[15] *H. Nozaki, Z. Yamaguti & R. Noyori*, Tetrahedron Letters *1965*, 37; *R. C. Cookson, A. G. Edwards, J. Hudec & M. Kingsland*, Chem. Commun. *1965*, 98.
[16] *A. Butenandt, A. Wolff & P. Karlson*, Chem. Ber. *74*, 1308 (1941); *H. Wehrli & K. Schaffner*, Helv. *45*, 385 (1962), und dortige Literaturhinweise; *R. J. Chambers & B. A. Marples*, Tetrahedron Letters *1971*, 3747, 3751.
[17] *C. G. Hatchard & C. A. Parker*, Proc. Roy. Soc. *A 235*, 518 (1956).
[18] *M. Hanck, C. E. Harding & J. L. Deroque*, Chem. Ber. *105*, 421 (1972).

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14. ESR. Spectra of Radical Anions in the Cyclazine Series

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Summary. The ESR. spectra of the radical anions of three cyclazines are described. Their π-spin distributions are discussed in terms of simple MO theory and compared with those of structurally related species.

In this paper we report the results of ESR. studies on the radical anions of 6-azacycl[3,2,2]azine (I), 6-nitrocycl[3,2,2]azine (II) and cyclopenta[h]cycl[4,2,2]-azine (III)[3]. These three compounds have been recently synthesized by *Jessep & Leaver* [1].

Experimental part. The radical anions $I^{\ominus}$, $II^{\ominus}$ and $III^{\ominus}$ can be prepared by both chemical and electrolytical methods. Electrolysis [N,N-dimethylformamide (DMF) as solvent and tetraethylammonium perchlorate as supporting salt] is, however, preferable to reaction with an alkali metal [potassium or sodium in 1,2-dimethoxyethane (DME)] for two reasons:

a) Controlled potential electrolysis inhibits the formation of diamagnetic dianions $I^{2\ominus}$, $II^{2\ominus}$, or $III^{2\ominus}$, if the applied voltage remains sufficiently low. In contrast, it is difficult to limit the alkali metal reduction to the uptake of only a single electron. This is particularly true for the cyclazines I and III, where the reaction with sodium or potassium favours the formation of the dianions.

b) The use of a relatively polar solvent (DMF) and bulky cations $[(C_2H_5)_4N^{\oplus}]$ for electrolysis prevents the radical anions from closely associating with their gegenions. Such an association, which is known to complicate the ESR. spectra [2a], occurs when $I^{\ominus}$, $II^{\ominus}$ and $III^{\ominus}$ are produced by alkali metal reduction in nonpolar ethers (DME) with $Na^{\oplus}$ or $K^{\oplus}$ as gegenions.

The radical anions $I^{\ominus}$ and $II^{\ominus}$ are sufficiently stable to be conveniently studied at room temperature. On the other hand, the halflife of $III^{\ominus}$ is only a few minutes at +25°, making low temperature studies desirable.

Results. Figs. 1, 2 and 3 show the ESR. spectra of the electrolytically generated radical anions $I^{\ominus}$, $II^{\ominus}$ and $III^{\ominus}$, along with the computer-simulated derivative curves.

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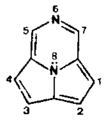
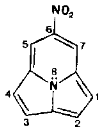
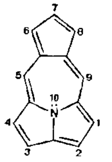
[3] For the sake of continuity the nomenclature and numbering of the parent compound IV [6] has been retained. To conform with the IUPAC rules: IV becomes pyridino[6,1,2-*cd*]pyrrolizine; hence I is pyrazino[6,1,2-*cd*]pyrrolizine, II is 6-nitro-pyridino[6,1,2-*cd*]pyrrolizine and III is cyclopenta[4,5]azepino[7,1,2-*cd*]pyrrolizine.

Table. *Coupling constants of protons and ^{14}N nuclei* (a_H and a_N in gauss), *and calculated π-spin populations* (ϱ) *in the radical anions* $I^{\ominus}$, $II^{\ominus}$ *and* $III^{\ominus}$.

	$I^{\ominus}$	$a_{H(1,4)} = 1.07 \pm 0.01$; $a_{H(2,3)} = 5.92 \pm 0.04$; $a_{H(5,7)} = 6.22 \pm 0.04$; $a_{N6} = 2.03 \pm 0.02$; $a_{N8} = 0.55 \pm 0.01$;	$\varrho_{1,4} = 0.045$ $\varrho_{2,3} = 0.233$ $\varrho_{5,7} = 0.237$ $\varrho_{6} = -0.066$ $\varrho_{8} = -0.013$
	$II^{\ominus}$	$a_{H(1,4)} = 1.28 \pm 0.01$; $a_{H(2,3)} = 0.47 \pm 0.01$; $a_{H(5,7)} = 3.42 \pm 0.02$; $a_{N8} = 0.82 \pm 0.01$; $a_N^{NO_2} = 9.75 \pm 0.05$;	$\varrho_{1,4} = 0.053$ $\varrho_{2,3} = -0.031$ $\varrho_{5,7} = 0.153$ $\varrho_{8} = 0.023$ $\varrho_{N} = 0.239$ $\varrho_{O} = 0.199$
	$III^{\ominus}$	$a_{H(1,4)} = 2.91 \pm 0.02$; $a_{H(2,3)} = 0.53 \pm 0.01$; $a_{H(5,9)} = 6.11 \pm 0.04$; $a_{H(6,8)} = 0.12 \pm 0.01$; $a_{H(7)} = 3.60 \pm 0.02$; $a_{N10} = 1.55 \pm 0.01$;	$\varrho_{1,4} = 0.115$ $\varrho_{2,3} = -0.057$ $\varrho_{5,9} = 0.318$ $\varrho_{6,8} = -0.017$ $\varrho_{7} = 0.116$ $\varrho_{10} = 0.047$

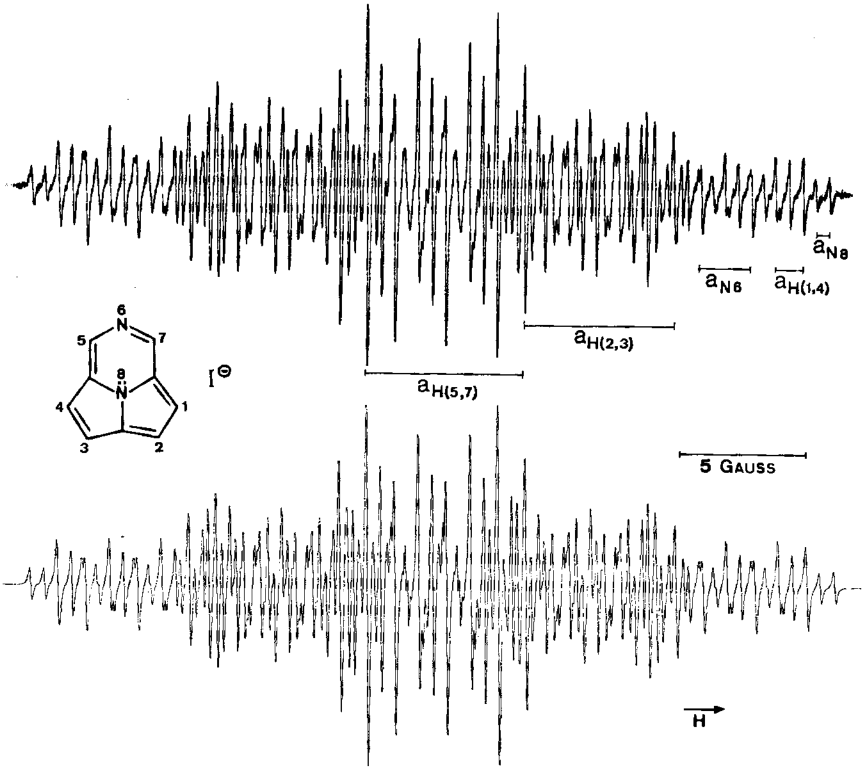


Fig. 1. *ESR. spectra of the radical anion* $I^{\ominus}$. Top: *Experimental spectrum.* Solvent: DMF; gegenion: $(C_2H_5)_4N^{\oplus}$; temp.: + 25°

Bottom: *Computer-simulated spectrum.* Coupling constants given in the Table; line-width: 0.1 gauss; line-form: Lorentzian

The proton and ^{14}N coupling constants are given in Table 1. Their assignment is based on analogy with related radical anions (see Discussion) and on the excellent correlation with π-spin populations calculated by the *McLachlan* procedure [3]. These values are also listed in the Table, beside the experimental data.

For the Coulomb integrals $\alpha_{\dot{N}}$ (I) and $\alpha_{\ddot{N}}$ (I, II and III) use was made of the standard values $\alpha+0.5\beta$ and $\alpha+1.5\beta$, respectively [4a]. In the case of the nitro group (II), the parameters of *Rieger* and *Fraenkel* [5] were adopted. The conventional value of 1.2 was taken for λ in the *Mc Lachlan* procedure [3]. No variation of parameters has been attempted in order to obtain an optimal fit between the calculated π-spin populations and the observed proton coupling constants.

Discussion. *6-Azacycl[3,2,2]azine* (I). The ESR. data for $I^{\ominus}$ (Table) are strikingly similar to those previously found for the radical anion of the parent cycl-[3,2,2]azine (IV): $a_{H(1,4)} = 1.13$; $a_{H(2,3)} = 5.34$; $a_{H(5,7)} = 6.02$; $a_{H(6)} = 1.20$ and $a_{N8} = 0.60$ gauss [6] [7]. Such a similarity points to an almost identical π-spin distribution in the two radical anions. It is consistent with theoretical considerations,

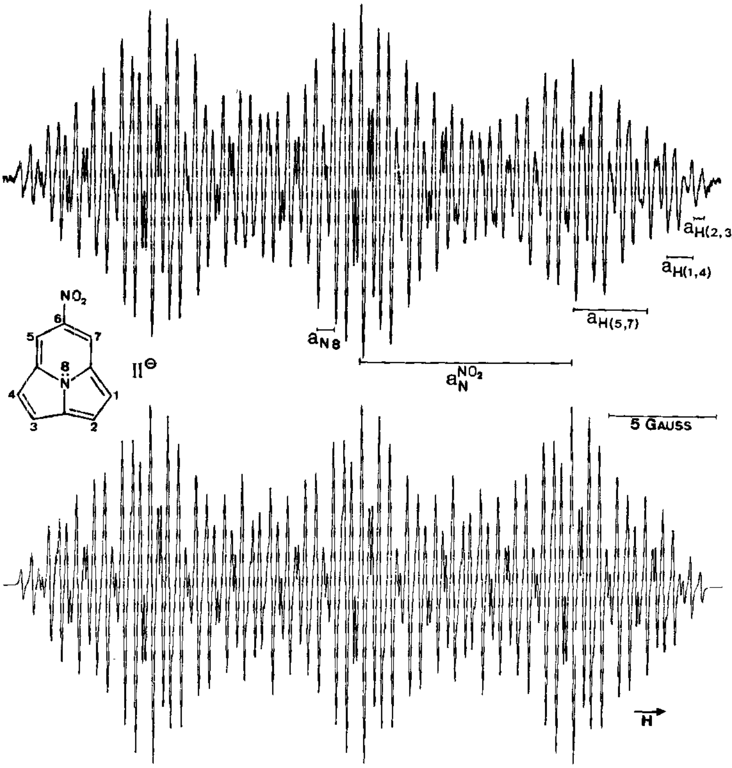


Fig. 2. *ESR. spectra of the radical anion $II^{\ominus}$.* Top: *Experimental spectrum.* Solvent: DMF; gegenion: $(C_2H_5)_4N^{\oplus}$; temp.: + 25°

Bottom: *Computer-simulated spectrum.* Coupling constants given in the Table; line-width: 0.1 gauss; line-form: Lorentzian. The simulated curve does not account for the relative broadening of the high-field group of lines since the 6-aza-nitrogen lies in a nodal plane of the lowest antibonding π-orbital [8] and its introduction into the cycl[3,2,2]azine system does not affect this orbital to a first approximation.

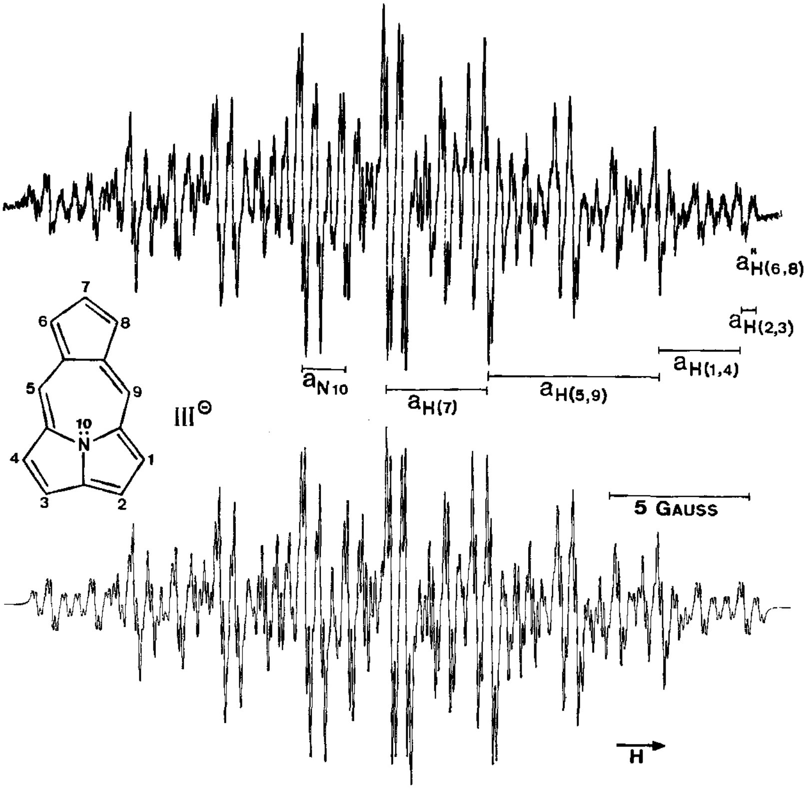


Fig. 3. *ESR. spectra of the radical anion III$^{\ominus}$.* Top: *Experimental spectrum.* Solvent: DMF; gegenion: $(C_2H_5)_4N^{\oplus}$; temp.: – 50°
Bottom: *Computer-simulated spectrum.* Coupling constants given in the Table; line-width: 0.1 gauss; line-form: Lorentzian.

An alternative approach is to regard IV and I as nitrogen-bridged [*10*]annulene and aza[*10*]annulene, respectively [7]. Experimental data for IV$^{\ominus}$ and I$^{\ominus}$ indicate that the singly occupied orbital of these radical anions resembles the antibonding perimeter HMO ψ_{a-} which is antisymmetric with regard to a mirror plane passing through two opposite π-centers and perpendicular to the molecular plane. This HMO is schematically depicted in Fig. 4, together with its degenerate symmetric counterpart ψ_{a+}.

The single occupancy of a perimeter-like orbital in IV$^{\ominus}$ and I$^{\ominus}$ can be interpreted as follows [7]: Of the two degenerate lowest antibonding HMO's (ψ_{a+} and ψ_{a-}) only ψ_{a+} can mix with the lone pair orbital (ψ_n) of the central nitrogen. Such a mixing yields modified orbitals ψ_n' and ψ_{a+}', the former being stabilized and the latter destabilized relative to ψ_n and ψ_{a+}, respectively. As a result, ψ_{a-} is lower in energy than ψ_{a+}' and takes up the odd electron in the radical IV$^{\ominus}$ (Fig. 4). The fact that the same holds for $I^{\ominus}$ implies no change in this energy sequence by the aza-substitution. Evidently, although such a substitution considerably stabilizes ψ_{a+} (or ψ'_{a+}) relative to ψ_{a-} (cf. the relevant coefficients in Fig. 4), it is not sufficient to counterbalance the effect of the amino-bridging.

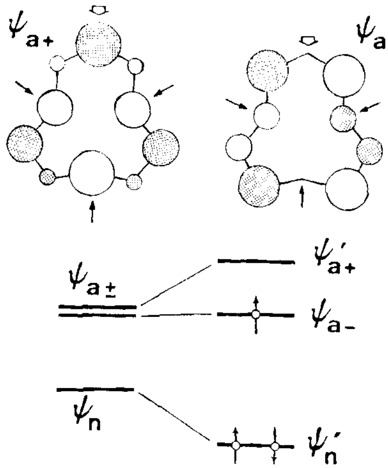


Fig. 4. Top: *Degenerate lowest antibonding HMO's* (ψ_{a+} and ψ_{a-}) *of the ten-membered perimeter* The radii of the circles are proportional to the absolute values of the LCAO-coefficients at the respective π-centers. The blank and dotted circles symbolize different signs of the coefficients. The centers which are bridged in the cycl[3,2,2]azine (IV) and its 6-aza-derivative (I) have been marked by solid arrows. The open arrows denotes the aza-substitution in I.

Bottom: *Splitting and occupancy of the HMO's* ψ_{a+} *and* ψ_{a-}, *and the lone pair orbital* ψ_n *in the radical anion* $IV^{\ominus}$ *of cycl[3,2,2]azine.*

Because the π-spin distributions in $IV^{\ominus}$ and $I^{\ominus}$ are almost identical, and the π-spin population ϱ_6 at the aza-nitrogen is of much smaller absolute magnitude than the values $\varrho_5 = \varrho_7$ at the neighbouring carbon centers, one can make a reliable estimate of the parameters Q_N and Q_{CN} in the formula $a_{N6} = Q_N\varrho_6 + Q_{CN}(\varrho_5+\varrho_7)$ [9]. As shown in a separate communication [10], values of $+27.5 \pm 1.0$ and -1.5 ± 0.2 are deduced, along with a negative sign for a_{N6}.

6-Nitrocycl[3,2,2]azine (II). In contrast to the 6-aza-substitution which does not markedly alter the π-spin distribution in the radical anion $IV^{\ominus}$, introduction of a nitro group in the 6-position of cycl[3,2,2]azine has a profound effect on such a distribution. Owing to its relatively high electron affinity, the nitro substituent in $II^{\ominus}$ retains the bulk of the π-spin population. As demonstrated by the diagrams of Fig. 5, the lowest antibonding HMO of II bears a strong resemblance to that of nitrobenzene (V)[4]. Accordingly, the nitro-^{14}N and *ortho*-proton coupling constants for $II^{\ominus}$ ($a_N^{NO_2} =$ 9.75 and $a_{H(5,7)} = 3.42$ gauss) are nearly equal to the analogous values for $V^{\ominus}$: $a_N^{NO_2} = 9.70$[5]) and $a_{H(2,6)} = 3.36$ gauss [5].

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[4]) The same heteroatom parameters were used here as in the calculation of the π-spin populations (see Results).

[5]) The coupling constant $a_N^{NO_2}$ for a nitro substituent is very sensitive to the nature of the solvent and of the gegenion. The value quoted for $V^{\ominus}$ [5] was measured under conditions analogous to those used for $II^{\ominus}$ (DME and tetraalkylammonium perchlorate as the solvent and gegenion, respectively).

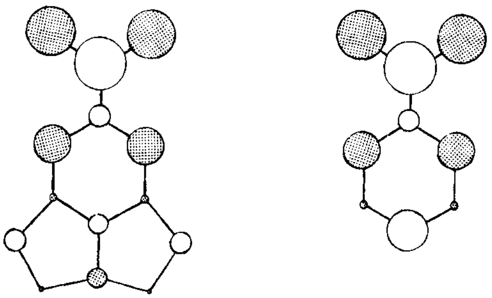

Fig. 5. *Lowest antibonding HMO's of 6-nitrocycl[3,2,2]azine (II) and nitrobenzene* (V)[4])
Schematic representation as in Fig. 4.

It is therefore not surprising that the approximate formula $a_N^{NO_2} = Q_N\varrho_N + 2Q_{ON}\varrho_O$, in which the parameters $Q_N = +99$ and $Q_{ON} = -36$ gauss were derived from the experimental data for $V^\ominus$ and its polysubstituted derivatives [5], also holds for $II^\ominus$. Use of the calculated π-spin populations ϱ_N and ϱ_O (Table) yields the coupling constant $a_N^{NO_2} = +9.33$, in fair agreement with experiment. (The positive sign of $a_N^{NO_2}$ can be deduced from the relative broadening of the highfield lines due to the ^{14}N hyperfine anisotropy [2b]: cf. Fig. 2).

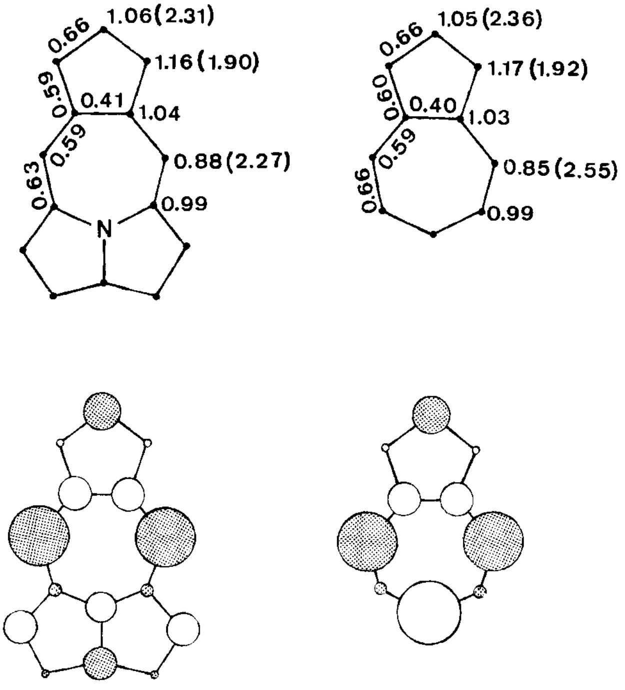

Fig. 6. Top: *Pertinent HMO charges, bond orders and atom localization energies*[6]) (in parentheses) *for cyclopenta[h]cycl[4,2,2]azine* (III)[4]) *and azulene* (VI).
Absolute values in units of ß are given for the localization energies.
Bottom: *Lowest antibonding HMO's of III*[4]) *and VI*.
Schematic representation as in Fig. 4.

Cyclopenta[h]cycl[4,2,2]azine (III). The numbers listed in Fig. 6 show that the pertinent π-charges, π-bond orders and atom localization energies 6) of the cyclazine III 4) are similar to those of azulene (VI), the framework of which is contained in III. There is also an essential correspondence in nodal properties of the HMO's which determine the long wavelength electronic transitions in the two molecules. Such a correspondence is illustrated by the diagrams of Fig. 6 for the lowest antibonding HMO's of III 4) and VI. In view of all these common features presented by the HMO models of the two compounds, one may expect that the chemical behaviour and physical properties of the cyclazine III will exhibit some characteristics of azulene (VI). Indeed, the facile electrophilic substitution in the 6,8-positions and the electronic spectrum of III [1] are reminiscent of VI [12].

The similarity in spectroscopic properties also holds for the radical anions $III^{\ominus}$ and $VI^{\ominus}$. According to the orbital diagrams of Fig. 6, the π-spin population in $III^{\ominus}$ should be largely localized on the azulene-like moiety and its distribution should closely follow the pattern of $VI^{\ominus}$. This prediction is nicely confirmed by experiment, since the relevant proton coupling constants for $III^{\ominus}$ ($a_{H(5,9)} = 6.11$; $a_{H(6,8)} = 0.12$ and $a_{H(7)} = 3.60$ gauss) compare favourably with the analogous values for $VI^{\ominus}$ ($a_{H(4,8)} = 6.22$; $a_{H(1,3)} = 0.27$ and $a_{H(2)} = 3.95$ gauss) [13].

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BIBLIOGRAPHY

[1] *M. A. Jessep & D. Leaver*, Chem. Commun. (London) *1970*, 790.

[2] *F. Gerson*, "High Resolution ESR Spectroscopy", J. Wiley and Sons Ltd., New York, and Verlag Chemie, Weinheim 1970; a) Appendix A.2.2; b) Appendix A.1.3.

[3] *A. D. McLachlan*, Molec. Physics. *3*, 233 (1960).

[4] *A. Streitwieser Jr.*, "Molecular Orbital Theory for Organic Chemists", J. Wiley & Sons, New York, 1961, a) p. 135; b) p. 335.

[5] *P. M. Rieger & G. K. Fraenkel*, J. chem. Physics *39*, 609 (1963).

[6] *F. Gerson & J. D. W. van Voorst*, Helv. *46*, 2257 (1963).

[7] *F. Gerson & J. H. Hammons* in "Nonbenzenoid Aromatics" (*J. P. Snyder* ed.), Academic Press, New York, 1971; Vol. II, p. 137–139.

[8] *N. M. Atherton, F. Gerson & J. N. Murrell*, Molec. Physics *6*, 265 (1963).

[9] *M. Karplus & G. K. Fraenkel*, J. chem. Physics *35*, 1312 (1961).

[10] *F. Gerson*, Molec. Physics, *24*, 445 (1972).

[11] *E. Heilbronner & H. Bock*, «Das HMO-Modell und seine Anwendung», Verlag Chemie, Weinheim, 1970; «Grundlagen und Handhabung», Kap. 12.6.

[12] *E. Heilbronner* in "Nonbenzenoid Aromatic Compounds" (*D. Ginsburg* ed.), p. 171–276; J. Wiley (Interscience), New York, 1959.

[13] *I. Bernal, P. H. Rieger & G. K. Fraenkel*, J. chem. Physics *37*, 1489 (1962).

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6) These are the energies required to localize an electron pair on a π-center (denoted L_r^+ in [4b] and $A_\mu^{\ominus}$ in [11]).