262. The Radical Anions of [2.2.2.2]Paracyclophane-1,9,17,25-tetraene and Some of its Heteroaromatic Analogues

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Summary

The radical anions of [2.2.2.2]paracyclophane-1,9,17,25-tetraene (I), [2](2,5)-furano[2]paracyclo[2](2,5)furano[2]paracyclophane-1,8,16,23-tetraene (II), [2]-(2,5)thiopheno[2]paracyclo[2](2,5)thiopheno[2]paracyclophane-1,8,16,23-tetraene (III) and [2.2.2.2](2,5)thiophenophane-1,8,15,22-tetraene (IV) have been studied by ESR. and ENDOR. spectroscopy. The assignment of the proton coupling constants, a_{H_μ}, is to a large extent based on investigations of deuteriated derivatives. These investigations impressively demonstrate the potential of ENDOR. spectroscopy as an analytical tool. The *Arrhenius* activation energies, E_a, for the rotation of phenylene fragments about the bonds linking them with the ethylenic parts in $I^{\ominus\cdot}$ and $II^{\ominus\cdot}$ are 36 ± 6 and 28 ± 4 kJ/mol, respectively. The value a_{H_μ} of the olefinic protons in $I^{\ominus\cdot}$ appears substantially smaller than expected for the corresponding planar radical anion. The hyperfine data for $II^{\ominus\cdot}$, $III^{\ominus\cdot}$ and $IV^{\ominus\cdot}$ are consistent with the conformations which should minimize the deviations of the macrocyclic π-systems from planarity. In the case of $II^{\ominus\cdot}$, tight ion pairs are formed by the radical anion and its counter-ion, $K^{\oplus}$, in DME, owing to the strong association of the alkali metal cation with one of the furan moieties. An analogous interaction of $K^{\oplus}$ with a thiophene moiety in $III^{\ominus\cdot}$ must be weaker, since no effects of ion pairing on the ESR. and ENDOR. spectra have been observed for this radical anion.

Introduction. - [2.2.2.2]Paracyclophane-1,9,17,25-tetraene (I), [2](2,5)furano-[2]paracyclo[2](2,5)furano[2]paracyclophane-1,8,16,23-tetraene (II), [2](2,5)thiopheno[2]paracyclo[2](2,5)thiopheno[2]paracyclophane-1,8,16,23-tetraene (III) and [2.2.2.2](2,5)thiophenophane-1,8,15,22-tetraene (IV) have recently been synthesized using the *Wittig* reaction [1-3].

The structure and conformation of the 4 macrocyclic π-systems, I to IV, which may be regarded as derivatives of [24]annulene, were studied by UV. and ^{1}H-NMR.

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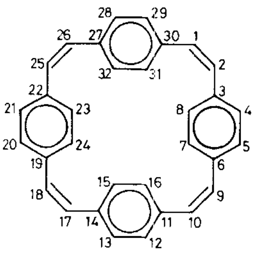
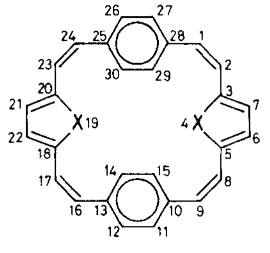
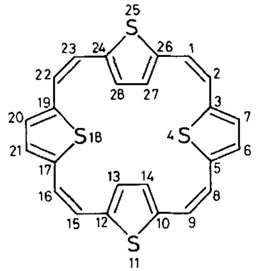


I



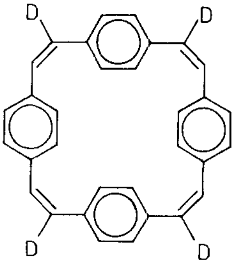
II, X = O

III, X = S

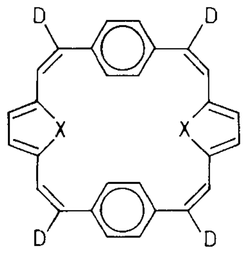


IV

spectroscopy [1–3] and, in the case of compound I, also by X-ray crystallography [4]. The formulae II, III and IV represent the conformations which are compatible with the results of these studies and, according to recent molecular mechanics calculations [5], should be the preferred ones if the cyclic π-systems tend towards planarity. For II and III, such conformations imply that the 2 heteroatoms lie inwards; these are considered to be more probable than those proposed originally [2]. In the present paper the available information is complemented by ESR. and ENDOR. investigations performed on the corresponding radical anions, $I^{\ominus\cdot}$ to $IV^{\ominus\cdot}$, as well as on their deuterio derivatives, I-1,10,17,26-$D_4^{\ominus\cdot}$ (I-$D_4^{\ominus\cdot}$), II-1,9,16,24-$D_4^{\ominus\cdot}$ (II-$D_4^{\ominus\cdot}$), III-1,9,16,24-$D_4^{\ominus\cdot}$ (III-$D_4^{\ominus\cdot}$) and III-11,12,14,15,26,27,29,30-$D_8^{\ominus\cdot}$ (III-$D_8^{\ominus\cdot}$).

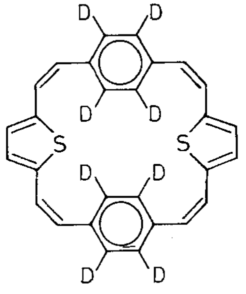


I-D_4



II-D_4, X = O

III-D_4, X = S

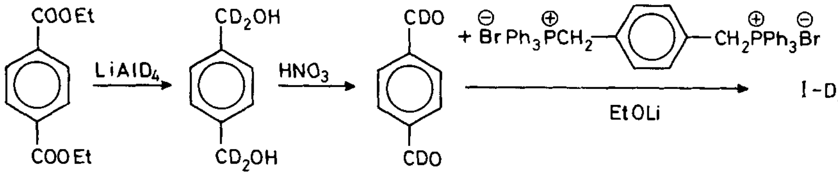


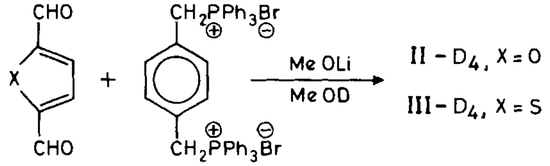
III-D_8

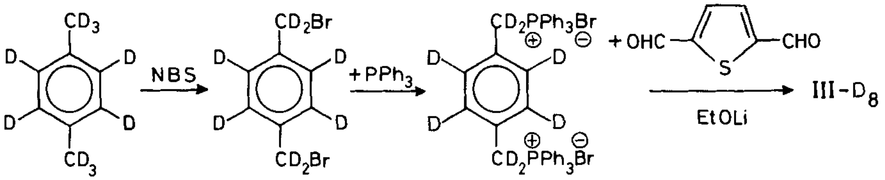
Experimental Part. – The syntheses of [2.2.2.2]paracyclophane-tetraene (I), [2](2,5)furano[2]paracyclo[2](2,5)furano[2]paracyclophane-tetraene (II), [2](2,5)thiopheno[2]paracyclo[2](2,5)thiopheno[2]-paracyclophane-tetraene (III) and [2.2.2.2](2,5)thiophenophane-tetraene (IV) have been described (I [1], II [2], III [2] and IV [3]). Their deuterio derivatives I-D_4, II-D_4, III-D_4 and III-D_8 were prepared by modifying these syntheses as indicated below.

The isotopic purities of I-D_4, II-D_4, III-D_4 and III-D_8 (^{1}H-NMR.) were 95, 70, 50 and 100 ± 5% respectively.

The radical anions $I^{\ominus\cdot}$ to $IV^{\ominus\cdot}$ and I-$D_4^{\ominus\cdot}$ to III-$D_8^{\ominus\cdot}$ were produced by reaction of the corresponding neutral compounds with potassium in 1,2-dimethoxyethane (DME). In a few experiments, DME was replaced by DME/hexamethylphosphoric triamide (HMPA) (2:1). The radical anions $I^{\ominus\cdot}$, I-$D_4^{\ominus\cdot}$ and $IV^{\ominus\cdot}$ exhibited sufficient stability to be conveniently studied by ESR. spectroscopy up to 333 K, while $II^{\ominus\cdot}$ and $III^{\ominus\cdot}$, and their deuterio derivatives decayed appreciably above 293 K. The ENDOR.







spectra were obtained at low temperatures (<213 K) with *Varian*-1700-system coupled to *Varian*-E-9-instrument.

The g-factors of $\mathrm{I}^{\dot{\ominus}}$, $\mathrm{II}^{\dot{\ominus}}$, $\mathrm{III}^{\dot{\ominus}}$ and $\mathrm{IV}^{\dot{\ominus}}$ in DME at 273 K (counter-ion $\mathrm{K}^{\oplus}$) are 2.0027, 2.0026, 2.0038 and 2.0023 ± 0.0001, respectively.

Results and Discussion. - *[2.2.2.2]Paracyclophane-1,9,17,25-tetraene (I). Figure 1* shows the ESR. spectra of the radical anion $\mathrm{I}^{\dot{\ominus}}$ in DME at 323, 263 and 203 K. Analysis of the hyperfine pattern at 203 K, assisted by corresponding ENDOR. signals *(Fig. 1)*, yields three coupling constants a_{H_μ}, each (0.050, 0.034 and 0.030 mT) for 8 equivalent protons. Comparison of the intensities of these signals with those

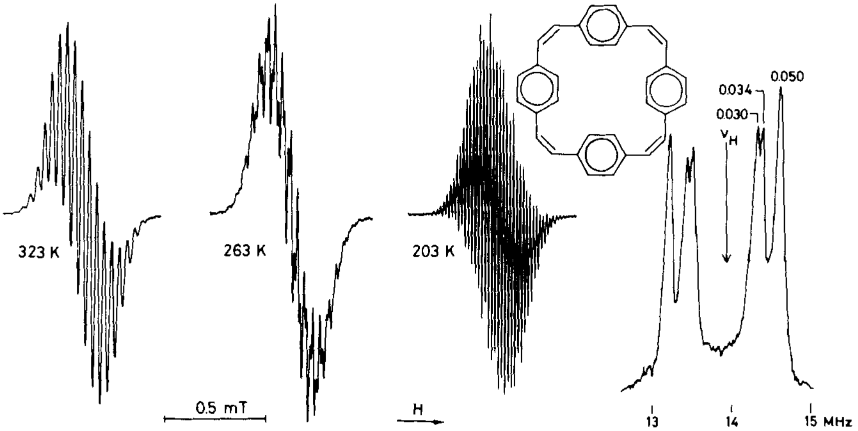


Fig. 1. *ESR. and ENDOR. spectra of the radical anion $I^{\dot{\ominus}}$.* Solvent: DME; counter-ion: $\mathrm{K}^{\oplus}$; temperature as indicated (ESR.) and 203 K (ENDOR.). The numbers above ENDOR. signals refer to the coupling constants a_{H_μ} in mT. ν_{H} = frequency of the free proton.

observed for I-$D_4^{\ominus}$ requires that the middle value a_{H_μ} (0.034 mT) should be assigned to the olefinic protons (positions $\mu = 1,2,9,10,17,18,25,26$), leaving the 2 remaining ones (0.050 and 0.030 mT) for the phenylene protons. Clearly, at 203 K, the rotation of the phenylene fragments about the bonds linking them to the ethylenic parts of the molecule is slow on the hyperfine time-scale, so that the inner ($\mu = 7,8,15,16,23,24,31,32$) and outer protons ($\mu = 4,5,12,13,20,21,28,29$) of these fragments are non-equivalent. At higher temperatures, the rate of rotation becomes comparable to the difference Δa_{H_μ} (*ca.* $10^6 s^{-1}$ in frequency units) of the relevant coupling constants, and specific line-broadening occurs (*Fig. 1*, 263 K). Upon further raising the temperature, a new hyperfine pattern emerges, in which the 16 phenylene protons display an averaged coupling constant a_{H_μ} of 0.040 mT (*Fig. 1*, 323 K)[3]). Such a pattern is diagnostic of the rapid rotation on the hyperfine time-scale.

Use of the two-jump model with the computer program developed by *Heinzer* [6] yields the *Arrhenius* activation energy

$$E_a = 36 \pm 6 \text{ kJ/mol}$$

for the rotation. This value should essentially hold for analogous motion in the neutral compound I as well, although, according to the HMO. bond orders $p_{\mu\nu}$, the linkages between the aromatic and the olefinic parts of the π-system ($\mu - \nu = 2$-3, 6-9, 10-11, 14-17, 18-19, 22-25, 26-27, 30-1) are predicted to acquire extra double bond character on going from I to $I^{\ominus}$. The height of the barrier to rotation would account for the fact that the 16 phenylene protons in I remain equivalent on the time-scale of chemical shift (*ca.* 100 s^{-1}) down to 213 K [5].

The π-spin populations ρ_μ calculated by means of the HMO. model and the *McLachlan* procedure ($\lambda = 1.0$) [7] depend only slightly on the angle of twist, θ, about the bonds $\mu - \nu$ linking the phenylene with the ethylenic fragments if the parameter $\beta_{\mu\nu}$ is set equal to $\beta \cos\theta$. Thus, on passing from $\theta = 0$ to 60°, the values ρ_μ change only from 0.017 to 0.011 at the proton-bearing centres μ of the phenylenes, and from 0.059 to 0.061 at the olefinic centres. Using the *McConnell* equation [8]

$$a_{H_\mu} = Q\rho_\mu \quad \text{with} \quad Q = -2.5 \text{ mT}$$

these π-spin populations ρ_μ are converted into the coupling constants $a_{H_\mu} = -0.043$ to -0.028 and -0.148 to -0.153 mT, of the phenylene and olefinic protons, respectively.

The theoretical values $|a_{H_\mu}|$ are in good agreement with the experimental data for the phenylene protons (0.050 and 0.030 mT), but not for the olefinic protons, where the calculated numbers $|a_{H_\mu}|$ considerably exceed the observed coupling constant (0.034 mT). An analogous discrepancy has been reported for the radical anion of *cis*-stilbene (V) [9], the π-system of which is contained in $I^{\ominus}$. For

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[3]) Since the coupling constant of the 16 phenylene protons (0.040 mT) is only slightly different from that of the 8 olefinic protons (0.034 mT), the spectrum of $I^{\ominus}$ at 323 K seems to be due to 24 nearly equivalent protons with a hyperfine splitting of 0.037 mT.

$\mathrm{V}^{\ominus\cdot}$, too, the coupling constants of the aromatic protons are in accord with the expected values, whereas those of the olefinic protons appear to be strongly reduced relative to such values. The latter finding has been rationalized [9] by deviations from planarity which are well documented by an electron diffraction study of V [10]. These deviations lead to a break-down of the $\pi-\sigma$ separation and thus to a direct spin transfer from the carbon $2p_z$-AO's into the 1s-AO's of the olefinic hydrogens. Since the contributions to the proton coupling constants by such $\pi-\sigma$ transfers have a positive sign, they partially cancel the negative values arising from $\pi-\sigma$ spin polarization [11]. This rationale should also apply to $\mathrm{I}^{\ominus\cdot}$. An X-ray crystallographic structure analysis of I indicates that the phenylene fragments are tilted by 27-40° towards the main molecular plane [4], and even larger deviations from planarity can be anticipated for I and $\mathrm{I}^{\ominus\cdot}$ in solution.

[2](2,5)Furano[2]paracyclo[2](2,5)furano[2]paracyclophane-1,8,16,23-tetraene (II). Figure 2 presents the ESR. spectrum of the radical anion $\mathrm{II}^{\ominus\cdot}$ in DME at 263 K, along with the ENDOR. spectra taken at 193 K in DME and DME/HMPA. Surprisingly, the proton ENDOR. signals of $\mathrm{II}^{\ominus\cdot}$ in DME point to at least 8 different coupling constants. A careful study yields 10 values a_{H_μ}, each (0.180, 0.099, 0.086, 0.068, 0.056, 0.051, 0.031, 0.027, 0.007 and < 0.003 mT) for 2 equivalent protons. When DME is replaced by DME/HMPA (2:1), the number of coupling constants a_{H_μ} is reduced to 5; their values are 0.105, 0.069, 0.052, 0.042 and 0.032 mT, each for 4 equivalent protons. The 2 sets of coupling constants, obtained for $\mathrm{II}^{\ominus\cdot}$ under different conditions, are

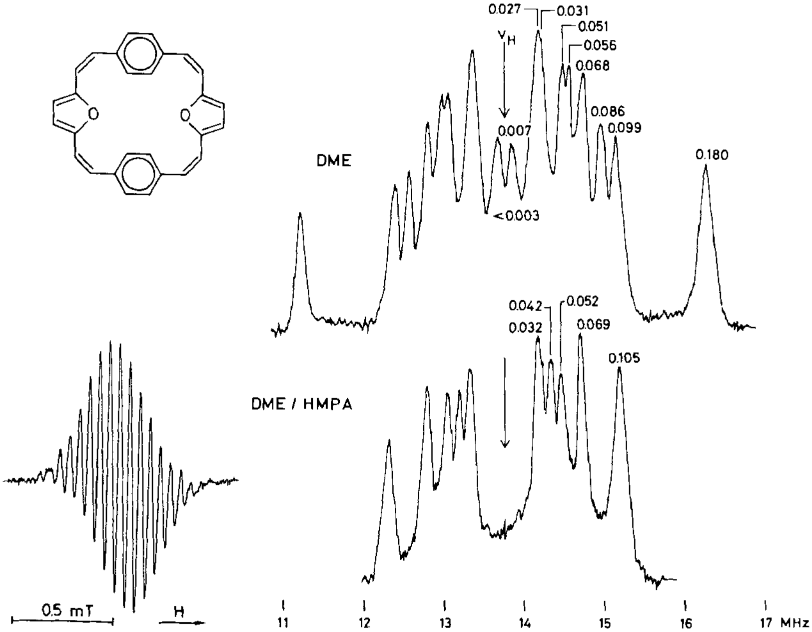


Fig. 2. *ESR. and ENDOR. spectra of the radical anion $II^{\ominus\cdot}$*. Solvent as indicated; counter-ion: $K^{\oplus}$; temp.: 263 K (ESR.) and 193 K (ENDOR.). The numbers above ENDOR. signals refer to the coupling constants a_{H_μ} in mT. ν_H = frequency of the free proton.

Table. *Proton coupling constants,* a_{H_μ} in mT, *for the radical anions* $I^{\ominus\cdot}$ *to* $IV^{\ominus\cdot}$. Solvent: DME, if not otherwise noted; counter-ion: $K^{\oplus}$; temp. as indicated. Experimental error in a_{H_μ}: ±0.001 mT

	$\mathrm{I}^{\ominus\cdot}$			$\mathrm{II}^{\ominus\cdot}$				$\mathrm{III}^{\ominus\cdot}$	$\mathrm{IV}^{\ominus\cdot}$	
Temp.	μ	$a_{H\mu}$ 203 K	$a_{H\mu}$ 323 K	μ	$a_{H\mu}$ 193 K	$a_{H\mu}$[a] 193 K	$a_{H\mu}$[a] 263 K	$a_{H\mu}$ 193 K	μ	$a_{H\mu}$ 223 K
Phenylene	4, 5 7, 8 12,13 15,16 20,21 23,24 28,29 31,32	0.050 0.030	0.040	11,12 14,15	0.086 0.051	0.069	0.051	0.046		
				26,27 29,30	0.056 0.007	0.032		0.041		
Furan or Thiophene				6, 7 21,22	0.180 0.031	0.105	0.105	0.104	6, 7 13,14	0.085
									20,21 27,28	0.115
Ethylene	1, 2 9,10 17,18 25,26	0.034	0.034	1, 9 16,24	0.099 <0.003	0.052	0.052	0.089	1, 2 8, 9	0.058
				2, 8 17,23	0.068 0.027	0.042	0.042	0.058	15,16 22,23	0.034

[a] Solvent DME/HMPA.

compared in the *Table* which summarizes the hyperfine data for all 4 radical anions investigated in the present work. As is evident from this *Table*, the 10 two-proton values found with DME can be arranged in such a way that the average of every pair almost matches one of the 5 four-proton values observed with DME/HMPA. The assignments of 0.099 and <0.003 mT (DME), and of 0.052 mT (DME/HMPA) to the olefinic protons in the positions $\mu = 1, 9, 16, 24$ follow from the comparison of the ENDOR. spectra of $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{II\text{-}D_4}^{\ominus\cdot}$; those of 0.086, 0.056, 0.051 and 0.007 mT (DME), and of 0.069 and 0.032 mT (DME/HMPA) to the phenylene protons *(Table)* are justified by the temperature dependence of ESR. spectra dealt with below. The remaining coupling constants a_{H_μ} are assigned only tentatively.

The ESR. spectra of $\mathrm{II}^{\ominus\cdot}$, both in DME and DME/HMPA, are rather poorly resolved in the temperature range below 223 K where the corresponding ENDOR. spectra can be recorded. However, with the solvent DME/HMPA, the resolution improves upon raising the temperature, and at 263 K the spectrum shown in *Figure 2* is observed. Its hyperfine pattern reveals that 2 of the 5 four-proton coupling constants a_{H_μ}, 0.069 and 0.032 mT, which have been determined from the ENDOR. spectrum at 193 K, are now replaced by a splitting of 0.051 mT, due to 8 equivalent protons. Obviously, at higher temperatures, the rotation of the phenylene fragments about the bonds linking them to the ethylenic parts of $\mathrm{II}^{\ominus\cdot}$ ($\mu - \nu = 2\text{-}3, 5\text{-}8, 9\text{-}10, 13\text{-}16, 17\text{-}18, 20\text{-}23, 24\text{-}25, 28\text{-}1$) becomes rapid on the hyperfine time-scale (*ca.* $10^6 \mathrm{s}^{-1}$), and the coupling constants of the inner ($\mu = 14, 15, 29, 30$) and the outer protons ($\mu = 11, 12, 26, 27$) are averaged. This finding not only leads to the assignment of the 2 four-proton coupling constants a_{H_μ} found with DME/HMPA, but also enables assignment of the pertinent pairs of the two-proton values observed with DME (see above).

By a procedure analogous to that used in the case of $\mathrm{I}^{\ominus\cdot}$, one obtains the *Arrhenius* activation energy

$$E_a = 28 \pm 4 \text{ kJ/mol}$$

for the rotation of the phenylene fragments in $\mathrm{II}^{\ominus\cdot}$. This value suggests that the barrier to such a motion is lower in $\mathrm{II}^{\ominus\cdot}$ than in $\mathrm{I}^{\ominus\cdot}$ ($E_a = 36 \pm 6$ kJ/mol). It is consistent with the ^{1}H-NMR. spectrum of II in which the 8 phenylene protons appear as equivalent above 213 K [5].

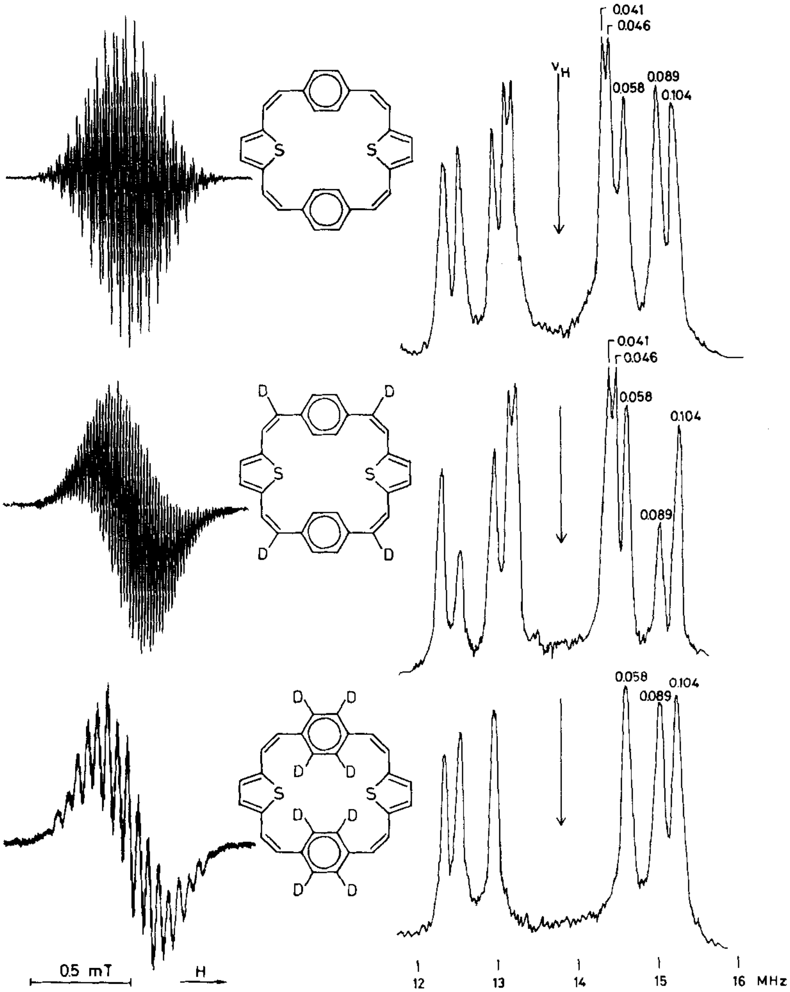


Fig. 3. *ESR. and ENDOR. spectra of the radical anions* $\mathit{III}^{\ominus\cdot}$ (top), $\mathit{III}\text{-}D_4^{\ominus\cdot}$ (middle) *and* $\mathit{III}\text{-}D_8^{\ominus\cdot}$ (bottom). Solvent: DME; counter-ion: $K^{\oplus}$; temp.: 193 K. The numbers above the ENDOR. signals refer to the coupling constants a_{H_μ} in mT. ν_H = frequency of the free proton.

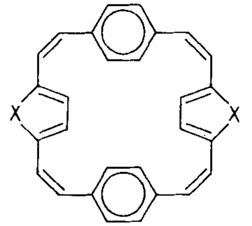
The strikingly different hyperfine data found for $\mathrm{II}^{\ominus\cdot}$ in DME and DME/HMPA by ENDOR. spectroscopy at 193 K - 10 coupling constants a_{H_μ} of 2 protons *vs.* 5 of 4 - indicate that in DME a tight ion pair is formed by the radical anion with its counter-ion $K^{\oplus}$. This ion pair, in which the cation presumably resides at one of the furan moieties, interconverts with its mirror image, whereby the cation migrates to an equivalent site at the second moiety. In DME, the interconversion is slow on the hyperfine time-scale. As a consequence the spectrum is characteristic of an individual ion pair, the symmetry of which is reduced relative to that of the unperturbed radical anion. The fact that addition of the polar solvent HMPA to DME effectively restores the full symmetry of the radical anion can be rationalized in terms of a loosening of the ion pairs, which renders their interconversion sufficiently rapid on the hyperfine time-scale. This interpretation is supported by the aforementioned finding that it is possible to reproduce the coupling constants a_{H_μ} for $\mathrm{II}^{\ominus\cdot}$ in DME/HMPA by the pair-wise averaging of the values observed with DME.

[2](2,5)Thiopheno[2]paracyclo[2](2,5)thiopheno[2]paracyclophane-1,8,16,23-tetraene (III). In contrast to $\mathrm{II}^{\ominus\cdot}$, the ESR. and ENDOR. spectra of the radical anion $\mathrm{III}^{\ominus\cdot}$, taken at 193 K, do not significantly differ in DME and DME/HMPA. These spectra shown in *Figure 3*, are analysed by means of 5 coupling constants a_{H_μ}, each (0.104, 0.089, 0.058, 0.046 and 0.041 mT) for a set of 4 equivalent protons. The identification of 0.089 mT with the coupling constant a_{H_μ} of one set of olefinic protons ($\mu = 1,9,16,24$), and of 0.046 and 0.041 mT with those of the 2 sets of phenylene protons ($\mu = 11,12,26,27$ and $14,15,29,30$) follows from the ENDOR. studies of the deuterio derivatives $\mathrm{III}\text{-}D_4^{\ominus\cdot}$ and $\mathrm{III}\text{-}D_8^{\ominus\cdot}$, respectively. The assignment of the 2 remaining values a_{H_μ} *(Table)* has not yet been confirmed by experiment.

For the sake of demonstration of the advantages offered by the ENDOR. technique, the ESR. and ENDOR. spectra of $\mathrm{III}\text{-}D_4^{\ominus\cdot}$ (*ca.* 50% deuteriation) and $\mathrm{III}\text{-}D_8^{\ominus\cdot}$ (almost 100% deuteriation) are reproduced in *Figure 3*, below the corresponding spectra of $\mathrm{III}^{\ominus\cdot}$. Whereas the ESR. spectra are very complex ($\mathrm{III}\text{-}D_4^{\ominus\cdot}$) or partially resolved ($\mathrm{III}\text{-}D_8^{\ominus\cdot}$), and their analysis is extremly tedious and highly unreliable, the ENDOR. spectra of the 2 radical anions are as simple as that of $\mathrm{III}^{\ominus\cdot}$, and the effect of deuteriation is conspicuous. Thus, on going from $\mathrm{III}^{\ominus\cdot}$ to $\mathrm{III}\text{-}D_4^{\ominus\cdot}$, a 50% decrease is found in the intensities of the signals pertaining to the coupling constant a_{H_μ} of 0.089 mT, so that this value has to be assigned to the 4 olefinic protons in the partially deuteriated positions $\mu = 1,9,16,24$. The passage from $\mathrm{III}^{\ominus\cdot}$ to $\mathrm{III}\text{-}D_8^{\ominus\cdot}$ is characterized by a total disappearance of the signals corresponding to the coupling constants 0.046 and 0.041 mT. These values must, therefore, belong to the 8 phenylene protons which have been replaced by deuterons.

The activation energy for the rotation of the phenylene fragments about the bonds linking them with the ethylenic parts in $\mathrm{III}^{\ominus\cdot}$ is expected to be similar to that found for $\mathrm{II}^{\ominus\cdot}$ (28 ± 4 kJ/mol). Its derivation from the temperature dependence of the ESR. spectra of $\mathrm{III}^{\ominus\cdot}$ is impeded by the small difference Δa_{H_μ} (0.005 mT) in the coupling constants of the inner and outer phenylene protons; this difference, which appears as a partial splitting of the pertinent ENDOR. signals at 193 K, cannot be resolved in the ESR. spectra.

The hyperfine data for $\mathrm{III}^{\ominus\cdot}$ in DME (5 coupling constants of 4 protons) indicate that, contrary to $\mathrm{II}^{\ominus\cdot}$ (10 values of 2), the ion pairs formed by $\mathrm{III}^{\ominus\cdot}$ and $K^{\oplus}$ interconvert rapidly on the hyperfine time-scale. This finding points to a looser structure of the ion pairs, which is readily interpreted by the less strong association of the counter-ion with the thiophene than with the furan moiety. On the other hand, the similarity in the hyperfine data for II$^{\overset{\ominus}{\cdot}}$ and III$^{\overset{\ominus}{\cdot}}$ in DME/HMPA suggests analogous conformations, at least under the conditions of loose ion pairing. These data are equally compatible with the conformations indicated in *Figures 2* and *3*, as well as with the alternative arrangements, IIa or IIIa, in which the 2 heteroatoms lie outwards.



IIa, X = O
IIIa, X = S

[2.2.2.2](2,5)Thiophenophane-1,8,15,22-tetraene (IV). From the ESR. and ENDOR. spectra of the radical anion IV$^{\overset{\ominus}{\cdot}}$ in DME at 223 K *(Fig. 4)* one derives 4 coupling constants a_{H_μ}, each (0.115, 0.085, 0.058 and 0.034 mT) for 4 equivalent protons. Their assignment *(Table)* is tentative, since no deuterio derivatives were available. As in the case of III$^{\overset{\ominus}{\cdot}}$, addition of HMPA to DME had a negligible effect on the spectra.

The hyperfine data for IV$^{\overset{\ominus}{\cdot}}$ are consistent with the sulfur atoms lying alternatively in- and outwards, which has been considered to be the preferred conformation of IV [3]. The relative stability of the radical anion allowed the temperature to be raised to 343 K, in the hope that conformational mobility of the molecule will affect the ESR. spectra. However, the observed unspecific line-broadening failed to be informative with respect to changes in conformation. It is noteworthy that 2 time-averaged signals, each for 8 equivalent protons, which have been found in the ^{1}H-NMR. spectrum of IV above 213 K [3], broaden considerably at 173 K [5], suggesting the approach of the coalescence temperature.

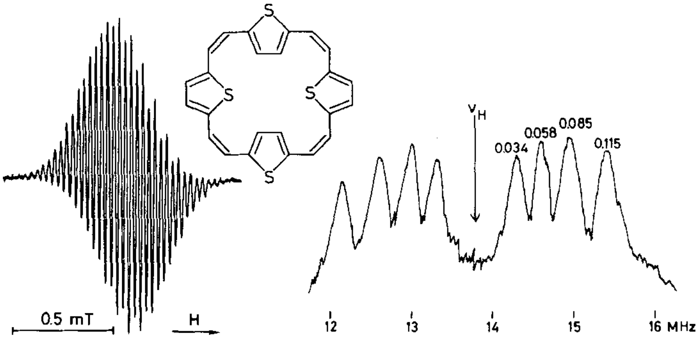


Fig. 4. *ESR. and ENDOR. spectra of the radical anion IV$^{\ominus}$.* Solvent: DME; counter-ion: K$^{\oplus}$; temp.: 223 K. The numbers above the ENDOR. signals refer to the coupling constants a_{H_μ} in mT. ν_H = frequency of the free proton.

Conclusion. - The present study of the macrocyclic radical anions, $I^{\ominus\cdot}$ to $IV^{\ominus\cdot}$ provides an instructive example of the potential and limits of magnetic resonance as a tool of choice in elucidation of structure and conformation. The ESR. spectra of such large radical anions are frequently complex or poorly resolved and defy reliable analysis, so that the ENDOR. technique is indispensible for unravelling the hyperfine pattern. This is particularly the case with deuterio derivatives, owing to an additional deuteron splitting and/or incomplete isotopic substitution. In contrast to ESR., the effect of deuteriation on the ENDOR. spectra consists merely in a disappearance or an intensity decrease of the pertinent proton signals, and the assignment of the coupling constants is made by a straightforward comparison of the spectra of the deuterio derivatives with that of the parent radical anion.

The use of an ENDOR. spectrometer and the availability of specifically deuteriated compounds can thus, in principle, afford the exact values and the assignment of the coupling constants. When these requirements are met, it is possible to derive structural information from the hyperfine data, despite the difficulties imposed by the size, non-planarity and conformational lability of the extended molecular framework.

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