188. π-Spin Distribution in the Radical Anion of Benzo[2.2]paracyclophane[1]) and its Relation to those in the Radical Anions of [2.2](1,4)Naphthalenophanes

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(7. VI. 77)

Summary

Radical anions of benzo[2.2]paracyclophane (V) and its 1,1,12,12,14,15,17,18-octadeuterio derivative (V-d_8) in three ethereal solvents (DME, THF and MTHF) and in the temperature range of −90 to −50° have been studied by ESR. and ENDOR. spectroscopy. The resulting hyperfine data provide a detailed picture of the π-spin distribution in $V\cdot^{\ominus}$ which is in full accord with expectation. In particular, it is noteworthy that the naphthalene moiety accommodates almost the entire π-spin population, as may be anticipated by the higher electron affinity of this π-system relative to benzene. The proton coupling constants for $V\cdot^{\ominus}$ have been compared with those values for the radical anions of *anti-* and *syn*-[2.2](1,4)-naphthalenophanes (II and III, respectively) which were obtained under conditions of low frequency electron transfer between the two equivalent naphthalene moieties. Such a comparison corroborates the interpretation of the results reported previously for $II\cdot^{\ominus}$ and $III\cdot^{\ominus}$.

Introduction. - In a recent paper [2], we reported briefly the proton hyperfine data for the radical anions of symmetric benzo derivatives of [2.2]paracyclophane (I), such as *anti-* and *syn-*[2.2](1,4)naphthalenophanes (II and III, respectively), and [2.2](9,10)anthracenophane (IV), in which the dimethylene bridges link two equivalent aromatic fragments.

The data for $II\cdot^{\ominus}$, $III\cdot^{\ominus}$ and $IV\cdot^{\ominus}$ furnish further experimental evidence that the frequency with which the unpaired electron is transferred from one aromatic moiety to the other is determined by the rate of migration of the counterion ($K^{\oplus}$) between two equivalent sites at each of the π-systems [3] [4]. This rate of migration, in turn, depends on the extent of association of the radical anion with its counterion. Since such an ion pairing becomes tighter with decreasing solvation of the cation, it is strengthened in the sequence 1,2-dimethoxyethane (DME) < tetrahydrofuran (THF) < 2-methyltetrahydrofuran (MTHF). Thus, in the two isomeric

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[1]) An alternative name for benzo[2.2]paracyclophane (V) is [2]paracyclo[2](1,4)naphthalenophane [1].

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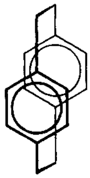
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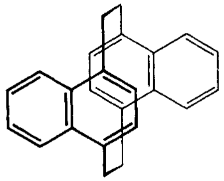
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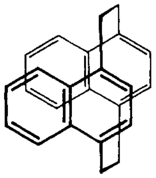
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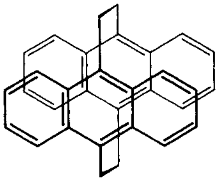
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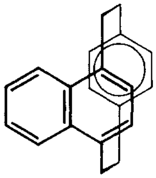
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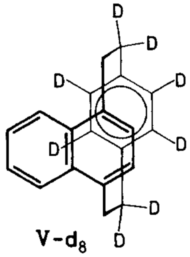


V-d_8

radical anions II$\cdot^{\ominus}$ and III$\cdot^{\ominus}$, the migration rate of the counterion and the transfer frequency of the unpaired electron are high on the hyperfine time-scale ($\sim 10^7$ s^{-1}) when DME or THF is used as the solvent; consequently, the π-spin populations appear to be evenly distributed between the two aromatic moieties. With MTHF, on the other hand, the two concomitant phenomena occur less frequently than $\sim 10^7$ s^{-1} so that the π-spin populations are found to a large extent on a single naphthalene π-system. The dramatic change in the hyperfine patterns upon replacement of DME (or THF) by MTHF as the solvent is illustrated by the ESR. spectra of II$\cdot^{\ominus}$ and III$\cdot^{\ominus}$ shown in *Fig. 1* and *2*. These spectra provide an additional opportunity for successful application of the ENDOR. spectroscopy to unravelling of complex ESR. splitting patterns. Without the benefit of this technique, the analysis of the hyperfine structures of II$\cdot^{\ominus}$ and III$\cdot^{\ominus}$ would be very tedious for the solvent DME or THF, and virtually impossible in the case of MTHF.

Table 1 lists the coupling constants, a_{H_μ}, which were determined from the positions of the proton ENDOR. signals at $-90°$ [2] and used for the computation of the ESR. derivative curves. As is evident from *Fig. 1* and *2*, an excellent agreement has thus been achieved between the simulated and observed spectra.

It is worthwhile to compare the π-spin distributions found for II$\cdot^{\ominus}$ and III$\cdot^{\ominus}$ in MTHF with that in the radical anion of benzo[2.2]paracyclophane (V) which contains two non-equivalent aromatic fragments. Since naphthalene has a substantially higher electron affinity than benzene, it should hold the bulk of the π-spin population in V$\cdot^{\ominus}$, irrespective of the solvent used. In the present paper we report on the ESR. and ENDOR. studies of V$\cdot^{\ominus}$; also investigated is the radical anion of the 1,1,12,12,14,15,17,18-octadeuterio derivative (V-d_8). The hyperfine data obtained therefrom are discussed, along with the corresponding values for II$\cdot^{\ominus}$ and III$\cdot^{\ominus}$.

Results. - The studies of V$\cdot^{\ominus}$ and V-$d_8\cdot^{\ominus}$, like those of II$\cdot^{\ominus}$ and III$\cdot^{\ominus}$, were performed with the three ethereal solvents, DME, THF and MTHF; the

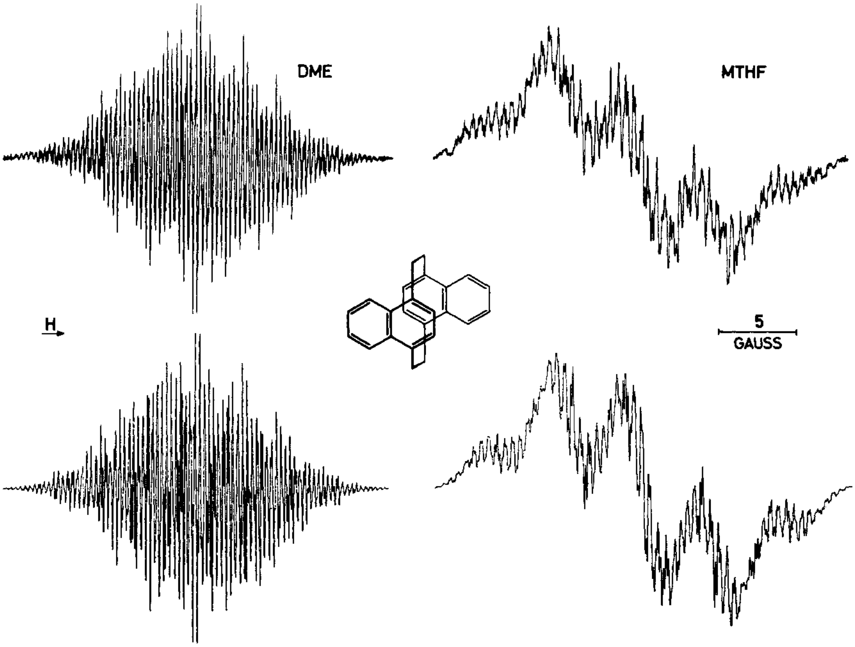
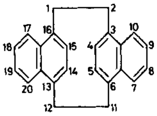
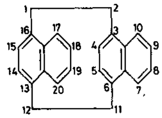


Fig. 1. *ESR. spectra of the radical anion* $II\cdot^{\ominus}$. Top: experimental spectra. Solvent: DME (left) or MTHF (right); Counterion: $K^{\oplus}$; Temp.: −90°. Bottom: computer simulated spectra. Coupling constants as given in *Table 1*. Line-shape: Lorentzian; line-width: 0.06 (left) or 0.11 Gauss (right)

Table 1. *Proton coupling constants* a_{H_μ} (in Gauss = 10^{-4} Tesla) *for the radical anions* $II\cdot\ominus$ *and* $III\cdot\ominus$ (Counterion: K⊕; Temp.: −90°)

	 II$^{\ominus}$ anti				 III$^{\ominus}$ syn			
solvent:	DME^{a})	THF^{a})	MTHF^{b})		DME^{a})	THF^{a})	MTHF^{b})	
μ = 2,11 1,12	2.13^{c})	2.11^{c})	3.80^{c}) 0.42^{c})	2.11^{d})	1.70^{c})	1.70^{c})	2.32^{c}) 0.90^{c})	1.61^{d})
2,11 1,12	0.28^{c})	0.26^{c})	0.46^{c}) 0.04^{c})	0.25^{d})	0.35^{c})	0.36^{c})	0.50^{c}) 0.16^{c})	0.33^{d})
4,5 14,15	0.60	0.57	0.95 0.16	0.56^{d})	1.00	1.00	1.43 0.55	0.99^{d})
7,10 17,20	3.00	3.02	4.48 1.09	2.79^{d})	2.42	2.39	3.64 1.06	2.35^{d})
8,9 18,19	0.98	0.97	1.59 0.35	0.97^{d})	1.32	1.27	1.91 0.60	1.26^{d})

^{a}) Each coupling constant for four equivalent protons. ^{b}) Each coupling constant for two equivalent protons. ^{c}) Coupling constant of methylene protons. ^{d}) Average value.

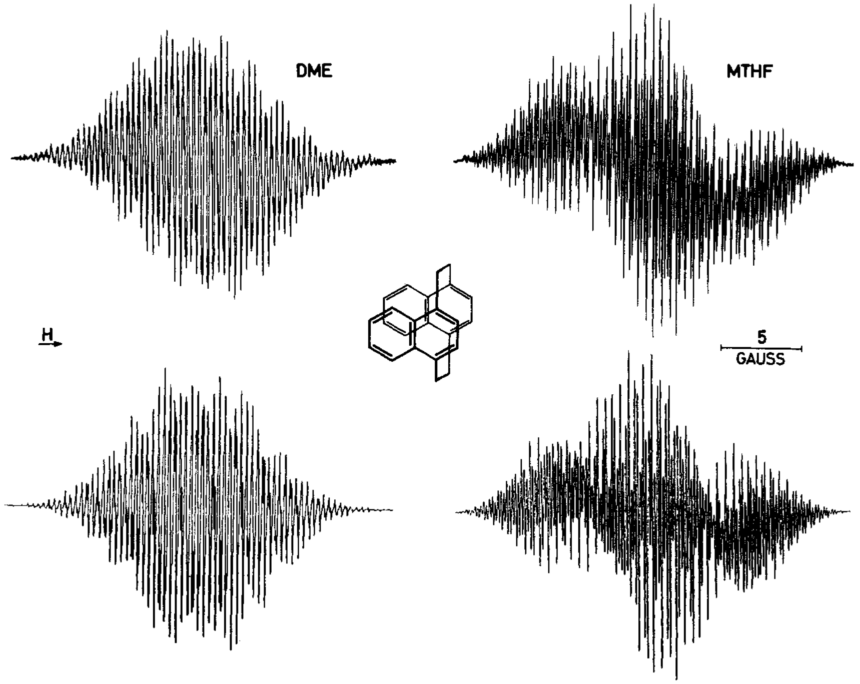


Fig. 2. *ESR. spectra of the radical anion* $III\cdot^{\ominus}$. Top: experimental spectra. Solvent: DME (left) or MTHF (right); Counterion: $K^{\oplus}$; Temp.: −90°. Bottom: computer simulated spectra. Coupling constants as given in *Table 1.* Line-shape: Lorentzian; line-width: 0.05 (left) or 0.09 Gauss (right)

temperature was varied between −90 and −50°. For each of the radical anions, $V\cdot^{\ominus}$ and $V\text{-}d_8\cdot^{\ominus}$, in DME and MTHF, a representative ESR. spectrum is displayed in *Fig. 3* and *4*, together with the corresponding computer simulated derivative curve. Through a combined use of ESR. and ENDOR. spectroscopies, proton coupling constants, a_{H_μ}, the magnitudes of which exceed 0.04 Gauss[3]), could be determined; they are collected in *Table 2*, with separate entries for −90 and −50°. Apart from the smallest measurable a_{H_μ} value (of the order of 0.1 Gauss), which was observed only for $V\cdot^{\ominus}$, all these coupling constants are identical for $V\cdot^{\ominus}$ and $V\text{-}d_8\cdot^{\ominus}$ within the limits of experimental error (±0.01 Gauss). No resolvable deuteron splittings were detected in the ESR. spectra of $V\text{-}d_8\cdot^{\ominus}$; considering the linewidth of 0.05 Gauss (*Fig. 4*), they are estimated to be smaller in magnitude than 0.03 Gauss.

The assignment of a_{H_μ} values listed in *Table 2* will be justified by arguments put forward in the Discussion. However, two features exhibited by these values stand out enough to be considered in advance. First, attention is drawn to the slight but significant changes which occur on passing from DME to THF and MTHF. is confirmed by the ESR. spectrum of $V\text{-}d_8\cdot\ominus$ (*Fig. 4*, right) where a ^{39}K hyperfine splitting, a_K of 0.05 ± 0.01 Gauss could be partially resolved at −50°. Secondly, one

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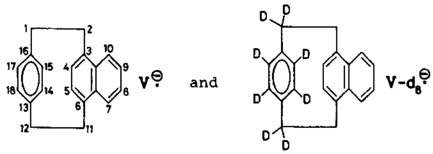
[3]) 1 Gauss $= 10^{-4}$ Tesla.

Table 2. *Proton coupling constants* a_{H_μ} (in Gauss = 10^{-4} Tesla) *for the radical anions* $V^{\cdot\ominus}$ *and* $V\text{-}d_8^{\cdot\ominus}$ (Counterion: $K^{\oplus}$)



temp.:	−90°			−50°		
solvent:	DME[a]	THF[a]	MTHF[a]	DME[a]	THF[a]	MTHF[a]
μ = 1,12	0.14[b][c] [d]	0.10[b][c] [d]	0.08[b][c] [d]	0.10[b][c] [d]	0.08[b][c] [d]	0.06[b][c] [d]
2,11	4.12[b] 0.70[b]	4.12[b] 0.67[b]	4.17[b] 0.74[b]	4.03[b] 0.76[b]	4.02[b] 0.78[b]	4.05[b] 0.80[b]
4,5	0.73	0.76	0.79	0.76	0.78	0.80
7,10	4.48	4.46	4.37	4.43	4.41	4.33
8,9	1.68	1.72	1.73	1.68	1.72	1.73
14,15	[d]	[d]	[d]	[d]	[d]	[d]
17,18	[d]	[d]	[d]	[d]	[d]	[d]

[a] Each coupling constant for two equivalent protons. [b] Coupling constant of methylene protons. [c] Observed only for $V^{\cdot\ominus}$. [d] Not observed either for $V^{\cdot\ominus}$ or for $V\text{-}d_8^{\cdot\ominus}$.

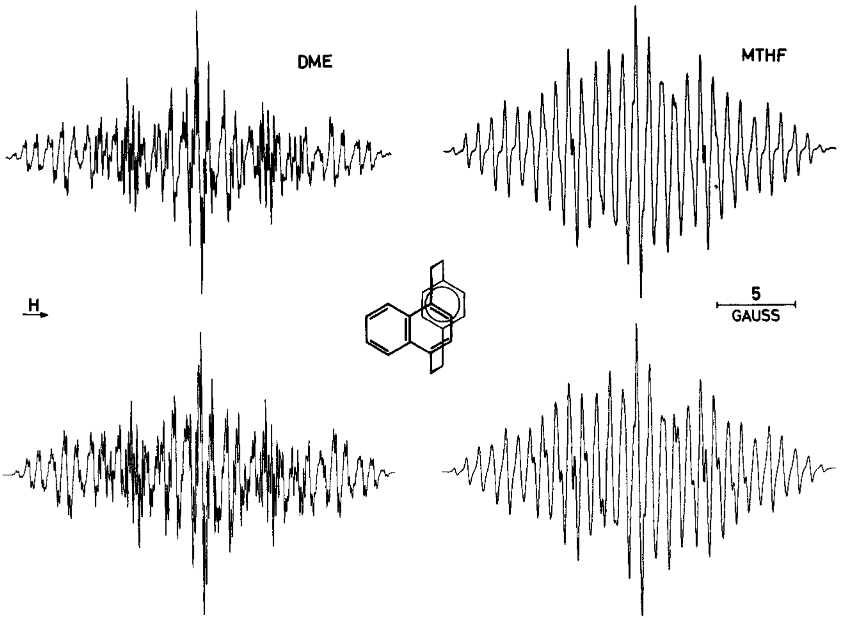


Fig. 3. *ESR. spectra of the radical anion* $V^{\cdot\ominus}$. Top: experimental spectra. Solvent: DME (left) or MTHF (right); Counterion: $K^{\oplus}$; Temp.: −90 (left) and −50° (right). Bottom: computer simulated spectra. Coupling constants as given in *Table 2*. Line-shape: Lorentzian; line-width: 0.12 (left) or 0.15 Gauss (right)

notes that some coupling constants are markedly dependent on temperature, a finding which will be useful in identifying the responsible protons.

In addition to the a_{H_μ} values *(Table 2)*, the two largest ^{13}C coupling constants could be determined from the spectral wings when the latter were amplified for V-$d_8 \cdot ^{\ominus}$ in DME at $-50°$ (*Fig. 4*, left). These coupling constants, a_{C_μ}, of 8.4 ± 0.1 and 7.5 ± 0.1 Gauss are attributed to the ^{13}C isotopes of the 3,6 and 7,10-carbon atoms, respectively, for reasons also given in the next section.

Discussion. - *Assignment of the coupling constants for* $V \cdot ^{\ominus}$. The expectation that the π-spin population in the radical anion of benzo[2.2]paracyclophane (V) will be largely localized on the naphthalene moiety (see Introduction) is fully borne out by the experimental data. In this regard, the ESR. spectra of V-$d_8 \cdot ^{\ominus}$ are particularly informative: The absence of deuteron splittings, as well as the lack of proton coupling constants smaller than 0.6 Gauss, certify that all a_{H_μ} values of substantial magnitude stem either from protons at the naphthalene π-centres or from those in the adjacent 2,11-methylene groups. In *Table 3* these values are compared with the hyperfine data found for the radical anions of naphthalene (VI) and its 1,4-dimethyl derivative (VII) under the same conditions. The assignment of the proton coupling constants for $V \cdot ^{\ominus}$, which results from such a comparison, is obvious. In the case of the pairwise equivalent 2,11-methylene protons, this assign-

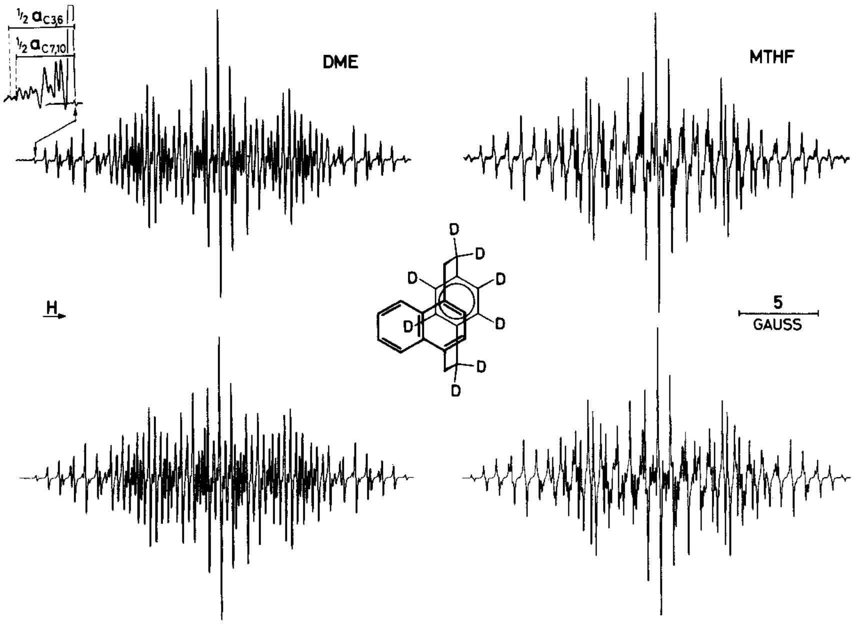


Fig. 4. *ESR. spectra of the radical anion* $V\text{-}d_8 \cdot ^{\ominus}$. Top: experimental spectra. Solvent: DME (left) or MTHF (right); Counterion: $K^{\oplus}$; Temp.: $-50°$. At the left, the lowfield part of the spectrum is reproduced under higher amplification. Bottom: computer simulated spectra. Proton coupling constants as given in *Table 2*, with the omission of the smallest value of 0.10 (DME) or 0.06 Gauss (MTHF). No account is taken of deuteron coupling constants, but a ^{39}K hyperfine splitting of 0.05 Gauss is included in the case of MTHF (see text). Line-shape: Lorentzian; line-widths: 0.05 Gauss

Table 3. *Comparison of the proton coupling constants* a_{H_μ} (in Gauss $= 10^{-4}$ Tesla) *for the radical anions* $VI\cdot^{\ominus}$, $VII\cdot^{\ominus}$, $V\cdot^{\ominus}$, $II\cdot^{\ominus}$ *and* $III\cdot^{\ominus}$ (Counterion: $K^{\oplus}$; Temp.: $-90°$)

	$VI\cdot^{\ominus}$		$VII\cdot^{\ominus}$			$V\cdot^{\ominus}(V\text{-}d_8\cdot^{\ominus})$		$II\cdot^{\ominus}$	$III\cdot^{\ominus}$
solvent:	DME	MTHF	DME	MTHF		DME	MTHF	MTHF	MTHF
$\mu = 1,4$	4.95	4.98	3.34[a])	2.93[a])	$\mu = 2,11$	4.12[b]) 0.70[b])	4.17[b]) 0.74[b])	3.80[b]) 0.46[b])	2.32[b]) 0.50[b])
2,3	1.85	1.87	1.85	1.85	4,5	0.73	0.79	0.95	1.43
5,8	4.95	4.98	5.41	5.89	7,10	4.48	4.37	4.48	3.64
6,7	1.85	1.87	1.67	1.75	8,9	1.68	1.73	1.59	1.91

[a]) Coupling constants of the six β-protons in the two methyl groups (substituted centres $\mu = 1,4$).
[b]) Coupling constant of two β-protons in the two 2,11-methylene groups (bridged centres $\mu = 3,6$).

ment is supported by the characteristic dependence of the two pertinent values on the temperature. The marked decrease in the larger value (~ 4.2 to ~ 4.0 Gauss) and the concomitant increase in the smaller one (~ 0.7 to ~ 0.8 Gauss), on going from -90 to $-50°$ *(Table 2)*, agree with the behaviour expected for such conformationally sensitive β-proton coupling constants[4]). Moreover, use of the ratio of the two values, along with the well established $<\cos^2\theta>$ relationship [5] leads to $\theta_1 = 5 \pm 5°$ and $\theta_2 = 115 \mp 5°$ as the estimates of the dihedral angles formed by the $C(2,11)-H(\beta)$ bonds and the $2p_z$-axes at the substituted 3,6 carbon atoms. Such estimates are consistent with a molecular model of V in which the benzene moiety does not eclipse the bridged ring of naphthalene, but it is displaced away from the larger aromatic system in an *anti*-like fashion.

Turning to the coupling constants of the α-protons[4]) in $V\cdot^{\ominus}$, those identified with $a_{H8,9}$ and $a_{H7,10}$ do not greatly differ in magnitude from the corresponding values for $VI\cdot^{\ominus}$ and $VII\cdot^{\ominus}$ ($a_{H5,8}$ and $a_{H6,7}$, respectively), whereas a larger discrepancy exists between $a_{H4,5}$ and its counterpart ($a_{H2,3}$). Such a discrepancy is, however, not surprising, since, according to the aforementioned molecular model, the two 4,5-protons in $V\cdot^{\ominus}$ should be situated directly above the π-cloud of the benzene moiety, and thus their coupling constant should be considerably altered relative to the $a_{H2,3}$ value for $VI\cdot^{\ominus}$ and $VII\cdot^{\ominus}$.

The only coupling constant of measurable magnitude (0.04 to 0.13 Gauss) which was observed in the spectra of $V\cdot^{\ominus}$, but failed to appear in those of $V\text{-}d_8\cdot^{\ominus}$, has been assigned to one pair of equivalent protons in the 1,12-methylene groups *(Table 2)*. The assignment of this value is indicated by its strong dependence on temperature, a behaviour anticipated for the protons in such an alkyl chain rather for those attached to the benzene ring.

The two ^{13}C coupling constants of 8.4 and 7.5 Gauss, determined from an ESR. spectrum of $V\text{-}d_8\cdot^{\ominus}$ (see Results), are reminiscent of the largest $a_{C\mu}$ values, $a_{C1,4,5,8} = 7.3 \pm 0.1$ Gauss and $a_{C5,8} = 7.7 \pm 0.2$ Gauss, which have been measured for the radical anions of naphthalene (VI) [6a] and its 1,4-dimethyl derivative (VII) [6b] respectively. The finding that one of the ^{13}C coupling constants for

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[4]) In ESR. spectroscopy, protons linked to π-electron centre *via* 0,1,2 ... sp^3-hybridized carbon atoms are denoted α, β, γ .... respectively.

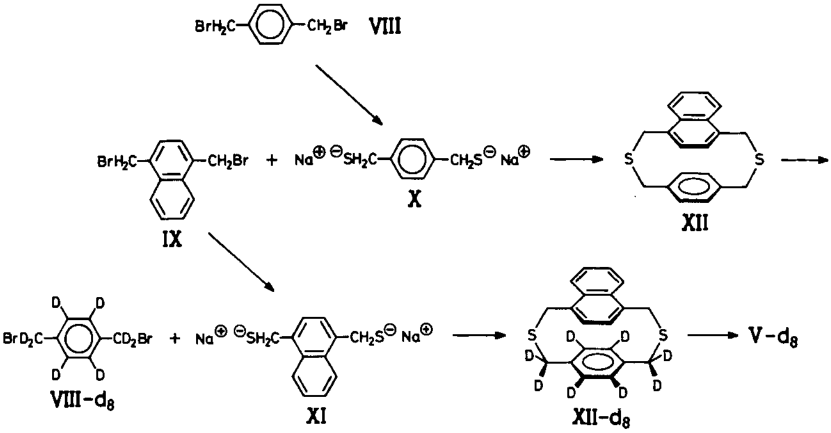
V-$d_8 \cdot ^{\ominus}$ substantially surpasses these values is of some interest, since such an increase does by no means follow from the π-spin distributions in V $\cdot ^{\ominus}$, VI $\cdot ^{\ominus}$ and VII $\cdot ^{\ominus}$, as inferred from the proton hyperfine data in *Table 3*. In this instance, it is tempting to invoke the strong deviations from planarity which undoubtedly occur at the bridged centers 3 and 6 of V, as they do at the corresponding carbon atoms in [2.2]paracyclophane (I) [7]. The non-planarity should endow the spin population at the two centres with a partial σ-character and thus should lead to an increase in the coupling constant $a_{C3,6}$ relative to the value expected for a planar π-system. Conforming to this argument, the larger coupling constant (8.4 Gauss) has been assigned to the ^{13}C nuclei of the 3,6-carbon atoms, leaving the smaller one (7.5 Gauss) to the like isotopes in the 7,10 positions.

Comparison of the proton hyperfine data for II $\cdot ^{\ominus}$ and III $\cdot ^{\ominus}$ with those for V $\cdot ^{\ominus}$. As stated in the Introduction, the π-spin distributions in the radical anions of the two isomeric [2.2](1,4)naphthalenophanes (II and III) can be compared with the spin distribution in V $\cdot ^{\ominus}$ if the rate of the counterion migration and the frequency of the attending electron transfer between the two equivalent aromatic moieties in II $\cdot ^{\ominus}$ and III $\cdot ^{\ominus}$ are low on the hyperfine time-scale. *Table 3* selects the α- and β-proton coupling constants observed under these conditions for those naphthalene fragments of II $\cdot ^{\ominus}$ and III $\cdot ^{\ominus}$ which accommodate the bulk of the π-spin population. It is evident in the case of II $\cdot ^{\ominus}$ that the pertinent coupling constants are very similar to the corresponding values for V $\cdot ^{\ominus}$, whereas such a resemblance is less conspicuous with III $\cdot ^{\ominus}$ and V $\cdot ^{\ominus}$. This result is just the one which is predicted by consideration of structure. Thus, on passing from benzo[2.2]-paracyclophane (V) to the *anti*-[2.2](1,4)naphthalenophane (II), the additional ring is brought into a position *away* from the naphthalene π-system of V $\cdot ^{\ominus}$ so that the π-spin distribution in this system will not be greatly affected by such a change. On the contrary, since an analogous annelation of V to yield the *syn*-isomer III places the additional ring essentially *above* the naphthalene π-system of V $\cdot ^{\ominus}$, the π-spin distribution in question will thereby be strongly altered. In other words, because of the different arrangement of the two naphthalene moieties, the interaction between their overlapping π-clouds is much more extensive in III $\cdot ^{\ominus}$ than in II $\cdot ^{\ominus}$, and, consequently, localization of the π-spin population on one moiety cannot be as efficient in the former as in the latter.

In conclusion, the following remark seems to be in order: Comparison of the hyperfine data for V $\cdot ^{\ominus}$ with those for II $\cdot ^{\ominus}$ and III $\cdot ^{\ominus}$ not only confirms the interpretation of the latter in terms of a concerted exchange of the counterion and the unpaired electron between the two equivalent naphthalene moieties, but also provides a substantial support for the assignment of these data, as made in *Table 1*.

Experimental Part. - Samples of *anti*- and *syn*-[2.2](1,4)naphthalenophanes (II and III respectively) were kindly provided by Prof. *H. H. Wasserman* and Dr. *P. M. Keehn* [8]. Preparation of benzo[2.2]paracyclophane (V) and its 1,1,12,12,14,15,17,18-octadeuterio derivative (V-d_8) followed the procedure of *Bruhin & Jenny* [9] [4] which essentially differs from the first synthesis of V, as described by *Cram et al.* [10].

p-Xylylene-dibromide (VIII), its perdeuterio derivative (VIII-d_8) and 1,4-bis(bromomethyl)-naphthalene (IX) were obtained by bromination of the corresponding methyl substituted compounds with *N*-bromosuccinimide in carbon tetrachloride. Treatment of VIII and IX with thiourea in ethanol



and subsequent basic hydrolysis yielded the sodium salts of 1,4-bis(mercaptomethyl)-benzene (X) and 1,4-bis(mercaptomethyl)-naphthalene (XI), respectively. 2,13-Dithia-benzo[3.3]paracyclophane (XII) was prepared by dropwise adding equimolar mixtures of IX and X to a solution of NaOH in methanol, whereas an analogous reaction of VIII-d_8 with XI resulted in the formation of the 1,1,14,14,16,17,19,20-octadeuterio derivative (XII-d_8). Pyrex-filtered UV.-irradiation of XII and XII-d_8 in trimethyl phosphite led to V and V-d_8 respectively, which were purified by chromatography on alumina (neutral, activity I) and recrystallization from heptane.

The identity of the products V and V-d_8, as well as the isotopic purity of the latter compound (96%), were checked by means of ^{1}H-NMR. and MS. spectroscopy.

Details of the preparation of XII and XII-d_8 will be given elsewhere [11].

The compounds II, III, V and V-d_8 were reduced with potassium in ethereal solvents to the corresponding radical anions which proved to be relatively stable in solution below −50°, but decayed at higher temperatures.

The ENDOR. spectra were taken with a *Varian*-E-1700-ENDOR. system linked to a *Varian*-E-9 ESR. instrument.

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REFERENCES

[1] *F. Vögtle & P. Neumann*, Topics in Current Chemistry *48*, 67-129 (1974).
[2] *F. Gerson, W. B. Martin, Jr., & Ch. Wydler*, J. Amer. chem. Soc. *98*, 1318 (1976).
[3] *F. Gerson*, Chimia *28*, 194 (1974) and references therein.
[4] *F. Gerson, W. B. Martin, Jr., & Ch. Wydler*, Helv. *59*, 1365 (1976).
[5] *C. Heller & H. M. McConnell*, J. chem. Physics *32*, 1535 (1960); *A. Horsfield, J. R. Morton & D. H. Whiffen*, Mol. Physics *4*, 425 (1961).
[6] a) *K. Markau & W. Maier*, Z. Naturforsch. A*36*, 615 (1961); b) *F. Gerson* & coworkers, unpublished results.
[7] *C. J. Brown*, J. chem. Soc. *1953*, 3265.
[8] *H. H. Wasserman & P. M. Keehn*, J. Amer. chem. Soc. *91*, 2374 (1969).
[9] *J. Bruhin & W. Jenny*, Tetrahedron Letters *1973*, 1215.
[10] *D. J. Cram, C. K. Dalton & G. R. Knox*, J. Amer. chem. Soc. *85*, 1088 (1963).
[11] *W. B. Martin, Jr., & P. M. Begley*, to be published.