The Aromatic Cation Radical from Bis(pentamethylphenyl)methane Oxidation. Structural Reassignment by X-Ray Crystallography

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The aromatic cation radical formed by the oxidation of bis(pentamethylphenyl)methane has been isolated as its crystalline hexachloroantimonate, and shown by X-ray crystallography to be the 1,2,3,4,5,6,7,8-octamethylanthracene cation radical.

We recently reported[1] an unusual structure of the aromatic cation radical resulting from the spontaneous oxidation of bis(pentamethylphenyl)methane (previously described as decamethyldiphenylmethane or DDM) that was promoted by the acidic solvent trifluoroacetic acid. Since the cation radical ($DDM^{+\bullet}$) was deduced from its diagnostic ESR spectrum, we sought its structural confirmation by isolation of the crystalline salt followed by X-ray crystallography. Repeated attempts to isolate the crystalline cation radical from trifluoroacetic acid were unfruitful, and we have now turned to the alternative (Lewis acid) oxidation of DDM based on antimony pentachloride.[2-4] Indeed the treatment of a dichloromethane solution of DDM at 25 °C with various amounts of $SbCl_5$ (or a combination of antimony pentachloride and tetra-n-butylammonium chloride) rapidly led to an insoluble black microcrystalline salt which afforded the same ESR spectrum reported previously.[1] However, the desired single crystals of the cation-radical salt that were suitable for X-ray crystallography could not be grown. Fortunately, overnight treatment of the homologous octamethyldiphenylmethane (ODM)[5] with an equivalent amount of $SbCl_5$ in dichloromethane at −10 °C led to black crystals of the paramagnetic salt, which also showed the characteristic ESR spectrum [a(2H, 12H, 12H) = 5.45, 3.34, 1.67 G].[1] Careful inspection of the crop of well-formed crystals revealed cocrystallization of a mixture of black thin plates **1** and parallelepipeds **2**, with the former predominating (~80%). X-Ray crystallography† established both **1** and **2** to consist of the $SbCl_6^-$ salt of 1,2,3,4,5,6,7,8-octamethylanthracene cation radical ($OMA^{+\bullet}$), as shown by

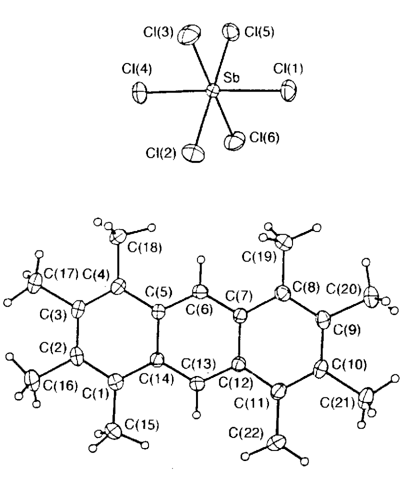

Fig. 1 ORTEP diagram of the 1,2,3,4,5,6,7,8-octamethylanthracene cation radical–hexachloroantimonate salt ($OMA^{+\bullet}$ $SbCl_6^-$)

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† *Crystal data* for **1**: $C_{22}H_{26}^{+\bullet}$ $SbCl_6^-$, M = 624.93, monoclinic, space group $P2_1/c$, a = 8.333(4), b = 10.984(4), c = 13.572(7) Å, β = 100.25(4)°, V = 1222 Å^3, Z = 2, Mo-Kα radiation (λ = 0.71073 Å), R = 0.031, crystal dimensions 0.50 × 0.44 × 0.12 mm. For **2**: $C_{22}H_{26}^{+\bullet}$ $SbCl_6^-$, M = 624.93, triclinic, space group $P\bar{1}$, a = 8.034(3), b = 12.465(5), c = 13.128(4) Å, α = 106.18(3), β = 97.28(3), γ = 89.83(3)°, V = 1252 Å^3, Z = 2, R = 0.023, crystal dimensions 0.44 × 0.28 × 0.26 mm. Both structures were solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares analysis. The 1616 and 2943 unique observed structure amplitudes [$I > 3\sigma(I)$] for **1** and **2**, respectively, were collected at 19 °C on a Nicolet R3m/V automatic diffractometer. All calculations were carried out with Nicolet's SHELXTL PLUS (1987) series of crystallographic programs. Atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

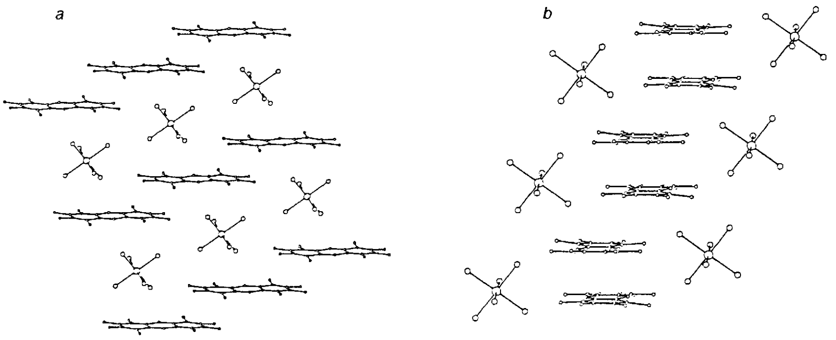

Fig. 2 Stacking arrangement of OMA$^{+\bullet}$ as separate and paired units in (*a*) **1** and (*b*) **2**, respectively

the ORTEP diagram in Fig. 1. Interestingly, the two crystalline habits differ primarily by the stacking of the aromatic planes. (The bond distances for OMA$^{+\bullet}$ in **1** and **2** are the same within 3σ.) Thus, the stacking diagram for **1** in Fig. 2(*a*) shows the essentially planar aromatic skeleton of OMA$^{+\bullet}$ (with the methyl groups slightly out of plane) to exist as single, separate cationic units. By contrast, the minor crystalline habit **2** consists of the cation radical lying in more or less vertical stacks [Fig. 2(*b*)]; each stack containing OMA$^{+\bullet}$ in pairwise units. The incipient interaction within such (OMA$^{+\bullet}$)$_2$ pairs is indicated by (*i*) the close (van der Waals) separation of 3.42 Å [compared to the significantly wider (3.95 Å) distance between the paired units] and (*ii*) the distortion (~0.3 Å) of the methyl groups away from the aromatic planes about the centre of inversion in the middle of (OMA$^{+\bullet}$)$_2$. Such a pairwise interaction of the cation radical is strongly reminiscent of the arrangement recently found in the crystals of the methylviologen cation radical (MV$^{+\bullet}$).[6,7]

The crystallographic results necessitate the structural reassignment of the ESR spectrum originally observed[1] to that of OMA$^{+\bullet}$, as also indicated recently by Eberson and Radner.[8] The facile formation of OMA$^{+\bullet}$ from the polymethylated diphenylmethanes DDM and ODM under the mildly oxidizing conditions (represented by trifluoroacetic acid and antimony pentachloride) points to the enhanced stabilization of OMA$^{+\bullet}$; sufficient for the facile loss of an *ortho*-methyl group of DDM,[8] and the gain of an additional carbon by ODM (most likely from the dichloromethane solvent). However, the structural reassignment does not preclude the existence of the stabilized cation radical DDM$^{+\bullet}$, since it would otherwise leave unexplained the stoichiometrically reversible NO$^+$ oxidation[9]–*N*-methylphenothiazine reduction, as well as the transient photochemical and electrochemical results presented earlier.[1] We hope that further studies in progress will resolve this ambiguity.

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