The synthesis of singlet ground state derivatives of non-Kekulé polynuclear aromatics

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It is known that a two-electron reduction of tetrabutylammonium 3,4-dioxo-4*H*,8*H*-dibenzo[*cd*,*mn*]pyren-12-olate gives a trioxy (tri-O^-) derivative of the non-Kekulé polynuclear aromatic compound dibenzo[*cd*,*mn*]pyrene (triangulene). This derivative is stable in solution and, like triangulene itself, has a triplet ground state. In exploring the generality of this strategy for the synthesis of high-spin derivatives of non-Kekulé polynuclear aromatic compounds we have investigated two electron reductions of 4,8-dioxo-4*H*,8*H*-dibenzo[*cd*,*mn*]pyrene (to give a dioxy derivative of triangulene), 7,8-dioxo-7*H*,8*H*-dibenzo[*de*,*hi*]naphthacene (to give a dioxy derivative of dibenzo[*de*,*hi*]naphthacene) and 7,9-dioxo-7*H*,9*H*-dibenzo[*de*,*jk*]pentacene (to give a dioxy derivative of dibenzo[*de*,*jk*]pentacene). Dibenzo-[*cd*,*mn*]pyrene (triangulene), dibenzo[*de*,*hi*]naphthacene and dibenzo[*de*,*jk*]pentacene should all have triplet ground states, but the presence of *two* O^- substituents on these aromatic nuclei will (just) lift the degeneracy of the putative singly occupied molecular orbitals. We have shown that the splitting this produces is sufficient to ensure that all of these dioxy derivatives have singlet ground states. Hence the strategy employed for making and stabilising triplet triangulene as its trioxy derivative does not provide a paradigm for other high-spin non-Kekulé polynuclear aromatics. The reduction reactions were studied by cyclic voltammetry, by UV–VIS spectroscopy, and by EPR spectroscopy. Improved synthetic routes are described for 7,8-dioxo-7*H*,8*H*-dibenzo[*de*,*hi*]naphthacene and for 7,9-dioxo-7*H*,9*H*-dibenzo[*de*,*jk*]-pentacene. Violent explosions were encountered in attempts to repeat the literature procedure for the synthesis of 4,6-dichlorobenzene-1,3-dicarboxylic acid.

In Ovchinnikov's seminal paper on organic molecular magnets[1] he made the imaginative suggestion that high-spin systems could be made by creating the 'triangularly bounded' series of polynuclear aromatic hydrocarbons **1**–**4**, *etc.* shown in Fig. 1. Hence the phenalenyl radical **1** has a doublet ground state, triangulene **2** a triplet ground state,[2–4] the hydrocarbon **3** should have a quartet ground state and so on. His suggestion involves exploiting the known stability of the phenalenyl radical. An alternative way of doing this, of 'creating' high-spin polynuclear aromatics, is not to extend from one edge of the molecule as in this sequence, but to linearly fuse the phenalenyl nuclei as in the series **1, 5**–**7**, *etc.* or in the series **1, 8**–**10** *etc.* (Fig. 1). In such linearly fused phenalenyl systems the detailed topology is all important. Hence, the second and third sequences shown in Fig. 1 should build up high-spin systems but, although it looks similar, the fourth sequence **1, 11**–**13**, *etc.* is expected to generate nothing more than doublet ground states. Whereas compounds **2**–**10** are non-Kekulé polynuclear aromatics,[3] compounds **11**–**13** are Kekulé in nature.

Although the structures shown in Fig. 1 may excite the theoretician, to the synthetic organic chemist they appear unrealistic targets. Like most polynuclear aromatics, the compounds themselves, and most of their precursors, are likely to be insoluble whilst their open-shell nature suggests that they will be highly unstable, particularly towards oxygen, to dimerisation and to polymerisation processes—a problematic combination of properties. However, it may be that the solubility problems can be overcome by suitable 'side-chain' substitution and recent success in the synthesis of the first derivative of a non-Kekulé polynuclear aromatic, the trioxy triangulene **14** (Fig. 2),[2–4] suggests, either that these systems are not as unstable as was at one time believed,[5,6] or that they can be stabilised by suitable substitution.[3] This paper describes the synthesis of the analogous dioxy derivative **15**–**17** of the non-Kekulé polynuclear aromatic compounds **2, 5** and **8** (as shown in Fig. 2). Unfortunately, they all prove to be singlet biradicals.

The parent hydrocarbons **2, 5** and **8** are all expected to have triplet ground states. This is because, as shown in Fig. 3, they all possess a degenerate pair of singly occupied molecular orbitals which are orthogonal but coextensive[7] (non-disjoint in Borden's terminology[8]). They have atomic sites in common. This is the classical Hund's Rule situation. For either atomic and molecular systems, degenerate, coextensive, orthogonal singly occupied orbitals lead to a strong exchange interaction and a high-spin ground state.[9] In the special case of the tris-O^- derivative of triangulene **14**, the introduction of the three O^- substituents into the hydrocarbon nucleus preserves the threefold-symmetry of the system and neither affects the degeneracy nor the coextensive nature of the singly occupied molecular orbitals.[4] This is, however a special case. In the analogous bis-O^- derivative **15** of compound **2,** the analogous bis-O^- derivative **16** of compound **5,** and the analogous bis-O^- derivative **17** of compound **8**, the presence of the two substituents lifts the degeneracy of the putative singly occupied molecular orbitals by between 0.09 and 0.15β (Fig. 2). In such cases there is a 'competition' between the exchange interaction, which in coextensive systems favours the high-spin state, and the perturbing effect of the substituents, which favours the low-spin state. The outcome of this competition cannot be predicted by simple molecular orbital methods. It requires an accurate calculation of correlation energies in what are relatively large molecules. Hence predictions must be based on analogies to known systems. In this case the obvious analogies are to derivatives of the related non-Kekulé polyene[3] trimethylenemethane[10] and of the related non-Kekulé quinomethane,[3] *m*-quinodimethane.[11] These show that unsymmetrically substituted, strongly perturbed derivatives with calculated splittings $>0.15\beta$ still have triplet ground states. This

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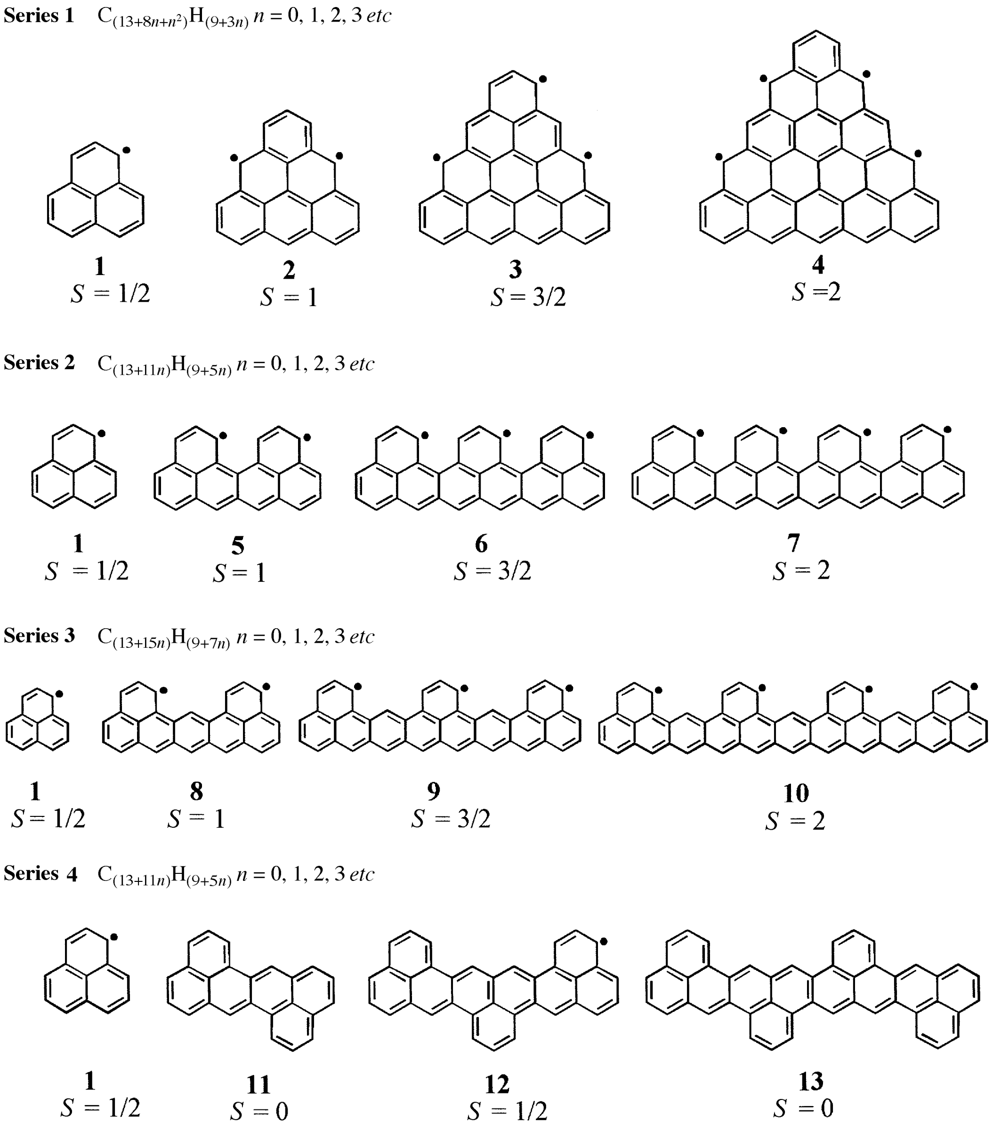


Fig. 1 Families of high-spin polynuclear aromatic compounds based on extended or repeated versions of the phenalenyl nucleus

suggests that, despite the magnitude of the splitting, it is not unreasonable to expect compounds **15**–**17** to have triplet ground states.

The HMO calculations of the splittings of the putative singly occupied molecular orbitals given in Fig. 2 assumed (of course) that all of these π systems are near planar. This is confirmed by the X-ray crystal structure of the tetrabutylammonium salt of compound **18**[4] and by RHF-MNDO optimisations of the geometry of compounds **18** **19**, and **21** but these same calculations suggest a significantly non-planar geometry for the dione **20**. This arises from a strong steric interaction between the hydrogens on carbons 1 and 14. As a result the 'terminal' benzene nuclei twist out of the plane and the molecule adopts a conformation in which these hydrogens lie one above the other.

This paper is concerned with the synthesis and the investigation of the spin ground states of the biradicals **15**–**17**. In doing this we have extended our work on the triangularly bound polynuclear aromatics[2–4] to include the two simplest linearly fused phenalenyl systems (the second members of both of the series 2 and 3 in Fig. 1) and have tried to lay a foundation for future work on solubilised/stabilised non-Kekulé polynuclear aromatics. The synthetic chemistry we have employed was based on the success of the two-electron reduction strategy used for the diketone **18** (Fig. 2), the relative ease by which the diketones **19**,[12] **20**[5] and **21**[5] can be made, the known ease of the one-electron reduction of phenalenone, and the known stability of the resultant radical anion.[13]

The synthesis of the biradical precursors 19–21

The synthesis of all three of these biradical precursors has been described in the literature. However, only the synthesis of compound **19** proved to be as straightforward as the literature suggests. As described by Weiss and Korczyn,[12] this can be obtained by a zinc–sodium hydroxide reduction of the potassium salt of compound **18**.[4]

As a first step in the synthesis of the bisdione **20,** the naphthylmalonic ester **22**[14] was prepared by the condensation of 1-naphthaldehyde with diethyl malonate. This was converted to the diester **23a** by reaction with the Grignard reagent derived from 1-bromonaphthalene[14] and this was hydrolysed to the diacid **23b**.[5] According to Clar and co-workers, when this acid is added to a refluxing mixture of phosphorus pentoxide and nitrobenzene and the mixture heated for a further ten minutes a red product is obtained which, on recrystallisation from xylene, gives a 'very small' yield of the desired red–brown ketone **20**, mp 250 °C decomp., although (also according to Clar) 'sometimes without reason' an unidentified colourless isomer, mp 250 °C, is obtained.[5] This and related 'Freidel–Crafts' processes have since been investigated by various groups with rather variable results. Gupte *et al.* investigated the reaction of the diacid **23b** with phosphorus pentoxide–phosphoric acid in chloro-

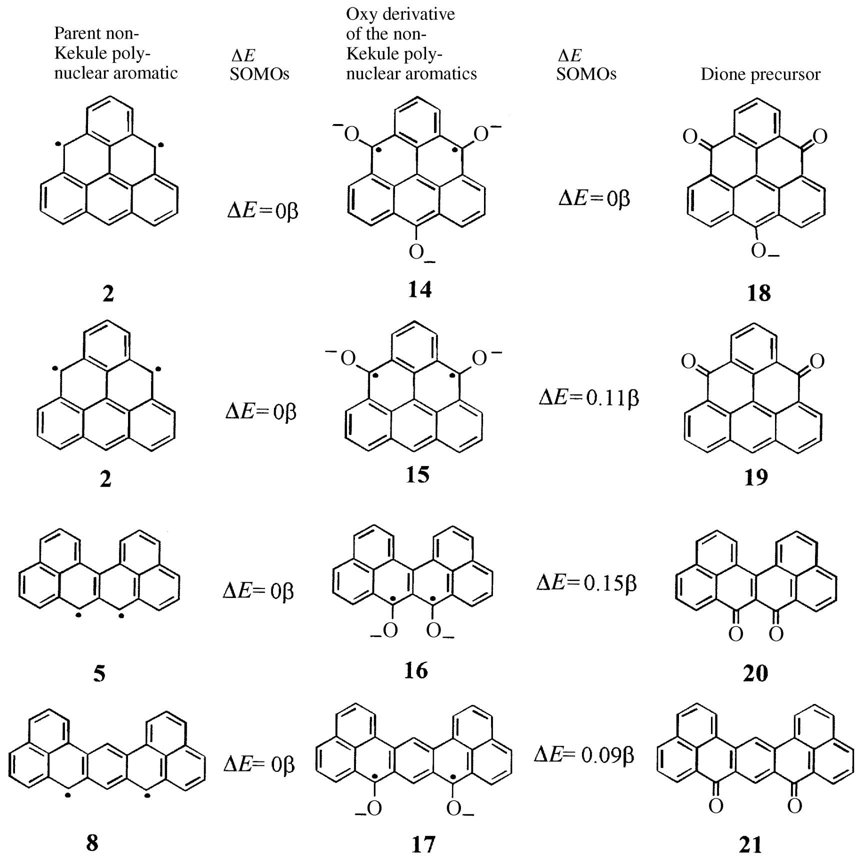


Fig. 2 The second member of each of the first three families of polynuclear aromatic compounds shown in Fig. 1. The triplet ground state molecules **2**, **5** and **8**, their dioxy and trioxy derivatives (compounds **14**–**17** which are the main subject of this paper), and the bis-diones (compounds **18**–**21**) from which they are made. In the HMO calculations of the differences in energy between the putative singly occupied molecular orbitals, h_O was taken as 2.0 and k_{CO} as 1.0.

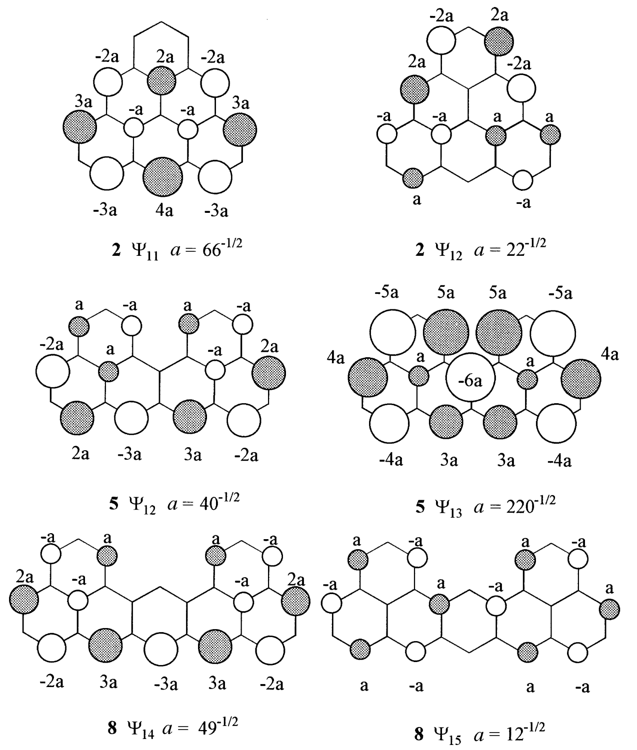
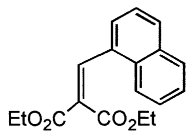


Fig. 3 Spatial distribution of the singly occupied molecular orbitals for the hydrocarbons **2**, **5** and **8** showing their orthogonal, coextensive (non-disjoint) nature

benzene at 130 °C and they isolated a colourless product, mp 248 °C, which they identified as an indanone.[15] When this reaction was reinvestigated by Shotter and co-workers[16] they revised the structure of Gupte's 'indanone' to that of the monocarboxylic acid **24a**. Gerasimenko and Didenko subsequently showed that treatment of the acid chloride **24b** with aluminium chloride gave the cyclised product **25** and its dehydroderivative **26**.[17]

Our attempts to repeat the cyclisation of the acid **23b** under Clar's conditions (*ca.* 10 min with phosphorus pentoxide in nitrobenzene at 130 °C) gave a crude product which was certainly red but which proved to be a complex mixture, separated only with difficulty by column chromatography. The main product, and the main source of the red colouration, proved to be the phenalenone **27**. The assignment of this particular structure to this product rests on the elemental composition $C_{23}H_{12}O$ and the ^1H NMR spectrum which shows the presence of a one-hydrogen singlet, one 'isolated' CHCH spin system, and three 'isolated' CHCHCH spin systems. The known compounds **25** and **26**[17] were also isolated from the chromatography column but in smaller yields. It seems that, at 130 °C, the main products are those of monodecarboxylation. The simplest explanation of the formation of these products would be one in which decarboxylation is the first step, *i.e.* **23b** ⟶ **24a** ⟶ **25** ⟶ **26** ⟶ **27** although more complex schemes could be envisaged. Even when authentic samples of the desired product **20** were available we were unable to detect any (by spectroscopic or chromatographic methods) in the crude product obtained under Clar's reaction conditions. Traces were, however, detected when the temperature of the reaction was lowered. The best yield was obtained when the reaction was carried out at room temperature. It seems probable that the variable results and yields ('very small' to 'non existent') reported by Clar resulted from poor temperature control and the use of high temperatures that favour decarboxylation rather than the desired cyclisation reaction.

Difficulties were also experienced in repeating Clar's synthesis of the dione **21**.[5] The dichloro compound **28** is readily



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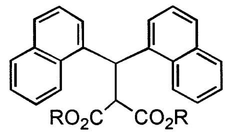
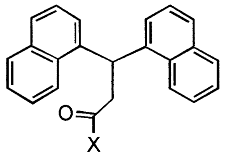
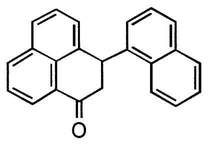


23a R = Et
23b R = H



24a X = OH
24b X = Cl



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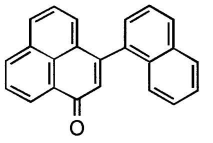

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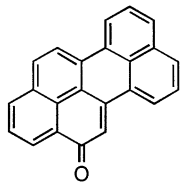

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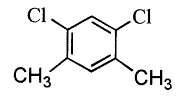

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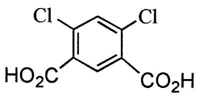

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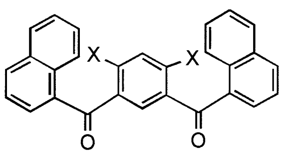
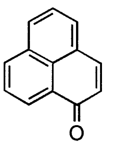


30a X = H
30b X = Cl
30c X = Br



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obtained from direct chlorination of *meta*-xylene,[18] in a rather low-yielding process but one that is easy to perform on a large scale. According to Koch[19] this dichloride can be converted to the dicarboxylic acid **29** by heating with concentrated nitric acid in a sealed tube at 220 °C for 10 h. **CAUTION** Although this was repeated successfully by Clar[5] and also by ourselves, our experience shows that **THIS IS AN EXTREMELY DANGEROUS PROCEDURE.** In all except three of about twenty attempts to repeat this reaction the tube has exploded. These explosions were extremely violent reducing standard Carius tubes with a wall thickness of 3.5 mm to the consistency of sand and on three occasions causing substantial damage to the door of a strongly built Carius tube oven. When, on the final attempt, a tube exploded after being cooled to room temperature and removed from the oven (but still within its guard tube) we concluded that **THIS PROCEDURE IS TOO DANGEROUS TO REPEAT.** The explosions were not the result of inexperience in the use of Carius tubes, nor of any obvious impurities in the starting materials (which were carefully checked), nor of the quantity of material in each tube (which was reduced to a lower level than that recommended). Since, on some occasions no significant pressure was developed and the desired product was obtained but on others high pressure developed and the tube exploded, it seems that there is some variability in the course of the reaction the cause of which we have not been able to identify.

The search for alternative oxidation methods was initially unsuccessful. Part of the problem is that compound **28** is a solid that is highly volatile and steam volatile. Hence any attempt to heat with a water-based oxidising agent such as permanganate or dichromate using conventional apparatus results in a rapid and quantitative transfer of the solid, unchanged dimethyl compound from the aqueous solution to the inner walls of the condenser. The procedure that eventually proved successful was based on an industrial procedure for oxidations with concentrated nitric acid. The acid was slowly dripped into a solution of the dichloride **28** in nitrobenzene at 160 °C in an apparatus fitted with a Dean and Stark separator.

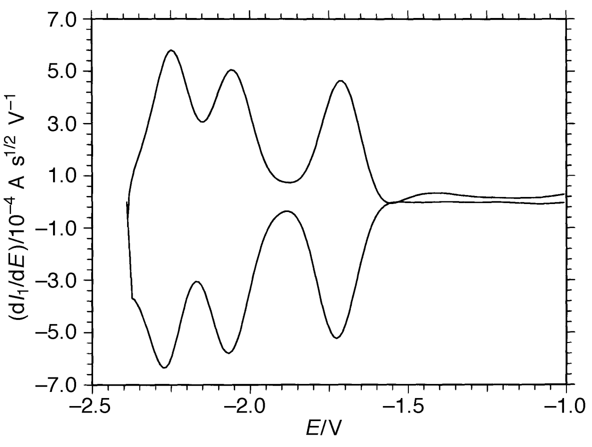

Fig. 4 Convolution–deconvolution voltammetry results for compound **18** in dimethylformamide, at a mercury droplet electrode, with tetrabutylammonium tetrafluoroborate as the supporting electrolyte, under an argon atmosphere, and with a silver–silver chloride reference electrode. For fast electron transfer the I_1 convolution is a function only of the potential and allows software compensation to be applied to the E axis to bring the peaks in the dI_1/dE plot into coincidence. In this case, hardware compensation at the potentiostat was itself almost adequate for this and only 30 Ω of additional software compensation was necessary. For this voltammogram the potential was swept in the cathodic direction (lower trace) and the upper trace represents the reverse sweep in the anodic direction.

This procedure has been carried out several times on a scale of up to 50 g without mishap although it is clear that the addition must be slow and that over-rapid addition of the acid can lead to an exothermic processes. The resultant acid **29** was converted to the acid chloride by reaction with phosphorus pentachloride[20] and reacted with naphthalene and aluminium trichloride to give the diketone **30a**. When heated with potassium hydroxide and quinoline this gave a low yield of the desired yellow dione **21**.[5] Attempted cyclisation reactions using other reagents or the related precursors **30b** and **30c** failed and these are detailed in the experimental section.

Although various salts of the dione **18** seem to be indefinitely stable at room temperature the diones **19**–**21** were all unstable. This probably explains the difficulty of obtaining high yields of these compounds. Samples stored for more than a few days at room temperature always showed traces (^{1}H NMR and thin layer chromatography) of decomposition products. Hence, for all of the reduction studies described herein, it was necessary to use freshly chromatographed material. The diones **20** and **21** also proved to be somewhat sensitive to acid conditions and it was necessary to chromatograph these materials on basic alumina rather than on silica.

In each case, conversion of the precursors **18**–**21** to the (potential) triplet, non-Kekulé polynuclear aromatic, level of oxidation requires a two-electron reduction. The reduction of these compounds has been studied in three ways, by cyclic voltammetry, by UV–VIS spectroscopy, and by EPR spectroscopy. These confirm that such a reduction is indeed feasible but that only the precursor **18** yields a triplet product.

The reduction of compounds 18–21 and 31—studies by cyclic voltammetry

Cyclic voltammetry results obtained for a solution of compound **18** in dimethylformamide, at a mercury droplet electrode, with tetrabutylammonium tetrafluoroborate as the

Table 1 Reduction potentials of compounds **18**–**21** and **31** obtained by cyclic voltammetry in dimethylformamide, at a mercury droplet electrode, with tetrabutylammonium tetrafluoroborate as the supporting electrolyte, under an argon atmosphere, and with a silver–silver chloride reference electrode

Compound	E_1/V	E_2/V	E_3/V	E_4/V
Phenalenone, **31**	−1.53	−2.53[a]		
Tetrabutylammonium 4,3-dioxo-4*H*,8*H*-dibenzo[*cd,mn*]pyren-12-olate, **18**	−1.718	−2.065	−2.263	
4,8-Dioxo-4*H*,8*H*-dibenzo[*cd,mn*]pyrene, **19**	−1.18	−1.92	−2.20[a]	−2.58[a]
7,8-Dioxo-7*H*,8*H*-dibenzo[*de,hi*]naphthacene, **20**	−1.20	−1.78	−1.95[a]	−2.75[a]
7,9-Dioxo-7*H*,9*H*-dibenzo[*de,jk*]pentacene, **21**	−0.70	−1.48	−1.95	−2.50

[a] Step chemically partially irreversible under these conditions.

supporting electrolyte, under an argon atmosphere, and with a silver–silver chloride reference electrode, are shown in Fig. 4. The symmetry of Fig. 4, shows that for compound **18** under these conditions the first three one-electron reduction steps ($E_1 = -1.718$, $E_2 = -2.065$, $E_3 = -2.263$ V) are simple electron transfer processes and that the intermediates are chemically stable. This was only the case when an argon atmosphere was maintained since the intermediates involved proved to be very oxygen sensitive. The width at half height of the peaks in the plot shown in Fig. 4 (*ca.* 120 mV) is somewhat broader than is normal for fast one-electron transfer (*ca.* 90.5 mV). The difference between the first and second reduction potentials (347 mV) is comparable to that found in related compounds in this solvent in which two electrons are placed in degenerate but coextensive orbitals. It arises mainly from coulombic factors and reflects the fundamentally coextensive nature of the orbitals themselves.[21] All of the compounds studied undergo between two and four reduction steps between 0 and *ca.* −3 V and the reduction potentials are detailed in Table 1. The potentials measured for the first reduction steps for these and related molecules correlate moderately well with the energy of the lowest unoccupied molecular orbital as derived by Hückel molecular orbital calculations.[22,27] Although these phenalenone structures superficially resemble quinones, they are substantially more difficult to reduce. For most simple quinones in dimethylformamide, E_1 generally lies between 0 and −0.75 V. From the standpoint of the production of molecular magnets, the fact that these reduction potentials are relatively high, is a disappointing observation. *A priori*, compound **18** (in particular) appears to be an ideal candidate for producing ‘charge transfer’ molecular ferromagnets[23] of the type first proposed by McConnell[24] and subsequently studied in depth by the groups of Breslow[25] and of Miller *et al.*[26] (except that in this case the ferromagnetic coupling would have to be driven by triplet anion rather than triplet cation character). The molecule has three-fold symmetry, the two-electron reduction product has a triplet ground state and it is thermally stable. However, the high reduction potentials of compound **18** make the production of charge-transfer complexes a difficult proposition unless a derivative with strong electron-withdrawing substituents could be prepared or a specific donor molecule designed for this particular acceptor.[27]

From the preparative standpoint the most significant fact arising from these cyclic voltammetry studies is that all four of the precursors of interest, **18**–**21**, gave the desired two-electron reduction and that this part of the process is reversible down to slow sweep rates (*ca.* 10 min). This suggests that the desired two-electron reduction products can be obtained and are stable in solution, at least on this timescale.

The reduction of compounds 20 and 21—studies by UV–VIS spectroscopy

When a solution of the dibenzonaphthacene **20** in degassed tetrahydrofuran and a small pellet of lithium metal were sealed under vacuum the yellow colour of the starting material slowly evolved through orange (*ca.* 2 h) to deep red (*ca.* 30 h). The spectrum of the starting material, characterised by an absorption maximum at *ca.* 410 nm, was replaced by one with λ_{max} *ca.* 445 nm (Fig. 5).

When a solution of the dibenzopentacene **21** was reduced in a similar manner the colour more slowly (*ca.* 2 weeks) evolved from yellow through orange to blood red (Fig. 6). The spectrum of the starting material, characterised by absorption maxima at 400 and 423 nm, was replaced by one with λ_{max} 540 nm. An attempt to carry out this reduction using potassium metal resulted in an almost immediate development of the red colouration but thereafter a brown precipitate rapidly formed and no spectrum could be obtained.

Figs. 5 and 6 also show calculated spectra for the starting materials, the corresponding singlet dianions and triplet dianions. In both the case of the naphthacene **20** (Fig. 5) and the pentacene **21** (Fig. 6) there is a reasonable match with the observed spectrum of the starting material whereas the product spectrum matches (reasonably well) that expected for either the singlet or triplet dianion but being rather closer to that for the singlet case.

These studies further confirmed that these substrates would undergo the desired two-electron reductions and that at least the lithium salts of the products of these reductions are reasonably stable in tetrahydrofuran. The extent to which ZNDO predictions of the UV–VIS spectra of such species can be relied on is not wholly clear but they provide the first indication that these biradicals may possess the singlet rather than the desired triplet ground state.

The reduction of compounds 18–21 and 31—studies by EPR spectroscopy

When a solution of phenalenone **1** in degassed tetrahydrofuran was sealed under vacuum (*ca.* 10^{-5} mmHg) and reduced with sodium, a bright green solution was obtained and an EPR spectrum which corresponds to that known for the radical anion:[13] *a*(5 H), 6.25; *a*(3 H), 2.0 G (1 G = 10^{-4} T). As in all of the monoradicals that are formal phenalenyl derivatives the hyperfine splittings to the α-hydrogens are substantially greater than those for the β-hydrogens. An HMO calculation on the parent phenalenyl radical yields large coefficients at the α-positions for the singly occupied molecular orbital but nodes at the β-positions. The small splittings observed for the β-hydrogens in this parent system are attributed to negative spin density. In this solvent and under these conditions the small differences due to the fact that not all of the α-hydrogens and β-hydrogens have quite equivalent hyperfine splittings could not be resolved.

In a similar manner, reduction of tetrabutylammonium 4,3-dioxo-4*H*,8*H*-dibenzo[*cd,mn*]pyren-12-olate **18** with sodium–potassium alloy in tetrahydrofuran gave the EPR spectrum of the monoradical dianion; *a*(6 H), 2.90; *a*(3 H), 0.80 G (ref. 2, Fig. 1). More prolonged reduction with sodium–potassium alloy in dimethylformamide resulted in the loss of the blue colour of the starting material and the formation of a brown–green solution. When this solution is frozen the strong triplet EPR spectrum of the two-electron reduction product, the diradical trianion **14**, was observed: $g = 2.0034$; $|D/hc| = 0.0064$ cm^{-1}; $|E/hc| = 0.0000$ (ref. 2, Fig. 2). The zero value of $|E/hc|$ is

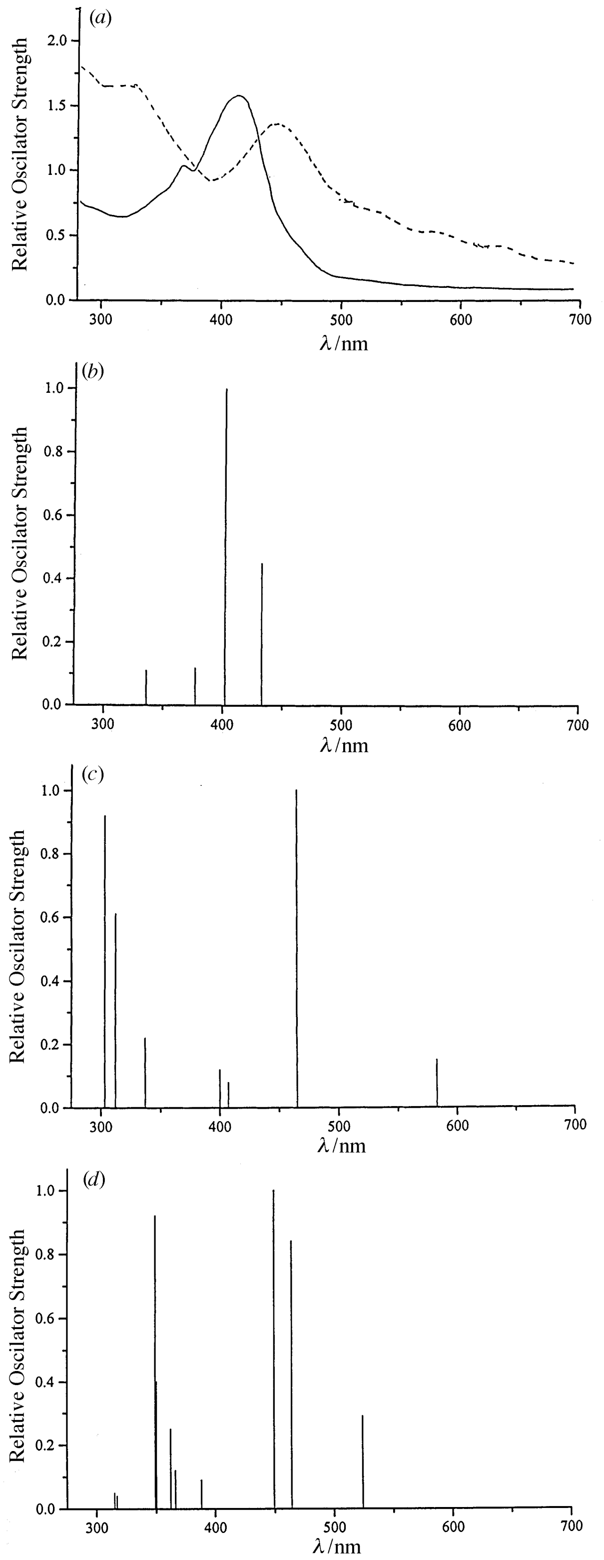

Fig. 5 (*a*) (top) The UV–VIS spectrum of the naphthacenedione **20** (continuous line) between 300 and 700 nm together with the spectrum assigned to the diradical dianion **16** (dashed line) obtained by reduction with lithium metal in tetrahydrofuran. (*b*) The spectrum of the neutral molecule calculated by the ZINDO/S method. (*c*) The calculated spectrum for the singlet dianion. (*d*) (bottom) The calculated spectrum for the triplet dianion.

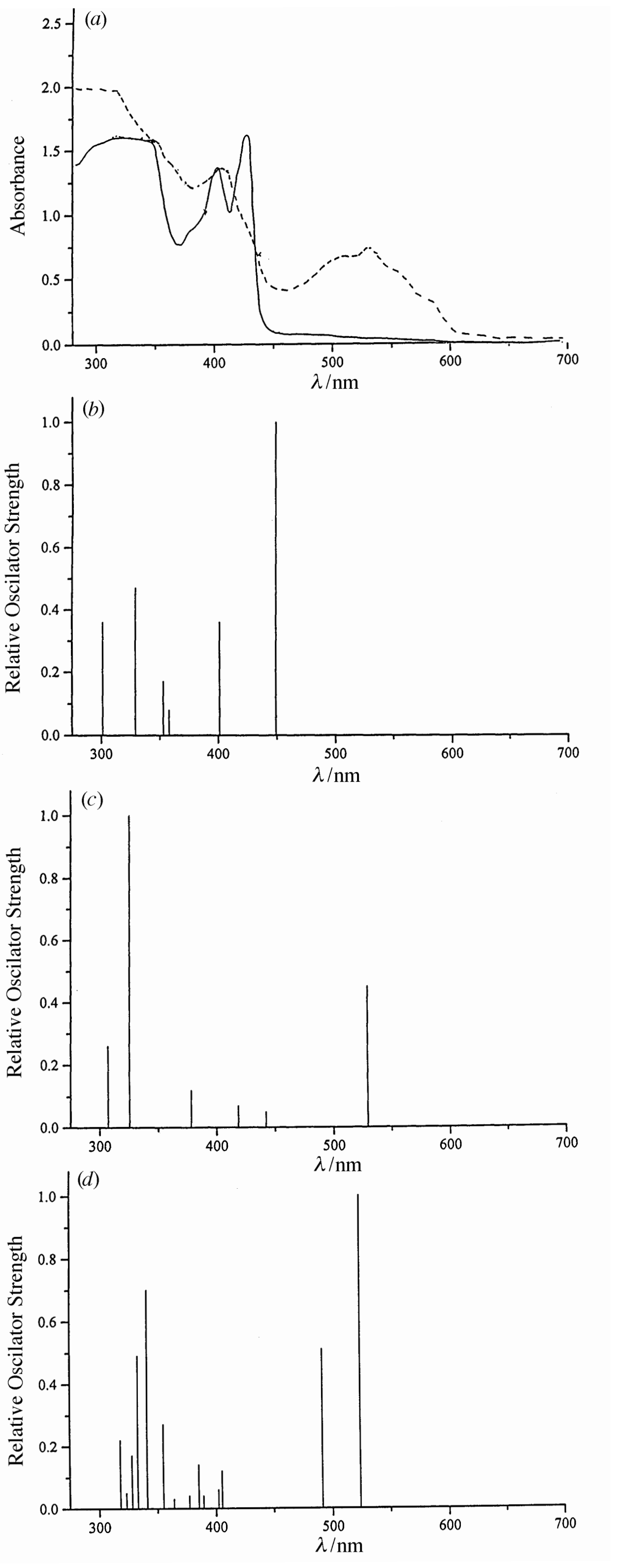

Fig. 6 (*a*) (top) The UV–VIS spectrum of the pentacenedione **21** (continuous line) between 300 and 700 nm together with the spectrum assigned to the diradical dianion **17** (dashed line) obtained by reduction with lithium metal in tetrahydrofuran. (*b*) The spectrum of the neutral molecule calculated by the ZINDO/S method. (*c*) The calculated spectrum for the singlet dianion. (*d*) (bottom) The calculated spectrum for the triplet dianion.

consistent with a triplet biradical which is uniaxial. The half field line is very weak. The intensity of the spectrum shows the ‘Curie Law’ temperature dependence expected for a ground state triplet. The same spectrum could be obtained using potassium metal.[2]

Reduction of 4,8-dioxo-4*H*,8*H*-dibenzo[*cd*,*mn*]pyrene **19** with potassium metal in tetrahydrofuran resulted in a transformation from a pale red to a strong ruby red coloured solution and the generation of an EPR spectrum which can be attributed to the radical anion: *a*(1 H), 7.0; *a*(4 H), 4.5; *a*(2 H), 0.9 G. Splittings due to the β-hydrogens could not be resolved. When the solution was frozen, the spectrum attributed to the doublet component broadened to the extent that the hyperfine structure was lost but at no stage, even when the reduction was allowed to proceed for several weeks, could a triplet EPR spectrum be detected.

When a solution of 7,8-dioxo-7*H*,8*H*-dibenzo[*de*,*hi*]naphthacene **20** was reduced with potassium, lithium or calcium in tetrahydrofuran the solution evolved from yellow to orange to red. The many line EPR spectrum attributed to the radical anion varied significantly according to the nature of the counterion and was strongest at the 'orange' stage. When solutions obtained with any of these reducing agents were frozen either at the 'orange' or the 'red' stage of the reduction no triplet EPR spectra were observed, simply broadening of the residual spectrum of the monoradical. As the reduction progressed further the EPR signal became progressively weaker.

When a solution of 7,9-dioxo-7*H*,9*H*-dibenzo[*de*,*jk*]pentacene **21** was reduced with lithium, potassium or sodium–potassium alloy very similar results were obtained, a many line spectrum attributable to the radical anion but when the solution was frozen, either at the 'orange' or at the 'red' stage of the reduction, no triplet EPR spectra were observed.

Conclusions

The cyclic voltammetry studies show that it is possible to carry out two-electron reductions of compounds **18–21** at an electrode surface and that the products of these reductions are stable in dimethylformamide. The UV–VIS spectroscopy studies confirm that for compounds **20** and **21**, this same two-electron reduction can be carried out using a group 1 metal in tetrahydrofuran and that the dilithium salts are stable. The EPR studies show that compounds **18**–**21** can all be reduced in this medium to the monoradical stage and these radicals observed by EPR spectroscopy. On further reduction only compound **18** gives a product showing a triplet EPR spectrum, the products of further reduction of compounds **19**–**21** being EPR silent. In the case of compounds **20** and **21**, the colour change matched that which corresponded to dianion formation but no triplet EPR spectra were observed. Furthermore calculated fits to the UV–VIS spectra of the dianions **16** and **17** were better for the singlet than for the triplet state. Although the main evidence is inevitably negative (the failure to observe EPR spectra) the weight of that evidence seems to indicate that we have succeeded in reducing the precursors **18**–**21** to the desired non-Kekulé polynuclear aromatic compounds **14–17** in a variety of different ways but that only **14** is triplet and that **15**–**17** have singlet ground states. Whereas dibenzo[*cd*,*mn*]pyrene (triangulene), dibenzo[*de*,*hi*]naphthacene and dibenzo[*de*,*jk*]pentacene should all have triplet ground states, the addition of the two O^- substituents to these aromatic nuclei seems to lift the degeneracy of the putative singly occupied molecular orbitals to such a degree that the derivatives **15**–**17** are no longer triplets. Hence, the strategy that proved successful for making trioxytriangulene **14** does not provide a general recipe for making high-spin non-Kekulé polynuclear aromatic compounds. Furthermore, since any progress in the area of high-spin non-Kekulé polynuclear aromatic chemistry must surely rely on making derivatives with stabilising and/or solublising substituents, and, in almost all cases, such substituents will lift the degeneracy of the singly occupied molecular orbitals, this seriously diminishes the prospects for making high-spin derivatives, particularly of those non-Kekulé polynuclear aromatic compounds shown in the second and third series of Fig. 1. Progress with those systems shown in the first series in Fig. 1 seems to be a more realistic option. For these, provided the substituents and/or heteroatoms are symmetrically placed, (as in the biradical **14**) the high-spin nature of the π system should be preserved and some high-spin derivatives of these polynuclear aromatics remain reasonably attainable if challenging synthetic targets.

Experimental

Melting points were determined either on a Reichart Hot Stage or in a Griffin melting point apparatus and are uncorrected. Samples for combustion analysis were routinely dried by heating at 65 °C and 0.5 mmHg for 3 d. UV–VIS spectra were recorded using a Pye-Unicam PU8800 UV–VIS spectrophotometer. IR spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrophotometer or a Philips PU 9706 spectrophotometer. Only significant or assignable absorbances are reported. NMR spectra were recorded on a General Electric QE300 or a Bruker AM400 instrument. Chemical shifts are relative to $SiMe_4$, coupling constants (J) are given in Hz. Mass spectra were obtained on a VG Autospec instrument. All peaks > 20% of the base peak (and less intense peaks of particular significance) are reported. Solvents were routinely purified according to the procedures recommended by Perrin *et al.*[28] Column chromatography on silica refers to the use of Merck Kieselgel 7731 Type 60 and TLC to Merck Kieselgel 7730 GF254. Column chromatography on alumina refers to the use of BDH 'active basic alumina'.

4,8-Dioxo-4*H*,8*H*-dibenzo[*cd*,*mn*]pyrene 19[12]

Potassium 4,3-dioxo-4*H*,8*H*-dibenzo[*cd*,*mn*]pyren-12-olate **14** (50 mg, 0.14 mmol)[4] and zinc powder (100 mg, 1.5 mmol) in 5% m/m aqueous sodium hydroxide (20 cm^3) was refluxed for 24 h. The mixture was cooled and filtered. Oxygen was bubbled through the filtrate for 15 min, the solution acidified (pH 1) with 36% hydrochloric acid. The resulting black precipitate was isolated by centrifugation and dried. Preparative TLC on silica eluting with dichloromethane–methanol (399:1) gave 4,8-dioxo-4*H*,8*H*-dibenzo[*cd*,*mn*]pyrene **19** as an air-sensitive red solid (2.5 mg, 5.8%); λ_{max}(EtOH)/nm 356 (ε/dm^3 mol^{-1} cm^{-1} 18 500), 392 (24 400), 332 (17 100), 466 (13 100), 492 (11 600) and 526 (12 500); ν_{max}/cm^{-1} (Nujol) 1720 (C=O); δ_H($CDCl_3$) 7.82 (1 H, t, J 8.0, C^6H), 7.92 (2 H, t, J 7.7, $C^{2,10}$H), 8.52 (2 H, d, J 8.0, $C^{5,7}$H), 8.86 (2 H, d, J 7.7), 8.88 (1 H, s, C^{12}H) and 8.99 (2 H, d, J 7.7).

Diethyl 1-naphthylmethylenemalonate 22[14]

A solution of benzoic acid (2.4 g, 20 mmol) and piperidine (3.6 g, 40 mmol) in benzene (8 cm^3) was added dropwise to a vigorously refluxing solution of 1-naphthaldehyde (40 g, 0.26 mol) and diethyl malonate (48 g, 0.30 mol) in benzene (160 cm^3). After refluxing for a further 3 h and cooling to room temp. the mixture was poured into 2 M hydrochloric acid (200 cm ^{3}). The organic phase was separated, washed with water (2 × 50 cm^3), dried (magnesium sulfate), filtered, the solvent removed under reduced pressure and the residue distilled under reduced pressure to give diethyl 1-naphthylmethylenemalonate **22** as a colourless oil (66 g, 86%) (Found: C, 72.6; H, 6.15. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.0%); λ_{max}(EtOH)/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 39 100), 240 (136 000) and 310 (95 700); ν_{max}/cm^{-1} (film) 1720 (C=O) and 1640 (C=C); δ_H($CDCl_3$) 1.04 (3 H, t, J 7.1, CH_3), 1.35 (3 H, t, J 7.15, CH_3), 4.15 (2 H, q, J 7.15, CH_2), 4.39 (2 H, q, J 7.1, CH_2), 7.43 (1 H, t, J 7.7), 7.5 (3 H, m), 7.59 (1 H, d, J 7.7), 7.84 (2 H, m), 7.89 (1 H, d, J 7.1) and 8.48 (1 H, s); δ_C($CDCl_3$) 13.5 (CH_3), 13.9 (CH_3), 61.1 (CH_2), 61.4 (CH_2), 123.7, 124.9, 126.1, 126.2, 126.6, 128.4, 129.0, 130.2, 130.5, 131.1, 133.1, 140.8, 163.6 (C=O) and 165.8 (C=O).

Diethyl bis(1-naphthyl)methylmalonate 23a[14]

A solution of 1-bromonaphthalene (4.3 g, 20 mmol) in tetrahydrofuran (15 cm^3) was added dropwise over 30 min to magnesium (0.5 g, 20 mmol) in tetrahydrofuran (15 cm^3). The mixture was refluxed until all of the magnesium had dissolved and a green solution had formed (about 3 h). A solution of the ester **22** (5.5 g, 18 mmol) in tetrahydrofuran (25 cm^3) was added dropwise over 30 min. The mixture was refluxed for a further 3 h, cooled to room temp., poured onto 2 M hydrochloric acid

(100 cm^3), the organic phase separated, washed with water (3 × 50 cm^3), saturated aqueous sodium hydrogen carbonate solution (2 × 50 cm^3), dried with magnesium sulfate, filtered, and the solvents removed under reduced pressure to give the ester **23a** as a white powder (2.4 g, 31%); mp 108–110 °C (from ethanol, lit.,[14] 113–114 °C) (Found: C, 78.9; H, 6.15. $C_{28}H_{26}O_4$ requires C, 78.9; H, 6.1%); λ_{max}(EtOH)/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 86 500) and 284 (31 000); ν_{max}/cm^{-1} (film) 1770 (C=O) and 1610 (C=C); δ_H($CDCl_3$) 0.90 (6 H, t, *J* 7.1, CH_3), 3.9 (4 H, q, *J* 7.1, CH_2), 4.26 (1 H, d, *J* 12.0, CHCH), 6.52 (1 H, d, *J* 12.0, CHCH), 7.5 (8 H, m), 7.75 (2 H, d, *J* 7.1), 7.85 (2 H, d, *J* 7.5) and 8.42 (2 H, d, *J* 7.5); δ_C($CDCl_3$) 13.2 (CH_3), 40.1 (CH), 58.3 (CH), 61.1 (CH_2), 123.2, 124.6, 124.9, 125.3, 126.1, 127.4, 128.5, 131.2, 133.7, 137.4 and 167.7 (C=O).

Bis(1-naphthyl)methylmalonic acid 23b [5]

A mixture of the foregoing ester **23a** (29.1 g, 68 mmol) and potassium hydroxide (112 g) in ethanol (750 cm^3) was refluxed for 3 h. The ethanol was distilled off and water added. This was also distilled off, a second volume of water (250 cm ^{3}) added, and the pH adjusted to pH 1 by addition of 36% HCl. The mixture was cooled to room temp. and filtered. The residue was recrystallised from ethanol to give the acid **23b** as colourless needles (19 g, 75%); mp 190–192 °C (lit.,[5] 196 °C) (Found: C, 78.1; H, 5.0. $C_{24}H_{18}O_4$ requires C, 78.1; H, 4.9%); λ_{max}(EtOH)/nm 246 (ε/dm^3 mol^{-1} cm^{-1} 75 100) and 280 (36 600); ν_{max}/cm^{-1} (film) 1710 (C=O) and 1610 (C=C); δ_H($CDCl_3$) 3.57 (1 H, d, *J* 3.6, CHCH), 6.52 (1 H, d, *J* 3.6, CHCH), 7.33 (2 H, t, *J* 7.6), 7.45 (6 H, m), 7.73 (2 H, d, *J* 7.9), 7.90 (2 H, d, *J* 7.9) and 7.98 (2 H, d, *J* 7.6); δ_C($CDCl_3$) 42.3 (CH), 53.4 (CH), 123.3, 125.2, 125.2, 126.1, 126.6, 126.8, 128.8, 131.1, 135.3, 139.5 and 173.5 (C=O).

7,8-Dioxo-7*H*,8*H*-dibenzo[*de*,*hi*]naphthacene 20. Attempted preparation by the Clar procedure [5]

Phosphorus pentoxide (2.4 g) was added to the acid **23b** (0.6 g, 1.6 mmol) in nitrobenzene (8 cm^3) at 155 °C under argon. After a further 15 min at 155 °C the mixture was cooled to room temp., water was added dropwise and the nitrobenzene was removed by steam distillation. The residue was dissolved in dichloromethane and the dichloromethane solution was washed with water, aqueous ammonia and water, dried with magnesium sulfate, filtered and the solvent removed under reduced pressure. The resulting red–brown gum (520 mg) was subjected to chromatography on silica eluting first with 9:1 light petroleum (bp 40–60 °C)–diethyl ether, then 1:1 light petroleum–dichloromethane, dichloromethane and finally 97:3 dichloromethane–methanol to give 2,3-dihydro-3-(1-naphthyl)phenalen-1-one **25** as a white crystalline solid (32 mg, 7%); mp 75–76 °C (lit.,[17] 75–76 °C) (Found: M$^+$, 308.1201. $C_{23}H_{16}O$ requires 308.1201); ν_{max}/cm^{-1} ($CHCl_3$) 1705 (C=O), 1590 and 1625 (C=C); δ_H($CDCl_3$) 2.70 (1 H, dd, *J* 18 and 1.5, CH_2), 3.60 (1 H, dd, *J* 18 and 8, CH_2), 5.82 (1 H, dd, *J* 8 and 1.5, CH), 6.70 (1 H, d, *J* 7), 7.22 (1 H, d, *J* 7), 7.3–8.2 (10 H, m) and 8.47 (1 H, dd, *J* 7 and 1); *m*/*z* 308 (M$^+$, 100%), 279 (27, M$^+$ − CHO), 265 (23, M$^+$ − C_2H_3O), 155 (25), 153 (22, 279 − $C_{10}H_6$), 152 (49, 279 − $C_{10}H_7$), 127 (27, $C_{10}H_7^+$) and 126 (21, $C_{10}H_6^+$): 3-(1-naphthyl)phenalen-1-one **26** as a white crystalline solid (35 mg, 7%); mp 189–190 °C (lit.,[17] 189–190 °C) (Found: M$^+$, 306.1035. $C_{23}H_{14}O$ requires 306.1044); ν_{max}/cm^{-1} ($CHCl_3$) 1640 (C=O), 1610 and 1570 (C=C); δ_H($CDCl_3$) 6.82 (1 H, s, vinyl CH), 7.2–8.1 (11 H, m), 8.24 (1 H, dd, *J* 8 and 1) and 8.76 (1 H, dd, *J* 7 and 1); *m*/*z* 306 (M$^+$, 28%), 305 (28, M$^+$ − H), 289 (56, M$^+$ − OH), 277 (21, M$^+$ − CHO), 276 (67, M$^+$ − CH_2O), 274 (24), 144 (20), 138 (71) and 137 (29): and the hexacycle **27** as a red solid (220 mg, 44%); mp 280–285 °C decomp. (Found: M$^+$, 304.0931. $C_{23}H_{12}O$ requires 304.0888); ν_{max}/cm^{-1} ($CHCl_3$) 1630 (C=O), 1600 and 1570 (C=C); δ_H($CDCl_3$) 7.31 (1 H, s), 7.45 (1 H, t, *J* 8), 7.48 (1 H, t, *J* 8), 7.67 (1 H, t, *J* 8), 7.73 (1 H, d, *J* 8), 7.81 (2 H, d, *J* 8), 7.98 (1 H, dd, *J* 8 and 1), 8.03 (1 H, d, *J* 8), 8.11 (1 H, d, *J* 8), 8.24 (1 H, d, *J* 8) and 8.54 (1 H, dd, *J* 8 and 1); *m*/*z* 304 (M$^+$, 100%), 276 (67, M$^+$ − CO), 274 (31, M$^+$ − CH_2O), 138 (45) and 137 (27).

7,8-Dioxo-7*H*,8*H*-dibenzo[*de*,*hi*]naphthacene 20. Improved procedure

A mixture of the acid **23b** (19 g, 51 mmol) and phosphorus pentoxide (18.5 g) in nitrobenzene (100 cm^3) was stirred at room temp. for 3 d under argon. Water (100 cm^3) was added dropwise and the nitrobenzene was removed by steam distillation. The resulting black solid was filtered off, dried and subjected to chromatography on alumina eluting first with light petroleum (bp 40–60 °C) then 1:1 light petroleum–dichloromethane, 1:3 light petroleum–dichloromethane, and finally 1:10 light petroleum–dichloromethane until the eluent was colourless. Then 1:339 methanol–dichloromethane gave 7,8-dioxo-7*H*,8*H*-dibenzo[*de*,*hi*]naphthacene **20** as an acid-sensitive yellow solid (90 mg, 5%); λ_{max}(EtOH)/nm 205 (ε/dm^3 mol^{-1} cm^{-1} 27 500), 244 (28 600), 362 (8530) and 410 (15 000); ν_{max}/cm^{-1} (Nujol) 1670 (C=O) and 1570 (C=C); δ_H($CDCl_3$) 7.75 (2 H, t, *J* 7.8), 7.82 (2 H, t, *J* 7.7), 8.18 (2 H, d, *J* 7.8), 8.23 (2 H, d, *J* 7.7), 8.25 (2 H, d, *J* 7.7) and 8.72 (2 H, d, *J* 7.8); δ_C($CDCl_3$) 125.4, 125.9, 127.6, 128.3, 129.9, 130.3, 131.3, 132.3, 133.3, 134.4, 135.3, 135.4 and 181.7 (C=O).

4,6-Dichloro-1,3-dimethylbenzene 28 [18]

Chlorine gas was bubbled for 30 h through a well-stirred mixture of 1,3-dimethylbenzene (240.5 g, 2.45 mol) and ferric chloride hexahydrate (18 g, 0.066 mol) maintained at 0–5 °C by external ice–salt bath cooling. When *ca.* 1 mol of chlorine had been absorbed (by mass) the mixture was washed with 2 M hydrochloric acid (2 × 500 cm^3), water (2 × 500 cm^3), dried ($CaCl_2$) and filtered. The filtrate was distilled under reduced pressure. The fraction boiling at 85–100 °C and 0.5 mmHg was refrigerated at −4 °C for 3 d and filtered to give colourless needles of 4,6-dichloro-1,3-dimethylbenzene **28** (60 g, 10%); mp 70 °C (from ethanol, lit.,[18] 68.5 °C); ν_{max}/cm^{-1} (Nujol) 1560 (C=C); δ_H($CDCl_3$) 2.25 (6 H, s, CH_3), 7.0 (1 H, s) and 7.25 (1 H, s); δ_C($CDCl_3$) 19.3 (CH_3), 128.7, 131.8, 132.6 and 134.2.

4,6-Dibromo-1,3-dimethylbenzene [29]

Iodine (0.5 g) was added over 30 min to a vigorously shaken mixture of 1,3-dimethylbenzene (26 g, 0.245 mol) and bromine (43.4 g, 0.27 mol). This mixture was shaken for a further 3 h, and then shaken with 2 M sodium hydroxide (200 cm^3) for 10 min. The resulting suspension was filtered, the residue washed with water, and recrystallised from ethanol to give 4,6-dibromo-1,3-dimethylbenzene (14.5 g, 22%); mp 67–69 °C (lit.,[29] 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%); ν_{max}/cm^{-1} (Nujol) 1560 (C=C); δ_H($CDCl_3$) 2.25 (6 H, s, CH_3), 7.0 (1 H, s) and 7.6 (1 H, s); δ_C($CDCl_3$) 22.0 (CH_3), 122.5, 132.5, 135.0 and 136.9.

4,6-Dichlorobenzene-1,3-dicarboxylic acid 29

A vigorously stirred solution of 4,6-dichloro-1,3-dimethylbenzene **28** (50 g, 0.29 mol) in nitrobenzene (50 cm^3) in an apparatus fitted with a Dean and Stark separator was heated to 150 °C. Concentrated nitric acid ($d = 1.4$, 25 cm^3) was added dropwise over 30 h at such a rate that the temperature of the reaction mixture neither fell below 150 °C nor rose above 180 °C. Over-rapid addition of the acid resulted in a highly exothermic process. The reaction was complete at the point at which (at 160 °C) a thick emulsion was produced. The mixture was cooled to room temp. Carbon tetrachloride (150 cm^3) was added, and the mixture filtered to give colourless needles of 4,6-dichlorobenzene-1,3-dicarboxylic acid (24 g, 38%); mp 276–278 °C (from ethanol, lit.,[18] 280 °C); λ_{max}(EtOH)/nm 221 (ε/dm^3 mol^{-1} cm^{-1} 39 400) and 244 (18 600); ν_{max}/cm^{-1} (Nujol) 2400–3200 (OH), 1700 (C=O) and 1590 (C=C); δ_H[$(CD_3)_2SO$] 7.6 (1 H, s) and 8.4 (1 H, s); δ_C[$(CD_3)_2SO$] 129.0, 132.2, 134.5, 136.1 and

165.0 (C=O); *m/z* 236 (^{37}Cl^{35}Cl M$^+$, 65%), 234 (^{35}Cl$_2$M$^+$, 98), 219 (^{37}Cl^{35}Cl M$^+$ − OH, 66) and 217 (^{35}Cl$_2$M$^+$ − OH, 100).

In a similar manner 4,6-dibromo-1,3-dimethylbenzene was converted to 4,6-dibromobenzene-1,3-dicarboxylic acid in 50% yield; mp 248–250 °C (from ethanol, lit.,[30] 250–254 °C) (Found: C, 29.6; H, 1.2; Br, 49.2. $C_8H_4Br_2O_4$ requires C, 29.6; H, 1.2; Br, 49.2%); λ_{max}(EtOH)/nm 221 (ε/dm^3 mol^{-1} cm^{-1} 78 000) and 243 (36 600); ν_{max}/cm^{-1} (Nujol) 2000–3300 (OH) and 1700 (C=O); δ_H[(CD$_3$)$_2$SO] 8.05 (1 H, s) and 8.4 (1 H, s); δ_C[(CD$_3$)$_2$SO] 124.7, 131.1, 133.5, 139.0 and 166.0 (C=O).

4,6-Dichlorobenzene-1,3-dicarboxylic acid dichloride[20]

A mixture of 4,6-dichlorobenzene-1,3-dicarboxylic acid **29** (10 g, 42 mmol) and phosphorus pentachloride (17.7 g, 85 mmol) in carbon tetrachloride (250 cm^3) was refluxed for 4 h. The resulting yellow solution was filtered and the solvent removed under reduced pressure. Phosphoryl chloride was removed at 100 °C and 0.5 mmHg. The residue was recrystallised from light petroleum (bp 40–60 °C) to give colourless needles of the unstable 4,6-dichlorobenzene-1,3-dicarboxylic acid dichloride (13.9 g, 86%); mp 74–76 °C (lit.,[20] 76.5 °C); ν_{max}/cm^{-1} (CHCl$_3$) 1755 (C=O) and 1585 (C=C); δ_H(CDCl$_3$) 7.72 (1 H, s) and 8.87 (1 H, s); δ_C(CDCl$_3$) 131.6, 134.2, 137.9, 140.0 and 163.3 (C=O).

In a similar manner 4,6-dibromobenzene-1,3-dicarboxylic acid dichloride was obtained as colourless needles (yield 87%); mp 70–72 °C (lit.,[31] 76.5 °C); ν_{max}/cm^{-1} (CHCl$_3$) 1760 (C=O) and 1570 (C=C); δ_H(CDCl$_3$) 8.1 (1 H, s) and 8.7 (1 H, s); δ_C(CDCl$_3$) 127.4, 134.1, 136.9, 140.8 and 164.1 (C=O).

4,6-Dichloro-1,3-di(1-naphthoyl)benzene 30a[5]

A mixture of 4,6-dichlorobenzene-1,3-dicarboxylic acid dichloride (2.6 g, 9.5 mmol), naphthalene (2.44 g, 19 mmol) and aluminium trichloride (7.72 g, 58 mmol) in dichloromethane (40 cm^3) was stirred at room temp. for 5 h. The mixture was poured into 2 M hydrochloric acid (150 cm^3). The organic phase was separated, washed with water (2 × 50 cm^3), dried (calcium chloride), filtered and the solvent removed under reduced pressure to give an orange–yellow gum. Column chromatography on silica eluting with 1 : 1 light petroleum (bp 40–60 °C)–dichloromethane gave 4,6-dichloro-1,3-di(1-naphthoyl)benzene **30a** (2.8 g, 65%) as a yellow powder, mp 50 °C (lit.,[5] 152 °C) (Found: M$^+$, 454.0519, 456.0491. $C_{28}H_{16}O_2{}^{35}Cl_2$ and $C_{28}H_{16}O_2{}^{35}Cl^{37}Cl$ require 454.0527, 456.0497); λ_{max}(EtOH)/nm 228 (ε/dm^3 mol^{-1} cm^{-1} 27 700) and 232 (20 000); ν_{max}/cm^{-1} (Nujol) 1660 (C=O) and 1585 (C=C); δ_H(CDCl$_3$) 7.6 (14 H, m) and 8.85 (2 H, d, *J* 8.7).

In a similar manner 4,6-dibromobenzene-1,3-dicarboxylic acid dichloride was converted to the pale-yellow 4,6-dibromo-1,3-di(1-naphthoyl)benzene **30b** in 19% yield; mp 68–74 °C; λ_{max}(EtOH)/nm 218 (ε/dm^3 mol^{-1} cm^{-1} 28 400) and 252 (16 800); ν_{max}/cm^{-1} (Nujol) 1665 (C=O) and 1580 (C=C); δ_H(CDCl$_3$) 7.6 (7 H, m), 7.8 (7 H, m) and 8.85 (2 H, d, *J* 9.0); *m/z* 544 (M$^+$, 4%), 155 (42, naphthoyl$^+$), 127 (38, naphthyl$^+$) and 80 (Br$^+$).

In a similar manner benzene-1,3-dicarboxylic acid dichloride was converted to the pale-yellow 1,3-di(1-naphthoyl)benzene **30c** in 26% yield; mp 170–178 °C (lit.,[32] 191° C); λ_{max}(EtOH)/nm 221 (ε/dm^3 mol^{-1} cm^{-1} 37 300); ν_{max}/cm^{-1} (Nujol) 1650 (C=O) and 1590 (C=C); δ_H(CDCl$_3$) 7.45 (9 H, m) and 7.7–8.5 (9 H, m).

7,9-Dioxo-7*H*,9*H*-dibenzo[*de*,*jk*]pentacene 21[5]

A mixture of 4,6-dichloro-1,3-di(1-naphthoyl)benzene **30a** (4.3 g, 9.5 mmol) and potassium hydroxide (0.85 g) was refluxed in quinoline (10 cm^3) for 3 h. The mixture was poured into 2 M hydrochloric acid (200 cm^3) and the resultant black solid filtered off. This was dried and purified by chromatography on alumina eluting first with light petroleum (bp 40–60 °C), then 1 : 1 light petroleum–dichloromethane, 1 : 3 light petroleum–dichloromethane and finally 1 : 10 light petroleum–dichloromethane until the eluent was colourless. Finally, 1 : 399 methanol–dichloromethane gave 7,9-dioxo-7*H*,9*H*-dibenzo-[*de*,*jk*]pentacene **21** as an air-sensitive yellow solid (118 mg, 5.2%); λ_{max}(EtOH)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 20 800), 320 (5730), 400 (5220) and 423 (6620); ν_{max}/cm^{-1} (Nujol) 1740 (C=O) and 1610 (C=C); δ_H(CDCl$_3$) 7.80 (4 H, t, *J* 6.8), 8.11 (2 H, d, *J* 6.8), 8.25 (2 H, d, *J* 6.8), 8.75 (2 H, d, *J* 6.8), 8.82 (2 H, d, *J* 6.8), 9.30 (1 H, s) and 9.59 (1 H, s); δ_C(CDCl$_3$) 125.1, 125.7, 125.8, 126.5, 126.7, 128.4, 128.8, 129.1, 129.7, 130.0, 130.1, 131.3, 135.2, 139.3 and 173.4 (C=O).

Attempts to prepare the same product through a potassamide–liquid ammonia mediated cyclisation of **30a** and **30b**,[33] by the reaction of **30b** with methylmagnesium bromide and cobalt chloride,[34] through the reaction of **30a–c** with aluminium trichloride,[35] through the reaction of **30b** with tributyltin hydride, and by photolysis of **30a–c**,[36] all failed to produce detectable amounts.

Studies by cyclic voltammetry[37]

These studies were carried out using 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 the 'CONDECON 310' cyclic voltammetry software. The cell consisted of a mercury droplet working electrode, a platinum wire counter electrode, and a silver–silver nitrate (0.01 M silver nitrate and 0.1 M tetrabutylammonium tetraflouroborate in DMF) reference electrode. The dimethylformamide used as the solvent was freshly purified by the procedures described in Perrin *et al.*,[28] passed through a short column of alumina and stored over 4 Å molecular sieves. The substrates **19**–**21** were all freshly purified by column chromatography before use. The supporting electrolyte was tetrabutylammonium tetrafluoroborate. The solutions were purged with argon for a minimum of 20 min prior to the start of data acquisition and argon flowed throughout the experiment. Anthracene was used as the standard and its reduction potential checked before each new set of experiments.

Studies of the reductions by UV–VIS spectroscopy

These studies were carried out using the apparatus and methods previously described.[38] A small pellet of lithium metal and a few (*ca.* 3) mg of the substrate **20** or **21** were placed in the 'anion generation chamber' of the cell (Fig. 4, ref. 38) which was attached to the vacuum line and evacuated to *ca.* 10^{-4} mmHg. Dry, deoxygenated tetrahydrofuran from a store over Na/K benzophenone ketyl (*ca.* 5 cm^3) was distilled through the manifold of the vacuum line into the 'anion generation chamber'. This was then frozen in liquid nitrogen, the system reevacuated to *ca.* 10^{-5} mmHg and the cell sealed and detached from the vacuum line by melting the glass at the constriction point. Ultrasound from a Kerry Ultrasonics Ltd. Type PUL55 ultrasound bath was used during the first 12 h to speed up the reduction process. From time to time a small portion of the solution was filtered into the Pyrex UV cell and was diluted to an appropriate level by distilling over some of the tetrahydrofuran. The calculated spectra shown in Figs. 5 and 6 were based on molecular structures for which the geometry of the neutral molecule was optimised at the MNDO-RHF level. The geometries of the ions were assumed to be the same as those of the neutral molecule and, indeed, MNDO calculations suggest that the reduction process has quite a small effect on the geometries. UV spectra were calculated using the ZINDO/S method[39] with a σ–σ atomic orbital overlap of 1.267 and a π–π overlap of 0.585 and with a configurational interaction in which the 36 lowest the singly excited states for the neutral molecules and all those with equivalent excitation energies (<5.5 eV) were included for the dianions. Finally, for all the results shown in Figs. 6 and 7 the energies of the transitions were scaled down by 15%.[40]

Studies of the reductions by EPR spectroscopy

These studies were carried out using very similar apparatus and procedures to that used in the UV–VIS spectroscopic studies.[38] EPR spectra were recorded on a Varian E-6 spectrometer fitted with a Bruker 4111 VT variable temperature unit.

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References

1 A. A. Ovchinnikov, *Theor. Chim. Acta*, 1978, **47**, 297.
2 G. Allinson, R. J. Bushby, J.-L. Paillaud, D. Oduwole and K. Sales, *J. Am. Chem. Soc.*, 1993, **115**, 2062.
3 G. Allinson, R. J. Bushby and J.-L. Paillaud, *J. Mater. Sci., Mater. Elect.*, 1994, **5**, 67.
4 G. Allinson, R. J. Bushby, J.-L. Paillaud and M. Thornton-Pett, *J. Chem. Soc., Perkin Trans. 1*, 1995, 385.
5 E. Clar, W. Kemp and D. G. Stewart, *Tetrahedron*, 1958, **3**, 325; E. Clar and I. A. MacPherson, *Tetrahedron*, 1963, **18**, 1411.
6 E. Clar, I. A. MacPherson and H. Schulz-Kiesow, *Justus Liebigs Ann. Chem.*, 1963, **669**, 44; E. Clar, *Chimia*, 1964, **18**, 375.
7 D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88.
8 W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1977, **99**, 4587; W. T. Borden, *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 195.
9 R. J. Bushby, D. R. McGill and K. M. Ng, in *Magnetism a Supramolecular Function*, ed. O. Kahn, Kluwer, Dordrecht, 1996, pp. 181–204.
10 B. K. Carpenter, R. D. Little and J. A. Berson, *J. Am. Chem. Soc.*, 1976, **98,** 5723; M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter and J. A. Berson, *J. Am. Chem. Soc.*, 1976, **98,** 5725; but compare F. Adams, R. Gompper, A. Hohenester and H.-U. Wagner, *Tetrahedron Lett.*, 1988, **29**, 6921.
11 D. E. Seeger, E. F. Hilinski and J. A. Berson, *J. Am. Chem. Soc.*, 1981, **103,** 720; M. Rule, A. R. Matlin, D. E. Seeger, E. F. Hilinski, D. A. Dougherty and J. A. Berson, *Tetrahedron*, 1982, **38,** 789; D. E. Seeger and J. A. Berson, *J. Am. Chem. Soc.*, 1983, **105,** 5144 and 5146; D. E. Seeger, P. M. Lathi, A. R. Rossi and J. A. Berson, *J. Am. Chem. Soc.*, 1986, **108,** 1251; T. A. Inglin and J. A. Berson, *J. Am. Chem. Soc.*, 1986, **108,** 3394; R. C. Fort, S. J. Getty, D. A. Hrovat, P. M. Lathi and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114,** 7549; D. A. Dougherty, in *Magnetism a Supramolecular Function*, ed. O. Kahn, Kluwer, Dordrecht, 1996, pp. 143–156.
12 R. Weiss and J. Korczyn, *Monatsch*, 1924, **45**, 207.
13 G. P. Rabold, K. H. Bar-Eli, E. Reid and K. Weiss, *J. Chem. Phys.*, 1965, **42**, 2438; E. Woischink, E. Ohmes and K. Volkamer, *Tetrahedron*, 1972, **28**, 4243.
14 M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, 1956, **78**, 4765.
15 S. D. Gupte, D. P. Nabar and S. V. Sunthankar, *J. Sci. Ind. Res. India*, 1960, **19B**, 411; *Chem. Abstr.*, 1961, **55**, 13396h.
16 J. M. Allen, K. M. Johnston and R. G. Shotter, *Chem. Ind.*, 1976, 108.
17 Yu. A. Gerasimenko and S. I. Didenko, *J. Org. Chem. USSR* (*Ed. Engl.*), 1979, **15**, 1520; (*Ed. Russ.*), 1979, **15**, 1698.
18 A. Claus and N. Bursert, *J. Pract. Chem.*, 1890, **41**, 556.
19 H. Koch, *Ber.*, 1890, **23**, 206.
20 R. L. Datta and N. R. Chatterjee, *J. Am. Chem. Soc.*, 1916, **38**, 2545.
21 R. J. Bushby, D. R. McGill, K. M. Ng and N. Taylor, *Chem. Commun.*, 1996, 2641; *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.
22 *C.R.C. Handbook Series in Organic Electrochemistry*, L. Meites and P. Zuman, CRC Press Inc., Cleveland, Ohio, 1976, vol. 1.
23 R. J. Bushby, in *Introduction to Molecular Electronics*, eds. M. C. Petty, M. R. Bryce and D. Bloor, E. Arnold, 1995.
24 H. M. McConnell in discussions reported at the end of R. W. Mulliken, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 1967, **11**, 109, but compare C. Kollmar and O. Kahn, *J. Am. Chem. Soc.*, 1991, **113**, 7987; C. Kollmar, M. Couty and O. Kahn, *J. Am. Chem. Soc.*, 1991, **113**, 7994.
25 R. Breslow, *Pure Appl. Chem.*, 1982, **54**, 927.
26 J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201.
27 G. Allinson, Ph.D. Thesis, Leeds, 1991.
28 *Purification of Laboratory Chemicals*, 2nd edn., ed. D. D. Perrin, W. L. F. Armarego and B. R. Perrin, Pergamon, Oxford, 1980.
29 A. Eckert and F. Seidel, *J. Prackt. Chem.*, 1921, **102**, 338.
30 L. Chardonneus and M. Schmidtz, *Helv. Chim. Acta*, 1956, **39**, 1981.
31 C. Seer and O. Discendorfer, *Monatsch*, 1924, **34**, 1493.
32 D. Sek, *Poly. J.*, 1981, **13**, 13.
33 S. V. Kesser, R. Sood, U. K. Nadir and M. Singh, *J. Chem. Soc., Chem. Commun.*, 1969, 316.
34 M. Tiecco, *J. Chem. Soc., Chem. Commun.*, 1965, 555; D. I. Davies, D. H. Hey and M. Tiecco, *J. Chem. Soc.*, 1965, 7062.
35 L. Ruzicka and H. Hosli, *Helv. Chim. Acta*, 1934, **17**, 470.
36 M. Sindler-Kulyk and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 187; W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, 185.
37 A. Blagg, S. W. Carr, G. R. Cooper, I. D. Dobson, J. B. Gill, D. C. Goodall, B. L. Shaw, N. Taylor and T. Boddington, *J. Chem. Soc., Dalton Trans.*, 1985, 1213.
38 R. J. Bushby and G. J. Ferber, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1688.
39 J. Ridley and M. C. Zerner, *Theor. Chim. Acta*, 1973, **32**, 223; J. Zerner, M. C. Zerner, G. H. Loew, R. F. Kirchner and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.*, 1980, **102,** 111.
40 N. Boden, R. J. Bushby, J. Clements and R. Luo, *J. Mater. Chem.*, 1995, **5**, 1741.

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