SOME PROPERTIES OF α-(6-METHYL-2-BENZOTHIAZOLYL)-α-PHENYL-β-PICRYLHYDRAZYL, α-(2-METHYL-6-BENZOTHIAZOLYL)-α-PHENYL-β-PICRYLHYDRAZYL, AND THEIR HYDRAZINES

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The structures and properties of α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-picrylhydrazyl, α-(2-methyl-6-benzothiazolyl)-α-phenyl-β-picrylhydrazyl, and their corresponding hydrazines and complexes were studied by means of IR, UV, and visible spectroscopy and electrical conductivity. The half-wave potentials and limiting currents for reduction on a dropping mercury electrode were found for the hydrazines. The charge and spin densities of the investigated compounds were calculated by the Hückel MO and MacLachlan methods. It is shown that in the case of strong interaction with a medium the characteristics of the trinitrophenyl groups of the picrylhydrazines are practically the same, regardless of the structure of the hydrazine residue bonded to them.

It is shown in [1, 2] that the simplest hydrazyl—diphenylpicrylhydrazyl (DPPH) — exists in solutions as a charge-transfer complex with solvent molecules.

The aim of this investigation is an explanation of the dependence between the structures and properties of two isomeric radicals and their hydrazines in solution, viz., α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-picrylhydrazyl (I), α-(2-methyl-6-benzothiazolyl)-α-phenyl-β-picrylhydrazyl (II), α-(6-methyl-2-benzothiazolyl)-α-phenyl-β-picrylhydrazine (III), and α-(2-methyl-6-benzothiazolyl)-α-phenyl-β-picrylhydrazine (IV).

For comparison, data were also obtained for DPPH and its hydrazine ($DPPH_h$) and for sym-trinitrobenzene (TNB).

It is known that the frequency of the asymmetrical vibrations of the nitro groups for aromatic compounds is more sensitive to a change in the structure of the aromatic residues than the frequency of the symmetrical vibrations. In III, IV, and $DPPH_h$, the frequencies of the symmetrical vibrations are constant, while the frequencies of the asymmetrical vibrations of the nitro groups for these hydrazines are also practically constant and are almost the same as those for TNB.

The potentials for the reduction of the nitro groups of TNB and the indicated picrylhydrazines differ only slightly (Table 3). The conductivities of the piperidine complexes of picrylhydrazines III and IV and $DPPH_h$ and TNB are practically identical (Fig. 1).

Benzene solutions of III and IV do not have maxima at 280-500 nm (Table 2). Two maxima at 320-340 and 420-440 nm appear when piperidine is added to them. The maximum at 430 nm is characteristic for the complex of TNB with piperidine [4], and the short-wave maximum (320-340 nm) is identified from the absorption maxima of the corresponding diarylhydrazines: α-(6-methyl-2-benzothiazolyl)-α-phenyl-

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TABLE 1. Characteristic Absorption Bands of Radicals and Hydrazines

Compound	Frequency, cm^{-1}			
	ν_{NH}	ν_{NO_2}†	$\nu_{C_{ar}-N<}$	$\nu_{>N-C_{ar}}$
DPPH$_h$*	3260	Асим. 1548 vs Сим. 1343 vs	1306 s	—
DPPH	—	Асим. 1530 vs Сим. 1330 vs	1295 s	1215 m
III	3288 w	Асим. 1542 vs Сим. 1344 m	1306 m	—
IV	3295w	Асим. 1546 s Сим. 1344 vs	1303 m	—
II	—	Асим. 1536 s Сим. 1330 vs	1300 w decrease in intensity	1214 w-m

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* The values presented for DPPH and DPPH$_h$ concur with the data in [3, 4].

† For 1,3,5-trinitrobenzene, asym 1550 cm^{-1} (vs) and sym 1340 cm^{-1} (vs).

TABLE 2. Electronic Absorption Spectra

Compound	λ_{max_1}, nm	λ_{max_2}, nm	ε_{max_1}, liter/mole · cm	ε_{max_2}, liter/mole · cm
I	360	570	9400	6750
II	340	540	10620	9800
DPPH	320	525	11900	8500
III	No absorption			
IV	No absorption			
DPPH$_h$	320	—	6200	—
DPPH$_h$ + piperidine	325	430	12300	16600
III + piperidine	320	440	24000	21000
IV + piperidine	345	430	18200	18000
DPPH + pyridine	320	525	12200	8600
I + pyridine	325	450	6000	4100
II + pyridine	340	540	11200	9500
III + pyridine	—	430	—	7400
α,α-Diphenylhydraz.	295		13750	
V	310		23750	
VI	317		13250	

hydrazine (V) and α-(2-methyl-6-benzothiazolyl)-α-phenylhydrazine (VI) (Table 4). A benzene solution of DPPH$_h$ has a maximum at 320 nm. A maximum appears at 430 nm during complexing, while a small shift and an increase in intensity is observed for the maximum at 320 nm [4].

On the basis of the above, it can be assumed that as a result of complexing of III, IV, and DPPH$_h$ with piperidine due to considerable charge transfer from piperidine there is a pronounced weakening of the bond of the picryl group with the hydrazine nitrogen atom, and by virtue of this, the individuality of the diarylhydrazine residue is manifested more here than in benzene solutions of the investigated hydrazines. In other words, the picryl residue in the examined compounds turns out to be, as it were, doubly bonded. In benzene solutions of III, IV, and DPPH$_h$ the intermolecular interactions are weaker as expressed in their different conductivities, which depend on the structure of the hydrazine bonded to the trinitrophenyl group. In addition, the reduction potentials of 2,6-dinitrophenylhydrazines V and VI and diphenylhydrazine and the conductivities and optical parameters of their benzene–piperidine solutions also depend on the peculiarities of the hydrazine component.*

All of this provides a basis to suppose that III, IV, and DPPH$_h$ form charge-transfer complexes in benzene–piperidine solutions, in the crystalline state, and during reduction on a dropping mercury electrode; within the limits of these complexes, the picryl grouping displays properties which are independent of the residue bonded to it.

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* This is the subject of a special communication.

TABLE 3. Half-Wave Potentials and Limiting Current Constants*

Compound	$[E_{1/2}]_1$ †	$[E_{1/2}]_2$ ‡	$[E_{1/2}]_3$	$[E_{1/2}]_4$	$[E_{1/2}]_5$ **	K_1	K_3	K_4
III	0,075	0,47	0,727	0,987	1,33	2,02	1,4	2,71
IV	0,058	0,47	0,692	0,985	1,34	1,17	1,94	4,27
$DPPH_h$	0,077	0,497	0,737	0,993	1,415	1,81	1,81	2,11
1,3,5-Trinitrobenzene	—	—	0,64	1,045	1,33	—	1,36	1,09

*Depolarizer concentration c = 0.8 mmole/liter.

† When the hydrazine concentration is increased above 0.8 mmole/liter the accurate determination of $E_{1/2}$ of the first wave is hindered as a consequence of distortion of the wave due to the maximum. For 1,3,5-trinitrobenzene the maximum appears when c = 0.2 mmole/liter.

‡ The height of the second wave remains almost unchanged when the concentration is increased. Nevertheless, this wave appears only for picrylhydrazines and does not appear for 2,6-dinitrophenylhydrazines and 1,3,5-trinitrobenzene.

** The fifth wave is markedly distorted by the maximum, particularly at concentrations above 0.8 mmole/liter. The accuracy of the determination of $E_{1/2}$ and K is consequently lowered. $K = J/cm^{2/3}T^{1/6}$, where J is in microamperes, c is in millimoles per liter, m is the dropping rate (in milligrams per second), and T is the dropping time (in seconds).

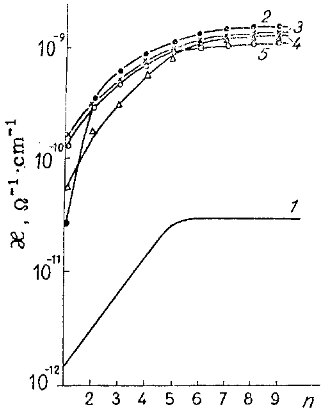

Fig. 1

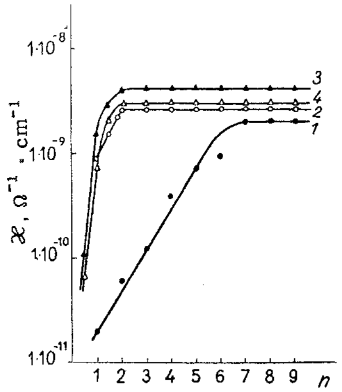

Fig. 2

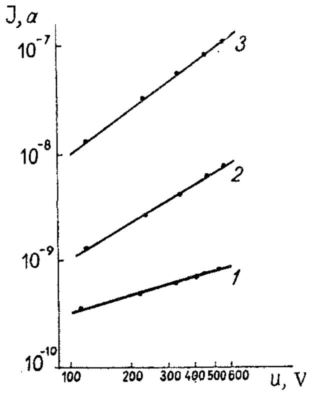

Fig. 3

Fig. 1. Specific conductivity of the benzene–piperidine–acceptor system as a function of the piperidine concentration (n is the volume ratio of piperidine and a benzene solution of the acceptor with a concentration of $1 \cdot 10^{-2}$ mole/liter): 1) in the absence of acceptor; 2) with sym-trinitrobenzene; 3) with $DPPH_h$; 4) with III; 5) with IV.

Fig. 2. Specific conductivity of the benzene–hydrazyl–pyridine system as a function of the pyridine concentration (n is the volume ratio of pyridine and a benzene solution of the hydrazyl with a concentration of $1 \cdot 10^{-2}$ mole/liter): 1) in the absence of hydrazyl; 2) with DPPH; 3) with I; 4) with II.

Fig. 3. Volt-ampere characteristics of benzene solutions of: 1) $DPPH_h$; 2) III; 3) IV.

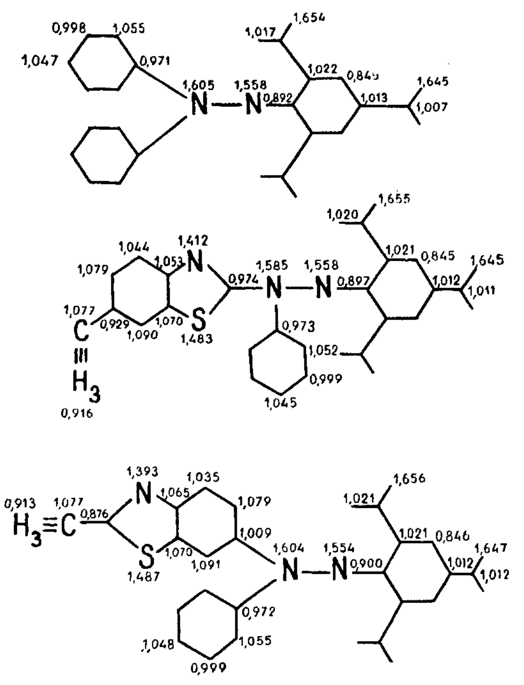

Fig. 4a

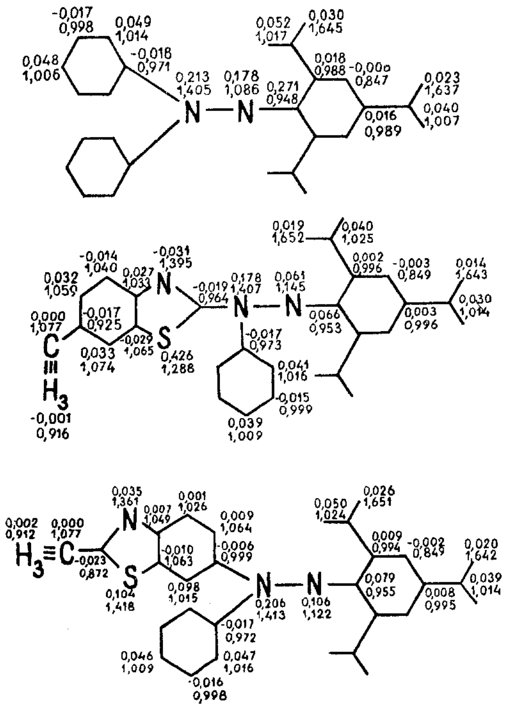

Fig. 4b

Fig. 4a. Charge densities (Hückel MO) of DPPH$_h$, III, and IV.

Fig. 4b. Spin densities (MacLachlan, upper number) and charge densities (Hückel MO) of DPPH, I, and II.

TABLE 4

Radical	A_1/A_2	A_1+A_2, Oe	A_1, Oe	A_2, Oe	δH±0.1 Oe
I	0,607	16,81	6,35	10,46	6,12
II	0,841	17,68	8,08	9,60	5,51
DPPH	0,83	17,68	8,03	9,65	5,29

Interesting results were obtained during an investigation of the properties of I, II, and DPPH. Thus, in the IR spectra of II and DPPH (the IR spectrum of I was not obtained since this radical is not isolated in the crystalline state) a decrease in the frequencies of the asymmetrical and symmetrical vibrations of the nitro groups from 1546 to 1536 cm^{-1} and from 1344 to 1330 cm^{-1} is observed, and the intensities of the band at 1300 cm^{-1} decrease appreciably for both radicals. Finally, a new band of medium-weak intensity appears at 1214 cm^{-1}. The latter can probably be assigned to the $>\dot{N}-C_{ap}$ grouping.

Close results are observed in a study of the conductivities of pyridine complexes of I, II, and DPPH. However, according to the parameters of the electronic and ESR spectra, the investigated radicals are different. The hydrazyls also differ substantially in reactivity. The rate constant of the reaction of I with benzylphenylamine is almost two orders of magnitude greater than for II. DPPH is virtually unreactive with this amine.

As already noted, in benzene solutions the interaction of I, II, and DPPH with the medium is small in comparison with such donors as piperidine or pyridine. A considerable difference is therefore observed in the electronic ESR spectra as a function of the structure of the hydrazine component of these radicals.

It is apparent that the reduction proceeds through the formation of an intermediate complex in which the picryl group is blocked, and the rate of hydrogen transfer from the amine to the hydrazyl nitrogen is already determined by the structure of the hydrazine residue.

It should be noted that both I, II, and DPPH as well as the complexes of their hydrazines with piperidine are characterized by the appearance of maxima at 320-360 nm. In addition, a decrease in the intensity at 1300 cm^{-1} and the appearance of a new band at 1208-1214 cm^{-1} are noted for DPPH and the complex of $DPPH_h$ with piperidine [4]. The formation of stable complexes apparently leads to substantial energy changes in the system. In this respect, the disappearance of the absorption maximum of I in the visible region with simultaneous preservation of the short-wave maximum and the appearance of the characteristic absorption of the complex of I with pyridine (Table 2) is remarkable; the solution remains paramagnetic in the process.

EXPERIMENTAL

Molecular Spectra. The IR spectra (Fig. 1) were obtained with a UR-20 double-beam IR spectrophotometer. The samples were prepared as KBr pellets. The spectra of identical substances investigated as pellets and mineral oil pastes coincided. In view of the complex structures of the compounds investigated, the spectra of model compounds were obtained. The results are presented in Table 1.

UV and Visible Spectra. The electronic absorption spectra of benzene solutions of the following were obtained with an SF-4 spectrophotometer: radicals DPPH, I, and II; hydrazines $DPPH_h$, III, and IV ($1 \cdot 10^{-3}$ mole/liter); complexes of these radicals with pyridine; and complexes of their hydrazines with piperidine (Table 2).

Conductivities. The conductivities of benzene–piperidine solutions of hydrazines III, IV, and $DPPH_h$ and of benzene–pyridine solutions of radicals I, II, and DPPH (Figs. 1 and 2) were investigated with a setup similar to that described in [5]. The conductivities of benzene solutions of hydrazines III, IV, and $DPPH_h$ are presented in Fig. 3.

Polarography. The reduction of 1,3,5-trinitrobenzene, III, IV, and $DPPH_h$ on a dropping mercury electrode was carried out with an LP-60 polarograph. Dimethylformamide solutions of the hydrazines (0.4 to 2 mmole/liter) with a background of a 0.1 M solution of tetraethylammonium iodide in anhydrous dimethylformamide were studied. Sludge mercury was used as the unpolarizable electrode. The capillary parameters were T = 2.6 sec, and m = 1.3 mg/sec for H = 400 mm. The recordings were obtained at from 0 to −2 V. In addition, the anode wave from +0.25 to −0.1 V was obtained. All of the investigations were carried out at 24°. The results of the polarographic investigations are presented in Table 3.

ESR Spectra. Degassed benzene solutions of I, II, and DPPH ($1 \cdot 10^{-3}$ mole/liter) were obtained with an RÉ-1301 radiospectrometer. The hfs constants were constructed with an M-20 computer via a method similar to that described in [6] (Table 4).

Quantum-Chemical Calculations. The calculation of the spin densities of I, II, DPPH were carried out according to the method of MacLachlan, while the charge densities for I, II, DPPH, III, IV, and $DPPH_h$ were calculated using the Hückel MO method. The results are indicated in the formulas in Figs. 4a and 4b. The major parameters for the calculation were the same as those used in [7], while the parameters for the CH_3 group were taken from [8].

LITERATURE CITED

1. B. Turchani, D. Kostersits, and F. Tyudesh, Acta Chem. Acad. Sci. Hung., 50, 293 (1966).
2. R. Z. Sagdeev and Yu. N. Molin, Zh. Strukt. Khim., 7, 3841 (1966).
3. W. Otting and H. Kainer, Ber., 87, 1205 (1954).
4. A. K. Chirkov, R. O. Matevosyan, L. A. Perelyaeva, L. L. Samarin, I. N. Getsova, and B. P. Manannikov, in: Quantum Chemistry and the Structures of Molecules [in Russian], Kiev (1969).
5. Kahson Masuda, Kenji Gamo, Matsuaki Nishijiama, and Juro Jamaguchi, Technology reports of Osaka University, 14, 507 (1964).
6. B. M. Kozyrev, Yu. V. Yablokov, R. O. Matevosyan, M. A. Ikrina, A. V. Il'yasov, Yu. M. Ryzhmanov, L. I. Stashkov, and L. F. Shatrukov, Optika i Spektroskopiya, 15, 625 (1963).
7. B. Pullman and A. Pullman, Quantum Biochemistry [Russian translation], Moscow (1965).
8. Yu. A. Kruglyak, V. S. Kvakush, G. G. Dyadyusha, and V. I. Khil'chenko, Computational Methods in Quantum Chemistry [in Russian], Kiev (1967).