SYNTHESIS AND INVESTIGATION OF THE PROPERTIES OF α-(6-METHYL-2-BENZOTHIAZOLYL)-α-PHENYL-β-(2,6-DINITROPHENYL)HYDRAZYL, α-(2-METHYL-6-BENZOTHIAZOLYL)-α-PHENYL-β-(2,6-DINITROPHENYL)-HYDRAZYL, AND THE CORRESPONDINGHYDRAZINES

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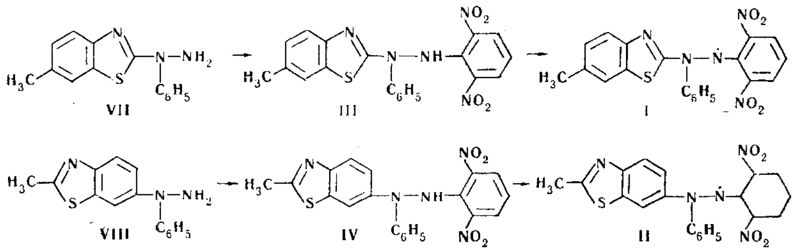
α-(6-Methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazyl and α-(2-methyl-6-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazyl and their corresponding hydrazines were synthesized. The properties of the compounds obtained were investigated by IR, UV, and visible spectroscopy. Their complexing ability was studied by an optical method and from their electrical conductivity. The ESR spectra of the radicals were recorded. The limiting currents and reduction potentials of the hydrazines on a dropping mercury electrode were found. The charge and spin densities of the compounds were calculated by means of the Hückel MO and MacLachlan methods. It was demonstrated that the hydrazines form unstable charge-transfer complexes in benzene–piperidine solutions; the characteristics of these complexes depend on the structure of the RR'N–NH–hydrazine residue.

The results of the investigations in [1, 2] provide a basis for assuming that the properties of solutions of hydrazyl radicals cannot be described without taking the peculiarities of the medium into account. The synthesis and investigation of the properties of α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazyl (I) and α-(2-methyl-6-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazyl (II) constitute the subject of this communication. The relationship between the structures and properties of α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazine (III), α-(2-methyl-6-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazine (IV), α,α-diphenyl-β-(2,6-dinitrophenyl)hydrazyl (V), and α,α-diphenyl-β-(2,6-dinitrophenyl)hydrazine (VI) is also examined. The synthesis of I-IV was accomplished via the following scheme:



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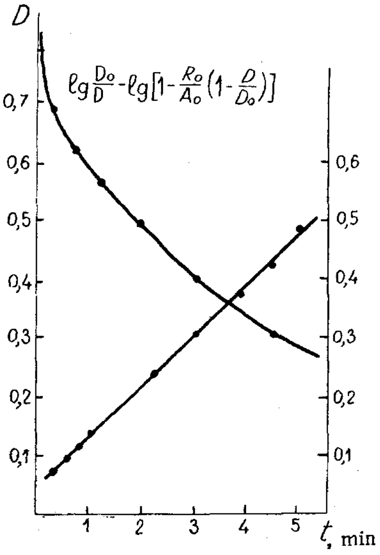

Fig. 1

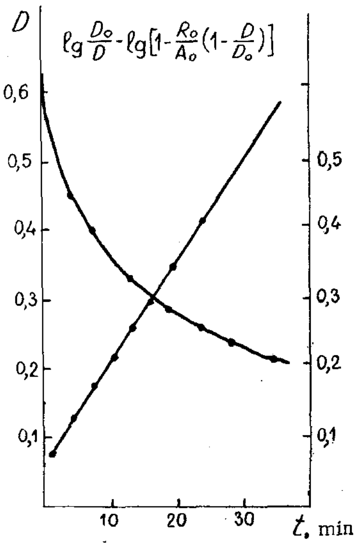

Fig. 2

Fig. 1. Experimental kinetic curve and anamorphosis for the reduction of the radical with N-phenyl-β-naphthylamine in toluene at 20° ($0.366 \cdot 10^{-4}$ mole/liter radical and $2.33 \cdot 10^{-5}$ mole/liter amine, layer thickness 4 cm, λ 620 nm).

Fig. 2. Experimental kinetic curve and anamorphosis for the reduction of the radical with N-phenyl-β-naphthylamine in toluene at 20° ($0.475 \cdot 10^{-4}$ mole/liter radical, $1.525 \cdot 10^{-2}$ mole/liter amine, layer thickness 4 cm, λ 620 nm).

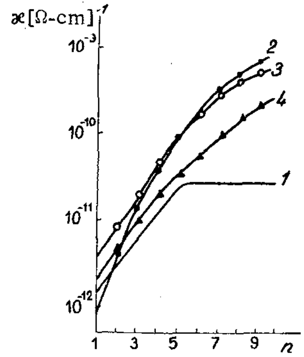

Fig. 3. Specific conductivity of the benzene–piperidine–hydrazine system as a function of the piperidine concentration (n is the volume ratio of piperidine and a benzene solution of hydrazine ($1 \cdot 10^{-2}$ mole/liter): 1) in the absence of hydrazine; 2) hydrazine III; 3) IV; 4) VI.

Hydrazines III and IV are readily oxidized by lead dioxide in benzene or chloroform solutions to the corresponding radicals (I, II). Only radical II could be isolated from solution.

To determine the reactivities of the radicals, we reduced them to the starting picrylhydrazine with N-phenyl-β-naphthylamine. The reaction is first-order in both the radical and amine. The experimental kinetic curves and their anamorphoses are presented in Figs. 1 and 2. The rate constants for the reduction of hydrazyls I and II are $1.36 \cdot 10^{-2}$ and $3.56 \cdot 10^{-2}$ liter/mole-sec.

The results of an investigation of benzene–piperidine solutions of hydrazines III, IV, and VI indicate that they exist as complexes with the medium. Thus the conductivity of benzene–piperidine solutions of hydrazines III, IV, and VI is considerably higher than the conductivity of benzene solutions of the hydrazines or piperidine–benzene solutions in the absence of hydrazine (Fig. 3). The appearance of a small characteristic maximum at 500 nm and of an intense maximum at 320 nm as the piperidine concentration rises (Table 1) is observed in the electronic spectra of III in benzene solutions. However, the absence of a clearly expressed inflection on the conductivity curves and the low intensity of the maximum in the long-wave region of the electronic spectrum indicate that the degree of charge transfer in the complexes of hydrazines III, IV, and VI with piperidine is small. The difference in the polarographic reduction potentials of III, IV, and VI (Table 2), however, as well as the difference in the optical properties of their complexes, indicate that the degree of charge transfer depends on the character of the RR'N–NH–hydrazine residue in these compounds. It is natural to assume that the complex of the β-dinitrophenyl substituent in these compounds with piperidine should be more stable, the lower the basicity

TABLE 1. Parameters of the Electronic Absorption Spectra

Compound	Solvent	λ_{max_1}, nm	λ_{max_2}, nm	$\lg \varepsilon_{max_1}$	$\lg \varepsilon_{max_2}$
I	Benzene	360	600	4,17	3,76
II	"	340	550	4,11	3,54
V	"	320	520	4,11	3,69
III	"	355	—	3,61	—
IV	"	585	—	3,50	—
VI	"	—	—	—	—
III	Piperidine	320	500	4,26	3,66
IV	"	385	—	3,50	—
VI	"	—	—	—	—

TABLE 2. Half-Wave Potentials and Limiting Current Constants

Hydrazine	$[E_{1/2}]_1$	K_1	$[E_{1/2}]_2$	K_2	$[E_{1/2}]_3$	K_3
III	0,22	2,82	0,895	2,5	1,26	26,8
IV	0,28	2,06	0,86	4,15	1,42	17,7
VI	0,29	3,47	0,89	4,39	1,465	29,34

TABLE 3. Characteristic Absorption Bands of Radicals and Hydrazines

Compound	ν_{NH}, cm^{-1}	Asymm. ν_{NO_2}, cm^{-1}	Symm. ν_{NO_2}, cm^{-1}	$\nu_{C_{ar}-\dot{N}}$, cm^{-1}	Other bands, cm^{-1}
II	—	1537 s	1346 s	1300 s	1208 — $\dot{N}-C_{ar}$ 1600 s — benzene 1498 s — ring
III	3288 m 1614 m	1532—1530 vs	1344 m	1318 vw 1295 m 838 w 712 m	655 w — C–S
IV	3312 mw	1537—1534 s	1344 w	1300 m 831 w 712 m	652 w — C–S
V	—	1530 vs	1343 m	1314 w 1287 m 820 w 718 m	1560 mw 1208* m — $N-C_{ar}$ 852 — marked increase in intensity 774 — new band, not in the starting hydrazine
VI	3320 w 1622 m	1536 s	1338 mw	1300 s 823 713 m	

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* Frequency of the band that corresponds to the presence of a $-\mathring{N}-C_{ar}$ bond in diphenylpicrylhydrazyl (DPPH), 1215 cm^{-1}. A similar band is also observed in the spectrum of tetraphenylhydrazine (1209 cm^{-1}).

of the hydrazine moiety in III, IV, and VI, and vice versa. The experimental data on the determination of the basicities of VII and VIII demonstrated that the basicities of these compounds are practically the same, and the K_B values are $9.93 \cdot 10^{-12}$ and $7 \cdot 10^{-12}$, respectively. The effect of a β substituent in the investigated systems is apparently more complex and is possibly associated with the structural peculiarities of the complex in solution.

An analysis of the IR spectra of III, IV, and VI (Table 3) demonstrated that the characteristic frequencies of the symmetrical and asymmetric vibrations of the nitro groups in these compounds are independent of the nature of the hydrazine component. In the crystalline state, the investigated hydrazines apparently form intermolecular complexes, the donor component in which is the hydrazine part of the molecule, while the acceptor component is the dinitrophenyl portion. In connection with the greater (in comparison with solutions) static character of the crystalline state, the stability of such intermolecular complexes is quite high. The latter stipulates the absence of an effect of the hydrazine portion of the molecules on the dinitrophenyl portion, and, in the end, one notes practically complete coincidence of the frequencies of the characteristic absorption bands of the dinitrophenyl residue. The electronic spectra of the investigated hydrazines

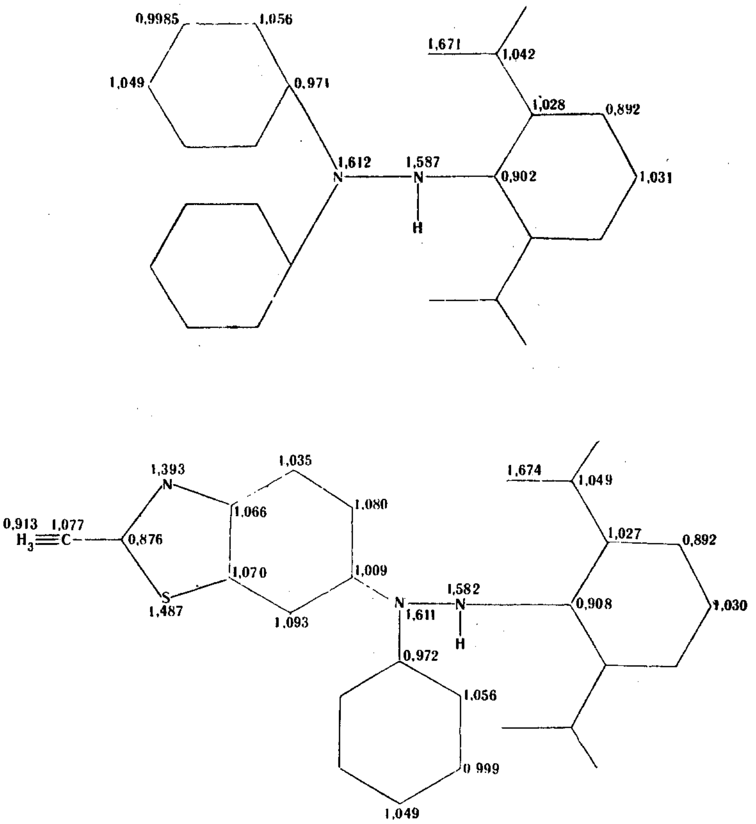

Fig. 4a. Hückel MO charge densities of hydrazines III, IV, and VI.

in benzene (Table 1) differ considerably from one another in connection with the high dynamic character of the system as compared with the crystalline state, and, consequently, with the considerable weakening – if not total destruction – of the intermolecular complex, which exists in the crystalline state.

It is noteworthy that 2,6-dinitrophenylhydrazyls, including I and II, are considerably less reactive compounds than their picryl analogs [3] in the dehydrogenation of secondary amines. If one takes into account that the picryl derivatives of diarylhydrazines form more stable complexes with amines than the 2,6-dinitrophenyl derivatives do, it can then be assumed that one of the determining steps in the reduction of the radicals with amines is the formation of complexes. The more stable the complex of the radical with the reducing agent, the higher the rate of reduction, and vice versa.

It is apparent that the certain correlation of the spin densities on the β-nitrogen atoms in I and II (Fig. 4) with the rate constant for their reduction by amines is accidental, since it has been demonstrated on the basis of a large amount of experimental data [4] that there is no such dependence in a series of hydrazyl radicals.

The quantum-chemical calculations of the spin densities of radicals I and II were performed according to the MacLachlan method, while the charge densities of radicals I and II and hydrazines III, IV, and VI were calculated by means of Hückel MO. An idealized planar molecule in which intermolecular interaction was disregarded was taken as the model for the calculations. However, since all of the experimental material presented above indicates nonmonomolecular structures for I-IV and VI, the certain correlation between the calculated spin densities and the experimental values that were obtained by ESR spectroscopy must be considered to be accidental.

In other words, quantum-chemical modeling for such systems (in which pronounced intermolecular interaction has been proved) proves to be invalid and does not correspond to the real state of the substance.

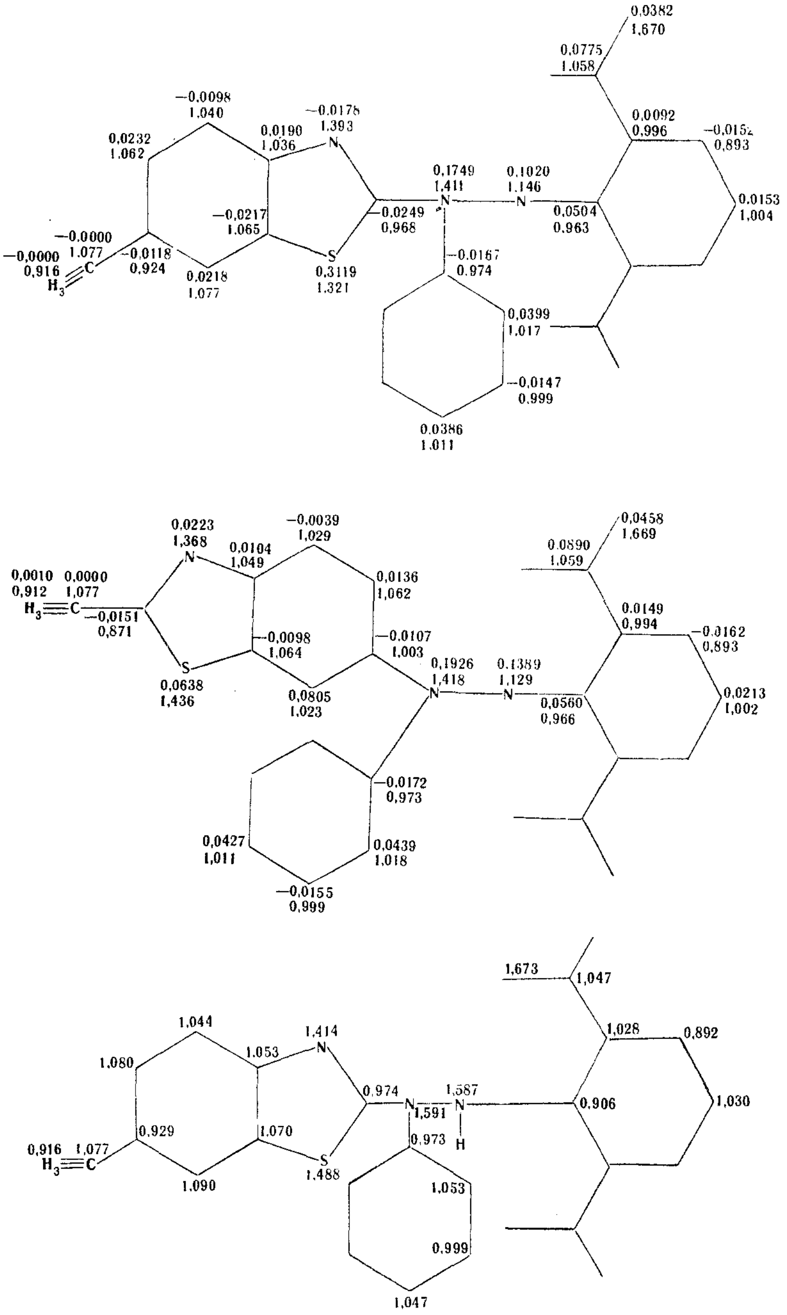

Fig. 4b. MacLachlan spin densities (upper) and Hückel MO charge densities of radicals I and II.

EXPERIMENTAL

The electronic absorption spectra were recorded with SF-4 and SF-10 spectrophotometers. The IR spectra of KBr pellets of the compounds were obtained with a UR-20 spectrophotometer.

The ESR spectra of degassed solutions of the radicals (10^{-3} mole/liter) were obtained with an RÉ-1301 radiospectrometer. The HFS parameters were calculated with an M-20 computer by means of optimization of the mean-square deviation of the ordinates of the experimental spectra from the theoretical (see Table 4). The electrical conductivities of benzene solutions of complexes of hydrazines III, IV, and VI with piperidine were measured in a thermostatted cell with palladized electrodes at 24°C and an electrode voltage of ~100 V. The results of the investigations are presented in Fig. 2.

TABLE 4. Isotropic HFS Parameters of the ESR Spectra

Compound	A_1/A_2	A_1+A_2, Oe	$A_1 \pm 0{,}15$, Oe	$A_2 \pm 0{,}15$, Oe	$\delta H \pm 0{,}15$, Oe
I	0,50	17,08	5,71	11,37	6,29
II	0,69	16,94	6,92	10,02	5,45
V	0,69	17,54	7,16	10,38	5,53

The polarographic reduction was performed with an LP-60 polarograph using $0.4\text{–}2.0 \cdot 10^{-4}$ M solutions of the hydrazines in anhydrous dimethylformamide with 0.1 M tetraethylammonium iodide as the background. A dropping mercury electrode was used as the cathode, and the unpolarizable anode was sludge mercury. The capillary parameters were: $t = 2.6$ sec when $H = 400$ and $m = 1.3$ m/sec. The recordings were made at 24° from 0 to − 2 V.*

α-(6-Methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)-hydrazine (III). A mixture of 5 g of VII and 4.2 g of 1,2,3-trinitrobenzene in ethanol was refluxed for 1 h. The precipitate that formed on cooling was crystallized from chloroform–alcohol (1 : 2) to give 2 g (24.4%) of yellow needles with mp 170-172° (dec.) that were slightly soluble in benzene and alcohol and quite soluble in chloroform and acetone. Found: C 56.76; H 3.83; N 16.70%. $C_{20}H_{15}N_5O_4S$. Calculated: C 57.00; H 3.59; N 16.62%.

α-(6-Methyl-2-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)-hydrazyl (I). This compound was obtained by the oxidation of III with a tenfold amount of lead dioxide in chloroform. All attempts to isolate the radical from the solution give its decomposition product – a colorless substance that we could not identify. Instantaneous decolorization of the solution was observed when the violet solution was treated with hydroquinone. The resulting mixture yielded an almost quantitative amount of III, which was identified from the authentic, synthesized compound. The results of investigations of the visible, UV, and IR spectra provide a basis for assuming that the product of the oxidation of III is radical I.

α-(2-Methyl-6-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)-hydrazine (IV). A mixture of 5 g of VIII and 4.2 g of 1,2,3-trinitrobenzene in 150 ml of ethanol was refluxed for 30 min. The alcohol was partially removed by distillation, and the resulting precipitate was separated and dissolved in chloroform. The solution was chromatographed over activity III Al_2O_3, and the eluate was evaporated to one third of its original volume. A twofold volume of ethanol was added to the hot chloroform solution, and the mixture was cooled to precipitate a resinous substance, which was converted to an orange powder by treatment with hydrochloric acid. The orange powder was washed thoroughly with water and vacuum-dried to give a product with mp 90° (dec.). The product was quite soluble in $CHCl_3$, ethanol, and benzene, and slightly soluble in hexane. The yield was 3 g (36.6%). Found: C 56.99; H 3.61; N 16.57%. $C_{20}H_{15}N_5O_4S$. Calculated: C 57.00; H 3.59; N 16.62%.

α-(2-Methyl-6-benzothiazolyl)-α-phenyl-β-(2,6-dinitrophenyl)hydrazyl (II). A 0.5-g sample of IV was oxidized by means of 5 g of lead dioxide in chloroform. The sediment was removed, and the chloroform was vacuum-distilled to one third of its original volume, diluted with heptane, and allowed to stand in the cold for a long time. The precipitate was removed by filtration and vacuum-dried (10^{-3} mm for 10 h at 20°) to give 0.3 g (60%) of almost black crystals with mp 81-82° (dec.) that were quite soluble in $CHCl_3$ and benzene, and slightly soluble in heptane. Reduction of II with hydroquinone gave starting IV, which was identified from an authentic, synthesized sample. Found: C 56.65; H 3.42%. $C_{20}H_{14}N_5O_4S$. Calculated: C 57.14; H 3.33%.

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*Hydrazyls could not be reduced under these conditions, since they interact with the background, and the violet color peculiar to the radicals vanishes. The polarogram of the product of this interaction is identical to those of the hydrazines.