

44. The Radical Anions of [2.2]Paracyclophane-1,9-diene and Some of its Derivatives. An Unexpected Conformational Interconversion

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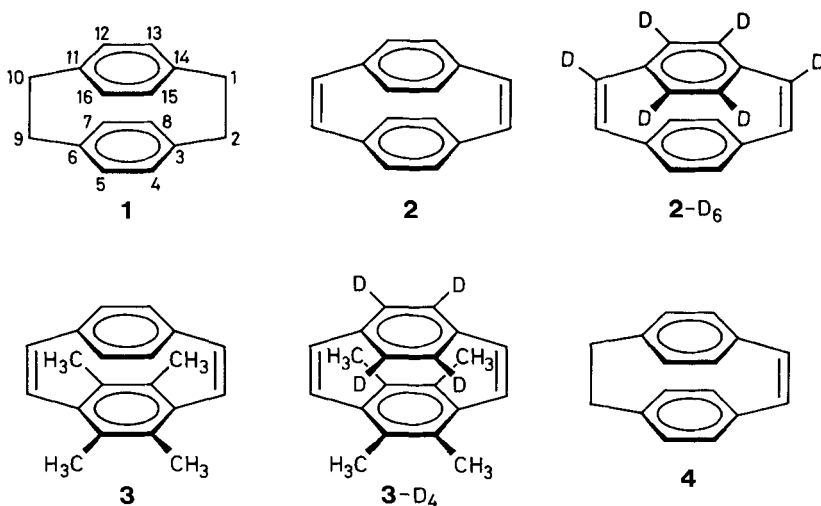
Dedicated to Prof. *Virgil Boekelheide* on the occasion of his 65th birthday

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The radical anions of [2.2]paracyclophane-1,9-diene (**2**) and its 1,10,12,13,15,16-hexadeuterio derivative **2-D₆**, as well as those of 4,5,7,8-tetramethyl[2.2]paracyclophane-1,9-diene (**3**) and its 12,13,15,16-tetradeterio derivative **3-D₄**, have been studied by ESR spectroscopy. The coupling constants for **2⁻** at 178 K are 0.422 mT for four equivalent olefinic protons and 0.046 and 0.020 mT, each for a set of four equivalent aromatic protons. This hyperfine pattern is consistent with either benzene ring bearing two pairs of equivalent protons and it points to a lowering of the anticipated *D_{2h}* symmetry. The ESR spectra of **2⁻** are strongly temperature dependent, due to modulation of the two coupling constants of 0.046 and 0.020 mT; these have opposite signs and average to 0.013 mT at 273 K. The experimental findings are interpreted in terms of a transition state of *D_{2h}* symmetry, 33 kJ/mol above two interconverting equivalent conformations of lower symmetry. Several pieces of evidence suggest that this symmetry is *D₂*, *i.e.*, the benzene rings in **2⁻** are twisted in opposite directions about the vertical axis. Temperature dependence of the ESR spectra, resulting from modulation of the hyperfine interactions with the aromatic protons, is also observed for **2-D₆⁻** and **3⁻**. In the case of **3⁻**, the olefinic protons are, as expected, only equivalent in pairs, the pertinent coupling constants being 0.560 and 0.325 mT. Upon standing at low temperatures, **2⁻** and **3⁻** gradually convert into the radical anions of [2.2]paracyclophane (**1**) and its 4,5,7,8-tetramethyl derivative, respectively. At higher temperatures, cleavage of one bridging chain in **2⁻** also occurs, with the formation of the radical anion of (*E*)-4,4'-dimethylstilbene (**7**). Both reactions of **2⁻** must involve the transient radical anion of [2.2]paracyclophane-1-ene (**4**) as proved by the observation of the spectra of **1⁻** and **7⁻** with **4** as the starting material.

Introduction. – Replacement of the single by the double bonds in the two bridging alkyl chains of [2.2]paracyclophane (**1**), to yield the 1,9-diene **2**, has only a small effect on the geometry and electronic structure. As shown by the X-ray analyses of **1** [1] and **2** [2], both molecules belong essentially to the same point group, *D_{2h}*, and the mean distances between their benzene decks are almost equal (298.5 and 302.5 pm, respectively). Likewise, the electron [3] and photoelectron spectra [4] of the two compounds are very similar, thus indicating that the olefinic π -systems of **2** do not appreciably interact with the aromatic ones, a finding which is not surprising in view of the essentially perpendicular arrangement of the double bonds and the benzene decks. Considering the common structural features of **1** and **2**, it is reasonable to expect that their radical anions **1⁻** and **2⁻** will also resemble each other in their properties such as symmetry, electron spin distribution and association with the positively charged counterion. The ESR studies reported here demonstrate that this expectation is not borne out by experiment.

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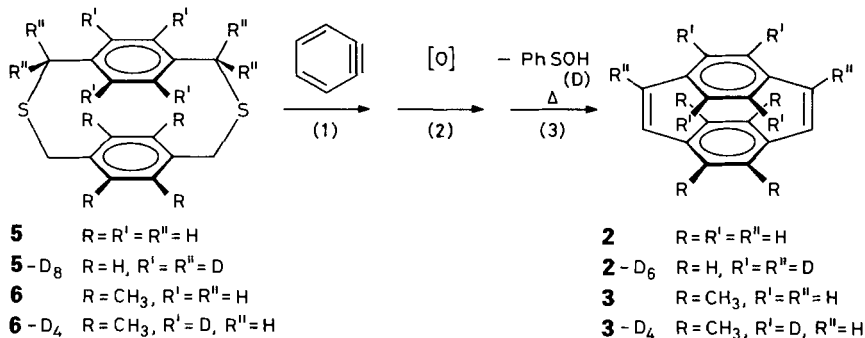


In addition to the radical anion of **2**, the paper deals with that of its 1,10,12,13,15,16-hexadeuterio derivative **2-D₆**, as well as with the radical anions of 4,5,7,8-tetramethyl-[2.2]paracyclophane-1,9-diene (**3**) and its 12,13,15,16-tetradeterio derivative **3-D₄**. Reduction of [2.2]paracyclophane-1-ene (**4**) is also described.

Some of the results obtained for **2^{•-}** and **3^{•-}** have been mentioned in a recent review article on the radical ions ofphanes [5], which, among others, gives a comprehensive account of the investigations carried out on **1^{•-}**.

Experimental. – *Syntheses.* – [2.2]Paracyclophane-1,9-diene (**2**) and its Derivatives **2-D₆**, **3**, and **3-D₄**. Whereas **2** has been known since 1958 [3], the syntheses of **2-D₆**, **3**, and **3-D₄** have not yet appeared in the literature. In the present work, all four compounds were prepared by following the synthetic route which is outlined in *Scheme 1*. This route started from the corresponding 2,11-dithia[3.3]cyclophanes **5** [6], **5-D₈** [7], **6** [8], and **6-D₄** [9] which were converted into **2**, **2-D₆**, **3**, and **3-D₄**, respectively, by three consecutive reaction steps: 1) treatment with benzynes, generated *in situ* by the reaction of anthranilic acid with isoamyl nitrite, 2) oxidation of the resulting Stevens-rearrangement products with *m*-chloroperbenzoic acid, and 3) olefination by pyrolysis of the sulfoxides. The three steps comply with the methodology introduced by *Otsubo* and *Boekelheide* [10], except for the replacement of the solvent *p*-xylene by chlorobenzene in step 3. Owing to this modification, 2,5,4'-trimethylbiphenylmethane [11] was not formed as a by-product and thus the isolation of the [2.2]paracyclophane-1,9-dienes was facilitated.

Scheme 1



4,5,7,8-Tetramethyl[2.2]paracyclophane-1,9-diene (**3**) was characterized by the following data: m.p. 132° (uncorrected); ¹H-NMR (CDCl₃, amb. temp., δ in ppm): s at 1.84 (12H, CH₃), 6.63 (4H, arom.) and 6.97 (4H, olef.). The two last values are comparable to those for the unsubstituted compound **2**: s at 6.56 (8H, arom.), and 7.20 (4H, olef.). MS basis peak *M*⁺ at *m/e* 260.

The isotopic purity of the deuteriated derivatives 2-D₆ and 3-D₄ was better than 90%, as estimated from the MS analysis.

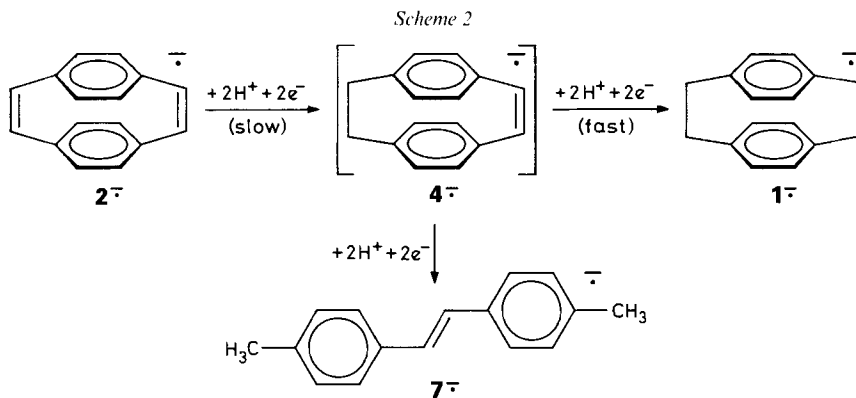
[2.2]Paracyclophane-1-ene (**4**). The first synthesis of **4** was described by Dewhirst and Cram in 1958 [3], along with that of **2**. Recently, Hopf and Psiorz prepared **4** via a more direct route [12], and a sample of **4** used in the present work was a generous gift from them.

(E)-4,4'-Dimethylstilbene (**7**). The preparation of **7**, which served as a reference compound (see below), involved a reaction of diphenylphosphinoyl sodium with 4-methylbenzaldehyde [13]. The properties of the product **7** thus obtained agree with those described in [14].

Generation and Reactions of the Radical Anions. Reduction of **2** and its derivatives, 2-D₆, **3**, and 3-D₄ to their radical anions was carried out with K metal in THF, 1,2-dimethoxyethane (DME) and in mixtures of DME with hexamethylphosphoric acid triamide (HMPT). In several experiments, the reaction mixture contained an excess of dissolved LiCl salt, so that Li⁺ superseded K⁺ as the counterion.

The radical anions 2⁻, 2-D₆⁻, 3⁻, and 3-D₄⁻ were moderately persistent below 213 K, but decayed markedly on raising the temp., as indicated by the decreasing intensity of their ESR signals. The persistence was enhanced by the addition of LiCl which also impeded the formation of secondary paramagnetic species. Two such species were identified by their ESR spectra in the case of 2⁻. One of them, gradually formed under not too rigorous conditions (short contact with the metal mirror and temp. below 253 K), was readily identified as the radical anion of **1** [15]. The second species, produced by a more severe treatment (prolonged contact with the metal mirror and higher temp.), proved to be the radical anion of **7**, as confirmed by the reduction of an authentic sample of **7**. The hyperfine data determined for 7⁻ in the present work closely agree with those reported for this radical anion in [16]. In the case of 3⁻ only the radical anion of 4,5,7,8-tetramethyl[2.2]paracyclophane [9] was identified as a secondary paramagnetic species.

Both radical anions 1⁻ and 7⁻ were also obtained with **4** as the starting material. However, in contrast to 2⁻, the primary radical anion 4⁻ was too short-lived to be characterized by its hyperfine data. Even at the lowest attainable temp. (153 K; DME/THF) the first ESR spectrum, which appeared immediately upon reduction of **4**, was that of 1⁻, and no signals attributable to 4⁻ could be detected. More rigorous conditions led to the formation of 7⁻ as in the case of 2⁻.



The behaviour of **2** and **4** upon reduction strongly suggests that the conversion of 2⁻ into 1⁻, and presumably also into 7⁻, proceeds according to Scheme 2. The reaction involves 4⁻ as a transient intermediate, whereby the first step, 2⁻ → 4⁻, is slow relative to the second one, 4⁻ → 1⁻. The H⁺ ions required for both steps must stem from protic impurities present in a minute amount.

Results. – [2.2]Paracyclophane-1,9-diene (**2**). The ESR studies of the radical anion 2⁻ were conducted in the range of 178 to 273 K²). The spectra were rather insensitive to the

²) A Varian-E9 ESR-spectrometer was used.

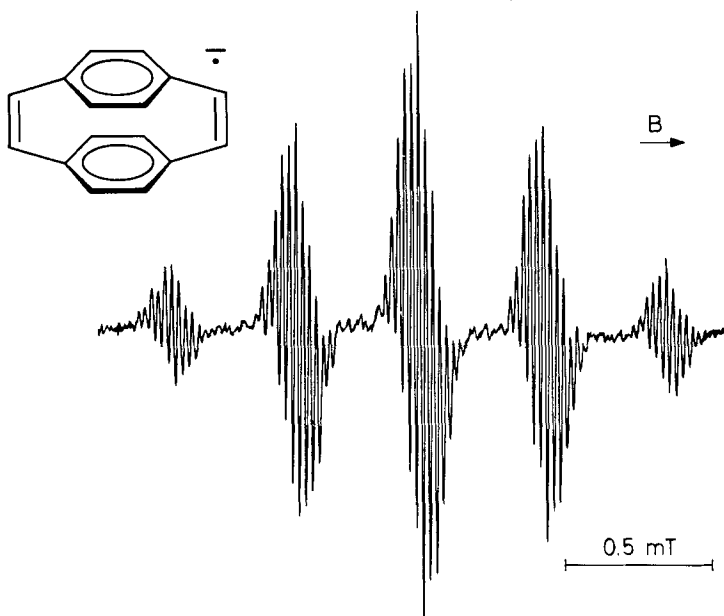


Fig. 1. ESR spectrum of the radical anion of 2. Solvent: DME; counterion: K^+ ; temp.: 178 K.

nature of the solvent (THF, DME, HMPT) and the counterion (K^+ , Li^+), but depended strongly on temperature. Fig. 1 shows the ESR spectrum taken at 178 K. The grouping of lines is due to four equivalent protons with the coupling constant of 0.422 ± 0.002 mT, whereas the hyperfine pattern within each group arises from two sets of four equivalent protons having the coupling constants of 0.046 ± 0.001 and 0.020 ± 0.001 mT. Careful examination of this pattern reveals slight deviations of the experimental line amplitudes from the expected ones, thus indicating the onset of a dynamic process. In fact, a rise in the temperature, while not significantly affecting the grouping of lines, leads to striking changes within each group. These changes are exemplified for the central group of lines by Fig. 2. The corresponding computer-simulated curves [17], also reproduced in Fig. 2, have been based on a two-jump model [18] which involves the two sets of four equivalent protons with the coupling constants of 0.046 and 0.020 mT. The changes in the hyperfine pattern observed on raising the temperature stepwise from $T = 178$ to 273 K thus point to an interconversion of two equivalent structural forms, whereby the two sets of protons exchange their environment and their coupling constants are modulated. It is evident from Fig. 2 that these changes are accurately simulated by a gradual increase in the interconversion rate from $k = 1.16 \cdot 10^5$ to $3.30 \cdot 10^8$ s^{-1} . The two coupling constants affected by the process have opposite signs and average in the fast exchange range ($T > 250$ K; $k > 10^8$ s^{-1}) to a value of ± 0.013 mT = $\frac{1}{2}(\pm 0.046 \mp 0.020)$ mT for eight equivalent protons. The Arrhenius plot, presented in Fig. 3, yields the following thermodynamic parameters: $\log A = 14.8 \pm 0.3$; $E_a = 33.2 \pm 1.3$ kJ/mol, $\Delta H^\ddagger = 30.7 \pm 1.3$ kJ/mol, $\Delta S^\ddagger = 30 \pm 5$ J/(mol · K) and $\Delta G^\ddagger = 21.6 \pm 0.5$ kJ/mol³⁾.

³⁾ The error limits are determined by experimental inaccuracies which amount to ± 1 K and 20% in T and k , respectively.

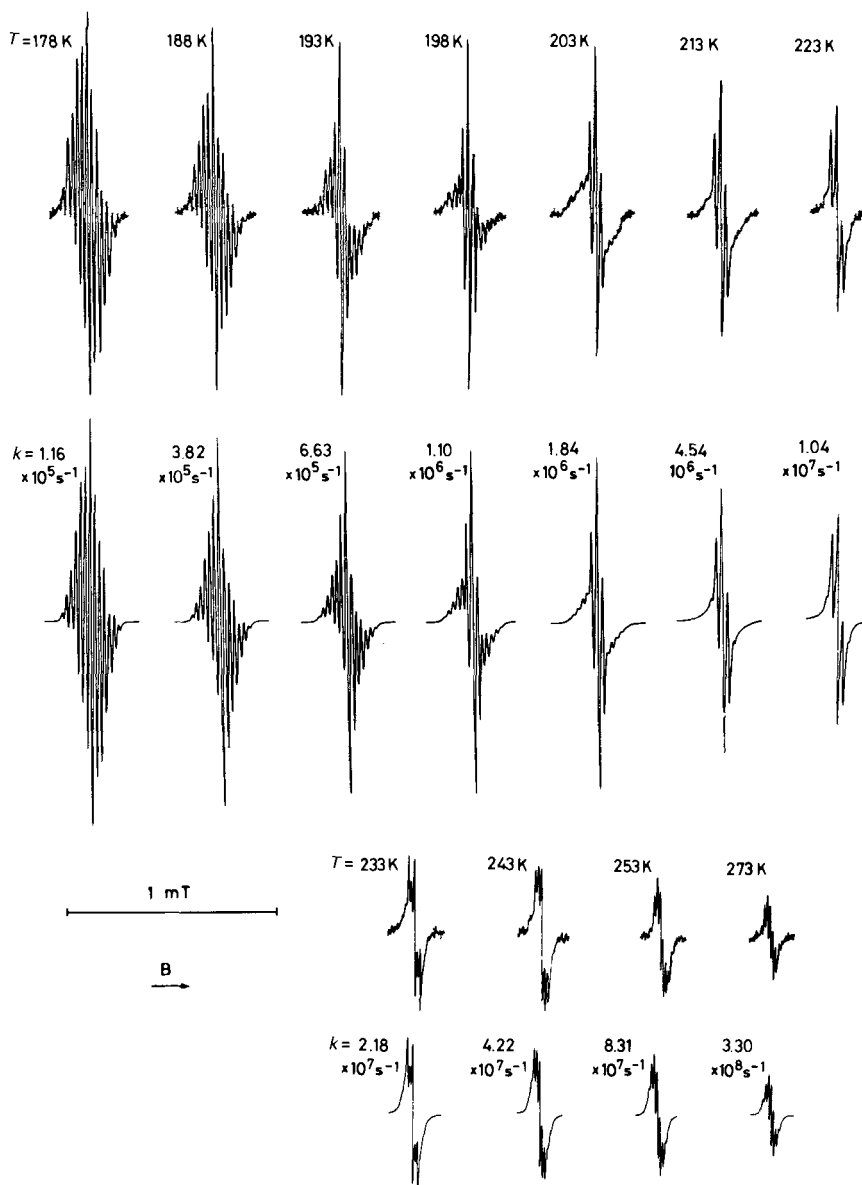


Fig. 2. First and third rows. *Central group of lines in the ESR spectrum of the radical anion of 2 at variable temperature (T). Solvent: DME; counterion: Li⁺. Second and fourth lines: Computer-simulated curves for a variable exchange rate (k). Modulated coupling constants: ± 0.046 (4H) and ∓ 0.020 mT (4H); line-shape: Lorentzian; line-width: 0.009 mT.*

A highly resolved ESR spectrum of 2^- , taken at 198 K, *i.e.*, at an intermediate exchange rate ($k = 1.10 \cdot 10^6 \text{ s}^{-1}$), is displayed in Fig. 4. It provides an impressive illustration of 'alternating' line-widths [18] in the rather rarely encountered case of proton-coupling constants of opposite signs [19]. Accordingly, the observed splitting within the groups equals 0.026 mT which is the difference of 0.046 and 0.020 mT. The computer simulation (Fig. 4), does

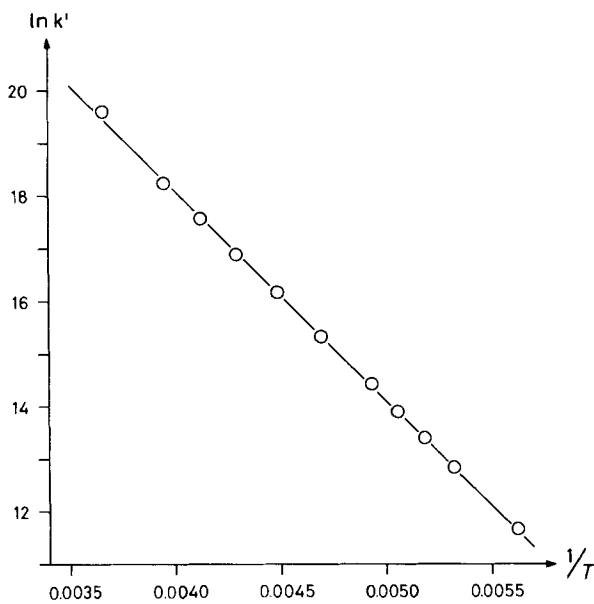


Fig. 3. Arrhenius plot of the exchange rate k for the radical anion of **2**. k' = numerical value of k .

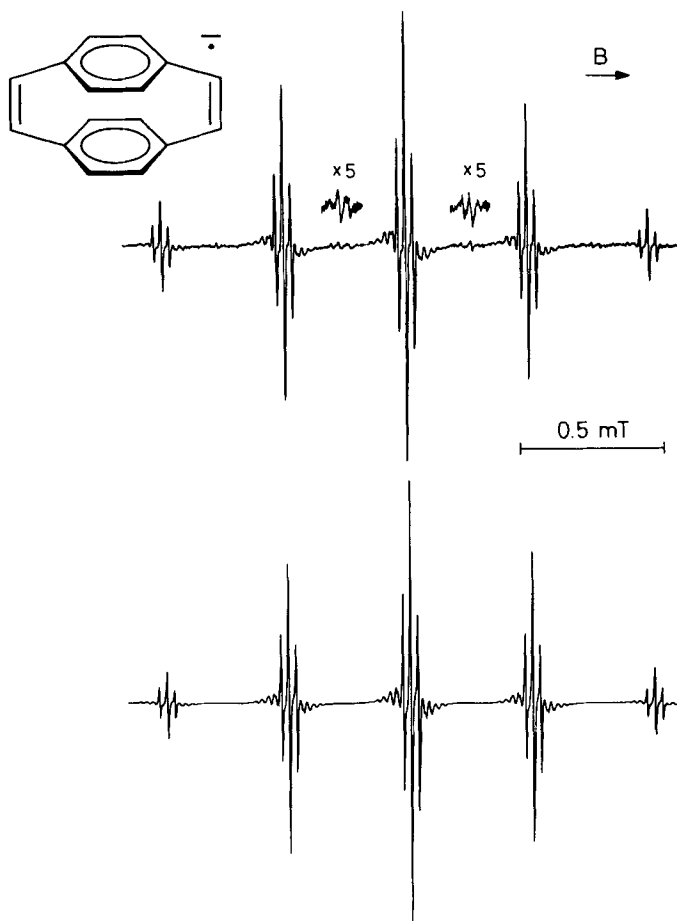


Fig. 4. Top: ESR spectrum of the radical anion of **2**. Solvent: DME; counterion: K^+ ; temp.: 198 K. Bottom: Computer-simulated curve for an exchange rate k of $1.10 \cdot 10^6 \text{ s}^{-1}$. Modulated coupling constants: ± 0.046 (4H) and ∓ 0.020 mT (4H); non-involved in the exchange: 0.422 mT (4H); line-shape: Lorentzian; line-width: 0.004 mT.

not account for the weak satellite lines stemming from naturally abundant ^{13}C isotopes in four equivalent C-sites. The ^{13}C -coupling constant associated with these lines is not affected significantly by the exchange. Since satellite lines due to ^{13}C isotopes in the remaining C-sites of 2^- are masked by the main spectrum, the pertinent ^{13}C -coupling constants must be smaller than 0.025 mT.

1,10,12,13,15,16-Hexadeuterio[2.2]paracyclophane-1,9-diene (2-D₆). The temperature dependence of the ESR spectra of 2-D_6^- was closely parallel to that observed for 2^- . Fig. 5 shows a spectrum taken at 203 K, along with its computer simulation. In the

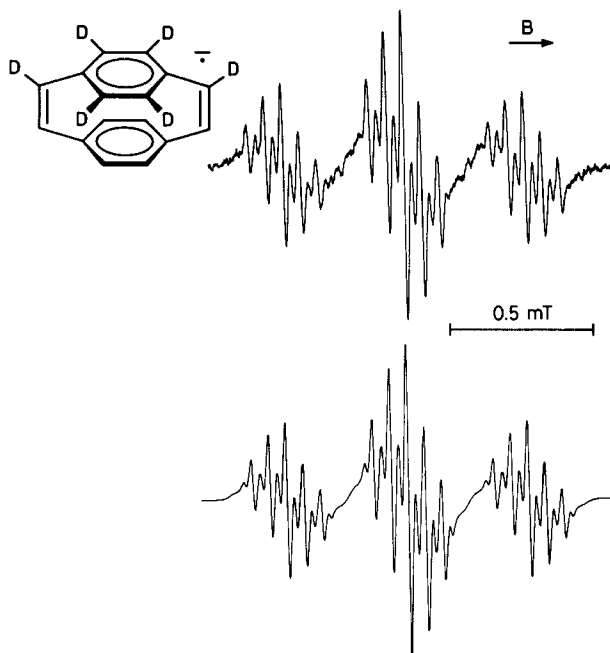


Fig. 5. Top: ESR spectrum of the radical anion of 2-D_6 . Solvent: DME; counterion: Li^+ ; temp.: 203 K. Bottom: Computer-simulated curve for an exchange rate k of $1.84 \cdot 10^6 \text{ s}^{-1}$. Modulated coupling constants: ± 0.046 (2H) and ∓ 0.020 mT (2H); non-involved in the exchange: 0.422 (2H) and 0.060 mT (2D); line-shape: Lorentzian; line-width 0.009 mT.

two-jump model, used in this simulation, two pairs of equivalent protons are involved. The opposite signs of their coupling constants, 0.046 ± 0.001 and 0.020 ± 0.001 mT, as well as the exchange rate k of $1.84 \cdot 10^6 \text{ s}^{-1}$ agree with the analogous findings for 2^- . A further pair of equivalent protons and a pair of equivalent deuterons, with the coupling constants of 0.422 ± 0.002 and 0.060 ± 0.001 mT, respectively, are not affected by the exchange. The simulation neglects the unresolved splitting from the four remaining deuterons (coupling constant < 0.01 mT).

4,5,7,8-Tetramethyl[2.2]paracyclophane-1,9-diene (3) and its 12,13,15,16-Tetradeterio Derivative 3-D₄. Fig. 6 presents the ESR spectra of 3^- at 178 (top) and 223 K (middle), as well as that of 3-D_4^- at 178 K (bottom). Their hyperfine pattern consists of nine components due to the major coupling constants of 0.560 ± 0.005 and 0.325 ± 0.005 mT, each for a pair of equivalent protons. In the spectra of 3^- , these components are very

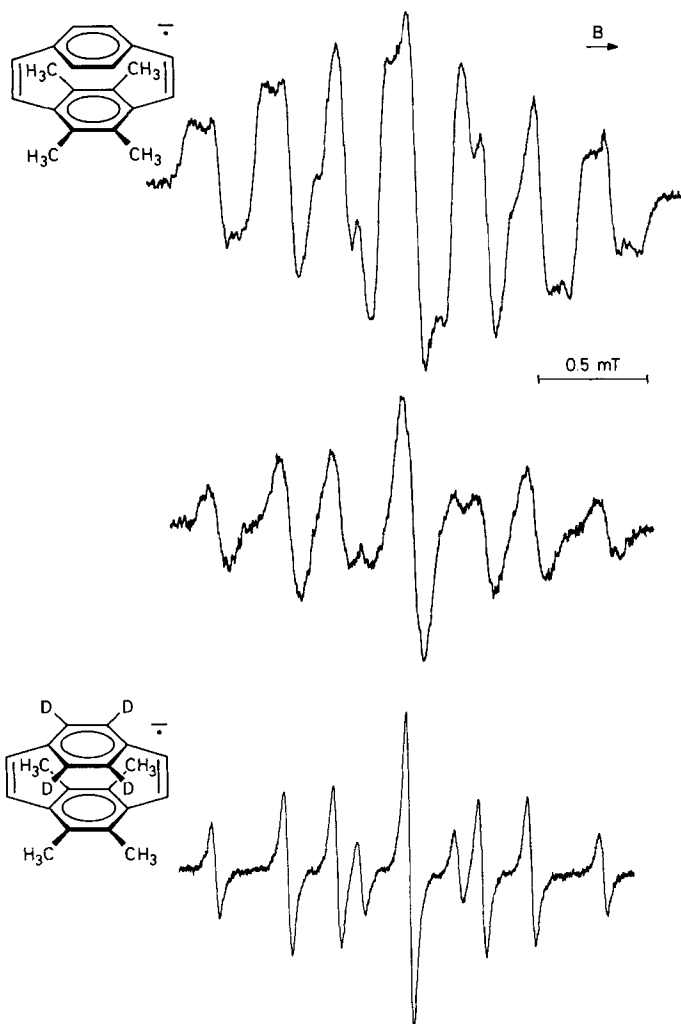


Fig. 6. Top and middle: *ESR spectra of the radical anion of 3*. Solvent: DME; counterion: K^+ ; temp. 178 (top) and 223 K (middle). Bottom: *ESR spectrum of the radical anion of 3-D₄*. Solvent: DME; counterion: K^+ ; temp.: 178 K.

broad and their widths and shapes strongly depend on the temperature. On passing to 3-D_4^- , the nine components narrow and their temperature dependence is substantially reduced. These findings indicate that the strong temperature dependence observed for 3^- arises from the unresolved hyperfine interaction with the four protons which are replaced by deuterons in 3-D_4^- . By analogy with 2^- and 2-D_6^- , it is assumed that the four protons are pairwise equivalent and that the two pairs are involved in an exchange process; their coupling constants have been estimated to lie in the range of 0.05 to 0.10 mT. A detailed analysis, like the one performed for 2^- and 2-D_6^- , was not practical in view of the poor resolution of the spectra. The unresolved hyperfine splittings from the 12 methyl protons in 3^- and 3-D_4^- and the four deuterons in 3-D_4^- must be smaller than 0.02 mT. The g value of the radical anions 2^- , 2-D_6^- , 3^- and 3-D_4^- is 2.0027 ± 0.0001 .

Discussion. – *Assignments of the Coupling Constants.* Since the two four-proton coupling constants of $(\pm)0.046$ and $(\mp)0.020$ mT, observed for the radical anion of **2**, average in the fast exchange limit to the eight-proton value of $(\pm)0.013$ mT, their overall assignment to the aromatic protons at the two benzene rings (4,5,7,8,12,13,15,16-positions) is straight-forward. The by far largest coupling constant of 0.422 mT, which is not affected by exchange, must, therefore, be assigned to the four olefinic protons at the two bridging double bonds of **2**⁻ (1,2,9,10-positions). The finding that these protons are throughout equivalent rules out the non-equivalence of the two benzene rings. This means that the eight aromatic protons do not separate into two sets of four in such a way that each set belongs to a different ring. On the contrary, *the four equivalent protons in each set must be distributed evenly over both benzene rings, each of them thus bearing two pairs of equivalent protons.*

The assignments made above for the coupling constants of the protons in **2**⁻ are fully confirmed by the hyperfine data for the radical anion of **2-D**₆. Since the hyperfine splittings from the four deuterons, replacing the four aromatic protons at one benzene ring (12,13,15,16-positions), are unresolved, the effect of the exchange on the coupling constants (0.046 and 0.020 mT) is observed only for the two pairs of protons at the undeuterated ring (4,5,7,8-positions). Also, as anticipated, both the two olefinic protons (2,9-positions) and the two olefinic deuterons (1,10-positions) are not involved in the exchange. It is noteworthy that the coupling constant of 0.060 mT, found for these deuterons, is markedly smaller than the expected value of $0.422 \text{ mT} \cdot 0.1535 = 0.065 \text{ mT}$.

The coupling constant of 0.46 mT, observed for ¹³C isotopes in four equivalent sites of **2**⁻ cannot be unambiguously assigned by experiment. However, guided by an MO model of **2**⁻ (see below), one favours the assignment of this value to the ¹³C-nuclei in the four bridged benzene C-atoms bearing the highest spin population (3,6,11,14-positions). Such an assignment is also in accord with the experimental finding that the observed ¹³C-coupling constant is not affected by the exchange process.

Assignments of the two largest coupling constants of 0.560 and 0.325 mT to the two pairs of equivalent olefinic protons in the radical anion of **3** follow unequivocally from a comparison of the hyperfine data for **3**⁻ and the radical anion of **3-D**₄. It is reasonable to assign the larger value (0.560 mT) to the protons adjacent to the non-methylated benzene ring (1,10-positions), thus leaving the smaller one (0.325 mT) for the protons neighbouring the tetramethyl-substituted ring (2,9-positions). These assignments are justified by the general tendency of the spin distribution in the radical anions to favour the π -system substituted by fewer alkyl groups (see, e.g. [9]). As expected, the mean of the two coupling constants (0.443 mT) is rather close to the corresponding value (0.422 mT) of the four equivalent olefinic protons in **2**⁻.

An uncertainty still remains with respect to the assignments of the two four-proton coupling constants (0.046 and 0.020 mT) to specific sets of aromatic protons in **2**⁻. It has been shown above that the four equivalent protons of either set are positioned at both benzene rings, so that each ring bears two pairs of equivalent protons. Obviously, this condition can be fulfilled by several conformations of different symmetry which will be considered in the next section.

Symmetry of the Radical Anion of [2.2]Paracyclophane-1,9-diene (2). As mentioned in the Introduction, an X-ray analysis of **2** [2] is consistent with D_{2h} molecular symmetry. The x-, y-, and z-directions of three two-fold axes in this point group are defined in Fig. 7; they

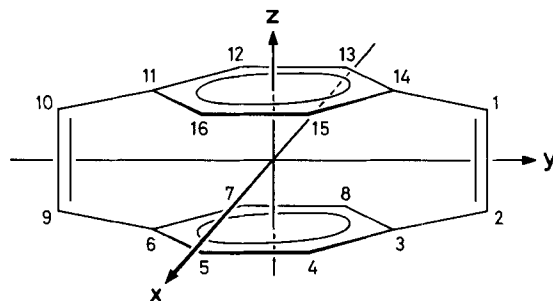


Fig. 7. Directions x , y and z , of the two-fold rotational axes for $\mathbf{2}^-$ in D_{2h} symmetry

also hold for $\mathbf{1}^-$ in the same point group. Prior to discussing the symmetry of the radical anion $\mathbf{2}^-$, it is appropriate to recall the corresponding results for $\mathbf{1}^-$. Lowering of the symmetry from D_{2h} to C_{2v} has been found for $\mathbf{1}^-$ as a consequence of the strong association with the positively charged counterion [15]. An ESR study of the radical anion of 1,1,10,10,12,13,15,16-octadeuterio derivative $\mathbf{1-D}_8$ [7] has shown that the counterion K^+ is situated on the z -axis above or below one of the benzene rings. The tightness of the ion pair and therewith the appearance of the ESR spectrum of $\mathbf{1}^-$ are very sensitive to the nature of the solvent and the counterion. Thus, replacing THF by a medium of higher solvating power, such as DME with a slight admixture of HMPT [15], or substituting K^+ by a smaller cation, such as Li^+ (through an excess of dissolved LiCl) [20], yields a loosely associated radical anion $\mathbf{1}^-$, the ESR spectrum of which exhibits the full symmetry D_{2h} . On the other hand, raising the temperature tightens the ion pair, because it leads to a decrease in the dielectric constant of the solvent.

None of these findings come true for $\mathbf{2}^-$: in contrast to $\mathbf{1}^-$, the ESR spectra of $\mathbf{2}^-$ are not sensitive to changes in the solvent and the counterion, and raising the temperature has an effect opposite to that expected for the strengthening of the association with the counterion. Ion pairing can thus be ruled out as the phenomenon responsible for the symmetry lowering in $\mathbf{2}^-$. An additional argument against such a role of the ion pairing for $\mathbf{2}^-$ is the equivalence of the four olefinic protons which would require that the counterion should be situated on the x -axis in the front or in the back of the benzene decks (Fig. 7). A structure of this type for the ion pair is highly improbable considering the distribution of the negative charge in $\mathbf{2}^-$, as indicated by the shape of the singly occupied orbital (see below).

In the absence of a substantial effect resulting from ion pairing, the lowering of the symmetry in $\mathbf{2}^-$ must be due to distortions of the C-framework. The temperature dependence of the ESR spectrum of $\mathbf{2}^-$ points to a double minimum energy profile with a barrier of 33 kJ/mol. Whereas the transition state is characterized by an undistorted structure of D_{2h} symmetry, the two energy minima correspond to a pair of equivalent conformations belonging to the point group D_2 , C_{2h} or C_{2v} . Fig. 8 depicts one conformation for each pair. These conformations, denoted by their symmetry, arise from the following displacements of the two benzene decks in opposite directions: D_2 : twisting about the z -axis; C_{2h} : gliding in parallel planes and in the direction of the x -axis; C_{2v} : rotating about the y -axis. Also indicated in Fig. 8 are the two sets of four aromatic protons which remain equivalent in the particular conformation.

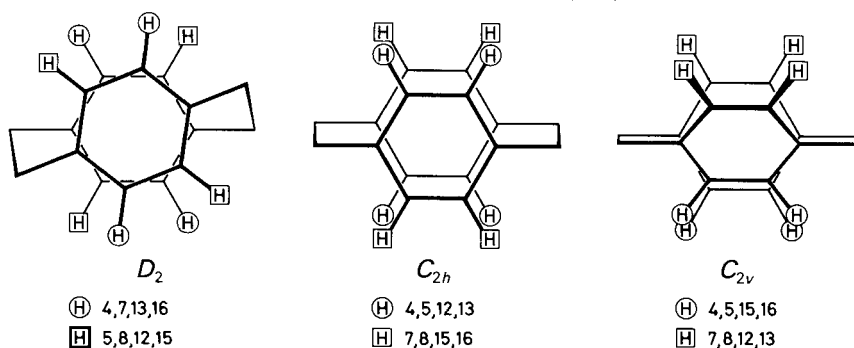


Fig. 8. D_2 , C_{2h} and C_{2v} conformations of **2**. ⊙ and ⊠ mark the two sets of four equivalent aromatic protons.

A C_{2v} conformation is the least probable, since it requires a close approach of the benzene rings on one 'side' of the radical anion. Of the two conformations D_2 and C_{2h} , the former is considered as the more probable, because distortions from D_{2h} to D_2 are strongly suggested by two independent studies of solid **1**. In a reinvestigation of the structure of **1** by X-ray crystallography [1b], the large apparent anisotropy of the atomic motion has been rationalized by a model in which each molecule is statistically disordered by a twist of the two benzene rings in opposite directions about the vertical axis. The half-twist angle was estimated as *ca.* 3° . The resulting two equivalent conformations, which correspond to those denoted D_2 for **2**⁻ (Fig. 8), must rapidly interconvert at room temperature, so that the molecule exhibits an effective D_{2h} symmetry. Another recent piece of evidence comes from a low-temperature ENDOR study of dibenzene vanadium diluted in crystals of **1** [21]. The results of this study point to a reduction of the site symmetry from D_{2h} to D_2 , which means that the two benzene rings in **1** are twisted in a way analogous to that leading to the D_2 conformation in **2**⁻ (Fig. 8). Surprisingly, such distortions were not considered in the X-ray analysis of the diene **2** [2], performed at ambient temperature 20 years ago. In this respect, it would be interesting to reinvestigate the crystallographic structure of **2**, preferably at various temperatures.

MO Model. Comparison of the coupling constants for the radical anions of **1** (0.297 for the eight aromatic and 0.103 mT for the eight methylene protons) [15] and **2** (0.013 for the eight aromatic and 0.422 mT for the four olefinic protons) indicates essential differences

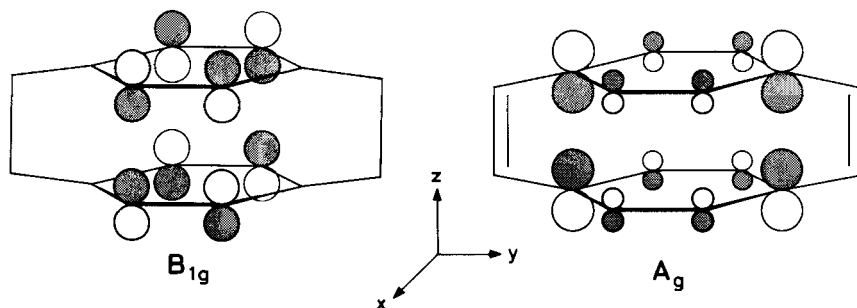


Fig. 9. Singly occupied orbitals in the radical anions of **1** and **2** as combinations of benzene-LUMO's in D_{2h} symmetry

in the spin distribution. Whereas the singly occupied orbital of $\mathbf{1}^-$ is usually regarded as a B_{1g} -combination of the two 'antisymmetric' benzene-LUMO's [15] [22], the corresponding orbital of $\mathbf{2}^-$ in D_{2h} symmetry is best represented as an A_g -combination of the two 'symmetric' ones (*Fig. 9*), with the bulk of the spin population located at the four bridged π -centres (3,6,11,14-positions). Since, in the undistorted radical anion $\mathbf{2}^-$ of D_{2h} symmetry, the π -systems of the double bonds do not conjugate with those of the benzene rings, the coupling constant ($a_{\text{H1},2,9,10}$) of an olefinic proton in this geometry is due to a hyperconjugative interaction between the pertinent C–H σ -orbital and the large π -spin population ($\rho_{3,6,11,14}$) at the adjacent bridged centre. The relevant relationship is [23]

$$a_{\text{H1},2,9,10} = B \rho_{3,6,11,14} \cos^2\theta \quad (1)$$

where θ is the dihedral angle between the directions of the C–H bond and the $2p_z$ -axis at the π -centre; for $\mathbf{2}^-$ in D_{2h} symmetry, $\theta = 0$. Taking +4.0 to +4.5 mT as the proportionality factor B for radical anions [24] and $\frac{1}{2} \cdot \frac{1}{3} = \frac{1}{6}$ (*i.e.*, half the squared LCAO coefficient of the 'symmetric' benzene-LUMO) as $\rho_{3,6,11,14}$, one estimates $a_{\text{H1},2,9,10}$ as +0.7 mT which is markedly larger than the observed value (0.422 mT). Agreement between theory and experiment is, however, greatly improved when deviations of the C-framework from D_{2h} symmetry are accounted for. The $a_{\text{H1},2,9,10}$ value, as calculated by *Eqn. 1*, is then considerably reduced not only by an increase in the angle θ but also by a decrease in the π -spin population $\rho_{3,6,11,14}$ through an induced conjugation with the π -systems of the double bonds. In addition, since this conjugation leads to a build-up of π -spin population ($\rho_{1,2,9,10}$) at the olefinic C-atoms, there will be a second contribution to $a_{\text{H1},2,9,10}$ due to the π - σ polarization in the respective C–H bond. This contribution is expressed by the *McConnell* relationship [25]

$$a_{\text{H1},2,9,10} = Q \rho_{1,2,9,10} \quad (2)$$

in which the proportionality factor Q has usually a value of -2.2 to -2.7 mT for radical anions [26]. Since $\rho_{1,2,9,10}$ is expected to be positive, the contribution to $a_{\text{H1},2,9,10}$ resulting from *Eqn. 2* should be negative and thus it should also reduce the positive value of this coupling constant as obtained by *Eqn. 1*.

The interpretation presented above in terms of a simple MO model is supported by calculations in the framework of the INDO approximation [27]. In these calculations, use was made of the atomic coordinates as determined by the X-ray analysis of $\mathbf{2}$ in D_{2h} symmetry [2], except for the underestimated C–H bond lengths (95–103 pm) which were given a more realistic value of 108 pm. The spin distribution in $\mathbf{2}^-$ yielded by the INDO approximation is, on the whole, consistent with the representation of the singly occupied orbital as an A_g -combination of the two 'symmetric' benzene-LUMO's (*Fig. 9*). Also, $a_{\text{H1},2,9,10}$ is predicted to be by far the most prominent proton-coupling constant, albeit its INDO value (+2.1 mT) is by a factor 3 in excess of that (+0.7 mT) obtained by means of *Eqn. 1*. Such a discrepancy is frequently encountered with INDO calculations involving hyperconjugative interactions [28]. The INDO value of $a_{\text{H1},2,9,10}$ markedly decreases when the symmetry of $\mathbf{2}^-$ is lowered from D_{2h} to D_2 by twisting the benzene ring about the z-axis. This result is demonstrated by *Fig. 10*, in which the coupling constant $a_{\text{H1},2,9,10}$ is plotted *vs.* the half-twist angle φ . In the INDO approximation, an angle φ of *ca.* 8° is required to arrive at the observed coupling constant of 0.422 mT. However, if the INDO

value of $a_{H_{1,2,9,10}}$ is scaled down by a factor of 3, twisting by *ca.* 5° should be sufficient to achieve an agreement between theory and experiment (*Fig. 10*).

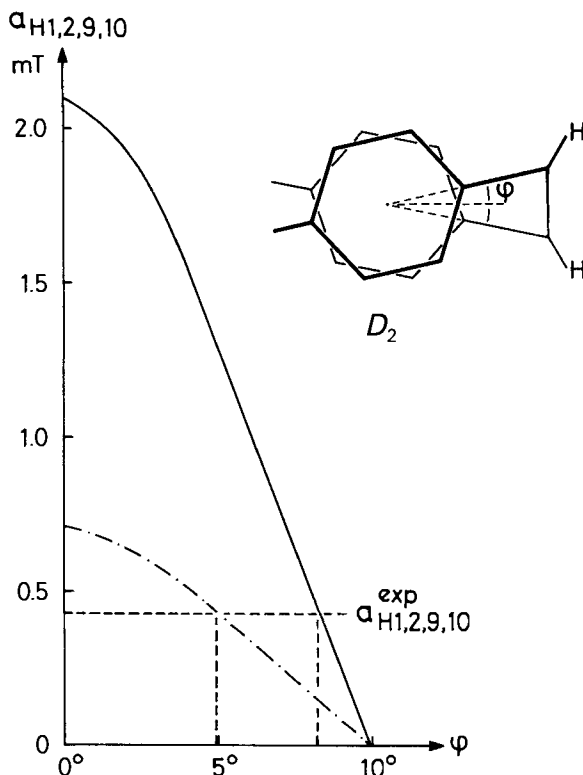


Fig. 10. Coupling constant, $a_{H_{1,2,9,10}}$, of the four equivalent olefinic protons in the radical anion of **2** as a function of the half-twist angle ϕ . — Value calculated in the INDO approximation; - - - the INDO value scaled down by the factor 3.

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