200. The Radical Ions of Indolizino[6,5,4,3-*aij*]quinoline and Some of its Derivatives

by **Fabian Gerson*** and **André Metzger**[1])

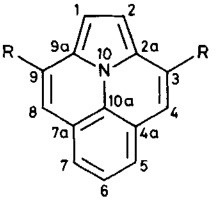
Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

(28.VI.83)

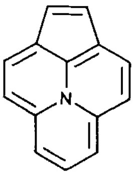
Summary

Indolizino[6,5,4,3-*aij*]quinoline (**1**) and its 3,9-dimethyl- (**2**), di-*tert*-butyl- (**3**) and diphenyl-(**4**) derivatives yield persistent radical cations which have been studied by ESR and ENDOR spectroscopy. The corresponding radical anions have also been prepared, but only that of **3** was amenable to a complete characterization by hyperfine data. The π-spin populations in the radical anions are essentially localized on the 13-membered C-perimeter, and thus both the HOMO and LUMO of **1** exhibit an 'annulenyl character'. The radical anions of **1** and **2** have gradually been converted into those of the corresponding 3,4-dihydro derivatives (**1**-H_2 and **2**-H_2) which have been unambiguously identified by a combination of preparative and spectroscopic methods.

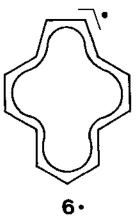
Introduction. – In [1], the synthesis of indolizino[6,5,4,3-*aij*]quinoline (**1**) and its 3,9-disubstituted derivatives, **2**, **3** and **4**, has been described.



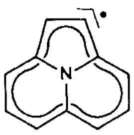
1 R = H
2 R = Me
3 R = *t*-Bu
4 R = Ph



5



6·



7·

The novel heteroarene **1**, for which the trivial name 'ullazine' has been suggested [1], is an isomer of cyclopenta[*ij*]pyrido[2,1,6-*de*]quinolizine (cyclopenta[*cd*]cycl[3.3.3]azine; **5**) synthesized several years ago [2]. Moreover, **1** is iso-π-

---

[1]) Present address: *Ciba-Geigy SA*, CH-4133 Schweizerhalle.

electronic with pyrene, to which it is related in the same way as pyrrole is to benzene. One also notes that **1** embraces both [13]annulenyl ($\mathbf{6}^{\cdot}$) and cycl[3.2.2]-azinyl ($\mathbf{7}^{\cdot}$) as sub-structures. Since the compound **1** and its derivatives **2**, **3** and **4** are electron-rich π-systems, they should readily form the radical cations. This expectation is borne out by the studies of $\mathbf{1}^{\oplus}$ to $\mathbf{4}^{\oplus}$ reported in the present paper which also deals with the corresponding radical anions $\mathbf{1}^{\ominus}$ to $\mathbf{4}^{\ominus}$.

Results. - *Half-Wave Potentials. Table 1* gives the half-wave oxidation and reduction potentials of **1**, **2**, **3** and **4**, which were measured at room temperature with *N,N*-dimethylformamide and tetraethylammonium tetrafluoroborate (0.1 M) as the solvent and the supporting salt, respectively. A Pt-wire was used as the working electrode for the oxidation, while S.C.E served as the counter-electrode. The reduction was conducted at a dropping Hg-electrode with a Pt-counter-electrode.

Table 1. *Half-Wave Oxidation and Reduction Potentials* (in V *vs.* S.C.E[a])) *of Indolizino[6,5,4,3-*aij*]-quinoline* (**1**) *and its 3,9-Disubstituted Derivatives* **2**, **3** *and* **4**

	1 (R=H)	**2** (R=Me)	**3** (R=*t*-Bu)	**4** (R=Ph)
Oxidation	+0.72	+0.66	+0.71	+0.76
Reduction	−2.48	−2.46	−2.49	−2.19; −2.46

[a]) Experimental error: ±0.01 V.

Radical Cations. ESR and ENDOR studies of $\mathbf{1}^{\oplus}$, $\mathbf{2}^{\oplus}$, $\mathbf{3}^{\oplus}$ and $\mathbf{4}^{\oplus}$ were performed on samples prepared by oxidation of the corresponding neutral compounds with $AlCl_3$ in CH_2Cl_2 at 298 K. The radical cations thus obtained were persistent; their concentrations in solution did not substantially decrease upon standing for several days. Analysis of the ESR spectra (*Fig. 1* and *2*), assisted by the ENDOR measurements *(Fig. 3)*, yielded the hyperfine data listed in *Table 2*. Assignments of the coupling constants are straightforward for the ^{14}N-nucleus and the single proton in the 6-position of $\mathbf{1}^{\oplus}$ to $\mathbf{4}^{\oplus}$, as well as for the six equivalent protons of the two methyl groups in $\mathbf{2}^{\oplus}$ and the 18 equivalent protons of the two *tert*-butyl groups in $\mathbf{3}^{\oplus}$. Also, the coupling constant of the two equivalent protons in the 3,9-positions of $\mathbf{1}^{\oplus}$ can reliably be assigned by comparison with that of the methyl protons in $\mathbf{2}^{\oplus}$. Assignments of the three remaining coupling constants to pairs of equivalent protons in the 1,2-, 4,8- and 5,7-positions of $\mathbf{1}^{\oplus}$ to $\mathbf{4}^{\oplus}$ are based on a MO model presented in the *Discussion.*

The *g*-value of all four radical cations is 2.0027±0.0001.

Radical Anions. Preparation of $\mathbf{1}^{\ominus}$, $\mathbf{2}^{\ominus}$, $\mathbf{3}^{\ominus}$ and $\mathbf{4}^{\ominus}$ for spectroscopic studies was carried out both 'chemically' (with K-metal) and electrolytically at 193 K. The solvents used in the chemical reduction were 1,2-dimethoxyethane (DME), 2-methyltetrahydrofuran (MTHF), and mixtures of DME and MTHF with hexamethylphosphoric acid triamide (HMPT). For the electrolysis, DME and tetrabutylammonium perchlorate (0.1 M) served as the solvent and the supporting salt, respectively. The radical anion of the unsubstituted compound **1** and those of its dimethyl- (**2**) and diphenyl derivative (**4**) gave rise to poorly resolved ESR spectra.

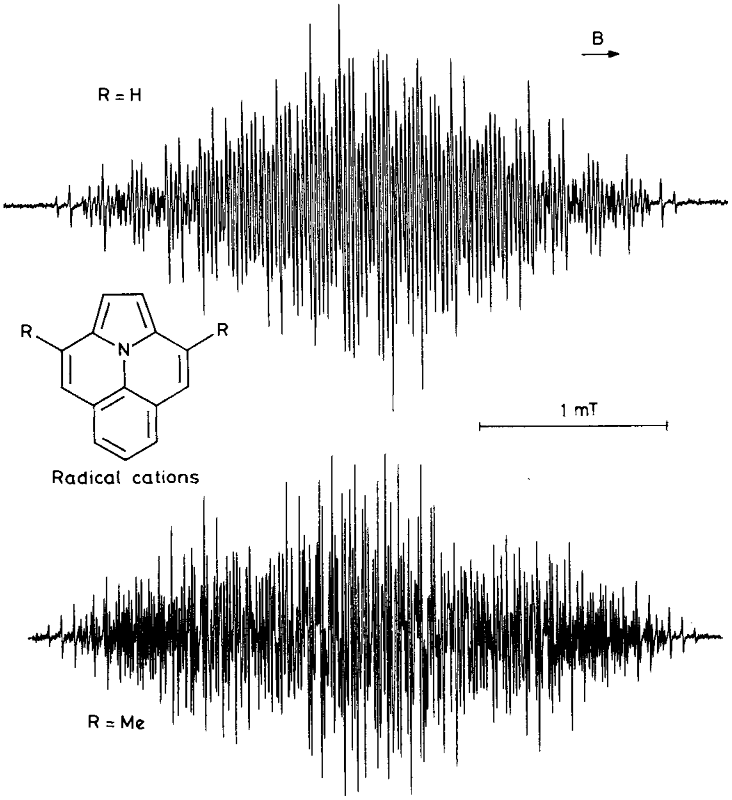


Fig. 1. *ESR spectra of the radical cations of indolizino[6,5,4,3-*aij*]quinoline* (**1**) (top) *and its 3,9-dimethyl derivative* (**2**) (bottom). Solvent: CH_2Cl_2; temperature 273 K.

Table 2. *^1H and ^{14}N Coupling Constants* (in mT[a]) *for the Radical Cations of Indolizino[6,5,4,3-*aij*]-quinoline* (**1**) *and its 3,9-Disubstituted Derivatives* **2**, **3** *and* **4**

Position	$\mathbf{1}^{\oplus}$ (R = H)	$\mathbf{2}^{\oplus}$ (R = Me)	$\mathbf{3}^{\oplus}$ (R = *t*-Bu)	$\mathbf{4}^{\oplus}$ (R = Ph)
1,2	0.181 (2 H)	0.180 (2 H)	0.179 (2 H)	0.165 (2 H)
3,9	0.071 (2 H)	0.070 (6 H)[b]	0.003 (18 H)[c]	< 0.010 (10 H)[d]
4,8	0.528 (2 H)	0.537 (2 H)	0.518 (2 H)	0.525 (2 H)
5,7	0.595 (2 H)	0.626 (2 H)	0.604 (2 H)	0.621 (2 H)
6	0.158 (1 H)	0.165 (1 H)	0.158 (1 H)	0.165 (1 H)
10	0.208 (1 N)	0.195 (1 N)	0.201 (1 N)	0.189 (1 N)

[a]) Experimental error: ± 1%. [b]) Equivalent protons of two methyl substituents. [c]) Equivalent protons of two *tert*-butyl substituents; coupling constant determined from the ESR line-widths. [d]) Protons of two phenyl substituents.

Since corresponding proton ENDOR signals could not be observed, complete analysis of these spectra was not possible. A few hyperfine data which were amenable to measurement are given in *Table 3*. Apart from the total extensions of the spectra, these data comprise rough estimates of the largest proton coupling constants for $\mathbf{1}^{\oplus}$ and $\mathbf{2}^{\oplus}$; in the case of $\mathbf{4}^{\oplus}$, even such estimates were out of reach.

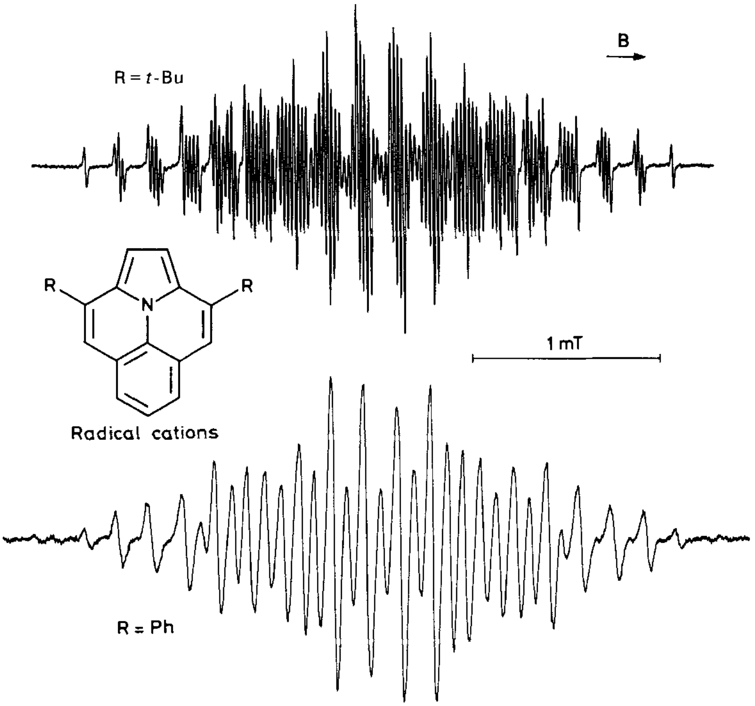


Fig. 2. *ESR spectra of the radical cations of 3,9-di-*tert*-butyl-* (**3**) (top) *and 3,9-diphenylindolizino-[6,5,4,3-*aij*]quinoline* (**4**) (bottom). Solvent: CH_2Cl_2; temperature: 293 K.

Table 3. *^1H and ^{14}N Coupling Constants for the Radical Anion of 3,9-Di-*tert*-butylindolizino[6,5,4,3-*aij*]-quinoline* (**3**) *and Some Partial Data for the Radical Anions of the Unsubstituted Compound* (**1**) *and its Disubstituted Derivatives* **2** *and* **4**. All values in mT.

Position	$\mathbf{1}^{\ominus}$ (R = H)[a]	$\mathbf{2}^{\ominus}$ (R = Me)[a]	$\mathbf{3}^{\ominus}$ (R = *t*-Bu)[b]	$\mathbf{4}^{\ominus}$ (R = Ph)
1,2	0.25 (2 H)		0.165 (2 H)	
3,9	0.60 (2 H)	0.45 (6 H)[c]	0.007 (18 H)[d]	
4,8			<0.001 (2 H)	
5,7	0.35 (2 H)	0.40 (2 H)	0.465 (2 H)	
6			0.078 (2 H)	
10			0.059 (1 N)	
Total extension:	2.8 ± 0.1	4.0 ± 0.1	1.58 ± 0.02	2.4 ± 0.1

[a] Experimental error: ±0.05 mT. [b] Experimental error: ±1%. [c] Equivalent protons of two methyl substituents. [d] Equivalent protons of two *tert*-butyl substituents.

Since the main hyperfine splitting observed in the spectrum of $\mathbf{2}^{\ominus}$ stems from six equivalent protons, it must be attributed to those of the two methyl substituents. By analogy, the large two-proton coupling constant found for $\mathbf{1}^{\ominus}$ can be assigned to the protons in the corresponding 3,9-positions. Both assignments are in accord with the total extensions of the ESR spectra of $\mathbf{1}^{\ominus}$ and $\mathbf{2}^{\ominus}$, which exceed that of the radical anion of the di-*tert*-butyl derivative (**3**) by 1.2 and 2.4 mT, respectively.

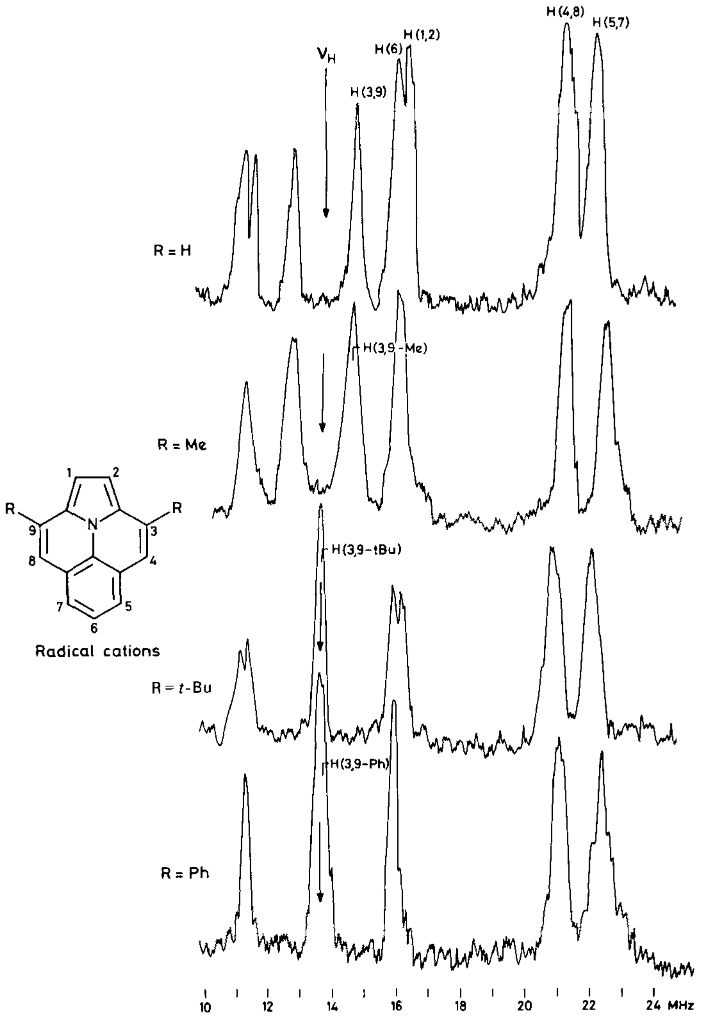


Fig. 3. *Proton ENDOR spectra of the radical cations of indolizino[6,5,4,3-*aij*]quinoline* (**1**) *and its 3,9-dimethyl-* (**2**), *di-*tert*-butyl-* (**3**) *and diphenyl derivative* (**4**) (from top to bottom). Experimental conditions as for the corresponding ESR spectra (*Fig. 1* and *2*). ν_H = frequency of the free proton.

In contrast to $\mathbf{1}^{\dot{\ominus}}$, $\mathbf{2}^{\dot{\ominus}}$ and $\mathbf{4}^{\dot{\ominus}}$, the radical anion $\mathbf{3}^{\dot{\ominus}}$ exhibited a fairly resolved ESR spectrum, along with measurable proton ENDOR signals *(Fig. 4)*. The hyperfine data obtained therefrom are also listed in *Table 3*. As for the radical cation $\mathbf{3}^{\dot{\oplus}}$, assignments of the coupling constants for $\mathbf{3}^{\dot{\ominus}}$ are unequivocal in the case of the ^{14}N-nucleus, the single proton in the 6-position and the 18 equivalent protons of the two *tert*-butyl groups. The remaining values, each for two equivalent protons, have been assigned by arguments advanced in the *Discussion*.

The *g*-value of all four radical anions is 2.0029 ± 0.0001.

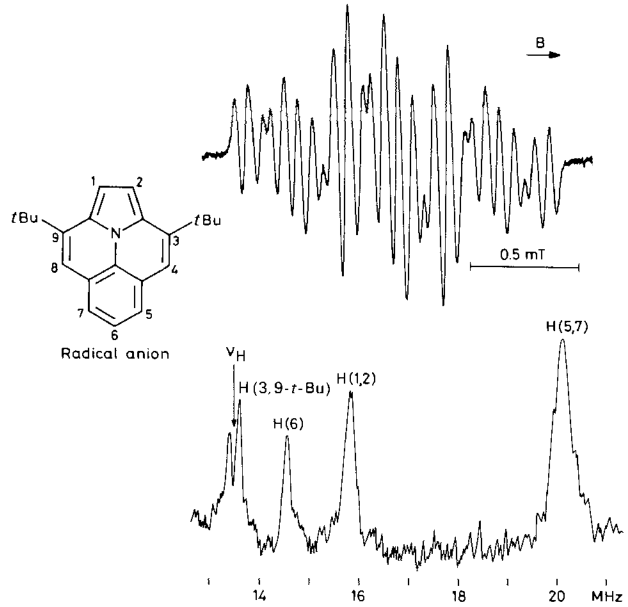
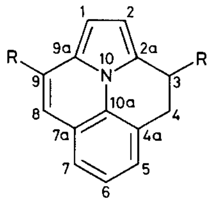


Fig. 4. *ESR* (top) *and proton ENDOR* (bottom) *spectra of the radical anion of 3,9-di-*tert*-butylindolizino-[6,5,4,3-*aij*]quinoline* (3). Solvent: MTHF; counter-ion: $K^{\oplus}$; temperature 183 K. ν_H = frequency of the free proton.

Secondary Paramagnetic Species. The radical anions $3^{\ominus}$ (R = *t*-Bu) and $4^{\ominus}$ (R = Ph) were relatively persistent. On the other hand, prolonged chemical or electrolytic reduction led to a gradual replacement of the ESR spectra of $1^{\ominus}$ (R = H) and $2^{\ominus}$ (R = Me) by those of secondary paramagnetic species having the same *g*-value. The conversion proceeded more rapidly for $1^{\ominus}$ than for $2^{\ominus}$ and, in the chemical reduction, it was favoured by addition of HMPT to DME or MTHF. Analysis of the complex ESR spectra of the two secondary species *(Fig. 5)* was greatly facilitated by the observation of the corresponding proton ENDOR signals *(Fig. 6)* which demonstrate the similar structures of these species. Their hyperfine data, listed in *Table 4*, clearly indicate that the secondary product of the reduction of **2** is a dimethyl derivative of the analogous product obtained from **1**. Both products possess two more protons than the corresponding starting materials and their symmetry is lower relative to that of their precursors. These findings strongly suggest that the secondary paramagnetic species are the radical anions of 3,4-dihydroindolizino[6,5,4,3-*aij*]quinoline (**1**-H_2) and its 3,9-dimethyl derivative (**2**-H_2).



1-H_2 R = H
2-H_2 R = Me

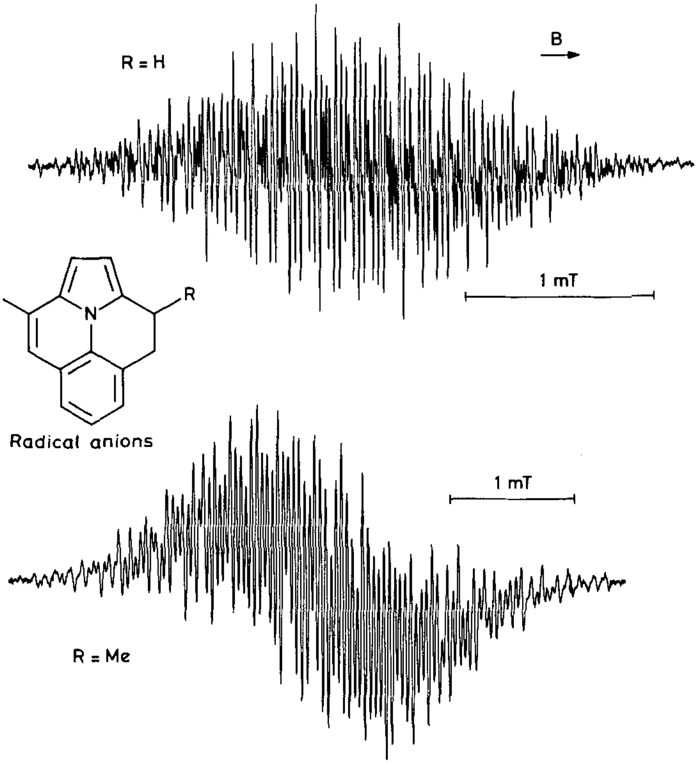


Fig. 5. *ESR spectra of the radical anions of 3,4-dihydroindolizino[6,5,4,3-*aij*]quinoline* (**1**-H_2) (top) *and its 3,9-dimethyl derivative* (**2**-H_2) (bottom). Solvent: MTHF/HMPT (10:1); counter-ion $K^{\oplus}$; temperature 233 K. Note the different scale of the magnetic field in the two spectra.

Table 4. *^1H and ^{14}N Coupling Constants* (in mT[a])) *for the Radical Anions of 3,4-Dihydroindolizino-[6,5,4,3-*aij*]quinoline* (**1**-H_2) *and its 3,4-Dimethyl Derivative* (**2**-H_2)

Position	**1**-$H_2^{\ominus}$ (R = H)	**2**-$H_2^{\ominus}$ (R = Me)
1	0.169 (1 H)	0.190 (1 H)
2	0.010 (1 H)	0.008 (1 H)
3	0.208 (2 H)	0.224 (1 H); <0.005 (3 H)[b])
4	0.239 (2 H)	0.299 (1 H); 0.190 (1 H)
5	0.270 (1 H)	0.285 (1 H)
6	0.101 (1 H)	0.088 (1 H)
7	0.538 (1 H)	0.511 (1 H)
8	0.443 (1 H)	0.435 (1 H)
9	0.685 (1 H)	0.687 (3 H)[b])
10	0.158 (1 N)	0.165 (1 N)

[a]) Experimental error: ±1% for **1**-$H_2^{\ominus}$ and ±2% for **2**-$H_2^{\ominus}$. [b]) Protons of methyl substituent.

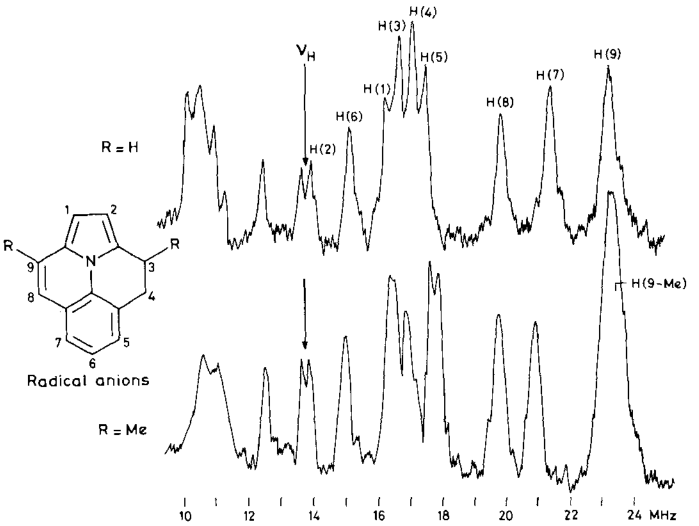


Fig. 6. *Proton ENDOR spectra of the radical anions of 3,4-dihydroindolizino[6,5,4,3-*aij*]quinoline* (**1**-H_2) (top) *and its 3,9-dimethyl derivative* (**2**-H_2) (bottom). Solvent: DME/HMPT (**1**-$H_2^{\ominus}$)or MTHF/HMPT (**2**-$H_2^{\ominus}$); counter-ion $K^{\oplus}$; temperature 233 K. ν_H = frequency of the free proton.

Support for the attribution of the structures **1**-$H_2^{\ominus}$ and **2**-$H_2^{\ominus}$ to the species in question has been provided by experiments, in each of which three 40 mg samples of **1** were exhaustively reduced with K-metal in DME (containing a few drops of HMPT) and the solutions of the radical anions thus obtained were quenched by air, dioxygen and MeOH, respectively. Whereas upon admission of air or dioxygen, the only isolated product was the starting material **1** (80%), addition of MeOH also yielded a small amount of an unknown product. This product (m.p. 142 °C, uncorrected) was identified as **1**-H_2 by its parent MS peak (m/e = 193) and, in particular, by its ^{1}H-NMR spectrum characterized by the following data ($CDCl_3$; ambient temperature). Narrow A_2B_2-multiplet centered at 3.23 ppm for H(3) and H(4); broad singlet at 6.46 ppm for H(1) and H(2); two AB-doublets, centered at 6.90 and 7.23 ppm for H(8) and H(9); ABC-multiplet at 7.1–7.6 ppm for H(5), H(6) and H(7). Reduction of **1**-H_2 led immediately to the radical anion **1**-$H_2^{\ominus}$, the ESR spectrum of which was identical with that observed for the secondary paramagnetic species in the reduction of **1** (*Fig. 5*, top).

The complexity of the ESR spectra of **1**-$H_2^{\ominus}$ and **2**-$H_2^{\ominus}$ rendered the studies of their temperature dependence rather difficult. Nevertheless, examination of these spectra in the range 193–293 K did not reveal the effects which might be expected for the 3,4-alkano chain inverting with a frequency comparable to the hyperfine time-scale. For want of experimental evidence, time-averaged coupling constants were assumed for the two protons in each CH_2-group of **1**-$H_2^{\ominus}$, while in the case of **2**-$H_2^{\ominus}$, as a consequence of the 3-methyl substitution, the hyperfine data were interpreted in terms of a frozen conformation. It is evident from *Table 4* that the complexity of the ESR spectra is due to the large number of different hyperfine splittings, most of them arising from single nuclei. Because of this diversity, assignments of several coupling constants *(Table 4)* based on an MO model (see *Discussion*) are subject to some uncertainty, especially for slightly differing values.

In a few reduction experiments on **1**, the ESR spectrum of **1**$^{\ominus}$ was not directly replaced by that of **1**-H$_2^{\ominus}$, but first gave place to an absorption by an intermediately formed paramagnetic species[2]. Its possible origin is considered in the *Discussion.*

Discussion. – *MO Models. Figure* 7 depicts those π-MO's of indolizino[6,5,4,3-*aij*]quinoline (**1**) (left) and its 3,4-dihydro derivative (**1**-H$_2$) (right) which are relevant to the discussion of the experimental results. They were calculated with the use of the standard *Hückel* parameters α and β, except for $\alpha_{\dot{N}}$ which was set equal to $\alpha + 1.5\beta$ [4] [5]. A prominent feature of the MO model of **1** is the high-lying HOMO ψ_8, in accordance with the low oxidation potential of **1** *(Table 1)*. This orbital, which is singly occupied in the radical cation **1**$^{\oplus}$, represents an 'antisymmetric' MO of the 13-membered perimeter ([13]annulenyl; **6**$^{\cdot}$) with a nodal plane

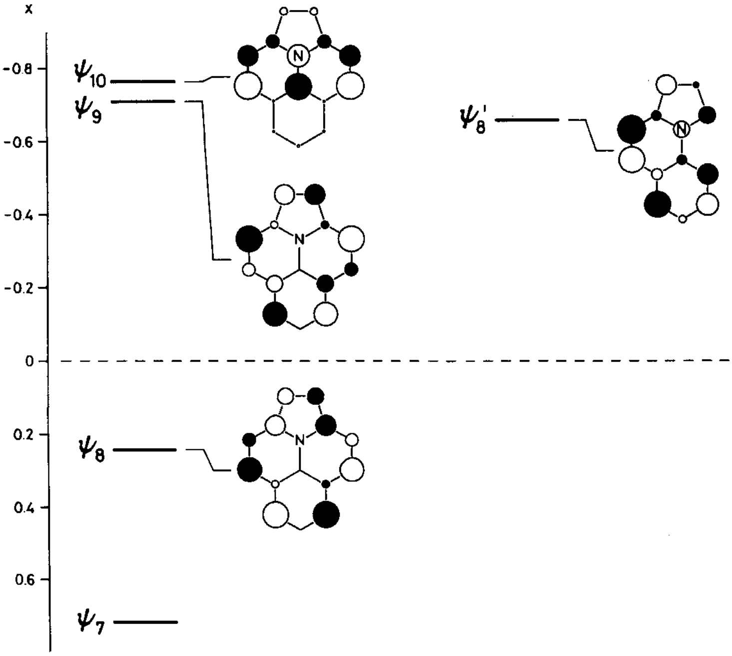
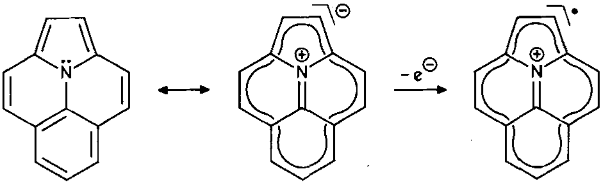


Fig. 7. Left: *The highest bonding* (ψ_8) *and the two lowest antibonding orbitals* (ψ_9 and ψ_{10}) *of indolizino[6,5,4,3-*aij*]quinoline* (**1**). Right: *The lowest antibonding orbital* (ψ_8') *of benzo[*e*]indolizine*, the π-*system of the 3,4-dihydro derivative* (**1**-H$_2$) *of* **1**. The areas of the circles are proportional to the squares of the LCAO coefficients. Full and open circles symbolize different signs of these coefficients. $x = (E - \alpha)/\beta$.

---

[2] The ESR and ENDOR spectra of this species are shown in [3].

passing through C(6) and bisecting the C(1)–C(2) bond. Such an 'annulenyl character' of the singly occupied orbital in $\mathbf{1}^{\oplus\cdot}$ can be visualized by considering the contribution of the 'ionic structure' **1a**.



1 **1a**

Table 5. *Calculated ^{1}H and ^{14}N Coupling Constants* (in mT) *for the Radical Ions of Indolizino[6,5,4,3-*aij*]quinoline* (**1**)

Position	$\mathbf{1}^{\oplus\cdot}$ [a]	$\mathbf{1}^{\ominus\cdot}$ [b]	$\mathbf{1}^{\ominus\cdot}$ [c]
1,2	−0.150 (2 H)	−0.303 (2 H)	+0.010 (2 H)
3,9	+0.039 (2 H)	−0.500 (2 H)	−0.140 (2 H)
4,8	−0.523 (2 H)	+0.020 (2 H)	−0.612 (2 H)
5,7	−0.644 (2 H)	−0.423 (2 H)	+0.016 (2 H)
6	+0.174 (1 H)	+0.124 (1 H)	+0.039 (1 H)
10	−0.239 (1 N)	+0.016 (1 N)	+0.314 (1 N)

[a] Single occupancy of ψ_8. [b] Single occupancy of ψ_9. [c] Single occupancy of ψ_{10}.

Table 5 gives the ^{1}H- and ^{14}N-coupling constants obtained from the *McLachlan* π-spin populations [6] for the single occupancy of ψ_8 in $\mathbf{1}^{\oplus\cdot}$ ($\lambda = 1.2$). Conversion of the spin populations ρ_μ (or ρ_ν) into the coupling constants, $a_{H(\mu)}$ and a_N in mT, was carried out with the use of the *McConnell* equation [7]

$$a_{H(\mu)} = -2.8\,\rho_\mu \tag{1}$$

and the relationship

$$a_N = +3.9\,\rho_\mu - 0.65\sum_{\nu}\rho_\nu \tag{2}$$

This relationship, in which the subscripts μ and ν refer to the N-centre and the adjacent C-centres, respectively (for **1**, $\mu = 10$, and $\nu = 2a$, 9a and 10a), has previously [5] been derived for radical ions of cyclazines. There is a good agreement between the calculated coupling constants *(Table 5)* and the corresponding hyperfine data observed for the radical cations $\mathbf{1}^{\oplus\cdot}$ to $\mathbf{4}^{\oplus\cdot}$ *(Table 2)*. The finding that the effect of the 3,9-substitution on these values is relatively weak is readily rationalized by the small magnitude of the coefficients at C(3) and C(9) in ψ_8 *(Fig. 7)*.

The MO energy scheme in *Figure 7* also accounts for the rather negative reduction potential of **1**, but it does not provide an unambiguous prediction with respect to the character of the LUMO. It is evident that two MO's, ψ_9 and ψ_{10}, must be considered, since they are energetically very close and thus their sequence depends on the choice of the *Hückel* parameters. The two MO's differ distinctly in their shapes. Whereas ψ_9, like the HOMO ψ_8, is essentially an 'antisymmetric' MO of the [13]annulenyl (**6**$^{\cdot}$), the character of ψ_{10} is best described as of 'cycl[3.2.2]azinyl (**7**$^{\cdot}$)-type' in view of the vanishingly small coefficients at C(5), C(6) and C(7).

Table 5 also lists the coupling constants predicted by the MO model for the single occupancy of either ψ_9 or ψ_{10} in the radical anion $\mathbf{1}^{\ominus}$. They were calculated by the same procedure as the analogous values of $\mathbf{1}^{\oplus}$, except for two modifications. In the case of ψ_{10} as the singly occupied orbital, the *Hückel* parameter β_{CN} was reduced from the standard value β to 0.9β to place this MO below ψ_9. Also, the proportionality factor in the *McConnell* equation was changed from −2.8 to −2.4 mT, thus allowing for the generally smaller magnitude of the coupling constants of the protons in the radical anions relative to the radical cations [8].

$$a_{H(\mu)} = -2.4\,\rho_\mu \tag{1'}$$

Comparison of the calculated coupling constants *(Table 5)* with those observed for $\mathbf{1}^{\ominus}$, $\mathbf{2}^{\ominus}$ and $\mathbf{3}^{\ominus}$ *(Table 3)* indicates that the singly occupied orbital is ψ_9. The strongest arguments in favour of ψ_9 are the large coupling constants found for the ring (0.60 mT) and the corresponding methyl protons (0.45 mT) in the 3,9-positions of $\mathbf{1}^{\ominus}$ (R=H) and $\mathbf{2}^{\ominus}$ (R=Me), respectively, as well as the rather small coupling constant (0.059 mT) of the ^{14}N-nucleus in $\mathbf{3}^{\ominus}$ (R=*t*-Bu). These data are compatible with the values predicted for the single occupancy of ψ_9 in $\mathbf{1}^{\ominus}$ ($|a_{H(3,9)}| = 0.500$ and $|a_N| = 0.016$ mT), but they disagree with those expected for such an occupancy of ψ_{10} ($|a_{H(3,9)}| = 0.140$ and $|a_N| = 0.314$ mT). It can therefore be concluded that not only the HOMO, but also the LUMO of **1** is of the 'annulenyl-type'.

The coupling constants calculated for the single occupancy of the LUMO ψ'_8 (*Fig. 7*, right) in the radical anion of 3,4-dihydroindolizino[6,5,4,3-*aij*]quinolizine (**1**-H$_2$) are given in *Table 6*. The procedure used in this calculation was the same

Table 6. *Calculated ^1H and ^{14}N Coupling Constants* (in mT) *for the Radical Anion of 3,9-Dihydroindolizino[6,5,4,3-*aij*]quinoline* (**1**-H$_2$)

Position	[a]		Position	[a]
1	−0.250 (1 H)		5	−0.325 (1 H)
2	+0.063 (1 H)		6	+0.100 (1 H)
3	+0.271 (1 H)	+0.193[b] (2 H)	7	−0.513 (1 H)
	+0.115 (1 H)		8	−0.455 (1 H)
4	+0.388 (1 H)	+0.276[b] (2 H)	9	−0.540 (1 H)
	+0.165 (1 H)		10	+0.170 (1 N)

[a] Single occupancy of ψ'_8. [b] Averaged value.

as that applied to ψ_9 in $\mathbf{1}^{\underset{\cdot}{\ominus}}$, apart from the conversion of π-spin populations into the coupling constants of CH_2-protons. In this case, the relationship [9] was applied

$$a_{H(\mu)} = +4.0\, \rho_\nu \cos^2\theta \tag{3}$$

where the subscripts μ and ν stand for the C-atom of the CH_2-group and the adjacent C-π-centre, respectively (for $\mathbf{1}$-H_2, $\nu = 2a$ when $\mu = 3$, and $\nu = 4a$ when $\mu = 4$). The dihedral angle θ between the C–H-bond of the CH_2-group and the $2p_z$-axis at the centre ν was estimated as 10° and 130° for the two protons in each group. The overall agreement of the calculated coupling constants *(Table 6)* with the corresponding hyperfine data observed for $\mathbf{1}$-$H_2^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}$-$H_2^{\underset{\cdot}{\ominus}}$ *(Table 4)* leaves no doubt that the interpretation of these data in terms of a single occupancy of ψ'_8 is essentially correct.

Reaction of the Radical Anions. Dihydrogenation of $\mathbf{1}^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}^{\underset{\cdot}{\ominus}}$ to yield $\mathbf{1}$-$H_2^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}$-$H_2^{\underset{\cdot}{\ominus}}$, respectively, deserves comment. Since this reaction occurs on prolonged reduction, its first step is presumably the formation of the dianions $\mathbf{1}^{\text{⊜}}$ and $\mathbf{2}^{\text{⊜}}$. The next step should then consist in a rapid protonation of the dianions which are then converted into the corresponding anions $\mathbf{1}$-$H^{\ominus}$ and $\mathbf{2}$-$H^{\ominus}$. The proton could be either abstracted from the solvent or provided by protic impurities present in minute amounts in solution. The second alternative is supported by the finding that dihydrogenation of $\mathbf{1}^{\underset{\cdot}{\ominus}}$ and $\mathbf{2}^{\underset{\cdot}{\ominus}}$ is accelerated by adding HMPT to DME or MTHF, since proton impurities are less readily removed from HMPT than from ethereal solvents. It is reasonable to assume that $\mathbf{1}$-$H^{\ominus}$ and $\mathbf{2}$-$H^{\ominus}$ are formed by protonation in the position 3 (or 9). MO models indicate not only that C(3) and C(9) bear a high negative charge in $\mathbf{1}^{\text{⊜}}$ (owing to the contribution of the doubly occupied orbital ψ_9; *cf. Fig. 7*, left), but also that the anion $\mathbf{1}$-$H^{\ominus}$, resulting from protonation of $\mathbf{1}^{\text{⊜}}$ in the position 3 or 9, is thermodynamically more stable (has larger π-electron energy) than the anions obtained by protonation of $\mathbf{1}^{\text{⊜}}$ in one of the remaining positions. Since dihydrogenation is found to proceed less rapidly with $\mathbf{2}^{\underset{\cdot}{\ominus}}$ (R = Me) than with $\mathbf{1}^{\underset{\cdot}{\ominus}}$ (R = H), and since it is not observed with $\mathbf{3}^{\underset{\cdot}{\ominus}}$ (R = *t*-Bu) and $\mathbf{4}^{\underset{\cdot}{\ominus}}$ (R = Ph), the 3,9-substituents R must exert some protecting effect which increases with growing size of the group R. This effect is probably steric in origin. The conversion of $\mathbf{1}^{\underset{\cdot}{\ominus}}$ to $\mathbf{1}$-$H_2^{\underset{\cdot}{\ominus}}$ can be formulated as

$$\mathbf{1}^{\underset{\cdot}{\ominus}} \xrightarrow{+e^{\ominus}} \mathbf{1}^{\text{⊜}} \xrightarrow{+H^{\oplus}} \mathbf{1}\text{-}H^{\ominus} \xrightarrow{+e^{\ominus}} \mathbf{1}\text{-}H^{\underset{\cdot}{\text{⊜}}} \xrightarrow{+H^{\oplus}} \mathbf{1}\text{-}H_2^{\underset{\cdot}{\ominus}}$$

with an analogous reaction scheme for $\mathbf{2}^{\underset{\cdot}{\ominus}}$. It is possible that the unknown paramagnetic species, intermediately observed in a few reduction experiments on **1**, is in fact the radical dianion $\mathbf{1}$-$H^{\underset{\cdot}{\text{⊜}}}$.

A comment on the results obtained by quenching exhaustively reduced solutions of **1** is also in order. Although, according to the spectroscopic evidence, such solutions contain the radical anion $\mathbf{1}$-$H_2^{\underset{\cdot}{\ominus}}$, admission of air or dioxygen yields **1** as the only product.

Both findings can be reconciled by assuming a reaction

$$\mathbf{1}\text{-}H_2^{\ominus\cdot} + \frac{3}{2}O_2 \rightarrow \mathbf{1} + H_2O + O_2^{\ominus\cdot}$$

in which **1** is regenerated by dioxygen. The relative ease of recovery of **1** from its dihydro derivatives complies with the chemical properties of this novel heteroarene [10].

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. We also thank Mr. *J. Knöbel* for taking several ESR spectra and Mr. *U. Buser* for carrying out the quenching experiments on radical anion solutions. Last but not least, we are indebted to Prof. *H. Balli* and Dr. *M. Zeller*, Institut für Farbenchemie der Universität Basel, for a generous gift of samples of **1**, **2**, **3** and **4**.

REFERENCES

[1] *H. Balli & M. Zeller*, Helv. Chim. Acta *66*, 2135 (1983).
[2] *R.P. Cunningham, D. Farquar, W.K. Gibson & D. Leaver*, J. Chem. Soc. (C) *1969*, 239.
[3] *A. Metzger*, Dissertation, Universität Basel, 1983.
[4] *F. Gerson, J. Jachimowicz, B. Kowert & D. Leaver*, Helv. Chim. Acta *56*, 238 (1973).
[5] *F. Gerson, J. Jachimowicz & D. Leaver*, J. Am. Chem. Soc. *95*, 6702 (1973).
[6] *A.D. McLachlan*, Mol. Phys. *3*, 233 (1960).
[7] *H.M. McConnell*, J. Chem. Phys. *24*, 632 (1956).
[8] See, e.g., *F. Gerson*, 'High-Resolution ESR. Spectroscopy', Verlag-Chemie, Weinheim, and J. Wiley, New York, 1970, Chapter 2.1.
[9] *C. Heller & H.M. McConnell*, J. Chem. Phys. *32*, 1535 (1960); *A. Horsfield, J.R. Morton & D.M. Whiffen*, Mol. Phys. *4*, 425 (1961).
[10] *M. Zeller*, Dissertation, Universität Basel, 1983; *H. Balli & M. Zeller*, unpublished work.