135. The Radical Cations of 4,5,7,13,15,16-Hexamethyl- and 4,5,7,8,12,13,15,16-Octamethyl[2.2]paracyclophane

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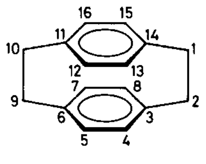
Summary

4,5,7,13,15,16-Hexamethyl- (**3**) and 4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane (**4**) have been oxidized to their radical cations in solution under relatively mild conditions. Substantial hyperfine splittings in the ESR. spectra of $\mathbf{3}^{\underset{\cdot}{\oplus}}$ and $\mathbf{4}^{\underset{\cdot}{\oplus}}$ arise from the methyl protons, whereas those from methylene protons are very small. This result indicates that the ethano bridges, unlike the methyl substituents, are rather ineffective in delocalizing the positive charge in $\mathbf{3}^{\underset{\cdot}{\oplus}}$ and $\mathbf{4}^{\underset{\cdot}{\oplus}}$. It is in line with the interpretation proposed previously to rationalize the gas-phase ionization potentials of multiply bridged $[2_N]$cyclophanes and methyl derivatives of [2.2]paracyclophane. The π-spin distributions in $\mathbf{3}^{\underset{\cdot}{\oplus}}$ and $\mathbf{4}^{\underset{\cdot}{\oplus}}$ are discussed in terms of a simple model in which the singly occupied orbitals are represented as the antibonding combinations of two benzene HOMO's.

Introduction. – [2.2]Paracyclophane (**1**) is relatively resistent to oxidation in solution, unless one or both of its benzene rings are substituted by several electron-donating groups. Recently, it has been reported that the radical cation of 4,5,7,8-tetramethyl[2.2]paracyclophane (**2**) was generated under rather rigorous conditions [1]. The present paper deals with the radical cations of more highly substituted derivatives of **1**, namely the 4,5,7,13,15,16-hexamethyl- (**3**) and 4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane (**4**) [2]. Both, $\mathbf{3}^{\underset{\cdot}{\oplus}}$ and $\mathbf{4}^{\underset{\cdot}{\oplus}}$ are prepared under milder



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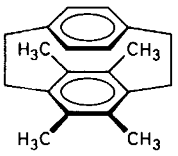

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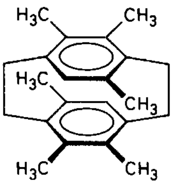

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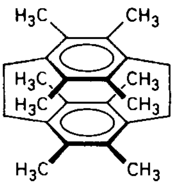

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conditions than $\mathbf{2}^{\cdot\oplus}$, in accord with the gas-phase ionization potentials of **2**, **3** and **4** which decrease in this order [3] [4].

Results. - Intensive ESR. spectra were observed upon electrolytic oxidation of **3** and **4** at 193 K, either in CH_2Cl_2 (with $Bu_4N^{\oplus}ClO_4^{\ominus}$ as the supporting salt), or in $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ 10:1:1 (*v/v/v*). By contrast, reaction of **3** with $AlCl_3$ in CH_2Cl_2 failed to produce signals amenable to analysis, while an analogous treatment of **4** led to an ESR. spectrum of low intensity. It is noteworthy that, in contrast to **2** [5], no dimeric radical cations were obtained by electrolysis of **3** and **4** in $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$.

The ESR. spectrum of $\mathbf{3}^{\cdot\oplus}$ (*Fig. 1*, top) was fitted by computer simulation (*Fig. 1*, bottom) with the use of three coupling constants $a_{H(4,16-CH_3)} = 0.660 \pm 0.008$, $a_{H(7,13-CH_3)} = 0.542 \pm 0.008$ and $a_{H(5,15-CH_3)} = 0.111 \pm 0.005$ mT, each for a set of six protons in two equivalent methyl substituents. The assignments of these values to protons in individual methyl groups of $\mathbf{3}^{\cdot\oplus}$ have been based on a MO-model presented in the *Discussion*. The hyperfine splittings from the two equivalent ring protons and the eight, pairwise equivalent methylene protons in $\mathbf{3}^{\cdot\oplus}$ are too small to be resolved (< 0.03 mT).

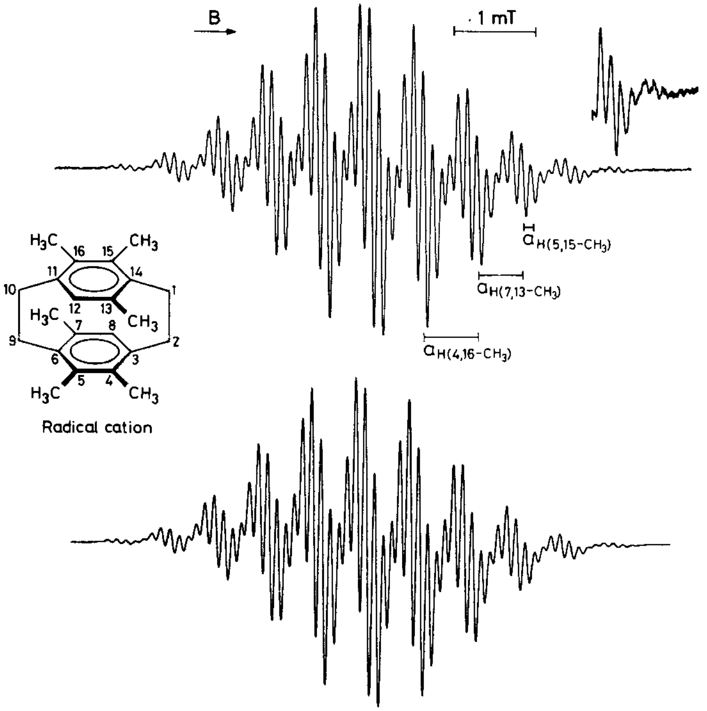

Fig. 1. Top: *ESR. spectrum of the radical cation of 4,5,7,13,15,16-hexamethyl[2.2]paracyclophane* (**3**) (Solvent $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ 10:1:1 (*v/v/v*), temperature 193 K). Bottom: *Computer simulated spectrum* (Coupling constants 0.660 (6 H), 0.542 (6 H) and 0.111 mT (6 H). Line-shape *Lorentzian*. Line-width 0.04 mT)

The simple ESR. pattern of $4^{\oplus}$ (*Fig. 2*, top) is due to a single set of 24 protons in the eight equivalent methyl substituents. The spacing of the equidistant lines yielded readily the coupling constant $a_{H(4,5,7,8,12,13,15,16-CH_3)} = 0.435 \pm 0.003$ mT.

Amplification of the spectrum (*Fig. 2*, bottom) gave prominence to two sets of ^{13}C-satellite lines which arise from isotopes in eight (outer set of broader lines) and four equivalent C-sites (inner set of narrower lines). They have been attributed to the ^{13}C-nuclei in the eight methyl-substituted and the four ethano-bridged

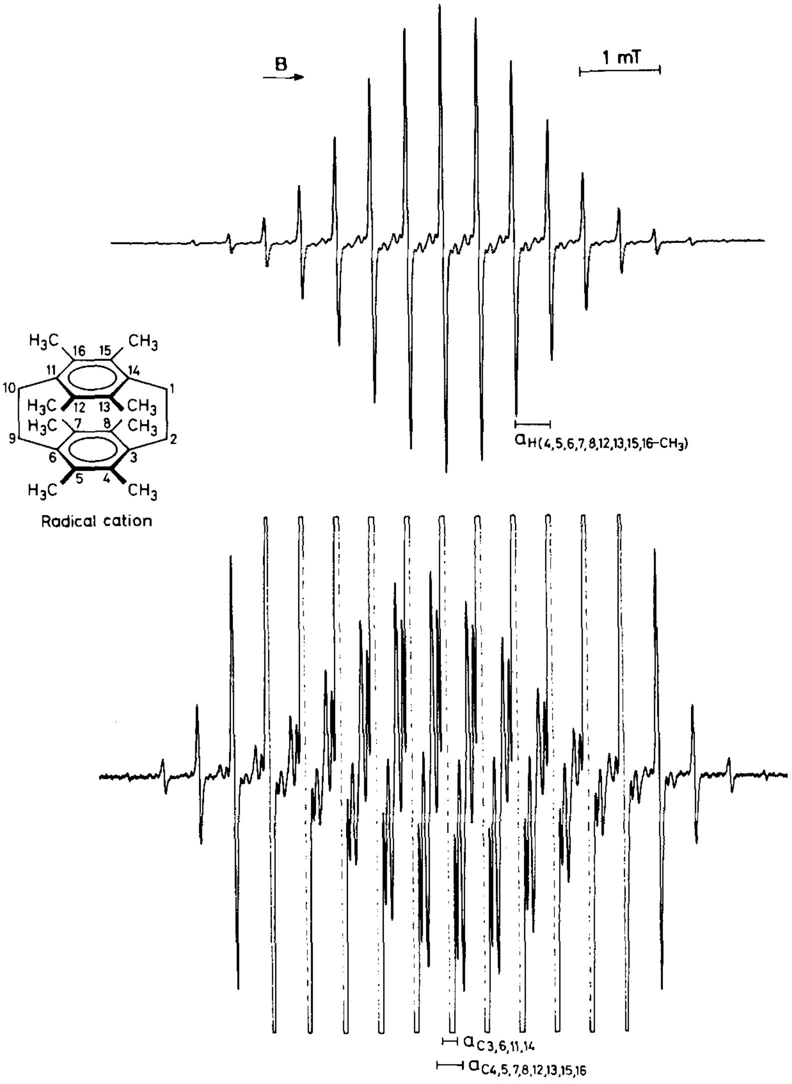

Fig. 2. Top: *ESR. spectrum of the radical cation of 4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane* (**4**) (Solvent $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ 10:1:1 (*v*/*v*/*v*), temperature 193 K). Bottom: *The same spectrum amplified* (in order to render the ^{13}C-satellite lines evident)

benzene π-centres, respectively. The pertinent coupling constants are $a_{\mathrm{C}(4,5,7,8,12,13,15,16)} = 0.328 \pm 0.003$ and $a_{\mathrm{C}(3,6,11,14)} = 0.182 \pm 0.002$ mT. The g-factor of $\mathbf{3}^{\oplus\cdot}$ and $\mathbf{4}^{\oplus\cdot}$ is 2.0026 ± 0.0001.

Discussion. - The orbitals of [2.2]paracyclophane (**1**), multiply bridged [2_{N}]-cyclophanes and substituted derivatives of **1** are conveniently represented by linear combinations of two benzene π-MO's [3] [4] [6]. For those orbitals which are singly occupied in the corresponding radical cations, the combinations are 'anti-bonding', *i.e.*, they exhibit a node between the benzene rings. It has been shown in a previous study [3] that the σ-MO's of the ethano bridges can not appreciably interact with the benzene HOMO's in such antibonding combinations. Thus, the ethano bridges are rather ineffective in lowering the gas-phase ionization potential of cyclophanes by delocalizing positive charge in the radical cations. On the other hand, introducing methyl substituents into the benzene rings of **1** reduces the ionization potential by an extent comparable to the effect of an analogous substitution on unsaturated and aromatic compounds [4]. The substantial coupling constants observed for the methyl protons in the radical cations of 4,5,7,13,15,16-hexamethyl- (**3**) and 4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane (**4**), when contrasted to the negligible splittings from the methylene protons, are fully consistent with these previous findings, since they point to a dominant effect of the methyl substituents in delocalizing the positive charge in $\mathbf{3}^{\oplus\cdot}$ and $\mathbf{4}^{\oplus\cdot}$.

The experimental results for $\mathbf{4}^{\oplus\cdot}$, $a_{\mathrm{H}(4,5,7,8,12,13,15,16-\mathrm{CH_3})} = 0.435$ mT and $a_{\mathrm{H}(1,2,9,10-\mathrm{CH_2})} \approx 0.008$ mT, compare favourably with the analogous data for the dimeric radical cation of durene (**5**), $a_{\mathrm{H}(1,2,4,5,1',2',4',5'-\mathrm{CH_3})} = 0.50$ mT and $a_{\mathrm{H}(3,6,3',6')} < 0.02$ mT [7], as well as with the halved values for the monomeric species $\mathbf{5}^{\oplus\cdot}$, $1/2\ a_{\mathrm{H}(1,2,4,5-\mathrm{CH_3})} = 1/2\ (1.059) = 0.530$ mT and $1/2\ a_{\mathrm{H}(3,6)} = 1/2\ (0.078) = 0.039$ mT [8]. This similarity strongly suggests that, due to the dominant effect of the methyl substituents, the π-spin distributions on the benzene rings are alike in the three radical cations. The 'antisymmetric' benzene HOMO ψ_{A}, which properly accounts for such distributions in $\mathbf{5}^{\oplus\cdot}$ and $(\mathbf{5})_2^{\oplus\cdot}$, should thus also be a suitable MO to deal with the π-spin populations on a benzene ring of $\mathbf{4}^{\oplus\cdot}$. This HOMO has large LCAO-coefficients at the methyl substituted π-centres and its nodal plane passes through the ethano bridges (*Fig. 3*, left). Beside being in accord with the proton hyperfine structure of $\mathbf{4}^{\oplus\cdot}$, such a model agrees with the larger width of the ^{13}C-satellite lines associated with the coupling constant $a_{\mathrm{C}(4,5,7,8,12,13,15,16)} = 0.328$ mT, relative to those pertaining to $a_{\mathrm{C}(3,6,11,14)} = 0.182$ mT, since the 'local' π-spin populations are high in the former ($\rho_{(4,5,7,8,12,13,15,16)} \approx 1/2 \cdot 1/4 = 1/8$) and low in the latter case ($\rho_{(3,6,11,14)} \approx 0$) [9][1]. The singly occupied orbital of $\mathbf{4}^{\oplus\cdot}$ (symmetry $D_{2\mathrm{h}}$) can consequently be regarded as the antibonding combination, $\mathrm{B}_{2\mathrm{g}}$[2], of the benzene HOMO's ψ_{A}.

On passing from $\mathbf{4}^{\oplus\cdot}$ to $\mathbf{3}^{\oplus\cdot}$ (symmetry C_{i}), the benzene HOMO's ψ_{A} or their 'symmetric' counterparts ψ_{S} are no longer proper basis MO's for a representation

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[1] Relationships between ^{13}C-coupling constants and π-spin populations [10] require a positive sign for 0.328 and negative for 0.182 mT.

[2] Corresponding to the combination $\mathrm{B}_{3\mathrm{g}}$ in [4].

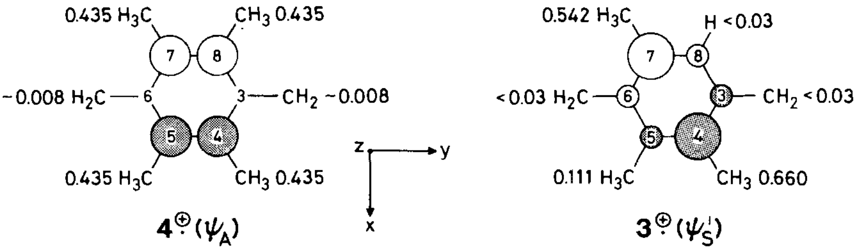

Fig. 3. *Benzene HOMO's* ψ_A *and* ψ'_S, *the antibonding combination of which may serve for an acceptable representation of the singly occupied orbitals in the radical cations of 4,5,7,8,12,13,15,16-octamethyl-* (**4**) *and 4,5,7,13,15,16-hexamethyl[2.2]paracyclophane* (**3**), *respectively.* (The values given along with the H-atoms are proton coupling constants in mT.)

of an orbital. Nevertheless, two alternative modes of π-spin distribution which bear a resemblance to such HOMO's may be suggested. Both of them allow for the dominant effect of the methyl substituents in delocalizing positive charge on the benzene C-centres. First, it is conceivable that replacing $H_3C-C(8)$ and $H_3C-C(12)$ by H-atoms, on going from $\mathbf{4}^{\oplus}$ to $\mathbf{3}^{\oplus}$, would not drastically alter the π-spin populations which will still be distributed approximately according to ψ_A. This means that all three methyl proton coupling constants would be comparable to the analogous value for $\mathbf{4}^{\oplus}$ (0.435 mT), and a relatively large hyperfine splitting ought to arise from the ring protons. Clearly, both expectations are at variance with experimental results. Alternatively it is reasonable to envisage a π-spin distribution which roughly follows a ψ_S-shaped HOMO on each of the benzene rings of $\mathbf{3}^{\oplus}$. For such an MO, denoted ψ'_S, the two opposite centres with the largest LCAO-coefficients will be substituted by methyl groups, and the nodal plane will cut the C(3), C(8)- and C(5), C(6)-bonds on one ring (*Fig. 3*, right), and C(11), C(12)- and C(14), C(15)-bonds on the other ring. If this model is acceptable, two of the three methyl-proton coupling constants should be larger by a factor 4/3 and the remaining one three times smaller than the analogous value for $\mathbf{4}^{\oplus}$; in addition only a small splitting from the ring protons is expected. The experimental data for $\mathbf{3}^{\oplus}$ are fully compatible with this model, since the average value of the two large methyl-proton coupling constants, 1/2 (0.660 + 0.542) = 0.601 mT, is close to 4/3 $(a_{H(4,5,7,8,12,13,15,16-CH_3)}) = 4/3\,(0.435) = 0.580$ mT, while the smallest one, 0.111 mT, has a magnitude similar to 1/3 (0.435) = 0.145 mT. Also, the unresolved splitting from the ring protons is rather small (< 0.03 mT). In a gross approximation, the singly occupied orbital of $\mathbf{3}^{\oplus}$ may thus be regarded as an antibonding combination, A_g, of the two benzene HOMO's ψ'_S. A slightly more elaborate model, which allows for the substituent effect of the methyl groups in the frame of the HMO-procedure, justifies the assignments of the three methyl-proton coupling constants 0.660, 0.542 and 0.111 mT to the positions 4,16; 7,13 and 5,15, respectively.

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