

Formation of 1,2,4,5,6,8-Hexamethylantracene and its Radical Cation from 2,2',3,4',5,5',6-Heptamethyldiphenylmethane in Trifluoroacetic Acid

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Upon dissolution in trifluoroacetic acid, 1,2,4,5,6,8-hexamethylantracene (HMA) gives an orange-red solution due to the presence of its protonated form. Under the influence of diffuse daylight, the radical cation of HMA was slowly formed and detected by its EPR spectrum. The hyperfine splitting constants were determined to be 0.543 (9,10-H), 0.079 (3,7-H), 0.348 (1,4,5,8-Me₄) and 0.231 (2,6-Me₂) by combining the EPR and ENDOR methods and the assignments were confirmed by the shapes of the EPR spectra of HMA^{•+} in TFA/dichloromethane (line-broadening) and TFA-*d* (exchange of the four 3,7,9,10-hydrogens). The same EPR spectrum was obtained by keeping 2,2',3,4',5,5',6-heptamethyldiphenylmethane in TFA solution for an extended period.

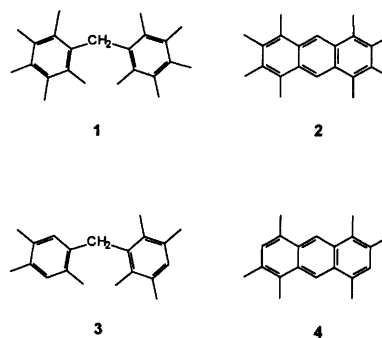
The ENDOR spectrum of HMA^{•+} in TFA was strongly temperature dependent, in that eight additional hf splittings due to a second radical appeared at lower temperatures (255–237 K). This fully reversible phenomenon is ascribed to equilibrium (i) being established at low temperature, the point of attack by trifluoroacetate ion being the 9-position.



It has recently been shown^{1–3} that 2,2',3,3',4,4',5,5',6,6'-decamethyldiphenylmethane (**1**) is rapidly cleaved by trifluoroacetic acid (TFA) and further converted, by a combination of methyl and hydride transfers, into a mixture of products, among which 1,2,3,4,5,6,7,8-octamethylantracene (**2**) is a minor (17% relative yield) but prominent one. A characteristic, very intense EPR spectrum of **2**^{•+} developed during the reaction, the oxidant being TFA alone and/or TFA in combination with light. Later,⁴ the same EPR spectrum was detected from treatment of highly methylated hexaphenyldistannanes and -germanes by aluminium chloride in dichloromethane; an ENDOR study confirmed earlier assignments of hyperfine splitting constants.^{1,2}

The oxidative self-coupling of durene by Co(III) or Mn(III) in TFA gave 2,2',3,4',5,5',6-heptamethyldiphenylmethane (**3**) as the major product, but a hexamethylantracene, most likely the 1,2,4,5,6,8-hexamethyl isomer, was formed as a by-product.⁵ The oxidation of

durene by Pd(II) in TFA likewise gave **3** as a product,⁶ and a well-resolved EPR spectrum with >120 lines accompanied the formation of **3** and was assigned to **3**^{•+}. In view of the facile **1** → **2** → **2**^{•+} conversion in TFA, this assignment was deemed less probable. Compound **3** indeed gave the same EPR spectrum merely upon being allowed to stand for a long period in TFA² (Fig. 1) and it was tentatively ascribed to the radical cation of 1,2,4,5,6,8-hexamethylantracene (**4**). We now provide full evidence that the EPR spectrum of Fig. 1 is that of **4**^{•+}, by showing that it is developed from authentic **4** upon treatment with TFA/light.



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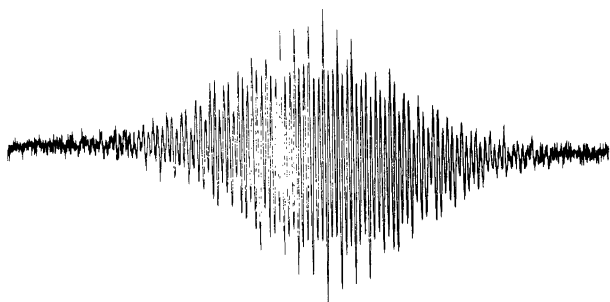


Fig. 1. EPR spectrum of a solution of 2,2',3,4,4',5,5'-heptamethyldiphenylmethane (**3**) in neat TFA, kept for ≈ 400 h in laboratory light (from Ref. 2). Sweep width 5.0 mT.

Results

Synthesis of 4. The synthesis of **4** was modeled upon that of **2**, in that a solution of 1,2,4,5-tetramethylbenzene (durene) and 2,4,5-trimethylbenzyl acetate was kept at ambient temperature in a solution of TFA, sulfuric acid and dichloromethane (2:2:1 by volume) for 1–2 h.² A 39% yield of crude **4** was obtained.

The same method was applied to several other systems, aiming at the preparation of less extensively methyl-substituted anthracenes, but led only to the formation of diphenylmethanes. The latter in principle are precursors to the anthracene derivatives, but apparently the oxidizing properties of the reaction mixture was not sufficient for cyclization to occur.

Electrochemistry of the $4^{\cdot+}/4$ system. Cyclic voltammetry of **4** in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 M) showed a quasi-reversible ($\Delta E_p = 80$ –90 mV) $1 e^-$ system with $(E_{pa} + E_{pc})/2 = 1.00$ V vs. Ag/AgCl and

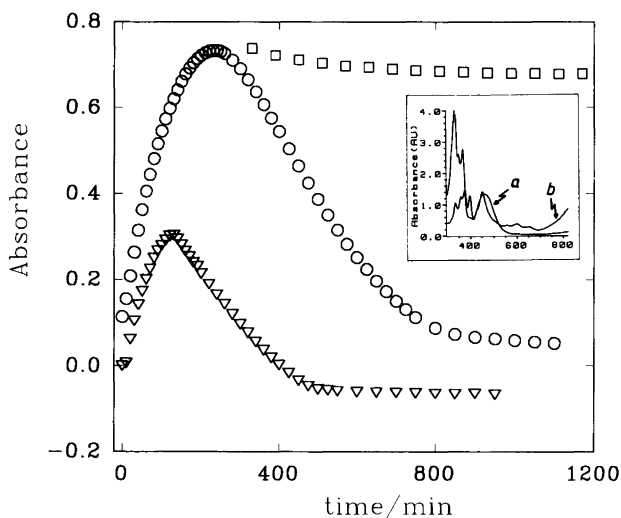


Fig. 2. Development of $[4^{\cdot+}]$ with time upon irradiation of a 0.35 mM solution of **4** in TFA (\circ) and TFA-*d* (Δ). The squares represent the case where irradiation was discontinued at $[4^{\cdot+}]_{\max}$ and the solution kept in the dark. The insert shows the spectrum of the TFA solution immediately after mixing (a) and at $[4^{\cdot+}]_{\max}$ (b).

an irreversible one with $E_{pa} = 1.53$ V at a sweep rate of 100 mV s^{-1} .

UV spectral behaviour of 4 in TFA and TFA-*d*. A 0.3–0.4 mM solution of **4** in dichloromethane/TFA (3/2 v/v), protected from light, initially had an orange–red colour due to the presence of the protonated form, 4-H^+ (Fig. 2, insert). Controlled irradiation by light from the spectrophotometer caused an increase in the radical cation concentration (Fig. 2, circles), as monitored by the average absorbance value for eleven wavelengths in the range 800–820 nm. Like $2^{\cdot+}$ (Ref. 2), $4^{\cdot+}$ exhibited a maximum in the near-infrared region around 900 nm, which, for technical reasons, could not be used for monitoring, so that the rising part of the maximum had to be used instead. $[4^{\cdot+}]$ rose to a maximum value after ≈ 4 h where the UV spectrum had the appearance of curve 2 of the insert of Fig. 2. This solution was dark green–brown. Continued irradiation over a period of 15 h eventually destroyed $4^{\cdot+}$. If irradiation was discontinued at some point, the resulting solution of $4^{\cdot+}$ was almost stable, as shown by the squares of Fig. 2. A 0.35 mM solution of **4** in dichloromethane/TFA-*d* (3/2 v/v) had a weaker, orange–yellow colour, and responded to irradiation in the same way as the TFA solution, (Fig. 2, triangles), except that the maximum in the radical concentration appeared earlier and was considerably lower. The initial rates of the two processes were 0.050 (in TFA) and 0.035 absorbance units per minute, respectively.

The EPR spectrum of $4^{\cdot+}$. When a saturated solution of **4** in neat TFA was thoroughly degassed with argon in an

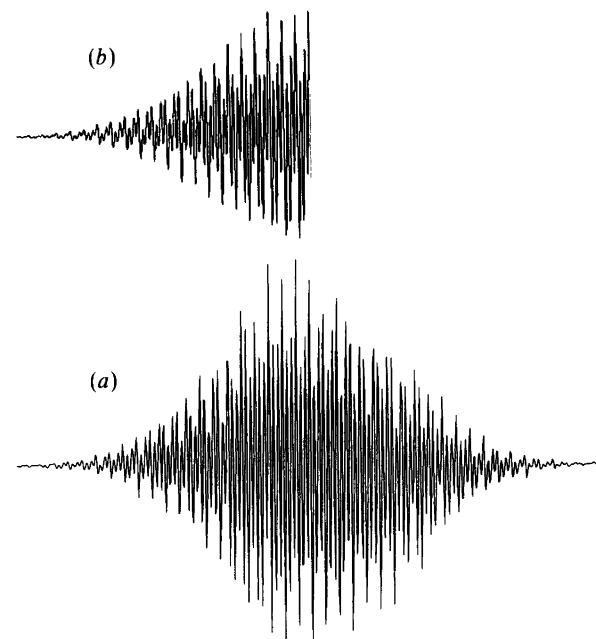


Fig. 3. (a) EPR spectrum of a solution of **4** in TFA, exposed to diffuse daylight for ≈ 10 h. (b) Simulated spectrum with $a = 0.543$ (2 H), 0.079 (2 H), 0.348 (12 H) and 0.231 mT (6 H), line width = 0.025 mT. Sweep width = 5.0 mT.

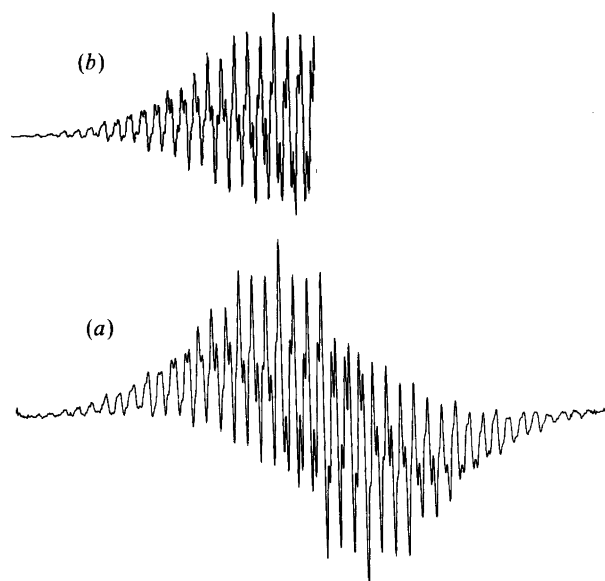


Fig. 4. (a) EPR spectrum of a solution of **4** in TFA/dichloromethane (50/50 v/v), exposed to diffuse daylight for ≈ 10 h. (b) Simulated spectrum with parameters as in Fig. 2(b), except with a line width of 0.040 mT. Sweep width = 5.0 mT.

EPR tube and kept in diffuse daylight, an intense signal [Fig. 3(a)] developed within a few hours. This spectrum was very stable and disappeared only after a period of 2–3 months in laboratory light. The same reaction occurred in TFA/dichloromethane (50/50 v/v) and gave a slightly less well resolved spectrum [Fig. 4(a)]. The light reaction of **4** in TFA-*d* was slower but eventually the EPR spectrum of Fig. 5(a) was recorded; its development could be

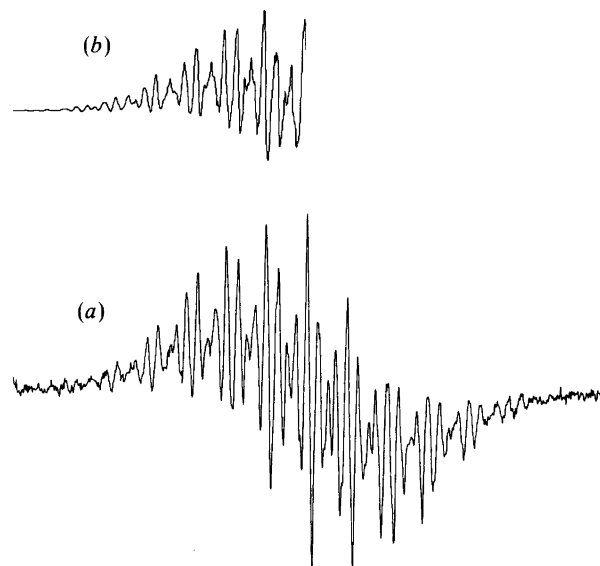


Fig. 5. (a) EPR spectrum of a solution of **4** in TFA-*d* after 24 h of H/D equilibration and addition of a small amount of 2,3-dichloro-5,6-dicyanobenzoquinone. (b) Simulated spectrum with $a = 0.083$ (2 D), 0.012 (2 D), 0.348 (12 H) and 0.231 mT (6 H), line width = 0.025 mT. Sweep width = 5.0 mT.

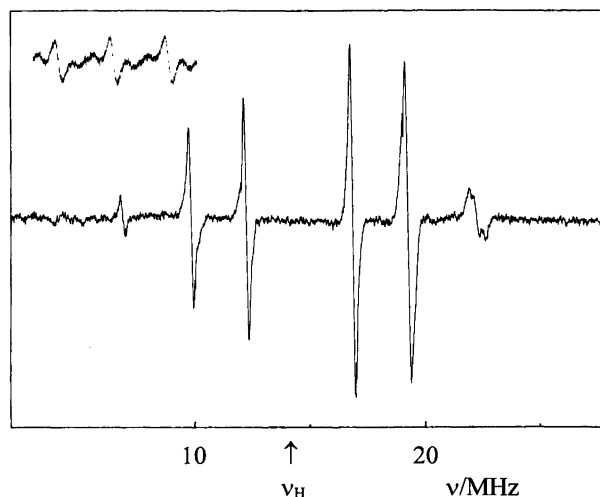


Fig. 6. ENDOR spectrum of $2^{+\bullet}$ in TFA at 237 K. The insert shows the middle part of the EPR spectrum (sweep width 0.50 mT). The Larmor frequency of hydrogen is indicated by ν_H .

speeded up drastically by the addition of an oxidant, such as 2,3-dichloro-5,6-dicyanobenzoquinone.

In order to determine the hfs values, ENDOR spectra were recorded at several temperatures. For calibration against published data on similar systems, the ENDOR spectrum of $2^{+\bullet}$ in TFA was first recorded. A spectrum of high quality (Fig. 6) could be obtained at 237 K, immediately above the freezing point of the solution. The hfs values determined from this spectrum were $a^{\text{H9,10}} = 0.543$, $a^{\text{methyl-1,4,5,8}} = 0.336$ and $a^{\text{methyl-2,3,6,7}} = 0.164$ mT, in good agreement with those derived from the ENDOR spectrum of $2^{+\bullet}$ at 193 K in dichloromethane,⁴ 0.539, 0.342 and 0.166 mT, and from the room-temperature EPR spectrum,^{1,2} 0.545, 0.334 and 0.167 mT, respectively. It was also noted that the ENDOR spectra of

Table 1. ENDOR and EPR spectral parameters associated with the radicals $2^{+\bullet}$, $4^{+\bullet}$ and $\text{CF}_3\text{COO-4}^\bullet$ in TFA.

Species	ENDOR hfs constant/MHz	EPR ^a hfs constant/mT	Multiplicity
$2^{+\bullet}$	15.33	0.547	2 H
	9.42	0.336	12 H
	4.60	0.164	12 H
$4^{+\bullet}$	15.21	0.543	2 H
	9.75	0.348	12 H
	6.64	0.237	6 H
	2.22	0.079	2 H
$\text{CF}_3\text{COO-4}^\bullet$	16.94	0.604	
	13.79	0.492	
	10.70	0.388	
	9.06	0.323	
	7.76	0.277	
	4.54	0.162	
	3.02	0.108	
	1.34	0.048	

^a At $g = 2.0026$.

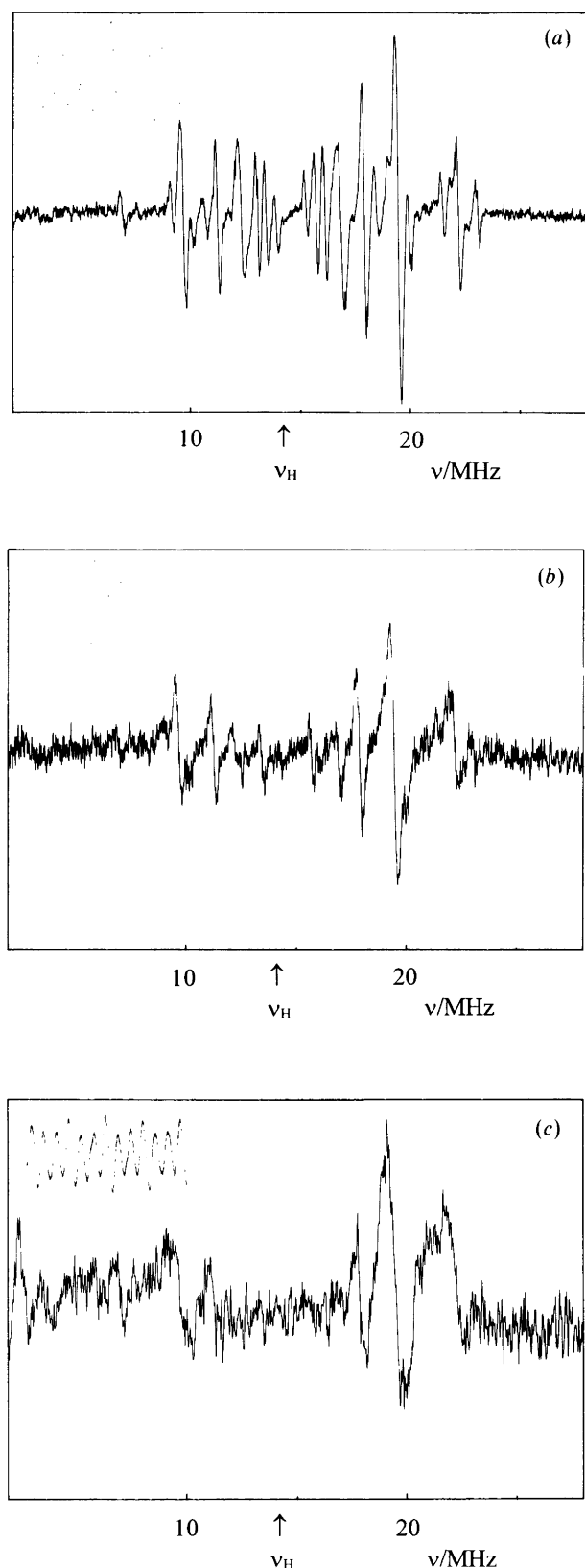


Fig. 7. ENDOR spectrum of a solution of **4** in TFA at (a) 237, (b) 270 and (c) 289 K. Inserts show the middle part of the corresponding EPR spectra (sweep width 0.50 mT). The Larmor frequency of hydrogen is indicated by ν_H .

2^+ exhibited a temperature effect, in that further splitting of the lines appeared at *higher* temperatures.

The ENDOR spectra of 4^{*+} in TFA, recorded in the interval from 237 to ≈ 290 K, showed a pronounced temperature effect. The low temperature signal contained 12 clearly detectable hf splittings due to hydrogen [Fig. 7(a) and Table 1], all of which remained detectable up to ≈ 255 K. At higher temperatures, the lines corresponding to eight of the splittings gradually became weaker, and at 270 K only five splittings could be discerned [Fig. 7(b)]. At 289 K, the spectrum was less distinct and only three splittings could be identified [Fig. 7(c)]. No temperature effect on the line positions (hf splittings) could be detected.

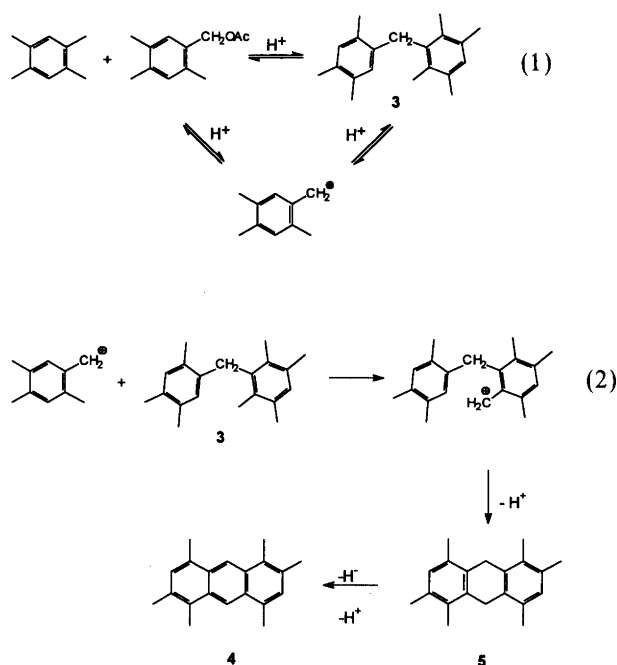
Four out of the 12 detected hfs constants (see Table 1) were consistent with simulations of the EPR spectra of 4^{*+} under the experimental conditions used in Figs. 3(a), 4(a) and 5(a), namely $a^{\text{H}9,10} = 0.543$, $a^{\text{H}3,7} = 0.079$, $a^{\text{methyl-1,4,5,8}} = 0.348$ and $a^{\text{methyl-2,6}} = 0.231$ mT [see Figs. 3(b) and 4(b)]. Note that the 6 H splitting of 0.231 mT is somewhat smaller than that obtained from the ENDOR spectrum, 0.237 mT, presumably because of the difference in temperature. The appearance of the simulated spectrum was extremely sensitive to this parameter, and use of $a^{6\text{H}} = 0.237$ mT led to a much worse fit. On the assumption that both types of ring hydrogen were exchanged in TFA-*d*, a simulation with $a^{\text{D}9,10} = 0.083$ and $a^{\text{D}3,7} = 0.012$ mT gave good agreement with the experimental spectrum [Fig. 5(b)]. The spectral width associated with these parameters could be approximately confirmed by spectral accumulation (~ 50000 spectra) in the outer wings of the spectra.

Returning to the analysis of the ENDOR spectra of 4^{*+} , the splittings appearing at low temperatures are assumed to originate from another radical in equilibrium with 4^{*+} . A logical candidate is the neutral radical formed by attack of trifluoroacetate ion at the 9-position of 4^{*+} , 9-CF₃COO-**4**^{*} (see below). Such a species would possess lower symmetry and, in fact, require eight hfs constants to hydrogen for a description of its EPR spectrum. By adding up the relative amplitudes of the two species at ≈ 240 K it was estimated that their relative concentrations are 1:1. The changes were fully reversible and support the suggestion of an equilibrium between the two radicals. We also noted that the EPR spectral lineshape changed in parallel with the appearance of the low-temperature ENDOR lines, indicating that a second spectrum becomes superimposed onto the spectrum of 4^{*+} . EPR spectra of an expanded portion around the central lines (sweep width 0.50 mT) are shown as inserts in Fig. 7.

Discussion

The synthetic and ENDOR/EPR spectral results demonstrate that the EPR-active species in solutions of **3** or **4** in TFA must be 4^{*+} , a radical cation which is stable for long periods of time under conditions of low light

intensity (laboratory light). At higher light intensities (unfiltered light from a spectrophotometer deuterium lamp) the radical cation was destroyed over a short period (Fig. 2). The ready formation of **4** from **3** or the precursor system of **3**, durene and 2,4,5-trimethylbenzyl acetate,^{2,6} can be explained in a similar way to the formation of **2** from **1** or precursor systems thereof. An equilibrium is set up [eqn. (1)], containing **3** and the benzylic cation preceding the formation of **3**, and then a hydride shift from **3** leads to cyclization to the dihydroanthracene derivative **5** [eqn. (2)]. A second hydride shift from the 9-position of **5** completes the transformation to **4**. This hydrocarbon has an $E^\circ(4/4^{+\bullet})$ of 1.00 V, ≈ 0.2 V above that of the $2^{+\bullet}/2$ redox couple, and should be easily oxidizable by the action of light upon its solution in TFA, as is known for similar aromatic and heteroaromatic compounds.⁷



Since the formation of **2** and/or $2^{+\bullet}$ was observed in a number of systems involving less methylated precursors and thus seems to represent an energy sink, one might wonder why the system discussed here stops at $4/4^{+\bullet}$. However, one critical step in the formation of more highly methylated derivatives from **4** or its precursors must be transfer of methyl cations from a suitable source, and this step may not be favourable in this system.

The appearance of a second radical in equilibrium with $4^{+\bullet}$ at lower temperatures deserves some comment. We ascribe it to the existence of the equilibrium of eqn. (3), an example of the initial step postulated for the mechanism



of most radical cation reactions with nucleophiles (oxidative substitution).⁸ Normally, this step is preceded

by fast electron transfer to some oxidant present and experimental evidence for the neutral radical is seldom obtained. The fact that this equilibrium is detectable in the system at hand is due to a lucky combination of factors: the high stability of $4^{+\bullet}$ and the weak oxidizing power of the system.

An alternative explanation might involve trifluoroacetoxylation of **4** in the 9-position with formation of 9-trifluoroacetoxy-1,2,4,5,6,8-hexamethylanthracene (**6**), as shown earlier⁹ for anthracene itself using Tl(III) trifluoroacetate/TFA as an oxidant. In that case, $6^{+\bullet}$ would correspond to the new radical. We deem this possibility less likely, since it is not easy to view the transformation $4 \rightarrow 6$ as being reversible. Further experimental and theoretical work is necessary to clarify in detail the temperature effect of both $2^{+\bullet}$ and $4^{+\bullet}$ in TFA, such as equilibrium constants and exchange rates. Such studies are underway.

Experimental

Materials and instrumentation. See Ref. 2 for details. ENDOR spectra were recorded using a Bruker ESP300/250 combined EPR and ENDOR spectrometer. The radio frequency was amplified using a 500 W EIN RF amplifier. The EPR microwave power was typically 0.5–2 mW and the RF power 400–500 W during the ENDOR experiments. The temperature was controlled using a Bruker VT4111 variable temperature unit.

1,2,4,5,6,8-Hexamethylanthracene (4). Durene (5.0 g, 37 mmol) and 2,4,5-trimethylbenzyl acetate (2.5 g, 13 mmol) were dissolved in a mixture of TFA (40 ml), concentrated sulfuric acid (20 ml) and dichloromethane (40 ml) and left at ambient temperature for 90 min. The precipitate (1.33 g of crude **4**, 39%) was filtered off and recrystallized once from toluene and once from cyclohexane, m.p. 206–208 °C. ¹H NMR (CDCl₃): δ 2.50 (s, 2,5-CH₃), 2.72, 2.79 (2 s of same intensity, 1,4,5,8-CH₃), 7.15 (2,3,7-H), 8.60 (s, 9,10-H). MS [m/z (% rel. int.)]: 262 (100, M^+), 247 (25), 231 (6), 131 (7).

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