The Radical Anions of [2.2]Metaparacyclophane and Some Derivatives. A Comprehensive ESR, ENDOR, and TRIPLE Resonance Study of Unstable Paramagnetic Species in Solution

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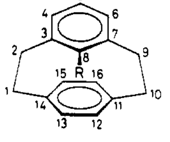
Abstract: The thermodynamically and kinetically unstable radical anion of [2.2]metaparacyclophane (**1**) has been fully characterized by its hyperfine data with the use of ESR, ENDOR, and TRIPLE resonance spectroscopy. For the sake of assignment of coupling constants to protons in individual positions, the investigations have been extended to include the radical anions of the first synthesized 1,1,10,10,12,13,15,16- and 1,1,2,2,9,9,10,10-octadeuterio derivatives (para-D_8-**1** and bridge-D_8-**1**, respectively), in addition to 8-deuterio[2.2]metaparacyclophane (8-D-**1**). The four major coupling constants belong to the pairs of protons at the para-bridged benzene ring of $\mathbf{1}^{\bullet-}$ (0.131 and 0.106 mT) and in the adjacent methylene groups (0.268 and 0.182 mT); they all have the same sign which is assumed to be positive. INDO calculations confirm that the spin population in $\mathbf{1}^{\bullet-}$ is largely localized on the para-bridged ring. The singly occupied orbital at this ring correlates with the "symmetric" LUMO of benzene rather than with its "antisymmetric" counterpart. In the radical anion of 8-cyano[2.2]metaparacyclophane (**2**), the spin population is shifted onto the cyano-substituted meta-bridged benzene ring, as verified by the study of the radical anion of the 1,1,10,10,12,13,15,16-octadeuterio derivative (para-D_8-**2**). The secondary reduction products of **1** and **2** have been identified by their ESR spectra as the radical anions of 3,4′-dimethylbibenzyl (**4**) and its 2-cyano derivative (**5**). This structure is confirmed by the spectral analysis of the analogous deuterated products obtained from 8-D-**1**, para-D_8-**1**, bridge-D_8-**1**, and para-D_8-**2**.

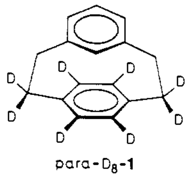
[2.2]Metaparacyclophane (**1**) was first prepared by Cram and co-workers[2a] via an acid-catalyzed rearrangement of [2.2]paracyclophane. Later on, **1** has become available owing to synthetic methods introduced by other research groups.[3,4] A versatile procedure, appropriate for the synthesis of substituted derivatives, makes use of 2,11-dithia[3.3]metaparacyclophane as a precursor.[3d,f,g,4] The meta-bridged benzene ring of **1** has been shown to undergo conformational flipping[2b,d,3b,c,f,4a,5] (Figure 1) with a substantial energy barrier (ca. 80 kJ/mol), so that elevated temperatures (about 400 K) were required for the interconversion to be revealed on NMR time scale. A great part of this energy is believed to arise from steric destabilization of the transition state in which the 8-hydrogen atom of the meta-bridged ring impinges into the electron cloud of the para-bridged one. Preliminary X-ray crystallographic studies of **1** were carried out by Trueblood and Crisp;[6] their results have recently been refined by Renault et al.[7] The deformations of the benzene rings in **1** are similar to those of the corresponding rings in para- and meta[2.2]cyclophanes, with the para- and meta-bridged rings being bent in a boat- and a chair-like form, respectively. The angle between the two aromatic planes defined by the carbon atoms 3, 4, 6, and 7, on one hand, and 12, 13, 15, and 17, on the other, is about 13°. It should be noted that the angle between the 11,12,16-plane and 10,11-bond vector (or between 13,14,15-plane and 1,14-bond vector) is even larger than the analogous angle in [2.2]paracyclophane. The para-bridged moiety of **1** is thus more strongly tilted than those of the isomeric compound. ^{13}C and ^{1}H NMR studies of **1**, performed by the same authors,[7] indicate that its molecular structure in solution does not significantly differ from the X-ray crystallographic one. These studies confirm the previous findings[2b,d,3b,c,f,4a,5] that the conformational flipping of the meta-bridged benzene ring in **1** is detectable only at relatively high temperatures.

In view of the unique arrangement of the two benzene rings in **1**, an investigation of the radical anion $\mathbf{1}^{\bullet-}$ appeared to be an attractive research project. Of particular interest was the spin distribution in $\mathbf{1}^{\bullet-}$, since it could not reliably be predicted by conventional MO methods and thus had to be elucidated by experiment. An ESR study, which was undertaken to this aim, has met with many difficulties due to the following properties of $\mathbf{1}^{\bullet-}$: (i) low thermodynamic and kinetic stability, making special techniques necessary for preparation and handling of the samples; (ii) lack of symmetry elements, except for a mirror plane, leading to a rather complex ESR spectrum which could hardly be analyzed without availability of efficient ENDOR instrumentation; (iii) need of specifically deuterated derivatives for the assignment of nine coupling constants to the seven proton pairs and the two single protons.

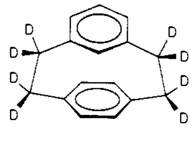
In the present work, the radical anions of **1** and three isotopically labeled derivatives have been subjected to a detailed study by ESR, ENDOR, and TRIPLE resonance spectroscopy. These derivatives are 8-deuterio[2.2]metaparacyclophane (8-D-**1**)[3f] as well as the hitherto unknown 1,1,10,10,12,13,15,16- and 1,1,2,2,9,9,10,10-octadeuterio[2.2]metaparacyclophanes (para-D_8-**1** and bridge-D_8-**1**, respectively).



1 R = H
8-D-**1** R = D



para-D_8-**1**



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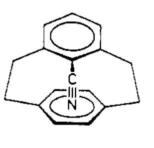

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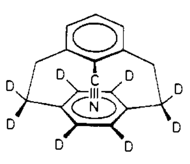

para-D_8-**2**

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[1] (a) Present address: F. Hoffmann-La Roche & Co., AG, Basel. (b) Permanent address: Department of Chemistry, Union College, Schenectady, NY 12308.

[2] (a) Cram, D. J.; Helgeson, D. L.; Lock, D.; Singer, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 1324. (b) Hefelfinger, D. T.; Cram, D. J. *Ibid.* **1970**, *92*, 1073. (c) Hefelfinger, D. T.; Cram, D. J. *Ibid.* **1971**, *93*, 4754. (d) Hefelfinger, D. T.; Cram, D. J. *Ibid.* **1971**, *93*, 4767.

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[5] Akabori, S.; Hayashi, S.; Mawa, M.; Shiomi, K. *Tetrahedron Lett.* **1969**, 3727.

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[7] Renault, A.; Cohen-Addad, C.; Lajzerowicz-Bonneteau, J.; Dutasta, J.-P.; Cris, M. J. *Acta Crystallogr., Sect. B* **1987**, *43*, 480.

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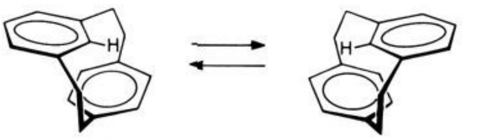

Figure 1. Flipping of the meta-bridged ring in **1**; reproduced (in part) from ref 3f.

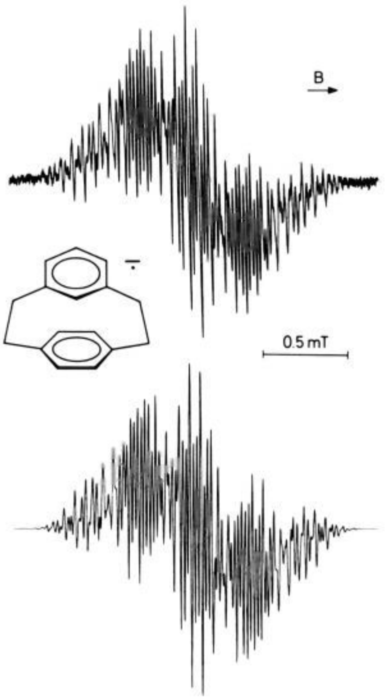

Figure 2. Top: ESR spectrum of $1^{\bullet-}$. Solvent DME–THF (4:1); counterion, K^+; temp, 168 K. Bottom: computer simulation. Coupling constants, see text; line shape, Lorentzian; line width, 0.020 mT.

In order to assess the effect of substitution in the sterically exposed 8-position, this study has been extended to the radical anions of 8-cyano[2.2]metaparacyclophane (**2**) and its first synthesized 1,1,10,10,12,13,15,16-octadeuterio derivative (para-D_8-**2**). Secondary paramagnetic products formed upon prolonged reduction of all these compounds have also been investigated. A few preliminary results were briefly mentioned in a review on the radical ions of phanes.[8]

Results

Source of Compounds. Samples of the unlabeled [2.2]metaparacyclophane (**1**) and its 8-cyano derivative (**2**) were kindly provided by Professor V. Boekelheide. The deuterated compounds 8-D-**1**, para-D_8-**1**, bridge-D_8-**1**, and para-D_8-**2** have been synthesized according to the procedures described in the Experimental Section.

Radical Anions of [2.2]Metaparacyclophane (1) and Its Deuterio Derivatives. As stated in the Introduction, the radical anion $1^{\bullet-}$ is both thermodynamically and kinetically unstable. The half-wave reduction potential, $E_{1/2}$, of **1** has been estimated to be substantially more negative than that of [2.2]paracyclophane (−3.00 V vs. SCE),[9,10] it is presumably close to the $E_{1/2}$ value of benzene (−3.42 V vs. SCE).[11,10] For that reason, conversion of **1** into $1^{\bullet-}$ required the strongest reducing agents such as potassium metal. The persistence of the radical anion thus obtained was very low, since $1^{\bullet-}$ has only a short lifetime at temperatures above 170 K. Its decay was, in particular, promoted by contact with the surface of the alkali metal. Efficient cooling of the solution and avoiding direct reaction of **1** with the metallic mirror were, therefore, prerequisites for the generation of a radical anion which was sufficiently long-lived for spectroscopic studies. These conditions have been met by reducing **1** with solvated electrons which were produced by dissolving potassium at 168 K in a 4:1 mixture of 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF).[12] (More details are given in the Experimental Section.)

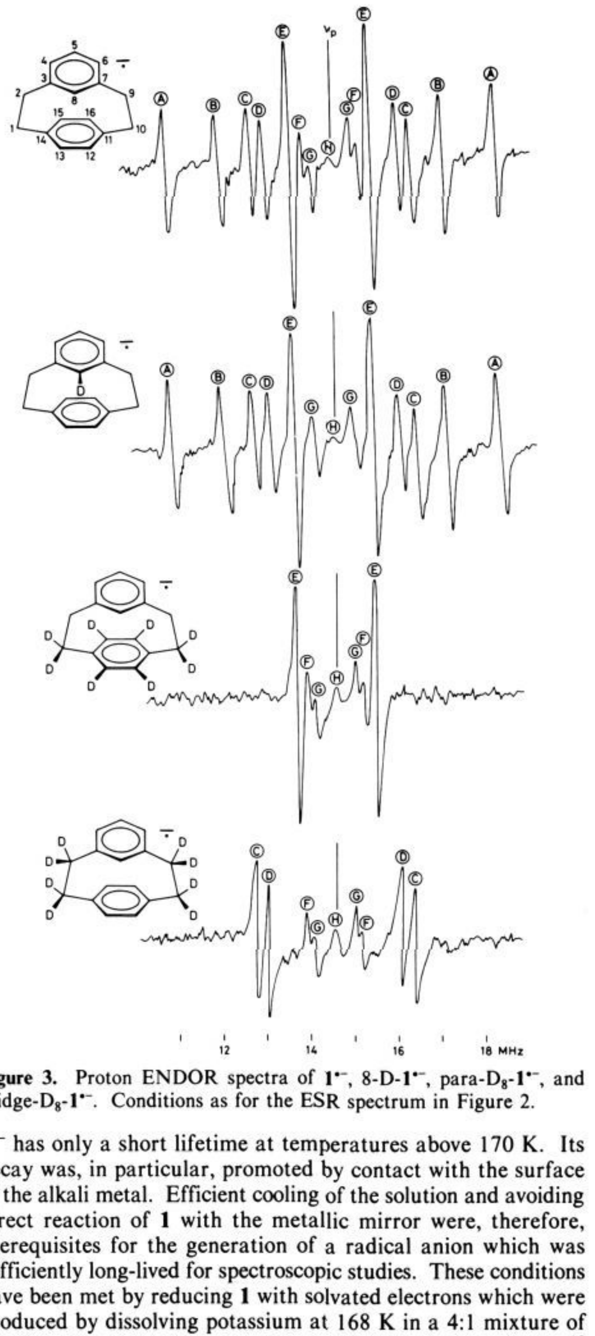

Figure 3. Proton ENDOR spectra of $1^{\bullet-}$, 8-D-$1^{\bullet-}$, para-D_8-$1^{\bullet-}$, and bridge-D_8-$1^{\bullet-}$. Conditions as for the ESR spectrum in Figure 2.

The poor persistence of $1^{\bullet-}$ and the relative complexity of its hyperfine pattern were handicaps in achieving an optimal ESR resolution. A typical ESR spectrum having a total width of 1.9 mT ($g = 2.0027 \pm 0.0001$) is shown in Figure 2, along with the simulated derivative curve. The proton coupling constants determined by the ENDOR technique (see below) and used for the simulation are (in mT) 0.268 (2 H), 0.182 (2 H), 0.131 (2 H), 0.106 (2 H), 0.065 (4 H), 0.044 (1 H), and 0.036 (1 H). In addition, an exact fitting of the ESR spectrum required the inclusion of a hyperfine splitting of 0.062 mT from the ^{39}K nucleus of the counterion.

The ESR spectrum of 8-D-$1^{\bullet-}$ was rather similar to that of $1^{\bullet-}$ and had almost the same total width, as one would expect for a deuteron substitution of a single proton having a small coupling constant. On the other hand, striking changes occurred in the

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Table I. Coupling Constants (in mT) for $\mathbf{1}^{\bullet-}$ and Their Assignments, as Determined from the Proton ENDOR Spectra of $\mathbf{1}^{\bullet-}$, 8-D-$\mathbf{1}^{\bullet-}$, para-D_8-$\mathbf{1}^{\bullet-}$, and bridge-D_8-$\mathbf{1}^{\bullet-}$

ENDOR signal[a]	A	B	C	D	E	F	G	H
coupling constant[b]	0.268	0.182	0.131	0.106	0.065	0.044	0.036	0.007
no. of protons	2	2	2	2	2 + 2	1	1	2
presence for $\mathbf{1}^{\bullet-}$[c]	√	√	√	√	√	√	√	√
8-D-$\mathbf{1}^{\bullet-}$	√	√	√	√	√	–	√	√
para-D_8-$\mathbf{1}^{\bullet-}$	–	–	–	–	√	√	√	√
bridge-D_8-$\mathbf{1}^{\bullet-}$	–	–	√	√	–	√	√	√
assignment	1,10(CH_2)		12,13,15,16		2,9(CH_2)	8	5	4,6
sign	pos	pos	pos	pos	pos/neg[d]	neg	neg	[e]

[a] See Figure 3. [b] Experimental error: ±0.001 mT. [c] The symbols √ and – mean the presence and the absence, respectively, of the signal in the ENDOR spectrum. [d] Opposite sign for the coupling constants of the two proton pairs with the same absolute value (see text). [e] Sign undetermined.

ESR spectrum on passing from $\mathbf{1}^{\bullet-}$ to para-D_8-$\mathbf{1}^{\bullet-}$ or to bridge-D_8-$\mathbf{1}^{\bullet-}$; both isotopically labeled radical anions gave rise to unresolved ESR signals having total widths of only 0.9 and 1.1 mT, respectively. Obviously, those protons in $\mathbf{1}^{\bullet-}$ which are replaced by deuterons in para-D_8-$\mathbf{1}^{\bullet-}$ and bridge-D_8-$\mathbf{1}^{\bullet-}$ must possess considerable coupling constants.

The conclusions drawn from the ESR spectra were substantiated by the ENDOR studies.[13] Figure 3 displays the proton ENDOR spectra of $\mathbf{1}^{\bullet-}$, 8-D-$\mathbf{1}^{\bullet-}$, para-D_8-$\mathbf{1}^{\bullet-}$, and bridge-D_8-$\mathbf{1}^{\bullet-}$. The information provided by these studies has not only allowed unravelling the ESR hyperfine pattern of $\mathbf{1}^{\bullet-}$ (Figure 2), but also has led to a complete and unequivocal assignment of all coupling constants to sets of equivalent protons.

As is evident from Figure 3, the ENDOR spectrum of $\mathbf{1}^{\bullet-}$ consists of seven pairs of signals which are here denoted by capital letters, A to G. Table I lists the coupling constants derived from the positions of these signals. Also given are the numbers of protons responsible for each coupling constant, roughly proportional to the intensities of the corresponding signals in the ENDOR spectrum. It is important to note that, in this way, only 14 out of 16 protons present in $\mathbf{1}^{\bullet-}$ are accounted for. By simulating the ESR spectrum of $\mathbf{1}^{\bullet-}$ (Figure 2), one finds out that the two "missing" protons have a coupling constant smaller than the line width of 0.02 mT. Accordingly, this coupling constant has been associated with the weak ENDOR absorption appearing at the free proton frequency ν_p and denoted H in Figure 3. A value of 0.007 mT estimated therefrom has been included in Table I.

The ENDOR spectrum of 8-D-$\mathbf{1}^{\bullet-}$ differs from that of $\mathbf{1}^{\bullet-}$ merely by the absence of the signals F which are thus attributed to the single proton in the 8-position of the meta-bridged benzene ring, leaving the other one-proton signal G for the 5-position of the same ring. In the ENDOR spectra of both octadeuterated radical anions, para-D_8-$\mathbf{1}^{\bullet-}$ and bridge-D_8-$\mathbf{1}^{\bullet-}$, one misses the signals A and B which must, consequently, arise from the two pairs of equivalent protons in the methylene groups adjacent to the para-bridged benzene ring (1,10-positions). Moreover, the absence of the signals C and D in the ENDOR spectrum of para-D_8-$\mathbf{1}^{\bullet-}$ requires that these signals represent the two pairs of equivalent protons attached directly to the para-bridged benzene ring (12,13- and 15,16-positions), whereas the failure of the signals E to appear in the spectrum of bridge-D_8-$\mathbf{1}^{\bullet-}$ indicates their association with the two pairs of equivalent protons in the methylene groups neighboring the meta-bridged benzene ring (2,9-positions). Finally, the weak absorption H has to be connected with the pair of equivalent protons in the 4,6-positions of the meta-bridged ring, since these protons are the only ones not yet accounted for. The complete solution to the "assignment puzzle" by specific deuteration is presented in Table I.

Figure 4 shows a general TRIPLE spectrum of $\mathbf{1}^{\bullet-}$.[13] According to this spectrum, the four largest two-proton coupling constants (0.268, 0.182, 0.131, and 0.106 mT), which are associated with the signals A, B, C, and D, have all the same sign. An opposite sign is indicated for the two one-proton coupling constants (0.044 and 0.036 mT) represented by the signals F and G. The failing response of the four-proton signals E to the TRIPLE resonance experiment strongly suggests that they arise from two two-proton coupling constants having the same absolute value (0.065 mT), but opposite signs. No information can be gleaned for the sign of the two-proton coupling constant attributed to the weak ENDOR absorption H, because of the vanishing small size of the value in question (0.007 mT). The last line of Table I summarizes the results of the TRIPLE resonance on the assumption that the sign of the four major coupling constants is positive (cf. Discussion).

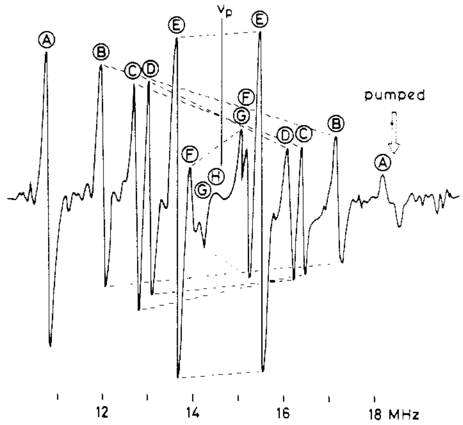
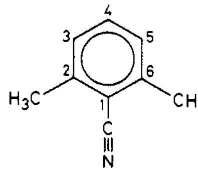


Figure 4. General TRIPLE resonance spectrum of $\mathbf{1}^{\bullet-}$. Conditions as for the ESR spectrum in Figure 2.

Radical Anion of 8-Cyano[2.2]metaparacyclophane (2) and Its Deuterio Derivative. Substitution of **1** by a cyano group in the 8-position to yield **2** greatly enhances both the thermodynamic and kinetic stabilities of the radical anion. The half-wave reduction potential, $E_{1/2}$, of **2** is −2.55 ± 0.05 V vs. SCE, as determined by cyclic voltammetry;[14] this value is practically the same as that of 2,6-dimethylbenzonitrile (**3**) (which is an intermediate product in the synthesis of **2** and para-D_8-**2**). Because of its relative ease of formation and its fairly high persistence at temperatures below 230 K, the radical anion $\mathbf{2}^{\bullet-}$ could be generated from **2** by standard chemical and electrolytic procedures (see Experimental Section). The observed (g = 2.0026 ± 0.0001) and simulated ESR spectra of $\mathbf{2}^{\bullet-}$ are shown in Figure 5, together with the corresponding proton ENDOR spectrum. Table II gives the proton and ^{14}N coupling constants used in the simulation; those of the protons have been derived from the positions of the ENDOR signals. Assignments to sets of equivalent nuclei in the individual positions of $\mathbf{2}^{\bullet-}$ are guided by comparison with the hyperfine data for $\mathbf{3}^{\bullet-}$ (g = 2.0026 ± 0.0001); these hitherto not reported values are also listed in Table II.



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(13) For a review on ENDOR and general TRIPLE resonance, see: Kurreck, H.; Kirste, B.; Lubitz, W. *Angew. Chem.* **1984**, *96*, 171; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 173.

(14) Solvent, MeCN; working electrode, HMDE; counterelectrode, glassy carbon; temperature, 298 K; scan, 300 mV/s.

Table II. Coupling Constants (in mT) for $2^{\bullet-}$, $3^{\bullet-}$, and $5^{\bullet-}$

$2^{\bullet-}$	coupl const[a]	0.808	0.247	0.159	0.047		0.022	0.200
	no. of nuclei	1 H	2 H	2 H	2 H		2 H + 2 H	1 ^{14}N
	assignment	5	2,9(CH$_2$)		4,6		1,10(CH$_2$)	8(CN)
$3^{\bullet-}$	coupl const[a]	0.851	0.397		0.047			0.242
	no. of nuclei	1 H	6 H		2 H			1 ^{14}N
	assignment	4	2,6(CH$_3$)		3,5			1(CN)
$5^{\bullet-}$	coupl const[a]	0.846	0.359	0.260	0.052	0.025	0.019	0.240
	no. of nuclei	1 H	3 H	2 H	1 H	1 H	2 H	1 ^{14}N
	assignment	5	3(CH$_3$)	7(CH$_2$)	4	6	7′(CH$_2$)	2(CN)

[a] Experimental error: ±0.005 for the largest (0.8–0.9 mT), ±0.002 for the middle-sized (0.1–0.4 mT), and ±0.001 mT for the smallest values (<0.1 mT).

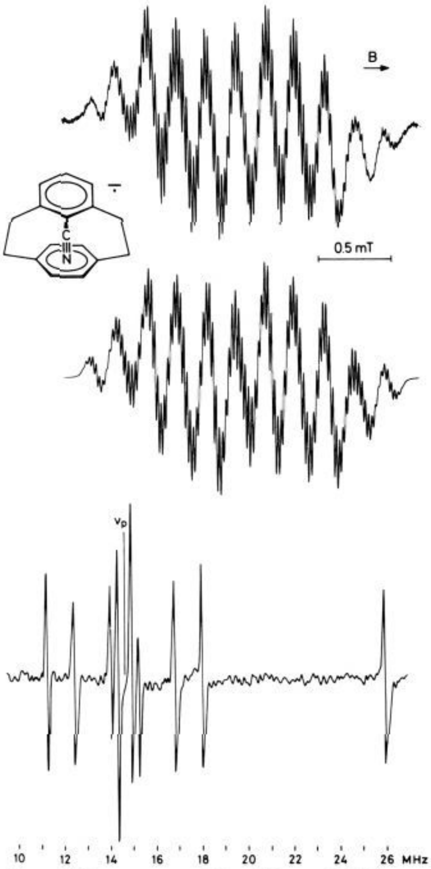


Figure 5. Top: ESR spectrum of $2^{\bullet-}$. Solvent, DME; counterion, K$^+$; temp, 193 K. Center: computer simulation. Coupling constants, see Table II; line shape, Lorentzian; line width, 0.020 mT. Bottom: proton ENDOR spectrum taken under the same conditions.

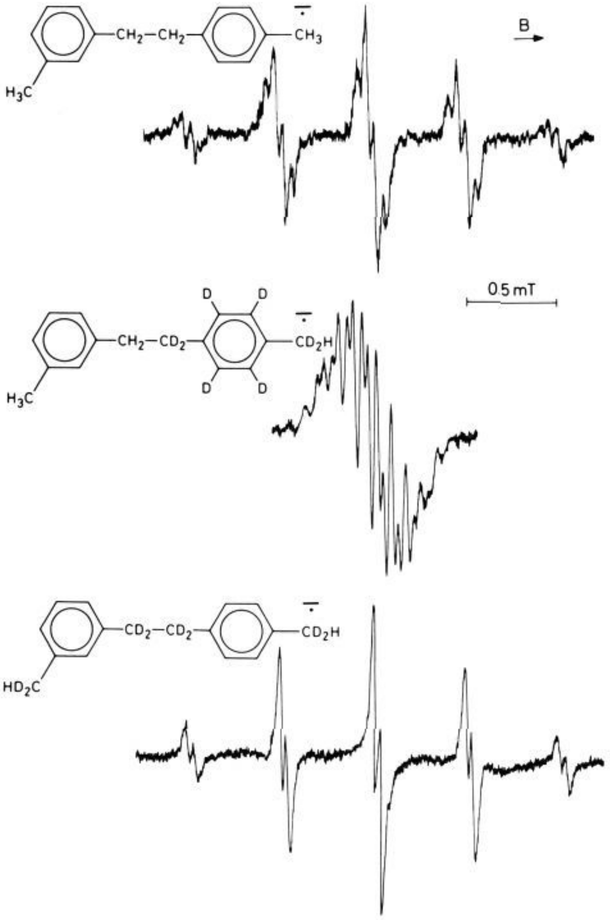


Figure 6. ESR spectra of $4^{\bullet-}$, para-D$_8$-$4^{\bullet-}$, and alkyl-D$_8$-$4^{\bullet-}$, obtained after exhaustive reduction of **1**, para-D$_8$-**1**, and bridge-D$_8$-**1**, respectively. Solvent, DME–THF (4:1); counterion, K$^+$; temp, 173 K.

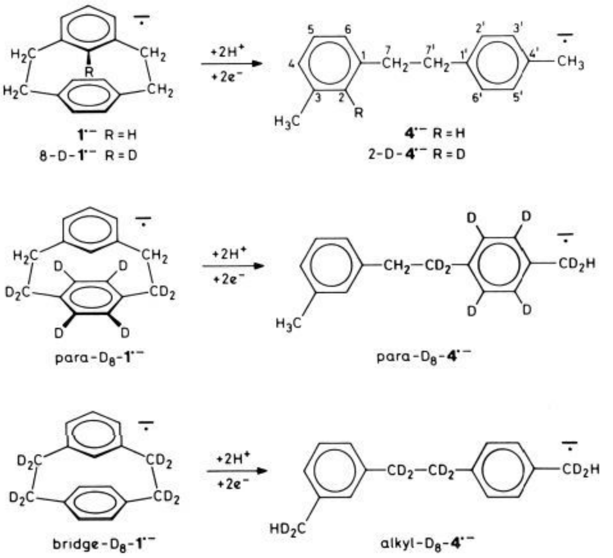
An experimental check of these assignments was provided by the ESR and ENDOR spectra of para-D$_8$-$2^{\bullet-}$ which differ from that of $2^{\bullet-}$ by the absence of the small four-proton coupling constant of 0.022 mT. This value must, therefore, belong to two pairs of protons replaced by deuterons in para-D$_8$-$2^{\bullet-}$, i.e., those at the para-bridged ring (12,13,15,16-positions) or in the adjacent methylene groups (1,10-positions). The tentative assignment of 0.022 mT to the methylene protons implies that the hyperfine splitting from the ring protons are unresolved and contribute essentially to the relatively large line widths in the ESR spectrum of $2^{\bullet-}$ (Figure 5).

TRIPLE resonance studies of $2^{\bullet-}$ indicate that the sign of the largest (0.808 mT) and the smallest observed coupling constant (0.022 mT) is opposite to that of 0.247, 0.159, and 0.047 mT. Theoretical considerations require a negative sign for 0.808 and 0.022 mT and a positive one for the three remaining values.

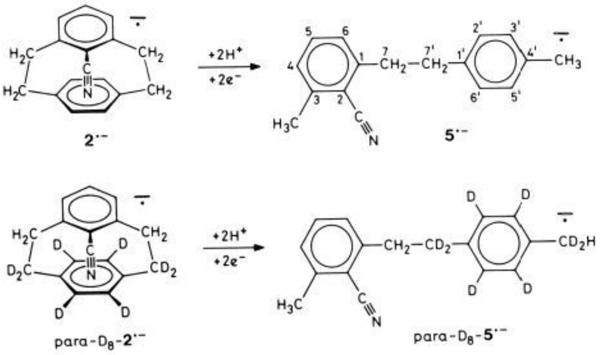
Secondary Reduction Products of 1 and 2. Hefelfinger and Cram[2c] reported that reaction of **1** with potassium in DME and subsequent quenching of the solution with water yielded 3,4′-dimethylbibenzyl (**4**). The formation of **4** from **1** at the stage of their radical anions has been verified in the present work by ESR spectroscopy.

When, following the decay of $1^{\bullet-}$, the DME–THF solution was brought into a prolonged contact with the potassium mirror, the ESR spectrum of a secondary radical anion appeared. This spectrum ($g = 2.0028 \pm 0.0001$) displayed at the top of Figure 6, has been analyzed in terms of the proton coupling constants of 0.520 ± 0.005 (4 H) and 0.048 ± 0.002 mT (3 H). An identical spectrum of a secondary radical anion was observed under the same conditions when 8-D-**1** replaced **1** as the starting material. On the other hand, exhaustive reduction of para-D$_8$-**1** and bridge-D$_8$-**1** led to different ESR spectra which are shown at the center and bottom, respectively, of Figure 6. Whereas in the former spectrum the four-proton coupling constant of 0.520 mT is preserved, it has been substituted in the latter by a four-deuteron splitting of 0.082 ± 0.001 mT. In both spectra the number of protons giving rise to the smaller coupling constant of 0.048 mT

Scheme I



Scheme II



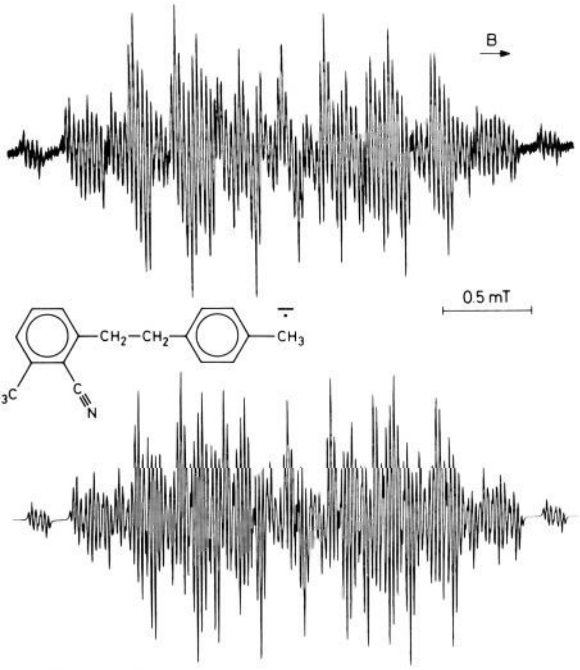


Figure 7. Top: ESR spectrum of **5**$^{\bullet-}$ obtained after exhaustive reduction of **2**. Solvent, *N*,*N*-dimethylformamide; counterion, Et_4N^+; temp, 298 K. Bottom: computer simulation. Coupling constants, see Table II; line shape, Lorentzian; line width, 0.010 mT.

has decreased from three to one.

The hyperfine data for the secondary reduction product of **1** strongly resemble the analogous values for the radical anions of bibenzyls[15] and 1,4-dialkylbenzenes.[16] Consequently, this product was identified as **4**$^{\bullet-}$ in which the unpaired electron is essentially localized on the para-substituted benzene ring. Likewise, the corresponding products from 8-D-**1** were disclosed as 2-D-**4**$^{\bullet-}$, para-D_8-**4**$^{\bullet-}$, and alkyl-D_8-**4**$^{\bullet-}$, respectively (Scheme I). Generation of these secondary radical anions from the primary ones implies a cleavage of the C–C bond in one ethano bridge followed by the uptake of two protons from the solvent[17] and two electrons from the alkali metal.[18]

The ESR spectrum of para-D_8-**4**$^{\bullet-}$ confirms that the four protons in **4**$^{\bullet-}$ which give rise to the large coupling constant (0.520 mT) are attached to the para-substituted benzene ring (2′,3′,5′,6′-positions). Furthermore, assignment of the smaller coupling constant (0.048 mT) to the three protons in the 4′-methyl substituent of **4**$^{\bullet-}$ is consistent with two of these protons being replaced by deuterons in both para-D_8-**4**$^{\bullet-}$ and bridge-D_8-**4**$^{\bullet-}$. The pertinent deuteron splittings are unresolved in the ESR spectra, as are those arising from the protons and deuterons in the dimethylene chain (7,7′-positions), at the meta-substituted ring (2,4,5,6-positions), and in the 3-methyl group.

Upon exhaustive reduction, either with the potassium mirror or by electrolysis, the cyano derivative **2** also yielded a secondary paramagnetic product which was identified by its ESR spectrum as the radical anion of 2-cyano-3,4′-dimethylbibenzyl (**5**). Starting from para-D_8-**2**, the radical anion para-D_8-**5**$^{\bullet-}$ was obtained under the same conditions (Scheme II). The reaction by which **2**$^{\bullet-}$ is converted into **5**$^{\bullet-}$ must thus proceed analogously to that transforming **1**$^{\bullet-}$ into **4**$^{\bullet-}$.

The ESR spectrum of **5**$^{\bullet-}$ ($g = 2.0026 \pm 0.0001$), observed upon prolonged electrolytic reduction of **2**, is shown in Figure 7. Its computer simulation, also presented therein, made use of the proton and ^{14}N coupling constants listed in Table II, below the corresponding values for **2**$^{\bullet-}$ and **3**$^{\bullet-}$. Assignments of these coupling constants to nuclei in individual positions of **5**$^{\bullet-}$ have been based on the similarity between the hyperfine data for **5**$^{\bullet-}$ and the two structurally related anions. As in the case of **2**$^{\bullet-}$, the substantial coupling constants stem from the ^{14}N nucleus of the cyano group and the protons in the benzonitrile moiety. In **5**$^{\bullet-}$, these protons are those at the pertinent benzene ring (4,5,6-positions), in its 3-methyl substituent, and in the adjacent methylene group (7-position). Accordingly, the ESR spectrum of para-D_8-**5**$^{\bullet-}$ differs from that of **5**$^{\bullet-}$ merely by the absence of the smallest coupling constant (0.019 mT) assigned to the two protons in the methylene group neighboring the other benzene ring (7′-position). The hyperfine splitting from the protons in this ring (2′,3′,5′,6′-positions) and its 4′-methyl substituent are obviously too small to be resolved.

Discussion

Conformation. The uptake of a single additional electron by [2.2]metaparacyclophane (**1**) is not expected to significantly change its molecular geometry, as determined by the X-ray crystallographic structure analysis.[7] In particular, the preferred conformation should not markedly be altered on passing from the neutral compound **1** to the radical anion **1**$^{\bullet-}$. It is thus reasonable to assume that the barrier to the flipping of the meta-bridged benzene ring in **1**$^{\bullet-}$ is comparable to the relatively high activation energy (ca. 80 kJ mol^{-1}) found for the analogous process in **1** by NMR studies at about 400 K.[2b,d,3b,c,f,4,5,7] Considering the different time scale of the experiment, an even more elevated temperature would be required for this interconversion in **1**$^{\bullet-}$ to be revealed by ESR or ENDOR spectroscopy. Conformational studies are therefore completely out of reach for **1**$^{\bullet-}$ in view of the poor persistence of the radical anion.

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(15) Gerson, F.; Martin, W. B., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1883.

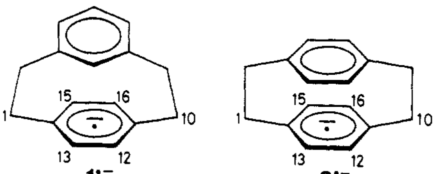
(16) Bolton, J. R.; Carrington, A.; Forman, A.; Orgel, L. E. *Mol. Phys.* **1962**, *5*, 43. De Boer, E.; Colpa, J. P. *J. Phys. Chem.* **1967**, *71*, 21.

(17) Minute amounts of proton impurities are always present in DME and THF, despite rigorous purification.

(18) A similar reaction yielding the radical anion of 4,4′-dimethylstilbene occurs on a prolonged reduction of [2.2]paracyclophane-1,9-diene: Bruhin, J.; Gerson, F.; Möckel, R.; Plattner, G. *Helv. Chim. Acta* **1985**, *68*, 377.

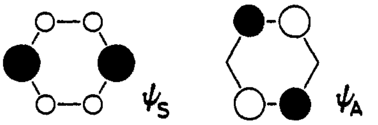
The energy barrier to the flipping of the meta-bridged ring should be still considerably higher in the 8-cyano derivative (**2**) and its radical anion ($\mathbf{2}^{\bullet-}$) than in **1** and $\mathbf{1}^{\bullet-}$, since the substitution of the H atom by the elongated CN group in the exposed 8-position strongly restricts the mobility of this ring. For that reason, although $\mathbf{2}^{\bullet-}$ is substantially more persistent than $\mathbf{1}^{\bullet-}$, observation of the conformational interconversion in $\mathbf{2}^{\bullet-}$ by ESR and/or ENDOR spectroscopy can hardly be envisaged.

Spin Distribution. The prominent feature of the hyperfine data for $\mathbf{1}^{\bullet-}$ is the confinement of the four major coupling constants (0.268, 0.182, 0.131, and 0.106 mT) to the protons at the para-bridged benzene ring and the adjacent methylene groups. This feature points to an essential localization of the unpaired electron on the para-bridged moiety of $\mathbf{1}^{\bullet-}$, in line with the 1,4-dialkylbenzenes having slightly higher electron affinity in solution than their 1,3-isomers.[19] Because of such a localization, it is instructive to compare the four major coupling constants for $\mathbf{1}^{\bullet-}$ with analogous values observed for the radical anion of [2.2]paracyclophane (**6**) in solvents promoting tight ion pairing.[8,15] Under these conditions, owing to an association of $\mathbf{6}^{\bullet-}$ with the counterion K^+, the unpaired electron in the radical anion appears to favor one of the two (otherwise equivalent) benzene rings.[8,20]



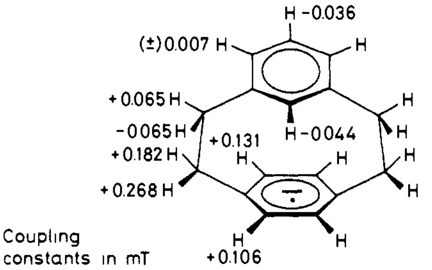
Coupling constants in mT	$\mathbf{1}^{\bullet-}$	$\mathbf{6}^{\bullet-}$
ring -12, 13, 15, 16	0.131 (2H) 0.106 (2H)	0.379 (4H)
methylene -1, 10	0.268 (2H) 0.182 (2H)	0.125 (4H)
solvent	DME/THF (4:1)	THF
temperature	168 K	178 K

The lack of similarity between the two sets of data strongly suggests that the shape of the singly occupied orbital at the pertinent benzene ring is different for $\mathbf{1}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$. In principle, such an orbital can correlate with either the "symmetric" (ψ_S) or the "antisymmetric" (ψ_A) LUMO of benzene, the degeneracy of these MO's being removed by the para substitution.



ESR studies clearly indicate that it is a ψ_A-like MO which is preferentially occupied by the unpaired electron in the radical anions of 1,4-dialkylbenzenes.[16,19,21] This MO lies, therefore, energetically lower than its ψ_S counterpart, in accord with the destabilizing effect of the inductive perturbation by the alkyl substituents.[21,22a] Diagnostic of the single occupancy of a ψ_A-like MO are the large coupling constants of the four ring α-protons[23] which by far surpass those of the alkyl β-protons. It is evident from the diagrams above that the singly occupied orbital at the favored benzene ring in $\mathbf{6}^{\bullet-}$ has also to be considered as a ψ_A-like.[8,15] By contrast, since the coupling constants of the four α-protons at the para-bridged benzene ring in $\mathbf{1}^{\bullet-}$ are *smaller* than those of the β-protons in the adjacent methylene groups, the single occupancy of an orbital correlating with ψ_S seems to be a more viable alternative.

INDO calculations,[24] performed on $\mathbf{1}^{\bullet-}$ with the use of the X-ray crystallographic geometry parameters,[7] bore out the expectation that the unpaired electron should essentially be located in the para-bridged benzene ring. As the ψ_S- and ψ_A-like LUMO's localized on this ring were predicted to differ only very slightly in their energy, the spin distribution in $\mathbf{1}^{\bullet-}$ was calculated for the single occupancy of either orbital. Although, in both cases the numerical agreement was rather poor, the characteristic features of the observed hyperfine data were much better reproduced by the INDO procedure when the unpaired electron was accommodated in a ψ_S- rather than in a ψ_A-like MO. With the singly occupied orbital resembling ψ_S at the para-bridged benzene ring, not only had the α-protons at this ring smaller coupling constants than the β-protons in the adjacent methylene groups, but also all four values exhibited the same sign, as required by the TRIPLE resonance experiment (see Results). This sign was predicted to be positive. Moreover, the INDO calculation for the single occupancy of a ψ_S-like orbital yielded opposite signs for the coupling constants of the protons in a methylene group neighboring the meta-bridged benzene ring (i.e., of γ-protons[23] with respect to the π-system of the para-bridged ring bearing the bulk of the spin population). This result, too, nicely tallies with the arguments used for the interpretation of the TRIPLE resonance spectrum. The diagram below combines the experimental data with the information provided by the INDO procedure; it presents a detailed characterization of $\mathbf{1}^{\bullet-}$ by its hyperfine parameters, since it distinguishes between the coupling constants of the "front" and "back" protons at the para-bridged benzene ring and in the methylene groups.



A few comments on these results are in order.

(i) One may ask why the singly occupied orbital of $\mathbf{1}^{\bullet-}$ should resemble ψ_S at the para-bridged benzene ring, whereas in the radical anions of **6** and 1,4-dialkylbenzenes such an orbital is ψ_A-like. A definite answer to this question is rather difficult, since slight structural differences can be crucial in determining the energetic sequence of ψ_S and ψ_A in derivatives of benzene.[25] It is noteworthy in this respect that tilting of the methylene groups at the para-bridged ring out of coplanarity with the benzene π-system is more severe in **1** than in **6**.

(ii) Single occupancy of a ψ_S-like MO at the para-bridged benzene ring of $\mathbf{1}^{\bullet-}$ implies large *positive* π-spin populations at the two bridged carbon centers and much smaller, but likewise *positive* populations at the four unsubstituted ones.[26] According to the current theory of spin transfer in planar π-radicals, the coupling constants of the two pairs of β-protons in the adjacent methylene groups should have substantial absolute values and a *positive* sign (π–σ spin delocalization), whereas those of the α-protons at the benzene ring ought to be lesser in size and *negative* (π–σ spin polarization).[22b] The positive sign allotted to the latter values (0.131 and 0.106 mT) is thus at variance with this theory. Since admixture of ψ_A to ψ_S would lead to an even more negative value,[27] it cannot account for the positive sign of the coupling

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[19] Lawler, R. G.; Tabit, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 5671.

[20] Gerson, F.; Martin, W. B., Jr.; Wydler, C. *Helv. Chim. Acta* **1976**, *59*, 1365.

[21] Carrington, A. *Q. R. Chem. Soc.* **1963**, *17*, 67.

[22] Gerson, F. *High Resolution ESR Spectroscopy*; Wiley and Verlag Chemie: New York and Weinheim (FRG), 1970: (a) Chapter 2.5. (b) Chapter 1.5. (c) Appendix A.2.2.

[23] In ESR spectroscopy, protons separated by 0, 1, 2, ... sp^3-hybridized carbon atoms from a π-center are denoted, α, β, γ, ...

[24] Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

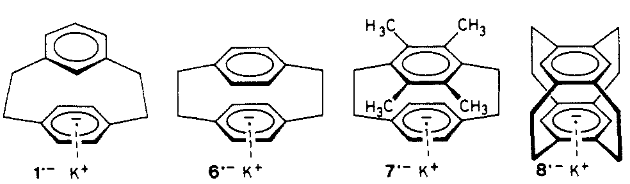
[25] Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370.

[26] Hobey, W. D. *J. Chem. Phys.* **1965**, *43*, 2187.

constants in question. Rationalization of this sign is, however, possible in terms of the particular geometry of the para-bridged benzene ring, because it is known[28] that deviations of a π-system from planarity result in *positive* contributions to α-proton coupling constants via π–σ spin delocalization. Such contributions will determine the sign of the coupling constants when the *negative* component brought about by the π–σ spin polarization (solely effective in *planar* π-radicals) is small.

(iii) The finding that the coupling constants of the protons in the positions 5 (0.036 mT) and 8 (0.044 mT) of the meta-bridged benzene ring are almost equal suggests that the hyperfine interaction with the 8-proton is not seriously affected by the proximity of the π-electron cloud in the para-bridged ring.

(iv) The coupling constant (0.062 mT) of the ^{39}K nucleus in the counterion exceeds by far the analogous values for $6^{\bullet-}$[8,15] and the radical anions of aromatic hydrocarbons associated with K^+ ions.[22c,29] However, as indicated below, this finding is not unprecedented, since ^{39}K coupling constants of similar magnitude have been observed for the tight ion pairs of the radical anions of 4,5,7,8-tetramethyl[2.2]paracyclophane (**7**)[8,30] and [2_4]-(1,2,4,5)cyclophane (**8**) with K^+.[8,31] The following diagram gives



	$1^{\bullet-}$ K^+	$6^{\bullet-}$ K^+	$7^{\bullet-}$ K^+	$8^{\bullet-}$ K^+
(a)	0.062	0 012	0 102	0 075
(b)	DME/THF(4 1)	THF	DME/THF(1 1)	DME
(c)	168	178	168	178
(d)	ψ_S	ψ_A	ψ_A	ψ_S

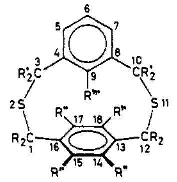
(a) the pertinent ^{39}K coupling constants, in mT, (b) the solvent, (c) temperature in K, and (d) the benzene LUMO correlating with the singly occupied orbital at the ring favored by the unpaired electron in the ion pairs.

In the formulas drawn in the diagram, the counterion K^+ is situated close to the center of this ring which bears the bulk of the spin and charge population. For the ion pair of $6^{\bullet-}$ such a structure has been corroborated by an ESR study on the radical anion of 1,1,10,10,12,13,15,16-octadeuterio[2.2]paracyclophane,[8,20] and it seems unlikely that a substantially different structure would be preferred by the ion pairs of $1^{\bullet-}$, $7^{\bullet-}$, and $8^{\bullet-}$. The large ^{39}K coupling constants for the counterions associated with these radical anions can thus hardly be rationalized in terms of changes in geometry of the ion pair. Neither are they explicable by a different shape of the singly occupied orbital at the favored benzene ring, since such an orbital resembles ψ_S in $1^{\bullet-}$ and $8^{\bullet-}$,[8,31] whereas it appears as ψ_A-like in $6^{\bullet-}$[8,15] and $7^{\bullet-}$.[8,30] It is generally assumed that the coupling constants in alkali metal nuclei in the ion pairs are due to the spin transfer from the π-system of the radical anion to the lowest vacant s-AO of the cation.[29] Considering the ^{39}K hyperfine data for $1^{\bullet-}$, $6^{\bullet-}$, $7^{\bullet-}$, and $8^{\bullet-}$, one has to admit that the mechanism of such a transfer is not yet fully understood.

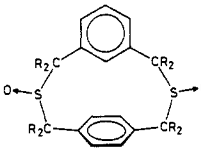
Introduction of the strongly electron-attracting cyano group into the 8-position of $1^{\bullet-}$ has a dramatic effect on the spin distribution. As indicated by the hyperfine data for the cyano-substituted radical anions $2^{\bullet-}$ and para-D_8-$2^{\bullet-}$, the spin population is then almost completely shifted onto the meta-bridged benzene ring, so that the coupling constants of the protons and ^{14}N nuclei in $2^{\bullet-}$ closely resemble the analogous values for the radical anions of 2,6-dialkylbenzonitriles, e.g., $3^{\bullet-}$. Because of the steric requirement of the cyano group, the two benzene rings in $2^{\bullet-}$ presumably adopt a conformation in which the mean aromatic planes are almost parallel. The hyperfine data for $2^{\bullet-}$ clearly indicate that the π-spin distribution in the cyano-substituted meta-bridged moiety is not greatly affected by the interaction with the π-system of the para-bridged benzene ring.

Experimental Section

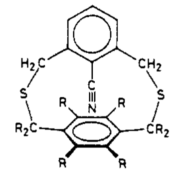
8-Deuterio[2.2]metaparacyclophane (8-D-1). 2-Bromo-*m*-xylene (Aldrich) was converted via the Grignard compound into 2-deuterio-*m*-xylene[32] which, upon treatment with *N*-bromosuccinimide (NBS), yielded 2-deuterio-1,3-bis(bromomethyl)benzene. This product was coupled with the K salt of 1,4-bis(mercaptomethyl)benzene to give 9-deuterio-2,11-dithia[3.3]metaparacyclophane (9-D-**9**).[33] The extrusion of the two S atoms from 9-D-**9** was performed by UV irradiation of a 5 × 10^{-3} M solution in $P(OMe)_3$ with a high-pressure TQ Hanovia lamp for 30 min at room temperature (N_2 atmosphere).[3d] 8-D-**1** thus obtained had a deuterium content of 88% of the expected value.



9 R = R' = R'' = R''' = H
9-D-**9** R = R' = R'' = H, R''' = D
para-D_8-**9** R' = R''' = H, R = R'' = D
bridge-D_8-**9** R'' = R''' = H, R = R' = D



10 R = H
bridge-D_8-**10** R = D



11 R = H
para-D_8-**11** R = D

1,1,10,10,12,13,15,16-Octadeuterio[2.2]metaparacyclophane (para-D_8-1). Bromination of perdeuterio-*p*-xylene (Aldrich) with NBS led to perdeuterio-1,4-bis(bromomethyl)benzene[20] which was reacted with the K salt of 1,3-bis(mercaptomethyl)benzene to yield 1,1,12,12,14,15,17,18-octadeuterio-2,11-dithia[3.3]paracyclophane (para-D_8-**9**).[33] When UV-irradiated under the conditions specified above, this compound lost two S atoms to afford para-D_8-**1** with a deuterium content of 99% of the expected value.

1,1,2,2,9,9,10,10-Octadeuterio[2.2]metaparacyclophane (bridge-D_8-1). Coupling of 1,3-bis(bromomethyl)benzene (Fluka) with the K salt of 1,4-bis(mercaptomethyl)benzene gave 2,11-dithia[2.2]metaparacyclophane (**9**)[33] which was converted into its disulfoxy derivative **10** by reaction with *m*-chloroperbenzoic acid in CH_2Cl_2. Subsequently the four bridging methylene groups of **10** were deuteriated by a MeO^--catalyzed H/D exchange in MeOD,[34] and the resulting labeled compound (bridge-D_8-**10**) was deoxygenated with *n*-Bu_4NI and $(CF_3CO)_2O$ in CH_2Cl_2 to yield 1,1,3,3,10,10,12,12-octadeuterio-2,11-dithia[3.3]metaparacyclophane (bridge-D_8-**9**).[35] UV irradiation of this cyclophane by a procedure described above led to the extrusion of two S atoms and formation of bridge-D_8-**1** with a deuterium content of 93% of the expected value.

8-Cyano-1,1,10,10,12,13,15,16-octadeuterio[2.2]metaparacyclophane (para-D_8-2). 2,6-Dimethylaniline (Fluka) was converted by the Sandmeyer reaction into 2,6-dimethylbenzonitrile (**3**) which upon bromination with NBS yielded 2,6-bis(bromomethyl)benzonitrile. This compound was coupled with the K salt of perdeuterio-1,4-bis(mercaptomethyl)benzene[33] obtained by the usual procedure from perdeuterio-1,4-bis(bromomethyl)benzene. The coupling product, 9-cyano-1,1,12,12,14,15,17,18-octadeuterio-2,11-dithia[3.3]metaparacyclophane (para-D_8-**11**), underwent a UV-photolytically induced extrusion of two S atoms (see above), affording para-D_8-**2** with a deuterium content of 99% of the expected value.

Radical Anions of 1 and Its Deuterio Derivatives. A deep blue solution of solvated electrons was prepared by condensing a cold 4:1 mixture of DME and THF on a freshly sublimed potassium mirror in a side arm of

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[27] An admixture of ψ_A to ψ_S would *increase* the *positive* π-spin populations at the four unsubstituted carbon centers and, therewith, give rise to *larger negative* α-proton coupling constants.

[28] Berndt, A. *Tetrahedron* **1969**, *25*, 37. Gerson, F.; Müllen, K.; Vogel, E. *Helv. Chim. Acta* **1971**, *54*, 2731; *J. Am. Chem. Soc.* **1972**, *94*, 2924.

[29] Symons, M. C. R. *J. Phys. Chem.* **1967**, *71*, 172. Sharp, J. H.; Symons, M. C. R. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. I, Chapter 5.

[30] Bruhin, J.; Gerson, F.; Ohya-Nishiguchi, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1045.

[31] Gerson, F.; Lopez, J.; Boekelheide, V. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1298.

[32] Sato, T.; Nishiyama, K. *J. Org. Chem.* **1972**, *37*, 3254.

[33] Reaction analogous to those described in ref 3g and 4.

[34] For a similar OD^--catalyzed deuteration of benzyl methyl sulfoxide in D_2O, see: Rauk, A.; Buncel, E.; Moir, R. Y.; Wolfe, S. *J. Am. Chem. Soc.* **1965**, *87*, 5498.

[35] Drabowicz, J.; Oae, S. *Synthesis* **1977**, 404. These authors used NaI and $(CF_3CO)_2O$ in acetone for deoxygenation of simple sulfides. Since para-D_8-**10** is not soluble in acetone, this solvent was replaced by CH_2Cl_2 which, however, does not dissolve NaI; consequently, NaI was substituted by *n*-Bu_4NI.

the sample container. Reduction of the cyclophane was carried out by tilting the container, so that the solution was poured onto the finely dispersed compound in a precooled narrow ESR sample tube. All operations were performed in vacuo at 168 K (coolant, hexane with liquid nitrogen).

Radical Anions of 2 and Its Deuterio Derivative. The chemical method of preparation implied a reaction of the compound with potassium mirror in DME. The electrolytic reduction made use of a cylindric cell containing a helical cathode of amalgamated gold and a platinum wire anode along the axis;[36] the solvent and supporting salt were *N*,*N*-dimethylformamide and Et_4NClO_4, respectively.

Instrumental. The equipment for cyclic voltammetry was a Metrohm-Polarecord E56 (VA Scanner 612/VA Stand 663). The ESR spectra were taken on a Varian-E9-instrument, while a Bruker-ESP 300 spectrometer system served for the ENDOR and TRIPLE resonance studies.

Acknowledgment. We thank Professor Virgil Boekelheide for samples of **1** and **2**, Dr. Hiroaki Ohya-Nishiguchi for performing some preliminary experiments, Mr. U. Buser for synthesizing para-D_8-**2**, and Dr. Claudine Cohen-Addad for communicating the X-ray crystallographic data of **1** prior to publication. The Swiss National Science Foundation is gratefully acknowledged for financial support.

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[36] Ohya-Nishiguchi, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2064.

Identification of High-Valent Fluoroiron Porphyrin Intermediates Associated with the Electrocatalytic Functionalization of Hydrocarbons

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Abstract: The difluoroiron(III) tetraphenylporphyrin complex undergoes a one-electron oxidation at 0.68 V (SCE) in contrast with values of 1.1 V measured for the monofluoroiron(III) porphyrin and the other five-coordinate iron(III) porphyrin complexes. Cyclic voltammetric oxidation of the difluoroiron(III) species in dichloromethane solution is quasi-reversible as a consequence of an EC mechanism. Reversible waves are favored at high scan rates and lower temperatures. Increased water content serves to make the oxidative cyclic voltammetric process irreversible presumably due to a disproportionation process. In the presence of added olefin substrates, this EC process permits efficient electrocatalytic oxidation to the epoxide, allylic alcohol, and enone. Tertiary carbon units are converted to the corresponding alcohol. Utilization of fluoride ion permits generation and low-temperature spectroscopic identification of a highly oxidized iron porphyrin species. The high-valent complex is produced at −78 °C through addition of *m*-chloroperbenzoic acid to monofluoroiron(III) tetraarylporphyrins or by fluoride ion promoted disproportionation of the dication radical μ-oxo dimeric iron(III) porphyrin derivative. The oxidized iron porphyrin species is competent to effect olefin epoxidation at −78 °C. Low-temperature ^1H and ^2H NMR spectroscopies demonstrate the porphyrin π-cation radical nature of the high-valent species, in that porphyrin phenyl resonances are drastically shifted in alternating upfield and downfield directions. The electron spin resonance spectrum is consistent with an $S = {}^3/_2$ ground state, and the high-valent intermediate is assigned a tentative fluorooxoiron(IV) porphyrin π-cation radical formulation.

High-valent iron oxo porphyrin species are proposed as intermediates in the reaction cycles of the peroxidases,[1] catalases,[1] cytochrome P-450,[2] and cytochrome oxidase.[3] Generation of such high-valent, isolated synthetic metalloporphyrin derivatives is of interest in terms of biomimetic studies and as a possible route to development of oxidative catalytic systems. Oxidation of metalloporphyrins may be ring-centered or metal-centered, meaning that the electron(s) may be removed from a molecular orbital that is centered predominantly either on the porphyrin ring or on the metal ion. One-electron oxidation of most simple five-coordinate high-spin iron(III) porphyrins has been shown to produce the corresponding iron(III) porphyrin π-cation radical species.[4] Recent evidence has been offered for metal-centered oxidation of hydroxide, methoxide, and aryl-ligated iron(III) porphyrins.[5] Metal-centered oxidation to the iron(IV) state (detectable at low temperature) is certainly dictated by a very basic oxo ligand[6] or two axial methoxide ligands.[7] Two-electron oxidation of the iron(III) porphyrin by oxo-transfer reagents seemingly yields an oxoiron(IV) porphyrin cation radical species[6c,8] analogous in electronic structure to the compound I state of peroxidases.

Binding of basic, "hard" axial ligands is expected to stabilize metal-centered oxidation, and in this regard fluoride coordination

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