54. The ESR. Spectrum of the Radical Anion of 1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane

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(28.XII.81)

Summary

The radical anion of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**1**) has been generated by electrolytic reduction of **1** in 1,2-dimethoxyethane (tetrabutylammonium perchlorate as the supporting salt). The hyperfine coupling constants of the eight ^{19}F-nuclei and the eight protons, $a_F = 3.35$ and $a_H \approx 0.10$ mT, are qualitatively reproduced by INDO. calculations. According to these calculations, the singly occupied orbital of $\mathbf{1}^{\ominus}$ can be represented by an A_g-combination of two 'symmetric' benzene LUMO's, with a substantial transfer of spin population into the 2s-AO's of the F-atoms. Line-width alternation in the ESR. spectrum of $\mathbf{1}^{\ominus}$ indicates an ion pairing of the radical anion with its counter-ion $Bu_4N^{\oplus}$. The energy barrier to the migration of the cation between two equivalent sites at the radical anion is determined as 14 ± 2 kJ/mol.

Introduction. – Although the 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**1**) was synthesized more than 10 years ago [1], its radical anion has not yet been characterized by ESR. spectroscopy. This fact might be due to the difficulty of generating $\mathbf{1}^{\ominus}$ in detectable concentration, because of the low persistence of this radical anion in solution. *Duke et al.* [2] have performed closed-shell CNDO. calculations on **1**, as well as on the parent [2.2]paracyclophane (**2**). Their results indicate that the lowest unoccupied orbital (LUMO) of **2** can be considered as the bonding combination, B_{1g}, of the 'antisymmetric' benzene MO's $\psi_A^{(1)}$ and $\psi_A^{(2)}$. This statement is in agreement with a previous interpretation of the ESR. spectrum of $\mathbf{2}^{\ominus}$ [3]. For the octafluoro-derivative **1**, the CNDO. calculations [2] suggest that its LUMO should resemble the bonding combination, A_g, of the 'symmetric' benzene MO's $\psi_S^{(1)}$ and $\psi_S^{(2)}$ *(Fig. 1)*. The present paper, which reports on the ESR. spectrum of $\mathbf{1}^{\ominus}$, verifies this prediction.

Results. – The radical anion $\mathbf{1}^{\ominus}$ was prepared by a continuous electrolysis of **1** in 1,2-dimethoxyethane (DME) with tetrabutylammonium perchlorate as the supporting salt. The electrolytic cell used in this experiment has been described else-

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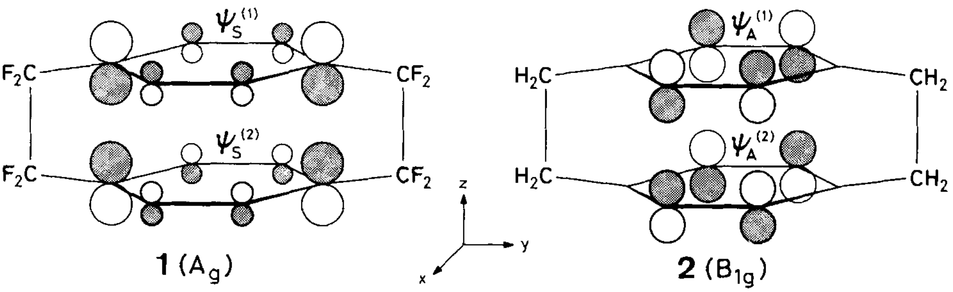

Fig. 1. *Lowest unoccupied orbitals* (LUMO's) *of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane* (**1**) *and [2.2]paracyclophane* (**2**) *represented as combinations of benzene MO's*

where [4]. The voltage required for the appearance of the ESR. spectrum of **1**$^{\ominus}$ was considerably less negative than in the case of **2**$^{\ominus}$ generated under the same experimental conditions [5], thus pointing to a substantially greater ease of reduction of the octafluoro-derivative **1**, as compared with the parent hydrocarbon **2**[2]). In view of the low persistence of **1**$^{\ominus}$, rather concentrated solutions of **1** (*ca.* 10^{-2} mol/dm^3) and temperatures below 200 K were essential for producing a measurable steady concentration of **1**$^{\ominus}$. Moreover, in order to enhance the intensity of the spectrum, high modulation amplitudes (0.05 to 0.1 mT) had to be applied to the ESR. signals.

Figure 2 shows the ESR. spectrum of **1**$^{\ominus}$ at 188 K. The observed hyperfine pattern, nine components spaced by 3.35 ± 0.01 mT, is attributed to the eight ^{19}F-nuclei, since protons bound to aromatic rings are unlikely to give rise to splittings of such magnitude. Computer-assisted analysis of the line-widths and the line-shapes leads to the following conclusions: *1)* the unresolved hyperfine splittings from the eight protons are 0.10 ± 0.02 mT. Together with the unresolved second order splittings from the ^{19}F-nuclei, they account for the inhomogeneous broadening of *ca.* 0.3 mT. The effect of the second-order splittings is particularly evident in the shape of the most intense component $[M_I(^{19}F) = 0]$ which exhibits a pronounced asymmetry about its centre *(Fig. 2)*; *2)* the inherent line-widths of *ca.* 0.1 mT arise from homogenous broadening by the use of high modulation amplitude and, presumably, by g-anisotropy. In contrast, the ^{19}F-hyperfine anisotropy appears not to be of major importance; *3)* there is a marked alternation in the line-widths, as the components with odd spin quantum numbers $[M_I(^{19}F) = \pm 1$ and $\pm 3]$ are considerably broader than those with the even ones $[M_I(^{19}F) = 0, \pm 2$ and $\pm 4]$ *(Fig. 2)*. This finding, which points to a time-dependent phenomenon, can be rationalized by a two-jump model involving a mutual exchange of the coupling constants, $a_F^{(1)}$ and $a_F^{(2)}$, between two sets of four equivalent ^{19}F-nuclei.

In the fast exchange limit, which holds for **1**$^{\ominus}$ in the investigated temperature range of T = 178 to 193 K, the rate k of exchange is given by

$$k = \frac{(\gamma \Delta a_F)^2}{8 \gamma \Delta B_{exch}} \quad \text{or} \quad \ln k = 2 \ln(\gamma \Delta a_F) - \ln(8 \gamma \Delta B_{exch}) \qquad (1)$$

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[2]) The greater ease of reduction of **1** relative to **2** was confirmed by cyclic voltammetry [6].

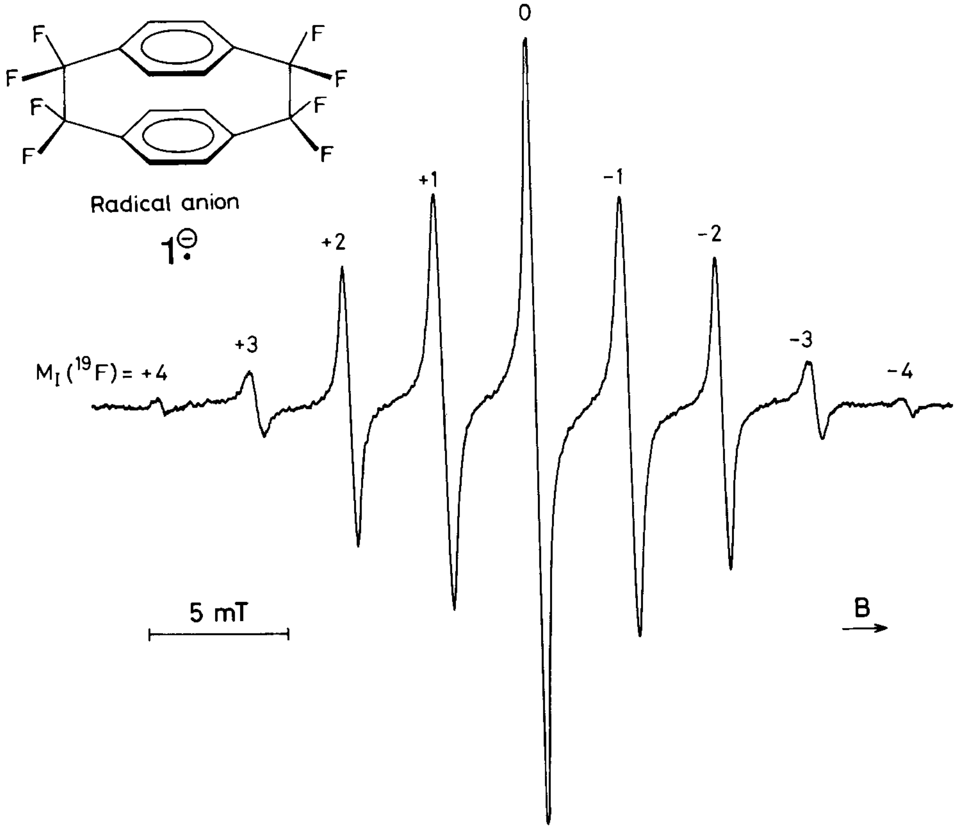

Fig. 2. *ESR. spectrum of the radical anion of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane* (**1**) (Solvent DME. Counter-ion $Bu_4N^{\oplus}$. Temperature 188 K). The signs of the spin quantum numbers M_I (^{19}F) are consistent with the positive sign of the spin populations at the F-atoms.

where $\Delta a_F = a_F^{(1)} - a_F^{(2)}$, in mT. The symbol ΔB_{exch}, in mT, stands for line-broadening due to the exchange, and $\gamma = 1.76 \cdot 10^8$ rad/(mT s) is the magnetogyric ratio which converts mT in rad/s. Assuming Δa_F to be temperature independent, one obtains *Equation 2* for the slope of the *Arrhenius* plot. *Equation 2* thus allows one

$$\frac{d\ln k}{d(1/T)} = -\frac{d\ln(8\gamma\Delta B_{exch})}{d(1/T)} \qquad (2)$$

to calculate the activation energy E_a without knowing the individual coupling constants $a_F^{(1)}$ and $a_F^{(2)}$, of which only their average, 3.35 mT, is experimentally available. The E_a-value, derived in this way from computer simulations [7] of the exchange-broadened ESR. spectra at 178, 183, 188 and 193 K, amounts to 14 ± 2 kJ/mol.

Discussion. - *Spin distribution.* In order to corroborate our ESR. spectroscopic results, we have carried out open-shell INDO. calculations on $1^{\ominus}$ with the use of the standard energy parameters for the C-, H- and F-valence AO's [8]. The coordinates of C- and F-atoms were those determined by X-ray crystallographic structure analysis [9]. The C—H bonds were placed on the lines bisecting the C—C—C angles, and their length was taken as 105 pm. A correspondence has been noted with the previous closed-shell CNDO. calculations on **1** [2] in that the singly occupied orbital of $1^{\ominus}$ in the INDO. model has the same nodal properties as the LUMO of **1** in the CNDO. model, *i.e.*, it can likewise be regarded as an A_g-combination of the benzene MO's $\psi_S^{(1)}$ and $\psi_S^{(2)}$ (see *Introduction* and *Fig. 1*). The ^{19}F- and ^{1}H-coupling constants calculated by the INDO. method are $+7.07$ and $+0.27$ mT, respectively. Although they are in only qualitative agreement with the observed values, comparison between theory and experiment leaves no doubt that the assignment, $a_F = 3.35$ and $a_H \approx 0.10$ mT, is correct. According to the INDO. calculations, the large value of a_F is mainly due to a substantial spin delocalization from the $2p_z$-AO's of the bridged C-atoms, bearing high π-spin populations *(Fig. 1)*, to the fluorine 2s-AO's. The essential s-character of these spin densities at the F-atoms accounts for the lack of a marked ^{19}F-hyperfine anisotropy (see *Results*).

Ion pairing. The perturbation, which lowers the symmetry of $1^{\ominus}$ from D_{2h} to probably C_{2v} and splits the set of eight equivalent ^{19}F-nuclei into two sets of four, is thought to be caused by an association of the counter-ion $Bu_4N^{\oplus}$ with $1^{\ominus}$ in DME-solution. An association of this kind has been amply investigated for the radical anion $2^{\ominus}$, of [2.2]paracyclophane and the counter-ion $K^{\oplus}$ in ethereal solvents [3][10], and the position of the cation in the ion pair $2^{\ominus}/K^{\oplus}$ was shown to be above (or below) the centre of one of the benzene rings [11]. It is reasonable to assume that the ion pair $1^{\ominus}/Bu_4N^{\oplus}$ will have a similar structure, but that the association of the radical anion with tetrabutylammonium will be less tight than with an alkali metal cation. The observed activation energy $E_a = 14$ kJ/mol, which is presumably determined by a barrier to migration of the counter-ion between two equivalent sites at the radical anion, seems compatible with such an association.

It is noteworthy that the ESR. spectrum of $2^{\ominus}$ does not exhibit line-width alternation, when **2** is reduced electrolytically under the same conditions as **1** [5]. This behaviour, contrasting with that of $1^{\ominus}$, is readily understood in terms of *Equation 1* which states that, all other things being equal, the line-broadening ΔB_{exch} should be proportional to the square of the difference in the coupling constants affected by the exchange. For $1^{\ominus}$, such a relationship is given by *Equation 3*, where the difference $\Delta a_F = a_F^{(1)} - a_F^{(2)}$ must be of the order 1 mT, as estimated from the a_F value

$$\gamma \Delta B_{exch} = \frac{1}{8k} (\gamma \Delta a_F)^2 \qquad (3)$$

of 3.35 mT and by analogy to structurally related ion pairs [10][11]. Considering the small magnitude of the coupling constant of the ring protons ($a_H \approx 0.1$ mT), the corresponding contribution of $\Delta a_H = a_H^{(1)} - a_H^{(2)}$ to ΔB_{exch} can be safely neglected. Turning to $2^{\ominus}$, one finds that the Δa_H-values for the ring and methylene protons in the ion pairs of this radical anion are of the order of 0.1 mT [3] [11], and thus the line-broadening, ΔB_{exch} is expected to be by a factor 10^2 smaller for $\mathbf{2}^{\ominus}$ than for $\mathbf{1}^{\ominus}$.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. Financial assistance by *Ciba-Geigy SA*, *Sandoz SA* and *F. Hoffmann-La Roche & Cie SA* is likewise acknowledged. We also thank Dr. *S. W. Chow*, Union Carbide, Bound Brook, New Jersey, for a generous gift of a sample of **1** and Drs. *J. Bruhin* and *W. B. Martin, Jr.*, for carrying out some experiments on **1**.

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