153. Electron-Transfer-Induced Conformational Changes. The Example of 1,8-Dimethyl[14]annulene

by **Walter Huber**

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

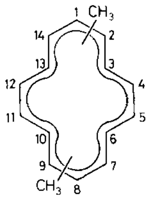
(15.V.84)

Summary

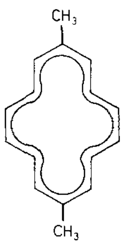
This communication reports ESR-spectroscopic investigations of the radical anion of 1,8-dimethyl[14]annulene (**1**) which possesses a flexible molecular framework allowing configurational and conformational mobility. The ESR and ENDOR spectra indicate that at higher temperatures (T > 160 K), $\mathbf{1}^{\bar{\cdot}}$ exists as a mixture of several distinct isomers. One of them, the sole product at T < 160 K, is found to be energetically preferred. The configuration and the conformation of this species can be determined by interpretation of the hyperfine data in terms of a singly occupied MO of the 14-membered π-perimeter.

Introduction. – Chemical and spectroscopic properties of [4n + 2]annulenes have aroused considerable interest in the past [1–5]. In particular, the study of ionic derivatives has proven of essential importance for understanding the most significant aspects: π-bond localization and delocalization [6–9], influence of nonplanarity and substitution [7] [8], conformational mobility [9] and the nature of the front orbitals (HOMO, LUMO) [6–9].

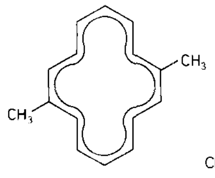
Investigations of charged 10- and 14-membered perimeters have so far been restricted to bridged [7] [8] and didehydro derivatives [6], since the parent compounds [1] [2] exhibit a pronounced reactivity even in the neutral state. Recently, we succeeded in synthesizing the 1,8-dimethyl[14]annulene (**1**) [10]. An X-ray analysis shows that **1** has the conformation **1a** in its crystalline state. From the ^{1}H-NMR studies, it is concluded that **1** exists in solution as an equilibrating mixture of the conformers **1a**, **1b** and **1c**. We were interested in studying the relative stabilities and dynamical behaviour of these



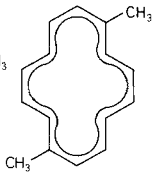
1



1a



1b



1c

conformers by adding one excess electron to this 14π-system. In this communication, we report ESR-spectroscopic investigations on $\mathbf{1}^{\overline{\cdot}}$. Considerations concerning the structure of $\mathbf{1}^{\overline{\cdot}}$ are based on the interpretation of the hyperfine data by symmetry arguments and qualitative MO theory.

Experimental. – The radical anion $\mathbf{1}^{\overline{\cdot}}$ was generated both by electrolytic and chemical reduction of the neutral compound. The electrolysis experiments were carried out in a cylindrical cell constructed at Basel [11]. 1,2-dimethoxyethane (DME) and tetrabutylammonium perchlorate served as the solvent and the supporting salt, respectively. Chemical reduction was performed by reaction of the neutral compound with potassium in ethereal solvents such as DME, tetrahydrofuran (THF), or a mixture of these ethers (DME/THF *ca.* 5:1), either by a direct contact of the solution with the metallic mirror or by the indirect method of solvated electrons [12]. The radical anion thus obtained was persistent up to a temperature of 280 K. The observed ESR spectra of $\mathbf{1}^{\overline{\cdot}}$ did not depend significantly on the method of preparation. The ESR data discussed in this communication were obtained in DME/THF (*ca.* 5:1), since this mixture allows measurements in solution down to 160 K. The ESR and ENDOR spectra of $\mathbf{1}^{\overline{\cdot}}$ were obtained using a *Varian E-9* ESR spectrometer with an attached *Varian E-1700* ENDOR unit.

Results. – *Fig. 1* (left-hand side) shows the ESR spectrum of $\mathbf{1}^{\overline{\cdot}}$ ($g = 2.0028$) in DME/THF at 160 K. The analysis of the hyperfine pattern, assisted by the corresponding ENDOR spectrum (*Fig. 1;* top, right-hand side), yields six coupling constants (in mT): 0.108 (8H), 0.204 (2H), 0.210 (2H), 0.325 (2H), 0.364 (2H) and 0.468 (2H). The ESR and the ENDOR spectra depend markedly on the temperature. Increasing the temperature to 200 K leads to the appearance of four additional ENDOR signals (*Fig. 1;* bottom, right-hand side). The corresponding coupling constants are 0.018, 0.264, 0.402 and 0.432 mT. The appearance of new signals in the ENDOR spectrum is accompanied by the loss of the symmetric shape of the corresponding ESR spectrum. The complexity of this spectrum prohibits its analysis. It is, however, important to mention that all observed temperature-dependent changes in the ESR and the ENDOR spectra are fully reversible.

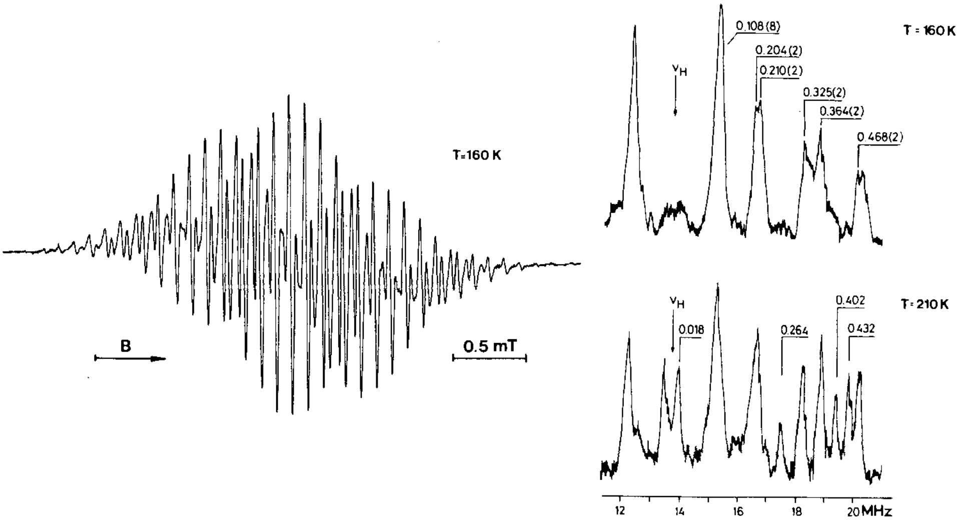


Fig. 1. *ESR spectrum* (left-hand side) *and ENDOR spectra* (right-hand side) *of* $\mathbf{1}^{\overline{\cdot}}$ (solvent DME/THF; counterion: K^+; temperature as indicated)

Discussion. – A qualitative interpretation of the hyperfine data of $\mathbf{1}^{\overline{\cdot}}$ must take into account the dynamical behaviour as well as π-bond localization and delocalization. In the neutral compound **1**, bond alternation is ruled out by the X-ray analysis which indicates a centrosymmetric molecular geometry and typically aromatic bond lengths. Furthermore, it is well-known from ESR studies of the radical anions of bridged and didehydro [14]annulenes [6–8], that there is no reduction of the original symmetry by π-bond fixation on passing from the neutral compounds to the corresponding paramagnetic ions. From these findings, one can assume that π-bond localization does not account for the observed number of coupling constants in $\mathbf{1}^{\overline{\cdot}}$. A further argument supporting this conclusion concerns the temperature dependence of the ENDOR and ESR spectra. Within the temperature ranges employed (ENDOR: 160 K $<$ T $<$ 220 K; ESR: 160 K $<$ T $<$ 280 K), one observes neither a broadening of the ENDOR signals nor a change in the ESR line-width which would indicate the presence of a slow π-bond shift with respect to the hyperfine time-scale.

The conclusions concerning the dynamical behaviour of $\mathbf{1}^{\overline{\cdot}}$ are analogously based on a qualitative interpretation of the ESR and ENDOR spectra. Obviously, the hyperfine data of $\mathbf{1}^{\overline{\cdot}}$ should reflect the highest possible symmetry (D_{2h}; 4 different coupling constants) if the radical anion exists as an equilibrating mixture of the conformers **1a**, **1b** and **1c**. However, the observation of six different coupling constants at 160 K rules out such dynamical behaviour. Increasing the temperature leads to the appearance of four additional ENDOR signals and to an asymmetric shape of the ESR spectrum. Since these changes are fully reversible, one can assume that they are not caused by a chemical conversion of $\mathbf{1}^{\overline{\cdot}}$. We interpret them as being due to the population of additional configurations and/or conformations of the radical anion. The interpretation of the high-temperature ESR spectra is rendered difficult by their complexity. This is explained by the fact that the species existing at higher temperatures differ spectroscopically from each other not only by their coupling constants but also by their g-values. There is no evidence (*e.g.* decreasing number of ENDOR signals and/or increasing symmetry of the ESR spectrum) for fast interconversion of such isomers up to 280 K.

The main question arising therefore concerns the energetically preferred structure of $\mathbf{1}^{\overline{\cdot}}$ at low temperatures (T $>$ 160 K). One can show that of the two configurations existing in the case of the unsubstituted [14]annulene, the *43*- and the *21*-configuration [13], only the former can be realized in $\mathbf{1}^{\overline{\cdot}}$. This conclusion, which is in acccordance with the findings for the neutral 1,8-dimethyl[14]annulene (**1**) [10], follows from the fact, that all conformations with a *21*-configuration possess two different CH_3-groups. The hyperfine data of $\mathbf{1}^{\overline{\cdot}}$, however, indicate equivalent coupling constants for the six protons of the two CH_3-substituents.

By interpreting the coupling constants of $\mathbf{1}^{\overline{\cdot}}$ in terms of the *43*-configuration, one has to consider the three conformations **1a**, **1b** and **1c** which are observed for the neutral compound in solution. Of these, **1a** can unambiguously be ruled out, since the observation of more than four different coupling constants at 160 K is not consistent with the D_{2h}-symmetry of this conformer. The two remaining conformers **1b** and **1c** exhibit C_{2h}-symmetry, leading to seven sets of equivalent coupling constants. (The observation of only six sets is due to an accidental equivalency of the six methyl and two ring protons.) Since a differentiation between **1b** and **1c** is impossible for $\mathbf{1}^{\overline{\cdot}}$ by symmetry criteria, one should, to this end, compare the observed coupling constants with those predicted for **1b** and **1c** by the use of the HMO-*McLachlan* procedure [14] and the *McConnell* relationship [15].

In terms of this model, **1**$^{\overline{\cdot}}$ is preferentially treated as a 14-membered π-perimeter disturbed by a positive inductive effect of the two CH_3-substituents and a conjugative interaction (crossconjugation) of formally nonbonded but spatially proximate π-centers. The inductive effect is taken into account by changing the coulomb integrals α_μ of the substituted π-centers ($\alpha_\mu = \alpha + d\alpha$; $\mu = 4{,}11$ in **1b** or 2,9 in **1c**), and the crossconjugation is simulated by introducing a bond integral $\beta_{\mu\nu}$ between the centers μ and ν ($\mu,\nu = 3{,}13$ and 6,10 in both **1b** and **1c**).

Carrying out such calculations, one must bear in mind that the two lowest antibonding orbitals of an ideal 14-membered π-perimeter (D_{14h}-symmetry) and, in the simple HMO model, those of the unperturbed perimeter of *43*-configuration (D_{2h}-symmetry) are degenerate. Moreover, investigations on bridged [14]annulenes [8] clearly demonstrate that the type of the singly occupied molecular orbital in radical anions with a disturbed 14-membered π-perimeter sensitively depends on perturbations such as inductive effects and crossconjugation (homoconjugation). To avoid misinterpretation, the parameters $d\alpha$ and $\beta_{\mu\nu}$ have been varied within a wide range ($d\alpha = -0.1$–-0.3β on the centers $\mu = 2{,}9$ for **1c** or $\mu = 4{,}11$ for **1b**; $\beta_{\mu\nu} = 0.1$–0.5β for $\mu,\nu = 3{,}13$ and 6,10). The correlation of computed and observed coupling constants is most satisfactory for a rather high value of $\beta_{\mu\nu}$ ($= 0.5\beta$) and favours the conformation **1c** (see *Table*). An inspection of the LCAO coefficients of the singly occupied molecular orbital shows that in **1**$^{\overline{\cdot}}$ the lowest antibonding orbital is ψ_S-like (see *Fig. 2*). Obviously the stabilization of this orbital with respect to a ψ_A-like is a consequence of the dominant C(3)–C(13)- and C(6)–C(10)-crossconjugation.

The postulation of such a crossconjugation certainly demands further comment. It may be argued that the interatomic distance between C(3)–C(13) and C(6)–C(10) which was determined for the neutral compound (conformation **1a**) by X-ray analysis (2.89 Å) [16] is too large for such an interaction. However, the example of the bishomocyclooctatetraene dianion [17] shows, that structural prerequisites, necessary for an overlap of atomic orbitals on formally nonbonded π-centers, can be brought about by the uptake of negative charge. Since **1** possesses a highly flexible molecular framework, it may be tentatively assumed, that the electron-transfer-induced changes of the structural features (*e.g.* interatomic distances and twist angles), on passing from the neutral compound to the radical anion **1**$^{\overline{\cdot}}$, increase an overlap between the π-orbitals on C(3,6,10,13).

Table. *Comparison of the Observed and Calculated Coupling Constants of* **1**$^{\overline{\cdot}}$ *in mT*

	μ						
	1,8	2,9	3,10	4,11	5,12	6,13	7,14
$a_{H\mu}$ (exp)	0.468	0.108a)	0.364	0.204	0.210	0.325	0.108a)
$a_{H\mu}$ (cal)b)	−0.401	0.127	−0.375	−0.172	−0.189	−0.351	0.121c)

a) Coupling constants of the methyl protons and of the protons on C(7,14) are accidentally equivalent.

b) Calculated coupling constants for the radical anion **1**$^{\overline{\cdot}}$ with the conformation **1c** ($\alpha_{2,9} = \alpha - 0.2\beta$; $\beta_{3,13} = \beta_{6,10} = 0.5\beta$).

c) Within the *McConnell* relationship the same proportionality between spin densities and methyl protons is used as for the α-protons ($Q = -2.5$ mT).

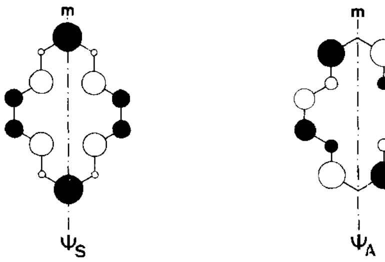


Fig. 2. *Schematical representation of the two lowest antibonding molecular orbitals of a 14-membered π-perimeter.* The orbitals are characterized as symmetric (ψ_S) of antisymmetric (ψ_A) with respect to the mirror plane m. The areas surrounded by the circles are proportional to the square of the LCAO coefficients whereby blank and filled circles signify different signs.

It is finally most important to note that for the radical anions of bridged [14]annulenes with a pyrene-type perimeter (*43*-configuration) a single occupancy of a ψ_S-like orbital has previously been observed [8]. For these radical anions, namely those of *trans*-10b,10c-dihydropyrene and its 10b,10c-dimethyl derivative as well as that of the *trans*-15,16-dimethyl-1,4:8,11-ethanediyliden[14]annulene, the stabilization of a ψ_S- relative to a ψ_A-like orbital has been rationalized in terms of a hyperconjugative interaction of the perimeter π-orbital with bridge σ-orbitals of adequate symmetry. In view of the present evidence it seems, however, appropriate to suggest that in these radical anions too, a homoconjugative interaction might play the dominant role in determining the energetic sequence of the lowest antibonding molecular orbitals.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. Financial assistance by *Ciba-Geigy SA*, *Sandoz SA* and *F. Hoffmann-La Roche & Cie., SA* is likewise acknowledged. The author thanks Prof. *F. Gerson* for his interest in this work and Prof. *K. Müllen* for samples of compound **1**.

REFERENCES

[1] a) *F. Sondheimer & Y. Gaoni*, J. Am. Chem. Soc. *82*, 5756 (1960). b) *Y. Gaoni, A. Melera, F. Sondheimer & R. Wolovsky*, Proc. Chem. Soc. *1964*, 397.

[2] a) *S. Massamune, K. Hojo, G. Bigam & D.L. Rabenstein*, J. Am. Chem. Soc. *93*, 4966 (1971). b) *S. Massamune & N. Darby*, Acc. Chem. Res. *5*, 272 (1972).

[3] a) *E. Vogel*, Pure Appl. Chem. *20*, 237 (1969). b) *E. Vogel*, Pure Appl. Chem. *28*, 355 (1971).

[4] *V. Boekelheide*, Pure Appl. Chem. *44*, 751 (1975).

[5] *W. Huber, J. Lex, T. Meul & K. Müllen*, Angew. Chem. *93*, 401 (1981); Angew. Chem. Int. Ed. *20*, 391 (1981).

[6] a) *F. Gerson, J. Jachimowicz, M. Nakagawa & M. Iyoda*, Helv. Chim. Acta *57*, 2141 (1974). b) *K. Müllen, W. Huber, T. Meul, M. Nakagawa & M. Iyoda*, J. Am. Chem. Soc. *104*, 5403 (1982).

[7] a) *F. Gerson, E. Heilbronner, W.A. Böll & E. Vogel*, Helv. Chim. Acta *48*, 1494 (1965). b) *F. Gerson, K. Müllen & E. Vogel*, Helv. Chim. Acta *54*, 2731 (1971). c) *F. Gerson, K. Müllen & Ch. Wydler*, Helv. Chim. Acta *59*, 1371 (1976).

[8] a) *F. Gerson, E. Heilbronner & V. Boekelheide*, Helv. Chim. Acta *47*, 1123 (1964). b) *Ch. Elschenbroich, F. Gerson & V. Boekelheide*, Helv. Chim. Acta *58*, 1245 (1975). c) *F. Gerson, K. Müllen & E. Vogel*, J. Am. Chem. Soc. *94*, 2924 (1972). d) *F. Gerson, W. Huber & J. Lopez*, submitted for publication in J. Am. Chem. Soc. e) *W. Huber*, Helv. Chim. Acta. *67*, 625 (1984).

[9] *J.F.M. Oth, E.P. Woo & F. Sondheimer,* J. Am. Chem. Soc. *95,* 7337 (1973).

[10] *E. Vogel, H.-W. Engels, W. Huber, J. Lex & K. Müllen,* J. Am. Chem. Soc. *104,* 3729 (1982).

[11] a) *F. Gerson, H. Ohya-Nishiguchi & Ch. Wydler,* Angew. Chem. *88,* 617 (1976); Angew. Chem. Int. Ed. *15,* 552 (1976). b) *H. Ohya-Nishiguchi,* Bull. Chem. Soc. Jpn. *52,* 2064 (1979).

[12] *F. Gerson, G. Moshuk & M. Schwyzer,* Helv. Chim. Acta *54,* 361 (1971).

[13] *J.F.M. Oth,* Pure Appl. Chem. *24,* 573 (1971).

[14] *A.D. McLachlan,* Mol. Phys. *3,* 233 (1960).

[15] *H.H. McConnell,* J. Chem. Phys. *24,* 632 (1956).

[16] *J. Lex,* private communication.

[17] *W. Huber, K. Müllen, R. Busch, W. Grimme & J. Heinze,* Angew. Chem. *94,* 294 (1982); Angew. Chem. Int. Ed. *21,* 301 (1982).