242. Dimeric Radical Cation of 4,5,7,8-Tetramethyl[2.2]paracyclophane

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Summary

Electrolytic oxidation of 4,5,7,8-tetramethyl[2.2]paracyclophane (I) yields a paramagnetic species which by ESR. spectroscopic evidence must be ascribed to the dimeric radical cation $I_2{\cdot}^{\oplus}$. Analogous dimers are obtained from the 12,13,15,16-tetradeuterio- and 1,1,10,10,12,13,15,16-octadeuterio-derivatives of I so that all coupling constants can be unequivocally assigned to sets of equivalent protons. The hyperfine data for $I_2{\cdot}^{\oplus}$ are consistent with an effective D_{2h} or D_{2d} symmetry, the four benzene rings lying in parallel planes.

Introduction. - It is well-known that benzenoid hydrocarbons and their methyl-substituted derivatives afford dimeric radical cations when oxidized under certain conditions [1]. Since the π-spin population in the dimers is evenly distributed between the two equivalent aromatic moieties, the identification of these paramagnetic species follows readily from their hyperfine data. The generally accepted proposal for the structure of the dimeric radical cations is that the two π-systems involved lie in parallel planes, on top of each other, the interplanar distance being *ca.* 3Å. Indirect experimental evidence in support of such a structure has recently been provided by the study of the monomeric radical cation of [2.2](9,10)anthracenophane [2].

In the present paper, we report the first observation that cyclophanes themselves can also form dimeric radical cations in which four aromatic moieties are successively superimposed. The pertinent compound yielding such a dimer is 4,5,7,8-tetramethyl[2.2]paracyclophane (I) [3] which has an ionization potential of 7.5 eV, *i.e.* 0.6 eV lower than the parent [2.2]paracyclophane (8.1 eV) [4]. The present paper describes the ESR. spectra of the dimeric radical cations produced from I and its 12,13,15,16-tetradeuterio- and 1,1,10,10,12,13,15,16-octadeuterio-derivatives (I-d_4 and I-d_8, respectively). The studies of the corresponding radical anions and monomeric radical cations will be reported elsewhere [5].

Results. - The paramagnetic species, of which the ESR. spectra will be considered below, were generated by electrolytic oxidation of the tetramethyl[2.2]paracyclophane I and its deuterated derivatives, I-d_4 and I-d_8, within a cell constructed in this laboratory [6]. This cell has a cylindrical shape and contains a helical gold anode with a straight platinum cathode along its axis. A mixture of methylene chloride, trifluoro-

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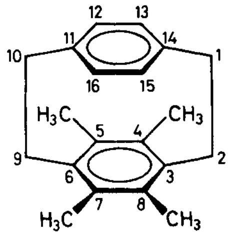
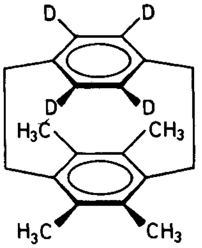
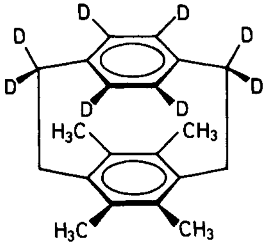


I



I-d$_4$

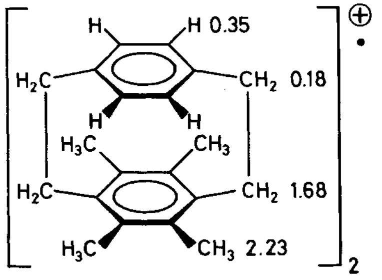


I-d$_8$

acetic acid and its anhydride in a 10:1:1 ratio [7] served as the solvent to which 0.01 M tetrabutylammonium perchlorate was added as the supporting salt. At the low temperatures (−70 to −90°) employed in the electrolysis, the half-lives of the formed paramagnetic species were *ca.* 20 min and no significant contributions from the monomeric radical cations [5] could be inferred from the ESR. spectra.

Figures 1, 2 and *3* show the ESR. spectra observed upon oxidation of I, I-d$_8$ and I-d$_4$, respectively, under the above-mentioned conditions; also reproduced are the corresponding computer simulated curves. In the case of I (*Fig. 1*), the simulation makes use of three coupling constants, 1.68, 0.35 and 0.18 Gauss[2]), each due to eight equivalent protons, in addition to a value of 2.23 Gauss arising from a set of twenty-four protons. On passing from I to I-d$_8$, the two minor proton coupling constants (0.35 and 0.18 Gauss) are superseded by unresolved splittings (0.054 and 0.028 Gauss, respectively) from two sets of eight equivalent deuterons so that the ESR. spectrum (*Fig. 2*) displays solely the two major values (2.23 and 1.68 Gauss). Replacement only of the larger one of the two minor proton coupling constants (0.35 Gauss) by an unresolved deuteron splitting (0.054 Gauss) occurs, on the other hand, in the spectrum obtained from I-d$_4$ (*Fig. 3*). Since, in this case, the smallest proton coupling constant (0.18 Gauss) persists, but cannot be resolved, substantial inhomogeneous line broadening results. It accounts for the apparent paucity of hyperfine components in the spectrum.

Discussion. – The hyperfine data determined from the ESR. spectra in *Figures 1, 2* and *3* leave no doubt that the paramagnetic species giving rise to them are the dimeric radical cations, $I_2 \cdot {}^{\oplus}$, $(I\text{-}d_8)_2 \cdot {}^{\oplus}$ and $(I\text{-}d_4)_2 \cdot {}^{\oplus}$, respectively. Interpretation of these data leads to the following unequivocal assignment of the coupling constants to sets of equivalent protons in the dimer $I_2 \cdot {}^{\oplus}$.



Experimental error: ±0.01;
all values in Gauss.

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[2]) 1 Gauss = 10^{-4} Tesla.

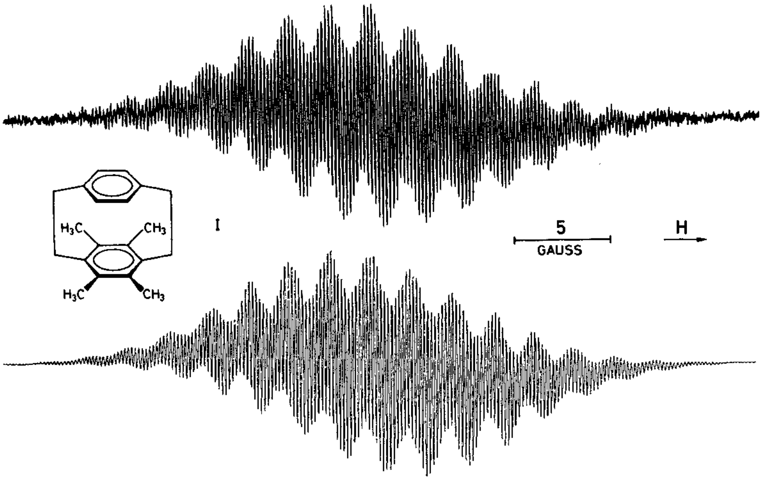

Fig. 1. *ESR. spectrum of the dimeric radical cation* $I_2{}^{\cdot\oplus}$. Top: experimental spectrum. Solvent: $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ 10:1:1; Temp.: −80°. Bottom: computer simulated spectrum. Coupling constants (Gauss): 2.23 (24H), 1.68 (8H), 0.35 (8H) and 0.18 (8H). Line-shape: Lorentzian; line-width: 0.16 Gauss.

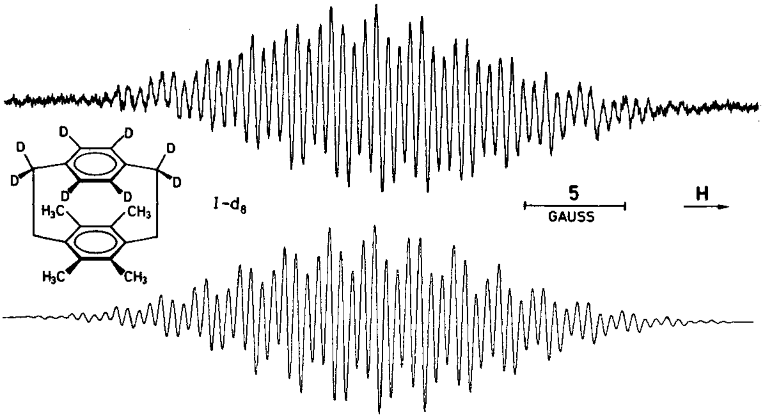

Fig. 2. *ESR. spectrum of the dimeric radical cation* $(I\text{-}d_8)_2{}^{\cdot\oplus}$. Top: experimental spectrum taken under the same conditions as that in *Figure 1*. Bottom: computer simulated spectrum. Coupling constants (Gauss): 2.23 (24H), 1.68 (8H), 0.054 (8D) and 0.028 (8D). Line-shape: Lorentzian; line-width: 0.16 Gauss.

The coupling constant of the methyl protons (2.23 Gauss) is by a factor 0.4 smaller than the corresponding value found for the monomeric radical cation $I^{\cdot\oplus}$ (5.7 Gauss) [5]. This factor compares nicely with the ratio of the analogous coupling constants for the dimeric and monomeric radical cations of 9,10-dimethylanthracene (3.51 *vs.* 8.00

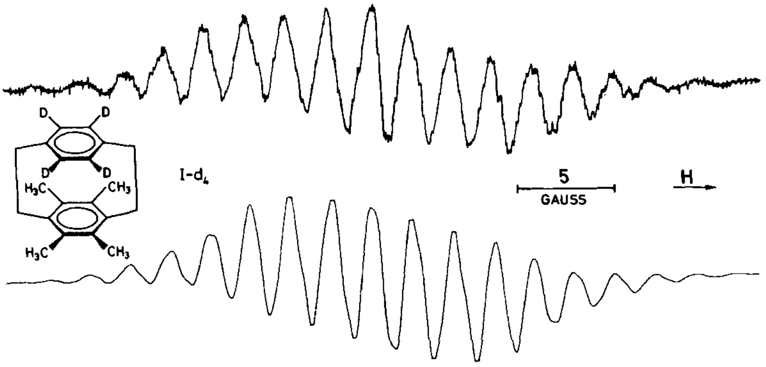

Fig. 3. *ESR. spectrum of the dimeric radical cation* (I-d$_4$)$_2$ · $^{\oplus}$. Top: experimental spectrum taken under the same conditions as that in *Figure 1*. Bottom: computer-simulated spectrum. Coupling constants (Gauss): 2.23 (24H), 1.68 (8H), 0.18(8H) and 0.054 (8D). Line-shape: Lorentzian; line-width: 0.20 Gauss.

Gauss) [2]. On the whole, the ESR. study of $I_2 \cdot {}^{\oplus}$ bears out the expectation that in the dimeric (as well as in the monomeric) radical cations of I the bulk of the π-spin population should be accommodated in the aromatic moieties having the lower ionization potential, i.e. in the more heavily substituted benzene rings.

The multiplicities found for the sets of equivalent protons in $I_2 \cdot {}^{\oplus}$ point to an effective symmetry of the dimer. 'Effective' means that the two molecules involved need not be held in a rigid geometry of the given symmetry, but can fluctuate among sterically and/or electronically more favourable orientations of lower symmetry. Such a motion must, however, be rapid on the hyperfine time-scale ($\sim 10^7$ s^{-1}) in order to account for the observed ESR. spectra in which no substantial exchange-broadening of lines is detected (see, *e.g. Fig. 1*; line-width: 0.16 Gauss).

The effective symmetry, in turn, provides some information on the structure of the dimeric radical cation. On the assumption that the four benzene rings lie in parallel planes and in an essentially eclipsed arrangement, the three structures (A, B and C) depicted in *Figure 4* are possible. Of these structures, the last one (C) has the symmetry

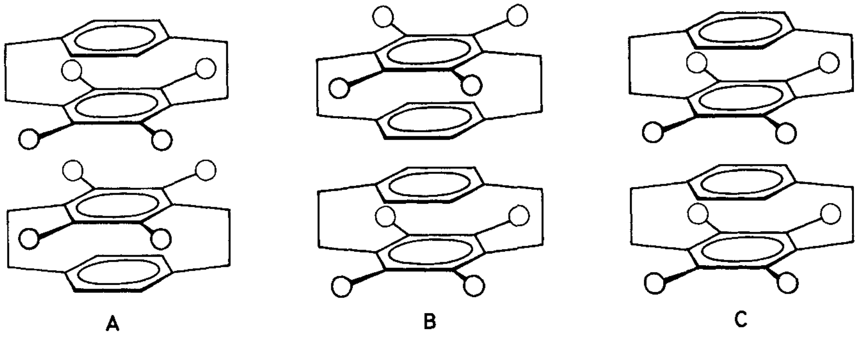

Fig. 4. *The three alternative structures for the dimeric radical cation* $I_2 \cdot {}^{\oplus}$ *in which the two molecules of 4,5,7,8-tetramethyl[2.2]paracyclophane (I) lie in parallel planes and in an essentially eclipsed arrangement.* The circles represent methyl groups.

C_{2v} and is thus inconsistent with the experimental data. On the contrary, the ESR. spectroscopic data are in perfect accord with an effective symmetry D_{2h} characteristic of both remaining structures (A und B). Theoretical arguments may be advanced in favour of either structure: whereas for steric reasons B should be preferred (closer approach of the molecules in absence of the methyl groups at the benzene rings), consideration of the electron distribution supports A (larger interaction energy of the relevant highest bonding orbitals which are essentially localized on the methyl substituted rings). The multiplicities of the sets of protons in $I_2 \cdot {}^{\oplus}$ can also be reconciled with an effective symmetry D_{2d}. The two structures of this symmetry are analogous to A and B, but one molecule is twisted by 90° relative to the other. Which of the four structures in question, A or B or one of their D_{2d} counterparts actually applies to $I_2 \cdot {}^{\oplus}$ cannot be decided on the grounds of the existing experimental evidence.

Source of compounds. – 4,5,7,8-Tetramethyl[2.2]paracyclophane (I) was synthesized by *Jenny & Davatz* [3]. Analogous procedure yielded the two deuterated compounds I-d_4 and I-d_8; their preparation will be described in another paper [5].

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