141. The Structure of the Ion Pairs Formed by the Radical Anion of [2.2] Paracyclophane and the Potassium Cation

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Summary. The structure of the title ion pairs has been established by ESR. studies of the radical anion produced from 1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane with potassium in tetrahydrofuran and 2-methyltetrahydrofuran. The counter-ion $K^{\oplus}$, which for steric reasons is forced to reside outside the framework of [2.2]paracyclophane, assumes a position above the centre of one benzene ring. Experimental support has been also obtained for the assignment of the coupling constants to those ring and methylene protons which are rendered non-equivalent by the ion pairing.

Introduction. – Reaction of [2.2]paracyclophane (I) with potassium in ethereal solvents at low temperatures yields the corresponding radical anion ($I^{\cdot\ominus}$) which exhibits well-resolved ESR. spectra [1]. Table 1 lists the coupling constants reported for $I^{\cdot\ominus}$ in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF) and 2-methyltetrahydrofuran [1] [2]. With DME as solvent, the hyperfine interaction is due to two sets of eight equivalent protons, in accordance with the full D_{2h} symmetry of the molecule. Upon replacement of DME by THF or MTHF, each of the two sets separates into two sets of four, and, in addition, a hyperfine splitting from the ^{39}K nucleus of the cation is observed. The data in Table 1 indicate an association of the radical anion $I^{\cdot\ominus}$ with its counter-ion $K^{\oplus}$, whereby two equivalent ion pairs of symmetry C_{2v} are interconverted by migration of the cation between two equivalent sites.

Table 1. *Coupling constants* (in Gauss = 10^{-4} Tesla) *for the radical anion of [2.2]paracyclophane (I)* [a])

Position	DME	THF		MTHF	
4, 5, 7, 8, 12, 13, 15, 16 (ring)	2.97 (8H)	3.79 (4H) 1.93 (4H)	2.86 [b])	3.84 (4H) 1.71 (4H)	2.78 [b])
1, 2, 9, 10 (methylene)	1.03 (8H)	1.25 (4H) 0.70 (4H)	0.98 [b])	1.28 (4H) 0.65 (4H)	0.97 [b])
counter-ion $K^{\oplus}$	–	0.12 (^{39}K)		0.13 (^{39}K)	

[a]) Numbers of equivalent nuclei are given in parentheses.
[b]) Average values.

The migration is slow on the hyperfine time-scale (10^6 to 10^7 s^{-1}) in THF and MTHF which solvate the cation rather poorly and thus favour its close association with the radical anion; in this case the actual symmetry C_{2v} of the ion pair is evident. On the other hand, the migration

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occurs more frequently in DME where better solvation of the cation results in formation of looser ion pairs; consequently, simplified hyperfine pattern and the higher symmetry D_{2h} are apparent in this solvent, though the large line-width of 0.25 Gauss[2]) (as compared to 0.06 Gauss for $I^{\cdot\ominus}$ in THF and MTHF) points to an incomplete averaging. Further increase in the frequency of migration along with the concomitant line narrowing, can readily be achieved by addition of hexamethylphosphoric triamide (HMPA) to the solution of $I^{\cdot\ominus}$ in DME.

Although the ESR. data for $I^{\cdot\ominus}$ (Table 1) provide a reliable information on the symmetry of the ion pairs, they do not specify their geometry. Obviously, the counterion cannot be located inside the carbon framework of $I^{\cdot\ominus}$, since the diameter of $K^{\oplus}$ is estimated as 2.7 to 3.4 Å [3], while the two benzene rings in [2.2]paracyclophane are at a distance of only 2.8 to 3.1 Å [4] (Fig. 1). It is inconceivable that the cation could be squeezed into the limited space inside the radical anion, and it is even more difficult to imagine how this space would accomodate two cation's sites separated by a sufficiently large barrier. The counter-ion $K^{\oplus}$ has therefore to occupy a position outside the carbon framework of $I^{\cdot\ominus}$ and, as required by the symmetry C_{2v}, such a position must lie on one of the three two-fold axes of the molecule. The ion pair structures corresponding to these three alternatives can be denoted as *left-right*, *front-back* and *top-bottom*, if account is taken of the two equivalent cation's sites in each case (Fig. 2). Intuitively, one may anticipate that the top-bottom structure will

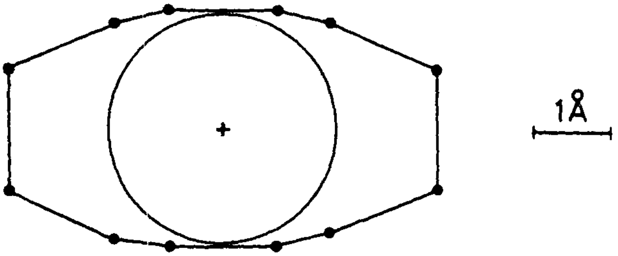

Fig. 1. *Carbon framework of [2.2]paracyclophane (I) vs. the circumference of the cation $K^{\oplus}$.* The radius of the cation (1.49 Å) is that derived from crystallographic measurements [5]

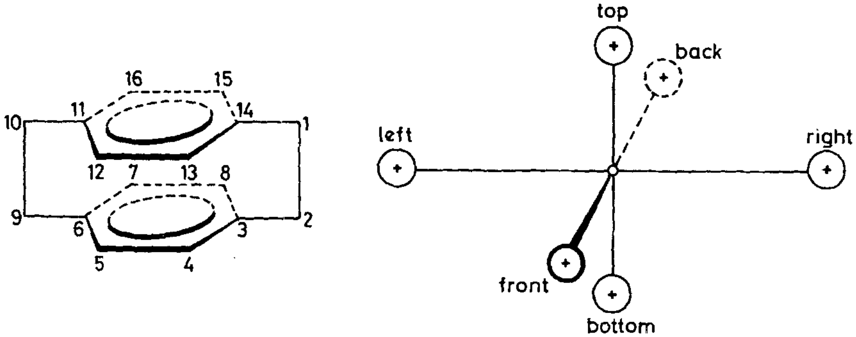

Fig. 2. *The potential positions of the counter-ion $K^{\oplus}$ relative to the radical anion of [2.2]paracyclophane (I)*

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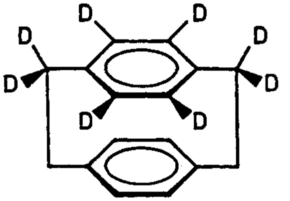
[2]) 1 Gauss = 10^{-4} Tesla.

be preferred, since it allows the counter-ion to be embedded in the π-cloud of one benzene ring. The observed ^{39}K coupling constant of *ca.* 0.1 Gauss[2]) (Table 1) compares, in fact, rather well with the analogous values found for the ion pairs [6] in which the cation $K^{\oplus}$ certainly resides above the plane of the aromatic radical anion [7]. In order to prove beyond doubt whether the *top-bottom* structure in question (Fig. 2) is the correct one, we have investigated the ESR. spectra of the radical anion produced from 1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane (I-d_8).



I-d_8

Results and Discussion. – Inspection of the three alternative structures for the ion pairs of I-$d_8{\cdot}^{\ominus}$ and $K^{\oplus}$ (Fig. 3) leads to the following prediction for the ESR. spectra taken with THF or MTHF as solvent:

(1) both *left-right* and *front-back* structures should give rise to the *same single* spectrum, *A*, for which the hyperfine interaction arises from *four pairs* of equivalent protons, *four pairs* of equivalent deuterons, and one ^{39}K nucleus;

(2) on the other hand, the *top-bottom* structure should be manifested by a 1:1 superposition of *two different* spectra, each exhibiting a hyperfine pattern due to *two sets of four* equivalent protons, *two sets of four* equivalent deuterons, and one ^{39}K nucleus. Since the ESR. data for the parent radical anion I$\cdot^{\ominus}$ in THF and MTHF (Table 1) do not indicate which sets of four ring and methylene protons should be assigned to the same xylylene moiety of the ion pair, two combinations of such superimposed spectra, *B* + *C* and *D* + *E*, must be considered in this case.

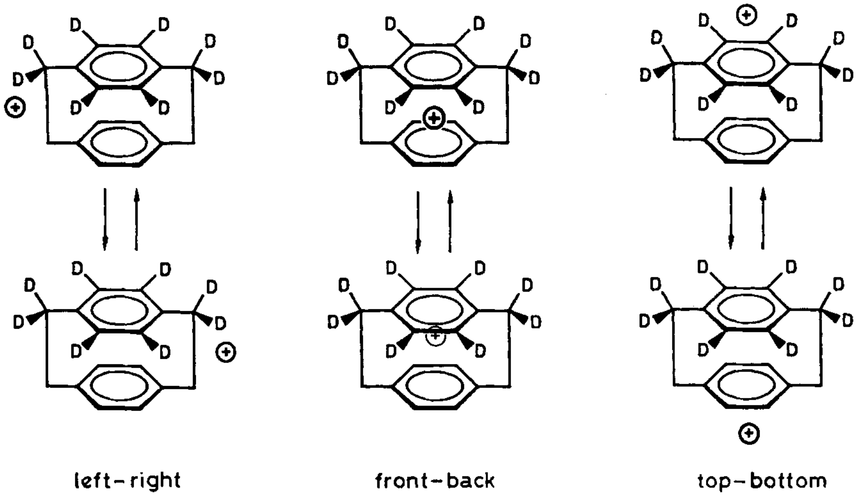


Fig. 3. *The alternative ion-pair structures for the radical anion of 1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane (I-d_8) associated with its counter-ion $K^{\oplus}$*

Table 2 lists the proton and deuteron coupling constants characteristic of the potential spectra (*A*, *B*, *C*, *D* and *E*) with THF as solvent; analogous values can readily be derived for $\text{I-d}_8\cdot^{\ominus}$ in MTHF.

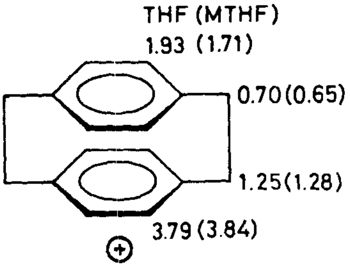
Table 2. *The five possible hyperfine patterns* (A, B, C, D and E) *predicted for the radical anion of 1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane* (*I-d*$_8$) *in THF*[a])

A	B	C	D	E
3.79 (2H); 1.93 (2H)	3.79 (4H)	1.93 (4H)	3.79 (4H)	1.93 (4H)
1.25 (2H); 0.70 (2H)	0.70 (4H)	1.25 (4H)	1.25 (4H)	0.70 (4H)
0.582 (2D); 0.296 (2D)	0.296 (4D)	0.582 (4D)	0.296 (4D)	0.582 (4D)
0.192 (2D); 0.107 (2D)	0.192 (4D)	0.107 (4D)	0.107 (4D)	0.192 (4D)
0.12 (^{39}K)	0.12 (^{39}K)	0.12 (^{39}K)	0.12 (^{39}K)	0.12 (^{39}K)

[a]) All coupling constants in Gauss (= 10^{-4} Tesla). Numbers of equivalent nuclei are given in parentheses. The deuteron coupling constants were calculated from the corresponding values for protons with the use of the conversion factor 0.1535.

Analysis of the ESR. spectra observed for the radical anion $\text{I-d}_8\cdot^{\ominus}$ in THF or MTHF shows unequivocally that they represent a *1:1 superposition of the hyperfine patterns predicted for D + E*. This finding is illustrated by a comparison of the experimental spectrum taken in THF with the derivative curves computed for *A*, *B* + *C* and *D* + *E* (Fig. 4). Clearly, only the *D* + *E* curve fits the observed spectrum; the agreement is as good as can be expected for a simulation which involves a superposition of two splitting patterns, each consisting of more than 8000 hyperfine lines.

Conclusions. – The investigations reported in the present paper not only establish the *top-bottom* structure of the ion pairs formed by the radical anion of [2.2]paracyclophane (I) and its counter-ion, but they also provide an experimental evidence for the assignment of the proton coupling constants, as indicated below.



(Values in Gauss)

Such an assignment, being consistent with the *D* + *E* (1:1) hyperfine patterns observed for $\text{I-d}_8\cdot^{\ominus}$ in THF or MTHF, meets the expectation that those sets of four equivalent ring and methylene protons, which have the *larger* coupling constants, will belong to *the same* xylylene moiety of $\text{I}\cdot^{\ominus}$. It is reasonable to assume that this moiety is the one which is proximate to the cation in the ion pair, since the positively charged counter-ion should enhance the electron affinity of the adjacent benzene

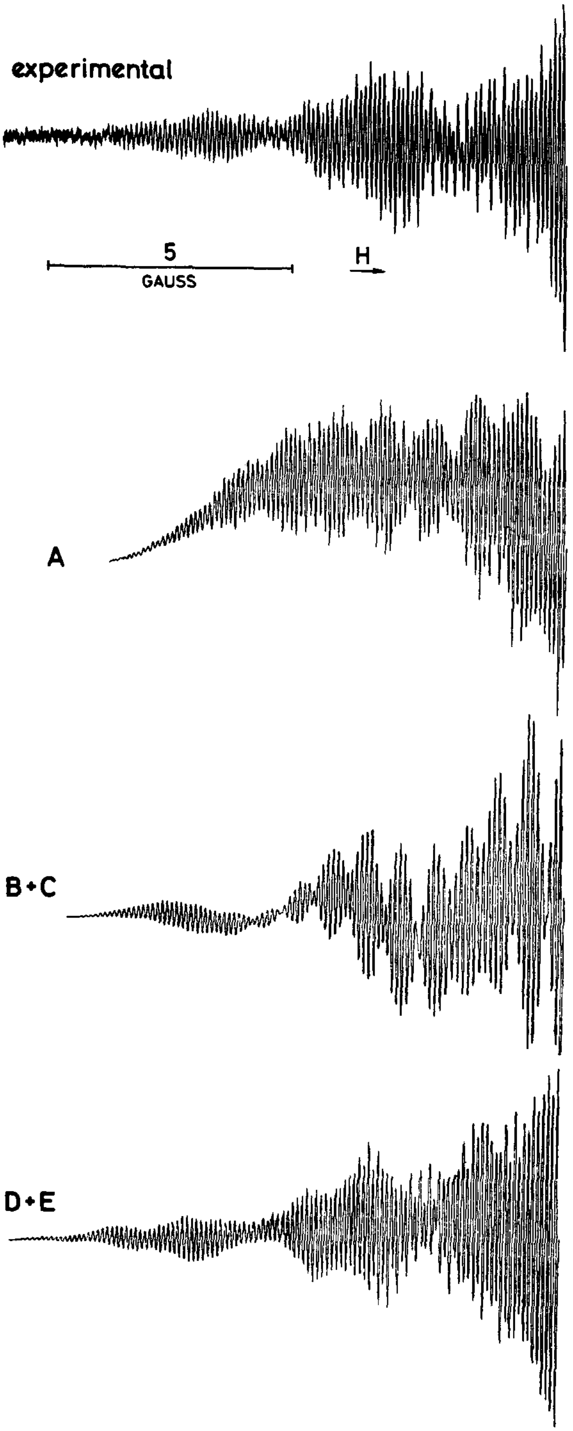
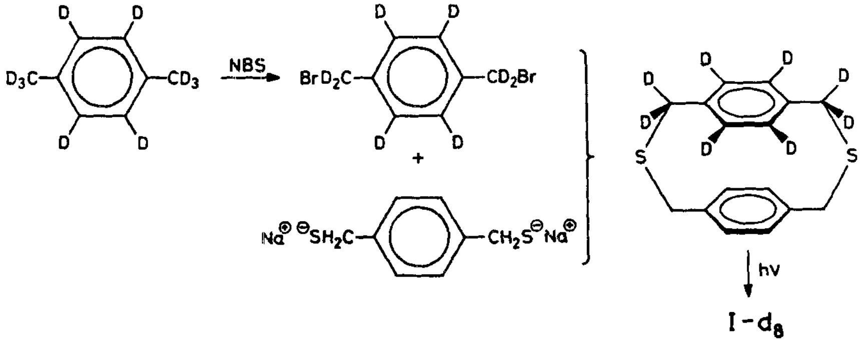


Fig. 4. Top: *Low-field half of the ESR. spectrum observed for the radicalanion of 1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane* (*1*-d_8). Solvent: THF; temp. –90°; counter-ion: $K^{\oplus}$. Below: *Corresponding spectra simulated with the aid of the coupling constants given in Table 2.* Line-shape: Lorentzian; line-width: 0.06 Gauss

π-system, and, as a result, the latter should accomodate the bulk of the π-spin population[3]).

Preparative Part. – 1,1,10,10,12,13,15,16-Octadeuterio[2.2]paracyclophane (I-d_8) was synthesized according to a procedure described by *Bruhin & Jenny* [8]. Equimolar mixture of perdeuterio-*p*-xylylene-dibromide [obtained by bromination of perdeuterio-*p*-xylene (*Aldrich*, Milwaukee, Wisconsin; isotopic purity 99 percent) with N-bromosuccinimide (NBS) in carbon tetrachloride] and of 1,4-bis(mercaptomethyl)benzene in tetrahydrofuran was added dropwise under nitrogen to a solution of NaOH in methanol at 50–60°. After the removal of the solvent, the crude product was extracted with benzene, purified by chromatography on alumina (*Merck*, Darmstadt, neutral, activity I) and recrystallized from hexane/chloroform 1:1. Pyrex-filtered UV. irradiation of the resulting 1,1,12,12,14,15,17,18-octadeuterio-2,11-dithia[3.3]paracyclophane in trimethyl phosphite yielded I-d_8 which was sublimed *in vacuo* at 100° (m.p. 287–289°).



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[3] The observed over-all π-spin distribution between the two benzene rings in the ratio of *ca.* 2:1 can be reproduced by a simple model suggested by *Reddoch* [6] for the ion pairs of hydrocarbon radical anions and alkali metal cations. In this model the positively charged counter-ion, which is located at a distance of 3.0–3.5 Å from the plane of the π-system, acts as an electrostatic perturbation of the HMO parameter α.