248. Aromatic Radical Anions with Parallel or Crossed Triple Bonds

by **Christoph Elschenbroich**1), **Fabian Gerson**, **Hiroaki Ohya-Nishiguchi**2) and **Christoph Wydler**

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel,

and **Axel Nissen**3)

Institut für Organische Chemie der Universität Heidelberg, Im Neuenheimer Feld 7, D-6900 Heidelberg

(3.X.77)

Summary

Proton hyperfine data are reported for the radical anions of 1,8-di(propyn-1-yl)-naphthalene (I), 7,8,12,13-tetradehydro-10,11-dihydro-9*H*-cyclodeca[*d,e*]naphthalene (II) and 2,2′-di(propyn-1-yl)-biphenyl (III), as well as of 5,6,11,12-tetradehydro-7,8,9,10-tetrahydro-dibenzo[*a,c*]cyclodecene (IV) and its 8,8,9,9-tetradeuterio-derivative (IV-d_4). The triple bonds in I and II can be regarded as roughly parallel, while those in IV (and IV-d_4) may be considered as crossed. The π-spin distributions in $\text{I}^{\ominus\cdot}$ to $\text{IV}^{\ominus\cdot}$ are discussed in terms of simple MO models which suggest a weakly bonding interaction between the acetylenic fragments in $\text{IV}^{\ominus\cdot}$, in contrast to $\text{III}^{\ominus\cdot}$ where such an effect appears to be negligible. The importance of an analogous interaction in $\text{I}^{\ominus\cdot}$ and $\text{II}^{\ominus\cdot}$ is difficult to deduce, since its inclusion into a MO model does not substantially affect the π-spin distribution in these radical anions.

Introduction. - A series of alkynyl-disubstituted naphthalenes [1] and biphenyls [2], such as 1,8-di(propyn-1-yl)-naphthalene (I), 7,8,12,13-tetradehydro-10,11-dihydro-9*H*-cyclodeca[*d,e*]naphthalene (II), 2,2′-di(propyn-1-yl)-biphenyl (III) and 5,6,11,12-tetradehydro-7,8,9,10-tetrahydro-dibenzo[*a,c*]cyclododecene (IV), has been synthesized several years ago.

X-ray crystallographic structure analyses of I [3], II [4] and IV [5] show that the two acetylenic fragments in these compounds are rather close in space, the interatomic distances between the formally not bonded sp-hybridized carbon atoms being in the range of 2.8 to 3.4 Å4). The triple bonds in the molecules I and II, which, on the whole, have a similar geometry, may be regarded as roughly parallel, while those in IV can be considered as having an approximately crossed arrangement. With respect to IV, it is also important to note that the two benzene rings

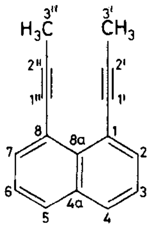
---

1) Present address: Fachbereich Chemie der Philipps-Universität, Lahnberge, D-3550 Marburg.

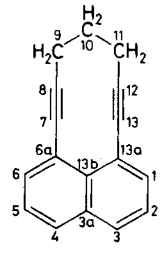
2) Present address: Department of Chemistry, Faculty of Science, University of Kyoto, Kyoto 606, Japan.

3) Present address: BASF, D-6700 Ludwigshafen.

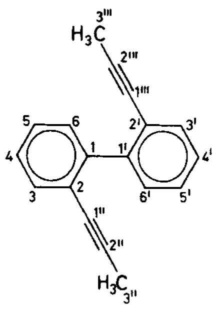
4) The following values (Å) were found for these distances: 2.874 (1′-1″) and 3.396 (2′-2″) in I; 2.795 (7-13) and 2.917 (8-12) in II; 3.036 (5-12) and 3.108 (6-11) in IV.



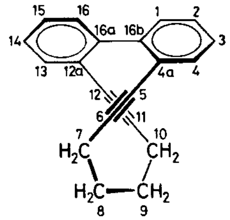
I



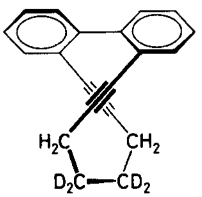
II



III



IV



IV-d_4

are twisted by *ca.* 60° about the essential single 16a–16b bond linking them. No X-ray crystallographic data are, to our knowledge, available for III, but molecular models indicate that this compound should prefer conformations in which the two acetylenic fragments are fairly remote (5 to 7 Å). Moreover, the two benzene rings in III are expected to be considerably more coplanar than in IV (twist angle of *ca.* 30° about the 1–1′ bond).

Although the structural parameters of I, II and IV, and to a smaller extent, those of III, strongly deviate from their standard values, investigations by UV., IR. and ^{1}H-NMR. have not revealed any marked effects on their spectroscopic properties [1] [2]. The purpose of the present work is to investigate whether this statement also holds for the corresponding radical anions $\mathrm{I}^{\overset{\ominus}{\cdot}}$, $\mathrm{II}^{\overset{\ominus}{\cdot}}$, $\mathrm{III}^{\overset{\ominus}{\cdot}}$ and $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ in regard to their hyperfine data. The pertinent ESR. studies include, in addition, the radical anion of the 8,8,9,9-tetradeuterio-derivative of IV (IV-d_4).

Experimental Part. – The syntheses of the alkynyl-disubstituted naphthalenes, I and II [1], as well as those of the analogous derivatives of biphenyl, III, IV and IV-d_4 [2], have been described previously. All compounds were reduced both by reaction with potassium in 1,2-dimethoxyethane (DME) and by electrolysis in *N,N*-dimethylformamide (DMF) with tetraethylammonium perchlorate as the supporting salt. The resulting radical anions proved to be rather unstable and readily yielded brown coloured polymers. Nevertheless, $\mathrm{I}^{\overset{\ominus}{\cdot}}$, $\mathrm{II}^{\overset{\ominus}{\cdot}}$ and $\mathrm{III}^{\overset{\ominus}{\cdot}}$, produced by either method, were sufficiently long-lived to be investigated at low temperatures (–90° in DME and –60° in DMF). On the other hand, in the case of $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ and IV-$d_4^{\overset{\ominus}{\cdot}}$, which exhibited the least stability, well-defined ESR. spectra could be observed only upon electrolytic generation with the use of a novel cylindrical cell [6]. The reaction of IV and IV-d_4 with potassium was less successful, even if the reduction was carried out by the method of solvated electrons [7] where a direct contact of the solution with the alkali metal mirror is avoided. The ESR. spectra obtained under such conditions presumably represented mixtures of $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ (or IV-$d_4^{\overset{\ominus}{\cdot}}$) and secondary radical anions arising from polymeric products; a reliable analysis of these spectra could not be achieved.

Results. - The ESR. and ENDOR. spectra of $\mathrm{I}^{\ominus\cdot}$, $\mathrm{II}^{\ominus\cdot}$ and $\mathrm{III}^{\ominus\cdot}$ have been reproduced elsewhere [8]. The pertinent proton coupling constants, a_{H_μ}, are listed in *Tables 1* and *2*. Within the limits of experimental error (±0.02 Gauss[5]), they do not differ for the solvent/counterion DME/$K^{\oplus}$ (−90 °C) and DMF/$Et_4N^{\oplus}$ (−60 °C). Also given in *Table 2* are the values a_{H_μ} for $\mathrm{IV}^{\ominus\cdot}$ and IV-$d_4^{\ominus\cdot}$ which, for reasons mentioned in the Experimental Part, were obtained only with DMF/$Et_4N^{\oplus}$. The ESR. spectra of these two radical anions are shown in *Figures 1* and *2*, respectively, along with the corresponding computer simulated derivative curves. The assignment of the coupling constants to sets of equivalent protons in $\mathrm{I}^{\ominus\cdot}$, $\mathrm{II}^{\ominus\cdot}$, $\mathrm{III}^{\ominus\cdot}$ and $\mathrm{IV}^{\ominus\cdot}$, wherever not inferred directly from experiment, is based on the arguments presented in the Discussion.

It is noteworthy that the multiplicities of the sets of equivalent protons in the radical anions $\mathrm{I}^{\ominus\cdot}$ to $\mathrm{IV}^{\ominus\cdot}$ agree with those of the respective neutral compounds in solution, as evidenced by the ^{1}H-NMR. spectra of I to IV [1] [2]. This finding is of

Table 1. *Proton coupling constants,* a_{H_μ} *in Gauss* (= 10^{-4} Tesla), *for the radical anions* $\mathrm{I}^{\ominus\cdot}$ *and* $\mathrm{II}^{\ominus\cdot}$. The values assigned to analogous positions *μ* of $\mathrm{I}^{\ominus\cdot}$ and $\mathrm{II}^{\ominus\cdot}$ are placed in the same line

$\mathrm{I}^{\ominus\cdot}$			$\mathrm{II}^{\ominus\cdot}$		
Nr. of nuclei	a_{H_μ}	Assignment μ	Nr. of nuclei	a_{H_μ}	Assignment μ
2 H	5.15	4,5(*α*)	2 H	5.15	3,4(*α*)
2 H	2.93	2,7(*α*)	2 H	2.96	1,6(*α*)
2 H	0.69	3,6(*α*)	2 H	0.70	2,5(*α*)
6 H	2.20	3′,3″(*β*)	2 H 2 H	3.42 1.11	9,11(*β*)
			1 H 1 H	0.14 0.06[a])	10(*γ*)

[a]) Splitting not resolved.

Table 2. *Proton and deuteron coupling constants,* a_{H_μ} *and* a_{D_μ} *in Gauss* (= 10^{-4} Tesla), *for the radical anions* $\mathrm{III}^{\ominus\cdot}$, $\mathrm{IV}^{\ominus\cdot}$ *and* IV-$d_4^{\ominus\cdot}$. The values assigned to analogous positions *μ* of $\mathrm{III}^{\ominus\cdot}$ and $\mathrm{IV}^{\ominus\cdot}$ are placed in the same line

$\mathrm{III}^{\ominus\cdot}$			$\mathrm{IV}^{\ominus\cdot}$			IV-$d_4^{\ominus\cdot}$		
Nr. of nuclei	a_{H_μ}	Assignment μ	Nr. of nuclei	a_{H_μ}	Assignment μ	Nr. of nuclei	a_{H_μ} or a_{D_μ}	Assignment *μ*
2 H	3.94	4,4′(*α*)	2 H	1.31	3,14(*α*)	2 H	1.30	3,14(*α*)
2 H	1.08	6,6′(*α*)	2 H	1.26	1,16(*α*)	2 H	1.26	1,16(*α*)
2 H	0.92	3,3′(*α*)	2 H	0.05[a])	4,13(*α*)	2 H	0.05[a])	4,13(*α*)
2 H	0.84	5,5′(*α*)	2 H	2.14	2,15(*α*)	2 H	2.14	2,15(*β*)
6 H	2.61	3″,3‴(*β*)	2 H 2 H	6.18 4.55	7,10(*β*)	2 H 2 H	6.16 4.54	7,10(*β*)
			2 H 2 H	1.75 0.36	8,9(*γ*)	2 D 2 D	0.27 0.06[a])	8,9(*γ*)

[a]) Splitting not resolved.

---

[5]) 1 Gauss = 10^{-4} Tesla.

particular interest for IV which in the crystalline phase exhibits a conformation of lower symmetry with all methylene β- and γ-protons[6]) being non-equivalent [5], whereas a two-fold axis passing through the centres of the 8-9 and 16a-16b bonds is apparent in solution. Molecular models of IV demonstrate that the higher conformational mobility in the liquid phase should, in effect, readily generate such a symmetry axis and thus render the methylene protons in the positions 7 (β) or 8 (γ) pairwise equivalent with those in the positions 10 and 9, respectively. On the other hand, since the two β- or γ-protons of one and the same methylene group in IV and IV$^{\ominus\cdot}$ are non-equivalent in the corresponding magnetic resonance spectra, the inversion of the 7-8-9-10 tetramethylene chain must be slow at the employed

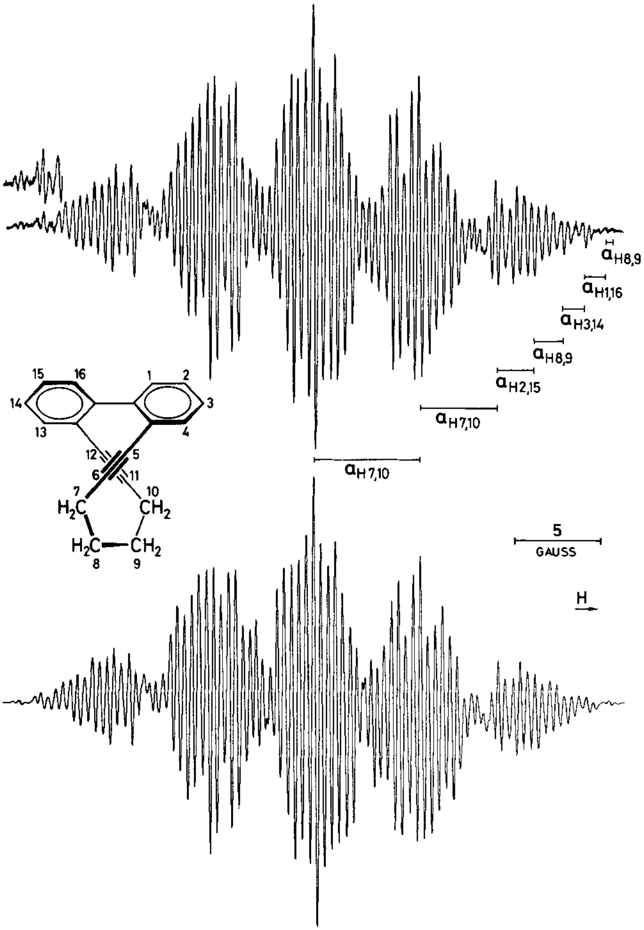


Fig. 1. *ESR. spectrum of the radical anion IV$^{\ominus\cdot}$*. Top: experimental spectrum. Solvent: DMF; counterion: $Et_4N^{\oplus}$; temp.: −60°. Bottom: computer simulated spectrum. Coupling constants as given in *Table 2.* Line-shape: Lorentzian; line-width: 0.12 Gauss

---

[6]) In ESR. spectroscopy, protons linked by 0,1,2··· sp^3-hybridized carbon atoms to a π-center are denoted $a, \beta, \gamma \cdots$ respectively.

temperatures and pertaining times-scales (NMR.: 25 °C, $\sim 10^2 s^{-1}$; ESR.: -60 °C, $\sim 10^7 s^{-1}$).

A coalescence of the NMR. signals from two β-protons of one methylene group in IV has been observed only at $+87$ °C [2]. On the assumption of a comparable activation energy ($\Delta G^{\ddagger} = 75$ kJ/mol) and considering the substantially faster time-scale, it may be anticipated that a much more elevated temperature would be required to bring about an analogous phenomenon in the ESR. spectrum of $IV^{\ominus}$. Such temperature is, however, not practicable, in view of the low stability of the radical anion (see Experimental Part).

Discussion. - *HMO models.* A HMO treatment starts conveniently with 1,8-divinylnaphthalene (V) in the case of I and II, and with 2,2′-divinylbiphenyl (VI) in that of III and IV. Subsequent modifications, aiming at a more realistic description of I to IV, are indicated in the diagrams of *Figure 3.* They yield in the models A_n to B_b' where the subscripts n and b stand for V and VI, respectively, referring to the aromatic moieties of these π-systems (naphthalene and biphenyl). In A_n and A_b, the only modification consists in the introduction of the triple bonds which is effected by increasing the pertinent parameter ($\beta_{C\equiv C} = 1.5\ \beta$) [9] relative to its standard value; no interaction between such bonds is taken in account. On the other hand, B_n and B_b allow for a weak interaction of this kind through the inclusion

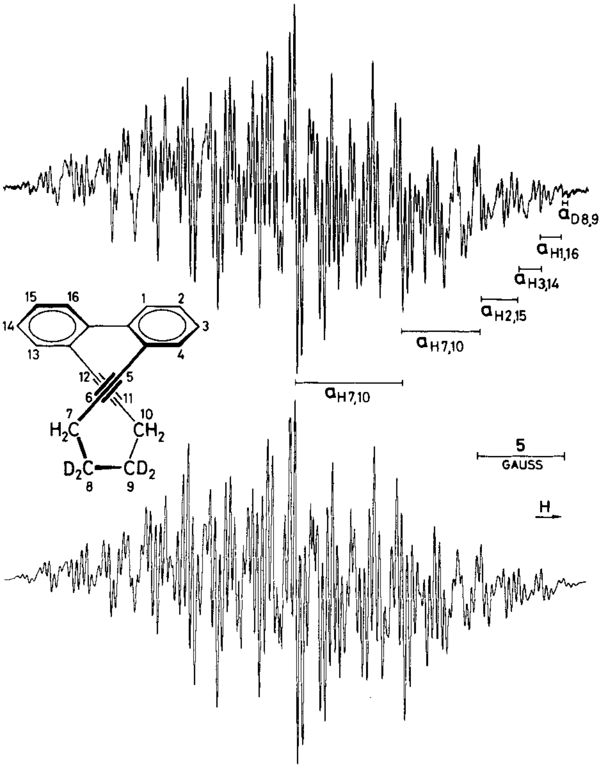


Fig. 2. *ESR. spectrum of the radical anion* $IV\text{-}d_4^{\ominus}$. Top: experimental spectrum taken under the same conditions as that in *Figure 1.* Bottom: computer simulated spectrum. Coupling constants as given in *Table 2.* Line-shape: Lorentzian; line-width: 0.12 Gauss

of a parameter ($\beta_{C\cdots C} = 0.2\ \beta$) between the formally not bonded sp-hybridized carbon atoms; in addition, the value adopted for the triple bonds in A_n and A_b is correspondingly decreased, ($\beta_{C\equiv C} = 1.3\ \beta$). The models A'_b and B'_b differ from A_b and B_b, respectively, in that, apart from the above-mentioned modifications, the parameter of the essential single 1-1′ bond linking the benzene rings of the biphenyl moiety is strongly reduced ($\beta_{C-C} = 0.5\ \beta$). This change simulates the twist of 60° about the bond in question (cos 60° = 0.5), as found by the X-ray crystallographic structure analysis of IV [5].

Use was made of all six models *(Fig. 3)* to compute the π-spin populations ρ_μ in the corresponding radical anions by the *McLachlan* procedure ($\lambda = 1.0$) [10]. These values are collected in *Table 3.* Of special interest is their behaviour upon the introduction of a weakly bonding interaction between the acetylenic fragments, *i.e.,* on going from A_n, A_b and A'_b to B_n, B_b and B'_b, respectively. In general, as a consequence of such an interaction, the π-spin population shifts from the aromatic moiety onto the terminal sp-hybridized carbon atoms. However, the shift is only very slight when this moiety is naphthalene ($A_n \rightarrow B_n$), whereas it is quite substantial with biphenyl as the aromatic component ($A_b \rightarrow B_b$ and $A'_b \rightarrow B'_b$). Furthermore, it is important to note that, according to the values in *Table 3,* a twist about the 1-1′ bond of the biphenyl moiety works in the same direction as the interaction between the acetylenic fragments. On passing from A_b to B'_b, the two effects thus reinforce each other, and, as a result, the π-spin populations on the terminal sp-hybridized atoms C(2″) and C(2‴) are strongly enhanced (+0.182 *vs.* +0.091) at the expense of those in the biphenyl moiety.

Assignment of the coupling constants. It is evident from the experimental data in *Table 1* that three values for $II^{\ominus\cdot}$, 5.15, 2.96 and 0.70 Gauss, are virtually equal to the α-proton coupling constants for $I^{\ominus\cdot}$. This finding indicates an assignment of these values to the three pairs of equivalent α-protons in the naphthalene moiety

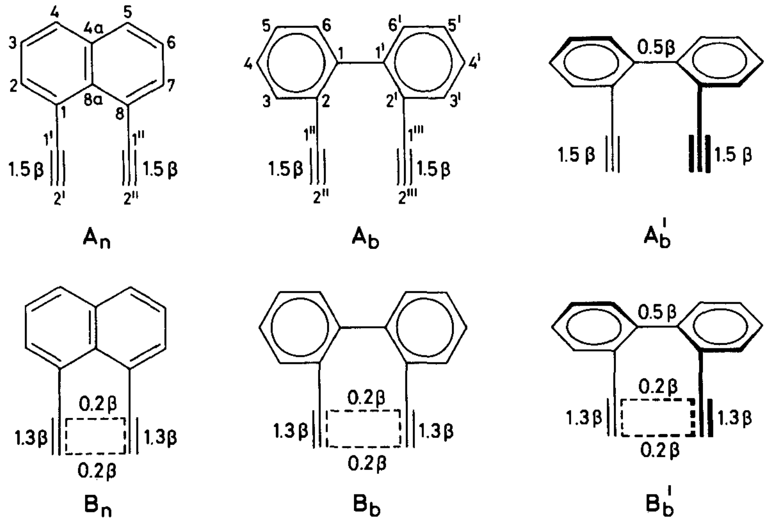


Fig. 3. *HMO models of the π-systems of I and II* (A_n and B_n), *and of III and IV* (A_b to B'_b)

of $\mathrm{II}^{\ominus\cdot}$, leaving the two remaining coupling constants of substantial magnitude, 3.42 and 1.11 Gauss, to the two pairs of equivalent β-protons in the positions 9 and 11. Moreover, the near equality of the α-proton coupling constants for $\mathrm{I}^{\ominus\cdot}$ and $\mathrm{II}^{\ominus\cdot}$ points to almost identical π-spin distributions in the two radical anions so that the same HMO model should apply to both of them. There is little to choose, in this case, between A_n and B_n, since, as stated in the preceding section, the π-spin populations ρ_μ are only slightly altered on passing from the former to the latter model. *Table 4* lists the 'theoretical' α-proton coupling constants $a_{H\mu}$ which were obtained by the use of the *McConnell* equation (1) [11]

$$a_{H\mu(\alpha)} = Q\,\rho_\mu \tag{1}$$

($Q = -27$ Gauss) and with the values ρ_μ calculated for $\mu = 2$ to 7 in A_n and B_n. These coupling constants compare favourably with their experimental counterparts, and the assignment made for the latter data is based on correlation between the two sets of values.

A glance at the experimental data in *Table 2* reveals that, in contrast to $\mathrm{II}^{\ominus\cdot}$ *vs.* $\mathrm{I}^{\ominus\cdot}$, the coupling constants due to pairs of equivalent protons in $\mathrm{IV}^{\ominus\cdot}$ bear little resemblance to those in $\mathrm{III}^{\ominus\cdot}$. In the case of $\mathrm{III}^{\ominus\cdot}$, all such coupling constants arise from α-protons and are readily assigned *via* eq. (1) in the same way as the analogous values for $\mathrm{I}^{\ominus\cdot}$ and $\mathrm{II}^{\ominus\cdot}$. It is noteworthy that the π-spin populations calculated for $\mu = 3,3'$ to $6,6'$ in the simplest available model A_b afford the best correlation between the 'theoretical' and experimental α-proton coupling constants for $\mathrm{III}^{\ominus\cdot}$.

Table 3. *π-Spin populations ρ_μ calculated for the radical anions of the model π-systems (cf. Fig. 3)*

μ	A_n	B_n	μ	A_b	B_b	A'_b	B'_b
1,8	+0.146	+0.149	1,1′	+0.118	+0.097	+0.133	+0.096
2,7	+0.084	+0.073	2,2′	+0.131	+0.117	+0.129	+0.097
3,6	+0.015	+0.019	3,3′	−0.040	−0.026	−0.028	+0.002
4,5	+0.204	+0.195	4,4′	+0.143	+0.087	+0.096	+0.037
4a	−0.034	−0.032	5,5′	+0.021	+0.039	+0.078	+0.080
8a	−0.026	−0.027	6,6′	+0.041	+0.011	−0.018	−0.024
1′,1″	−0.011	−0.023	1″,1‴	−0.006	+0.012	+0.001	+0.030
2′,2″	+0.093	+0.117	2″,2‴	+0.091	+0.164	+0.109	+0.182

Table 4. *Comparison of theoretical and experimental α-proton coupling constants,* $a_{H\mu}$ *in Gauss* ($= 10^{-4}$ Tesla), *for the radical anions $\mathrm{I}^{\ominus\cdot}$ to $\mathrm{IV}^{\ominus\cdot}$*

$a_{H\mu}$ (theor.)			$a_{H\mu}$ (exp.)			$a_{H\mu}$ (theor.)			$a_{H\mu}$ (exp.)		
μ	A_n	B_n	$\mathrm{I}^{\ominus\cdot}$	$\mathrm{II}^{\ominus\cdot}$	(μ[a])	μ	A_b	B'_b	$\mathrm{III}^{\ominus\cdot}$	$\mathrm{IV}^{\ominus\cdot}$	(μ[b])
2,7	−2.27	−1.97	2.93	2.96	(1,6)	3,3′	+1.08	−0.05	0.92	0.05	(4,13)
3,6	−0.41	−0.51	0.69	0.70	(2,5)	4,4′	−3.86	−1.00	3.94	1.31	(3,14)
4,5	−5.51	−5.26	5.15	5.15	(3,4)	5,5′	−0.57	−2.16	0.84	2.14	(2,15)
						6,6′	−1.11	+0.65	1.08	1.26	(1,16)

[a] Numbering according to II.

[b] Numbering according to IV.

Consequently, the assignment of the experimental data for this radical anion relies on such a correlation, as demonstrated in *Table 4.*

More problematic is the assignment of the coupling constants for $\mathrm{IV}^{\ominus\cdot}$. In view of the dissimilarity between the hyperfine data for $\mathrm{III}^{\ominus\cdot}$ and $\mathrm{IV}^{\ominus\cdot}$, the π-spin distribution in the latter radical anion must differ essentially from that predicted by the model $\mathrm{A_b}$. In fact, B'_{b}, *i.e.*, the model which is considerably altered relative to $\mathrm{A_b}$ *(Fig. 3)*, seems to be the proper choice for $\mathrm{IV}^{\ominus\cdot}$, as shown by an examination of the main hyperfine features of this radical anion. It begins preferably with the coupling constants of the γ-protons, 1.75 and 0.36 Gauss, since their assignment to the two pairs of such protons in the positions 8 and 9 follows unequivocally from the comparison of the experimental data for $\mathrm{IV}^{\ominus\cdot}$ and $\mathrm{IV\text{-}d_4}^{\ominus\cdot}$. The magnitude of one of these values, which is surprisingly large for a γ-proton coupling constant, can be rationalized by the unusual geometry of the molecule. In a single conformation, characteristic of the X-ray crystallographic structure of IV [5], one of the γ-protons is rather close to that triply bound centre μ which is separated from it by a larger number of $\mathrm{sp^3}$-hybridized carbon atoms ($\mu = 6$ and 11 for the γ-proton in the position 9 and 8, respectively). A direct π-σ spin transfer can thus occur from the $2\mathrm{p_z}$-AO at the centre 6 or 11 into the 1s-AO of this particular γ-proton, giving rise to a huge increase in its coupling constant. In a solution of $\mathrm{IV}^{\ominus\cdot}$, the increase must necessarily appear to be shared with a second γ-proton which becomes equivalent to the first one through a rotation about the effective two-fold axis (see Results). Such an interpretation presupposes a high π-spin population $\rho_{6,11}$ at the relevant acetylenic carbon atom C(6) or C(11), a condition which is met by the corresponding value $\rho_{2'',2'''} = +0.182$ in the model B'_{b}.

The high π-spin population $\rho_{6,11}$ should also manifest itself in large coupling constants of the two pairs of equivalent β-protons in the positions 7 and 10. Indeed, the spectrum of $\mathrm{IV}^{\ominus\cdot}$ exhibits such coupling constants, 6.18 and 4.55 Gauss, which considerably exceed in magnitude the values $\mathrm{a_{H\mu}}$ for $\mathrm{III}^{\ominus\cdot}$. Use of the well-known relationship [12]

$$\mathrm{a}_{\mathrm{H}7,10(\beta)} = \mathrm{B}\,\rho_{6,11}\langle\cos^2\theta\rangle \tag{2}$$

(B = +40 Gauss [13]) and the reasonable assumption of a positive sign for the experimental data $\mathrm{a_{H7,10}}$ leads to π-spin population $\rho_{6,11} = +0.181$, along with $\theta = 22.5$ and 142.5° as the dihedral angles between the C–H(β) bonds and the $2\mathrm{p_z}$-axis at the centre 6 or 11. While the 'experimental' value $\rho_{6,11}$ is found to be in perfect accord with the corresponding number $\rho_{2'',2'''}$ in the model B'_{b}, it is rather difficult to assess the significance of the angles θ in a non-planar and flexible molecule like IV.

The assignment of the four coupling constants considered above to the β- and γ-protons in $\mathrm{IV}^{\ominus\cdot}$, leaves the four remaining ones to pairs of equivalent α-protons. Again, these values can be assigned by correlating them with their theoretical counterparts which were obtained *via* eq. (1) from the π-spin populations ρ_μ for $\mu = 3,3'$ to $6,6'$ in the model B'_{b} *(Table 4).*

In order to provide further support for the assignment of the hyperfine data in $\mathrm{IV}^{\ominus\cdot}$, an attempt has been made to predict the coupling constants of the protons in this radical anion by the use of the

INDO technique [14]. The geometry adopted in this method was the one determined by the X-ray crystallographic structure analysis of IV (see above) so that the resulting values had to be pairwise averaged prior to their comparison with the experimental data. The general agreement thus achieved was satisfactory for the α-protons, the coupling constants of which are expected not to be very sensitive to conformational changes of the tetramethylene chain. On the other hand, the averaging procedure was less successful in the case of β- and γ-protons where the theoretical coupling constants appeared to be much smaller than their experimental counterparts. This result casts some doubt on the applicability of the INDO technique to conformationally labile molecules.

Interactions between the triple bonds. As stated in the Introduction, the present study of $\mathrm{I}^{\overset{\ominus}{\cdot}}$ to $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ has been undertaken in a search for the effect of an unusual geometry on the π-spin distribution. More specifically, one asks whether the spatial proximity of the triple bonds in $\mathrm{I}^{\overset{\ominus}{\cdot}}$, $\mathrm{II}^{\overset{\ominus}{\cdot}}$ and $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ (and to a much lesser extent in $\mathrm{III}^{\overset{\ominus}{\cdot}}$) affects the hyperfine data. The answer to this question is a cautious yes, at least as far as $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ is concerned. Since $\mathrm{III}^{\overset{\ominus}{\cdot}}$ and $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ contain essentially the same π-electron system, the great differences in their proton coupling constants must be due to different geometries of the molecules. Moreover, the finding that the experimental data for $\mathrm{III}^{\overset{\ominus}{\cdot}}$ and $\mathrm{IV}^{\overset{\ominus}{\cdot}}$ can be accomodated by the models A_b and B'_b, respectively, suggests that a weak bonding interaction between the acetylenic carbon atoms is important in $\mathrm{IV}^{\overset{\ominus}{\cdot}}$, whereas, in accord with the expectation, it is negligible in $\mathrm{III}^{\overset{\ominus}{\cdot}}$. In the case of $\mathrm{I}^{\overset{\ominus}{\cdot}}$ and $\mathrm{II}^{\overset{\ominus}{\cdot}}$ the models do not provide a clear-cut answer to the question posed above, since they do not predict a marked effect of the analogous interactions on the π-spin distributions in the two structurally related radical anions.

One of us *(A.N.)* thanks Professor *H.A. Staab,* now at *Max-Planck*-Institut für Medizinische Forschung, Heidelberg, for having introduced him into the intriguing field of alkynyl-disubstituted aromatics. We are also obliged to Dr. *G. Plattner,* Physikalisch-Chemisches Institut der Universität Basel, for carrying out the INDO calculations of $\mathrm{IV}^{\overset{\ominus}{\cdot}}$. This work was supported by the *Swiss National Science Foundation* (project 2.523.76). Financial assistance by *Ciba-Geigy SA, Sandoz SA* and *F. Hoffmann-La Roche & Cie, SA,* Basel, is also acknowledged.

REFERENCES

[1] *A. Nissen & H.A. Staab,* Chem. Ber. *104,* 1191 (1971).
[2] *H.A. Staab, H. Mack & A. Nissen,* Chem. Ber. *105,* 2310 (1972).
[3] *A.E. Jungk,* Chem. Ber. *105,* 1595 (1972).
[4] *H. Irngartinger & A.E. Jungk,* Chem. Ber. *110,* 749 (1977).
[5] *H. Irngartinger,* Chem. Ber. *105,* 1184 (1972).
[6] *F. Gerson, H. Ohya-Nishiguchi & Ch. Wydler,* Angew. Chem. *88,* 617 (1976); Angew. Chem., Int. Ed. Engl. *15,* 552 (1976). *H. Ohya-Nishiguchi,* to be published.
[7] *F. Gerson, G. Moshuk & M. Schwyzer,* Helv. *54,* 361 (1971).
[8] *Ch. Wydler,* Dissertation, Universität Basel 1977.
[9] *F. Gerson, J. Jachimowicz, M. Nakagawa & M. Iyoda,* Helv. *57,* 2141 (1974); *F. Gerson, W.B. Martin,* jr., *G. Plattner, F. Sondheimer & H.N.C. Wong,* ibid. *59,* 2038 (1976).
[10] *A.D. McLachlan,* Mol. Physics *3,* 233 (1960).
[11] *H.M. McConnell,* J. chem. Physics *24,* 632 (1956).
[12] *C. Heller & H.M. McConnell,* J. chem. Physics *32,* 1535 (1960); *A. Horsfield, J.R. Morton & D.H. Whiffen,* Mol. Physics *4,* 425 (1961).
[13] See, e.g., *G.A. Russell,* in: 'Radical Ions' (E.T. Kaiser & L. Kevan, ed.), Interscience Publishers, New York 1967; pp. 110-112.
[14] *J.A. Pople & D.L. Beveridge,* 'Approximate Molecular Orbital Theory', McGraw-Hill, New York 1970.