THE PROBLEM OF CONJUGATION THROUGH KEY HETEROATOMS IN ARENE-2,1,3-X-DIAZOLES (X = O, S, Se)

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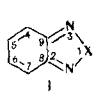
Potassium metal and an electrochemical method are used to prepare anion radicals from benz-2,1,3-oxa-, -thia-, and -selenadiazoles, and also from naphtho-1,2-furazane and naphtho-1,2-selenadiazoles. The EPR spectra of these anions are analyzed, and the results compared with the calculated distributions of spin densities in the anions. It is concluded that the key heteroatoms in the molecules of the compounds investigated participate in conjugation in a definite way. This conclusion is also based on analysis of the electronic absorption spectra of arene-2,1,3-X-diazoles. Apparently the distribution of spin density in the heterocyclic ring does not change substantially from benzologs to naphthologs.

The participation of elements of Group VI, O, S, Se, in conjugation, is still a subject of discussion [1, 2]. Optical spectra of compounds of the type ROR, RSR (where R is a phenyl radical), show no signs of conjugation between rings [3,4]. One reason for this may be the nonplanar structure of compounds of this type. To compare the capacities for conjugation of the above heteroatoms, steric effects should be excluded. Benz-2,1,3-X-diazoles I, whose molecules are planar [5], are suitable models for the purpose.

The structure and properties of benzofuran (I X = = O) [6], piazthiol (I, X = S, see [7]) piaselenole (I, X = Se [8]) and their derivatives have been the subjects of a number of researches. Mostly they have been studied from the point of view of the interaction between the benzene ring and the heterocyclic one, the properties of the latter being known to be determined by the nature of the key heteroatom.

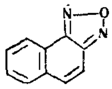


I

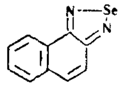
X = O, S, Se

The electronic spectra of these molecules exhibit a systematic shift of absorption bands towards the red on passing from oxygen to sulfur and selenium [6,9], obviously bound up with the effect of different electronegativities and capacities for conjugation of key heteroatoms.

We attempted to arrive at an answer to the question of the participation of these atoms in conjugation by studying the EPR spectra of the anion radicals obtained from arene-2,1,3-X-diazoles by different methods. At the same time it was contemplated comparing the EPR data with the electronic spectra of the molecules, from which these anion-radicals were prepared. Benz-2,1,3-X-diazoles (I, X = O, S, Se) were selected as subjects of research. In addition it appeared to be of interest to investigate the EPR spectra of anion-radicals whose molecules contained nonequivalent nitrogen atoms: of naphtho-1,2-furazan (II), and naphtho-1,2-selenodiazole (III).

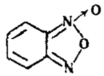


II

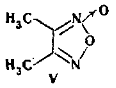


III

Attempts were made to investigate the EPR spectra of the anion-radicals benzofuroxan (IV) and dimethylfuroxan (V).



IV



V

Recent papers reveal the existence of inter-ring exchanges of oxygen between nitrogen atoms in the benzofuroxan molecule [10]. It was important to determine the possibility, from EPR spectra, of such exchanges in anion-radical molecules from benzoforoxan and dimethylfuroxan.

The anions of the compounds investigated were prepared electrochemically at a mercury electrode in dimethylformamide, and by reduction with metallic potassium in 1,2-dimethoxyethane. In general, the reduction potentials of furazans and furoxans have been found in aqueous solution [11], and only in the case of naphtho-1,2-furazan (II) has a determination been made in dimethylformamide [12]. The first wave in the polarographic reduction of II $E_{1/2}^{I} = -1.43$ V (relative to a saturated calomel electrode) corresponds, as has been shown in [12], to a single electron transfer. The second wave appears at a much lower negative potential ($E_{1/2}^{II} = -1.824$ V) [12].

The electrochemical reduction was carried out in the cell of Fig. 1. It consists of three parts: (A) cathode portion of cell with a branch for measuring EPR spectra; at the end of the branch (3 mm diam.) is sealed in a platinum wire (0.3 mm diam.); drops of mercury at the end of the branch formed the cathode; (B) capillary for bubbling through inert gas; to remove oxygen it is enough to bubble through argon or helium for 10–15 min; (C) anode part, a cylinder with a ground glass bottom. There are some openings at the bottom. A platinum disc area 1.5 cm^2 was the anode. Just as in paper [13], the anode space is separated from the cathode one by a teflon membrane 6–10 nm thick. The concentration of the reducible compound is $5 \cdot 10^{-3}$ mole/l. The electrically conducting base electrolyte used was tetramethylammonium iodide, at concentration 0.1 mole/l. The cell resistance was 20–100 kohm, and was determined to a large extent by the resistance of the electrical contact at the edges of the teflon membrane.

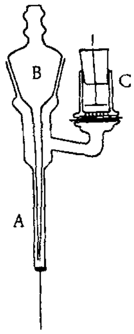


Fig. 1. Diagram of electric cell: A) cathode part; B) capillary; C) anode part.

A 1 M solution of KCl was poured into the anode portion. During the reduction process the cathode potential was found, relative to a saturated calomel electrode, to be 200–300 mV more negative than the potential of the half-wave corresponding to a single electron transfer during polarographic reduction. The spectra were recorded with an IKhF-2 type spectrometer, with a 1 Mc magnetic field frequency modulation.

1. EPR SPECTRA OF ANION-RADICALS FROM BENZ-2,1,3-DIAZOLES

Figure 2 shows halves of spectra of anion-radicals of benzofuran (I, X = O), piazthiole (I, X = S), piaselenole (I, X = Se), prepared electrochemically. Also recorded were the EPR spectra of anions from compounds I, X = O, and I, X = S, obtained by reducing with potassium metal in 1,2-dimethoxyethane. The appearance of the piaselenole spectrum is independent of the method of preparation. Whether benzofuran is reduced by potassium metal or electrochemically, the same EPR spectra are recorded, with identical hyperfine structures, but in the former case the width of the individual components of the hyperfine structure are different, and the spectrum has an unsymmetrical appearance.

The hyperfine structure of all spectra obtained corresponds to interaction of an unpaired electron with two nitrogen nuclei and four protons of the benzene ring. The hyperfine structural constants in the spectrum of the anion from benzofurazan were: $a_N = 5.9$ G, $a_4^H = 3.5$ G, $a_5^H = 2.1$ G; the anion from piazthiole gave $a_N = 5.6$ G, $a_4^H = 2.9$ G, $a_5^H = 1.6$ G; the anion from piaselenole gave $a_N = 6{,}4$ G, $a_4^H = a_5^H = a_5^H = 2.1$ G. The proton splittings in the spectra of these anions are assigned from the spin density splitting as calculated by the MO method.

Results in agreement with the present ones have also been obtained very recently, where an exchange reaction with the anions of propiophenone or 9,10-dihydroanthracene was used to generate union-radicals of benz-2,1,3-X-diazoles (I, X = O, S, Se) [14].

In analyzing the EPR spectra of anions of nitrogen ring compounds, use is usually made of equations analogous to those used by Karplus and Fraenkel to describe the mechanism of hyperfine interaction of an unpaired electron with the magnetic moment of the nucleus of C_{13} in aromatic radicals:

$$a_N = Q_N^N O_N^\pi + \Sigma Q_{X_iN}^N \rho_{X_i}^\pi,$$

where the term $Q_N^N \rho_N^\pi$ represents the relationship between the value of the splitting at the nitrogen nucleus and the density $2pZ^-$ of an electron at the nitrogen atom; the terms of the sum $\Sigma Q_{X_iN}^N \rho_{X_i}^\pi$ express the relationship between a_N and the existence of spin density at neighboring atoms. According to existing data used in spin density calculations, the quantity Q_N^N is 25–28 G, while Q_{CN}^N lies in the limits $2.6 \geqslant Q_{CN}^N \geqslant -3.9$ G [16–19]. To calculate the spin density distribution in the anions, we took Q_N^N as 27 G, and decided to neglect terms $Q_{X_iN}^N$ due to their smallness. The relationship $a_i = Q_{CH}^H \rho_C^\pi$ was used to calculate the density of an unpaired electron at a carbon atom, taking the constant $Q_{CH}^H = 24.4$ [20]. Table 1 gives the unpaired electron densities obtained using this constant. A paper [14] shows that spin density at a key heteroatom increases in the order O, S, Se. However this does not allow for spin density at nitrogen atoms. Calculation of this factor shows that differences in spin densities at the fragments C_8, C_9, Se and C_8, C_9, S are negligible.

We carried out calculations of spin density distribution by the simple MO method, using parameters varying inside wide limits. The following parameters were employed:

$$\alpha_N = \alpha_C + \beta_{CC};\ \beta_{NC} = \beta_{CC};\ \alpha_X = \alpha_C + h_X\beta;\ h_X = 0, 1, 2, 3;$$

$$\beta_{NX} = \gamma_{NX}\beta_{CC};\quad \gamma_{NX} = 0.5;\ 1,\ 1.5.$$

In the case $\gamma_{NX} = 0$, when conjugation between the heteroatom and the rest of the π system is ignored, the calculation is carried out with the varying values $\alpha_N = \alpha_C + h_N\beta_{CC}$; $h_N = 0$; 0.25; 0.50; 0.75 1.25; 1.50. The limits of variation of the parameters were chosen so as to include $h_O = 3.2$ [21], $h_O = 2$ [22], $h_S = 1$ [22] previously used in the literature. We know of no data for h_{Se} and γ_{Se}, but starting from the less electronegative selenium, we can put $h_{Se} < h_O$ and h_S. Data relating to γ_{NX} values are at least few; the following values have been given $\gamma_N \cong 0.6$–0.75 [21,22], $\gamma_{NS} = 0.566$ [14], but they are quite inadequately based, and depend on choice of values of other parameters. Carrying out calculations using a wide range of changes in parameters, we attempted in a general form to analyze spin density distribution in molecules of anion-radicals of benz-2,1,3-X-diazoles.

Figure 3(A) shows how spin densities vary in corresponding positions of the anion of benz-2,1,3-X-diazole, in the absence of exchange interaction between the key heteroatom and the nitrogen atoms.

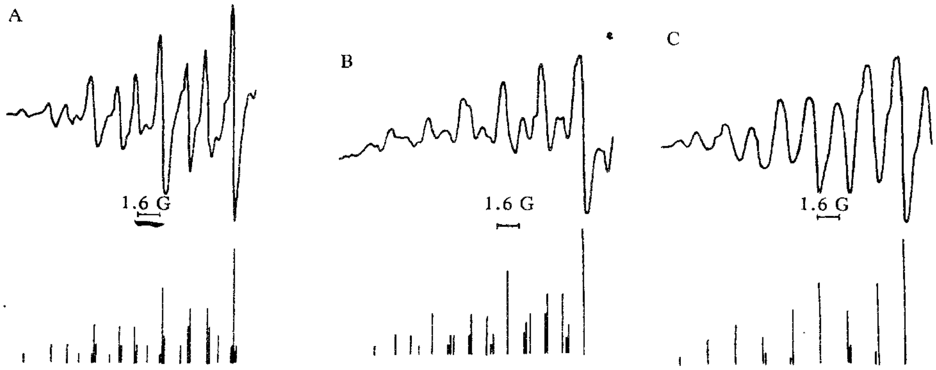


Fig. 2. EPR spectra of anions: A) benzofuran; B) piazthiole; C) piaselenole, generated by electrochemical reduction in dimethylformamide.

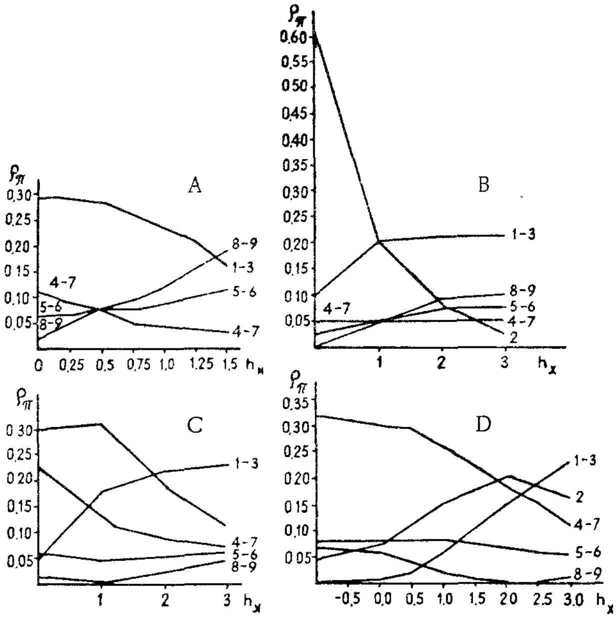


Fig. 3. Plots of spin density distribution at atoms in the anions of benz-2,1,3-diazoles: A) $\gamma_{NX} = 0$; $\alpha_N = \alpha_C + h_N$; B) $\gamma_{NX} = 0.5$; C) $\gamma_{NX} = 1$; D) $\gamma_{NX} = 1.5$.

Table 1

Unpaired Electron Density in Anions from Benz-2,1,3-X-diazoles (I, X = O, S, Se)

Anion		Density at atoms			$\Sigma 2\left(\rho_N^\pi+\rho_{C_4}^\pi+\rho_{C_5}^\pi\right)$
		N	C_4	C_5	
Benzofurazan (I, X=O)	Expt.	0.22	0.145	0.087	0.904
	Calc.	0.20^{1*}	0.15^{1*}	0.05^{1*}	0.80^{1*}
Piazthiole (I, X=S)	Expt.	0.21	0.107	0.066	0.776
	Calc.	0.20^{2*}	0.10^{2*}	0.05^{2*}	0.70^{2*}
Piaselenole (I, X=Se)	Expt.	0 24	0.087	0.087	0.828
	Calc.	0.25^{3*} 0.205^{4*}	0.075^{3*} 0.050^{4*}	0.075^{3*} 0.050^{4*}	0.828^{3*} 0.600^{4*}

1* Calculated using parameters $h_0=2.7$, $\gamma_{NO}=1.5$. 2* Calculated using parameter $h_S=1.5$, $\gamma_{NS}=1$. 3* Calculated using parameters $h_{Se}=0.5$, $\gamma_{NSe}=0$. 4* Calculated using parameters $h_{Se}=1$, $\gamma_{NSe}=0.5$.

Here the effect of the key heteroatom led only to an inductive effect, changing the value of h_N. Figure 3(B–D) shows the change in spin density distribution for different values of γ_{NX}: B $\gamma_{NX} = 0.5$; C $\gamma_{NX} = 1$; D $\gamma_{NX} = 1.5$, with h_X varying from 0 to 3. Analysis of the plots shows that for the cases $\gamma_{NX} = 1$ and 1.5, for all h_X values $\rho_{4-7} > \rho_{5-6}$. This region of changes of the parameter γ_{NX} can provisionally denote a naphthelenic one, since in the naphthalene anion the density of an unpaired electron at an α carbon atom is 2.7 times that at a β one [23]. Decrease in γ_{NX} to 0.5 and 0 results in ρ_{5-6} becoming greater than ρ_{4-7} for some values of h_X and h_N. Such a spin density distribution corresponds more closely to the distribution in the anion of ortho-benzosemiquinone, where the splitting at hydrogen atoms in positions 5–6 is 4 G, and that at hydrogen atoms at positions 4–7 is 1 G [24] (the numbering of the quinoid system is the same as that given in Eq. I). However the spin densities at the nitrogen and carbon atoms calculated for $\gamma_{NX} = 0$ and 0.5, are in worse agreement with experiment for the anions I, X = O and I, X = S, than for $\gamma_{NX} = 1$; 1.5. For the benzfuran and piazthiole anions the best agreement between calculated and found values for spin densities is found for the following values of the parameters: $\alpha_O=\alpha+2.7\beta_{CC}$; $\beta_{NO}=1.5\beta_{CC}$; $\alpha_S=\alpha_C+1.5\beta_{CC}$; $\beta_{NS}=\beta_{CC}$ (see Table 1).

Table 2

Energies of Transitions Between the Basic and First Excited Levels in β_{CC} units

γ_{NX}	h_N			
0	0	1	2	3
	0.58	0.40	0.30	—
	h_X			
	0	1	2	3
0.5	0.89	0.87	0.62	0.58
1	1.58	1.24	0.98	0.86
1.5	—	—	1.4	—

These values may be a little too high, due to the choice of $h_N = 1$. However as reliable data for h_X and γ_{NX} are lacking, these results are of some interest. Strom and Russell secured agreement with experiment using somewhat different values of the parameters: $\alpha_O=\alpha_C+2.0\beta_{CC}$, $\alpha_N=\alpha_C+0.5\beta_{CC}$; $\beta_{NO}=0.7\beta_{CC}$; $\alpha_S=\alpha_C+\beta_{CC}$; $\beta_{NS}=0.566\beta_{CC}$; but they had to raise the value of B_{CN} to 1.25–1.0 β_{CC} [14]. It follows from the equality of the hyperfine splitting constant for the hydrogen atoms at the 4th and 5th carbon atoms in the spectrum of the anion of piaselenole, and from comparison of plots A and B in Fig. 3, that β_{Se} lies within the limits $0 \leq \beta_{NSe} \leq 0.5\ \beta_{CC}$. It is precisely at these values of β_{NSe} that intersection of plots 4–7 and 5–6 in Fig. 3 (A and B) are found. The result of calculating the spin density distribution in the anion of piazthiole, taking into account the d-orbital of sulfur using the results of [14], and our results agree with the results of calculations inside the framework of pure π-electron models.

Thus, comparison of calculated and experimental data on the distribution of spin density in the anions shows that the key heteroatoms in the molecules of the compounds studied participate in a definite way in conjugation.

The results obtained, as well as literature data [14,21,22], enable the inequality $\alpha_O > \alpha_S > \alpha_{Se}$; $\beta_{NO} > \beta_{NS} > \beta_{NSe}$ to be deduced, characterizing the electronegativity of key heteroatoms and their abilities to conjugate with nitrogen. This inequality is in qualitative agreement with the data of electronic absorption spectra of benz-2,1,3-diazoles (I, X = O, S, Se) [6–9]. Table 2 gives transition energies between the basic level Ψ_1 and the first excited level Ψ_{-1}, calculated by the MO method in β_{CC} units.

Of course it is difficult to satisfactorily compare the results of a theory which does not take into account inter-electron interaction, with experiment. However, by analyzing the results in Table 2, it is possible to separate some tendencies. Decrease in β_{NX} with α_X fixed results in decrease in transition energy; decrease in α_X acts in the reverse direction. The changes are basically connected with the shift in energy level corresponding to nonbonding orbital Ψ_{-1}. The observed bathochromic shift [9] of the long-wave maximum in the series of compounds I, X = O 270, X = S 307, X = Se 330 nm, confirms the qualitative dependence of ΔE on β_{NX}. In view of this, the maximum bathochromic shift should be found with an interrupted heterocyclic ring, when $\gamma_{NX} = 0$. It is possible to follow similar behavior of longwave optical bands in the cases of naphtho-1,2-furazane (λ_{max} 330 nm) [25]. When the heterocyclic ring is interrupted, the longwave maximum suffers a bathochromic shift of 40 nm. The electronic spectra of quinoxaline and o-benzoquinone are to be recalled in connection with the problem considered. While for the former λ_{max} 339 nm, for the latter it is 610 nm [26], which is also in qualitative agreement with the views put forward.

2. EPR SPECTRA OF ANION-RADICALS FROM NAPHTHO-1,2-FURAZAN (II) AND NAPHTHO-1,2-SELENADIAZOLE (III).

The EPR spectra of anions of naphtho-1,2-furazan (II, potassium reduction) and naphtho-1,2-selenadiazole (III, potassium and electrochemical reduction) consists of 5 hyperfine structure lines, 6 G splitting, and relative intensities 1:2:3:2:1 (Fig. 4). The intensity ratios in the spectra indicate interaction of an unpaired electron with two equivalent nitrogen nuclei. Due to a large number of hydrogen atoms, the proton structure is ill-resolved. Analysis of EPR spectra of anions of compounds II and III shows the hyperfine splitting constants at the nitrogen nuclei to be equal (with an accuracy up to the width of a line). That result is not obvious, since the nitrogen atoms are not equivalent. The conservation of the splitting values a_N in the spectra of the anions of naphtho-1,2-furazan (II) and naphtho-1,2-selenadiazole (III), compared with the anions of benzofurazan (I, X = O), and, correspondingly piaselenole (I, X = Se) obviously means that on passing from benzologs to naphthologs, spin density distribution in the heterocyclic ring changes negligibly.

3. INVESTIGATION OF EPR SPECTRA OF PRODUCTS OF ELECTROCHEMICAL REDUCTION OF BENZOFUROZAN (IV) AND DIMETHYLFUROXAN (V).

In the process of electrochemical reduction of benzofuroxan (IV) an EPR spectrum was recorded which was the same, both in appearance and in respect of splitting constant value, as the EPR spectrum of benzofurazan (I, X = O). The same results are obtained by reducing benzofuroxane with potassium metal in 1,2-dimethoxyethane.

Some of the reasons for the agreements found may be indicated: 1) reduction of benzofuroxan under the conditions employed may be accompanied by splitting off of the oxygen in the ring to give the anion-radical of benzofurazan; 2) exchange of ring oxygen in the benzofuroxan-anion occurs, but at a rate over 10^7 sec^{-1} (splitting value in frequency units). Then the observed agreement of splitting values in the EPR spectra must be considered to be fortuitous.

At the start of the electrolysis process when reducing dimethylfuroxan (V, the observed spectrum has 5 hyperfine splitting components intensity ratios 1:2:3::2:1 and resolution 0.5 G. After some minutes at room temperature, the 5-line spectrum changes to a 7-line one with intensity ratios close to binomial, resolution 2.2 G. At –20° to –30° the 5-line spectrum lasts a long time. The spectra obtained so far do not enable the structure of the paramegnetic particles formed during electrochemical reduction of dimethylfuroxan, to be determined. The basic difficulty, connected with the interpretation of the spectrum obtained under these conditions, is that the 5-line spectrum shows only splitting due to 2 nitrogen nuclei, and there is a lack of the splitting due to protons of methyl groups which it would seem, should be observed.

Fig. 4. EPR spectrum of the anion obtained from naphtho-1,2-selenadiazole by reduction in 1,2-dimethoxyethane using potassium metal.

Using the method described for dimethylfuroxan (V), it has so far not been possible to record the spectrum of anions from dimethylfurazan, the N-base of compound V.

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