

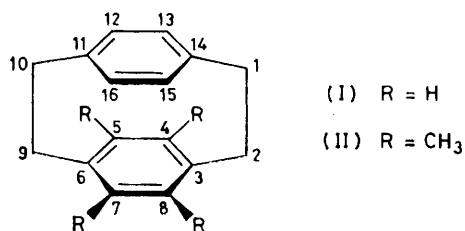
The Radical Ions of 4,5,7,8-Tetramethyl[2.2]paracyclophane

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By the use of strong oxidising and reducing agents, 4,5,7,8-tetramethyl[2.2]paracyclophane (II) has been converted to its radical cation ($\text{II}^{\bullet+}$) and to its radical anion ($\text{II}^{\bullet-}$). These radical ions, as well as those generated from the 12,13,15,16-tetradeuterio ($[\text{H}_4]\text{II}$) and the 1,1,10,10,12,13,15,16-octadeuterio-derivative ($[\text{H}_8]\text{II}$), have been studied by e.s.r. and, in part, by e.n.d.o.r. spectroscopy. In ($\text{II}^{\bullet+}$), the bulk of the spin population is located on the methyl-substituted benzene ring, whereas, in ($\text{II}^{\bullet-}$), it is found on the ring bare of methyl groups. This result corresponds to the effect of the alkyl substitution which enhances the donor and weakens the acceptor character of a π -system. Comparison of the hyperfine data for ($\text{II}^{\bullet+}$) with those of the dimeric radical cation ($\text{II}_2^{\bullet+}$) reveals considerable deviations from the ratio of ca. 0.5, expected for the coupling constants of the protons in such two species. In the e.s.r. spectra of ($\text{II}^{\bullet-}$) the large splittings from the nuclei of the counterions (^{39}K 0.102 and ^{133}Cs 0.596 mT) are notable; they exceed by one order of magnitude the corresponding values for the radical anion of [2.2]paracyclophane (I).

In the last two decades, the radical anions of many cyclophanes have been studied by e.s.r.¹⁻⁹ and, more recently, also by e.n.d.o.r. spectroscopy.⁵⁻⁹ The corresponding radical cations are, in general, not sufficiently stable to be investigated in solution. Only in the case of [2.2](9,10)anthracenophane, which contains two rather extended and readily ionisable π -systems, could both the radical anion^{3,4,8} and the radical cation⁸ be characterised by hyperfine data.

Among the derivatives of [2.2]paracyclophane (I), a promising candidate for the generation of the radical cation is the 4,5,7,8-tetramethyl-substituted compound (II)¹⁰ which possesses an ionisation potential of 7.5 eV, *i.e.* 0.6 eV lower than that of the parent hydrocarbon (I)



(8.1 eV).¹¹ Some time ago, it has been reported that the compound (II) yields a dimeric radical cation ($\text{II}_2^{\bullet+}$) when it is oxidised electrolytically at low temperature (183–203 K) in methylene chloride–trifluoroacetic acid–trifluoroacetic anhydride (10:1:1 ratio).¹² The hyperfine data for this dimer are consistent with an effective symmetry D_{2h} or D_{2d} ; thus the four benzene rings lie in parallel planes, on top of each other.

Under the relatively mild conditions used for the generation of ($\text{II}_2^{\bullet+}$) no significant amounts of the monomeric radical cation ($\text{II}^{\bullet+}$) were formed, because the conversion of (II) into ($\text{II}^{\bullet+}$) requires a more rigorous treatment. For reduction of (II) to the radical anion ($\text{II}^{\bullet-}$) strong agents are likewise necessary, since the tetramethyl-substituted compound (II) possesses an even lower electron affinity than the parent [2.2]paracyclophane (I).¹³ The present paper deals with the

preparation and the hyperfine data of the radical cation ($\text{II}^{\bullet+}$) and of the radical anion ($\text{II}^{\bullet-}$). The radical ions produced from the 12,13,15,16-tetradeuterio- and the 1,1,10,10,12,13,15,16-octadeuterio-derivatives have also been investigated.

RESULTS

Radical Cation ($\text{II}^{\bullet+}$).—Although formation of ($\text{II}^{\bullet+}$) could be brought about by alternative methods, such as reaction of (II) with AlCl_3 in nitromethane at 333 K, e.s.r. spectra of good quality were preferentially obtained for ($\text{II}^{\bullet+}$) upon dissolving (II) in unpurified SbCl_3 at 353 K.¹⁴ The oxidising agent, responsible for the generation of ($\text{II}^{\bullet+}$) by this procedure, is thought to be SbCl_5 (or HSbCl_6) present in trace amounts.¹⁵ Figure 1 shows an e.s.r. spectrum of ($\text{II}^{\bullet+}$), taken in SbCl_3 at 323 K; very similar spectra were observed with the 12,13,15,16-tetra- and 1,1,10,10,12,13,15,16-octa-deuterio-derivatives ($[\text{H}_4]\text{II}$) and ($[\text{H}_8]\text{II}$), as starting materials. Obviously, at least partial dedeuteriation must have occurred under the rigorous conditions of the experiment, due to protic impurities which are inevitable in hygroscopic SbCl_3 . These conditions (polar solvent and relatively high temperature) also precluded the observation of the corresponding e.n.d.o.r. spectra.

The e.s.r. spectrum of ($\text{II}^{\bullet+}$) was satisfactorily fitted with the use of three coupling constants, 0.574 (12 H), 0.188 (4 H), and 0.112 mT (4 H), as is evident from the computer simulation of the experimental curve (Figure 1). The assignment of the largest value (0.574 mT) to the twelve equivalent protons of the four methyl groups ($\alpha_{\text{H}4,5,7,8}(\text{CH}_3)$) is straightforward. Unfortunately, this does not hold for the remaining coupling constants, each from a set of four equivalent protons, because specific deuteriation fails to provide the relevant information (see above). According to experience,^{8,16,17} it is, however, reasonable to assume that the relative magnitudes of these values follow the sequence of the corresponding coupling constants for the dimer ($\text{II}_2^{\bullet+}$), in which case the assignment was unambiguous, based on comparison between the e.s.r. spectrum of ($\text{II}_2^{\bullet+}$) with those of $\{([\text{H}_4]\text{II})_2^{\bullet+}\}$ and $\{([\text{H}_8]\text{II})_2^{\bullet+}\}$.¹² (No dedeuteriation took place under the milder conditions required for generation of the dimeric radical cations.)

With such an assumption, the larger (0.188 mT) and the smaller (0.112 mT) of the two four-proton coupling constants observed for (II⁺) have been assigned to the sets of four equivalent protons in the 2- and 9-methylene groups ($a_{H2,9(CH_2)}$) and the benzene ring ($a_{H12,13,15,16}$), respectively.

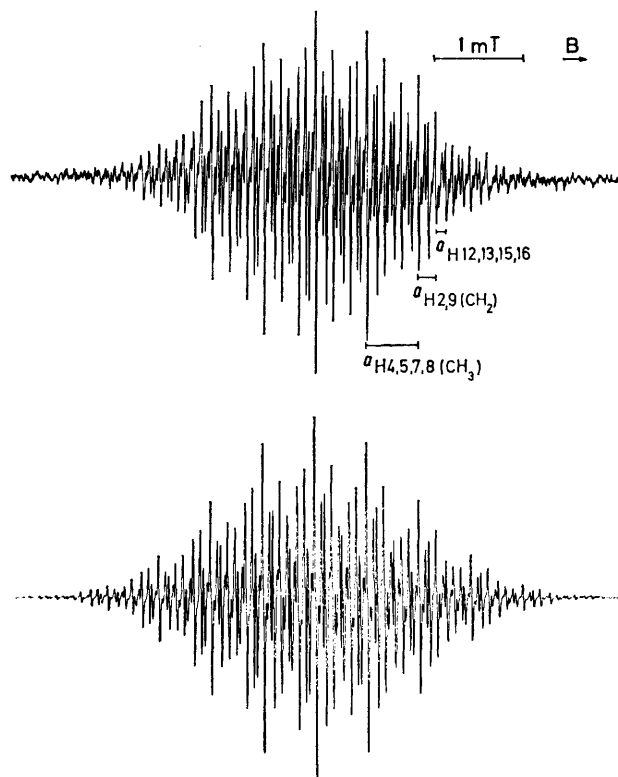


FIGURE 1 E.s.r. spectrum of the radical cation of 4,5,7,8-tetramethyl[2.2]paracyclophane (II). Top: experimental spectrum; solvent $SbCl_3$, temperature 323 K. Bottom: spectrum simulated with the use of the coupling constants 0.574 (12 H), 0.188 (4 H), and 0.112 mT (4 H); line-shape Lorentzian, line-width 0.014 mT

This assignment implies that the splitting from the four equivalent protons in the 1- and 10-methylene groups ($a_{H1,10(CH_2)}$) is too small to be resolved (<0.01 mT). The finding that both $([{}^2H_4]II)$ and $([{}^2H_8]II)$ yield upon oxidation the same e.s.r. spectrum as (II) can then be rationalised by a rapid D-H exchange at the 12,13,15,16-positions of the benzene ring. Owing to such an exchange, $([{}^2H_4]II)$ is converted into (II^+) , while analogous reactions of $([{}^2H_8]II)$ lead to the radical cation of the 1,1,10,10-tetradeuterio-derivative $([{}^2H_4]II^+)$. It is to be expected that the e.s.r. spectra of (II^+) and of this radical cation will not differ significantly if the coupling constant $a_{H1,10(CH_2)}$ for (II^+) and an even smaller deuterium splitting $a_{D1,10(CD_2)}$ for $([{}^2H_4]II^+)$ escape observation.

Radical Anion (II^-) .—Reaction of (II) with potassium or cesium mirrors in 1:1 1,2-dimethoxyethane (DME)–tetrahydrofuran (THF) at low temperature proved to be a suitable procedure for the generation of (II^-) in a sufficient concentration. Figure 2 shows an e.s.r. spectrum of (II^-) in such a solvent mixture, taken at 163 K with K^+ as the counter-ion. The corresponding spectra of $([{}^2H_4]II^-)$ and $([{}^2H_8]II^-)$, which are not reproduced in this paper, were poorly resolved and rather uninformative. In contrast the effect of deuteration was very conspicuous in the e.n.d.o.r.

spectra obtained under the same conditions. The potential of this technique is illustrated by Figure 3 which displays the 1H e.n.d.o.r. signals for (II^-) , $([{}^2H_4]II^-)$, and $([{}^2H_8]II^-)$. Thus, the high-frequency part ($\nu > \nu_H$) of the e.n.d.o.r. spectrum of (II^-) consists merely of four signals which correspond to the four coupling constants. The most intense of these signals, at 15.2 MHz (0.099 mT), stems from the twelve equivalent protons of the four methyl groups, as is confirmed by the multiplicity of the corresponding splitting, $a_{H4,5,7,8(CH_3)}$, in the e.s.r. spectrum (Figure 2). Of the three remaining signals, due to sets of four equivalent protons, the outermost one, at 17.9 MHz (0.295 mT) disappears on going from (II^-) to $([{}^2H_4]II^-)$. Further deuteration to $([{}^2H_8]II^-)$ causes the second outermost signal, at 16.1 MHz (0.168 mT) to vanish. These two signals must therefore be assigned to the sets of four equivalent protons in the benzene ring ($a_{H12,13,15,16}$) and the

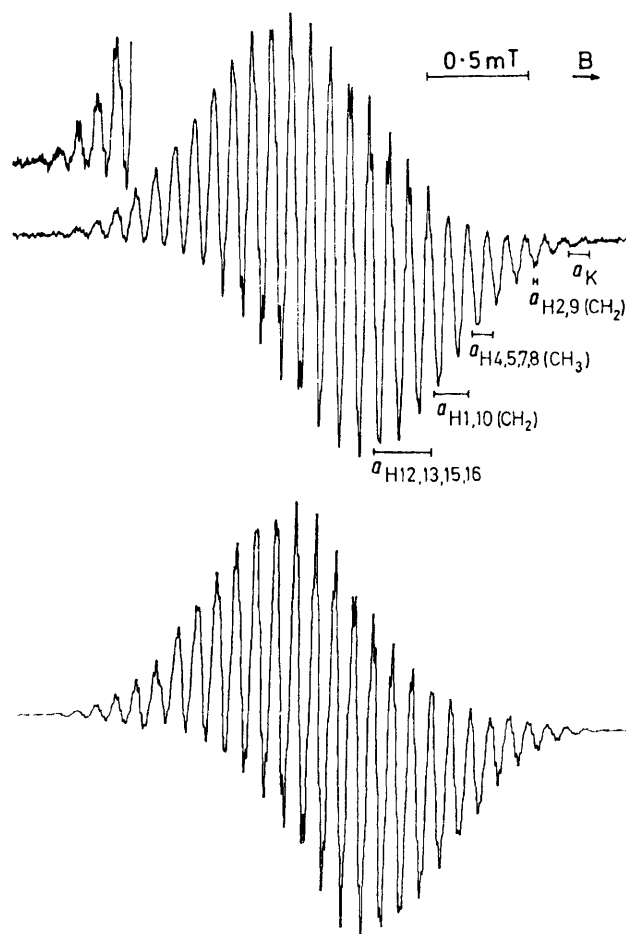


FIGURE 2 E.s.r. spectrum of the radical anion of 4,5,7,8-tetramethyl[2.2]paracyclophane (II). Top: experimental spectrum; solvent DME–THF (1:1), counter-ion K^+ , temperature 163 K. Bottom: spectrum simulated with the use of the coupling constants 0.295 (4 H), 0.168 (4 H), 0.099 (12 H), 0.015 (4 H), and 0.102 mT (${}^{39}K$); line-shape Lorentzian; line-width 0.015 mT

1- and 10-methylene groups ($a_{H1,10(CH_2)}$) of (II^-) , respectively. As a consequence, the innermost signal, at 14.0 MHz (0.015 mT) is left for the four equivalent protons in the 2- and 9-methylene groups ($a_{H2,9(CH_2)}$).

Analysis by computer simulation (Figure 2) indicates

that the e.s.r. spectrum of ($\text{II}^{\cdot-}$) exhibits, in addition to the four above-mentioned proton coupling constants, a sub-

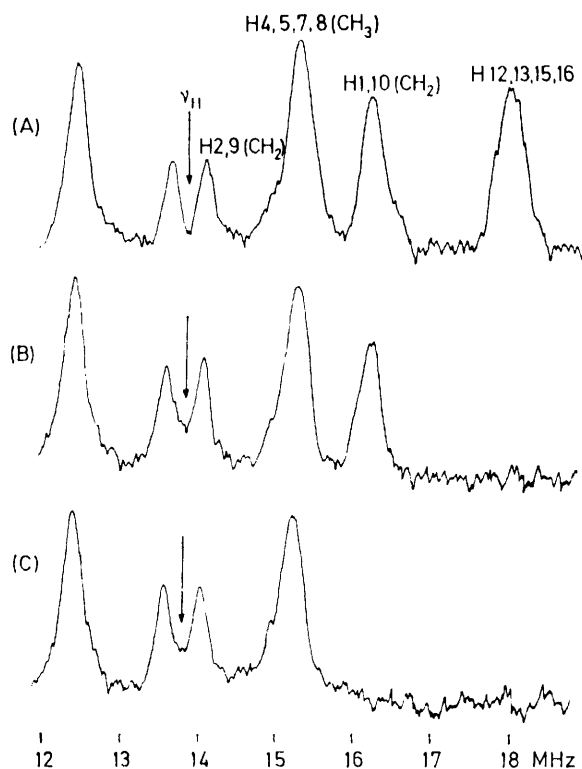


FIGURE 3 E.n.d.o.r. spectra of the radical anions of 4,5,7,8-tetramethyl[2.2]paracyclophane (II) (A), and its 12,13,15,16-tetradeuterio-([$^2\text{H}_4$]II) (B) and 1,1,10,10,12,13,15,16-octadeuterio-derivatives ([$^2\text{H}_8$]II) (C). Solvent DME-THF (1 : 1), counter-ion K^+ , temperature 163 K. ν_{H} = frequency of the free proton

stantial hyperfine splitting, a_{K} 0.102 mT, from the ^{39}K nucleus (I 3/2) of the counter-ion. Using cesium instead

the analogous values for the dimeric radical cation ($\text{II}_2^{+\cdot}$) and for the radical anion ($\text{I}^{\cdot-}$) of the parent [2.2]paracyclophane. According to the proton coupling constants for ($\text{II}^{+\cdot}$) and ($\text{II}^{\cdot-}$), the bulk of the π -spin population in the radical cation is accommodated on the methyl-substituted benzene ring, whereas the π -spin distribution in the radical anion favours the alternative ring which is bare of methyl groups. The preference of the unpaired electron for different aromatic moieties in ($\text{II}^{+\cdot}$) and ($\text{II}^{\cdot-}$) is thus consistent with the effect of the alkyl substitution which enhances the donor, and weakens the acceptor, character of a π -system.

On passing from a monomeric to a dimeric radical cation, one expects that the corresponding coupling constants will be approximately halved. In fact, the ratios of such values have been found to be in most cases close to, or slightly lower than 0.5.^{16,17} For ($\text{II}^{+\cdot}$) and ($\text{II}_2^{+\cdot}$), the ratio, $0.223 \text{ mT} : 0.574 \text{ mT} = 0.39$, of the largest coupling constants $a_{\text{H4,5,7,8}(\text{CH}_3)}$ is still comparable to the analogous values, $0.50 \text{ mT} : 1.10 \text{ mT} = 0.45$ and $0.351 \text{ mT} : 0.808 \text{ mT} = 0.43$, obtained for the methyl protons in dimeric and monomeric radical cations of durene¹⁷ and 9,10-dimethylantracene,^{8,17} respectively. However, the remaining smaller coupling constants of the protons in ($\text{II}^{+\cdot}$) and ($\text{II}_2^{+\cdot}$) exhibit much larger deviations from 0.5. One may argue that the structure of ($\text{II}_2^{+\cdot}$) is essentially different from those of other dimeric radical cations which consist of only *two* parallel π -systems.^{8,16,17} The observed symmetry, D_{2h} or D_{2d} , of ($\text{II}_2^{+\cdot}$) requires that four benzene rings should lie in parallel planes whereby the two molecules of (II) must have the equivalent rings (*i.e.* both bearing methyl groups or both not substituted) in adjacent positions.¹² The π -systems of these two adjacent rings can thus interact more strongly upon dimerisation than those of the remaining, distant ones, and, as a consequence, the

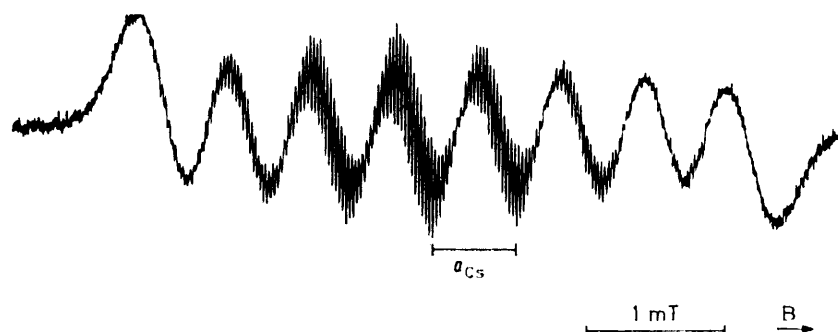


FIGURE 4 E.s.r. spectrum of the radical anion of 4,5,7,8-tetramethyl-1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane ([$^2\text{H}_8$]II). Solvent DME-THF (1 : 1), counter-ion Cs^+ , temperature 163 K

of potassium as a reducing agent, this splitting was replaced by the one from the ^{133}Cs nucleus (I 7/2). The large magnitude of a_{Cs} , which amounts to 0.596 mT, is particularly evident in the case of the deuterio-derivatives, as shown by the e.s.r. spectrum of ([$^2\text{H}_8$]II $^{\cdot-}$) in Figure 4.

DISCUSSION

Figure 5 summarizes the hyperfine data and the g factors for the radical ions ($\text{II}^{+\cdot}$) and ($\text{II}^{\cdot-}$), along with

π -spin distribution in ($\text{II}_2^{+\cdot}$) need no longer faithfully reflect that in ($\text{II}^{+\cdot}$). Changes in geometry, which can occur on passing from ($\text{II}^{+\cdot}$) to ($\text{II}_2^{+\cdot}$) and do not substantially alter the π -spin distribution, should also be considered. Such changes would affect $a_{\text{H4,5,7,8}(\text{CH}_3)}$ to a lesser extent than the remaining coupling constants, namely $a_{\text{H12,13,15,16}}$ (due to its sensitivity to the distortion of the benzene ring from planarity¹⁸), as well as $a_{\text{H1,10}(\text{CH}_2)}$

and $a_{\text{H}2,9(\text{CH}_3)}$ (because of the well known dependence on the conformation of the dimethylene bridges¹⁹).

The most striking results for $(\text{II}^{\cdot-})$ are the unusually large coupling constants due to the ^{39}K and ^{133}Cs nuclei of the counter-ions (a_{K} ca. 0.1 and a_{Cs} ca. 0.6 mT).

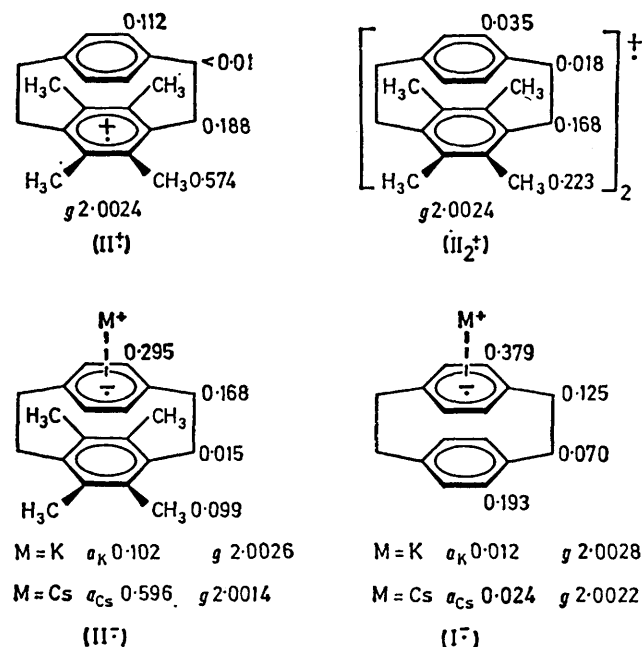


FIGURE 5 Coupling constants (mT) and g factors for the radical cation, the radical anion, and the dimeric radical cation of 4,5,7,8-tetramethyl[2.2]paracyclophane (II), and for the radical anion of [2.2]paracyclophane (I). (II⁺), solvent SbCl_5 , temperature 323 K; (II^{·-}), solvent DME-THF (1 : 1), temperature 163 K; (II₂⁺), solvent $\text{CH}_2\text{Cl}_2\text{-CF}_3\text{CO}_2\text{H-(CF}_3\text{CO)}_2\text{O}$ (10 : 1 : 1), temperature 193 K; (I^{·-}), solvent THF, temperature 193 (M = K) and 173 K (M = Cs).

Values of this magnitude have hitherto been observed only in exceptional cases where the alkali-metal cations are bound in a chelate-like fashion to two oxygen atoms of a radical anion; the best known example are the ketyls of *o*-dimesitylbenzenes.²⁰ By contrast, for the counter-ions associated with the radical anions of hydrocarbons, the coupling constants a_{K} and a_{Cs} are much smaller,

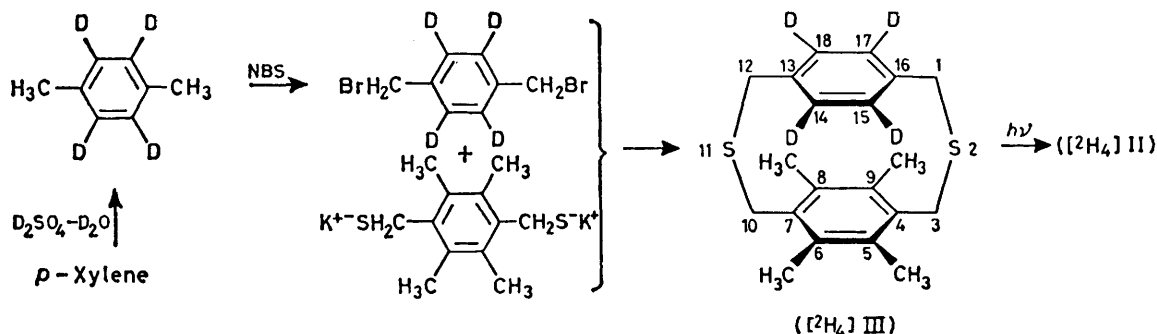
because the structure of the ion pair formed by (I^{·-}) with K^+ has been clarified in a previous work.⁴ In this ion pair, the cation is located above the centre of one benzene ring which accommodates the larger part of the π -spin population; as a consequence, the symmetry of the radical anion is lowered from D_{2h} to C_{2v} . It is reasonable to assume that a similar structure of C_{2v} symmetry is encountered not only with the ion pairs of (I^{·-}) and Cs^+ , but also with those of (II^{·-}) and K^+ or Cs^+ . According to the π -charge distribution in (II^{·-}), the counter-ion should be situated above the benzene ring which is not substituted by the methyl groups (Figure 5). The fact that (II^{·-}) has only one such preferred site, whereas two equivalent sites of this kind are present in (I^{·-}), constitutes a distinctive mark of the ion pairs in question. Correspondingly, the ion pairs of (II^{·-}) should be longer lived and, presumably, tighter than those of (I^{·-}), for which the replacement of the solvent THF by DME suffices to speed up the intramolecular migration of the counter-ion to a frequency that is high on the hyperfine time scale.² The answer to the question whether this distinction alone can account for the differences of one order of magnitude in the coupling constants must await the results of further studies on ion pairs of structurally related radical anions. It is noteworthy that the large value a_{Cs} for (II^{·-}) is combined with a low g factor (Figure 5).

EXPERIMENTAL

4,5,7,8-Tetramethyl[2.2]paracyclophane (II).—The undeuteriated compound (II) was synthesized by Jenny and Davatz¹⁰ and generously donated to us by Professor W. Jenny.

4,5,7,8-Tetramethyl-12,13,15,16-tetradeuterio[2.2]paracyclophane ([²H₄]II) and 4,5,7,8-Tetramethyl-1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane ([²H₈]II).—The preparation of ([²H₄]II) was carried out according to Scheme 1.

Repeated treatment of an emulsion of *p*-xylene in $\text{D}_2\text{SO}_4\text{-D}_2\text{O}$ (molar ratio 1 : 1)²² led to the 2,3,5,6-²H₄-derivative (97% isotopic purity) which was subsequently reacted with two equivalents of *N*-bromosuccinimide (dibenzoyl peroxide as initiator), to afford the correspond-



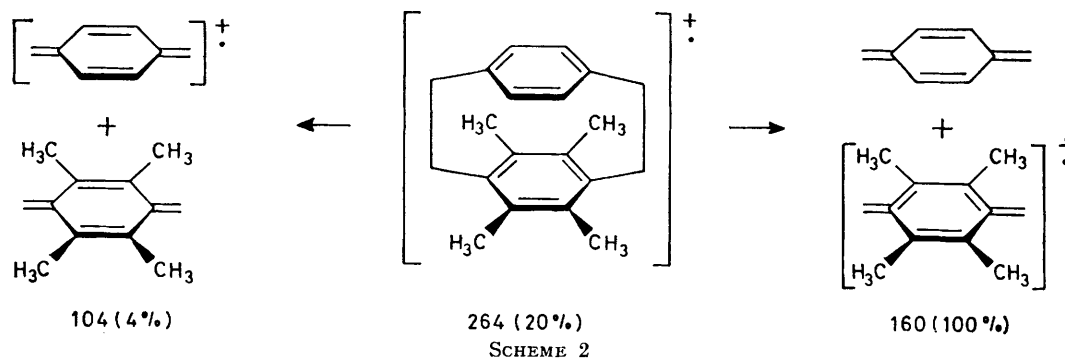
SCHEME 1

generally by one order of magnitude.²¹ This finding is exemplified in Figure 5 by the data for (I^{·-}) (a_{K} ca. 0.01 and a_{Cs} ca. 0.02 mT; see also Appendix). Their comparison with those for (II^{·-}) is of particular interest,

ing *p*-xylylene dibromide (40%), m.p. 145 °C. An equimolar mixture of this dibromide and 3,6-bis(mercaptomethyl)durene in tetrahydrofuran was added dropwise to a solution of KOH in methanol (5% H₂O), at 60 °C, with vigorous

stirring and under nitrogen. After removal of the solvent, the resulting 2,11-dithia-5,6,8,9-tetramethyl-14,15,17,18-tetradeuterio[3.3]paracyclophane ($[^2\text{H}_4]\text{III}$) was extracted with chloroform, purified by chromatography on alumina

by the method introduced previously in the synthesis of non-symmetrically substituted [2.2]paracyclophanes.²³ A 10^{-3}M solution of ($[^2\text{H}_4]\text{III}$) in trimethyl phosphite was u.v.-irradiated for 4 h under nitrogen by an immersed high-pres-



(Fluka, neutral, activity I, benzene as eluting agent) and recrystallised from hexane-chloroform (2 : 1) (45%), m.p. 200 °C. Sulphur extrusion from ($[^2\text{H}_4]\text{III}$) was carried out

sure mercury lamp (Hanau TQ 150; Pyrex filter). Evaporation of the solvent afforded crude product ($[^2\text{H}_4]\text{II}$) which was chromatographed on alumina (Fluka neutral, activity I, hexane as eluting agent), recrystallised from ethanol and sublimed at 60 °C and 0.1 Torr (35%), m.p. 109 °C.

An analogous reaction sequence starting with perdeuterio-*p*-xylene (Aldrich; Gold Label) led to 2,11-dithia-5,6,8,9-tetramethyl-1,1,12,12,14,15,17,18-octadeuterio[3.3]paracyclophane ($[^2\text{H}_8]\text{III}$) which was converted into ($[^2\text{H}_8]\text{II}$), m.p. 110 °C.

The isotopic purities of ($[^2\text{H}_4]\text{II}$) and ($[^2\text{H}_8]\text{II}$), determined by comparison of their ^1H n.m.r. spectra with that of (II), were 97 and 99%, respectively. The mass spectrum of (II) impressively demonstrated the higher tendency of the tetramethyl-substituted moiety to accept a positive charge, as is indicated (Scheme 2) by the m/e values of the relevant peaks and their relative intensities (in parentheses). Similar intensities were also found for the deuterio-derivatives, for which the m/e numbers 264 and 104 were increased by 4 and 8, in the case of ($[^2\text{H}_4]\text{II}$) and ($[^2\text{H}_8]\text{II}$), respectively.

E.s.r. spectra were taken with a Varian ESR-E9-spectrometer coupled to a Varian ENDOR-1700-system. The experimental error is ± 0.002 and ± 0.001 mT for coupling constants larger and smaller, respectively, than 0.1 mT. The accuracy in the g factors is ± 0.000 1.

APPENDIX

The radical anion of [2.2]paracyclophane (I) has been studied only at low temperatures (below 193 K),²⁻⁵ although, due to its higher stability relative to the radical anion of the 4,5,7,8-tetramethyl derivative (II), such an investigation can be carried out up to 243 K. Moreover, no data are yet available for ($\text{I}^{\cdot-}$) with the counter-ion Cs^+ . In order to make up for these deficiencies and to provide data for comparison with the corresponding values of ($\text{II}^{\cdot-}$), the e.s.r. spectra of ($\text{I}^{\cdot-}$) in THF were taken in the range between 163 and 243 K, with both K^+ and Cs^+ as counterions. Contrary to the coupling constants of the protons, which were only slightly affected by the changes in experimental conditions, those of the ^{39}K and ^{133}Cs nuclei proved to be strongly temperature-dependent. The Table lists the values of a_{K} and a_{Cs} obtained over 163–243 K, along with the g factors which also exhibit a marked sensitivity to variations in temperature. It is interesting to note that the coupling constant a_{Cs} changes its sign at ca. 193 K, at which temperature its

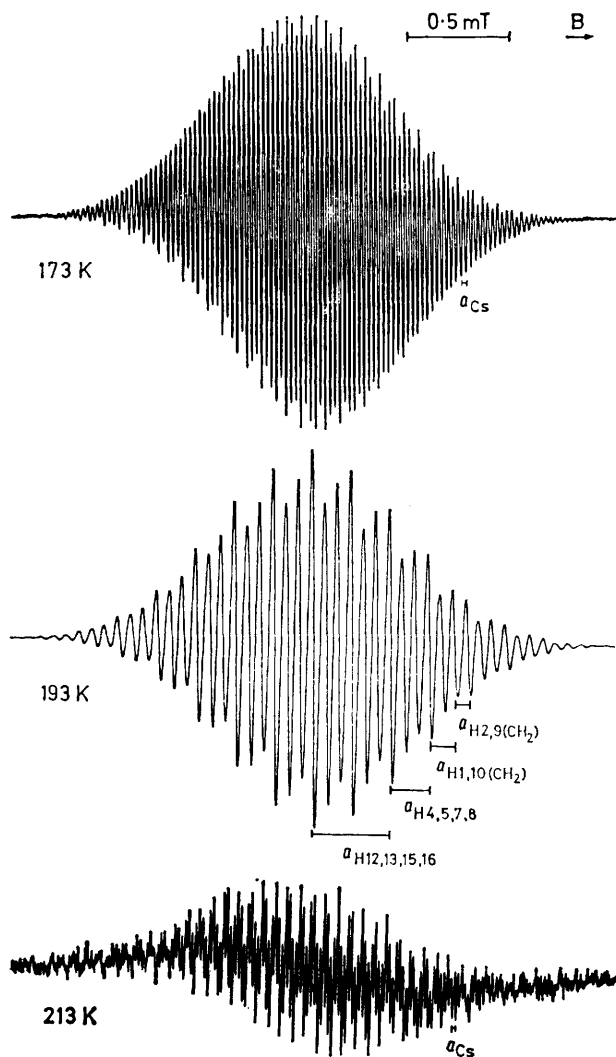


FIGURE 6 E.s.r. spectra of the radical anion of [2.2]paracyclophane (I). Solvent THF, counter-ion Cs^+ , temperature as indicated

value is *ca.* 0. This finding is illustrated in Figure 6 by the e.s.r. spectra of (I⁻) at 173, 193, and 213 K. According to previous reports on analogous systems, the sign of a_{Cs}

Temperature dependence of the g factor and of the ^{39}K and ^{133}Cs coupling constants [a_{K} and a_{Cs} (mT)] for the ion pairs formed between the radical anion of [2.2]paracyclophane (I) and the alkali-metal counter-ions (M^+)^a

T/K	$\text{M} = \text{K}$		$\text{M} = \text{Cs}$	
	a_{K}	g	a_{Cs}	g
163	<0.008	2.0029	0.038	2.0020
173	0.0080		0.024	2.0022
183	0.0090	2.0028	0.016	2.0023
193	0.0115		<0.005	2.0024
203	0.0135	2.0028	0.007	
213	0.0150		0.017	2.0027
223	0.0165		0.019	
233	0.0180			
243	0.0195			

^a Experimental error: ± 0.0005 mT in a_{K} , ± 0.001 mT in a_{Cs} , and ± 0.0001 in g

should be negative and positive, respectively, below and above 193 K.²⁴

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REFERENCES

- S. I. Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 6462; A. Ishitani and S. Nagakura, *Mol. Phys.*, 1967, **12**, 1.
- F. Gerson and W. B. Martin, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 1883.
- D. J. Williams, J. M. Pearson, and M. Levy, *J. Amer. Chem. Soc.*, 1971, **93**, 5483.
- F. Gerson, W. B. Martin, jun., and C. Wydler, *Helv. Chim. Acta*, 1976, **59**, 1365.
- F. Gerson, W. B. Martin, jun., and C. Wydler, *J. Amer. Chem. Soc.*, 1976, **98**, 1318.
- J. Bruhin, F. Gerson, W. B. Martin, jun., and C. Wydler, *Helv. Chim. Acta*, 1977, **60**, 1915.
- Ch. Elschenbroich, F. Gerson, and J. A. Reiss, *J. Amer. Chem. Soc.*, 1977, **99**, 60.
- F. Gerson, G. Kaupp, and H. Ohya-Nishiguchi, *Angew. Chem.*, 1977, **89**, 666; *Angew. Chem. Internat. Edn.*, 1977, **16**, 657.
- F. Gerson, W. Huber, and O. Wennerström, *Helv. Chim. Acta*, 1978, **61**, 2763; P. Fürderer, F. Gerson, H. Ohya-Nishiguchi, I. Böhm, and H. Hopf, *ibid.*, 1979, **62**, 2569.
- W. Jenny, J. Bruhin, and A. Davatz, *Chimia*, 1973, **27**, 641; A. Davatz, Ph.D. Thesis, Universität Bern, 1976.
- J. P. Maier, unpublished data.
- J. Bruhin, F. Gerson, and H. Ohya-Nishiguchi, *Helv. Chim. Acta*, 1977, **60**, 2471.
- F. Gerson, H. Ohya-Nishiguchi, and C. Wydler, *Angew. Chem.*, 1976, **88**, 617; *Angew. Chem. Internat. Edn.*, 1976, **15**, 552.
- F. Gerson and J. Heinzer, *Helv. Chim. Acta*, 1967, **50**, 1852.
- E. C. Baughan, T. P. Jones, and L. G. Stoodley, *Proc. Chem. Soc.*, 1963, 274.
- I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 1965, **43**, 2712; O. W. Howarth and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1966, **88**, 4514; *J. Chem. Phys.*, 1970, **52**, 6258; H. van Willigen, E. de Boer, J. T. Cooper, and W. F. Forbes, *ibid.*, 1968, **49**, 1190; W. F. Forbes and J. T. Cooper, *Canad. J. Chem.*, 1968, **46**, 1158; T. C. Chiang and A. H. Reddoch, *J. Chem. Phys.*, 1970, **52**, 1371; S. Shih and R. M. Dessau, *ibid.*, 1971, **55**, 3757; H. Yoshimi and K. Kuwata, *Mol. Phys.*, 1972, **23**, 297.
- F. Gerson and H. Ohya-Nishiguchi, unpublished results.
- A. Berndt, *Tetrahedron*, 1969, **25**, 37; F. Gerson, K. Müllen, and E. Vogel, *Helv. Chim. Acta*, 1971, **54**, 2731; *J. Amer. Chem. Soc.*, 1972, **94**, 2924; F. Gerson, K. Müllen, and C. Wydler, *Helv. Chim. Acta*, 1976, **59**, 1371.
- C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535; A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, 1961, **4**, 425.
- B. J. Herold, A. F. Neiva-Correia, and J. dos Santos Veiga, *J. Amer. Chem. Soc.*, 1965, **87**, 2661; B. J. Herold, L. J. Alcácer, A. J. Ferrer Correia, A. J. Pereira Domingos, M. Celina R. Lazana, and J. dos Santos Veiga, *Rev. Port. Quím.*, 1969, **11**, 188; B. J. Herold, H. M. Novais, M. Celina R. Lazana, and P. B. Correia, *ibid.*, 1971, **13**, 78.
- F. Gerson, 'High Resolution E.S.R. Spectroscopy,' Verlag Chemie, Weinheim; Wiley, New York, 1970, ch. A.2.2; M. C. R. Symons, *J. Phys. Chem.*, 1967, **71**, 172; J. H. Sharp and M. C. R. Symons, in 'Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley, New York, 1972, vol. II, ch. 5.
- D. Grime and I. M. Ward, *Trans. Faraday Soc.*, 1958, **54**, 959.
- J. Bruhin and W. Jenny, *Tetrahedron Letters*, 1973, 1215.
- G. W. Canters, C. Corvaja, and E. de Boer, *J. Chem. Phys.*, 1971, **54**, 3026; G. W. Canters and E. de Boer, *Mol. Phys.*, 1973, **26**, 1185; R. D. Rieke and S. E. Bales, *Chem. Phys. Letters*, 1972, **12**, 631.