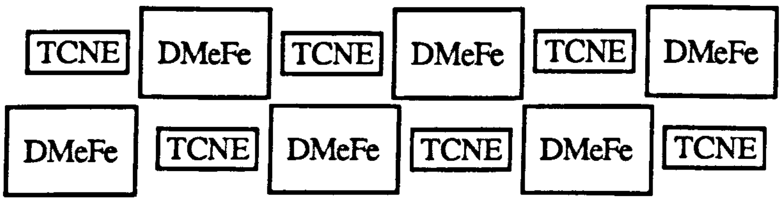
Figure 4.4 : Chain alignment in complex **148** .

Alignment 1

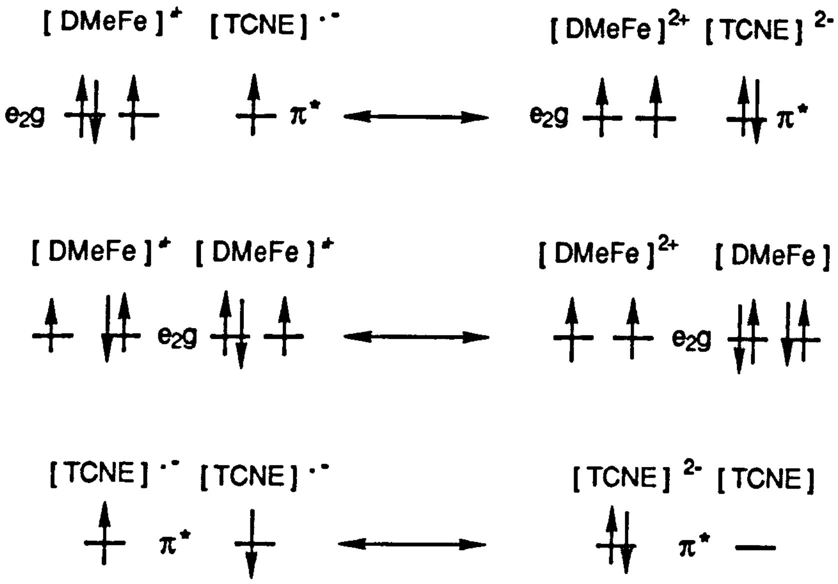


Alignment 2



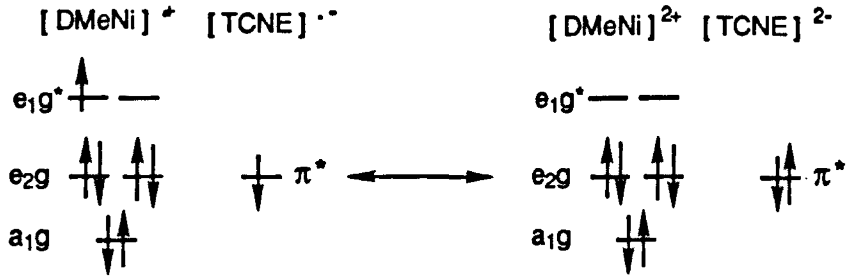
By referring to Figure 4.4 it may be seen that these last two couplings are minimised by the spatial distribution of the ions in the " alignment 2 " stacking whilst maximising $[DMeFe]^{\cdot +}$ ion / $[TCNE]^{\cdot -}$ ion interactions .

Figure 4.5

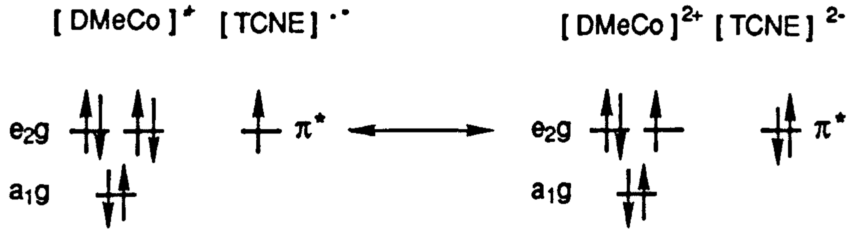


Miller and Epstein have studied the effects of chemical changes on the magnetic properties of the system . Modifications to the electron acceptor ion and the donor ion ligands did not produce any significant increase in the Curie temperature of the complexes . In 1987 they suggested that by adding two elecrons antiferromagnetic behaviour could be induced .They have tested this theory by varying the metal ion present in the system and their results are illustrated in Figure 4.6 . Replacing iron with nickel adds two electrons to the system and an antiferromagnetic complex is the result . Cobalt adds one extra electron to the complex but there is now no co-operation between the spins of the unpaired electrons and so the complex is paramagnetic . When the iron is replaced by manganese as the metal ion , one electron is effectively removed from the complex but a ferromagnetic complex is still observed . However , when chromium replaces the iron as the metal ion , two electrons are effectively removed from the system and a ferrimagnetic complex results .

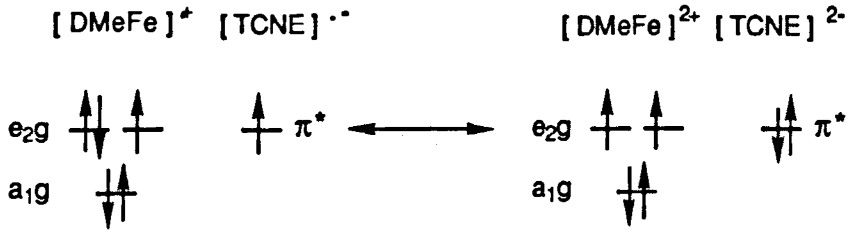
Figure 4.6



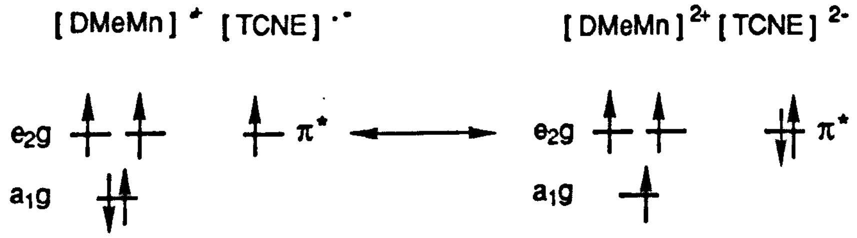
Antiferromagnet



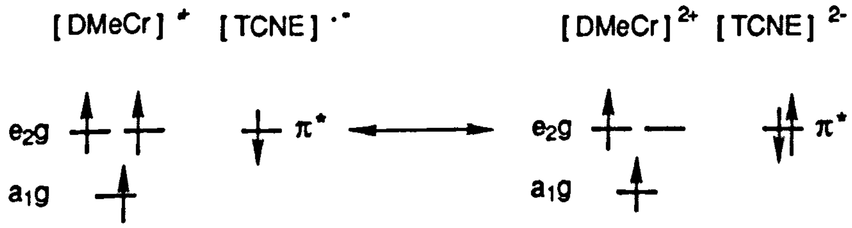
Paramagnet



Ferromagnet $T_c = 4.8$ K

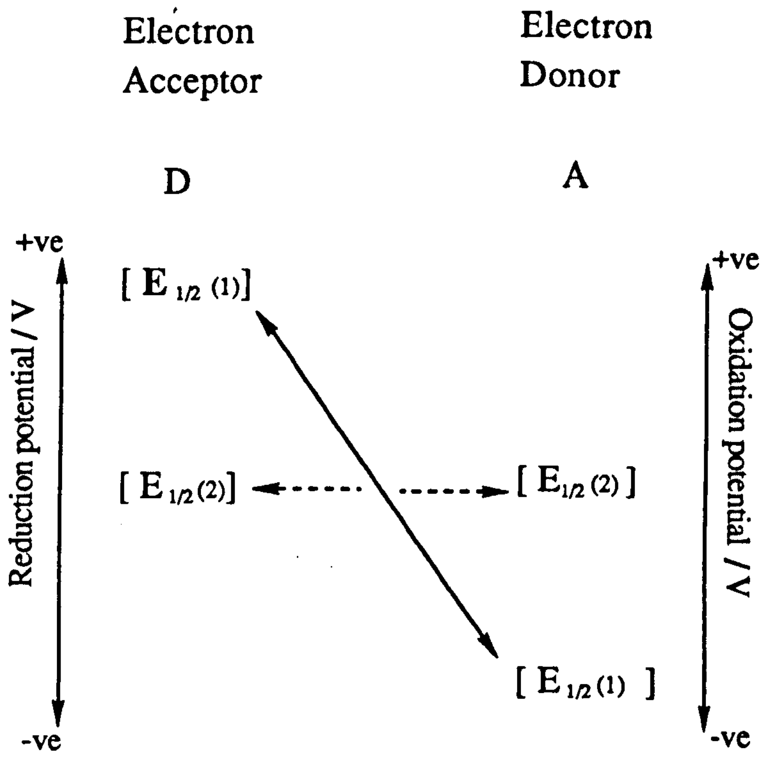


Ferromagnet $T_c = 6.2$ k



Ferrimagnet

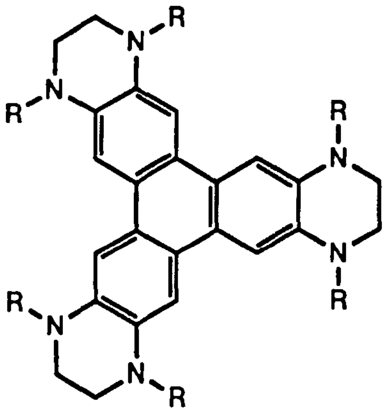
Figure 4.7



McConnell's charge transfer model is quite general in its applicability and so it ought to be possible to design purely organic systems based on the principles underlying this model . However , for the correct type of charge transfer complex to be formed the redox potentials of the acceptor and the donor molecules must be matched . This situation is illustrated in Figure 4.7 . In this case the first reduction potential of the acceptor is more positive than the first oxidation potential of the donor and therefore the first electron transfer from the donor to the acceptor would be complete (solid arrow) . However , the second reduction potential of the acceptor is not more positive than the second oxidation potential of the donor and therefore the second electron transfer would be incomplete (dotted arrow) . A ferromagnetic complex would be expected if either of A^{2-} or D^{2+} were a triplet .

Breslow [11] has endeavoured to produce purely organic charge transfer complexes of this type with ferromagnetic properties using derivatives of the hexaaminotriphenylene system **149** . He has found that these derivatives are easily oxidised to cation radicals and that the dications have triplet ground states . The hexacyano compound **150** can be reduced to the dianion at potentials that are a good match to the oxidation potentials available with the hexaaminotriphenylene derivatives **149** . The measured redox potentials are displayed in Figure 4.8 in which , as with figure 4.7 , the solid arrows represent electron transfers that would be " complete " and the dotted arrows those that would be " incomplete " .

Breslow comments that the infra red spectrum of the complex resulting from a mixture of compounds **150** and **149** , R = Et , indicated that the heaxaethyl derivative was too good an electron donor since in the infra red spectrum the CN stretch of the complex corresponded to the dianion of compound **150** . Compound **149** R = CF_3 proved to be a poor reducing agent since the CN stretch of the complex corresponded to that of a mono anion . However , with compound R = CH_2CHF_3 a mixed valence complex of the right type was formed . However , magnetic susceptibility measurements indicated that the system was antiferromagnetically coupled . Breslow comments that this alignment may be due to one of two factors : either the dication derived from compound **149** does not have the triplet ground state in the charge transfer complex , being distorted in some manner and hence losing its C_{3V} symmetry , or the two and three dimensional interactions may be too inadequate to permit bulk ferromagnetism . The recent studies of Miller *et al* [12] support the former suggestion .



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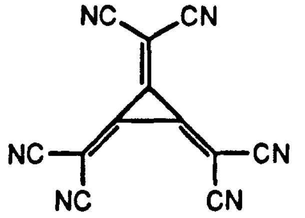

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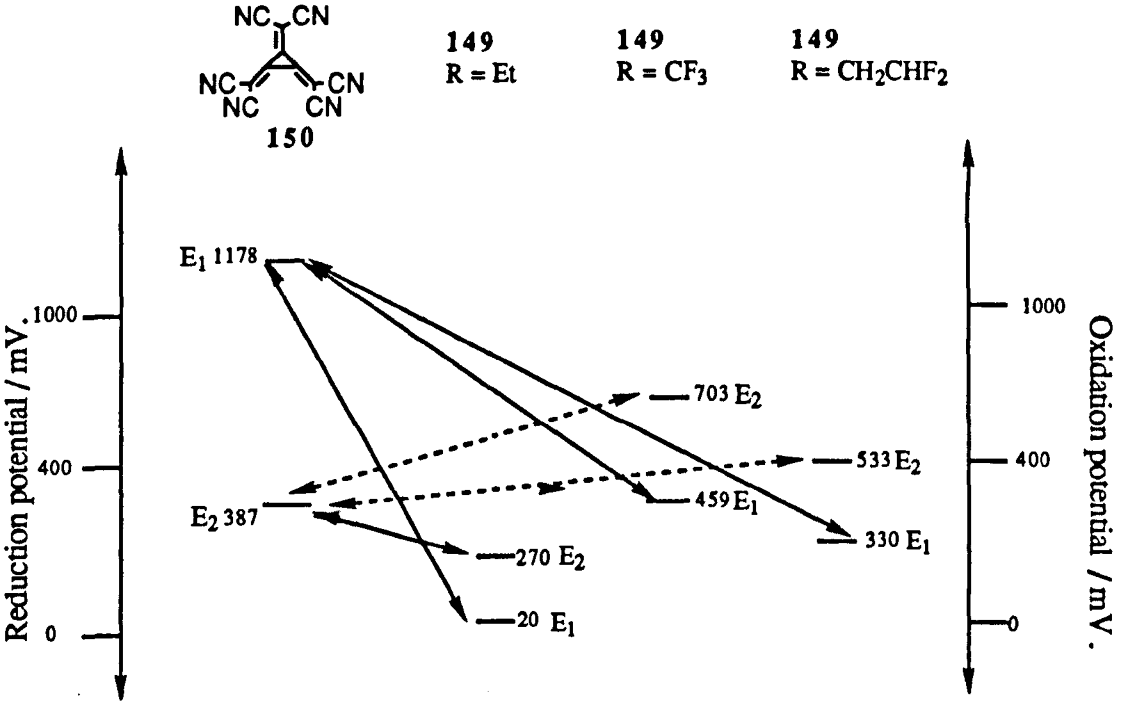
Figure 4.8



4.3 Non-Kekule Polynuclear Aromatics as components in Charge Transfer Systems.

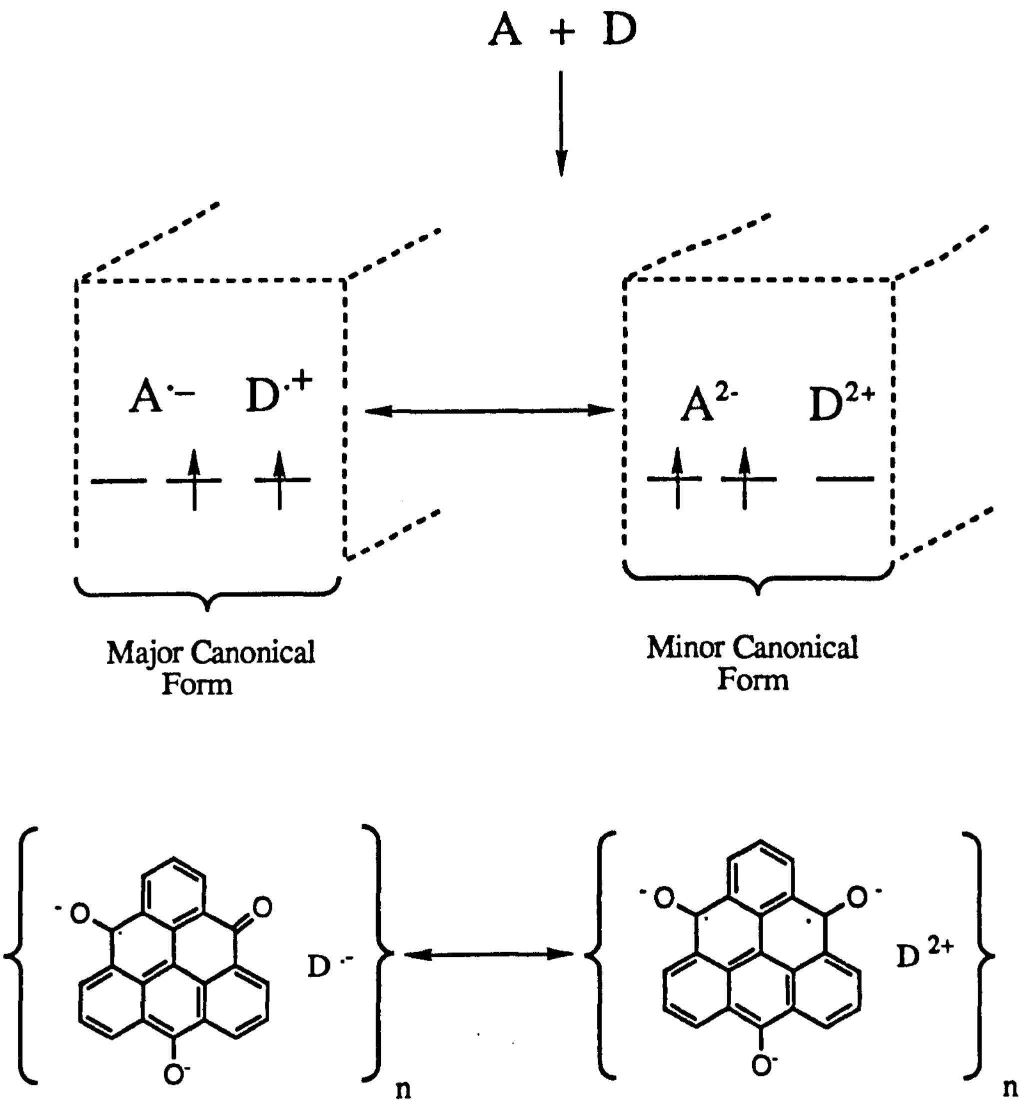
Although Breslow has been unable to obtain bulk ferromagnetism in his complexes , his studies have illustrated the point made earlier - that the reduction potentials of the electron acceptors must be more positive than the oxidation potentials of the donors . The non-Kekulé polynuclear aromatics **3** , **9** , **10** , **15** are all biradicals and all can , in theory , be prepared by addition of two electrons to an appropriate derivative . Our Hückel molecular orbital calculations suggested that the diradical dianions of the diketone **16** - **19** and the diradical of the trioxotriangulene **34** should all have triplet ground states . As such they appeared tailor-made as electron acceptors in M^{c}Connell type charge transfer complexes . This strategy is illustrated in Figure 4.9 using the trioxotriangulene as a model .

However , several important conditions needed to be met for this strategy to be successful . Firstly , that the aforementioned compounds must have triplet ground states and maintain this state within a charge transfer complex . Secondly , a suitable electron donor must be found . Thirdly , the redox potentials of the diketones and the trioxotriangulene must be determined and be in the correct range . Fourthly , the products of the redox processes must be stable and the reactions reversible . This last point is important . If any of the transitions

$$[A] \rightleftharpoons [A^{\bullet -}] \rightleftharpoons [A^{2-}]$$

were irreversible , with either $[A^{\bullet -}]$ or $[A^{2-}]$ also chemically unstable , then this would in effect render the charge transfer complex and any associated magnetism unstable .

Figure 4.9 : Ferromagnetic coupling in charge -transfer complexes of the type ($A^{\cdot -}$ $D^{\cdot +}$)$_n$ where the acceptor molecule is the tri-oxo-triangulene and A^{2-} is a triplet .



4.3.1 The Determination of the Redox Potentials of Organic Molecules .

It is the aim of this next short section to introduce one of the principle methods for determining the redox potentials of organic molecules , namely cyclic voltammetry , in a qualitative and non-mathematical manner .

Cyclic Voltammetry is an experimental technique which may be used to obtain many sorts of information about electrochemical reactions [13] . However we shall limit the scope of this discussion to the determination of redox potentials . The apparatus used in our experiments is illustrated in Figure 4.13 and was basically an unstirred three electrode cell containing a working electrode , a counter electrode and a reference electrode . In cyclic voltammetry the potential of the working electrode is swept in one direction from an initial voltage E_1 to a final voltage E_2 , and then the potential is swept back in the reverse direction toward E_1 . Throughout this process the current I flowing between the working electrode and the counter electrode is monitored . Typical cyclic voltammograms for reduction processes are illustrated in Figure 4.10 , but analogous behaviour may be observed for oxidation processes .

The cylic voltammogram for the reversible reduction of a species O to its reduced form R is illustrated in Figure 4.11. At **a** no current flows when the circuit is closed since the electrode potential is too small . The voltage is swept from **a** in the cathodic direction . Reduction of O begins at **b** and the current flow increases with electrode potential until **c** where depletion of the substrate in the region around the working elecrode brings about a decrease in current . The voltage sweep is reversed at **d** and an oxidation peak observed at **e** . For a rapid reversible one electron process both the potential separation ΔE between the anodic and cathodic peaks **c** and **e** and the peak width are approximately equal to 59 mV .

For an irreversible process , a cyclic voltammogram similar to that illustrated in Figure 4.10 (b) would be obtained in which there would be complete absence of any measurable anodic current on sweep reversal .

Figure 4.10 : Representative cyclic voltammograms .
(a) Reversible Process (b) Irreversible Process
(c) EC process

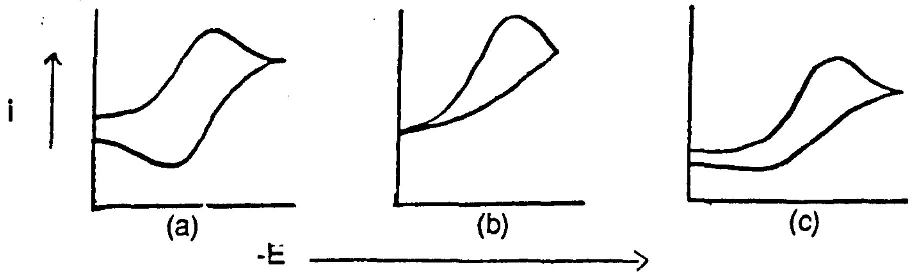
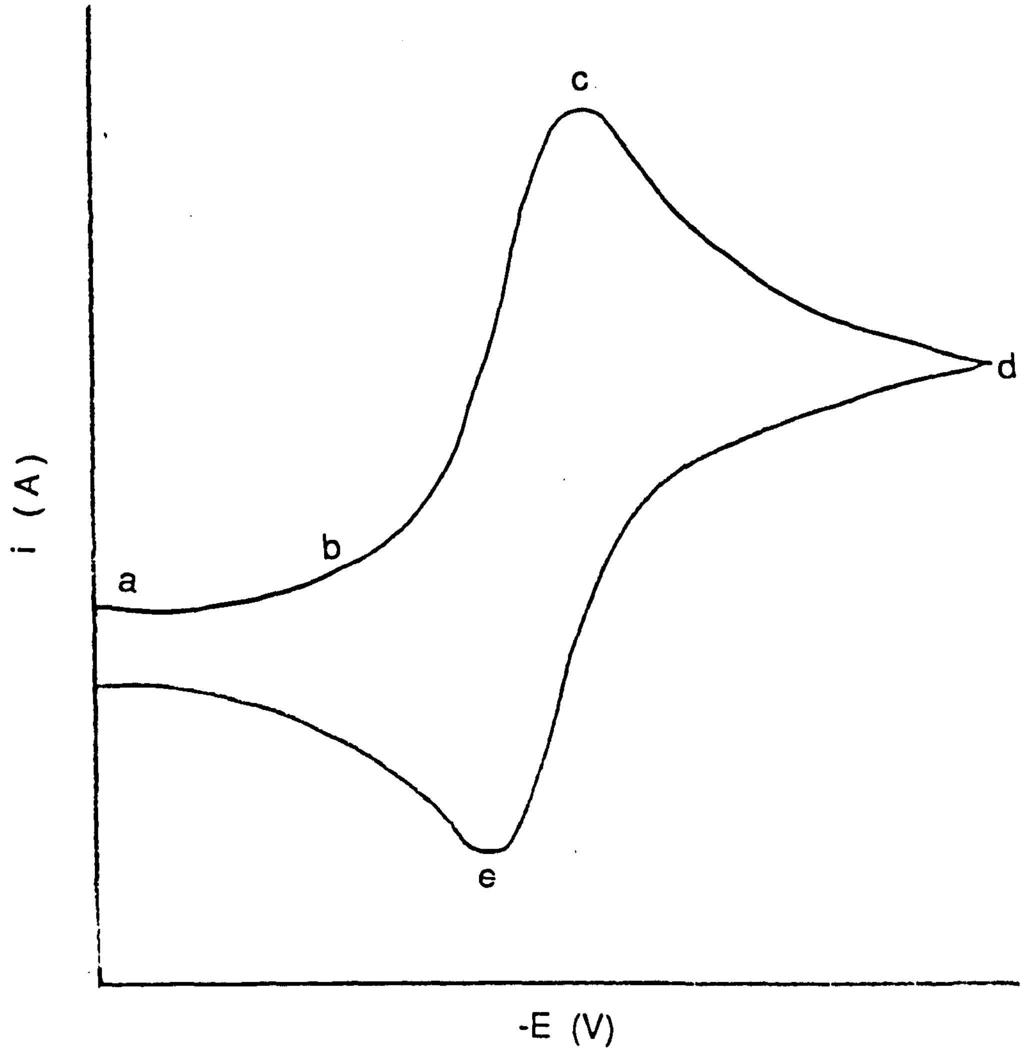


Figure 4.11



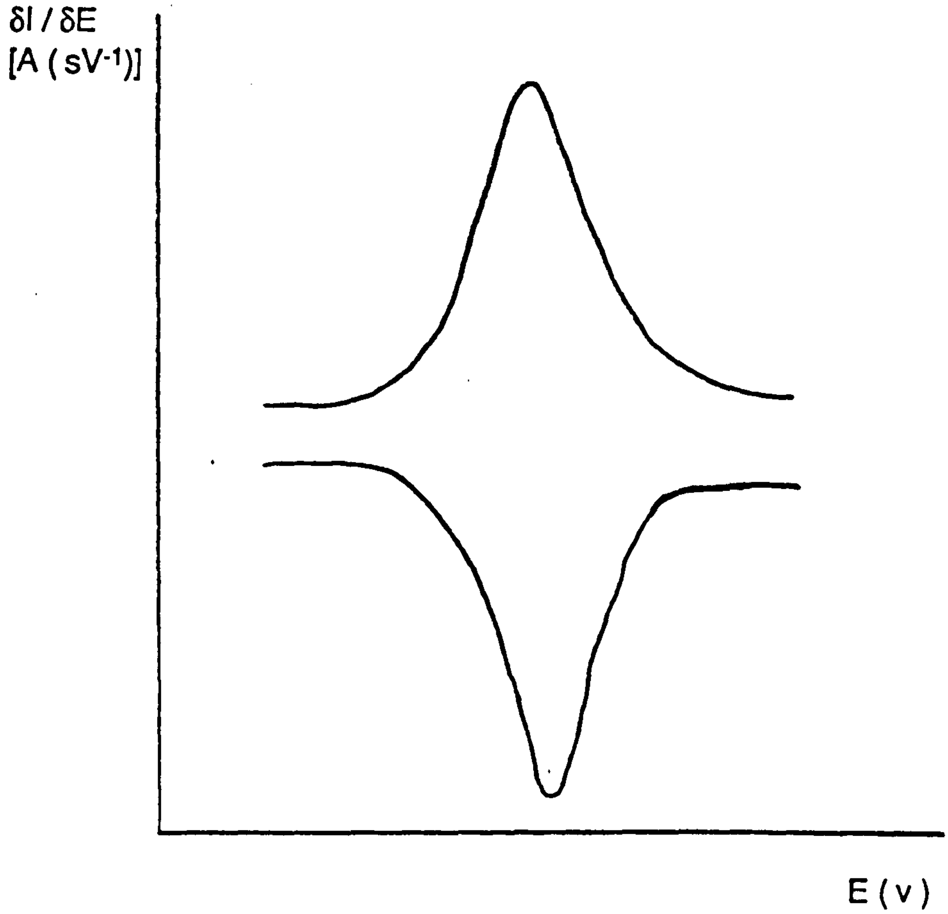


Figure 4.12 : Cyclic process

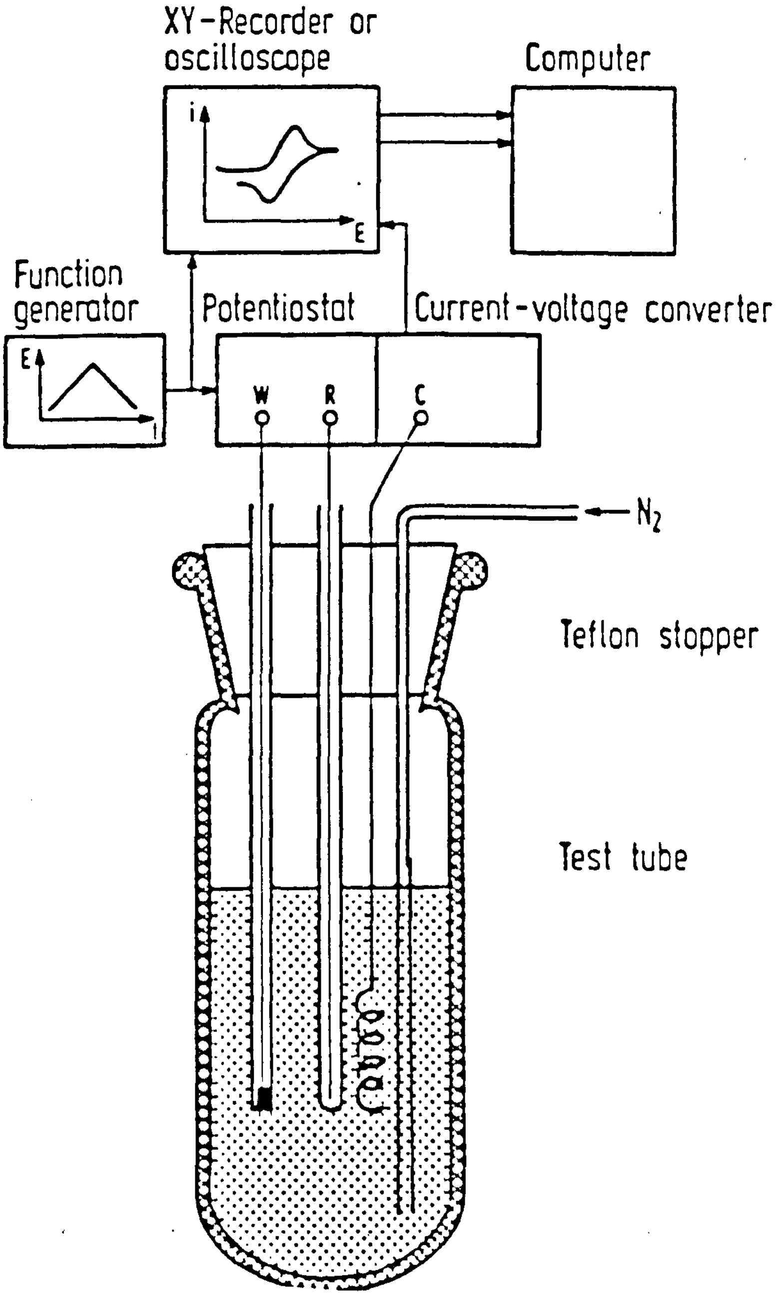


Figure 4.13 : Experimental set up for cyclic voltammetry . W = working electrode ; R = reference electrode ; c = counter electrode . Reproduced from Baizer and Lund[13] .

Figure 4.10(c) illustrates the case where there is chemical reaction subsequent to electron transfer . An anodic peak is observed on scan reversal but is considerably smaller than the cathodic peak . This is defined as an EC process , indicating that electron transfer is followed by chemical reaction .

When cyclic voltammetry is used as a direct electrochemical measurement technique there is no difficulty evaluating the current on the forward scan but establishing the baseline for the return scan may be troublesome . This problem may be overcome by employing the first derivative of the current response and plotting dI / dE against electrode potential . Figure 4.12 illustrates the line shape for a reversible one electron process from which it is possible to measure the half wave reduction (or oxidation) potential $E_{1/2}$, which corresponds to the reduction (or oxidation) potential for the one electron process .

The essential components of a typical cyclic voltammetry system are illustrated in Figure 4.13 . When recording the cyclic voltammograms discussed later in this chapter we used an EG & G PARC Model 303 SMDE voltammetry stand coupled to an EG & G Model 362 Scanning Potentiostat with the system controlled by an Amstrad PC 1640 Personal Computer running a cyclic voltammetry programme " Condecon 310" developed by Dr. N. Taylor and Mr. D. Mills . The working electrode was a small hanging mercury droplet , the counter electrode a platinum wire and the reference electode a silver / silver nitrate electrode . The reference electrolyte was a 0.01M solution of silver nitrate in a 0.1M solution of tetrabutylammonium tetrafluoroborate in either DMF or THF . DMF was purified according to the procedures described in ' Perrin and Perrin '[14] , passed through a short (5cm) column of alumina and then stored over 4Å molecular sieve . THF was distilled from sodium benzophenone ketyl and then stored over sodium wire under argon .

The diketones **16 - 18** were dissolved in a 0.1M solution of tetrabutylammonium tetrafluoroborate in either DMF or THF , the potassoxy triangulene **116** was dissolved in a 0.1M solution of tetrabutylammonium tetrafluoroborate in DMF . Unfortunately time and experimental constraints

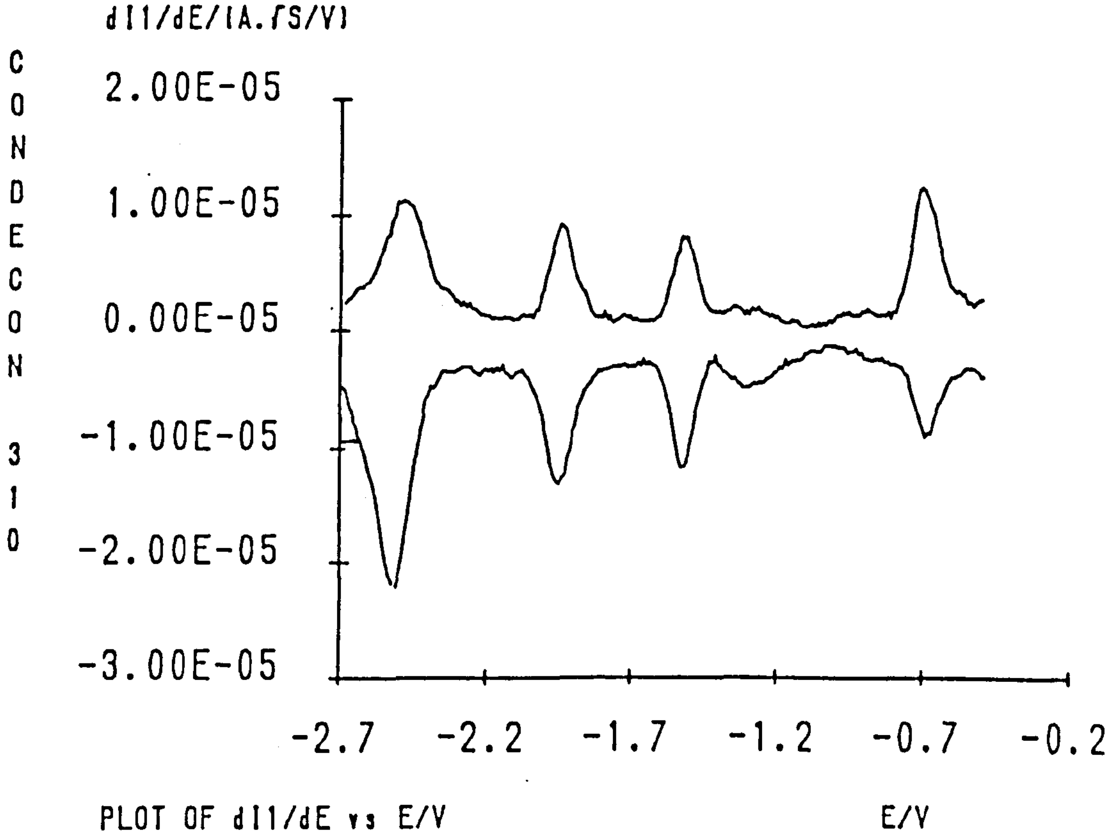
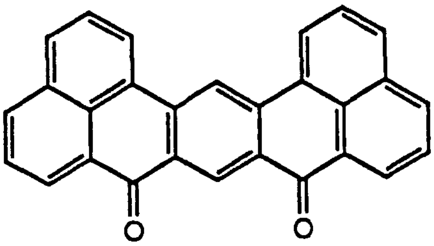


Figure 4.14 : Cyclic voltammogram obtained from the reduction of dibenzpentacenequinone .



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prevented us from investigating the reduction of the diketone **19**. The solutions were purged with oxygen free nitrogen or argon for a minimum of twenty minutes prior to acquiring the cyclic voltammetry data to remove oxygen.

As has been mentioned, we employed a small droplet of mercury as the working electrode. This hung from the end of a narrow bore capilliary tube. The capilliary itself was filled with mercury from which the droplet was refreshed. The circuit was closed through this mercury column. Any breaks in the capilliary, either through the entry of air or solvent, caused the circiut to be broken and / or the mercury droplet to fall off. Thus, although collecting data was quick, the preparation of a stable mercury column was often a long and painstaking task occupying many hours, or even days. In order to calibrate the system, anthracene was used as a ' standard ' and its reduction potentials checked before the system was used each day.

For the cyclic voltammograms shown in Figures 4.14 - 4.18 the potential was swept in the cathodic direction, which is represented by the lower line on the voltammograms and runs from right to left. When the potential was reversed in the anodic direction, the upper line running from left to right was produced. All voltammograms are first derivative. The derived redox potentials are quoted relative to the internal standard - a silver / silver nitrate electrode and are accurate to ±10mV.

4.3.2 The Reduction of Dibenzpentacenequinone

The cylic voltammogram obtained from dibenzpentacenequinone **17** in DMF under argon is illustrated in Figure 4.14. There are four reversible one electron processes corresponding to the formation of the radical anion ($E_{1/2}$ (1) -0.70V), the diradical dianion ($E_{1/2}$ (2) -1.48V) and then a radical trianion ($E_{1/2}$ (3) -1.95V) and tetraanion species ($E_{1/2}$ (4) -2.50V). The observation of four fast one electron transfer processes was not completely unexpected since many quinones also show four redox potentials[16].

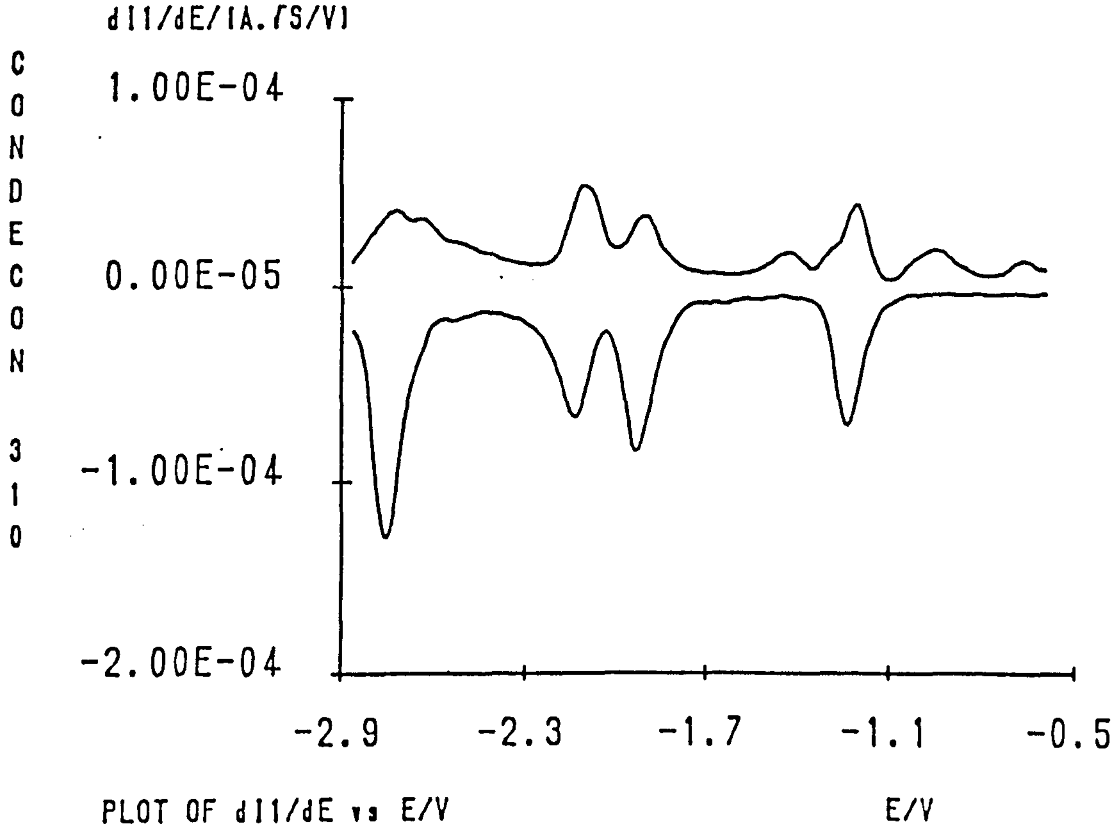
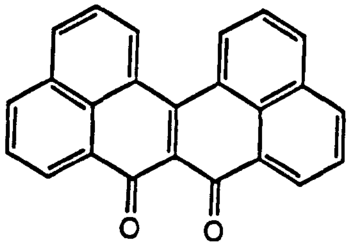


Figure 4.15 : Cyclic voltammogram obtained from the reduction of dibenznaphthacenequinone .



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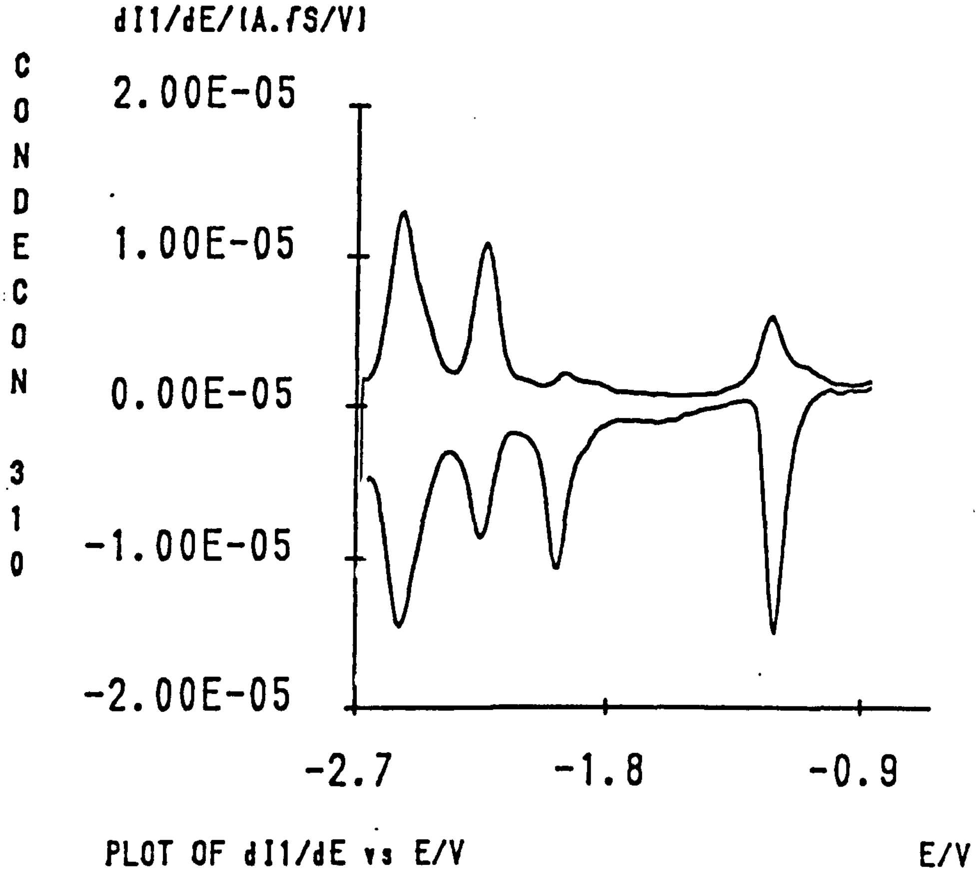
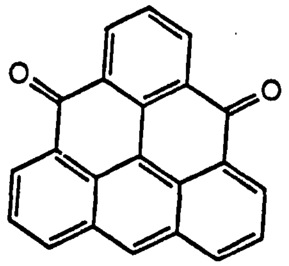


Figure 4.16 : Cyclic voltammogram obtained from the reduction of triangulenequinone .



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4.3.3 The Reduction of Dibenznaphthacenequinone

The cyclic voltammogram obtained from the electrochemical reduction of compound **18** in DMF under argon is illustrated in Figure 4.15 and , like compound **17** , it shows four fast one electron processes . Again these correspond to formation of first the radical anion ($E_{1/2}$ (1) -1.20V) , then the diradical dianion ($E_{1/2}$ (2) -1.78V) followed by the radical trianion ($E_{1/2}$ (3) -1.95V) and tetraanion ($E_{1/2}$ (4) -2.75V) species . However in this case the fourth reduction potential is irreversible indicating that at this point the tetraanion species rapidly undergoes either chemical reaction or decomposition . Experience gained in the synthesis of compounds **17** and **18** suggested that they were unstable . For example , recoveries from chromatography were always poor . The electrochemical studies reinforced this impression and solutions of **17** and **18** both deteriorated quickly on standing .

4.3.4 The Reduction of Triangulenequinone

The cyclic voltammogram obtained from the reduction of triangulenequinone **16** in DMF under argon is illustated in Figure 4.16 and again shows four fast one electron processes . The radical anion has $E_{1/2}$ (1) -1.18V and the diradical dianion $E_{1/2}$ (2) -1.92V . In this case the third and fourth redox processes were stable and reversible , with $E_{1/2}$ (3) -2.20V and $E_{1/2}$ (4) -2.58V . However , the second redox process was irreversible suggesting that the diradical dianion is a highly reactive species . The first reduction gave a cylic voltammogram trace sug gestive of an EC process , indicating that the radical anion underwent chemical reaction .

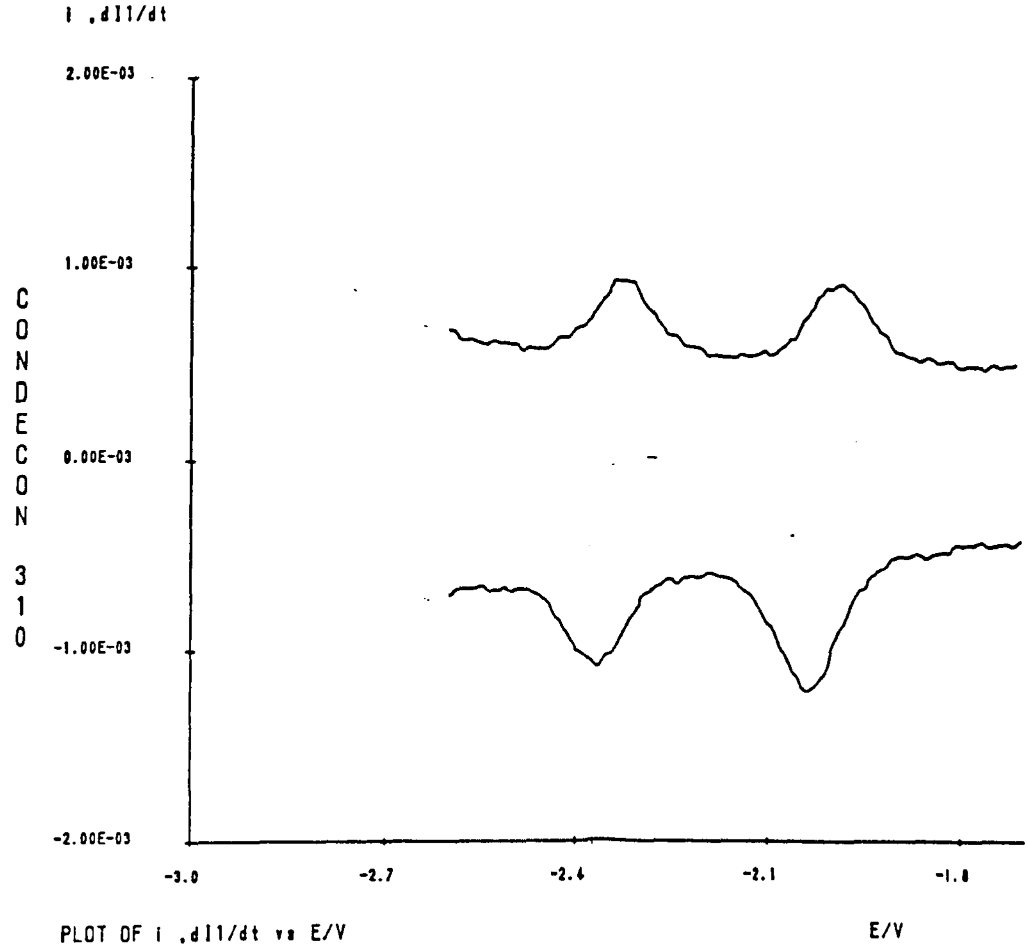
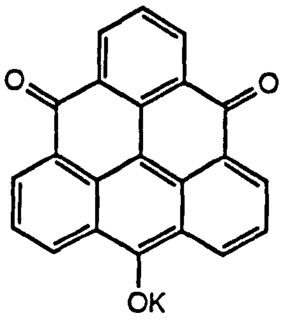


Figure 4.17 : Cyclic voltammogram obtained from the reduction of potassoxytriangulenequinone .



116

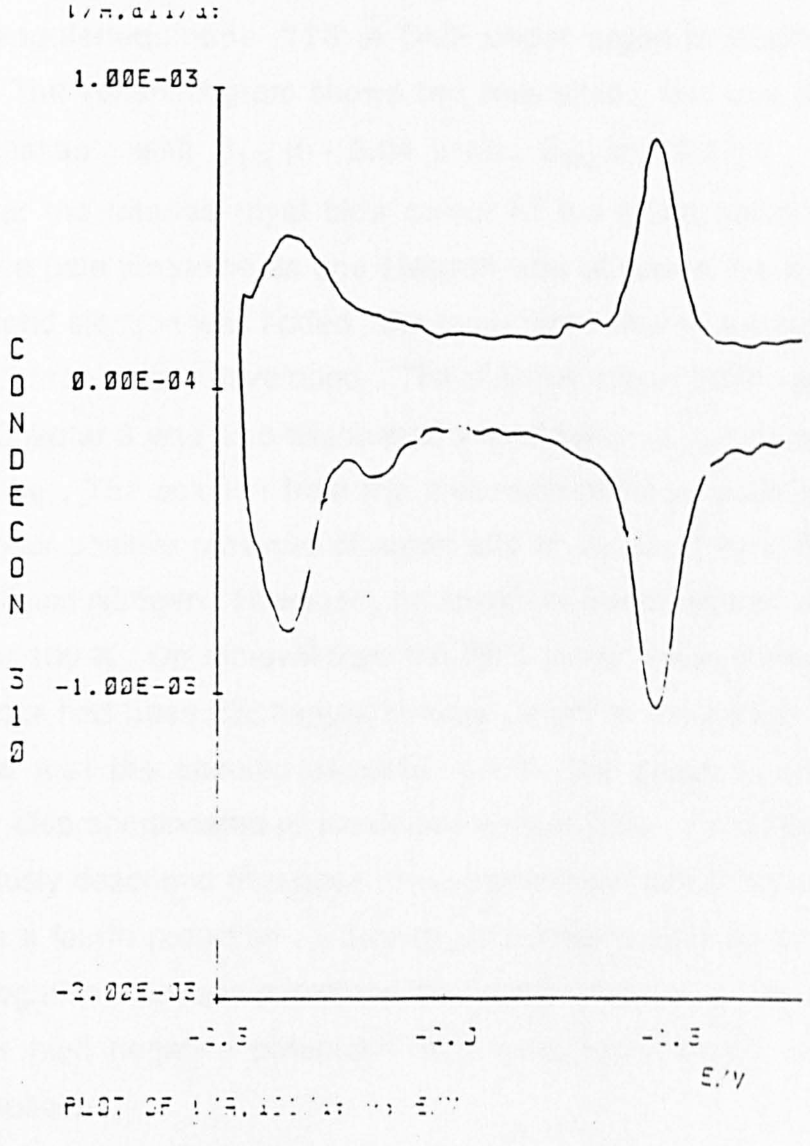
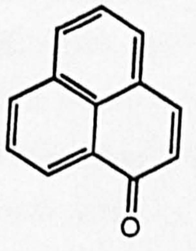


Figure 4.18 : Cyclic voltammogram obtained from the reduction of perinaphthenone .



73

4.3.5 The reduction of Potassoxytriangulenequinone [15]

The cyclic voltammogram obtained from the reduction of potassoxytriangulenequinone **116** in DMF under argon is illustrated in Figure 4.17 . The voltammogram shows two reversible , fast one electron transfer processes , with $E_{1/2}$ (1) - 2.04 V and $E_{1/2}$ (2) - 2.37 V . It was noticeable that the intense royal blue colour of the initial solution was discharged to a pale turquoise as one electron was added to the system . When the second electron was added , the turquoise colour was discharged and in turn a green colour developed . The putative triplet ESR spectrum described in Chapter 3 was also associated with a green colour developing in the ESR tube . The solution from the electrochemical experiment was transferred under positive pressure of argon into an argon filled ESR tube and frozen in liquid nitrogen . However , no spectrum was observed at room temperature or 100 K . On removal from the ESR cavity it was noticed that the green colour had been discharged to blue , even in the frozen state . This indicated that the species associated with the green colouration decomposed , disproportionated or reoxidised very quickly . It may be that , like the previously described diketones , these processes are followed by a third , or even a fourth reduction . However , we were unable to sweep to more highly negative electrode potentials than approximately -2.7 V in DMF since at these high negative potentials drop becomes unstable and the solvent decomposes .

4.3.6 The Reduction of Perinaphthenone [15]

The chemical routes to non-Kekulé polynuclear aromatics were derived from those reactions pioneered on phenalenone (perinaphthenone) to give the phenalenyl radical . We decided that it would be useful to compare the reduction of phenalenone with those of the diketones **16 - 18** and that of compound **116** . The cyclic voltammogram obtained from the reduction of perinaphthenone in DMF under argon is illustrated in Figure 4.18 . Again it shows two fast one electron transfer processes . The first , with $E_{1/2}$ (1) -1.53 V is fully reversible and electrochemically stable . However , the second , with $E_{1/2}(2)$ - 2.35 is irreversible .

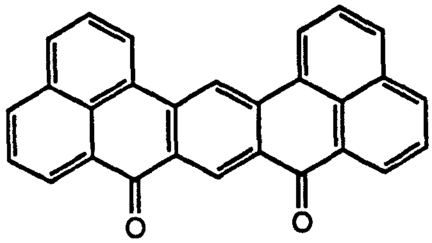
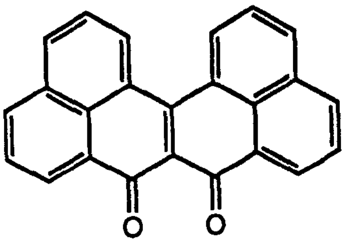
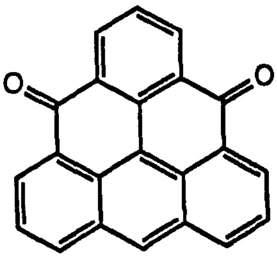
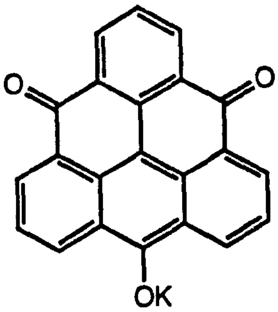
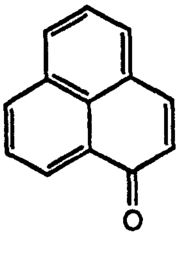
4.4 Conclusion

The redox potentials for the quinones **16 - 18** and the tri-oxo-triangulene **116** are summarised in Figure 4.19 . *The reduction potentials* required to reduce these compounds were high when compared with those of other quinones , such as p-benzoquinone or tetrachloro-p-benzoquinone . This raised the question of whether the first two redox potentials we were recording were in fact the first and second redox potentials and not , say , the third and fourth . Given that we were not observing any other redox potentials in the range -1 - 0 V we were fairly certain that our redox potentials were truly the first two such potentials . However , to answer the question more fully we constructed the graph of E_{LUMO} vs. $E_{(1/2)(1)}$ for a range of quinones [16] (Figure 4.20) , where E_{LUMO} is the energy of the lowest unoccupied molecular orbital and hence the orbital into which the first electron would be added during reduction . The compounds and data points used to construct the graph are illustrated in Figure 4.21 . The E_{LUMO} for the reference compounds was calculated using a Hückel Molecular orbital computer program developed by Dr. R.J. Bushby and took into account orbital overlap ie. for C=O $k_{C-O} = 0.8$, whilst C=C $k_{C-C} = 1.0$. For truly keto-like quinone oxygens we used $h_O = 1.0$, whilst for truly hydoxy-like oxygen functions $h_O = 2.0$.

It may be seen from the graph that the compounds **16 - 18** , and **116** straddle the best fit line of the graph and thus we can be confident in saying that we were indeed observing the first and subsequent reduction potentials in our cyclic voltammetry experiments .

The ESR experiments described in Chapter 3 indicated that when the diketones **16 -19** were converted to the corresponding diradicals that these biradicals had a singlet ground state and as such were not viable as the acceptor components of charge transfer complexes .

Figure 4.19

Compound	$E_{1/2}$ /V
 **17**	- 2.50 - 1.95 - 1.48 - 0.70
 **18**	- 2.75 - 1.95 - 1.78 - 1.20
 **16**	- 2.58 - 2.20 - 1.92 - 1.18
 **116**	- 2.37 - 2.04
 **73**	- 2.35 - 1.57

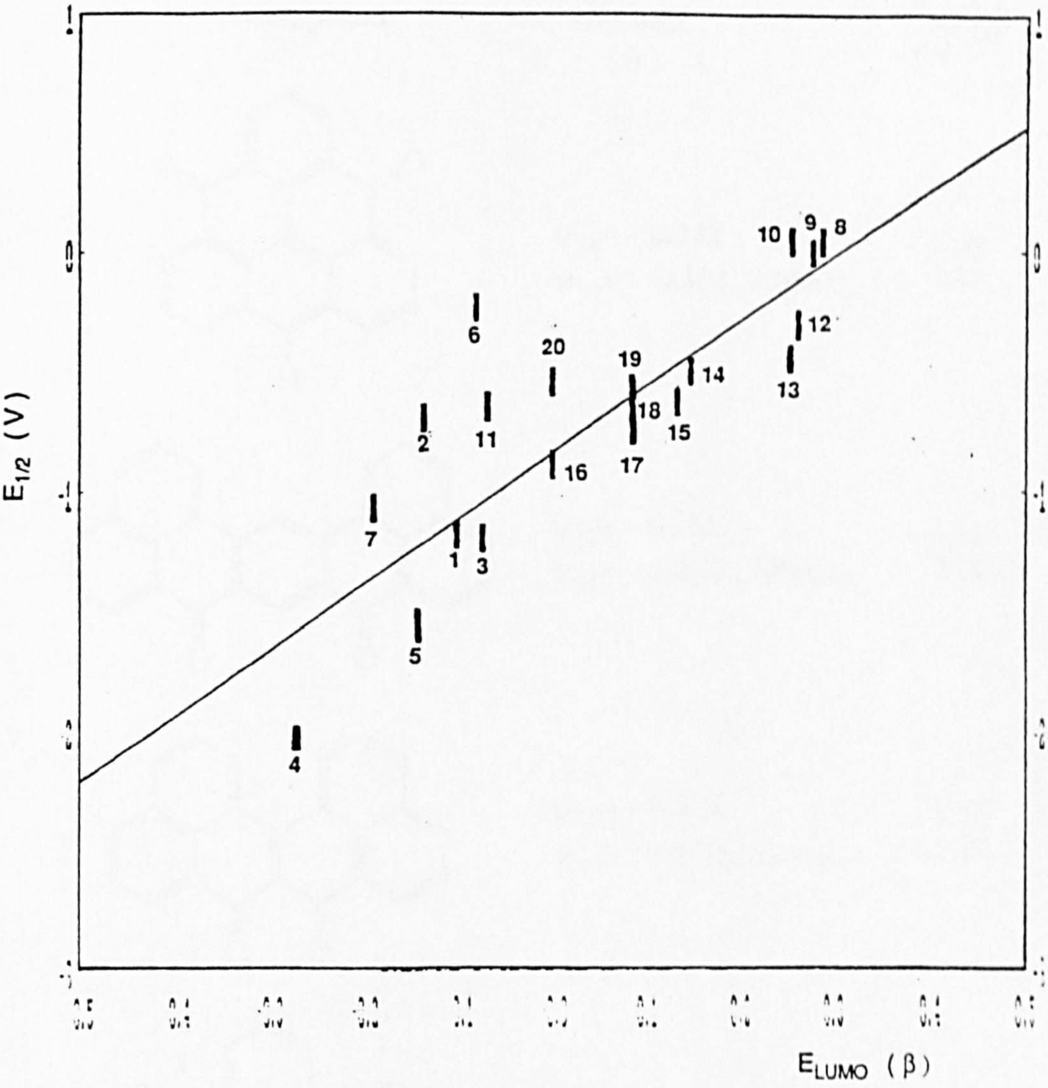


Figure 4.20 : Graph of E_{LUMO} vs. $E_{1/2}$

Figure 4.21

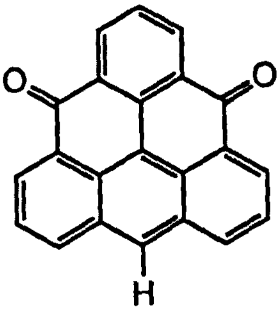
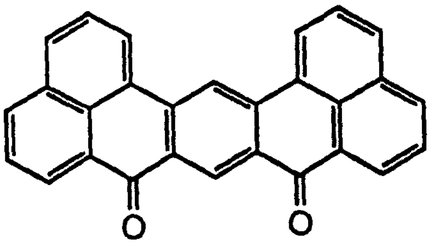
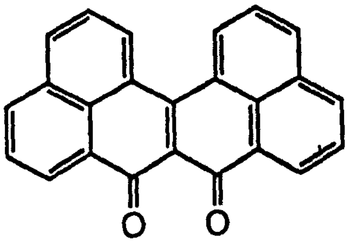
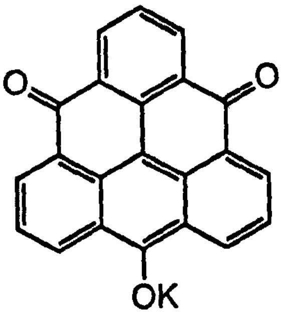
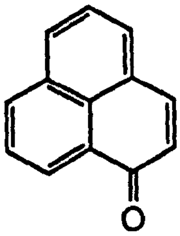
	Compound	E_{NBMO} (β)	$E_{1/2}{}^{(2)}_{(1)}$ (V)
1		ψ_{14}= - 0.272 ψ_{13}= - 0.102...LUMO.........	- 1.92 - 1.18
2		ψ_{17}= - 0.266 ψ_{16}= - 0.138...LUMO.........	- 1.48 - 0.70
3		ψ_{15}= - 0.303 ψ_{14}= - 0.074...LUMO.........	- 1.78 - 1.20
4		ψ_{15}= - 0.272 ψ_{14}= - 0.272...LUMO.........	- 2.37 - 2.04
5		ψ_9 = - 1.000 ψ_8 = - 0.138...LUMO.........	- 2.35 - 1.53

Figure 4.21 (cont .)

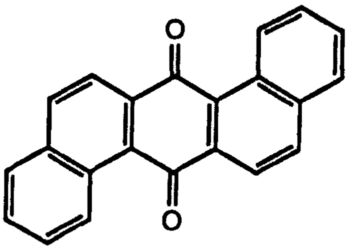
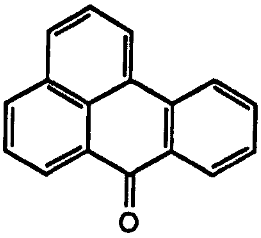
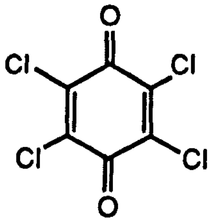
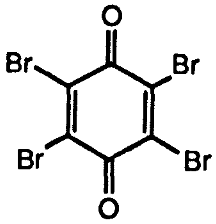
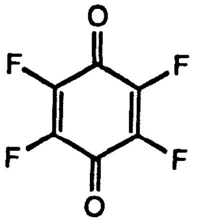
	Compound	E_{NBMO} (β)	$E_{1/2}{}^{(2)}_{(1)}$ (V)
6		ψ_{13}= - 0.082...LUMO.........	- 0.41 - 0.24
7		ψ_{10}= - 0.190...LUMO.........	- 1.25 - 1.07
8		ψ_9 = + 0.288...LUMO.........	- 0.88 +0.04
9		ψ_9 = +0.278...LUMO.........	- 0.72 0.00
10		ψ_9 = +0.256...LUMO.........	- 0.82 +0.04

Figure 4.21 (cont .)

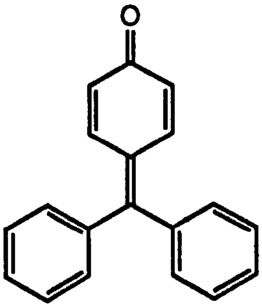
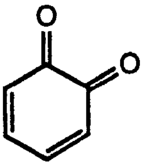
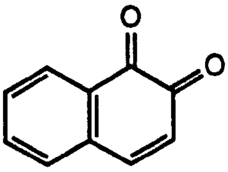
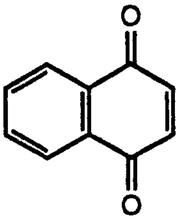
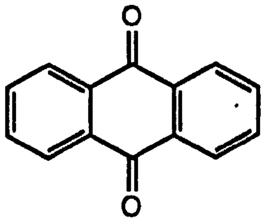
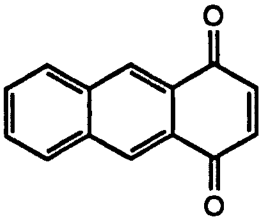
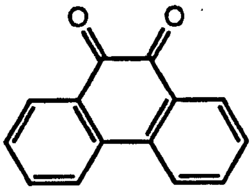
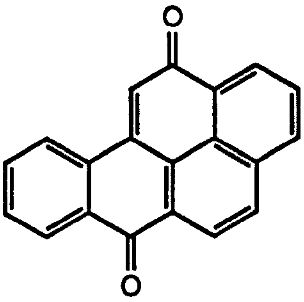
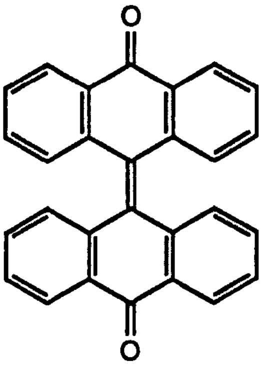
	Compound	E_{NBMO} (β)	$E_{1/2}{}^{(2)}_{(1)}$ (V)
11		ψ_{13}= - 0.069...LUMO.........	- 0.65
12		ψ_5 = +0.262...LUMO.........	- 0.90 - 0.31
13		ψ_5 = + 0.254...LUMO.........	- 1.28 - 0.45
14		ψ_7 = +0.147...LUMO.........	- 1.12 - 0.51
15		ψ_7 = +0.133...LUMO........	- 1.35 - 0.63

Figure 4.21 (cont .)

	Compound	E_{NBMO} (β)	$E_{1/2}{}^{(2)}_{(1)}$ (V)
16		ψ_9 = 0.000...LUMO.........	- 1.54 - 0.89
17		ψ_9 = +0.085...LUMO........	- 1.25 - 0.75
18		ψ_9 = + 0.084...LUMO........	- 1.22 - 0.66
19		ψ_{12} = +0.084...LUMO.........	- 0.90 - 0.58
20		ψ_{16} = 0.000...LUMO........	- 1.25 - 0.55

The tri-oxo-triangulene , on the other hand , does appear to have a triplet ground state and as such fits the bill as an acceptor in a charge transfer complex . However , its first reduction potential at - 2.04V has a high negative potential . Figure 4.22 illustrates a range of molecules that have been used as donors in charge transfer systems and it is immediately obvious that their first oxidation potentials are considerably more positive than the first reduction potential of tri-oxo-triangulene . Thus it seems unlikely that the tri-oxo-triangulene can be used as an acceptor in a charge transfer complex . Figure 4.23 was constructed using the same format as Figure 4.8 for a mixture of the tri-oxo-triangulene with a typical donor molecule . It is clear that even the first electron transfer is unfavourable under these circumstances .

Although the tri-oxo-triangulene system does have high negative reduction potentials , the very fact that it does appear to have a triplet ground state gives this system some promise as an electron acceptor component of a charge transfer complex . This leaves two avenues of research open ; either one could design (or find) electron donors with comparably low first

Figure 4.23

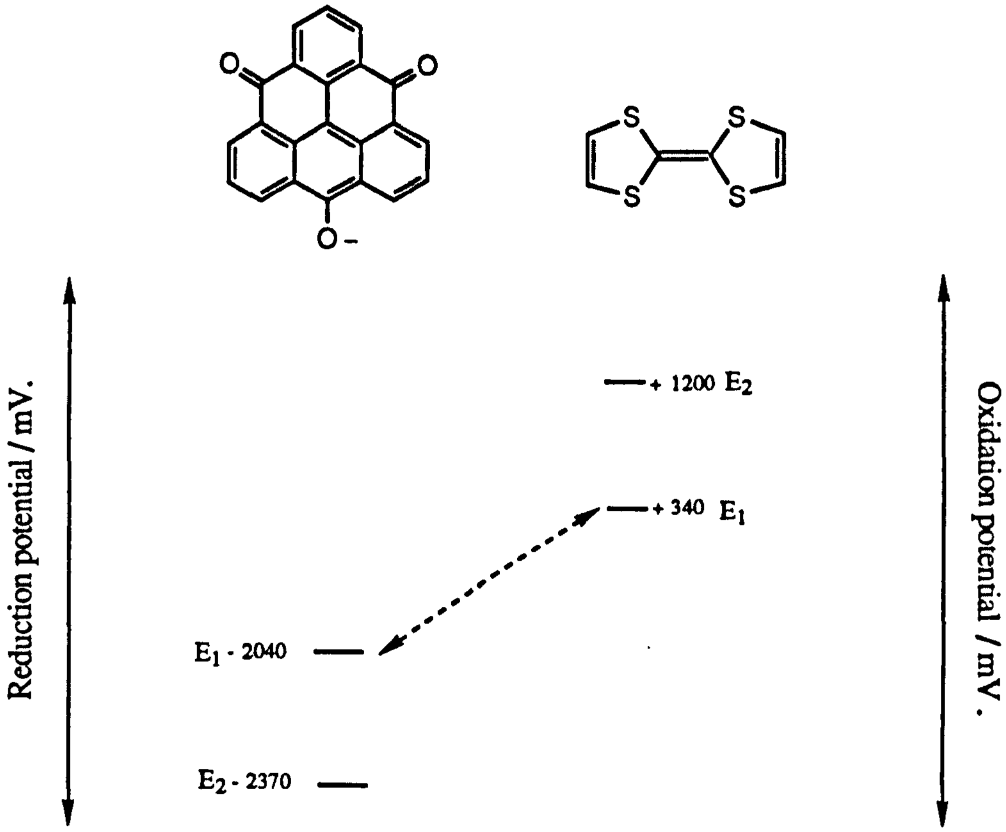
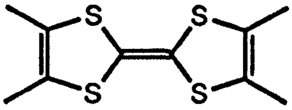
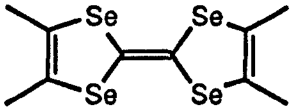
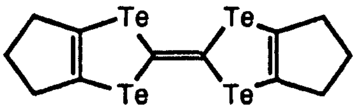
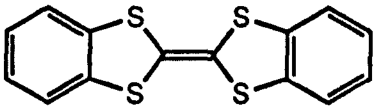
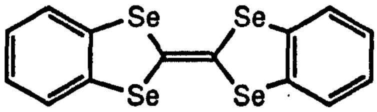
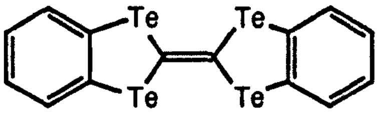
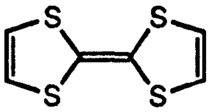
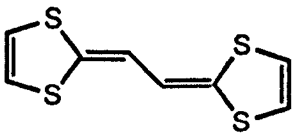
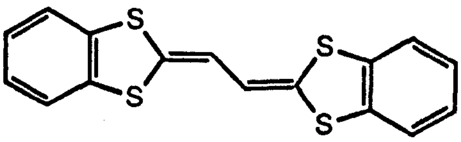
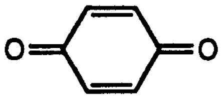
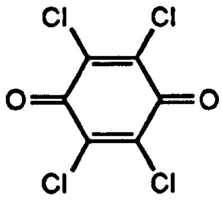
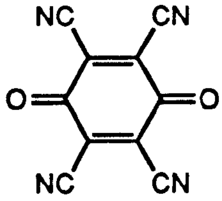


Figure 4.22

Compound	$E_{1/2}{}^{(2)}_{(1)}$ (V)
	+ 0.73 + 0.24
	+ 0.81 + 0.42
	+ 0.69 + 0.40
	+ 1.14 + 0.71
	+ 1.17 + 0.78
	+ 1.14 + 0.71
	+ 0.71 + 0.34
	+ 0.36 + 0.20
	+ 0.64 + 0.47

and second oxidation potentials or one could derivatise the tri-oxo-triangulene system in such a way that the redox potentials are made less negative .

Figure 4.24

Compound	E_{LUMO} (β)	$E_{1/2}(1)$ (V)
	$\psi_5 = 0.254$	- 0.51
	$\psi_9 = 0.288$	+ 0.04
	$\psi_9 = 0.347$	+ 0.1 (calc)

When the graph illustrated in Figure 4.20 was being compiled it was noticed that there was a marked decrease in E_{LUMO} when the p-benzoquinone nucleus was *per* - halogenated . This effect is illustrated in Figure 4.24 . Some interesting effects on E_{LUMO} were noticed when this strategy was applied to the tri-oxo-triangulene system . The results of our Huckel molecular orbital calculations for a range of substituted triangulenes are tabulated in Figure 4.25 . These Hückel molecular orbital calculations indicated that *per* - chlorination would indeed lower E_{LUMO} which , by utilising the graph drawn in Figure 4.20 , gave a predicted first redox

Figure 4.25

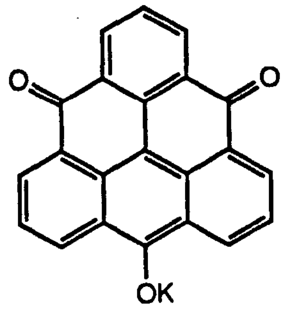
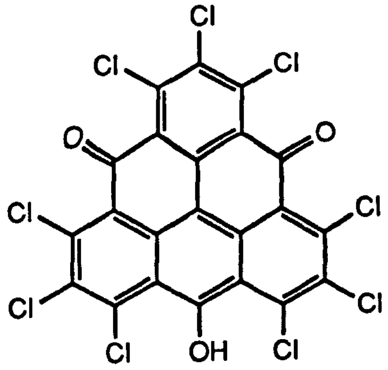
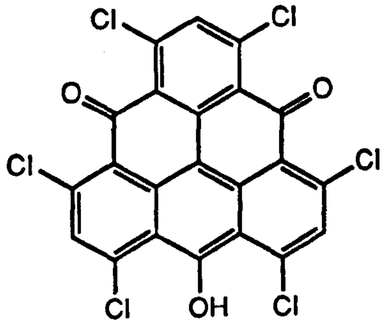
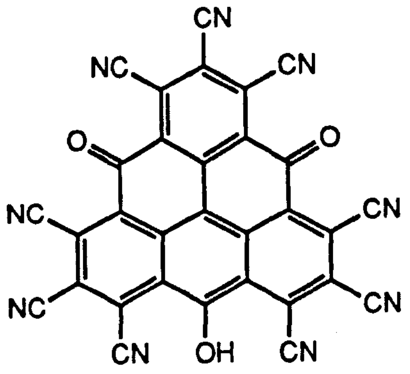
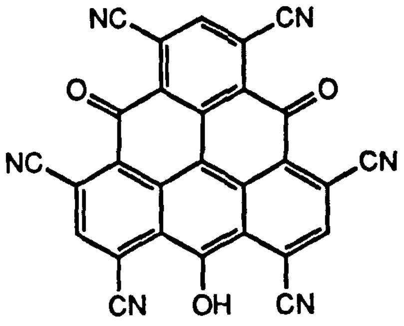
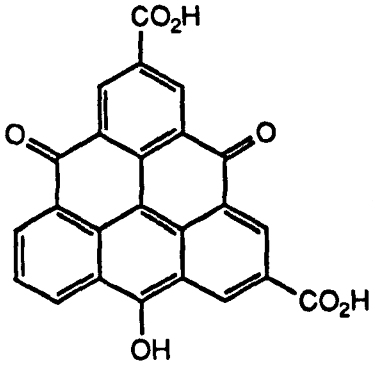
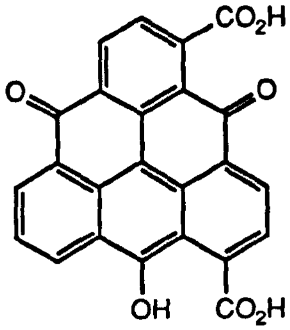
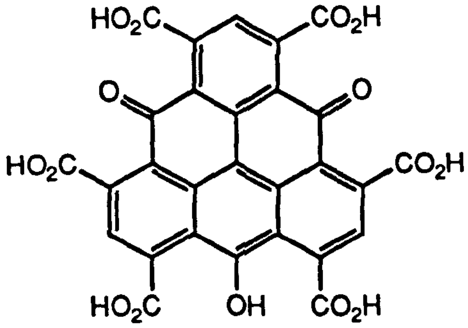
Compound	E_{NBMO} (β)	$E_{1/2}{}^{(1)}$ (V) (predicted)
	$\Psi_{14}\Psi_{15} = -0.272$	- 2.04 (exp.)
	$\Psi_{23}\Psi_{24} = -0.132$	- 1.25
	$\Psi_{20}\Psi_{21} = -0.057$	- 1.0
	$\Psi_{23}\Psi_{24} = -0.134$	- 1.25

Figure 4.25 (cont.)

Compound	E_{NBMO} (β)	$E_{1/2}(1)$ (V) (predicted)
	$\Psi_{20}\Psi_{21}$ = + 0.134	- 0.45
	$\Psi_{18}\Psi_{19}$ = - 0.115	- 0.9
	Ψ_{19}= - 0.002 Ψ_{18} =+ 0.127	- 0.45
	$\Psi_{26}\Psi_{27}$ = + 0.209	- 0.25

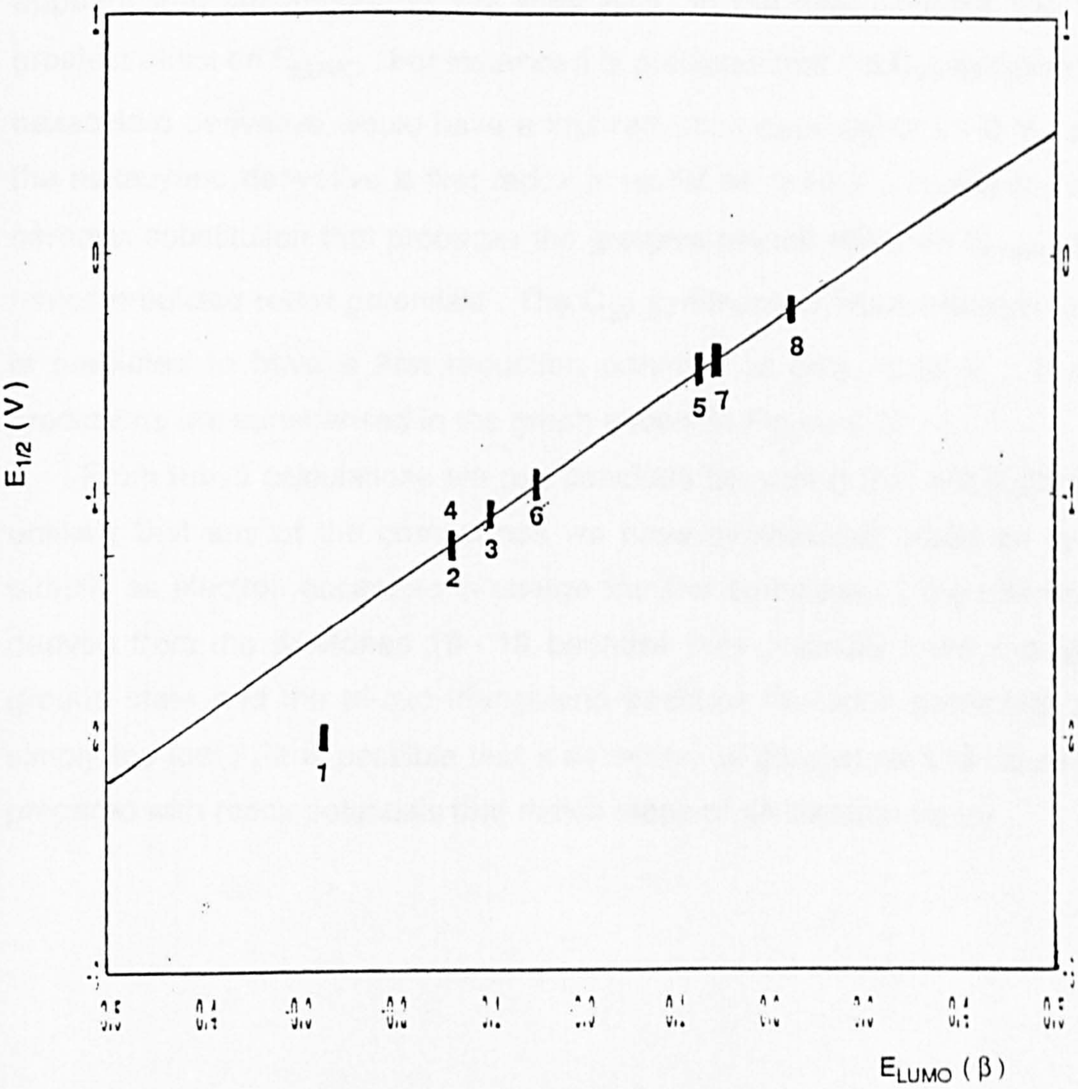


Figure 4.25 : Graph of E_{LUMO} vs. $E_{1/2}$ giving the predicted redox potentials for the triangulene derivatives illustrated in Figure 4.24

potential of approximately -1.25 V , an increase of approximately 0.8 V . It appears that substitution at the sites *peri* to the oxo-functions has the greatest effect on E_{LUMO} . For instance it is predicted that the C_{3v} symmetrical hexachloro derivative would have a first reduction potential of - 1.0 V , and the hexacyano derivative a first redox potential of -0.45 V . However , it is carboxyl substitution that produces the greatest overall effect on E_{LUMO} and hence predicted redox potentials . The C_{3v} symmetrical hexacarboxylic acid is predicted to have a first reduction potential of only -0.25 V . These predictions are summarised in the graph shown in Figure 4.26 .

From these calculations we can conclude by saying that although it is unlikely that any of the compounds we have synthesised could be used directly as electron acceptors in charge transfer complexes (the biradicals derived from the diketones **16 - 18** because they probably have a singlet ground state and the tri-oxo-triangulene because its redox potentials are simply too low) , it is possible that a derivative of compound **116** could be prepared with redox potentials that match those of an electron donor .

4.5 References

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