Chemistry of Heterocyclic Compounds, Vol. 36, No. 2, 2000

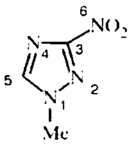
ESR AND POLAROGRAPHY OF NITROAZOLES.
7*. ANION-RADICALS OF ISOMERS OF N-METHYL-C-NITRO-1,2,4-TRIAZOLE

T. I. Vakul'skaya, V. A. Shagun, L. I. Larina, and V. A. Lopyrev

The anion-radicals of N-methyl-substituted 3-nitro-1,2,4-triazole have been studied by polarography, ESR, and quantum-chemical methods. The difference in electrochemical behavior of the N-methyl isomers of 3-nitro-1,2,4-triazole has been analyzed. The spin distributions in their anion-radicals have been investigated by quantum-chemical methods. The theoretical data obtained are in poor agreement with experiment. By varying the structural characteristics of the anion-radicals internal geometric parameters have been separated out which prove to have the greatest effect on spin distributions. Geometric structures were established for the investigated isomers by minimizing the functional describing the disagreement of the theoretical and experimental spin distributions on the magnetic nuclei. The calculated hyperfine structure constants for the magnetically active nuclei for the structures obtained were in good agreement with experiment. The influence of solvation effects on the electronic structure parameters of the nitrotriazole anion-radicals has been investigated. Hydrated complexes containing four molecules of water proved to be the most stable. Structural deformation of the solvated anion-radicals occurs in the same direction as on minimizing the functional.

Keywords: N-methyl-C-nitro-1,2,4-triazoles, anion-radicals, quantum-chemical calculations, ESR.

Replacement of hydrogen at nitrogen atom in nitroazoles by methyl group leads to a shift of the reduction potentials towards negative values. As a result of this replacement transfer of the first electron becomes a reversible process, which permits observation of primary anion-radicals of N-methylated nitroazoles [1-3]. In the present work the stereoselectivity of the effect of the methyl group on the electrochemical reduction of the isomers of N-methyl derivatives of C-nitro-1,2,4-triazole has been investigated. These isomers are important from the point of view of synthetic chemistry [4] and are 1-methyl-3-nitro- (**1**), 1-methyl-5-nitro- (**2**), and 4-methyl-3-nitro- (**3**) 1,2,4-triazole. The main quantum-chemical models of the effect of intramolecular conformational deformations on the main magnetoresonance parameters of the ESR in the anion-radicals of compounds **1-3**[*2] were considered.



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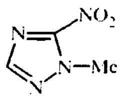

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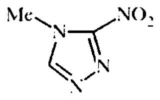

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[*] For part 6 see [1].

[*2] The numbering of the atoms in the molecules used in the calculations is given in the structural formula **1**.

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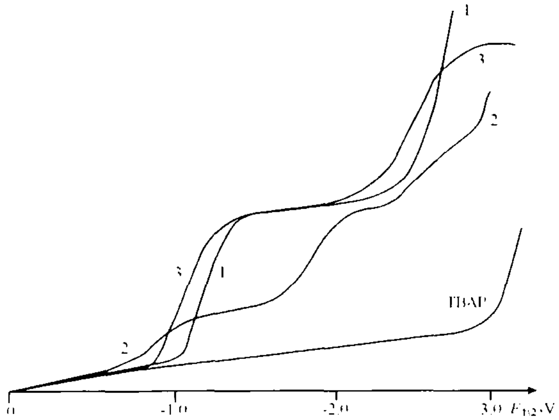

Fig. 1. Polarograms of compounds **1-3** in acetonitrile on a background of TBAP.

All three isomers are reduced in acetonitrile at the dropping mercury electrode at more negative potentials than 3(5)-nitro-1,2,4-triazole itself [1]. A clear dependence of the electrochemical behavior of compounds **1-3** on the position of the methyl group in the triazole ring is observed (Fig. 1). Shifts of potentials of the first and second waves are different for all isomers while the length of the plateau between them is increased in the following order: **3** < **2** < **1** (Table 1).

An increase is observed in the same sequence of the degree of hindrance of transfer of both the first and second electron compared with 3(5)-nitro-1,2,4-triazole [1]. This means that there exists a significant effect of the methyl group on the size of the gap between the energy levels of the lower vacant MO. Reduction of **1** in acetonitrile occurs in two stages. The first wave is a reversible one-electron wave, and the second is a 3-electron wave (polarogram 1 in Fig. 1). Isomer **2** is reduced in two one-electron stages, and the first wave also corresponds to reversible transfer of electron (polarogram 2 in Fig. 1). In difference to derivatives **1** and **2** compound **3** gives three waves on the polarogram. The total height of the two first waves barely reaches the one-electron level (the waves are sloping, irreversible). Isomer **3** is reduced significantly more readily than the rest (polarogram 3 in Fig. 1; Table 1). On increasing the concentration of the depolarizer by an order of magnitude to 5×10^{-3} M the first wave acquires a branched character, but the ratio of the wave heights remains unchanged. This indicates increased adsorption of the substance on the electrode.

In spite of the difference in reduction mechanisms of isomers **1-3**, at potentials corresponding to the first reduction wave well-resolved signals are observed in the ESR spectra for compounds **1** and **2** for the primary anion-radicals (Table 1, Fig. 2a,b). A well-resolved ESR signal (Fig. 2c) is also recorded for compound **3** which in hyperfine structure character must also refer to a primary anion-radical, but arising at potentials greater than 2 V, i.e. at the potentials of the second wave. Probably destruction of the adsorbed layer occurs only at these potentials and reduction of neutral molecules to the primary anion-radicals becomes possible. The hyperfine structure of the ESR signals is caused by all the magnetic nuclei of the molecules, while approximately half the spin density is centered on the nitro group in all the anion-radicals (Table 1).

TABLE 1. Reduction Potentials (V) of the Isomeric N-Methyl-C-nitro-1,2,4-triazoles and Hyperfine Structure Constants (mT) of Their Anion-Radicals

Isomer	$E_{1/2}$	$E''_{1/2}$	$a_N^{NO_2}$	$a_{N_{(1)}}$	$a_{N_{(2)}}$	$a_{N_{(4)}}$	a_H	$a_H^{CH_3}$
1	-1.17	-2.68	1.150	0.050	0.150	0.120	0.460	0.050
2	-1.06	-2.43	1.180	0.140	0.110	0.400	0.280	0.025
3	-0.85	-1.80						
		-2.54	1.105	0.130	0.240	0.130	0.120	0.020

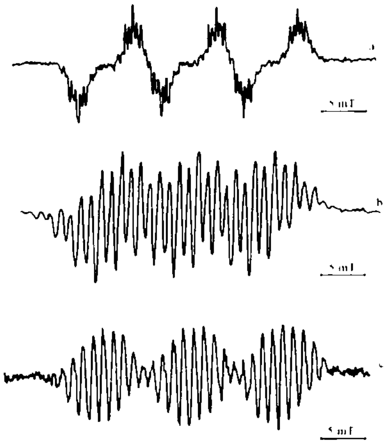

Fig. 2. ESR spectra obtained in the electrochemical reduction of compounds a) **1**; b) **2**; c) **3**.

A change in the position of the methyl group causes a significant redistribution of spin density between the nitrogen atoms of the triazole ring and shows up particularly strongly in the proton constant. The values of the constant $a_N^{NO_2}$ vary within 5-7%. Analysis of the spin densities on the magnetic nuclei of the triazole ring shows that in the anion-radical of compound **1** the pyridine nitrogen atoms are practically equivalent, while in the anion-radicals of isomers **2** and **3** one of the pyridine and the pyrrole nitrogen atoms are equivalent (Table 1). Such a character of the spin distributions related to the disposition of the methyl group in the triazole ring is reflected in the structures of the lowest unoccupied molecular orbitals (LUMO) of the most stable stationary states of the isolated neutral molecules **1-3**. A comparative analysis of the LUMO composition enables a clear traceable qualitative link to be recorded between the corresponding spin populations and the values of the hyperfine structure constants (Tables 1 and 2). This fact forms a basis for relying on a satisfactory transmission of spin distribution and, as a result, of the experimental hyperfine structure constants by quantum-chemical methods.

However test calculations carried out by the UMP2/6-31G* method led to values of the hyperfine structure constants not in agreement with experiment even qualitatively (Tables 1 and 3). Two states of the anion-radicals of compounds **1-3** were considered (excluding pseudodegenerate states). The first (a) was the most stable with an almost planar disposition of the nitro group relative to the five-membered ring, and the second (b) with it close to an orthogonal orientation. The differences of the main geometric parameters of these rotamers are small except for the dihedral angle α (Table 4).

TABLE 2. Contributions (ρ^{π}) of the AO of the Magnetically Active Atoms of the Triazole Ring to the LUMO, Relative Stabilities (ΔE, kcal/mole), and Barriers to the Internal Rotation of the Nitro Group (E_{RO}, kcal/mole) of the Neutral Isolated Isomers **1-3** (data by MNDO method)

Compound	$(\rho^{\pi})^2 \cdot 10^2$			ΔE*	E_{RO}
	$N_{(1)}$	$N_{(2)}$	$N_{(3)}$		
1	0.10	0.36	0.32	0.0	2.3
2	0.33	0.31	1.41	5.0	1.6
3	0.38	0.97	0.41	1.8	1.3

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* $\Delta Hf(I)$ = 58.4 kcal/mole.

TABLE 3. Calculated Isotropic Hyperfine Structure Constants (mT) of the Anion-Radicals of Compounds **1-3**

Radical	State	a_1	a_2	a_4	a_6
1	a	0.12	1.10	0.56	1.54
	b	0.41	0.87	0.06	2.69
2	a	0.55	0.58	0.52	1.57
	b	0.21	0.01	0.32	3.11
3	a	0.42	0.81	0.35	1.75
	b	0.39	0.16	0.47	2.43

The application of narrow-focused methods with the aim of improving agreement with experimental data led to an insignificantly positive result in certain variants. The geometric characteristics of the anion-radicals of compounds **1-3**, used subsequently in semiempirical calculations, were optimized in an UHF/MNDO approach. Geometric sets (Table 4) were also used, leading on the whole to no improvement. The spin populations obtained by INDO and UHF/MNDO methods differed fairly substantially, while in both variants the hyperfine structure constants, calculated according to the relationship [5], *viz.* $a = k\rho^s$, where ρ^s is the spin population of an atomic *s*-orbital, k – a constant equal to 379.34 Gs for the nitrogen atom nucleus, were in poor agreement with experiment (Table 5). Attempts to use semiempirical equations derived for nitro compounds in acetonitrile [6] and for aromatic nitroxyl radicals [7] in calculations of the $a_N^{NO_2}$ values, did not give any significant improvement of the results. The semiempirical methods (MNDO-UHF-QA, MINDO/3-RHF-CI, MNDO-RHF-CI), analysis of the applicability of which had demonstrated adequate efficiency of the two latter approaches for the assessment of hyperfine structure constants of a large series of π-radicals in [8], also led to no significant improvement in the agreement with experiment (Table 5).

The results obtained indicate that the actual (solvated) structures of the radicals of compounds **1-3** differ somewhat from those used in the calculations. On the other hand the analysis of the electron structure of the rotational isomers shows that the distribution of spin density depends strongly on the stereochemistry of the radicals. Attempts were therefore undertaken with the aid of an independent geometric variation to separate out the basic quantitatively significant structural parameters showing the greatest effect on spin populations. Assessment of the response of the distribution of spin density on the geometric deformation was effected in the neighborhood of the stationary states of the radicals of compounds **1-3** by alternate variation of the internal coordinates and also certain combinations of them with optimization of all the residual parameters. A similar approach, having moved little from the starting stationary state on the potential surface of intramolecular deformations, enabled assessment of the degree and direction of the changes of the spin populations of the various atoms. In view of the large volume of calculations and using the initially obtained values of the constants (Tables 3 and 5), the scanning of the geometric parameters was carried out within the framework of an UHF/MNDO approach.

As a result of carrying out this approach three parameters were separated variations of which, while not leading to a sharp reduction of the relative stability of the corresponding radical, chiefly influenced the spin populations. These parameters were the characteristics of the pyramidality of the nitro group nitrogen atom (d_1) and of the pyrrole nitrogen atom (d_2), and also the dihedral angle (α) between the planes of the triazole ring and the nitro group. It is not difficult to note that all three parameters determine primarily the orientation of the unshared electron pairs and their mutual influence. The variation of the dihedral angle (in the example of anion-radical of compound **1**, Fig. 3) in a stiff rotator approach in the neighborhood of the stationary state in the range 0-90°C gives a wide range of a_i values. This range at least includes the experimental values of the spin populations of the nitrogen atoms of pyrrole type and of the nitro group. The free variation of the dihedral angle, which in essence implies the rejection of the stiff rotator approach, and the implication of the pyramidality parameter in the variation process, leads to a substantial change in the behavior of the a_i values (Fig. 3). This indicates the significant effect of pyramidality on the character of the spin distribution. The independent variation of the pyramidality parameter of the pyrrole nitrogen atom (Fig. 4) within the limits of 0.0-0.3 Å also changes this constant significantly. The experimental value lies in the range of acceptable values.

TABLE 4. Geometric Parameters, Relative Stabilities (ΔE, kcal/mole)*, and Barriers to the Internal Rotation of the Nitro Group (E_{RO}, kcal/mole) of the Anion-Radicals of Compounds **1-3**

Radical	State	l_{ij},Å					φ_{ijk}, deg				α*^{2}	ΔE	E_{RO}
		1-2	2-3	3-4	4-5	3-6	1-2-3	2-3-4	3-4-5	2-3-6			
1	a	1.351	1.326	1.371	1.288	1.366	102.6	113.7	102.9	123.1	0.0	0.0	2.0
	b	1.347	1.319	1.362	1.294	1.381	101.6	114.1	101.2	122.9	67.8	1.7	2.0
2	a	1.352	1.351	1.318	1.338	1.369	108.8	109.9	102.6	123.6	0.0	0.0	3.8
	b	1.346	1.348	1.304	1.349	1.460	107.2	113.2	101.3	121.9	88.2	3.1	3.8
3	a	1.364	1.302	1.347	1.355	1.370	107.4	110.1	103.1	127.0	0.0	0.0	3.6
	b	1.355	1.294	1.365	1.348	1.385	107.0	112.3	102.9	125.8	84.6	2.9	3.6

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* The total energies of conformers **1a**, **2a**, and **3a** were 483.4201, 483.4410, and 483.4250 arbitrary units respectively.

*^{2} With the aim of retaining clarity allowing for the dependence of the $N_{(6)}$ atom on the angle of rotation, it is assumed that α is the angle formed between the planes $N_2C_3N_4$ and $C_3O_7O_8$.

TABLE 6. Geometric Parameters of the Anion-Radical Structures of Compounds **1-3** Minimized According to Functional F

Radical	l_{ij},Å					φ_{ijk}, deg				d_1*, Å	d_2*^{2}, Å	α, deg.
	1-2	2-3	3-4	4-5	3-6	1-2-3	2-3-4	3-4-5	2-3-6			
1	1.393	1.283	1.532	1.382	1.380	108.4	112.1	101.1	123.7	0.170	-0.081	10.9
2	1.403	1.422	1.362	1.420	1.420	104.7	109.8	103.0	126.3	0.058	0.102	3.3
3	1.312	1.309	1.419	1.417	1.428	109.1	108.0	104.6	130.2	-0.017	-0.120	1.9

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* The minus sign denotes the emergence of the nitro group nitrogen atom from the $C_3O_7O_8$ plane into the halfspace of the $N_{(4)}$–$C_{(5)}$ bond.

*^{2} The minus sign denotes divergence of the nitrogen atom from the plane of the atoms valence-bonded to it, increasing the interatomic distance from the oxygen atom closest to it.

TABLE 5. Hyperfine Structure Constants (mT) of the Anion-Radicals of Compounds **1-3**

Radical	Centre	UHF QA MNDO	UHF MNDO	RHF CI MNDO	INDO	RHF CI MINDO/3
1	1	0.02	0.05	0.03	0.18	0.04
	2	0.03	0.10	0.08	0.44	0.08
	4	0.00	0.00	-0.01	0.34	-0.05
	6	1.07	3.26	2.01	1.25	2.43
2	1	0.02	0.10	0.05	0.06	-0.01
	2	0.01	0.02	0.01	0.17	0.02
	4	0.06	0.15	0.10	0.34	0.11
	6	0.99	3.31	1.91	1.61	1.35
3	1	0.00	0.00	-0.02	0.06	-0.02
	2	0.05	0.15	0.09	0.35	0.10
	4	0.07	0.21	0.10	0.12	0.15
	6	0.91	2.91	1.63	1.35	1.87

A cross section of the potential energy surface in coordinates of α and d_1 is given in Fig. 5. Independent variation of parameters α, d_1, and d_2 was carried out in the neighborhood of the stationary state with an acceptable variation of the total energy not exceeding 20 kcal/mole and was effected in this way in order to minimize the functional F:

$$F(a_1(x_i),a_2(x_i),a_N(x_i)) = \sum_{i=1}^{N} |a_i\text{theor.} - a_i\text{exp.}|$$

where x_i are the internal coordinates of the anion-radical. It is thereby secretly assumed that energies of no more than 20 kcal/mole are required in the MNDO approach on transition from the isolated state to the solvated for the geometric reorganization of the anion-radicals of isomers **1-3**. This is demonstrated below. The present approach enabled the establishment of the structure of radicals of compounds **1-3** (Table 6) with a distribution of spin density and correspondingly with hyperfine structure constants, which are practically quantitatively in agreement with experiment (Tables 1 and 7).

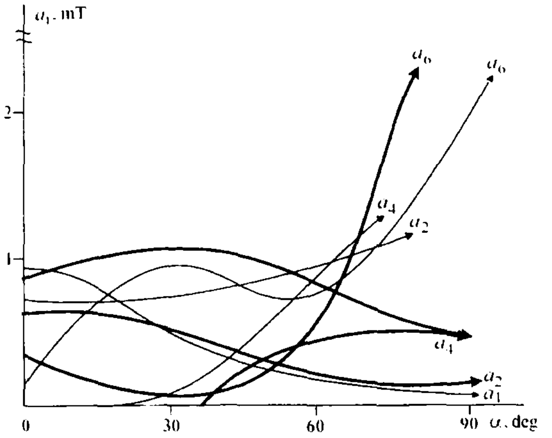


Fig. 3. Dependence of the hyperfine structure constants of the anion-radical of compound **1** on the angle of rotation α (fine line is for stiff rotator approach, bold line is for free rotation).

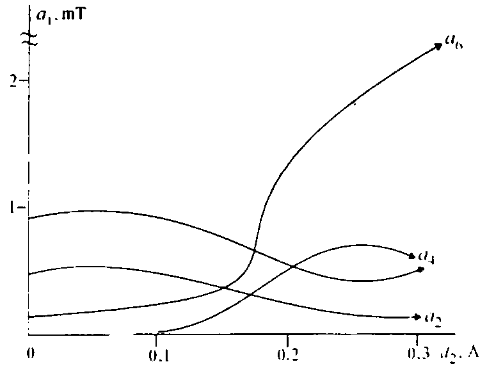


Fig. 4. Dependence of the hyperfine structure constants of the anion-radicals of compound **1** on the degree of pyramidality of the $N_{(4)}$ atom.

TABLE 7. Hyperfine Structure Constants (mT) of the Aniȯn-Radicals of Compounds **1-3**

Radical	a_1	a_2	a_4	a_6
1	0.13	0.25	0.14	1.12
2	0.13	0.11	0.31	1.19
3	0.05	0.18	0.15	1.16

Naturally there is a need if only on a qualitative basis for the results of the geometric reorganization carried out. With this object a quantum-chemical model has been considered of the effect of the solvate environment on the structural parameters and the electronic state of the anion-radicals of isomers **1-3**. Water molecules play the role of solvate envelope. The solvation energy is estimated as the difference between the total energies of the polyhydrated complex and of the isolated substrate and water molecules. In order to be consistent, in a comparative analysis of the data obtained all quantum-chemical calculations were carried out by the UHF/MNDO semiempirical method.

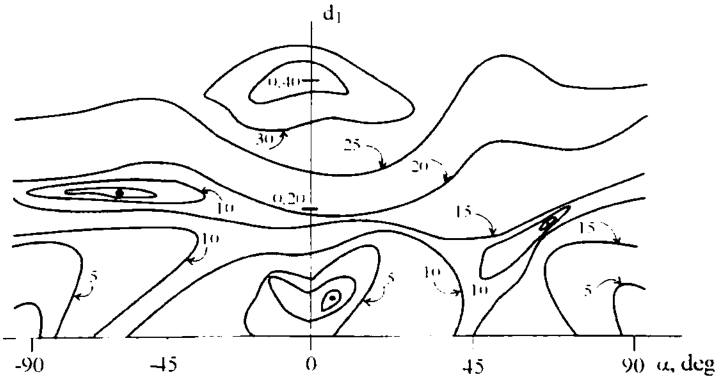


Fig. 5. Cross section of the potential energy surface in coordinates of α and d_1.

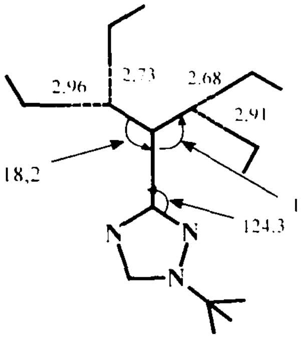
TABLE 8. Geometric Parameters and Hyperfine Structure Constants (mT) of Tetrahydrate Complexes of the Anion-Radicals of Compounds **1-3**

Radical	a_1	a_2	a_4	a_6	d_1, A	d_2, A	α, deg.
1	0.02	0.05	0.04	1.10	0.141	-0.046	8.6
2	0.08	0.13	0.28	1.23	0.087	0.064	7.4
3	0.08	0.24	0.10	1.21	0.021	-0.96	3.7

To determine the optimum number of particles in the first hydrate envelope of the anion-radicals of compounds **1-3**, the energies of complexes with 3, 4, 6, and 7 water molecules were calculated. The most preferred was the form with four water molecules, the solvation energy of which in a recalculation on one water molecule was -22.1, -17.4, and -18.6 kcal/mole for compounds **1**, **2**, and **3** respectively. With a further increase in the number of water molecules the system becomes destabilized. Solvation is accompanied by an insignificant electron transfer from the anion-radical to the hydrate envelope. The excess negative charge on the water molecules was 0.04-0.06 on average.

The more substantial structural reconstruction of the substrate was that leading to a drawing together of the appropriate geometry obtained by *F*-minimalization. In this way the energy of the intramolecular geometric deformation of the anion-radicals of compounds **1-3** did not exceed 20 kcal/mole, i.e. the maximum value which was allowed in the search for *F*-stationary states. Although the hyperfine structure constants calculated for $AP^{\cdot}\cdots nH_2O$ complexes were not comparable quantitatively with experimental (Table 8), the main trends of their changes were relayed qualitatively.

The calculated splittings in the magnetic nucleus of the nitro group nitrogen atom in the anion-radicals of isomers **1-3** in aqueous medium were close to experimental. A less satisfactory agreement was observed for the nitrogen atoms of the triazole rings, which may be explained by an imperfection in the solvation model considered in the following structure of the tetrahydrate complex corresponding only for the nitro group:



The implication of additional water molecules in interaction with the triazole ring may probably lead to an improvement of the results.

One of the possible proofs of the high effectiveness of the *F*-minimization approach or the solvate model compared with the standard method of evaluation of splitting is the calculation of the hyperfine structure constants for the $H_{(5)}$ atom in the anion-radicals of compounds **1-3**. The obtained values $a_H = k\rho^s$, where k = 539.86 Gs and ρ^s is the spin population of the atomic *s*-orbital, do not agree badly with experiment in the variant first mentioned above [a_H = 0.36 (**1**), 0.21 (**2**), 0.08 (**3**)], correlate satisfactorily in the second [a_H = 0.53 (**1**), 0.24 (**2**), 0.23 (**3**)], and partially in the third [a_H = 0.64 (**1**), 0.19 (**2**), 0.21 (**3**)]. The use of *F*-minimization procedures in the variation of quantitatively significant internal geometric parameters may help to assess moderately the electronic and structural transformations related to external influences.

EXPERIMENTAL

Nitroazoles **1-3** were obtained by the procedure of [9,10] and were purified by vacuum sublimation directly before use. Polarograms were recorded on OH-102 and OH-105 polaragraphs (Hungary) relative to the saturated calomel electrode on a background of tetra-*n*-butylammonium perchlorate (TBAP) using the dropping mercury electrode with forced breaking off of the drops ($m^{2/3}t^{-1/6}$ = 1.5 $mg^{2/3}sec^{-1/2}$). Freshly purified nitrobenzene was used as standard substance. The operating concentration of depolarizer was 5×10^{-4} M.

The ESR studies of anion-radicals were effected in special electrochemical cells, previously deoxygenated by sequential freezing and thawing of solutions under vacuum, and then filled with argon purified over potassium–sodium alloy. The EPR spectra were taken on a RE-1307 spectrometer with stabilization of the resonance conditions. Simulation of EPR spectra was carried out with regard to the Lorentz form of a line and the width of an individual component within the limits of 0.015-0.04 mT [1].

Calculation of the geometric characteristics of compounds **1-3** by the UMP2/6-31G* method was effected using the GAMMES-95 set of programs [11]. The isotropic (spherically symmetric) component of splitting was determined nonempirically through the spin density on a nucleus [12]. The main part of the semiempirical calculations was carried out using the computer packages MOPAC and AMPAC. The procedure for minimizing the functional was constructed on the basis of the method of alternate change of variables (Gauss–Seidel). The structural parameters d_1, d_2, and α were selected as independent coordinates. On attaining limiting conditions ($\Delta E \geq 20$ kcal/mole) return in the region energetically permitted for variations was effected using the vector-gradient projection method. Variation of the linear parameters in the minimization process was effected with a step of 0.05 Å and 3° for angles. In the neighborhood of F stationary states the step was reduced to 0.005 Å and 0.2° respectively.

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