187. The Radical Anions of [2.2]Metaparacyclophane-1,9-diene and Some Derivatives: an ESR and ENDOR Study

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The radical anion of [2.2]metaparacyclophane-1,9-diene (**1**) has been fully characterized by its hyperfine data with the use of ESR, ENDOR, and TRIPLE-resonance spectroscopy. Assignments of all proton-coupling constants are based on comparison with the spectra of the radical anions of the 8-deuterio-, 1,2,9,10-tetradeuterio-, and 1,10,12,13,15,16-hexadeuterio derivative. The spin distribution in $\mathbf{1}^{\bar{\cdot}}$ drastically differs from that in the radical anion of [2.2]metaparacyclophane (**4**), and it is not readily interpreted by semi-empirical MO-methods. The radical anions of 8-fluoro- (**2**) and 8-cyano[2.2]metaparacyclophane-1,9-diene (**3**) have also been investigated. Substitution of **1** by an F-atom in the 'exposed' 8-position, to yield **2**, has only a minor effect on the π-spin distribution in the radical anion, as evidenced by the similar proton-hyperfine data for $\mathbf{1}^{\bar{\cdot}}$ and $\mathbf{2}^{\bar{\cdot}}$. The ^{19}F-coupling constant for $\mathbf{2}^{\bar{\cdot}}$ is much smaller than expected, thus indicating a pronounced '*ortho*-effect' in the pertinent position. The ESR and ENDOR spectra of $\mathbf{3}^{\bar{\cdot}}$ in 1,2-dimethoxyethane (counterion K^+) reveal an equilibrium between a tightly and a loosely ion-paired radical anion. Whereas the former is present exclusively in 2-methyltetrahydrofuran (K^+), the latter prevails in *N,N'*-dimethylformamide (Et_4N^+) and in mixtures of 1,2-dimethoxyethane with *N,N,N',N',N'',N''*-hexamethylphosphoric triamide (K^+). The high temperatures required for the conformational flipping of the *meta*-bridged benzene ring in $\mathbf{1}^{\bar{\cdot}}$, $\mathbf{2}^{\bar{\cdot}}$, and $\mathbf{3}^{\bar{\cdot}}$ to be fast on the hyperfine time-scale are well above the range appropriate for the studies of these radical anions.

Introduction. – The synthesis of [2.2]metaparacyclophane-1,9-diene (tricyclo-[9.2.2.1^{4,8}]hexadeca-2,4,6,8(16),9,11,13,14-octaene; **1**) was first reported in 1968 [1]; it has been modified in the following years [2]. In addition to the parent compound **1**, 8-fluoro- and 8-cyano[2.2]metaparacyclophane-1,9-dienes (16-fluoro- and 16-cyano-tricyclo[9.2.2.1^{4,8}]hexadeca-2,4,6,8(16),9,11,13,14-octaenes; **2** and **3**, respectively) have been prepared [2b]. The radical anion of **1** has not yet been characterized by its hyperfine data; detailed ESR and ENDOR studies on the radical anion of [2.2]metaparacyclophane (tricyclo[9.2.2.1^{4,8}]hexadeca-4,6,8(16),11,13,14-hexaene; **4**) were reported only two years ago [3][2]).

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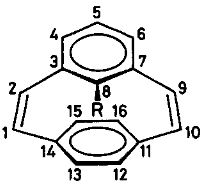
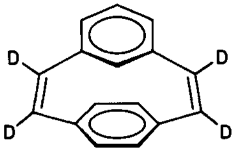
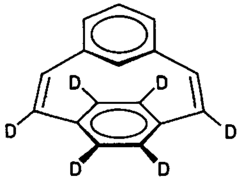
[2]) A few preliminary results on $\mathbf{1}^{\bar{\cdot}}$, $\mathbf{2}^{\bar{\cdot}}$, $\mathbf{3}^{\bar{\cdot}}$, and $\mathbf{4}^{\bar{\cdot}}$ have been mentioned in [4].



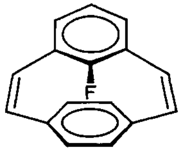
1 R = H
(8-D)-**1** R = D



(1,2,9,10-D_4)-**1**



(1,10,12,13,15,16-D_6)-**1**



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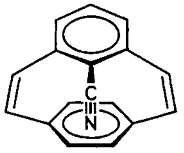

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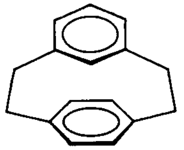

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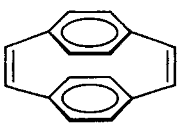

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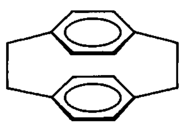

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An X-ray crystallographic structure analysis of **1** [5] indicates that the *meta*-bridged benzene ring is only mildly distorted from planarity, whereas the distortion of the *para*-bridged ring is even more severe than in the [2.2]paracyclophane-1,9-diene (tricyclo[8.2.2.2^{4,7}]hexadeca-2,4,6,8,10,12,13,15- octaene; **5**)[6]. The mean planes of the benzene rings are inclined to each other by an angle of 41°, whereby the π-planes of the ethenic double bonds form angles of *ca.* 30° and 75° with the mean planes of the *meta*- and *para*-bridged rings, respectively. The free activation energy, $\Delta G^{\ddagger}$, for the conformational flipping of the *meta*-bridged ring is considerably less (*ca.* 35 kJ/mol) than the corresponding value (85–90 kJ/mol) for **4** [7]. This difference suggests that, in the transition conformation which demands a perpendicular arrangement of the two rings, the H-atom in the 8-position has to penetrate less deeply in **1** than in **4** into the π-cloud of the *para*-bridged ring.

A drastic change in the spin distribution has been found on going from the radical anion of [2.2]paracyclophane (tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene; **6**) [4][8] to that of its 1,9-diene **5** [9]. It is, therefore, of interest to investigate the effect of analogous change in the [2.2]metaparacyclophane series, *i.e.*, on passing from **4**$^{\cdot-}$ [3] to **1**$^{\cdot-}$. The present paper deals with the ESR and ENDOR spectra of the radical anions of **1** and of its deuterated derivatives (8-D)-**1**, (1,2,9,10-D_4)-**1**, and (1,10,12,13,15,16-D_6)-**1** (16-deuterio-, 2,3,9,10-tetradeuterio-, and 2,10,12,13,14,15-hexadeuteriotricyclo-[9.2.2.1^{4,8}]hexadeca-2,4,6,8(16),9,11,13,14-octaenes). Also reported are the hyperfine data for the radical anions of the 8-fluoro- and 8-cyano-substituted compounds **2** and **3**.

Results. – The radical anions **1**$^{\cdot-}$, (8-D)-**1**$^{\cdot-}$, (1,2,9,10-D_4)-**1**$^{\cdot-}$, (1,10,12,13,15,16-D_6)-**1**$^{\cdot-}$, **2**$^{\cdot-}$, and **3**$^{\cdot-}$ were prepared by reaction of the corresponding neutral compounds with K in 1,2-dimethoxyethane (DME) and in mixtures of DME with *N,N,N',N',N'',N''*-hexamethylphosphoric triamide (HMPT). The radical anion **3**$^{\cdot-}$ was also generated by reaction of **3** with K in 2-methyltetrahydrofuran (MTHF) and by electrolytic reduction of **3** at a Hg cathode in *N,N*-dimethylformamide (DMF) with Et_4NClO_4 as the supporting salt. All these radical anions were considerably more persistent than those of the analogous [2.2]metaparacyclophanes [3]. Thus, **1**$^{\cdot-}$ could be studied by ESR and ENDOR spectroscopy up to 243 K, and even **2**$^{\cdot-}$ was sufficiently long-lived below 193 K to be fully characterized by its hyperfine data. The persistence of **3**$^{\cdot-}$ allowed this radical anion to be investigated up to the ambient temperature. The g-factor of all three radical anions is 2.0027±0.0001.

[2.2]*Metaparacyclophane-1,9-diene* (**1**) *and Its Deuterio-Derivatives. Fig. 1* presents a highly resolved ESR spectrum of **1**$^{\cdot-}$, along with its simulation which was computed using the following proton-coupling constants [mT]: 0.498±0.003 (2 H), 0.316±0.002

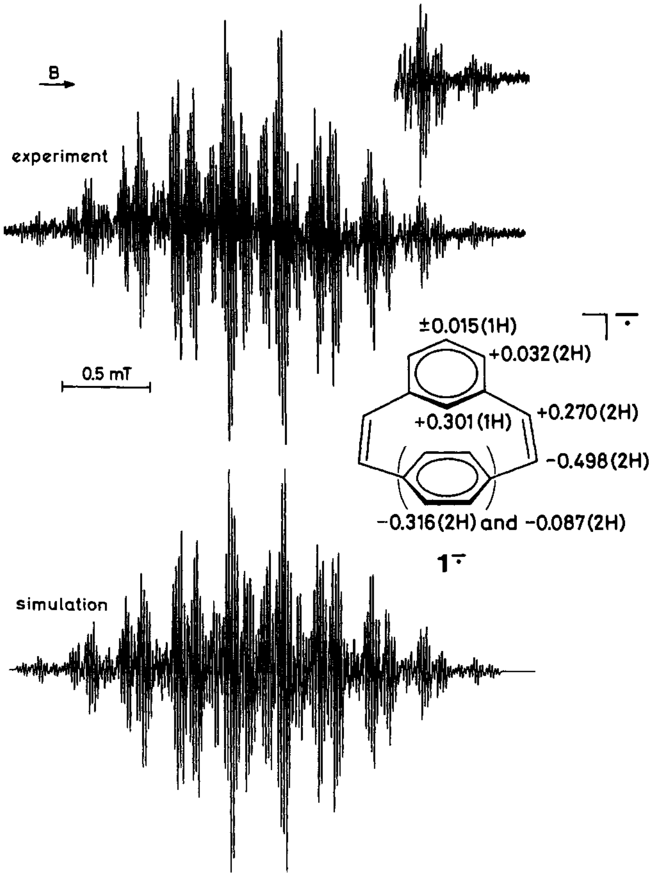

Fig. 1. *ESR spectrum of* **1**$^{\cdot-}$. Solvent: DME/HMPT (10:1); counterion: K^+; temp.: 223 K. Coupling constants [mT] used in the simulation are indicated on the formula; line-shape: *Lorentz*ian; line-width: 0.010 mT.

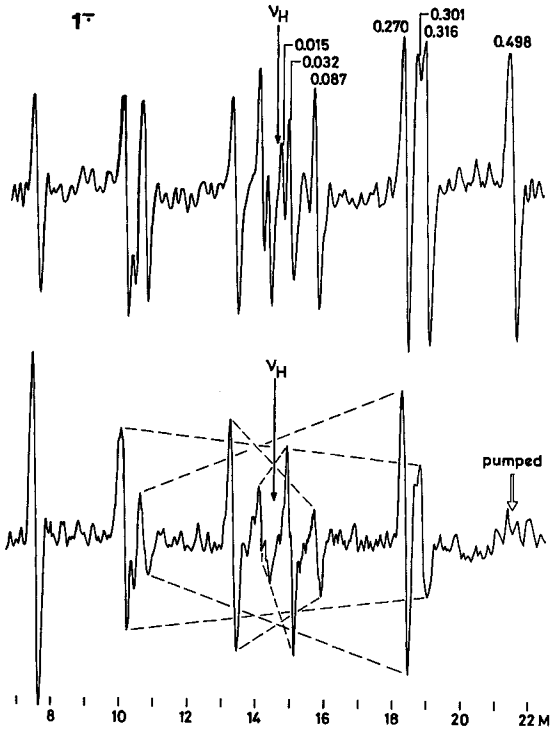

Fig. 2. *^{1}H-ENDOR* (top) *and general TRIPLE-resonance* (bottom) *spectra of* **1**$^{\cdot-}$. Experimental conditions as for the ESR spectrum in *Fig. 1*. The numbers [mT] are the proton-coupling constants associated with the ENDOR spectra.

(2 H), 0.301±0.002 (1 H), 0.270±0.002 (2 H), 0.087±0.001 (2 H), 0.032±0.001 (2 H), and 0.015±0.001 (1 H). These values did not significantly depend on the small amounts of HMPT admixed to the solvent DME. They were corroborated by the corresponding ^{1}H-ENDOR spectrum displayed in *Fig. 2* which also shows how a general TRIPLE-resonance experiment affects the intensities of the ENDOR signals. Accordingly, the sign of 0.270 and 0.032 mT is opposed to that of 0.498, 0.316, and 0.087 mT [10]. As the one-proton ENDOR signals associated with 0.301 mT were largely masked by the stronger signals due to two protons having the coupling constant of 0.316 mT, the relative sign of 0.301 mT could not be unambiguously determined from this spectrum. However, the sign in question proved to be the same as that of 0.270 mT by a general TRIPLE-resonance experiment performed on the ^{1}H-ENDOR spectrum of (1,10,12,13,15,16-D_6)-**1**$^{\cdot-}$ (see below) in which the signals due to the two protons with 0.316 mT have been eliminated by deuteration. No information was obtained with respect to the sign of the smallest one-proton coupling constant of 0.015 mT.

Unequivocal assignments of all coupling constants to sets of equivalent protons in individual positions of **1**$^{\cdot-}$ were made by comparing the ESR and, in particular, the ^{1}H-ENDOR spectra of **1**$^{\cdot-}$ with those of the radical anions of the deuterated derivatives, (8-D)-**1**, (1,2,9,10-D_4)-**1**, and (1,10,12,13,15,16-D_6)-**1**. These assignments are indicated on the structural formula of **1**$^{\cdot-}$ in *Fig. 1*. The absolute signs allotted to the coupling constants imply the assumption that the absolutely largest value of 0.498 mT for the protons in the 1,10-positions is negative. This assumption is justified by semi-empirical MO methods which all require a negative sign for 0.498 mT (see *Discussion*).

8-Fluoro[2.2]metaparacyclophane-1,9-diene (**2**). ESR and ^{1}H-ENDOR spectra of **2**$^{\cdot-}$ are displayed in *Fig. 3*. The coupling constants determined therefrom are: 0.436±0.003

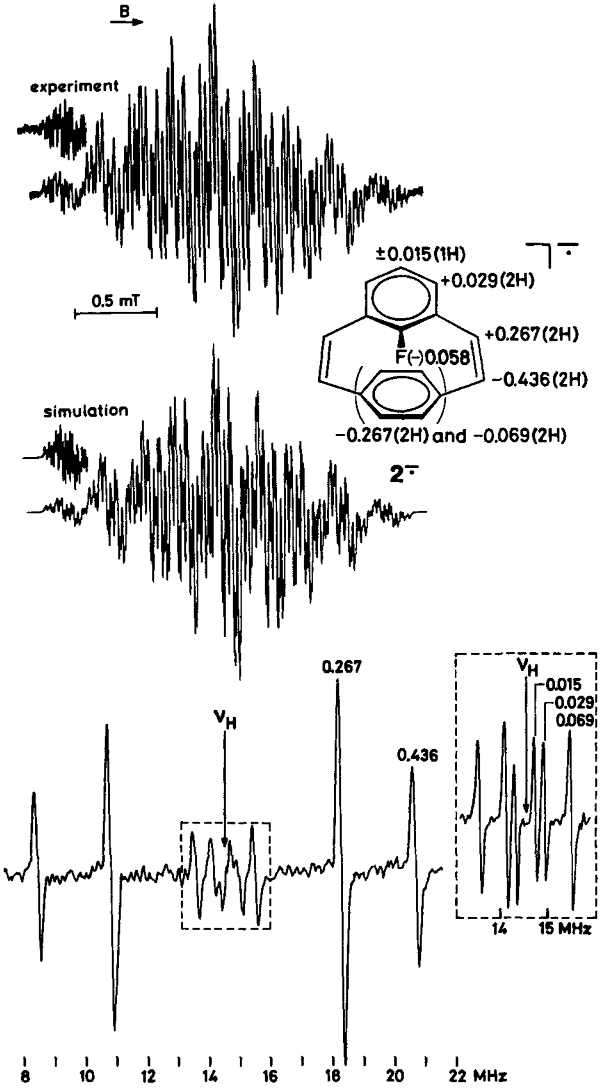

Fig. 3. *ESR* (top) *and* ^{1}*H-ENDOR* (bottom) *spectra of* **2**$^{\cdot-}$. Solvent: DME/HMPT (10:1); counterion: K$^+$; temp. 183 K. Coupling constants [mT] used in the simulation of the ESR spectrum are indicated on the formula; line-shape: *Lorentz*ian; line-width: 0.021 mT (0.015 mT for the inset at the low-field side). The number in the ENDOR spectrum are the proton-coupling constantss [mT] associated with the signals. The central part of the ENDOR spectrum is reproduced in the inset at the right on an expanded frequency scale and with better resolution.

(2 H), 0.267±0.002 (2 × 2 H), 0.069±0.001 (2 H), 0.029±0.001 (2 H), and 0.015±0.001 (1 H) [mT]. No signals associated with the ^{19}F-coupling constants could be detected by the ENDOR technique at the low temperature (193 K), conditioned by the poor persistence of $\mathbf{2}^{\cdot-}$, but the pertinent value of 0.058±0.002 mT was readily derived by a computer simulation of the ESR spectrum (*Fig. 3*). As in the case of $\mathbf{1}^{\cdot-}$, all these values were not sensitive to the admixture of HMPT to DME. A general TRIPLE-resonance experiment, performed on the ^{1}H-ENDOR spectrum, indicated that the sign of 0.029 mT is opposite to that of 0.436 and 0.069 mT. The ENDOR signals, associated with 0.267 mT and due to *two* pairs of equivalent protons, did not respond to the TRIPLE-resonance technique. Hence, the two pairs of protons must (within the limits of experimental resolution) have coupling constants of the same absolute value, but of opposite signs. Again, the relative sign of the smallest coupling constant (0.015 mT) could not reliably be determined from the TRIPLE-resonance spectrum.

The similarity of the coupling constants of the protons in $\mathbf{1}^{\cdot-}$ and $\mathbf{2}^{\cdot-}$ allowed the assignments of these values for $\mathbf{2}^{\cdot-}$ to be made by analogy to those for $\mathbf{1}^{\cdot-}$. The assignments and the signs resulting therefrom are indicated on the structural formula of $\mathbf{2}^{\cdot-}$ in *Fig. 3*. A negative sign was allotted to the ^{19}F-coupling constant (0.058 mT), as the corresponding proton value (0.301 mT) for $\mathbf{1}^{\cdot-}$ is positive, and a change in sign should occur on replacing a proton at a π-centre by a ^{19}F-nucleus in an F-substituent (see *Discussion*).

8-Cyano[2.2]*metaparacyclophane-1,9-diene* (**3**). The ESR spectra of $\mathbf{3}^{\cdot-}$ in DME (counterion K$^+$) at low temperatures (193–263 K) revealed the presence of two radical anions having markedly different hyperfine patterns. The radical anion, which gave rise to the hyperfine pattern with the larger total width, is considered as tightly ion-paired with K$^+$, because its ESR lines are split by an additional coupling with a ^{39}K-nucleus. The other radical anion, exhibiting a smaller total width and no observable ^{39}K-hyperfine splitting, is regarded as loosely associated with K$^+$. Upon raising the temperature and/or prolonged contact of the solution with K metal, the equilibrium between the two radical anions shifted in favour of the tightly ion-paired $\mathbf{3}^{\cdot-}$, whereas a reverse effect followed on addition of HMPT to DME. In MTHF as the solvent (counterion K$^+$), only the tightly paired radical anion was observed, irrespective of the temperature and the extent of reduction; its ESR and ^{1}H-ENDOR spectra are shown in *Fig. 4*. The proton-coupling constants derived from the ENDOR signals and used for the computer simulation of the ESR spectrum (*Fig. 4*) are: 0.499±0.004 (1 H), 0.268±0.002 (2 H), 0.182±0.002 (2 H), 0.127±0.002 (2 H), and 0.006±0.001 (2 × 2 H) [mT]; hyperfine interaction with paramagnetic nuclei other than protons gives rise to splittings 0.154±0.002 (1 ^{14}N) and 0.017±0.001 (1 ^{39}K) mT. According to a general TRIPLE-resonance experiment, the sign of 0.182 and 0.127 mT is opposite to that of the remaining proton-coupling constants. The hyperfine data for all paramagnetic nuclei in this tightly paired radical anion are indicated on the structural formula of $\mathbf{3}^{\cdot-}$ in *Fig. 4*. Their assignments to individual positions and their absolute signs have been based on a MO model presented in the *Discussion*³).

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³) It has tentatively been assumed that the coupling constant of –0.006 mT is due to *two* pairs of protons in the *para*-bridged ring. As the number of protons having this coupling constant has not experimentaly been ascertained, a hyperfine interaction with only *one* pair cannot be excluded (in such case, the second pair of the protons in the *para*-bridged ring would give rise to a splitting that is too small to be observed).

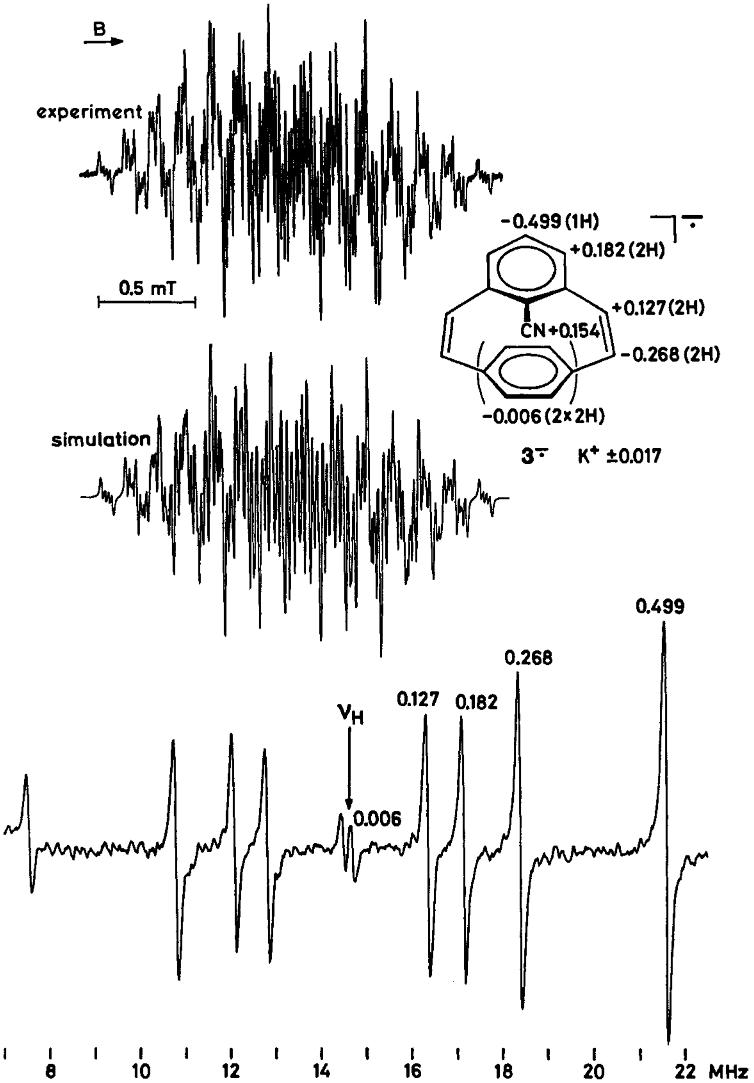

Fig. 4. *ESR* (top) *and* ^{1}*H-ENDOR* (bottom) *spectra of* **3**$^{-\cdot}$. Solvent: MTHF; counterion: K$^+$; temp.: 203 K. Coupling constants [mT] used in the simulation of the ESR spectrum are indicated on the formula (see *Footnotes 3* and *4* for −0.006 mT); line-shape: *Lorentz*ian; line-width: 0.013 mT. The numbers in the ENDOR spectrum are the proton-coupling constants [mT] associated with the signals.

An ESR spectrum of a loosely paired radical anion, obtained upon electrolytic reduction of **3** in DMF (counterion Et_4N^+), is displayed in *Fig. 5*, along with its simulation computed by the use of the following coupling constants: 0.468±0.004 (1 H), 0.251±0.003 (2 H), 0.171±0.002 (2 H), 0.115±0.002 (2 H), 0.006±0.001 (2 x 2 H), and 0.156±0.002 (1 ^{14}N) [mT]. Their assignments and signs, which have been chosen by analogy to those for the

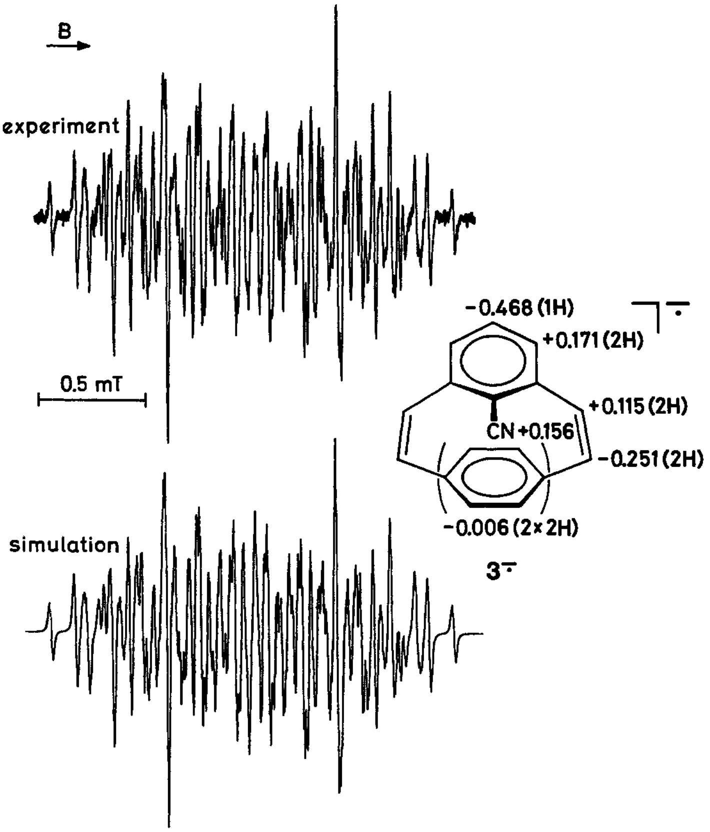

Fig. 5. *ESR spectrum of* **3**$^{\cdot-}$. Solvent: DMF; counterion: Et_4N^+; temp.: 298 K. Coupling constants [mT] used in the simulation are indicated on the formula (see *Footnote 3* for −0.006 mT); line-shape: *Lorentz*ian; line-width: 0.012 mT.

tightly paired radical anion, are indicated on the structural formula of **3**$^{\cdot-}$ in *Fig. 5*. The presence of electrodes in the ESR cavity foiled application of the ENDOR technique[4]), but both ESR and ENDOR spectra of a loosely paired radical anion were readily observed for the **3**$^{\cdot-}$ in DME/HMPT (counterion K^+). The coupling constants determined therefrom are: 0.468±0.004 (1 H), 0.252±0.003 (2 H), 0.167±0.002 (2 H), 0.105±0.002 (2 H), 0.006±0.001 (2 × 2 H), and 0.159±0.002 (1 ^{14}N) [mT]. Thus, with one exception (0.115 *vs.* 0.105 mT), these values do not significantly differ from those found for the electrolytically generated radical anion. Their relative signs, as determined by the general TRIPLE-resonance technique, agree with those of the corresponding values obtained by the same technique for the tightly paired **3**$^{\cdot-}$ in MTHF.

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[4]) With no ENDOR spectrum available for the electrolytically generated **3**$^{\cdot-}$, the very small coupling constant of −0.006 mT could not, in this case, be directly measured. It has been taken over from the hyperfine data of the radical anions produced with K in an ethereal solvent.

Discussion. – *Spin Distribution.* The total widths of the ESR spectra are compared in *Fig. 6* for the radical anions of [2.2]paracyclophane (**6**) [8], [2.2]metaparacyclophane (**4**) [3], and their respective dienes, **5** [9] and **1**. This comparison demonstrates how difficult it is to predict the spin distribution in this class of radical ions. In the case of the paracyclophanes, the drastic *decrease* in the total width, on going from the radical anion of the parent compound **6** to that of its diene **5**, has been rationalized in terms of a symmetry change in the singly occupied π-orbital which is considered as a combination of benzene LUMO's [9]. Unfortunately, an analogous interpretation is not at hand to account for the large *increase* in the total width on passing from the radical anion of the metaparacyclophane **4** to that of its diene **1**. This failure is not only due to the lower symmetry of the metaparacyclophanes **4** and **1** (C_{2v}) relative to their *para*-counterparts **6** and **5** (D_{2h}), but it is also a consequence of semi-empirical MO methods being incapable to reproduce the proton-coupling constants observed for $\mathbf{1}^{\cdot-}$. The simplest of these models is that of the radical anion of 1,3-diethenylbenzene in which the planes of the exocyclic double bond and the aromatic ring deviate by 30° (see *Introduction*). The complete omission of the *para*-bridged ring seems justified by the near-orthogonality of this ring to the residual π-system. The *Table* gives the proton-coupling constants calculated by the

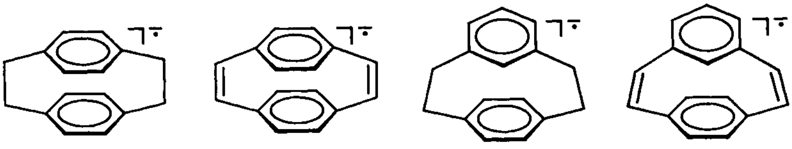
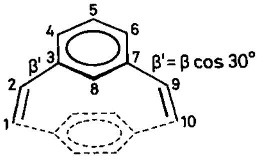

$\mathbf{6}^{\cdot-}$: 3.20 **$\mathbf{5}^{\cdot-}$: 1.90** **$\mathbf{4}^{\cdot-}$: 1.95** **$\mathbf{1}^{\cdot-}$: 2.72**

Fig. 6. *Total widths* [mT] *of the ESR spectra of* $\mathbf{6}^{\cdot-}$, $\mathbf{5}^{\cdot-}$, $\mathbf{4}^{\cdot-}$, *and* $\mathbf{1}^{\cdot-}$

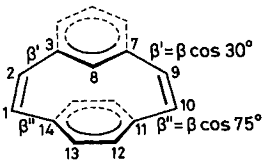
Table . *Calculated and Experimental Coupling Constants* [mT] *for the Radical Anion of [2.2]Metaparacyclophane-1,9-diene* (**1**)

Position	1,10	2,9	4,6	5	8	12,13,14,15
Model A[a])	–0.566	–0.057	–0.554	+0.156	+0.108	–
Model B	–0.225	+0.549	–0.462	+0.256	+0.192	+0.076 +0.056
Model C[a])	–0.622	+0.250	–	–	+0.314	–0.002
Experiment	–0.498	+0.270	+0.032	±0.015	+0.301	–0.316 –0.087

[a]) Q = –2.4 mT as the proportionality factor in the *McConnell* equation [12].



Model A



Model C

Hückel-McLachlan procedure ($\lambda = 1.2$) [11] for the radical anion of 1,3-diethenylbenzene ($\beta' = \beta \cos 30°$; *Model A*). Agreement of these values with their experimental counterparts is rather poor. Apart from not accounting for the substantial coupling constants of the protons at the *para*-bridged ring, the model overestimates the absolute values for the positions 4, 5, and 6 and underestimates those for 2, 9, and 8. Agreement with experiment is not improved by applying to $\mathbf{1}^{\cdot-}$ the more sophisticated INDO-procedure [13] which makes use of the geometry determined by the X-ray crystallographic structure analysis of **1** [5]. This conclusion is drawn from the inspection of the coupling constants calculated by such a procedure and also listed in the *Table* (*Model B*). Surprisingly, the coupling constants observed for the protons in the positions 1,2,8,9, and 10 of $\mathbf{1}^{\cdot-}$ are rather well reproduced by performing *Hückel-McLachlan* calculations on a 11-membered monocyclic π system formed by the centres 1–3 and 7–14 and occupied by 11 electrons (*Table; Model C*). Deviations of the constituent parts in this system from planarity are simulated by modifying the bond parameters of the pertinent linkages ($\beta' = \beta \cos 30°$; $\beta'' = \beta \cos 75°$).

According to the proton-hyperfine data (*Figs. 1* and *3*), the π-spin distribution is not much altered on passing from $\mathbf{1}^{\cdot-}$ to $\mathbf{2}^{\cdot-}$, although the greater steric demand of the F- relative to the H-atom should increase deviations of the constituent π systems from planarity. In general, the absolute value of the ^{19}F-coupling constant in an F-substituent of a π-system exceeds the corresponding value for the replaced proton by a factor of 2–2.5 [14][15], whereby the signs of the two constants are opposite [16]. Deviations from this factor have been found for F-atoms in *ortho*-positions to substituent groups at the benzene ring, as the absolute values of the ^{19}F-coupling constants were considerably smaller than expected [15]. Such an '*ortho*-effect' is very pronounced on the 8-fluoro substitution of $\mathbf{1}^{\cdot-}$ to yield $\mathbf{2}^{\cdot-}$. The ratio of the absolute values for the ^{19}F- and ^{1}H-coupling constants is, in this case, as low as 0.058 mT/0.301 mT = 0.19, but the signs of the two values are assumed to be still opposite (*Figs. 1* and *3*).

No X-ray structural data are available for **3**, but molecular models require that deviations of constituent π systems from planarity should be larger in **3** than in **1** and **2**. Thus, the π-spin population in $\mathbf{3}^{\cdot-}$ must be essentially restricted to the *meta*-bridged benzene ring with its electron affinity being strongly enhanced by the CN substitution. An appropriate model for $\mathbf{3}^{\cdot-}$ is the radical anion of 1-cyano-2,6-diethenylbenzene, in which the two exocyclic double bonds are not quite coplanar with the aromatic ring. Applying the *Hückel-McLachlan* procedure to this radical anion and making use of appropriate parameters, which account for the deviations from planarity and the presence of the CN group [17], one obtains coupling constants in fair agreement with experiment. This agreement justifies the assignments of the coupling constants to protons in the individual positions of $\mathbf{3}^{\cdot-}$ (*Figs. 4* and *5*).

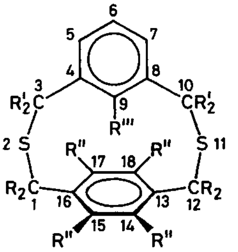
The marked increase in the absolute values of the proton-coupling constants on going from the loosely paired radical anion $\mathbf{3}^{\cdot-}$ (*Fig. 5*) to the tightly paired one (*Fig. 4*) can be simulated in the frame of the *Hückel-McLachlan* procedure by making the *Coulomb* parameter of the N-centre more negative (*i.e.* enlarging h_N in $\alpha_N = \alpha + h_N\beta$). This result bears out the expectation that the positively charged counterion is close to the heteroatom N, of which the electronegativity is enhanced by tight ion pairing.

Conformational Flipping. The NMR signals of the two proton pairs at the *para*-bridged benzene ring in **1** coalesce at $T_c = 177$ K [2b]. From this temperature and the chemical-shift difference, $\Delta\nu = 91$ Hz, of the pertinent protons, an activation energy, $\Delta G^{\ddagger} = 35$ kJ/mol, has been estimated for the conformational flipping of the *meta*-bridged ring [2b]. The same relation between $\Delta G^{\ddagger}$, T_c, and $\Delta\nu$ [18] can be used to predict the coalescence temperature, T_c, for the ESR and/or ENDOR signals of the two proton pairs in **1**$^{\cdot-}$. Taking $\Delta G^{\ddagger} = 35$ kJ/mol as for **1** and setting $\Delta\nu = 28.04 \cdot 10^6 \cdot [-0.087 - (-0.316)]$Hz, which is the difference in the coupling constants of these proton pairs, one obtains $T_c \approx 320$ K. This temperature is far above the upper limit of the range conditioned by the persistence of **1**$^{\cdot-}$.

As the NMR signals of the two proton pairs in **2** do not coalesce even at 463 K [19], the activation barrier to the conformational flipping of the *meta*-bridged ring must be considerably higher than in **1**. In general, due to the different time-scale of the NMR and ESR experiments, the coalescence temperatures T_c for the radical anions are at least 100 K above those for the neutral compounds. Thus, considering the poor persistence of **2**$^{\cdot-}$, a chance to observe T_c for this radical anion is still less realistic than for **1**$^{\cdot-}$.

As expected, conformational flipping in **3** is very slow on the NMR time-scale [2b] and must be even slower in **3**$^{\cdot-}$ on the ESR hyperfine time-scale. As the small coupling constants assigned to the two proton pairs at the *para*-bridged ring are hardly distinguishable (*Figs. 4* and *5*)^3), the coalescence of the pertinent ESR and/or ENDOR signals is not likely to be detected. Nevertheless, it has been found that, except for their influence on the equilibrium between the ion-pairs in DME, changes in the temperature have little effect on the ESR spectra in the range of 183–298 K. This finding is in accord with the rate of conformational flipping being negligibly small in **3**$^{\cdot-}$ under the applied experimental conditions.

Experimental. – *Syntheses.* The compounds **1**, (8-D)-**1**, (1,2,9,10-D_4)-**1**, and (1,10,12,13,15,16-D_6)-**1** were prepared from 2,11-dithia[3.3]metaparacyclophane (3,11-dithiatricyclo[11.2.2.1^{5,9}]octadeca-5,7,9(18),13,15,16-hexaene; **7**) and correspondingly deuterated derivatives, (9-D)-**7**, (1,1,3,3,10,10,12,12-D_8)-**7**, and (1,1,12,12,14,15,17,18-D_8)-**7** (18-deuterio-, 2,2,4,4,10,10,12,12-octadeuterio-, and 2,2,12,12,14,15,16,17-octadeuterio-3,11-dithiatricyclo[11.2.2.1^{5,9}]octadeca-5,7,9(18),13,15,16-hexaenes). The syntheses of **7** and its deuterio derivatives have been described in [3]. The extrusion of the S-atoms from these dithia-compounds and introduction of the double bonds was carried out in the same way as the conversion of the analogous 2,11-dithia[3.3]paracyclophanes into **5** and its deuterio derivatives [9]. In the last step of this reaction sequence [2c][9], a substantial amount of diphenyl disulfide is formed. This by-product could readily be separated from a [2.2]metaparacyclophanediene by reduction with *threo*-1,4-dimercaptobutane-2,3-diol (racemate) to thiophenol and chromatography on Al_2O_3 in cyclohexane [20].



7	R = R' = R'' = R''' = H
(9-D)-**7**	R = R' = R'' = H, R''' = D
(1,1,3,3,10,10,12,12-D_8)-**7**	R'' = R''' = H, R = R' = D
(1,1,12,12,14,15,17,18-D_8)-**7**	R' = R''' = H, R = R'' = D

The F- and CN-substituted derivatives **2** and **3**, resp., used in the present work, were synthesized by the Eugene (Oregon, USA) research group [2b].

Instrumental. The ESR spectra were taken on a *Varian-E9* instrument, while the *Bruker-ESP-300* system served for the ENDOR and TRIPLE- resonance studies.

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