The Radical Anion of $[2_4]$(1,2,4,5)Cyclophane

By **Fabian Gerson** * and **Javier Lopez**, Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH–4056 Basel, Switzerland
Virgil Boekelheide, Department of Chemistry, University of Oregon, Eugene, Oregon 97403, U.S.A.

The radical anion of $[2_4]$(1,2,4,5)cyclophane (I) has been investigated by e.s.r. and e.n.d.o.r. spectroscopy under a variety of conditions. In dimethylformamide (counterion Et_4N^+) and in 1,2-dimethoxyethane–hexamethylphosphoric triamide (3 : 1) (counterion K^+) a 'free' or loosely associated radical anion ($If^{-\bullet}$) is formed (effective symmetry D_{2h}), whereas in tetrahydrofuran and 2-methyltetrahydrofuran (counterion K^+ or Cs^+) a tightly ion paired species ($Ip^{-\bullet}$) is present (symmetry C_{2v}; a_K *ca.* 0.1 or a_{Cs} *ca.* 0.6—0.8 mT). In 1,2-dimethoxyethane (counterion K^+), at low temperatures, ($If^{-\bullet}$) and ($Ip^{-\bullet}$) give rise concurrently to distinct e.s.r. and e.n.d.o.r. spectra; the interconversion ($If^{\bullet+}$) + $K^+ \rightleftharpoons$ ($Ip^{\bullet-}$)K^+ must thus be slow on the hyperfine time-scale. The concentration ratio $[(Ip^{-\bullet})]/[(If^{-\bullet})]$ in 1,2-dimethoxyethane is *ca.* 5 at 178 K and increases upon raising the temperature.

In the last few years, many multiply bridged cyclophanes have been synthesized,[1] and their behaviour upon reduction is currently under study.[2] The present paper deals with the radical anion of $[2_4]$(1,2,4,5)cyclophane (I) [1] which deserves special consideration for several reasons. (*a*) The compound (I) may be regarded as a counterpart of [2.2]paracyclophane ($\equiv [2_2]$(1,4)cyclophane) (II), since the bridged and unbridged atoms in (I) and (II) are interchanged. Both molecules belong to the D_{2h} symmetry group and, as shown by X-ray crystallography,[3] their benzene rings undergo distortions to boats by almost the same amount, but in the opposite sense (Figure 1). (*b*) The radical anion of (I) is relatively stable (persistent) and can be investigated by e.s.r. and e.n.d.o.r. spectroscopy under a variety of experimental conditions. (*c*) The high symmetry of (I) (D_{2h}), which is preserved in its 'free' or loosely associated radical anion, facilitates the analysis of the spectra and the interpretation of the hyperfine data. (*d*) In ethereal solvents, the radical anion of (I) forms tight ion pairs with alkali metal cations. Distinct e.s.r. and e.n.d.o.r. spectra of such ion pairs of lower symmetry (C_{2v}) can be observed in the same solution along with those of the 'free' radical anion.

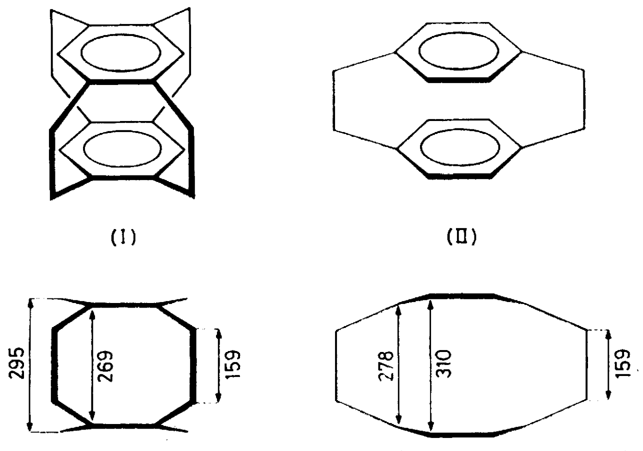

FIGURE 1 Structures and geometries of the carbon frameworks in $[2_4]$(1,2,4,5)cyclophane (I) and [2.2]paracyclophane (II). The distances are given in pm

EXPERIMENTAL

The synthesis of $[2_4]$(1,2,4,5)cyclophane (I) has been described elsewhere.[1e] The radical anion of (I) was generated electrolytically in *NN*-dimethylformamide (DMF) (tetraethylammonium perchlorate as the supporting salt) and 'chemically', *i.e.*, by reaction of (I) with potassium in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), or a 3 : 1 mixture of DME with hexamethylphosphoric triamide (HMPT). In one experiment, performed with MTHF, potassium was replaced by caesium as the reducing agent. While e.s.r. spectra could be obtained for the radical anion prepared by any of the above mentioned procedures, e.n.d.o.r. studies had to be restricted to the chemically produced species. The upper limits of the temperature range were 293 and 213 K for the e.s.r. and e.n.d.o.r. studies, respectively. The apparatus used consisted of a Varian ESR-E9 spectrometer coupled to a Varian ENDOR-1700 system.

RESULTS

'Free' or Loosely Associated Radical Anion.—Figure 2 shows the e.s.r. spectrum of the radical anion of $[2_4]$(1,2,4,5)-cyclophane (I) in DMF at 213 K with Et_4N^+ as the counterion. This spectrum, which only slightly depends on temperature, is readily analysed in terms of the three following coupling constants: $a_{H\,(ring)}$ 0.409 mT, due to the four equivalent protons in the two benzene rings, and $a_{H\,(endo)}$ 0.033 and $a_{H\,(exo)}$ 0.245 mT, due to the two sets of eight equivalent protons in the four ethano-bridges.

The notation of the protons is specified in Figure 2. Assignment of the smaller and larger coupling constant of the methylene protons to the *endo*- and *exo*-positions, respectively, is based on INDO calculations presented in the Discussion section. The g factor is 2.0028 ± 0.0001.

Henceforth, the radical anion giving rise to the spectrum shown in Figure 2 and exhibiting the full effective symmetry D_{2h} of the molecule will be denoted ($If^{-\bullet}$), where f stands for 'free' or loosely associated species.

The e.s.r. spectrum of ($If^{-\bullet}$) is likewise observed with DME–HMPT (v/v 3 : 1) and the counterion K^+, but striking changes appear when this mixture is replaced by THF or MTHF. In the following, the results obtained with MTHF, which also hold for THF, will be described in some detail. Pure DME represents a special case dealt with in a separate section.

Ion Paired Radical Anion.—In contrast to the e.s.r. spectra attributed to ($If^{-\bullet}$), those of the radical anion of

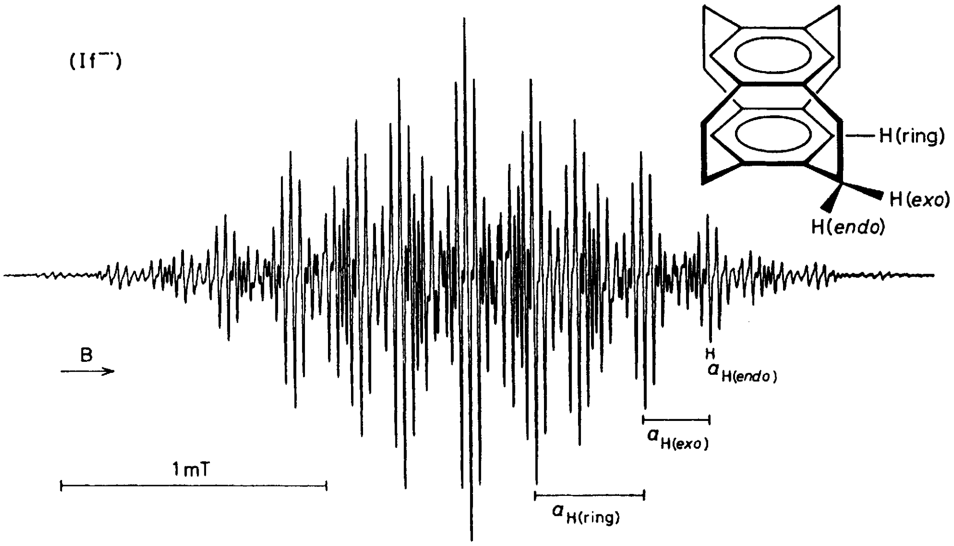

FIGURE 2 E.s.r. spectrum of the radical anion of $[2_4]$(1,2,4,5)-cyclophane (I). Solvent DMF, counterion Et_4N^+, temperature 213 K. In the formula at top right, one hydrogen is indicated for each of the three equivalent sets

$[2_4]$(1,2,4,5)cyclophane (I) in MTHF or THF, with K^+ as the counterion, are very complex and strongly temperature dependent. Their analysis was rendered possible by the use of the e.n.d.o.r. technique. In Figure 3, the proton e.n.d.o.r. signals observed with the solvent MTHF at 153 K are displayed against the corresponding signals of $(\mathrm{If}^{-\bullet})$ in DME–HMPT at 178 K. Evidently, on passing from DME–HMPT to MTHF, the effective symmetry is lowered from D_{2h} to C_{2v}. As a consequence, the set of four equivalent ring protons separates into two sets of two, and either of the two sets of eight equivalent methylene protons is split into two sets of four. Concurrently, each of the three coupling constants, $a_{\mathrm{H\,(ring)}}$, $a_{\mathrm{H}\,(endo)}$, and $a_{\mathrm{H}\,(exo)}$, found for $(\mathrm{If}^{-\bullet})$ is nearly matched by the mean of the two corresponding values obtained with MTHF. Such a relationship is also apparent from the Table which collects the hyperfine data determined for the radical anion of $[2_4]$(1,2,4,5)cyclophane (I) under various experimental conditions. The marked temperature dependence of the e.s.r. spectra taken with MTHF is accounted for by listing the coupling constants measured at 153 and 213 K. The precision of the analysis of these complex spectra is illustrated by Figure 4 which reproduces the experimental spectrum taken at 213 K, along with the corresponding computer-simulated derivative curve. Apart from the coupling constants for two sets of two equivalent ring

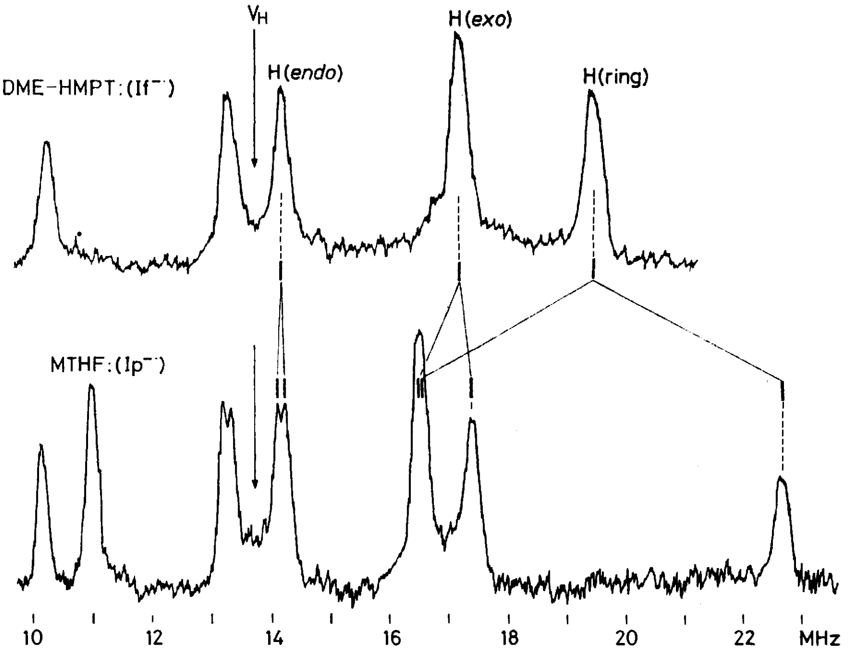

FIGURE 3 Proton e.n.d.o.r. spectra of the radical anion of $[2_4]$(1,2,4,5)cyclophane (I). Top: solvent DME–HMPT (3 : 1), counterion K^+, temperature 178 K. Bottom: solvent MTHF, counterion K^+, temperature 153 K

Proton and ^{39}K coupling constants, a_H and a_K in mT,[a] for the radical anion of $[2_4](1,2,4,5)$cyclophane (I). Number of equivalent protons in parentheses

	(If$^{-\bullet}$)			(Ip$^{-\bullet}$)		
Solvent	DMF	DME–HMPT	DME	DME	MTHF	MTHF
Counterion	Et_4N^+	K^+	K^+	K^+	K^+	K^+
T/K	213	178	178	178	153	213
$a_{H\,(ring)}$/mT	0.409(4)	0.407(4)	0.407(4)	0.598(2) 0.234(2)	0.645(2) 0.195(2)	0.637(2) 0.209(2)
$a_{H\,(endo)}$/mT	0.033(8)	0.033(8)	0.033(8)	0.038(4) 0.028(4)	0.038(4) 0.028(4)	0.038(4) 0.028(4)
$a_{H\,(exo)}$/mT	0.245(8)	0.248(8)	0.248(8)	0.259(4) 0.213(4)	0.260(4) 0.195(4)	0.253(4) 0.186(4)
a_K/mT				0.075	0.085[b]	0.103[c]

[a] Experimental error: ±0.001 mT for $a_H < 0.1$ mT and a_K, and 0.002 mT for $a_H > 0.1$ mT. [b] Corresponding ^{133}Cs coupling constant a_{Cs} 0.625 ± 0.004 mT. [c] Corresponding ^{133}Cs coupling constant a_{Cs} 0.823 ± 0.004 mT.

protons and four sets of four equivalent methylene protons, the simulation requires the inclusion of a hyperfine splitting due to the ^{39}K nucleus ($I\ \frac{3}{2}$) of the counterion. The unusually large value of this splitting, a_K 0.085 at 153 and 0.103 mT at 213 K (Figure 4), points to a close association of the radical anion with the cation K^+. Such an association, which is responsible for the reduced symmetry C_{2v} of the radical anion, justifies the notation (Ip$^{-\bullet}$), where p symbolises pairing with the counterion.

For (Ip$^{-\bullet}$) associated with K^+, the g factor is slightly lower than that of (If$^{-\bullet}$) (2.0028), but the difference does not exceed the systematic experimental error of ±0.0001 and, therefore, is difficult to determine exactly on an absolute scale (see, however, next section). The effect of the ion pairing on the g factor is much more pronounced with the counterion Cs^+. When Cs^+ replaces K^+ in MTHF, the g factor is lowered to 2.0020 ± 0.0001 within the temperature range 153—213 K. The most conspicuous feature of the e.s.r. spectra of (Ip$^{-\bullet}$) taken under these conditions (and not analysed in full detail) is the hyperfine splitting from the ^{133}Cs nucleus ($I\ \frac{7}{2}$). The coupling constant a_{Cs} amounts to 0.625 and 0.823 mT at 153 and 213 K, respectively, and is thus almost one order of magnitude larger than a_K.

Mixtures of ' Free ' and Ion Paired Radical Anions.—At temperatures below 193 K, the e.s.r. spectra of the radical anion of $[2_4](1,2,4,5)$cyclophane (I) in pure DME, with K^+ as the counterion, bear a superficial resemblance to that (Figure 2) of the ' free ' or loosely associated species (If$^{-\bullet}$). However, the S shaped curvature of these spectra, and the deviations from the symmetry about their centres, reveal an underlying absorption due to a second paramagnetic species with a slightly differing g factor. The e.n.d.o.r. technique

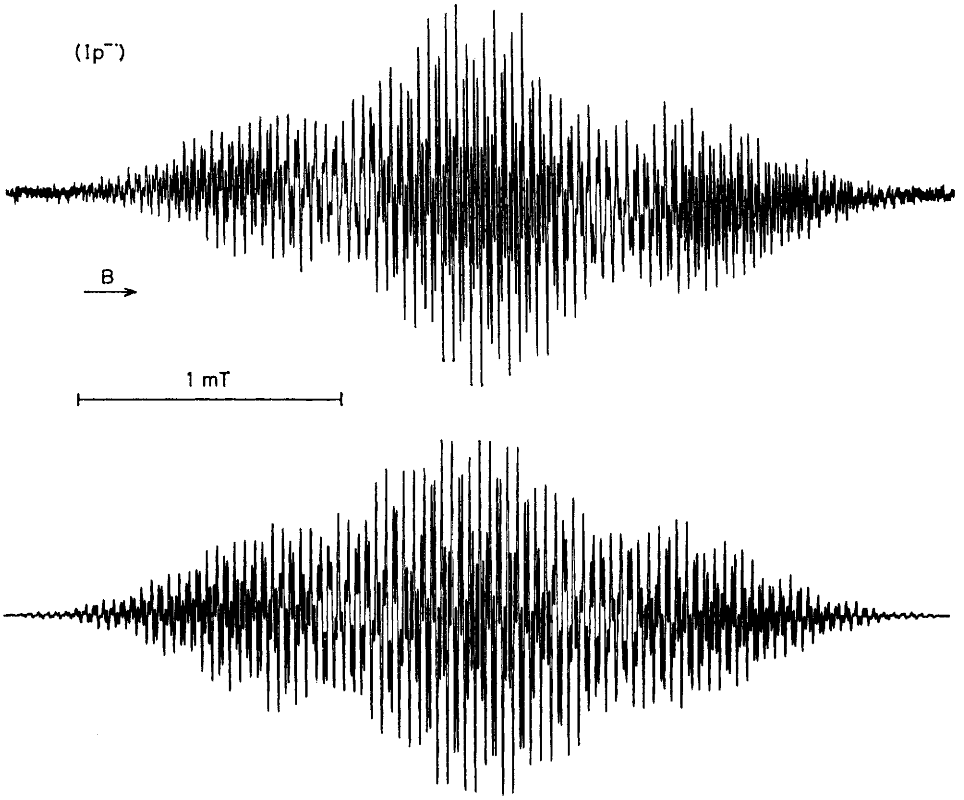

FIGURE 4 E.s.r. spectrum of the radical anion of $[2_4](1,2,4,5)$-cyclophane (I). Top: experimental spectrum; solvent MTHF, counterion K^+, temperature 213 K. Bottom: spectrum simulated with the use of the coupling constants given in the Table (last column); line-shape, Lorentzian, line-width 0.007mT

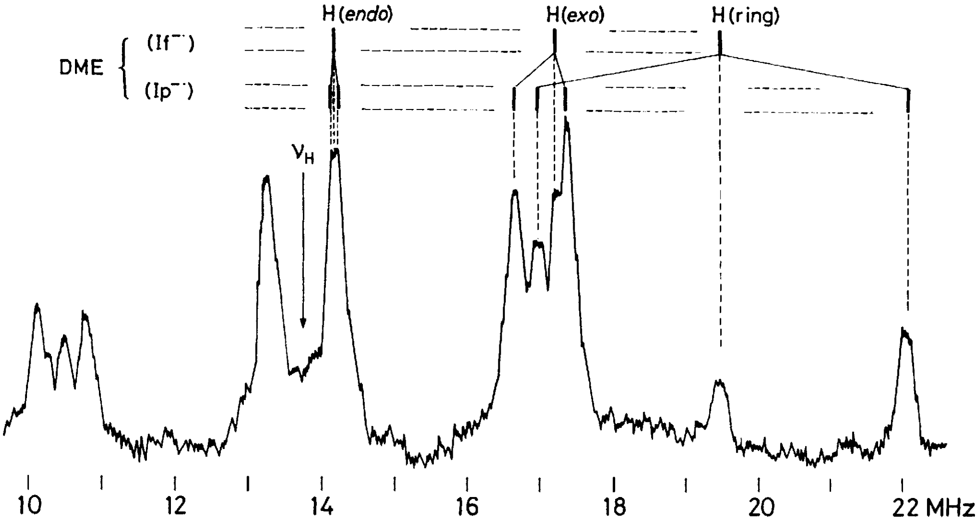

FIGURE 5 Proton e.n.d.o.r. spectrum of the radical anion of $[2_4](1,2,4,5)$cyclophane (I). Solvent DME, counterion K^+, temperature 178 K

attests that this species is the ion paired radical anion $(Ip^{-\bullet})$, as demonstrated by the spectrum shown in Figure 5. This e.n.d.o.r. spectrum, observed at 178 K, exhibits proton signals from both $(If^{-\bullet})$ and $(Ip^{-\bullet})$. Despite the poor reliability of the e.n.d.o.r. intensities as a quantitative measure of number of protons giving rise to them, it is tempting to estimate the relative concentrations of the two species from the pertinent signals (Figure 5). The ratio $[(Ip^{-\bullet})]/[(If^{-\bullet})] \approx 5:1$ derived in this way seems, at first sight, to be unreasonably high in view of the apparent predominance of the hyperfine lines from $(If^{-\bullet})$ in the corresponding e.s.r. spectrum. However, one should bear in mind that the number of such lines is $5 \times 9^2 = 405$ against $3^2 \times 5^4 \times 4 = 22\,500$ expected for $(Ip^{-\bullet})$. The total e.s.r. absorption of $(Ip^{-\bullet})$ is thus distributed over a 50-fold number of lines compared with $(If^{-\bullet})$, and this fact more than compensates for the lower concentration of the 'free' relative to the ion paired radical anion.

Upon raising the temperature to 273 K, the hyperfine pattern of $(If^{-\bullet})$ in the e.s.r. spectra becomes increasingly less prominent and is finally superseded by that of $(Ip^{-\bullet})$. As confirmed by the e.n.d.o.r. technique, which could be applied up to 213 K, the concentration of $(If^{-\bullet})$ must be vanishingly small at higher temperatures.

Like the g factor of $(Ip^{-\bullet})$ associated with K^+ in MTHF, that of the corresponding ion pair in DME is lowered relative to the value of $(If^{-\bullet})$ by <0.0001. However, contrary to the case of MTHF, the presence of both $(Ip^{-\bullet})$ and $(If^{-\bullet})$ in the same solution enables one to measure the small difference in their g factors, irrespective of the larger systematic experimental error. This difference is found to be $0.000\,05 \pm 0.000\,02$.

DISCUSSION

π-Spin Distribution and Proton Coupling Constants.— Figure 6 depicts the degenerate lowest antibonding π-MOs of benzene, which are classified as symmetric (ψ_S) and antisymmetric (ψ_A) with respect to the vertical mirror plane (m) passing through two opposite centres. It has been shown in a previous paper[4] that the singly occupied orbital in the radical anion of [2.2]paracyclophane (II) can be regarded as a bonding combination of two benzene MOs ψ_A, with the two bridged carbon atoms lying in the plane m. Such a combination is energetically favoured relative to that of the MOs ψ_S, due to the electron-donating substituent effect of the two ethanobridges.

An analogous simple model is also applicable to the radical anion of $[2_4](1,2,4,5)$cyclophane (I). Contrary to (II), the mirror plane m in (I) contains the two unbridged carbon atoms. The substituent effect of the four ethanobridges in (I) should thus render a bonding combination of the MOs ψ_S more stable than that of their antisymmetric counterparts ψ_A. Accordingly, such a combination of the MOs ψ_S is expected to be an acceptable description of the singly occupied orbital in the radical anion of (I).

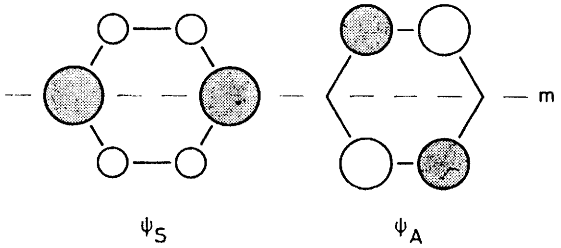

FIGURE 6 Degenerate lowest antibonding orbitals of benzene. The areas of the circles are proportional to the squares of the LCAO coefficients. Blank and shaded areas symbolize opposite signs of these coefficients. The dashed line is the trace of the vertical mirror plane m

This expectation is, in fact, borne out by the observed coupling constants of the ring protons. The relevant relationship between experimental and theoretical values is (1)[5] in which Q and $\rho_{\mathrm{C,unbr}}$ are the proportionality

$$a_{\mathrm{H\,(ring)}} = Q\rho_{\mathrm{C,unbr}} \qquad (1)$$

parameter and the π-spin population at an unbridged benzene carbon atom, respectively. The value $\rho_{\mathrm{C,unbr}}$ in the simple model is given by one-half the squared LCAO coefficient at this atom for the MOs ψ_S or ψ_A, where the factor of 1/2 accounts for the distribution of the π-spin population between two benzene rings. In this approximation, $\rho_{C,unbr}$ is $1/2 \times 1/3 = 1/6$ for the radical anion of (I) (MOs ψ_S) and $1/2 \times 1/4 = 1/8$ for that of (II) (MOs ψ_A). Taking $|Q|$ as 2.3 mT (which is the total spectral spread of the benzene radical anion at 178 K), the predicted coupling constants are 0.38 and 0.29 mT, respectively, in good agreement with the corresponding experimental values of 0.409 mT for ($If^{-\bullet}$) (this work) and 0.297 mT for the corresponding ' free ' or loosely associated radical anion ($IIf^{-\bullet}$) of [2.2]paracyclophane.[4]

The coupling constants of protons which are separated by one sp^3-hybridized carbon atom from a π-centre usually obey the $\cos^2 \theta$ relationship.[6] For the methylene protons in ($If^{-\bullet}$) such a relationship is expressed by (2) and (3) in which θ_{endo} and θ_{exo} are the dihedral angles

$$a_{H\,(endo)} = B_0 + B \langle \cos^2 \theta_{endo} \rangle \rho_{C,br} \qquad (2)$$

$$a_{H\,(exo)} = B_0 + B \langle \cos^2 \theta_{exo} \rangle \rho_{C,br} \qquad (3)$$

formed by the $2p_z$ axis at the bridged carbon atom (C,br) with the C–H(*endo*) and C–H(*exo*) bonds, respectively, and B_0 and B are parameters ($|B_0| \ll |B|$). According to equations (2) and (3), different values $a_{H\,(endo)}$ and $a_{H\,(exo)}$ should arise from different angles θ_{endo} and θ_{exo}. However, molecular models, which conform to the *X*-ray structural data of (I), indicate that such a dependence alone can hardly rationalize the observed large difference in the two coupling constants. (This statement holds even if some uncertainty in the position of the pertinent $2p_z$ axis, due to the distortion of the benzene rings from planarity, is taken into consideration.[7]) Consequently, the difference in question must, to a great extent, be caused by effects which are not allowed for in equations (2) and (3), *e.g.*, interactions through space and/or through bonds. In order to provide some support for this conclusion, the standard INDO procedure [8] was applied to the radical anion ($If^{-\bullet}$). The co-ordinates of the carbon atoms were used as determined by *X*-ray crystallography of (I).[3b] The C–H bonds were placed in planes which are perpendicular to those formed by the two adjacent C–C bonds and which contain the lines bisecting the C–C–C angles. These lines yielded the directions of the C–H(ring) bonds, as well as the bisectors of the H(*endo*)–C–H(*exo*) angles (109°) in the methylene groups. For the length of all C–H bonds a value of 105 pm was adopted.

The results of the INDO calculations are consistent with the model of ($If^{-\bullet}$) in which the singly occupied orbital is regarded as a bonding combination of ψ_S-like MOs of two benzene π-systems. The predicted proton coupling constants are $a_{H\,(ring)}$ -0.27, $a_{H\,(endo)}$ $+0.03$, and $a_{H\,(exo)}$ $+0.26$ mT. In particular, the values calculated for the methylene protons are gratifying, since they agree well with those found experimentally (0.033 and 0.245 mT). This agreement justifies the assignment made for the two coupling constants in the present paper.

Ion Pairing.—Several features exhibited by the ion paired radical anion ($Ip^{-\bullet}$) of $[2_4]$(1,2,4,5)cyclophane are noteworthy, in particular by comparison with the analogous findings for the ion paired radical anion ($IIp^{-\bullet}$) of [2.2]paracyclophane.[4,9]

First, the hyperfine splittings from the ^{39}K and ^{133}Cs nuclei of the counterions associated with ($Ip^{-\bullet}$) (a_K *ca.* 0.1 and a_{Cs} *ca.* 0.6—0.8 mT) exceeded by far the corresponding values for ($IIp^{-\bullet}$) (a_K *ca.* 0.01 and $a_{Cs} < 0.04$ mT [4,10]). ^{39}K and ^{133}Cs coupling constants of such a great magnitude are unusual for the alkali metal cations paired with the radical anions of pure hydrocarbons. In fact, to our knowledge, the only case where comparably large values a_K and a_{Cs} were observed in the e.s.r. spectra of a hydrocarbon radical anion was that of 4,5,7,8-tetramethyl-[2.2]paracyclophane.[10]

Secondly, on going from ($If^{-\bullet}$) to ($Ip^{-\bullet}$), the coupling constant $a_{H\,(ring)}$ (*ca.* 0.4 mT) splits into two values in an approximate ratio of 3 : 1 (*ca.* 0.6 and 0.2 mT), whereas the analogous effect on $a_{H\,(endo)}$ and $a_{H\,(exo)}$ is rather small (*cf.* Table and Figures 3 and 5). In contrast, the passage from ($IIf^{-\bullet}$) to ($IIp^{-\bullet}$) affects the coupling constants of both ring and methylene protons to roughly the same extent (approximate splitting ratio 2 : 1).[4,9]

Thirdly, the use of DME is not sufficient to generate exclusively ($If^{-\bullet}$), although, in general, this solvent is much more effective than THF and MTHF in loosening the association between radical anions of hydrocarbons and alkali metal cations.[11] Actually, not ($If^{-\bullet}$), but ($Ip^{-\bullet}$), clearly predominates in DME, as is indicated by the concentration ratio $[(Ip^{-\bullet})]/[(If^{-\bullet})]$ which is *ca.* 5 : 1 at 178 K and which increases upon raising the temperature and the concomitant decrease in the dielectric constant of the solvent. The finding that, even at 178 K, it is ($Ip^{-\bullet}$), and not ($If^{-\bullet}$), which prevails in DME should again be compared with the corresponding results for the radical anion of (II). Previous reports [4,9] merely stated that this radical anion is present as ($IIf^{-\bullet}$) in DME at low temperatures. The concurrent existence of ($IIp^{-\bullet}$) in the same solution was not mentioned in that work, although examination of the pertinent e.s.r. spectra reveals the appearance of lines which do not make part of the hyperfine pattern of ($IIf^{-\bullet}$) and which vanish upon addition of HMPT to DME. The obvious assumption that these lines arise from ($IIp^{-\bullet}$) has now been confirmed by e.n.d.o.r. studies. At 178 K, the ratio $[(IIp^{-\bullet})]/[(IIf^{-\bullet})]$ estimated from the e.n.d.o.r. spectra is actually *ca.* 2 : 1 and is thus lower than the value $[(Ip^{-\bullet})]/[(If^{-\bullet})]$ under these conditions.

Conclusions.—A common feature of the ion pairs formed by the radical anions ($Ip^{-\bullet}$) and ($IIp^{-\bullet}$) with alkali metal cations is the effective C_{2v} symmetry. The lowering relative to the full symmetry D_{2h} exhibited by ($If^{-\bullet}$) and ($IIf^{-\bullet}$) signifies that the positively charged counterion is situated on only one of the three two-fold axes characteristic of this symmetry group. For ($IIp^{-\bullet}$) associated with K^+, this axis is the one passing through the centres of the benzene rings, *i.e.*, the position of the cation is outside the carbon framework of the molecule and above (or below) the centre of one benzene π-system.[9a]

It is reasonable to expect that the analogous structure of the ion pair should also be preferred by (Ip$^{-\bullet}$) and K$^+$, although, in the absence of further experimental evidence, alternative structures cannot be excluded. Irrespective of this uncertainty, one may conclude that (Ip$^{-\bullet}$) forms tighter ion pairs with alkali metal cations than (IIp$^{-\bullet}$). This conclusion can be drawn from the three features mentioned above and distinguishing (Ip$^{-\bullet}$) from (IIp$^{-\bullet}$): (*a*) strikingly larger coupling constants of the ^{39}K and ^{133}Cs nuclei in the counterions, (*b*) stronger predominance of the ion paired radical anions (Ip$^{-\bullet}$) in DME at 178 K, and (*c*) the more pronounced splitting of the coupling constant of the ring protons on passing from (If$^{-\bullet}$) to (Ip$^{-\bullet}$). The only finding which does not seem to be consistent with the tighter ion pairing of (Ip$^{-\bullet}$) is the rather slight effect of such a pairing on the coupling constants of the methylene protons. This finding is difficult to rationalize at present.

Presumably, the most interesting observations reported in the present paper are the distinct e.s.r. and e.n.d.o.r. spectra of both ' free ' and ion paired radical anions of (I) and (II) in DME. Thus, at least in the low temperature range (178—198 K) where such spectra were concurrently observed with the same solution, the interconversions (If$^{-\bullet}$) + K$^+$ $\rightleftharpoons$ (Ip$^{-\bullet}$)K$^+$ and (IIf$^{-\bullet}$) + K$^+$ $\rightleftharpoons$ (IIp$^{-\bullet}$)K$^+$ must be slow on the hyperfine time-scale (10^6—10^8 s^{-1}). The behaviour of the radical anion of [2.2]paracyclophane (II) in DME is now being investigated.

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