142. Methyl Substitution as a Probe for π-Spin Distribution in the Radical Anion of 1,6-Methano[10]annulene

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(30. III. 76)

Summary. ESR. and ENDOR. spectra are reported for the radical anion of the 2-methyl derivative (III) of 1,6-methano[10]annulene (I). Comparison of the hyperfine data for $\mathrm{I}^{\cdot\ominus}$ and $\mathrm{III}^{\cdot\ominus}$ with those for the radical anions of naphthalene (II) and its 1-methyl derivative (IV), respectively, confirms the suggestion that – despite the vastly different α-proton coupling constants – the π-spin distributions should be similar in the two series. This result provides further support for the view that the π-spin distribution, in particular, and the cyclic π-delocalisation, in general, are not seriously perturbed by moderate deviations of the π-perimeter from planarity.

Introduction. – The ESR. data for the radical anion of 1,6-methano[10]annulene (I) have been amply discussed in the literature [1]. Their prominent features are the low absolute values observed for the coupling constants of the protons at the ten-membered ring (α-protons[3])). This finding has been rationalized by the deviations of the cyclic π-electron system from planarity [2] and the resulting 'leakage' of π-spin population from $2p_z$-AO's at the carbon centres into 1s-AO's of the ring hydrogen atoms. Since the contributions provided by such a π-σ transfer have positive sign, they cancel to a large extent the negative spin populations which, due to the so called π-σ spin polarization, are generally present in the ring hydrogen 1s-AO's. On the other hand, one may argue that the non-planarity of $\mathrm{I}^{\cdot\ominus}$, in spite of its striking effect on the α-proton coupling constants (a_{H_μ}), should only slightly affect the spin distribution in the cyclic π-system. This statement is justified in view of (1) the almost unimpaired π-electron delocalization over the ten-membered perimeter [3] [4] and (2) the insignificantly small amounts (< 0.005) of spin population involved in the π-σ transfer and required to bring about the observed reduction in the $|a_{H_\mu}|$ values. The π-spin distribution in $\mathrm{I}^{\cdot\ominus}$ should thus hardly differ from that predicted for the radical anion of a hypothetical 1,6-methano[10]annulene having a planar π-system. One can even anticipate that the π-spin populations in $\mathrm{I}^{\cdot\ominus}$ should be similar to those in the radical anion of naphthalene (II), since the pertinent singly occupied HMO's of $\mathrm{I}^{\cdot\ominus}$ and $\mathrm{II}^{\cdot\ominus}$ are identical in the first approximation [1b]. A suitable probe to test whether this expectation is borne out by experiment is provided by a methyl substitution, because the coupling constants of the protons in such a substituent (β-protons[3])) are less sensitive to moderate deviations of the

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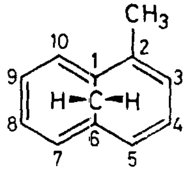
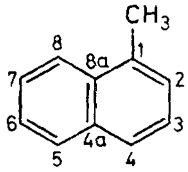
[3]) In ESR. spectroscopy protons linked to a π-electron centre *via* 0, 1, 2 ... sp^3-hybridized carbon atoms are denoted α, β, γ ..., respectively.

π-system from planarity [5]. Accordingly we have studied the radical anion of 2-methyl-1,6-methano[10]annulene (III) [6], and compared its ESR. data with those for the radical anion of 1-methylnaphthalene (IV).



III



IV

Results and Discussion. – The Figure shows the ESR. and ENDOR. spectra taken of the radical anion $III^{\cdot\ominus}$ in 1,2-dimethoxyethane (DME), at –90°, with $K^{\oplus}$ as the counter-ion. Also reproduced is the computed derivative curve which simulates the ESR. spectrum with the aid of the proton coupling constants obtained from the ENDOR. signals. The pertinent values are listed in the Table against the analogous data for $IV^{\cdot\ominus}$. The proton coupling constants for the latter radical anion, which have been now reexamined by ESR. and ENDOR. spectroscopy under the same conditions as those for $III^{\cdot\ominus}$, agree excellently with the values reported previously by other authors [7].

The assignment of the coupling constants to the three β-protons of the methyl substituents in $III^{\cdot\ominus}$ and $IV^{\cdot\ominus}$ is straightforward. The observed values (3.77 and 3.87 Gauss[4]), respectively) are *almost equal*, which indicates *nearly identical* π-spin populations at the methyl substituted centres of the two radical anions.

For the coupling constants (a_{H_μ}) of the seven non-equivalent α-protons in $IV^{\cdot\ominus}$, the assignment made by *Moss et al.* [7] was adopted. This assignment is based on an additivity model in which the changes Δa_{H_μ} caused by a methyl substitution are considered as additive and transferable from one alkyl derivative of naphthalene to another. It has been shown [7] that such a model consistently interrelates the ESR. data for the radical anions of ten methyl substituted naphthalenes, and enables one to assign them more reliably than by means of HMO calculations.

In the case of $III^{\cdot\ominus}$, the coupling constants of the nine remaining non-equivalent protons can be separated into three sets according to their absolute values which are either considerably higher (3.46, 2.87 and 1.95 Gauss), substantially lower (0.54, 0.32, 0.23 and 0.13 Gauss) or slightly larger (1.16 and 1.07 Gauss) than 1 Gauss. Little ambiguity exists with respect to the origin of the two middle-sized coupling constants (1.16 and 1.07 Gauss); they are so close to the value (1.16 Gauss) found for the two equivalent β-protons in the 1,6-methano bridge of $I^{\cdot\ominus}$ [1b] that their assignment to the two corresponding non-equivalent β-protons of $III^{\cdot\ominus}$ is obvious. In addition, since one of the two coupling constants exactly equals the value for $I^{\cdot\ominus}$, it is tempting to assign it to that β-proton which points towards the unsubstituted moiety of $III^{\cdot\ominus}$.

Also, by analogy with the values $|a_{H_\mu}|$ observed for the two sets of four equivalent α-protons in $I^{\cdot\ominus}$ ($\mu = 2,5,7,10$: 2.73 Gauss; $\mu = 3,4,8,9$: 0.09 Gauss) [1b], an over-all assignment of the three large and the four small coupling constants to the two sets

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

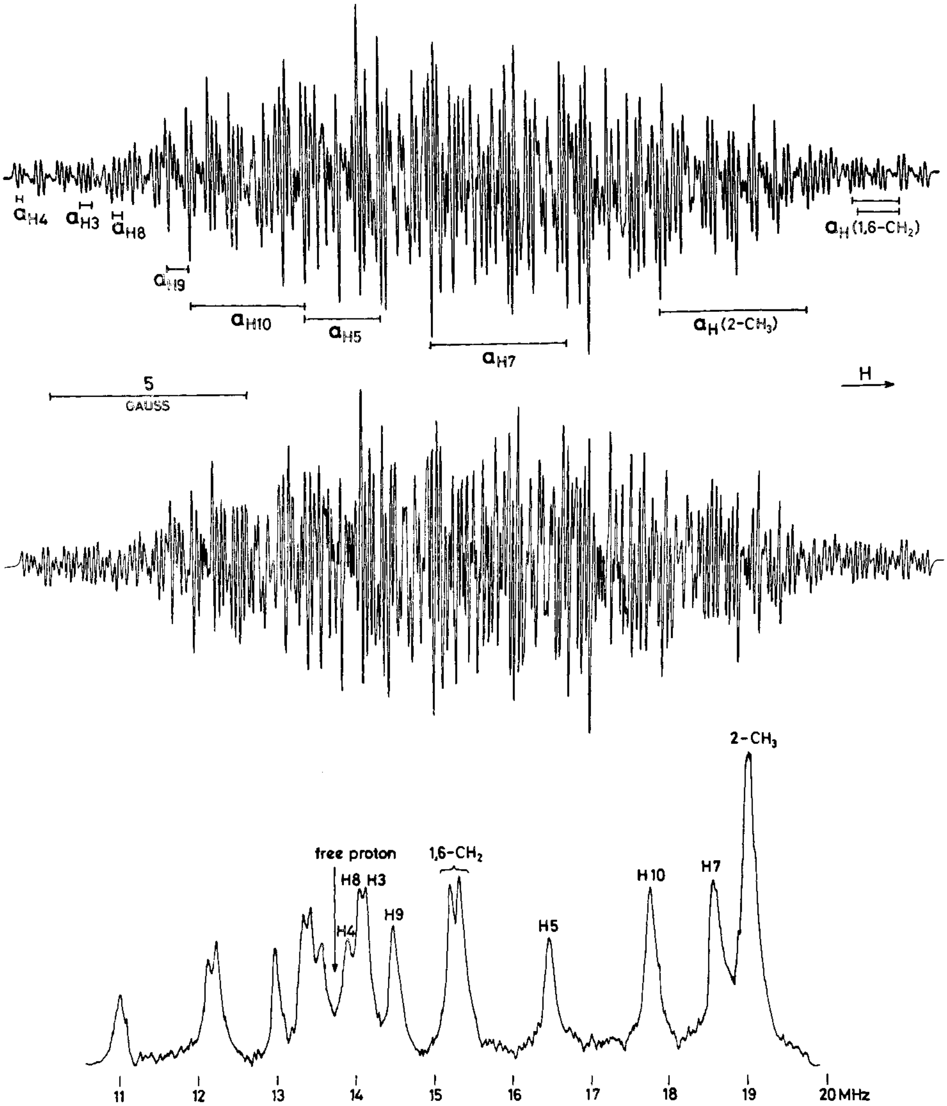

Fig. *ESR. and ENDOR. spectra of the radical anion of 2-methyl-1,6-methano[10]annulene (III).* Top: Experimental ESR. spectrum. Solvent: 1,2-dimethoxyethane; temp.: – 90°; counter-ion: K$^{\oplus}$. Bottom: ENDOR. spectrum taken under the same conditions. Middle: Computer simulated ESR. spectrum. Coupling constants as given in the Table; line-shape: Lorentzian; line-width: 0.06 Gauss

of corresponding non-equivalent α-protons at the unsubstituted centres of III·$^{\ominus}$ is readily accomplished (μ = 5,7,10: 3.46, 2.87 and 1.95 Gauss; μ = 3,4,8,9: 0.54, 0.32, 0.23 and 0.13 Gauss). More problematic is, however, the assignment to the protons at the individual centres μ. In this context, use can be made of the following arguments.

Since the 2-methyl substitution of 1,6-methano[10]annulene (I) to yield the derivative III is not likely to alter substantially the geometry of the ten-membered perimeter, the non-planarity of the π-system should affect the coupling constants a_{H_μ} of the α-protons in $III^{\cdot\ominus}$ to nearly the same extent as in $IV^{\cdot\ominus}$. This means that the changes Δa_{H_μ} on passing from $I^{\cdot\ominus}$ to $III^{\cdot\ominus}$ would mainly be caused by the substituent effect of the methyl group and thus would parallel the corresponding changes for $II^{\cdot\ominus}$ and $IV^{\cdot\ominus}$ in the naphthalene series. Verification of such a hypothesis presupposes that the signs of the values a_{H_μ} under consideration are fairly secured. This is the case with all coupling constants of the α-protons in $II^{\cdot\ominus}$ and $IV^{\cdot\ominus}$, as well as with values a_{H_μ} for the centres $\mu = 2,5,7,10$ of $I^{\cdot\ominus}$ and $\mu = 5,7,10$ of $III^{\cdot\ominus}$. As is evident from the data given in the Table, the changes $\Delta a_{H_\mu} = a_{H_\mu}$ ($III^{\cdot\ominus}$) $-$ a_{H_μ} ($I^{\cdot\ominus}$) for $\mu = 5,7,10$ are readily correlated with $\Delta a_{H_\mu} = a_{H_\mu}$ ($IV^{\cdot\ominus}$) $-$ a_{H_μ} ($II^{\cdot\ominus}$) for $\mu = 4,5,8$, so that a reliable assignment of the three large coupling constants a_{H_μ} to the α-protons at the individual centres $\mu = 5,7,10$ of $III^{\cdot\ominus}$ could be based on such a relationship. An analogous procedure was also applied to the four small values a_{H_μ} for the centres $\mu = 3,4,8,9$ of $III^{\cdot\ominus}$, despite the fact that the signs of the pertinent coupling constants a_{H_μ} ($III^{\cdot\ominus}$) and a_{H_μ} ($I^{\cdot\ominus}$), required for the calculation of the differences Δa_{H_μ}, are uncertain. To overcome this handicap, the signs in question were chosen in such a way as to yield an optimal correlation between the changes Δa_{H_μ} in the 1,6-methano[10]annulene ($\mu = 3,4,8,9$) and naphthalene series ($\mu = 2,3,6,7$). Clearly, the resulting assignment of the four small coupling constants a_{H_μ} to the α-protons at the individual centres $\mu = 3,4,8,9$ of $III^{\cdot\ominus}$ must be regarded as tentative.

Table. *Proton coupling constants* a_{H_μ} (in Gauss = 10^{-4} Tesla) *for the radical anions* $I^{\cdot\ominus}$ *to* $IV^{\cdot\ominus}$

	$a_{H\mu}$				$a_{H\mu}$		
μ	$III^{\cdot\ominus}$	$I^{\cdot\ominus}$	$\Delta a_{H\mu}$	μ	$IV^{\cdot\ominus}$	$II^{\cdot\ominus}$	$\Delta a_{H\mu}$
2	+3.77[a]	−2.73		1	+3.87[a]	−4.95	
5	−1.95		+0.78	4	−4.43		+0.52
7	−3.46		−0.73	5	−5.41		−0.46
10	−2.87		−0.14	8	−5.07		−0.12
3	+0.31[b]	−0.09[b]	+0.40	2	−1.43	−1.85	+0.42
4	−0.13[b]		−0.04	3	−1.98		−0.13
8	+0.23[b]		+0.32	6	−1.54		+0.31
9	−0.54[b]		−0.45	7	−2.30		−0.45
1,6	(±)1.16[c] (±)1.07[c]	(±)1.16[c]					

[a] Coupling constant of three β-protons in a methyl substituent.

[b] Sign uncertain; see text.

[c] Coupling constant of one ($III^{\cdot\ominus}$) or two β-protons ($I^{\cdot\ominus}$) in the 1,6-methano bridge; sign undetermined.

Temperature dependence. – As has been mentioned above, all the data in the Table refer to measurements at −90°. However, it was observed in the case of $I^{\cdot\ominus}$ [1b] that the α-proton coupling constants (a_{H_μ}) strongly depend on temperature. This behaviour has been attributed to slight changes in geometry which ought to exert a more pronounced effect on the values a_{H_μ} for $I^{\cdot\ominus}$ than on those for a planar π-radical. In particular, the larger coupling constant of four equivalent α-protons (2.73 Gauss) was found to exhibit a remarkably negative temperature coefficient ($d|a_{H_\mu}|/dT = -0.003$ Gauss/degree) which is mainly responsible for the decrease in the total extension of the ESR. spectrum from 13.6 Gauss at −90° to 12.1 Gauss at +20°.

Analogous changes should also occur for III $\cdot^{\ominus}$ if our assumption that this radical anion has essentially the same geometry as I $\cdot^{\ominus}$ is correct. Unfortunately, a detailed analysis of the complex ESR. spectrum of III $\cdot^{\ominus}$ (Figure) proves to be increasingly more difficult at higher temperatures, because the resolution of the hyperfine pattern becomes poorer[4] and the ENDOR. signals weaker under these conditions. Nevertheless, a distinct decrease in the three larger $|a_{H_\mu}|$ values of the α-protons (3.46, 2.87 and 1.95 Gauss) is apparent, along with a concomitant shortening in the total extension of the ESR. spectrum from 23.1 Gauss at −90° to 21.7 Gauss at +20°. In contrast, the coupling constant of the three β-protons in the 2-methyl substituent (3.77 Gauss) seems to be much less affected by the raise in temperature.

Conclusions. – The considerations, which motivated the present studies (see Introduction), have been corroborated by the experiment. In accordance with the simplest MO models, not only the π-spin populations themselves, but also their responses to a methyl substitution are very similar in the radical anions of 1,6-methano[10]annulene (I) and naphthalene (II). Thus, *the π-spin distribution in I*$\cdot^{\ominus}$ *must be perturbed only slightly by the deviations of the ten-membered perimeter from planarity.*

Some generalization of these results is possible. It is in line with the idea [8] that moderate deviations from planarity are distributed over a π-perimeter in such a way as not to impair seriously the cyclic π-electron delocalization. Consequently, at least for the discussion of their spectroscopic properties, compounds like I and III can serve as suitable models for the corresponding, synthetically inaccessible planar annulenes. On the other hand, it would be risky to state that the effects of 1,6-bridging in I and of forming a 4a,8a-bond in II are comparable since the similarity of the π-spin distributions in I$\cdot^{\ominus}$ and II$\cdot^{\ominus}$ is due to the particular shape of the pertinent singly occupied orbital which exhibits a nodal plane through the two centres in question.

We thank Prof. *E. Vogel* and Dr. *W. Klug*, Universität Köln, for a sample of 2-methyl-1,6-methano[10]annulene. Support by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Project Nr. 2.313.75), is acknowledged, as well as financial assistance by *Ciba-Geigy* SA, *Sandoz* SA and *F. Hoffmann-La Roche & Co* SA, Basel.

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[4] The line-width increases from 0.06 Gauss at −90° to 0.15 Gauss at +20°. A similar broadening was observed for I $\cdot^{\ominus}$ (see Fig. 1 of [1b]).