9. The Radical Anion of 1,2:9,10-Dibenzo[2.2]paracyclophane[1]).
An ESR, ENDOR, and TRIPLE Resonance Study

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The radical anion of 1,2:9,10-dibenzo[2.2]paracyclophane (**3**) has been studied by ESR, ENDOR, and TRIPLE resonance spectroscopy under a variety of experimental conditions. The coupling constants of the eight protons in the deck-benzene rings, and of the four inner and four outer protons in the side-benzene rings are 0.234, 0.123, and 0.036 mT, respectively (solvent: 1,2-dimethoxyethane; counterion: K$^+$). All three values have the same sign which is predicted to be negative. Comparison of the largest coupling constant (0.234 mT) with the corresponding value (0.297 mT) for the radical anion of the parent [2.2]paracyclophane (**1**) points to similar nodal properties of the singly occupied orbitals in **1**$^{\tau}$ and **3**$^{\tau}$. Notwithstanding this similarity, **3**$^{\tau}$ seems to associate less readily than **1**$^{\tau}$ with alkali metal counterions, since tight ion pairs of **3**$^{\tau}$ with K$^+$ are formed only in solvents of low solvating power. Effects of conformational changes on the ESR spectra, such as those previously observed for the radical anion of [2.2]paracyclophane-1,9-diene (**2**), are not apparent for **3**$^{\tau}$ in the temperature range of investigation. Hyperfine data are also reported for the radical anion of a derivative **4** which has a CH$_3$ substituent in one of the side-benzene rings of **3**.

Introduction. – While [2.2]paracyclophane (**1**) [2] and its 1,9-diene **2** [3] had been known for several decades, the 1,2:9,10-dibenzo derivative **3**[1]) has only recently been synthesized [1]. The average D_{2h} symmetry of **1** and **2** is preserved in **3**, with the two additional 'side'-benzene rings being orthogonal to the mean planes of the two 'deck'-benzene rings.
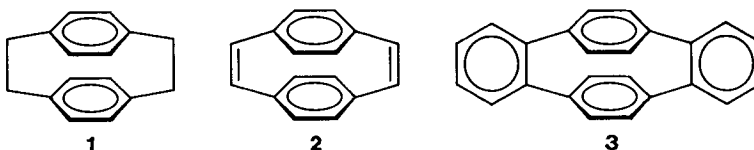
The radical anion **1**$^{\tau}$ has been the subject of extensive ESR and ENDOR studies which provided detailed information on its spin distribution and the structure of the ion pairs formed with an alkali metal cation [4]. Later, an investigation of **2**$^{\tau}$ by ESR spectroscopy [5] showed that, contrary to expectation, this radical anion markedly differs from **1**$^{\tau}$ in its properties. It is, therefore, of interest to examine how **3**$^{\tau}$ compares with **1**$^{\tau}$ and **2**$^{\tau}$ in regard to spin distribution, association with the positively charged counterion,

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and conformational mobility. To this aim, the present paper deals with the ESR, EN-DOR, and TRIPLE resonance spectra of **3**⁻ recorded under a variety of experimental conditions, and the results are discussed in the light of those previously obtained for **1**⁻ and **2**⁻.

Experimental. – The synthesis of 1,2:9,10-dibenzoparacyclophane (**3**) has been described in [1]. Reduction of **3** to its radical anion was performed with K or Cs metal in THF, 2-methyl-THF (MTHF), Et₂O, 1,2-dimeth-oxyethane (DME), or DME/hexamethylphosphoric-acid triamide (HMPT) 10:1. In several experiments, the soln. contained an excess of LiCl salt, so that Li⁺ replaced K⁺ or Cs⁺ as the counterion. Such a procedure could not, however, be applied to **3**⁻ in Et₂O, because of the low solubility of LiCl in this solvent. The radical anion **3**⁻ was fairly persistent below 233 K in all solvents used, except for Et₂O, in which it decayed above 203 K. Conversion into secondary paramagnetic species was not observed. The ESR spectra were taken on a *Varian-E9* instrument between the freezing points of the reaction mixtures and 273 K, while a *Bruker-ESP 300* spectrometer system served for the ENDOR and TRIPLE resonance studies which were conducted at low temp. (183 or 193 K).

Results. – It is advantageous to arrange the experimental findings for **3**⁻ in the order of decreasing solvating power of the solvents, *i.e.,* DME/HMPT > DME > THF > MTHF > Et₂O.
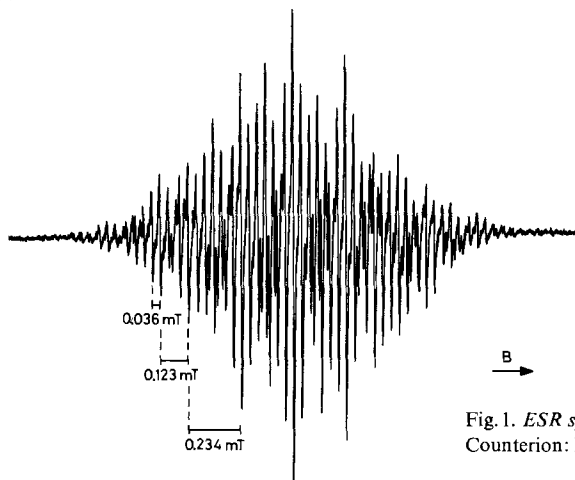

Fig. 1. *ESR spectrum of* **3**⁻ *in DME.* Counterion: K⁺; temp.: 213 K.

DME/HMPT, DME, THF. Fig. 1 shows an ESR spectrum of **3**⁻ in DME with K⁺ as the counterion (g = 2.0031 ± 0.0001). The hyperfine pattern is readily analyzed in terms of three coupling constants of 0.234 ± 0.001, 0.123 ± 0.001, and 0.036 ± 0.001 mT, due to sets of eight, four, and four equivalent protons, respectively. The largest value can be assigned in a straightforward way to the eight protons in the two 'deck'-benzene rings, whereas the two smaller ones must be connected with the two sets of four protons in the 'side'-benzene rings. Comparison of the hyperfine data for **3**⁻ with the corresponding values for the radical anion of the methyl derivative **4** (see *Appendix*) indicates that the
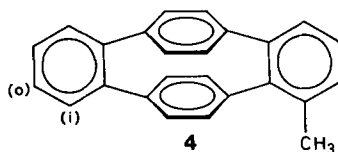
coupling constant of 0.123 mT should be assigned to the protons in the inner positions (i) of the 'side'-benzene rings, leaving 0.036 mT for the protons in the outer positions (o).

Addition of HMPT to DME or replacement of DME by THF as the solvent slightly modifies the hyperfine pattern of $3^{\bar{}}$, owing to small but regular changes in the coupling constants upon decreasing solvating power of the medium *(Table 1)*. On the other hand,

Table 1. *Coupling Constants* [mT][a]) *for L Ion Pairs*[b]) *of* $3^{\bar{}}$

Solvent Counterion		DME/HMPT K$^+$	DME K$^+$	THF K$^+$ or Li$^+$	MTHF K$^+$ or Cs$^+$ or Li$^+$
'Deck' rings	8 H	0.235	0.234	0.232	0.232
'Side' rings	4 H (i)[c])	0.120	0.123	0.125	0.126
	4 H (o)[d])	0.036	0.036	0.037	0.037

[a]) Exper. error: ±0.001 mT.　[b]) See *Discussion*.　[c]) i = inner positions.　[d]) o = outer positions.
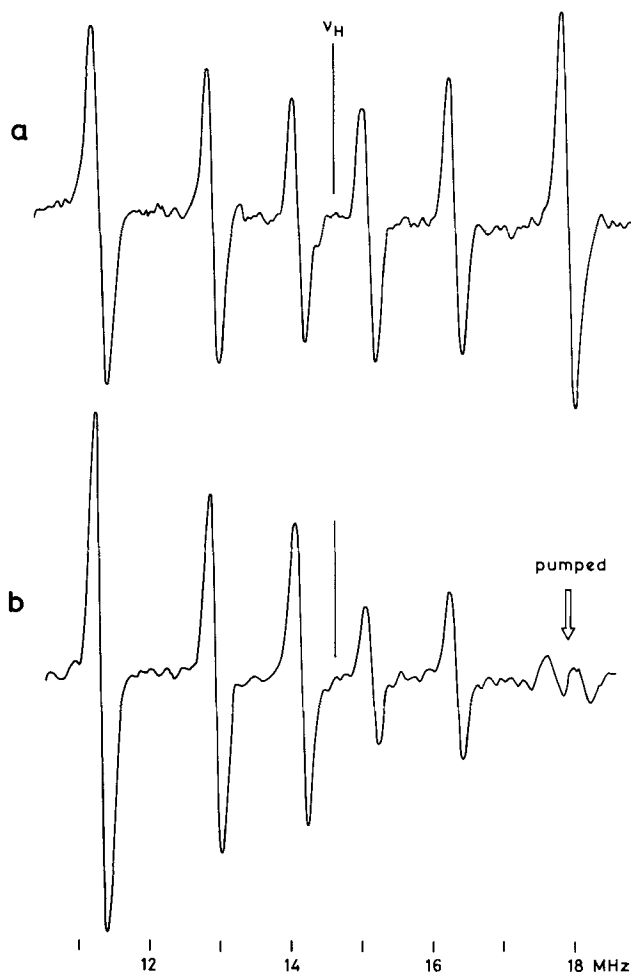

Fig. 2. *Proton ENDOR* (a) *and general TRIPLE resonance* (b) *spectra of* $3^{\bar{}}$ *in DME.* Counterion: K$^+$; temp.: 193 K.

these values are neither sensitive to substitution of K^+ by Li^+ as the counterion nor do they markedly depend on the temperature in the range of investigation (183–273 K). In particular, no line-width effects characteristic of a conformational interconversion are observed[3].

A proton ENDOR spectrum of $3^{\cdot-}$ in DME (counterion K^+) is reproduced in *Fig. 2a*; similar spectra have been obtained for $3^{\cdot-}$ in DME/HMPT and THF with either K^+ or Li^+.
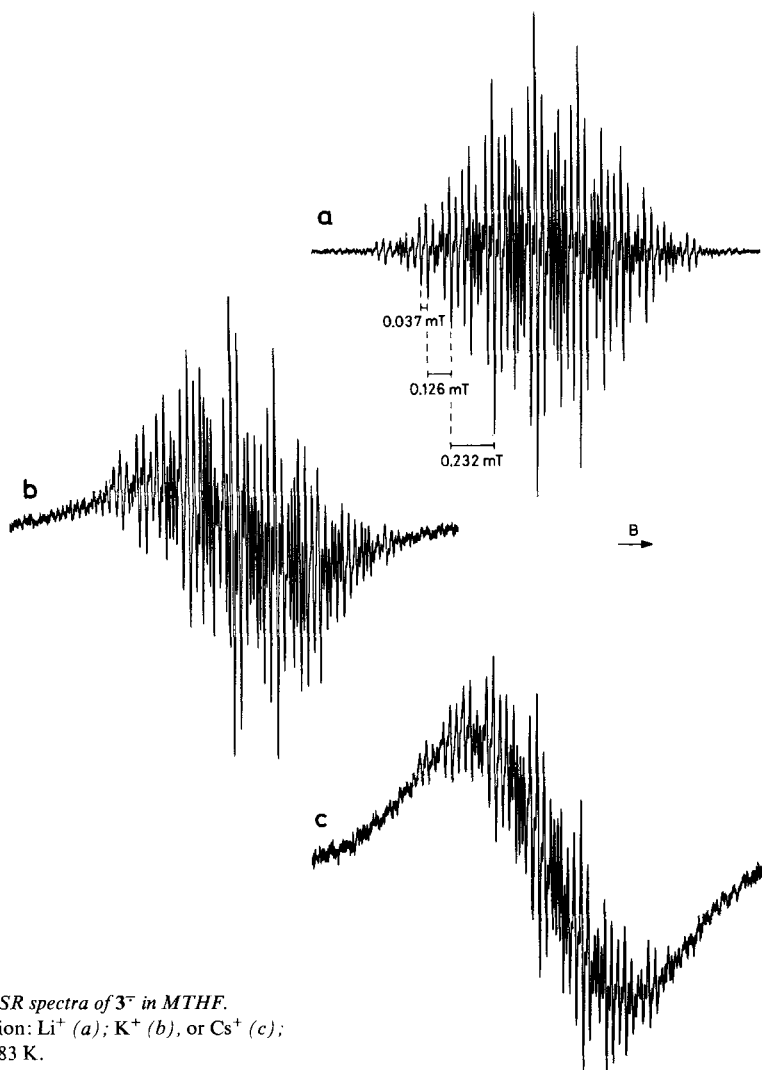

Fig. 3. *ESR spectra of* $3^{\cdot-}$ *in MTHF.*
Counterion: Li^+ *(a)*; K^+ *(b)*, or Cs^+ *(c)*;
temp.: 183 K.

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[3]   At 183 K, the low-field lines are distinctly wider than their high-field counterparts; the line-width difference gradually diminishes at higher temperatures. Interpretation of this phenomenon in terms of hyperfine aniso-tropy [6] is questionable, considering the absence of interacting nuclei other than protons and the modest sizes of the coupling constants.

The observed three pairs of ENDOR signals confirm the analysis of the ESR spectra in terms of the three coupling constants *(Table 1)*. Moreover, the general TRIPLE resonance spectrum *(Fig. 2b)*, indicates that all three values have the *same* sign. (This is because pumping of the signal at 17.9 MHz causes a simultaneous decrease in the relative intensities of the two remaining signals in this high-frequency half of the spectrum [7].)

MTHF. An ESR spectrum of $3^{\cdot-}$ in MTHF with K^+ as the counterion is displayed in *Fig. 3b*. It closely resembles those obtained for $3^{\cdot-}$ in THF under the same conditions, except for an S-shaped curvature which points to an underlying broad absorption. The curvature disappears when K^+ is superseded in MTHF by Li^+; in this case the ESR spectrum shown in *Fig. 3a* is observed. This spectrum is virtually identical with that of $3^{\cdot-}$ in THF with either K^+ or Li^+. By contrast, a marked enhancement of the S-shaped curvature occurs when Cs^+ is the counterion of $3^{\cdot-}$ in MTHF. As is conspicuous from *Fig. 3c*, the underlying structureless absorption becomes then a prominent feature of the ESR spectrum.
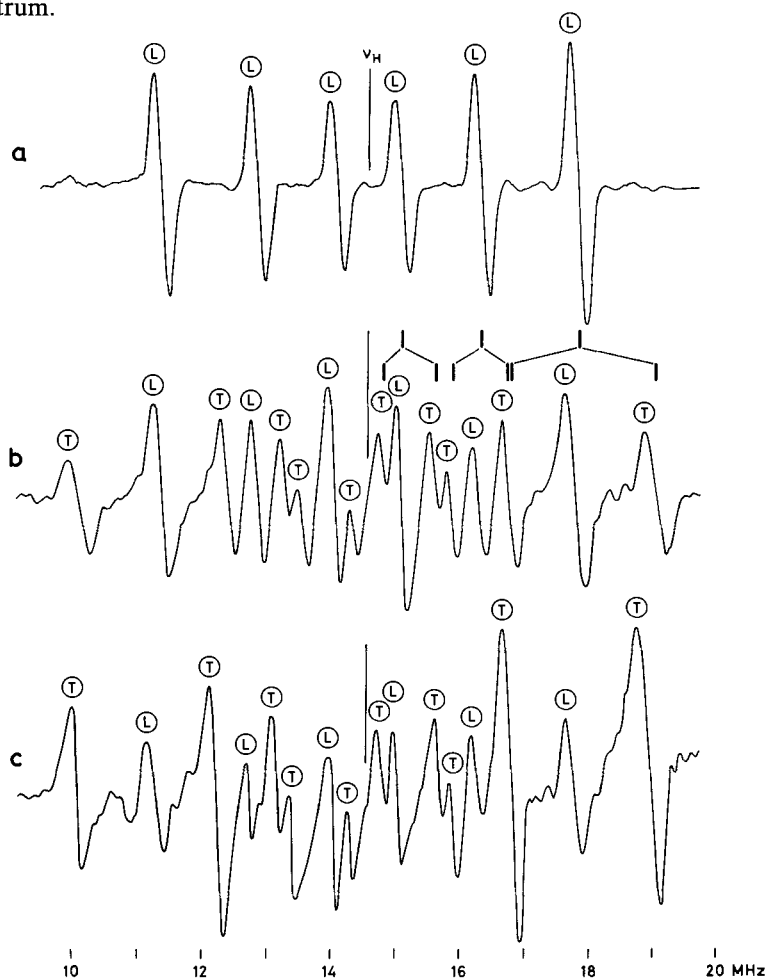

Fig. 4. *Proton ENDOR spectra of* $3^{\cdot-}$ *in MTHF.* Counterion: Li^+ *(a)*, K^+ *(b)*, or Cs^+ *(c)*; temp.: 183 K.

The origin of this absorption has been clarified with the aid of the ENDOR technique. In *Fig.4*, the pertinent proton ENDOR spectra of 3^- in MTHF are presented. *Fig.4a* (counterion Li^+) corresponds to the ESR spectrum without the S-shaped curvature *(Fig.3a)*; the three pairs of signals appearing therein and labelled ⓛ [4]) are analogous to those observed in DME/HMPT, DME *(Fig.2a)*, and THF. Additional ENDOR signals emerge, when K^+ *(Fig.4b)* or Cs^+ *(Fig.4c)* are the counterions of 3^- in MTHF, *i.e.* when the corresponding ESR spectra *(Fig.3b and c*, respectively) exhibit the broad structureless absorption along with the resolved hyperfine pattern; these signals have been labelled ⓣ [4]). It is evident that each of the ⓛ signals is flanked by two ⓣ [5]), and that the intensities of the latter increase relative to the former, on going from K^+ *(Fig.4b)* to Cs^+ *(Fig.4c)* as the counterion. This increase parallels the intensification of the broad absorption in the ESR spectra, when one replaces the counterion K^+ *(Fig.3b)* by Cs^+ *(Fig.3c)*. The ⓣ signals can, therefore, unequivocally be attributed to this absorption which, in that way, is characterized by hyperfine data not accessible from the ESR spectra. Assignments to sets of equivalent protons in 3^- *(Table 2)* take advantage of the finding that an average of two coupling constants derived from two ⓣ signals is close to the value associated with a ⓛ signal about which the two ⓣ are centered. Thereby, each set of n protons (n = 8 or 4) responsible for a ⓛ signal is split into two sets of n/2 protons giving rise to the corresponding ⓣ signals.

Table 2. *Coupling Constants* [mT]^a)) *for T Ion Pairs*^b)) *of* 3^-

Solvent		MTHF		MTHF		Et$_2$O	
Counterion		K$^+$		Cs$^+$		K$^+$	
Deck rings	4 H	0.324	0.241^c)	0.318	0.241^c)	0.335	0.233^c)
	4 H	0.158		0.163		0.131	
Side rings	2 H (i)^d)	0.158	} 0.126^c)	0.163	} 0.129^c)	0.083	} 0.072^c)
	2 H (i)	0.094		0.095		0.061	
	2 H (o)^e)	0.077	} 0.048^c)	0.082	} 0.050^c)	0.038	} 0.026^c)
	2 H (o)	0.018		0.018		0.013	
^{39}K or ^{133}Cs		^f)		^f)		0.011^g)	

^a)) Exper. error: ±0.002 mT. ^b)) See *Discussion*. ^c)) Average. ^d)) i = inner positions. ^e)) o = outer positions. ^f)) Hyperfine splitting not measured. ^g)) Coupling constant of one ^{39}K nucleus.

Et$_2$O. An ESR spectrum of 3^- in Et$_2$O with K^+ as the counterion (g = 2.0029 ± 0.0001) is presented in *Fig.5a*; it consists of a few hundred closely spaced lines. Its computer simulation *(Fig.5b)* makes use of two four-proton and four two-proton coupling constants, in addition to a hyperfine splitting from one ^{39}K nucleus *(Table 2)*. The proton coupling constants have been determined from the six pairs of signals in the ENDOR spectrum reproduced in *Fig.6a*. They possess the *same* sign as indicated by the general TRIPLE resonance technique *(Fig.6b)*. Their assignments to sets of equivalent protons in 3^- *(Table 2)* are guided by analogy with the hyperfine data acquired from the ⓣ

[4]) The labelling ⓛ and ⓣ of the proton ENDOR signals refer to *l*oose (or solvent-separated) and *t*ight ion pairs (see *Discussion*).

[5]) Of the six pairs of ⓣ signals thus expected, only five pairs are actually observed, because two ⓣ flanking different ⓛ coincide at 12.3 and 16.8 MHz (see splitting scheme on the high-frequency half; *Fig.4*).
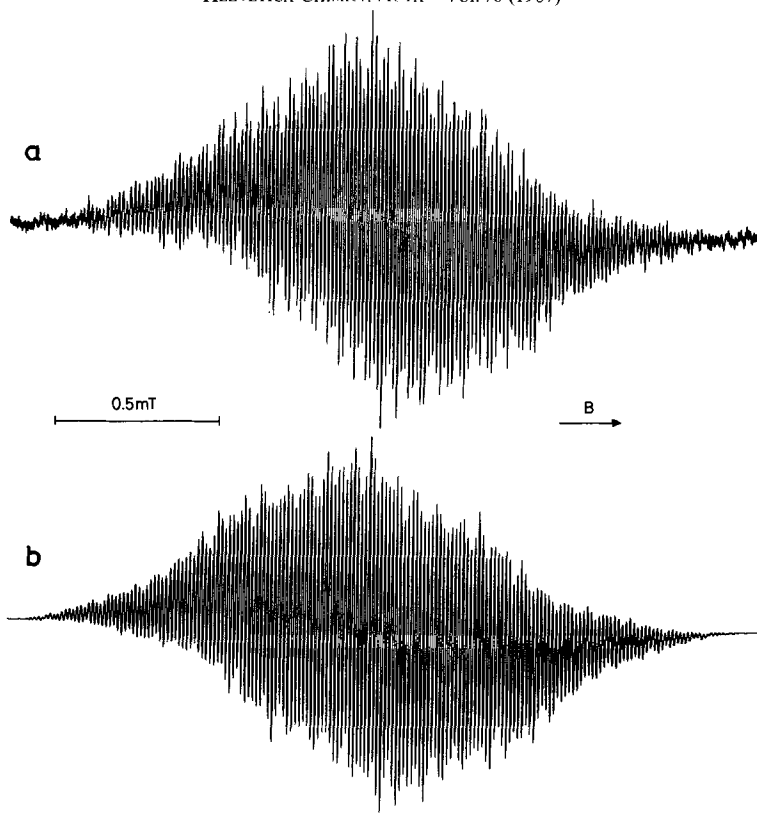
Fig. 5. a) *ESR spectrum of* **3**⁻ *in Et₂O*. Counterion: K⁺; temp.: 183 K. b) *Computer simulation*. Coupling constants as given in *Table 2*; line-shape: *Gaussian*; line-width: 0.006 mT.
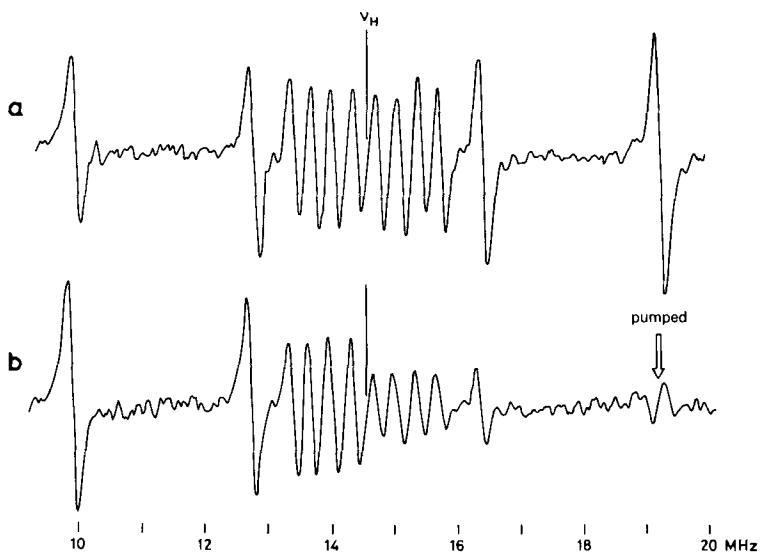

Fig. 6. *Proton ENDOR* (a) *and general TRIPLE resonance* (b) *spectra of* **3**⁻ *in Et₂O*. Counterion: K⁺; temp.: 183 K.

signals of 3^- in MTHF. Attempts to supersede the counterion K^+ in Et_2O by Li^+ through addition of LiCl salt have failed (see *Experimental*), as have those to replace K^+ by Cs^+ *via* reduction of **3** with Cs instead of K metal in this solvent.

Discussion. – *Spin Distribution and Sign of the Coupling Constants.* The substantial value (0.234 mT) of the coupling constant observed for the eight protons in the deck-benzene rings of 3^- strongly suggests that the singly occupied orbital of this radical anion should be considered as a B_{1g} combination of two 'antisymmetric' benzene-LUMO's rather than an A_g combination of their two 'symmetric' counterparts. In this respect, 3^- resembles the radical anion of [2.2]paracyclophane (**1**) and differs from that of the 1,9-diene **2**, as illustrated by the orbital diagram in *Fig. 7*. Assuming the B_{1g} representation
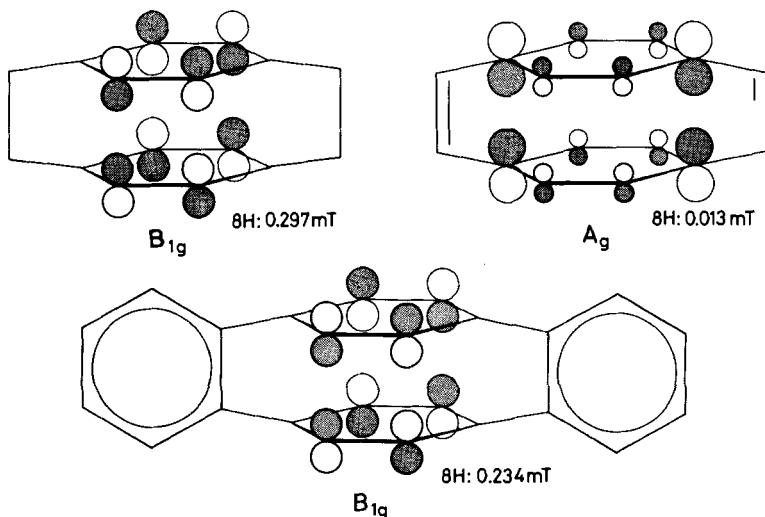

Fig. 7. *Singly occupied orbitals of* 1^-, 2^-, *and* 3^- *as combinations of two benzene-LUMO's.* The given values are the coupling constants of the eight protons in the 'deck'-benzene rings.

for the singly occupied orbital of 3^-, the following arguments concerning the sign of the proton coupling constants can be considered: *i)* Since the protons in the 'deck'-benzene rings are directly attached to C-atoms bearing the bulk of (positive) π-spin population, the coupling constant of these protons should be brought about by the usual mechanism of spin polarization and, therefore, have a negative sign [8a]. *ii)* As no spin delocalization is expected onto the 'side'-benzene rings lying in a nodal plane of the singly occupied orbital, the hyperfine interaction with the protons in these rings should also arise from spin polarization which should again bestow a negative sign upon the pertinent coupling constants (0.123 and 0.036 mT).

The same sign of the three coupling constants has been attested to 3^- by the general TRIPLE resonance technique (see *Results*). Moreover, the INDO method [9][6] applied to

3^- has confirmed that this sign is negative. The calculated coupling constants are −0.214 mT for the eight protons in the 'deck'-benzene rings and −0.054 and −0.009 mT for the protons in the four inner and the four outer positions, respectively, of the 'side'-benzene rings. Whereas there is a good agreement between the experimental and calculated absolute values for the largest coupling constant (0.234 vs. 0.214 mT), those of the two smaller ones seem to be underestimated by the INDO method (0.123 vs. 0.054 and 0.036 vs. 0.009 mT).

It is noteworthy that the general TRIPLE spectra require opposite signs for the coupling constants of the two sets of eight protons in 1^- [12]. Since the coupling constant of the protons in the 'deck'-benzene rings of 1^- (0.297 mT) [4], like its counterpart for 3^- (0.234 mT), is expected to be negative, that of the CH_2 protons (0.103 mT) should have a positive sign. This is a reasonable result, considering the positions of the CH_2 protons in 1^-. In contrast to the protons in the 'side'-benzene rings of 3^-, these protons lie outside the nodal planes of the singly occupied orbital (Fig. 7) and their hyperfine interaction should arise from spin delocalization rather than from spin polarization.

Ion Pairing and Conformation. The finding that the D_{2h} symmetry of 3^- is lowered in the solvents MTHF and Et$_2$O, with K$^+$ or Cs$^+$ as the counterions, must be ascribed to an association between the radical anion and the cation. Such an association, generally referred to as ion pairing, is known to be promoted by a decrease in the solvation power of the solvent (DME/HMPT > DME > THF > MTHF > Et$_2$O) and, in the case of hydrocarbon π-radical anions, also by an increase in the size of the alkali metal counterion (Li$^+$ < Na$^+$ < K$^+$ < Cs$^+$) [8b]. In the present paper, ion pairs of 3^- exhibiting a reduced symmetry are denoted 'tight' Ⓣ to be distinguished from 'loose' Ⓛ (or solvent separated) ion pairs which, on the hyperfine time-scale, preserve effectively the full symmetry D_{2h}. It has previously been established [13] that the ion pairs of 1^- and K$^+$ have the symmetry C_{2v}, with the counterion being situated in an external position above (or below) the centre of one deck-benzene ring. A closely related structure of this symmetry is expected for the ion pairs of 3^-, since the similar nodal properties of the singly occupied orbitals (Fig. 7) point to an essentially same distribution pattern of the negative charge in the two radical anions. In view of the common structural features, it is appropriate to consider the solvents in which 1^- and 3^- form L and/or T ion pairs with K$^+$.

	DME/HMPT	DME	THF	MTHF	Et$_2$O	
1^-	L	L + T	T	T	T	[4] [12]
3^-	L	L	L	L + T	T	

Clearly, the tendency to associate with an alkali metal counterion is considerably weaker for 3^- than for 1^-, since, on passing from the latter to the former, the dividing line between the L and the T ion pairs markedly shifts to the right, i.e. towards solvents of lower solvating power. This finding may be rationalized in terms of the substantial enlargement of molecular dimensions which makes the electronic and steric factors less favourable for a T ion pairing. It is remarkable that L and T ion pairs coexist in a particular solvent such as DME for 1^- and MTHF for 3^-. Under these conditions, the interconversion between the two species must thus be slow on the hyperfine time scale (10^6–10^8 s^{-1}) in the temperature range of investigation (183–273 K).

It is the split of each set of n equivalent protons into two sets of n/2, which is diagnostic of lowering the symmetry from D_{2h} to C_{2v} and, therewith, of changing the L into T ion pairs. In the ESR and ENDOR spectra of 1^{τ} and 3^{τ}, such a split is most conspicuous for the eight protons in the 'deck'-benzene rings, since these protons have by far the largest coupling constants. Again, it is informative to compare the pertinent hyperfine data acquired for the two radical anions under the same conditions (counterion: K^+; temperature 193 K).

	DME/HMPT	MTHF	Et₂O	
1^{τ}	8 H: 0.297 mT	{ 4 H: 0.384 mT	0.388 mT	[4] [12]
		{ 4 H: 0.172 mT	0.146 mT	
		average: 0.278 mT	0.267 mT	
		ratio: 2.23	2.66	
3^{τ}	8 H: 0.235 mT	{ 4 H: 0.324 mT	0.335 mT	(Table 2)
		{ 4 H: 0.158 mT	0.131 mT	
		average: 0.241 mT	0.233 mT	
		ratio: 2.05	2.56	

The similar ratios of the 'split values' for 1^{τ} and 3^{τ} strongly support the postulated structural relationship of the ion pairs formed by the two radical anions. The slight decrease in these ratios on going from 1^{τ} to 3^{τ} is consistent with the weaker tendency of the larger radical anion to associate with K^+, while the increase by ca. 20% on passing from MTHF to Et₂O reflects the lower solvating power of the latter solvent.

An analogous comparison seems not indicated for the remaining hyperfine data, since the protons in the CH_2 groups of 1^{τ} and those in the 'side'-benzene rings of 3^{τ} not only greatly differ in the character of their bonds and in their positions relative to the charge bearing π-centres, but also the opposite signs of their coupling constants indicate different mechanism of spin transfer (see above). As is evident from Table 2, there is an unexpectedly large reduction in the coupling constants found for the 'side'-ring protons in the T ion pairs of 3^{τ}, when MTHF is replaced by Et₂O as the solvent. Curiously enough, the averages of these split values approach the absolute numbers calculated by the INDO method (0.072 vs. 0.054 and 0.026 vs. 0.009 mT).

No detailed studies have been performed on the association of 2^{τ} with its counterions, since, in this case, the interest focused on the conformational interconversion [5]. The investigation was, therefore, restricted to the solvents DME/HMPT, DME, and THF in which 2^{τ}, like 3^{τ}, is only loosely associated with the counterion Li^+ or K^+, and the ion pairing does not interfer in the ESR spectra with other phenomena. It has been found that two ground conformations of 2^{τ}, having presumably D_2 symmetry, interconvert in the range of 193–233 K at a rate comparable to the hyperfine time scale. The interconversion gives rise to temperature-dependent ESR spectra from which an activation barrier of 33 kJ/mol has been determined [5]. The transition state of 2^{τ}, having the full D_{2h} symmetry, thus lies well above the ground conformations. As has been stated in the Results, analogous temperature-dependent effects are not observed in the ESR spectra of 3^{τ} which, in the absence of T ion pairing, exhibit the full D_{2h} symmetry of the radical anion. This finding indicates that either 3^{τ} lacks conformational mobility or the activation

barrier is too low for an interconversion to be perceived on the hyperfine time-scale in the temperature range of investigation.

Appendix. – The derivative **4** of 1,2:9,10-dibenzo[2.2]paracyclophane (**3**), in which an inner position of one 'side'-benzene ring has been substituted by a CH_3 group [14], was reduced to its radical anion by reaction with K in DME. The ESR spectrum of **4**$\bar{\cdot}$ *(Fig. 8a)* (g = 2.0031 ± 0.0001) could be exactly fitted by computer-simulation *(Fig. 8b)* with the use of coupling constants determined from the proton ENDOR signals *(Fig. 8c)*. The four pairs of these signals yield the values of 0.240, 0.129, 0.082, and 0.035 mT which are due to eight, five, one, and four protons, respectively (exper. error: ± 0.002 mT). It is reasonable to assign the largest coupling constant (0.240 mT) to the eight protons in the 'deck'-benzene rings and the smallest one (0.035 mT) to the four protons in the outer positions of the 'side'-benzene rings. The five protons responsible for the next largest coupling constant (0.129 mT) are identified with the two protons in the inner positions of the unsubstituted 'side'-benzene ring and with the three CH_3 protons. This assignment leaves the remaining value (0.082 mT) for the single proton in the inner position of the substituted 'side'-benzene ring (*para* to the CH_3 group).
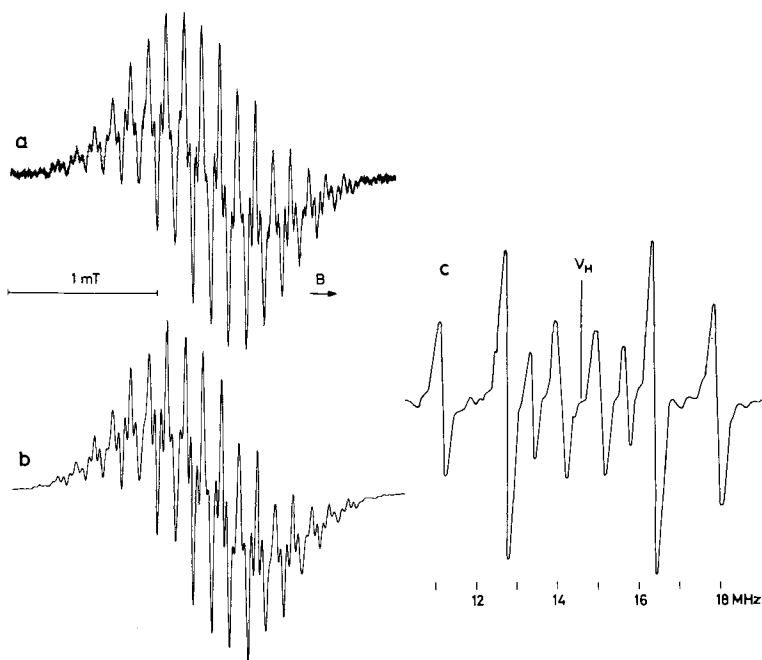

Fig. 8. *ESR* (a) *and proton ENDOR* (c) *spectra of* **4**$\bar{\cdot}$ *in DME.* Counterion: K$^+$; temp.: 203 K. b) *Computer simulation of the ESR spectrum.* Coupling constants as given in the text; line-shape: *Lorentzian;* line-width: 0.050 mT.

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