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Formation of the Radical Cation of 1,2,3,4,5,6,7,8-Octamethylanthracene from Bis(pentamethylphenyl)methane in Trifluoroacetic Acid

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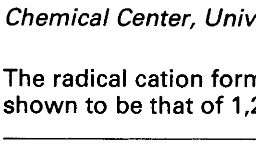
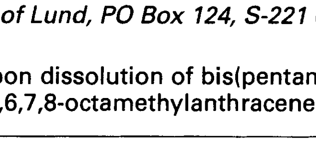
The radical cation formed upon dissolution of bis(pentamethylphenyl)methane in trifluoroacetic acid has been shown to be that of 1,2,3,4,5,6,7,8-octamethylanthracene.

It was recently claimed[1] that bis(pentamethylphenyl)methane **1** is converted to a π-stabilized radical cation, **1**$^{+\bullet}$, upon dissolution in trifluoroacetic acid (TFA) or oxidation by nitrosonium ion in dichloromethane. The structure of **1**$^{+\bullet}$ was inferred by ESR and time-resolved spectroscopy, and its stability with respect to the 'normal' radical cation, **2**$^{+\bullet}$, was estimated to be ≈ 10 kcal mol^{-1} (1 cal = 4.184 J) from cyclic voltammetry data.

In view of the propensity of polymethylaromatics to undergo intermolecular alkyl shifts during anodic or metal ion oxidation[2,3] and their high reactivity toward proton attack,[4] we deemed it more likely that the ESR spectrum referred to above would be that of a particularly stable system, accessible from **1** under acidic conditions *via* a series of alkyl/hydride transfer steps. An obvious candidate would be the radical cation of 1,2,3,4,5,6,7,8-octamethylanthracene **3**.



1$^{+\bullet}$



2$^{+\bullet}$

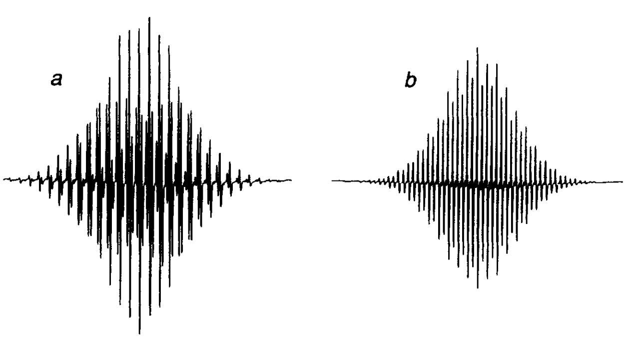


Fig. 1 ESR spectrum of (*a*) 1,2,3,4,5,6,7,8-octamethylanthracene in TFA after 15 h and (*b*) in $[^2H_1]$TFA after 20 h. The sweep width was 5 mT; note that the outer, very weak lines fall outside this range.

Synthesis of **3**[5] and inspection of the ESR spectrum of its stable radical cation [Fig. 1(*a*), for the spectrum of a **1**–TFA solution and its simulation, *cf.* ref. 1] in TFA confirmed this assumption. Upon dissolution of **3** in TFA an orange-red coloured solution (λ_{max} = 466 nm) was obtained which according to its visible spectrum (Fig. 2) contained only a very low concentration of **3**. The ESR spectrum of this solution, taken immediately after mixing, was rather weak but could be strongly enhanced by keeping the solution overnight or addition of tris(4-bromophenyl)aminium hexachloroantimonate. This spectrum is identical in all respects to the one obtained from a solution of **1** in TFA.

We suggest that the initial orange-red species is the protonated anthracene, existing in equilibrium with **3** in TFA. This was substantiated by performing the reaction in $[^2H_1]$-TFA which provided an ESR spectrum of **3**$^{+\bullet}$ where the hyperfine coupling to the 9,10-hydrogens had been changed in the expected way [Fig. 1(*b*), a^{2D} changing from 0.545 mT to 0.083 mT and I from 1/2 to 1]. An identical spectrum was obtained by dissolution of **1** in $[^2H_1]$TFA.

Upon work-up of a solution of **1** in TFA, kept at room temperature for 48 h, a 3% yield of **3** was obtained. Cyclic voltammetry of **3** in dichloromethane–Bu_4NPF_6 (0.1 mol dm^{-3}) displayed a reversible redox system with $(E_p + E_c)/2$ = 0.86 V (*vs.* Ag/AgCl, at a sweep rate of 50 mV s^{-1}). The ESR spectrum of **3**$^{+\bullet}$ appeared with high intensity in TFA solutions of the following systems: pentamethylbenzyl acetate + mesitylene, durene or pentamethylbenzene; 2,2′,3,3′4,4′,5,5′,6- or 2,2′,3,3′,4,4′,5,6,6′-nonamethyldi-

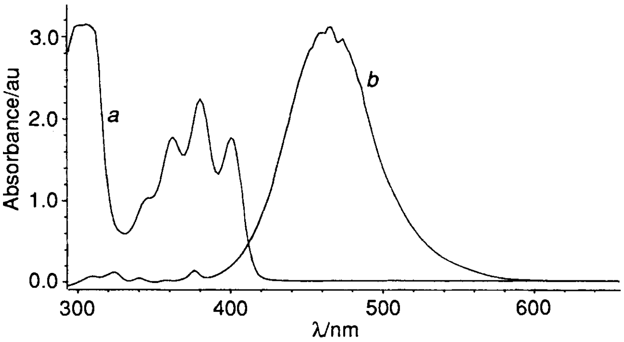


Fig. 2 UV-VIS spectrum of 1,2,3,4,5,6,7,8-octamethylanthracene in (*a*) dichloromethane (0.93 mmol dm^{-3}) and (*b*) TFA (1.28 mmol dm^{-3})

phenylmethane; 1,2,3,4-tetramethylbenzene + formaldehyde; 2,2′,3,3′,4,4′,5,5′-octamethyldiphenylmethane + formaldehyde. It thus seems that $\mathbf{3}^{+\bullet}$ is a ubiquitous species in acidic solutions of polymethylbenzenes.

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