9. Radical Cations of Tetrazinodi(heteroarenes): An ESR and ENDOR Study

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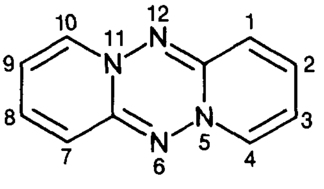
^{14}N- and ^{1}H-Coupling constants, determined by ESR, ENDOR, and general-TRIPLE-resonance spectroscopy, are reported for the radical cations of tetrazinodi(heteroarenes) **1**–**8**. The results comply with the expectation that donor properties of these compounds are mainly due to the electron-rich dihydrotetrazine ring.

Introduction. – The title compounds [1] [2], a novel class of heteroarenes containing 1,4-dihydro-1,2,4,5-tetrazine as the electron-rich moiety, are powerful donors [3] [4] which have very low oxidation potentials in solution (0–0.5 V *vs.* Ag/AgCl) [2] [3] and quite moderate ionization energies in the gas phase (6.0–6.5 eV) [5]. Accordingly, forma-



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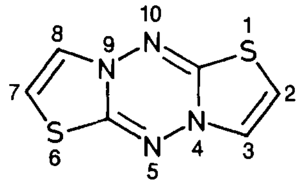

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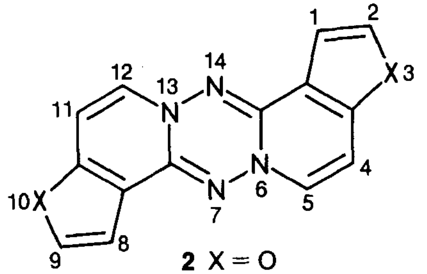
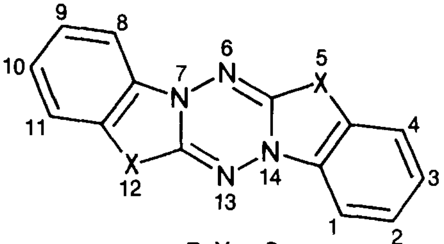
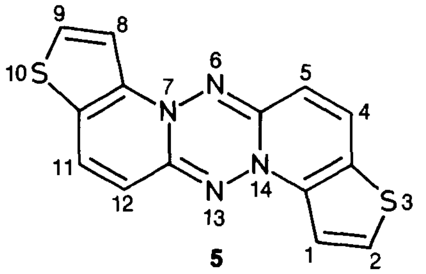


2 X = O
3 X = S
4 X = MeN



7 X = S
8 X = EtN



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tion of their radical cations is extremely facile, and the corresponding salts were isolated in several cases [2]. Here, we characterize the radical cations of the tetrazinodi(heteroarenes) **1**–**8** by hyperfine data with the use of ESR, ENDOR, and general-TRIPLE-resonance spectroscopy.

Experimental. – The syntheses of the eight compounds are described elsewhere: **1** [1], **2**–**6** [2], **7** [1], **8** [1] [2]. Five of their radical cations, $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$, $\mathbf{6}^{+\cdot}$, and $\mathbf{8}^{+\cdot}$, which were isolated as perchlorate salts [2], were studied in both MeCN and CH_2Cl_2/CF_3COOH 1:2 solutions. (In most cases, pure CH_2Cl_2 proved not sufficiently polar to dissolve the salts.) For the three remaining radical cations $\mathbf{1}^{+\cdot}$, $\mathbf{5}^{+\cdot}$, and $\mathbf{7}^{+\cdot}$, the CH_2Cl_2/CF_3COOH mixture was exclusively used as the solvent, in which the paramagnetic ions were generated from their neutral precursors by oxidation with the acid. All radical cations $\mathbf{1}^{+\cdot}$–$\mathbf{8}^{+\cdot}$ were very persistent and could be kept for months in solution at r.t., provided that exposure to light and air was avoided. Their ESR spectra were recorded on *Varian-E9* instrument, while *Bruker-ESP-300* system was employed for ENDOR and TRIPLE-resonance studies.

Results and Discussion. – The ESR spectra of $\mathbf{1}^{+\cdot}$–$\mathbf{8}^{+\cdot}$, taken in the range of 243–293 K, exhibited a marked ^{14}N-hyperfine anisotropy, in particular at lower temperatures. The lines were broadened at the wings of the spectrum, whereby the effect was more pronounced at the high- than at the low-field half. This behavior is characteristic of ^{14}N nuclei having large and positive coupling constants [6]. For each radical cation, precise $|a_{N_\mu}|$ and $|a_{H_\mu}|$ values of the ^{14}N- and ^1H-coupling constants were derived from the corresponding ENDOR spectra and served for the simulation of the ESR derivative curves. The procedure is illustrated in *Figs. 1* and *2* by the spectra of the two basic radical cations $\mathbf{1}^{+\cdot}$ and $\mathbf{6}^{+\cdot}$. General-TRIPLE-resonance experiments carried out on the ENDOR signals [7] led to the relative signs of a_{H_μ}.

The hyperfine data and g factors of $\mathbf{1}^{+\cdot}$–$\mathbf{8}^{+\cdot}$ are listed in the *Table*. The coupling constants a_{N_μ} and a_{H_μ} are arranged in such a way that values for nuclei in topologically similar positions μ of the π-systems are placed in the same line. The assignments to individual positions are based on *Hückel-McLachlan* calculations [8] using the conventional parameters for hetero-π-centers and adjacent bonds [5] [9] [10]; a further guidance for these assignments was provided by the consistency of the data within the series $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$ and $\mathbf{6}^{+\cdot}$–$\mathbf{8}^{+\cdot}$. The signs of a_{H_μ} are in accord with the results of the TRIPLE-resonance experiment, on the reasonable assumption that, in each case, the absolutely largest value is negative. The coupling constants of the ^{14}N nuclei in the positions $\mu = 3,10$ of $\mathbf{4}^{+\cdot}$ and 5,12 of $\mathbf{8}^{+\cdot}$, as well as those of the protons in the *N*-alkyl substituents at these positions, escape observation, because of their apparent smallness (< 0.005 mT); accordingly, the pertinent values are missing in the *Table*. All data refer to 253 K and to the solvent CH_2Cl_2/CF_3COOH 1:2. Their dependence on the temperature in the range of investigation is only slight. For $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$, $\mathbf{6}^{+\cdot}$, and $\mathbf{8}^{+\cdot}$, the values measured with the solvent MeCN (see *Experimental*) are very similar to those obtained with CH_2Cl_2/CF_3COOH 1:2 and are, therefore, not presented here.

The expectation that the donor properties of **1**–**8** are mainly due to the central dihydrotetrazine ring (*Fig. 3*) is borne out by the large ^{14}N-coupling constants. Interestingly, the sums of a_{N_μ} at the four N-atoms μ are almost constant for $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$ (1.81 ± 0.03 mT) and $\mathbf{6}^{+\cdot}$–$\mathbf{8}^{+\cdot}$ (1.95 ± 0.04 mT). These sums may be compared with the corresponding values for the radical cations of 1,4-dihydro-1,2,4,5-tetrazine and its substituted derivatives (2.4 ± 0.1 mT) [11–13]. From such a comparison, one concludes that *ca.* 80% of the 'hole', created by the removal of an electron from **1**–**8**, resides on the dihydrotetrazine ring.

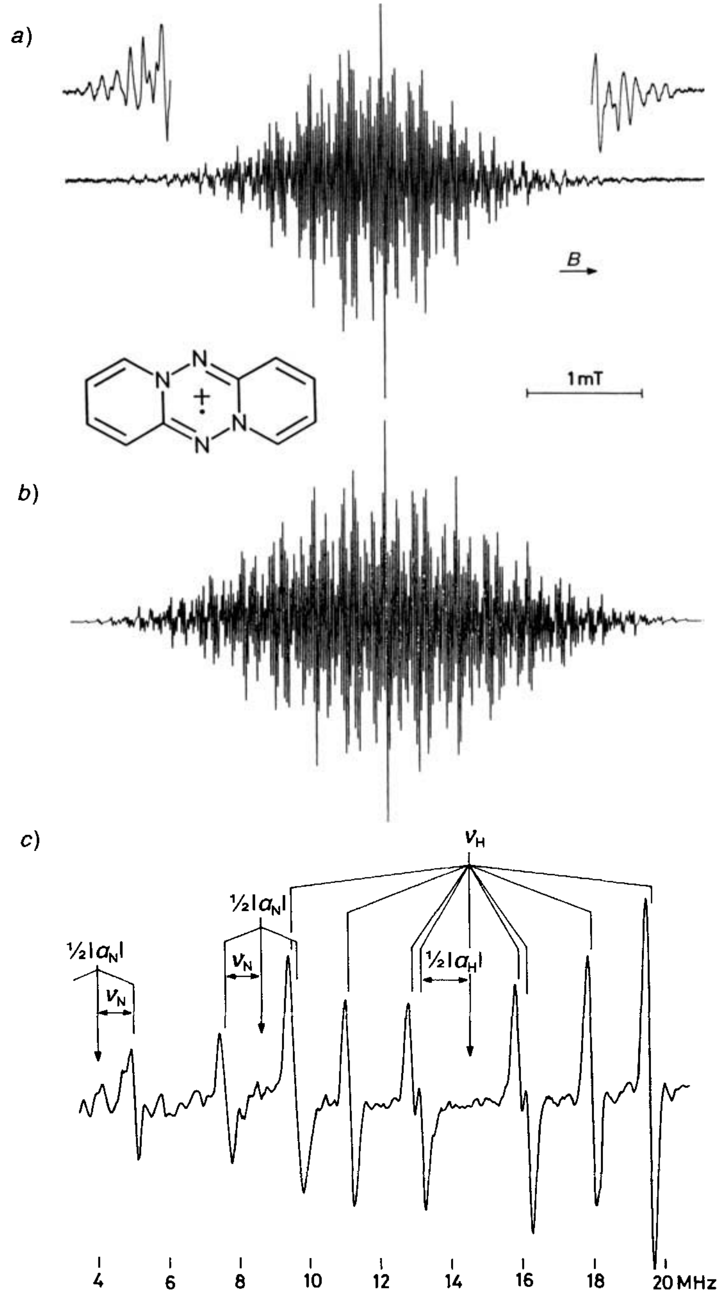

Fig. 1. a) *ESR Spectrum of the radical cation* $1^{+\cdot}$ *in* CH_2Cl_2/CF_3COOH *1:2* (counterion CF_3COO^-; temp. 253 K). b) *Simulation of the ESR spectrum* (coupling constants in the *Table*; line-shape *Lorentzian*, line-width 0.018 mT; no allowance is made for the effect of ^{14}N-hyperfine anisotropy). c) *Corresponding* ^{14}*N- and* ^{1}*H-ENDOR spectrum*. The low-frequency signal of the smaller coupling constant a_N could not be detected, because of the poor performance of the ENDOR system below 4 MHz.

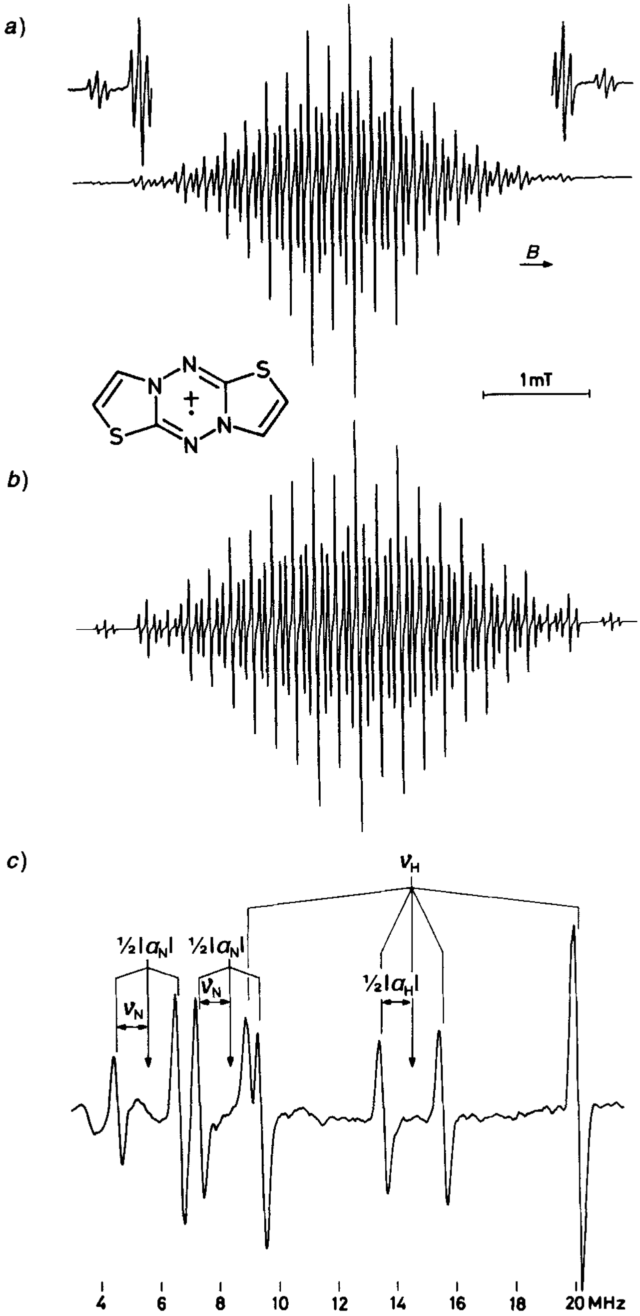

Fig. 2. a) *ESR Spectrum of the radical cation* **6**$^{+\cdot}$ *in* CH_2Cl_2/CF_3COOH *1:2* (counterions ClO_4^- and CF_3COO^-; temp. 253 K). b) *Simulation of the ESR spectrum* (coupling constants in the *Table*; line-shape *Lorentzian*, line-width 0.018 mT; no allowance is made for the effect of ^{14}N-hyperfine anisotropy). c) *Corresponding* ^{14}*N- and* ^{1}*H-ENDOR spectrum*

Table. *^{14}N- and ^{1}H-Coupling Constants,* $a_{\mathrm{N}\mu}$ *and* $a_{\mathrm{H}\mu}$ [mT], *and* g *Factors*^{a})
for the Radical Cations $\mathbf{1}^{+\cdot}$–$\mathbf{8}^{+\cdot}$

	$\mathbf{1}^{+\cdot}$	$\mathbf{2}^{+\cdot}$	$\mathbf{3}^{+\cdot}$	$\mathbf{4}^{+\cdot}$	$\mathbf{5}^{+\cdot}$
$a_{\mathrm{N}\mu}$(2 ^{14}N)	+0.618	+0.570	+0.554	+0.557	+0.599
μ	6, 12	7, 14	7, 14	7, 14	6, 13
$a_{\mathrm{N}\mu}$(2 ^{14}N)	+0.280	+0.330	+0.347	+0.339	+0.323
μ	5, 11	6, 13	6, 13	6, 13	7, 14
$a_{\mathrm{H}\mu}$(2 ^{1}H)	−0.358	−0.361	−0.364	−0.341	
μ	3, 9	4, 11	4, 11	4, 11	
$a_{\mathrm{H}\mu}$(2 ^{1}H)	+0.117	+0.110	+0.103	+0.094	
μ	4, 10	5, 12	5, 12	5, 12	
$a_{\mathrm{H}\mu}$(2 ^{1}H)	−0.243				−0.184
μ	1, 7				5, 12
$a_{\mathrm{H}\mu}$(2 ^{1}H)	+0.099				+0.081
μ	2, 8				4, 11
$a_{\mathrm{H}\mu}$(2 ^{1}H)		−0.090	−0.084	−0.080	
μ		2, 9	2, 9	2, 9	
$a_{\mathrm{H}\mu}$(2 ^{1}H)		+0.015	+0.019	+0.005	
μ		1, 8	1, 8	1, 8	
$a_{\mathrm{H}\mu}$(2 ^{1}H)					−0.049
μ					1, 8
$a_{\mathrm{H}\mu}$(2 ^{1}H)					+0.009
μ					2, 9
g	2.0038	2.0036	2.0037	2.0036	2.0039
	$\mathbf{6}^{+\cdot}$	$\mathbf{7}^{+\cdot}$	$\mathbf{8}^{+\cdot}$		
$a_{\mathrm{N}\mu}$(2 ^{14}N)	+0.596	+0.531	+0.568		
μ	5, 10	6, 13	6, 13		
$a_{\mathrm{N}\mu}$(2 ^{14}N)	+0.400	+0.465	+0.388		
μ	4, 9	7, 14	7, 14		
$a_{\mathrm{H}\mu}$(2 ^{1}H)	−0.394				
μ	2, 7				
$a_{\mathrm{H}\mu}$(2 ^{1}H)	+0.074				
μ	3, 8				
$a_{\mathrm{H}\mu}$(2 ^{1}H)		−0.180	−0.173		
μ		3, 10	3, 10		
$a_{\mathrm{H}\mu}$(2 ^{1}H)		−0.134	−0.128		
μ		1, 8	1, 8		
$a_{\mathrm{H}\mu}$(2 ^{1}H)		+0.053	+0.043		
μ		4, 11	4, 11		
$a_{\mathrm{H}\mu}$(2 ^{1}H)		+0.022	+0.010		
μ		2, 9	2, 9		
g	2.0044	2.0040	2.0036		

^{a}) Exper. error: ±0.002 mT in $|a_{\mathrm{N}\mu}|$ and in $|a_{\mathrm{H}\mu}| > 0.1$ mT, ±0.001 mT in $|a_{\mathrm{H}\mu}| < 0.1$ mT, and ±0.0001 in g.

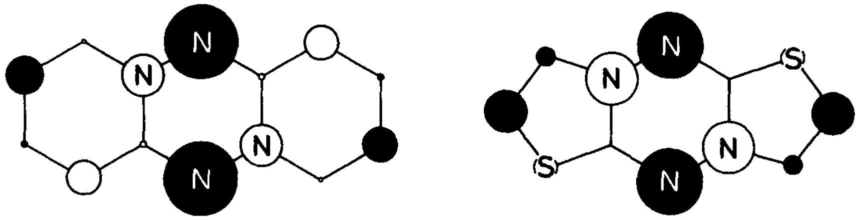

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Fig. 3. *Diagrams of the HOMO's of* **1** *and* **6** *in the frame of the* Hückel *model.* Heteroatom parameters: $h_{\dot{N}} = 0.75$, $h_{\ddot{N}} = 1.5$, $h_S = 1.0$, $k_{C-\ddot{N}} = 0.8$, and $k_{C-S} = 0.7$. All remaining parameters *h and k* have their standard values.

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