Formation and EPR Spectral Detection of Methyl-substituted Naphthalene Radical Cations and Products of their Further Transformations: Binaphthalene Formation

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The EPR spectral behaviour of a number of methyl-substituted naphthalenes (ArH), as well as the corresponding 1,1′-binaphthalenes and perylenes, upon oxidation by any of the four methods mentioned below has been investigated. A study of these compounds by cyclic voltammetry is also reported. The substrates ArH included 1-methyl-, 1,2-, 1,3-, 1,4-, 1,5-, 1,7- and 1,8-dimethylnaphthalene as well as acenaphthene, and the oxidation methods were: (*i*)–(*iii*) photolysis of ArH and a good electron acceptor [tetranitromethane, DDQ or Hg^{II} trifluoroacetate] in dichloromethane–TFA (0.4–0.8 mol dm^{-3}) at a temperature between −60 and −70 °C, or (*iv*) thermal oxidation by Tl^{III} trifluoroacetate in dichloromethane–TFA (0.4–0.8 mol dm^{-3}) at room temperature, followed by recording of the EPR spectrum at −60 °C. Except in cases where a *peri* methyl group can interfere (1,4- and 1,5-dimethylnaphthalene) with σ coupling at the 1-position, these methods directly generated the EPR spectra of the radical cations of the corresponding 1,1′-binaphthalenes $\mathrm{Ar{-}Ar}^{\bullet+}$, previously interpreted as originating from π dimer radical cations, $(\mathrm{ArH})_2^{\bullet+}$. No evidence was obtained for further oxidation of the 1,1′-binaphthalenes to perylene derivatives under the prevailing reaction conditions.

The one-electron oxidation of aromatic compounds (ArH) leads primarily to the corresponding radical cations which exist either in monomeric ($\mathrm{ArH}^{\bullet+}$) or dimeric form [$(\mathrm{ArH})_2^{\bullet+}$], the latter usually being formulated as a π-dimer with two ArH arranged face-to-face and with the hole delocalized over both rings.[1,2] Both types of ion have been characterized by EPR spectroscopy, and as a rule of thumb, the hyperfine splitting constants of $(\mathrm{ArH})_2^{\bullet+}$ are about half of those of the monomeric radical cation.[3]

However, radical cations are reactive species and can undergo further reactions yielding more persistent radical cations even under what normally would be considered mild reaction conditions. For example, it was shown early on by EPR spectroscopy that Co^{III} trifluoroacetate oxidation of *tert*-butylbenzene in dichloromethane–trifluoroacetic acid at −30 °C or Tl^{III} trifluoroacetate oxidation of toluene or *o*-xylene in trifluoroacetic acid at −16 °C gave the radical cations of 4,4′-di-*tert*-butylbiphenyl, 4,4′-bitoluene or 3,3′,4,4′-tetramethylbiphenyl, obviously products of further σ-coupling, proton loss and further one-electron oxidation [eqns. (1)–(3)].[4,5] This is the pathway of biaryl dehydrodimerization, synthetically well known and, for example, explored in anodic and metal-ion oxidation of ArH.[6] On the other hand, higher polymethylbenzenes on Tl^{III} oxidation gave monomeric or π-dimeric radical cations, as judged by the EPR criterion, even though anodic biaryl dehydrodimerization has been demonstrated even for pentamethylbenzene.

$$\mathrm{ArH} \xrightarrow{-e^-} \mathrm{ArH}^{\bullet+} \qquad (1)$$

$$2\mathrm{ArH}^{\bullet+} \longrightarrow \mathrm{Ar(H){-}Ar(H)}^{2+} \qquad (2)$$

$$\mathrm{Ar(H){-}Ar(H)}^{2+} \xrightarrow{-2\mathrm{H}^+} \mathrm{Ar{-}Ar} \qquad (3)$$

The latter substrate is a prime example of another facile and extensive reaction following one-electron oxidation under seemingly mild conditions, in that it eventually gives the persistent 1,2,3,4,5,6,7,8-octamethylanthracene radical cation *via* the diphenylmethane dehydrodimerization pathway.[7] This mechanism is initiated by proton loss from one of the methyl groups of the radical cation. Other aromatic compound classes with high reactivity in σ-coupling are alkoxy- and amino-substituted ArH.[8] Thus a risk with EPR-spectroscopic characterization of radical cations is that 'hardy survivors' and not primary radical cations are detected.

The case of photochemical oxidation of 1-methoxynaphthalene (**1**-H) by tetranitromethane illustrates well the difficulties with EPR characterization of radical cations.[9] This reaction leads through excitation of the charge transfer (CT) complex between tetranitromethane and **1**-H to a triad of $\mathbf{1}\text{-H}^{\bullet+}$, trinitromethanide ion and NO$_2$ [eqn. (4)],[10] and it was expected that the EPR spectrum of $\mathbf{1}\text{-H}^{\bullet+}$ would be detectable at a sufficiently low temperature, especially because preparative photolysis at −20 °C gave products of monomeric type only. Photolysis in the temperature range −60 to −80 °C gave rise to a well-resolved EPR spectrum which was not obtained at temperatures above −60 °C. In the presence of TFA (0.4 mol dm^{-3}), photolysis produced a strong, unresolved EPR signal over the whole temperature range studied (up to 0 °C), indicating that the elimination of trinitromethanide ion from the reaction by protonation had removed the favoured pathway for disappearance of $\mathbf{1}\text{-H}^{\bullet+}$ *via* nucleophilic interaction with trinitromethanide ion [eqn. (5)], and left it to react with NO$_2$ [eqn. (6)], the slower pathway of the two leading from the triad.

$$\mathbf{1}\text{-H}\cdots\mathrm{C(NO_2)_4} \xrightarrow{h\nu} \underbrace{\mathbf{1}\text{-H}^{\bullet+}\ \mathrm{(NO_2)_3C^-}\ \mathrm{NO_2}}_{\text{triad}} \qquad (4)$$

$$\mathbf{1}\text{-H}^{\bullet+} + \mathrm{(NO_2)_3C^-} \longrightarrow \mathbf{1}\mathrm{(H)C(NO_2)_3}^{\bullet} \qquad (5)$$

$$\mathbf{1}\text{-H}^{\bullet+} + \mathrm{NO_2} \longrightarrow \mathbf{1}\text{-}\mathrm{(H)NO_2}^{+} \qquad (6)$$

Table 1 Redox potentials of methyl-substituted naphthalenes and the corresponding 1,1′-binaphthalenes and perylenes, as measured i dichloromethane–Bu_4NPF_6 (0.15 mol dm^{-3}) at 0.1–0.4 V s^{-1}, unless otherwise stated. All potentials are given in V *vs.* the Ag/AgCl electrode

Substituent in naphthalene	Redox potential of naphthalene			Redox potential of the corresponding 4,4′-coupled binaphthalene			Redox potential of the corresponding perylene		
	E_{pa}	E_{pc}	E_{rev}	E_{pa}	E_{pc}	E_{rev}	E_{pa}	E_{pc}	E_{rev}
1-CH_3	1.74	—	—	1.53[a]	1.45[a]	1.49	0.98	0.91	0.95
1,2-$(CH_3)_2$	1.60	—	—	1.44	1.37	1.41	0.89	0.80	0.85
1,3-$(CH_3)_2$	1.60[b]	1.48[b]	1.54	1.59	1.51	1.55			
1,4-$(CH_3)_2$	1.63	1.53	1.58				—	—	—
1,5-$(CH_3)_2$	1.67	1.59	1.63				—	—	—
1,8-$(CH_3)_2$	1.65	—	—	1.41	1.35	1.38	0.84	0.73	0.78
1,7-$(CH_3)_2$	1.70	—	—	1.44	1.36	1.40	0.91	0.76	0.84
1,8-$(CH_2)_2$[c]	1.45			1.29	1.22	1.26			

[a] At 2 V s^{-1}. [b] At 40 V s^{-1}. [c] Acenaphthene.

However, the preparative photolysis of **1**-H, tetranitromethane and TFA in dichloromethane at +20 or −50 °C gave exclusively the dehydrodimer, **1**–**1**, as the primary product, showing that reaction (7) takes preference over reaction (8) when the trinitromethanide ion is removed. The dehydrodimer was obtained in significant yield at −80 °C even in the absence of TFA, showing that, at this temperature, the coupling process [eqn. (7)] can compete favourably even with the trinitromethanide reaction, owing to the differing temperature coefficients of these reactions. Accordingly, it was shown eventually that all EPR spectral observations relating to **1**-H photolysis with tetranitromethane or Hg^{II} trifluoroacetate, or oxidation by Tl^{III}[11] or DDQ, were due to the dehydrodimer radical cation, **1**–$\mathbf{1}^{\bullet+}$, revealing that **1**-$H^{\bullet+}$ is a reactive species in self-coupling, but is less reactive in coupling with the moderately reactive radical NO_2.

$$2\,\mathbf{1}\text{-H}^{\bullet+} \longrightarrow \mathbf{1}(\text{H})\text{–}\mathbf{1}(\text{H})^{2+} \longrightarrow \longrightarrow \mathbf{1}\text{–}\mathbf{1}^{\bullet+} \qquad (7)$$

The application of the tetranitromethane–ArH–TFA EPR spectroscopic method to a closer study[12] of the reactivity of a series of methylnaphthalene radical cations with trinitromethanide ion and/or NO_2 has posed the same question as for 1-methoxynaphthalene: what is the observed radical cation—$ArH^{\bullet+}$, $(ArH)_2^{\bullet+}$ or possibly a survivor of the Ar–$Ar^{\bullet+}$ type? Radical cations derived from the oxidation of methylnaphthalenes, either anodically at −80 °C or by $AlCl_3$ oxidation at −(60–80) °C in SO_2 have recently been characterized by EPR spectroscopy,[13,14] either as monomeric $ArH^{\bullet+}$ or $(ArH)_2^{\bullet+}$ or radical cations (derived from the perylene structure) resulting from the occurrence of the Scholl reaction.[15] However, the possibility of Ar–$Ar^{\bullet+}$ formation was not explicitly considered. Some inconsistencies between our EPR spectral data[12] and the published ones,[13] noted in connection with the 1-methoxynaphthalene work[9] suggested a more widespread occurrence of dehydrodimer formation, and caused us to extend our study. We now report EPR spectral results from the oxidation of the systems 1-methyl-, 1,2-, 1,3-, 1,4-, 1,5-, 1,7- and 1,8-dimethylnaphthalene, as well as the related compound, acenaphthene.

Results

Cyclic Voltammetry.—The compounds studied are listed in Table 1, together with their electrochemical characteristics as measured by cyclic voltammetry in dichloromethane–tetrabutylammonium hexafluorophosphate (0.15 mol dm^{-3}). This technique is often useful for the detection of possible further reactions of the primary radical cation,[1] since any secondary radical cation of reasonable stability is reduced during the reverse scan, and its reduced form can then be detected during further cycling. Prominent examples of such behaviour have been found earlier among alkoxy- and amino-aromatics.[8] For the naphthalenes employed in this study, any secondary couple is present normally only in low concentration. This is illustrated in Fig. 1 by the behaviour of 1,2-dimethylnaphthalene which upon cycling between 0.5 and 1.8 V at a sweep rate of 20 V s^{-1} developed a secondary redox couple in low concentration, E_{pa} 1.41 and E_{pc} 1.34 V. These values are close to those measured for authentic 3,3′,4,4′-tetramethyl-1,1′-binaphthalene (Table 1) and suggest that the primary radical cation has been converted partially into the dehydrodimer radical cation during the anodic sweep.

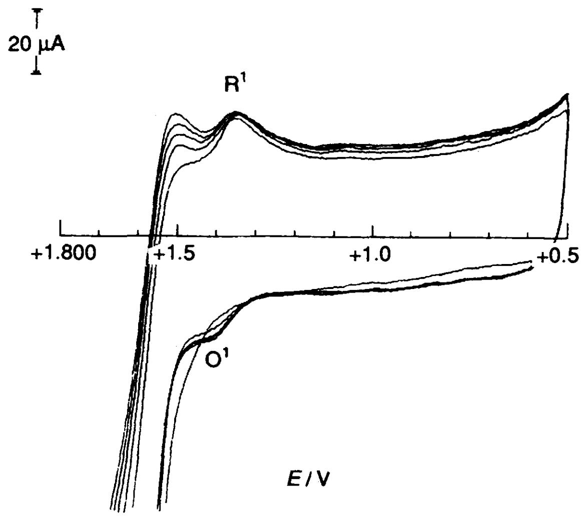

Fig. 1 Enlarged part of a cyclic voltammogram (five cycles) of 1,2-dimethylnaphthalene (1.8 mmol dm^{-3}) in dichloromethane–Bu_4NPF_6 (0.15 mol dm^{-3}) at a sweep rate of 20 V s^{-1}. The redox couple R^1–O^1 is derived from 3,3′,4,4′-tetramethyl-1,1′-binaphthalene, formed in the anodic oxidation of 1,2-dimethylnaphthalene.

Methods for Generating Radical Cations for EPR Spectroscopy.—The methods employed here to generate radical cations were: photolysis of ArH and a good electron acceptor in dichloromethane–TFA (0.4–0.8 mol dm^{-3}) at a temperature between −60 and −70 °C, or thermal oxidation by Tl^{III} trifluoroacetate in dichloromethane–TFA (0.4–0.8 mol dm^{-3}) at room temperature, followed by recording of the EPR spectrum at −60 °C. Electron acceptors were tetranitromethane,[12] 2,3-dichloro-4,5-dicyanoquinone (DDQ),[16] or Hg^{II} trifluoroacetate (the Kochi method).[17] The trifluoroacetic acid in the first two cases was added to protonate instantly the anionic species formed (trinitromethanide ion or $DDQ^{\bullet-}$) and thus avoid very rapid nucleophilic/electron transfer follow-up reactions of ArH$^{\bullet+}$. In some cases DDQ reacted thermally upon mixing and was then replaced by tetrachlorobenzoquinone (chloranil), a weaker electron acceptor.

The Hg$^{\mathrm{II}}$ trifluoroacetate method is known[18] sometimes to give EPR spectra of mercuriated products, easily recognizable by g values <2 and large ^{199}Hg coupling constants. This aspect was checked in all Hg$^{\mathrm{II}}$–light promoted runs and found not to occur under the conditions employed.

It is sometimes possible to obtain good EPR spectra merely by photolysing a solution of ArH in the presence of TFA,[7a] and here this method (the 'TFA method') was used in dichloromethane–0.8 mol dm^{-3} TFA at -60 °C. TFA is a weak electron acceptor, as reported by Bunce *et al.*[19] This method does not work with all compounds and was used only occasionally.

1,4-*Dimethylnaphthalene* (1,4-*DMN*).—This compound exhibited reversible behaviour upon cyclic voltammetry at a sweep rate of 10 V s^{-1} and no secondary, low-potential couple was detected. From this criterion, oxidation of 1,4-DMN would be expected to give the monomeric or π-dimeric radical cation. The EPR spectra of both species are known,[13,14] and from simulations using known hfs constants it was obvious that most of the methods listed above (not the TFA method) generated a moderately well resolved spectrum of the π dimer, (1,4-DMN)$_2^{\bullet+}$ (*ca.* 30 visible lines of 0.107 mT spacing), compared with the simulated spectrum of the π dimer using a linewidth of 0.12 mT (*ca.* 35 visible lines of 0.107 mT spacing). The TFA method gave a better resolved spectrum of larger width, in best agreement with the simulated 1,4-DMN$^{\bullet+}$ spectrum.

1,5-*Dimethylnaphthalene* (1,5-*DMN*).—Cyclic voltammetry of 1,5-DMN at 1 V s^{-1} indicated that a low-potential couple ($E_{\mathrm{pa}}/E_{\mathrm{pc}}$ = 1.33/1.28 V) was formed from the primary radical cation in very low concentration. The Tl$^{\mathrm{III}}$ method in this case did not produce any radical cation by thermal reaction at room temperature. However, by UV irradiation at -65 °C a moderately well resolved EPR spectrum was obtained (Fig. 2), simulated by the known hfs constants of the π dimer using a linewidth of 0.055 mT. Similar spectra were obtained by the tetranitromethane and Hg$^{\mathrm{II}}$ method, whereas the TFA method did not work.

Preparative attempts to dehydrodimerize 1,5-DMN by oxidation with Tl$^{\mathrm{III}}$–BF$_3$ gave a mixture of three dehydrodimers in very low yield (proportions 60:30:10; the NMR spectrum indicated that the unsymmetrical dimer was the major one), which could not be separated. The mixture gave a very weak EPR spectrum by the tetranitromethane method at -65 °C and a moderately strong one by the Tl$^{\mathrm{III}}$ method. The spectrum was very complex, with >300 lines over a width of *ca.* 5 mT, but seemed to originate from a single species, not unexpectedly since the thermodynamically most stable radical cation should be formed from the mixture.

1,2-*Dimethylnaphthalene* (1,2-*DMN*).—As shown in Fig. 1, cyclic voltammetry indicated that the dehydrodimer radical cation is formed from 1,2-DMN$^{\bullet+}$. EPR spectra generated from 1,2-DMN by any of the methods listed above were well resolved and identical. In its best resolved form [Fig. 3(*a*)], this spectrum was shown to be identical with that of authentic 3,3′,4,4′-tetramethylbinaphthalene radical cation [Fig. 3(*b*)], generated by the same methods. The earlier assignment of this spectrum[13] was to the π dimer, (1,2-DMN)$_2^{\bullet+}$, perhaps not so surprising in view of the difference being between two systems of 7 or 8 hfs constants, respectively, and nearly the same number of hydrogen atoms (22 or 24). The corresponding perylene was synthesized, and its radical cation had an EPR spectrum significantly different from that of the dehydrodimer radical cation (Fig. 4).

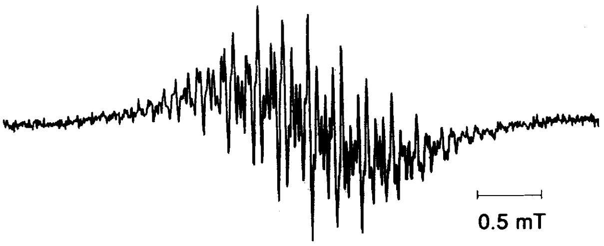

Fig. 2 EPR spectrum obtained by UV irradiation of a solution of 1,5-dimethylnaphthalene (2.5 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and Tl$^{\mathrm{III}}$ trifluoroacetate (20 mmol dm^{-3}) in dichloromethane at -65 °C

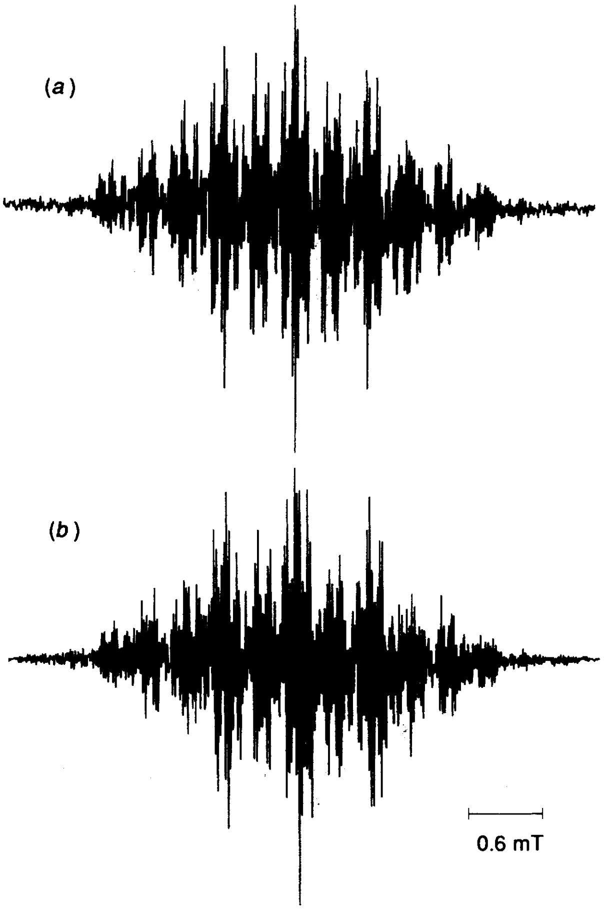

Fig. 3 EPR spectrum obtained by (*a*) UV irradiation of a solution of 1,2-dimethylnaphthalene (70 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and DDQ (20 mmol dm^{-3}) in dichloromethane at -60 °C and (*b*) irradiation by light of λ > 430 nm of a solution of 3,3′,4,4′-tetramethyl-1,1′-binaphthalene (1.5 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and DDQ (20 mmol dm^{-3}) in dichloromethane at -60 °C

1,3-*Dimethylnaphthalene* (1,3-*DMN*).—Cyclic voltammetry had no diagnostic value for this compound since 1,3-DMN and its dehydrodimer, 2,2′,4,4′-tetramethyl-1,1′-binaphthalene are oxidized at about the same potential (Table 1).

The tetranitromethane method did not generate an EPR spectrum from either 1,3-DMN or 2,2′,4,4′-tetramethyl-1,1′-binaphthalene at -65 °C, indicating high reactivity of the corresponding radical cations toward NO$_2$, the remaining component from tetranitromethane reduction after protonation of the trinitromethanide ion. The Tl$^{\mathrm{III}}$ method, applied to 1,3-DMN, produced a well-resolved spectrum of the 2,2′,4,4′-tetramethyl-1,1′-binaphthalene radical cation, identical with

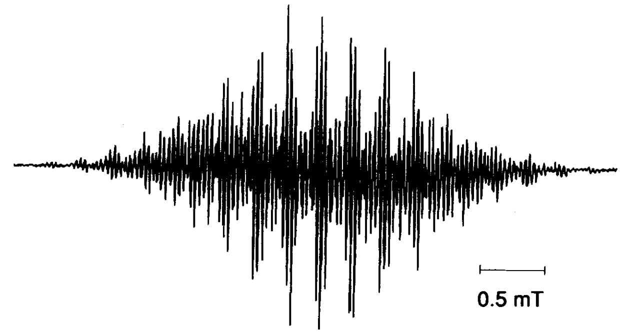

Fig. 4 EPR spectrum obtained by mixing a solution of 2,3,10,11-tetramethylperylene (2.5 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and Tl^{III} trifluoroacetate (20 mmol dm^{-3}) in dichloromethane at room temperature and recording at −60 °C

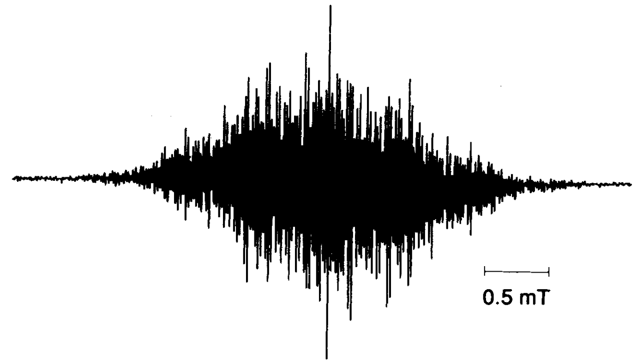

Fig. 5 EPR spectrum obtained by mixing a solution of 1,3-dimethylnaphthalene (10 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and Tl^{III} trifluoroacetate (20 mmol dm^{-3}) in dichloromethane at room temperature and recording at −65 °C

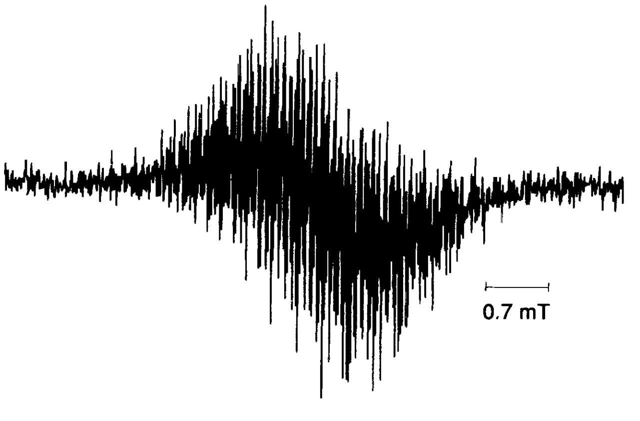

Fig. 6 EPR spectrum obtained by UV irradiation of a solution of 1,8-dimethylnaphthalene (70 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and Hg^{II} trifluoroacetate (20 mmol dm^{-3}) in dichloromethane at −60 °C

that of Tl^{III} oxidation of the authentic dehydrodimer (Fig. 5). The Hg^{II} method also gave the EPR spectrum of the dehydrodimer radical cation, although weaker, whereas the DDQ method gave a spectrum of lower resolution.

1,8-*Dimethylnaphthalene* (1,8-*DMN*).—Cyclic voltammetry of 1,8-DMN at a sweep rate of 20 V s^{-1} indicated the formation of two low-potential couples in low concentration upon cycling through 10 scans, with E_{pa}/E_{pc} equal to 1.45/1.35 and 0.91/0.88 V. The former might correspond to the dehydrodimer (see Table 1) whereas the latter differs too much from that of the corresponding perylene, 3,4,9,10-tetramethylperylene (0.84/0.73 V), to be tentatively identified as such.

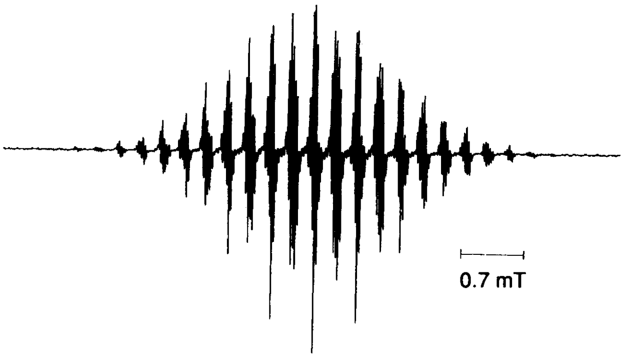

Fig. 7 EPR spectrum obtained by mixing a solution of 3,4,9,10-tetramethylperylene (5 mmol dm^{-3}) and Tl^{III} trifluoroacetate (10 mmol dm^{-3}) in dichloromethane at room temperature and recording at −20 °C. The addition of TFA led to fast destruction of the substrate.

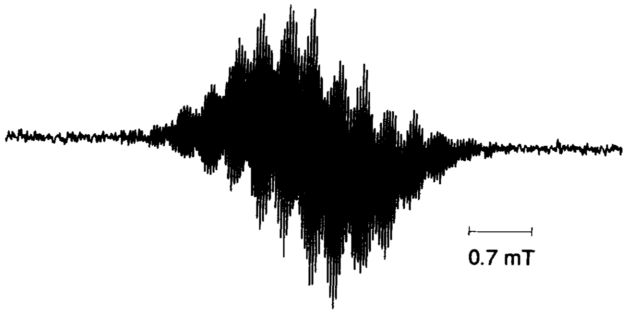

Fig. 8 EPR spectrum obtained by irradiation at $\lambda > 430$ nm of a solution of 1,7-dimethylnaphthalene (70 mmol dm^{-3}), TFA (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at −65 °C

Any of the generation methods, applied to 1,8-DMN or an authentic sample of its dehydrodimer, produced the same spectrum which we assign to the 4,4′,5,5′-tetramethyl-1,1′-binaphthalene radical cation. This spectrum in its most well-resolved form is shown in Fig. 6; visual inspection shows it to be very similar to that previously assigned to the π dimer, (1,8-DMN)$_2^{\bullet+}$, and was well simulated by the hfs constants given for this species.[13] An authentic sample of 3,4,9,10-tetramethylperylene showed a significantly different EPR spectrum (Fig. 7).

1,7-*Dimethylnaphthalene* (1,7-*DMN*).—Cyclic voltammetry indicated the formation of a redox couple centred around 1.05 V upon cycling at a sweep rate of 0.4 V s^{-1} whereas nothing was to be seen around the potential of the dehydrodimer redox couple, 1.40 V (Table 1).

One and the same radical cation spectrum (Fig. 8) was generated from 1,7-DMN or 4,4′,6,6′-tetramethyl-1,1′-binaphthalene by all methods, and this spectrum is accordingly assigned to 4,4′,6,6′-tetramethyl-1,1′-binaphthalene radical cation. The corresponding 2,4,9,11-tetramethylperylene upon oxidation by the Tl^{III} or tetranitromethane method gave a complex spectrum of >400 lines (Fig. 9) which was not compatible with a previous simulation[14] of a spectrum obtained by $AlCl_3$–SO_2 oxidation of 1,7-DMN at −60 °C. The latter spectrum has a characteristic 7-group appearance owing to one dominant hfs constant to six methyl hydrogens.

Acenaphthene.—Formally, acenaphthene is 1,8-ethanonaphthalene, and would thus be expected to behave like 1,8-dimethylnaphthalene. However, further complications might be expected due to oxidation of the five-membered ring(s) at the monomer, dehydrodimer and/or perylene level, with additional complexity of CV and EPR spectral behaviour to be expected.

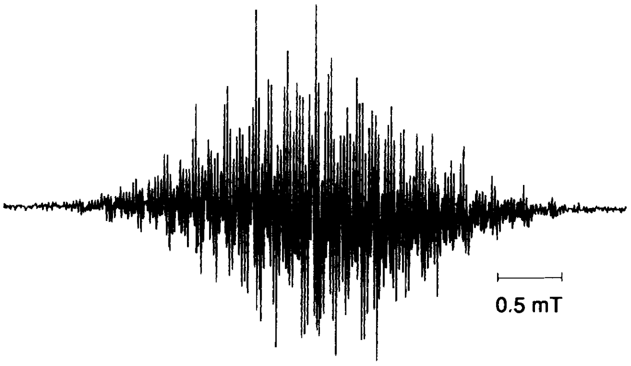

Fig. 9 EPR spectrum obtained by irradiation (λ > 430 nm) of a solution of 2,4,9,11-tetramethylperylene (5 mmol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA (0.4 mol dm^{-3}) in dichloromethane at −65 °C

Therefore we conducted only a limited study of this substrate since a more detailed treatment would fall outside the scope of this investigation.

Cyclic voltammetry in the range 0–1.8 V at a sweep rate of 0.4 V s^{-1} showed that acenaphthene is the most easily oxidizable naphthalene derivative of Table 1 and that a redox couple centred around 0.25 V appeared upon repeated cycling. The latter had a peak height of about half of the original oxidation peak of acenaphthene and is most probably due to the generation of acid by proton abstraction from the acenaphthene radical cation. In addition a low concentration redox couple, centred around 1.0 V, developed; it became larger when the upper limit of the cycling range was extended to 2.2 V. This couple does not correspond to that of the authentic dehydrodimer, 4,5;4′,5′-bis(ethano)-1,1′-binaphthalene (Table 1).

The EPR spectral behaviour of acenaphthene differed between the different methods employed. The tetranitromethane method at −65 °C gave a characteristic 9-group spectrum (Fig. 10) which was obtained previously[20] by anodic oxidation of acenaphthene at −60 °C in dichloromethane–TFA and assigned the structure of the π dimer, (acenaphthene)$_2^{\bullet+}$. The DDQ method gave the same spectrum, although weaker. A different spectrum was obtained by Tl^{III} oxidation (Fig. 11). and this was identical with that of authentic dehydrodimer, 4,5;4′,5′-bis(ethano)-1,1′-binaphthalene. The Hg^{II} method did not generate any EPR activity from acenaphthene at −65 °C even upon prolonged UV irradiation. In view of the finding[18] that Hg^{II} trifluoroacetate readily bismercuriates acenaphthene in neat TFA at −11 °C, the EPR sample [in dichloromethane–TFA (0.4 mol dm^{-3})] was kept at room temperature overnight; however, no sign of mercuriation was evident in the EPR spectrum of the aged sample.

A check was performed of the behaviour of acenaphthylene in the tetranitromethane method, but the only detectable EPR spectrum was a weak version of Fig. 10, evidently caused by the presence of a small proportion of acenaphthene as an impurity (even as little as 2% of acenaphthene in a sample was found to cause the appearance of the EPR spectrum of Fig. 10).

1-*Methylnaphthalene* (1-*MN*).—Cyclic voltammetry at 10 V s^{-1} in the range 0.6–2.0 V developed a low concentration redox couple around 1.0 V, about the same position as for authentic 3,10-dimethylperylene.

At −60 °C, the tetranitromethane method did not generate an EPR signal owing to rapid follow-up reactions of the radical cation(s) formed. At −70 °C, the spectrum of Fig. 12(*a*) developed, identical with that obtained by the same or Tl^{III} treatment of 4,4′-dimethyl-1,1′-binaphthalene [Fig. 12(*b*)]. 3,10-Dimethylperylene by both the tetranitromethane and Tl^{III} methods gave a spectrum [Fig. 12(*c*)] distinctly different from that of the dehydrodimer radical cation.

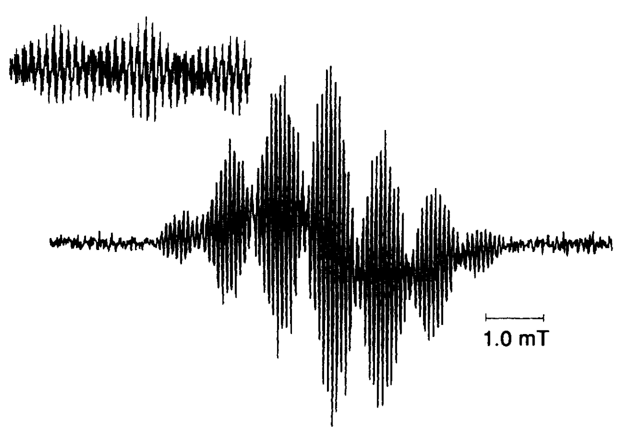

Fig. 10 EPR spectrum obtained by irradiation by light of λ > 430 nm of a solution of acenaphthene (60 mmol dm^{-3}), TFA (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at −65 °C. Insert: spectrum run over the three middle groups (3.0 mT) at highest possible resolution.

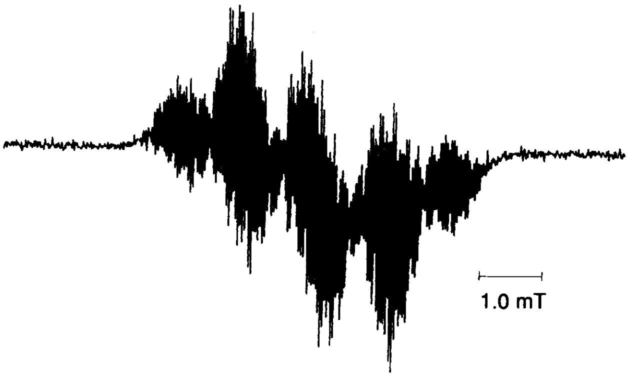

Fig. 11 EPR spectrum obtained by mixing a solution of acenaphthene (5 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and Tl^{III} trifluoroacetate (20 mmol dm^{-3}) in dichloromethane at room temperature and recording at −70 °C

Discussion

Radical Cations Obtained by Oxidation of Methyl-substituted Naphthalenes and their Structures.—Anodic or metal-ion promoted oxidation of aromatic hydrocarbons is known to lead to the formation of dehydrodimers of the biaryl and/or diphenylmethane type,[6] the latter of course being confined to hydrocarbons with at least one hydrogen at the 1-position of a side-chain. These coupling reactions were found to be favoured in media of low or non-existent nucleophilicity and/or by the presence of an acid, such as TFA, which acts mainly by suppressing the reactivity of any nucleophilic species which might accidentally be present. These principles were extended later to other types of substrate, such as alkoxyaromatics.

The naphthalenes employed in this study correspond to reactive or moderately reactive radical cations, as judged by the range of redox potentials listed in Table 1. When generated by any method in a sufficiently non-nucleophilic environment, they will still have several important pathways available for further reactions, such as (*i*) association with a parent molecule to form a π dimeric radical cation [eqn. (8)], or (*ii*) coupling with a

$$\mathrm{ArH}^{\bullet+} + \mathrm{ArH} \longrightarrow (\mathrm{ArH})_2^{\bullet+} \qquad (8)$$

second monomeric radical cation into a σ-bound dication

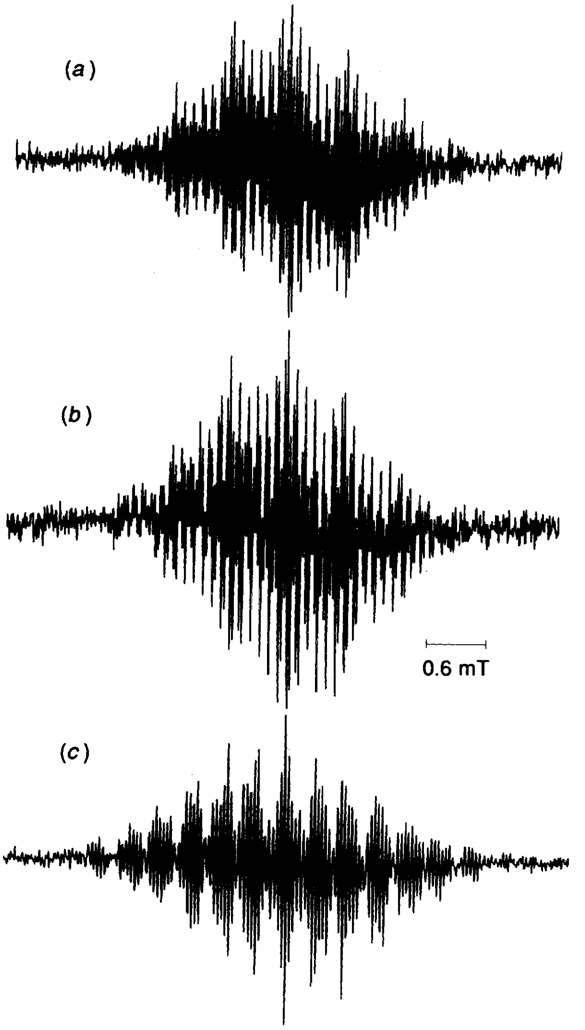

Fig. 12 EPR spectrum obtained by (*a*) irradiation by light of $\lambda > 430$ nm of a solution of 1-methylnaphthalene (70 mmol dm^{-3}), TFA (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at −70 °C; (*b*) irradiation at $\lambda > 430$ nm of a solution of 4,4′-dimethyl-1,1′-binaphthalene (25 mmol dm^{-3}), TFA (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) in dichloromethane at −70 °C, and (*c*) mixing a solution of 3,10-dimethylperylene (5 mmol dm^{-3}), TFA (0.8 mol dm^{-3}) and $\mathrm{Tl^{III}}$ trifluoroacetate (20 mmol dm^{-3}) in dichloromethane at room temperature and recording at −70 °C

followed by further transformation of the latter into the dehydrodimer [eqn. (9)]. The π dimer likewise can be thought to

$$\mathrm{ArH}^{\bullet +} + \mathrm{ArH}^{\bullet +} \longrightarrow \mathrm{Ar(H){-}Ar(H)}^{2+} \xrightarrow{-2\mathrm{H}^+} \mathrm{Ar{-}Ar} \qquad (9)$$

develop into a σ-bound radical cation which by one-electron oxidation will lead to the dehydrodimer [eqn. (10)]. The latter

$$\begin{tikzcd}
(\mathrm{ArH})_2^{\bullet +} \arrow[r] & \mathrm{Ar(H){-}Ar(H)}^{\bullet +} \arrow[r, "-e^-"] & \mathrm{Ar(H){-}Ar(H)}^{2+} \arrow[d, "-2\mathrm{H}^+"] \\
 & & \mathrm{Ar{-}Ar} \qquad (10)
\end{tikzcd}$$

can in principle undergo analogous reactions, leading to further coupling processes until eventually radical cations of sufficiently low reactivity are formed. Extreme results of these reactivities are crystallized radical cation salts[21]—essentially stacks of π dimers—on one side, and conducting polymers—σ bonded dehydropolymers[22]—on the other.

Two of the naphthalenes studied, 1,4- and 1,5-dimethylnaphthalene, showed reversible electrochemical behaviour at low sweep rate, which can, presumably, be ascribed to the fact that σ coupling, directed to the α position because of its higher spin density, is sterically prohibited by the strong *peri* interaction in the transition state. Thus the reaction stops at the π dimer level and this is the species detected by EPR spectroscopy.

1,3-Dimethylnaphthalene behaved reversibly at 40 V s^{-1}, indicating some stability of its radical cation. However, the EPR spectrum observed must be assigned to the dehydrodimer radical cation, a more stable species, showing that steric hindrance from a methyl group at an adjacent carbon atom is not detrimental to coupling in a naphthalene 1-position. This is in line with the preparative results.[23]

The remaining naphthalenes of Table 1 all have at least one unhindered 1-position and thus are not blocked for σ coupling. Accordingly, the reaction does not stop until the dehydrodimer radical cation has been formed. Under the mild conditions prevailing during the generation methods employed here, no further reaction to give the perylene derivative takes place. Some comments on the individual compounds are pertinent.

In a previous study,[14] 1-methylnaphthalene upon treatment with $\mathrm{AlCl_3{-}SO_2}$–dichloromethane at −60 °C gave a spectrum assigned to its monomeric radical cation, simulated by 5 hfs constants: 4.77(6), 2.306(2), 0.44(4), 0.27(2) and 0.02(2) G. A simulation of this EPR spectrum is distinctly different from that of the 4,4′-dimethyl-1,1′-binaphthalene radical cation [Fig. 12(*b*)] but has features in common with that of the 3,10-dimethylperylene radical cation [Fig. 12(*c*)]. They both consist of 15 major groups of signals, each split into 8–9 lines. However, their spectral width differs by about 0.5 mT and in all probability they correspond to different species. The spectrum obtained earlier by anodic oxidation at low temperature[13] was identical with that of Fig. 12(*b*), and was simulated by six hfs constants: 0.589(6), 0.093(2), 0.031(2), 0.476(2), 0.186(2) and 0.124(2).

1,2-Dimethylnaphthalene radical cation was generated by anodic oxidation at *ca.* −80 °C, and the resulting EPR spectrum was assigned to the π dimeric radical cation.[13] The spectrum was simulated by six hfs constants: 0.580(6), 0.106(6), 0.023(4), 0.342(2), 0.212(4) and 0.083(2). However, as shown above, this spectrum belongs to the 3,3′,4,4′-tetramethylnaphthalene radical cation.

Anodic oxidation of 1,8-dimethylnaphthalene was claimed[13] to give the π dimeric radical cation although a somewhat distorted geometry had to be assumed in order to explain the necessity of seven hfs constants for simulating the spectrum [0.586(6), 0.364(2), 0.222(2), 0.080(2), 0.284(8), 0.061(2) and 0.019(2) mT]. In fact, this spectrum is derived from the 4,4′,-5,5′-tetramethylnaphthalene radical cation.

Acenaphthene, superficially similar to 1,8-dimethylnaphthalene, at least in principle might be expected to show more complex behaviour due to the extended possibility of oxidation of the five-membered ring(s). The tetranitromethane method gives the same spectrum (Fig. 10) as that obtained earlier[20] by anodic oxidation of acenaphthene at −60 °C and assigned to the π dimeric radical cation. Four hfs constants [0.91(8), 0.238(4), 0.088(4) and 0.070(4)] simulate this spectrum satisfactorily. The relative simplicity of the spectrum might seem to indicate a perylene structure, but this cannot be correct. Under conditions of highest resolution possible (see the insert of Fig. 10) one can estimate that the experimental spectrum has > 320 lines whereas the perylene structure can have maximally 225 lines.

However, later studies[13] gave another spectrum for the π dimeric radical cation [hfs constants: 0.962(2), 0.567(2), 0.080(4), 0.882(4), 0.064(4), 0.400(2) and 0.016(2)], pointing to a lower degree of symmetry of this species. This spectrum does not agree with our spectrum of the dehydrodimer (Fig. 11) and may be derived from its further transformations by oxidation of the five-membered ring(s).

The EPR spectrum obtained by oxidation of 1,7-dimethylnaphthalene in all probability was due to the dehydrodimer (4,4′,6,6′-tetramethyl-1,1-binaphthalene) radical cation. $AlCl_3$ oxidation in SO_2–dichloromethane at −60 °C gave a different spectrum,[14] assigned to the 2,4,9,11-tetramethylperylene radical cation formed in a Scholl condensation. This spectrum was not seen in our study.

Possible Limitations of the Tetranitromethane Method of Generating Radical Cations.—The photolysis of a substrate with tetranitromethane in an inert organic solvent in the presence of an acid (TFA or methanesulfonic acid) is potentially a useful method for generating radical cations. Obviously, the method is limited to radical cations which do not react rapidly at the prevailing temperature with NO_2, the triad component [eqn. (4)] which is left after protonation of trinitromethanide ion [eqn. (11)]. With the temperature limitations dictated by the

$$ArH\cdots C(NO_2)_4 \xrightarrow{h\nu,\ H^+} ArH^{\bullet +} + NO_2 + HC(NO_2)_3 \quad (11)$$

physical properties of the solvents used so far (dichloromethane or acetonitrile), the upper limit of reactivity seems to be *primary* radical cations with a redox potential of 1.7–1.8 V. However, the primary radical cation has the option to undergo self-coupling in competition with the NO_2 reaction, leading to secondary products which can give less reactive radical cations. This complication is common to all methods for generating radical cations in fluid solution, and as far as one can tell from the limited number of applications described until now, the tetranitromethane method is equivalent to others, be they based on organic or inorganic electron acceptors.

Previously we used the tetranitromethane method for a different purpose,[12] namely to study the competition between the reactions of $ArH^{\bullet +}$ and trinitromethanide ion or NO_2. The photolysis of a solution of tetranitromethane and ArH in dichloromethane at −60 °C in most cases gives an EPR-silent system, signifying that one or both of reactions (12) and (13) are

$$ArH^{\bullet +} + (NO_2)_3C^- \longrightarrow Ar(H)C(NO_2)_3^{\bullet} \xrightarrow{NO_2} \text{adducts} \quad (12)$$

$$ArH^{\bullet +} + NO_2 \longrightarrow Ar(H)NO_2^{+} \quad (13)$$

too fast for any $ArH^{\bullet +}$ to accumulate. With an acid present during photolysis, a radical cation signal develops in most cases, implying that protonation of trinitromethanide ion has removed the most reactive component, leaving behind the slower $ArH^{\bullet +}$–NO_2 reaction. Based on the then available EPR spectral information,[13,14] we assigned the radical cation spectra obtained to either $ArH^{\bullet +}$ or $(ArH)_2^{\bullet +}$, which obviously was not always correct in view of the findings reported above. Under the conditions employed, the dehydrodimerization reaction [eqn. (14)] can also sometimes compete with the $ArH^{\bullet +}$–NO_2

$$2ArH^{\bullet +} \longrightarrow Ar(H)\text{–}Ar(H)^{2+} \quad (14)$$

process, particularly for those types of radical cation which are prone to self-coupling. 1-Methoxynaphthalene, the case which alerted us to the possibility of dehydrodimer formation, is such a substrate.[9]

The predominance of the NO_2 reaction over the trinitromethanide reaction in the acidic medium [eqn. (13) *vs.* (12)] could be approximately quantified as the ratio of the EPR signal intensity between the acidified and the neutral solution, denoted ξ. It was expected that this quantity, plotted against some accepted measure of radical cation reactivity, like $E°(ArH^{\bullet +}/ArH)$,[24] should go through a maximum for a series of radical cations ranging from very reactive ones [$\xi \approx 1$, since both reactions (12) and (13) are fast] to unreactive ones [$\xi \approx 1$, now because both reactions are slow]. However, this correlation failed, and one can now give an additional reason: the radical cations formed were in some cases derived from dehydrodimers which are far less reactive than their precursors. However, even with the revised $E°(ArH^{\bullet +}/ArH)$ for the 1-methyl- and dimethyl-naphthalene systems (those of the corresponding 1,1′-binaphthalenes were used instead; Table 1) the expected relationship did not appear for the range of compounds studied. The class of radical cations which are unreactive under both sets of conditions is difficult to study, since the corresponding ArH react spontaneously with tetranitromethane.

However, we stress that $\xi > 1$ still qualitatively signifies that the $ArH^{\bullet +}$/trinitromethanide reaction has become retarded or completely blocked. The primary radical cation, $ArH^{\bullet +}$, has had time to undergo reactions other than that of eqn. (12), particularly *via* eqn. (14), in cases where it is not detected. The general conclusion remains that the tetranitromethane/acid method demonstrates beyond reasonable doubt that $ArH^{\bullet +}$ is significantly more reactive toward trinitromethanide ion than NO_2.

Experimental

Materials and Methods.—Melting points are uncorrected. ^1H NMR spectra were recorded on a Varian 200 MHz spectrometer with $SiMe_4$ as an internal standard. Tetranitromethane was purchased from Aldrich and DDQ from Merck. Thallium(III) trifluoroacetate was from Strem Chemicals and mercury(II) trifluoroacetate was from Johnson Matthey. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and trifluoroacetic acid was from Merck.

EPR spectra were recorded by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using the 50 W high-pressure Hg lamp from Bruker (ER 202) and a filter with cut-off at <430 nm from Schott, Germany. The following methods were used to generate radical cations from the substrates: (*i*) photolysis of substrate (8–80 mmol dm^{-3}), tetranitromethane (0.8 mol dm^{-3}) and TFA (0.4–0.8 mol dm^{-3}) in dichloromethane at −60 to −70 °C, (*ii*) photolysis of substrate (4–80 mmol dm^{-3}), mercury(II) trifluoroacetate (50 mmol dm^{-3}) and TFA (0.4–0.8 mol dm^{-3}) at −60 to −70 °C, (*iii*) photolysis of the substrate (5–50 mmol dm^{-3}), DDQ (20 mmol dm^{-3}) and TFA (0.4–0.8 mol dm^{-3}) in dichloromethane, and (*iv*) oxidation of the substrate (5 mmol dm^{-3}) by thallium(III) trifluoroacetate (20–30 mmol dm^{-3}) in TFA (0.8 mol dm^{-3})–dichloromethane.

Cyclic voltammetry was performed in dichloromethane–Bu_4NPF_6 (0.15 mol dm^{-3}), using a BAS-100 instrument.

Substrates.—The substrates were either purchased in highest commercial quality possible or synthesized according to known methods, as detailed below. The following compounds were of commercial origin: 1-methyl- (Aldrich, 98%), 1,2-dimethyl- (Aldrich, 98%), 1,3-dimethyl- (Janssen, 98%), 1,4-dimethyl- (Merck, >96%), 1,5-dimethyl- (Fluka, >97%), 1,8-dimethylnaphthalene (Fluka, 85–95%, purified by flash chromatography, or Merck, 98%) and acenaphthene (Aldrich, >97%). The purity was checked by GLC and/or GLC–MS.

1,7-*Dimethylnaphthalene.*—Triflic acid (3 cm^3) was added to a solution of 1.0 g (6.4 mmol) of 1,8-dimethylnaphthalene in dichloromethane (10 cm^3). The mixture was vigorously stirred until the reaction was complete (3 h, GLC), poured onto ice and neutralized with sodium carbonate. Extraction with dichloromethane, drying with magnesium sulfate and evaporation of the solvent gave a yellow oil. Column chromatography on silica with pentane as the eluent gave 0.70 g (70%) of 1,7-dimethylnaphthalene, the NMR spectrum of which was identical with the published one.[25]

General Method for the Preparation of Binaphthalenes.[6j]—Thallium trifluoroacetate (1.76 g, 3.2 mmol) was added to a solution of the naphthalene derivative (6.4 mmol) in dry acetonitrile (10 cm^3). The mixture was cooled to -60 °C and boron trifluoride–diethyl ether (3.2 cm^3) was added dropwise. The reaction mixture was then allowed to warm slowly to room temperature and was further stirred until a Tl^{III} test was negative. The mixture was poured into water (20 cm^3), extracted with dichloromethane (2 × 20 cm^3) and dried with magnesium sulfate. The solvent was evaporated off and the crude product was purified by column chromatography on silica, using pentane–dichloromethane (10:1) as the eluent.

4,4′-*Dimethyl*-1,1′-*binaphthalene*. Mp 146–147 °C, lit.,[6j] 145–147 °C, δ_H(CDCl$_3$) 2.82 (s, 6 H), 7.30 (ddd, 2 H, 8.4, 6.6, 1.2 Hz), 7.40–7.45 (m, 6 H), 7.52 (ddd, 2 H, 8.6, 6.6, 1.4 Hz) and 8.11 (d, 2 H, 8.6 Hz).

2,2′,4,4′-*Tetramethyl*-1,1′-*binaphthalene*. ^{1}H NMR spectrum as reported.[23] Mp 176–177 °C.

3,3′,4,4′-*Tetramethyl*-1,1′-*binaphthalene*. Mp 173–174 °C, lit.,[6j] 160–163 °C, δ_H(CDCl$_3$) 2.54 (s, 6 H), 2.71 (s, 6 H), 7.21 (ddd, 2 H, 8.4, 6.5, 1.1 Hz), 7.39 (d, 2 H, J = 8.4 Hz), 7.31 (s, 2 H), 7.47 (ddd, 2 H, J = 8.7, 6.5, 1.3 Hz) and 8.13 (d, 2 H, J = 8.7 Hz).

4,4′,5,5′-*Tetramethyl*-1,1′-*binaphthalene*. ^{1}H NMR spectrum as reported,[26] mp 186–187 °C, lit.,[26] 185–186 °C.

4,4′,6,6′-*Tetramethyl*-1,1′-*binaphthalene*. Mp 195–196 °C, δ_H(CDCl$_3$) 2.54 (s, 6 H), 2.78 (s, 6 H), 7.12 (dd, 2 H, J = 8.6, 1.6 Hz), 7.30 (d, 2 H, J = 7.1 Hz), 7.32 (d, 2 H, J = 8.6 Hz), 7.40 (dd, 2 H. J = 7.1, 0.8 Hz) and 7.86 (s, 2 H).

5,5′-*Biacenaphthene*. ^{1}H NMR spectrum as reported.[26] Mp 174–176 °C, lit.,[26] 169 °C.

Oxidative Coupling of 1,5-*Dimethylnaphthalene*.—An attempt to use 1,5-dimethylnaphthalene in the general procedure above resulted in a mixture of three isomers of the dehydrodimer (GLC–MS) in very poor total yield. The ^{1}H NMR spectrum of the dehydrodimer mixture, separated by flash chromatography, indicated that the predominant product (*ca.* 60%) was the unsymmetrically bonded dehydrodimer 1′,4,5′,7-tetramethyl-1,2′-binaphthalene.

General Method for the Preparation of Perylenes.—Lithium powder (0.90 g, 130 mmol) was added to a solution of the binaphthalene derivative (1.6 mmol) in dry THF (100 cm^3) under Ar atmosphere. The reaction mixture was refluxed until the reaction was complete (2–4 h) according to TLC analysis. Then oxygen was bubbled into the solution until the colour changed from dark blue or green to orange. The lithium powder was removed by filtration and washed several times with dry THF. The THF solution was poured into water (100 cm^3) and the solution was extracted with dichloromethane (3 × 20 cm^3). Drying with magnesium sulfate and evaporation of the solvent gave a product which was further purified by column chromatography on silica, using pentane–dichloromethane (10:1) as the eluent.

3,10-*Dimethylperylene*. ^{1}H NMR spectrum as reported.[26] Mp 177–180 °C, lit.,[26] 199–200 °C.

2,3,10,11-*Tetramethylperylene*. Mp 175–177 °C, δ_H(CDCl$_3$) 2.53 (s, 6 H), 2.55 (s, 6 H), 7.48 (dd, 2 H, 8.5 Hz, J = 7.1 Hz), 7.85 (d, 2 H, J = 8.5 Hz), 7.99 (s, 2 H) and 8.14 (d, 2 H, J = 7.1 Hz).

2,4,9,11-*Tetramethylperylene*. Mp 245–247 °C, δ_H(CDCl$_3$) 2.58 (s, 6 H), 2.62 (s, 6 H), 7.28 (d, 2 H, 7.6 Hz), 7.59 (s, 2 H), 7.99 (d, 2 H, 7.6 Hz) and 8.07 (s, 2 H).

3,4,9,10-*Tetramethylperylene*. ^{1}H NMR spectrum as reported.[26]

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