2. H. Gilman and J. Eisch, J. Am. Chem. Soc., 77, 3862 (1955).
3. N. Kornblum, J. W. Powers, G. J. Anderson, N. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, J. Am. Chem. Soc., 79, 6562 (1957).
4. H. Saikachi and J. Matsuo, Yakugaku Zasshi, 88, 1308 (1968).
5. N. P. Grin', A. N. Krasovskii, and P. M. Kochergin, Khim. Geterotsikl. Soedin., No. 9, 1271 (1972).
6. N. O. Saldabol and S. A. Giller, Khim. Geterotsikl. Soedin., No. 10, 1396 (1976).
7. Norwich Pharmaceutical Co., Ltd. Belgian Patent No. 623469 (1963); Chem. Abstr., 59, No. 8, 8761 (1963).
8. N. P. Buu-Hoi and N. D. Xuong, Bull. Soc. Chim. France, No. 7, 1344 (1961).
9. N. O. Saldabol, G. Ya. Zarinya, and S. A. Giller, Khim. Geterotsikl. Soedin., No. 1, 178 (1968).
10. L. Pentimalli, G. Cogo, and A. M. Guerra, Gazz. Chim. Ital., 97, 488 (1967).
11. N. O. Saldabol and Yu. Yu. Popelis, Khim. Geterotsikl. Soedin., No. 5, 691 (1972).
12. N. O. Saldabol and I. B. Mazheika, Khim. Geterotsikl. Soedin., No. 1, 118 (1969).
13. N. O. Saldabol, L. L. Zeligman, S. A. Giller, Yu. Yu. Popelis, A. É. Abele, and L. N. Alekseeva, Khim. Geterotsikl. Soedin., No. 10, 1353 (1972).
14. N. O. Saldabol, L. L. Zeligman, Yu. Yu. Popelis, and S. A. Giller, Khim. Geterotsikl. Soedin., No. 1, 55 (1975).

INTRAMOLECULAR HYDROGEN BONDING IN 1-NITRO-5,10-DIHYDROPHENAZINE DERIVATIVES

I. N. Borukhova, V. F. Gryazev,
E. G. Kovalev, and Z. V. Pushkareva

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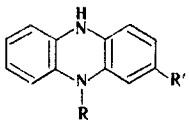
The formation of free radicals only for derivatives with a nitro group in the 1 position was observed in the oxidation of a number of 5-substituted 5,10-dihydrophenazines with lead dioxide. A long-wave absorption band was observed in the electronic spectra of the derivatives with a nitro group in the 1 position. The assumption of the formation of an intramolecular hydrogen bond in dihydrophenazines with a nitro group in the 1 position was confirmed by quantum-chemical modeling of the three structures of the 1,3-dinitro-5-phenyl-5,10-dihydrophenazine molecule. By comparison of the integral intensities of the bands of the stretching vibrations of the N–H bond in 5-substituted dihydrophenazines it was concluded that this bond is depolarized in derivatives with an intramolecular hydrogen bond.

In the oxidation of substituted 5,10-dihydrophenazines Ia-e and IIa-e with lead dioxide generation of phenazyl radicals was observed only for compounds with a nitro group in the 1 position. It was assumed that an intramolecular hydrogen bond is formed in these molecules [1, 2]. A similar hypothesis was expressed in [3].



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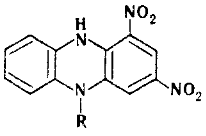

II

I a) R=CH_3, R'=H; b) R=$COCH_3$, R'=H; c) R=COC_6H_5, R=H; d) R–CO-(4-$NO_2C_6H_4$), R'=H; e) R==C_6H_5, R'=NO_2. II n) R=eC_4H_9; b) R=C_6H_5; c) R=4-CH_3-C_6H_4; d) R=2,4-$(NO_2)_2$-C_6H_3; e) R==2,4,6-$(NO_2)_3$-C_6H_2

During a comparison of the electronic spectra of dihydrophenazines Ia-e and IIa-e we observed that a long-wave band with λ_{max} 530-565 nm is characteristic only for the second group

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S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 263-265, February, 1978. Original article submitted April 21, 1977.

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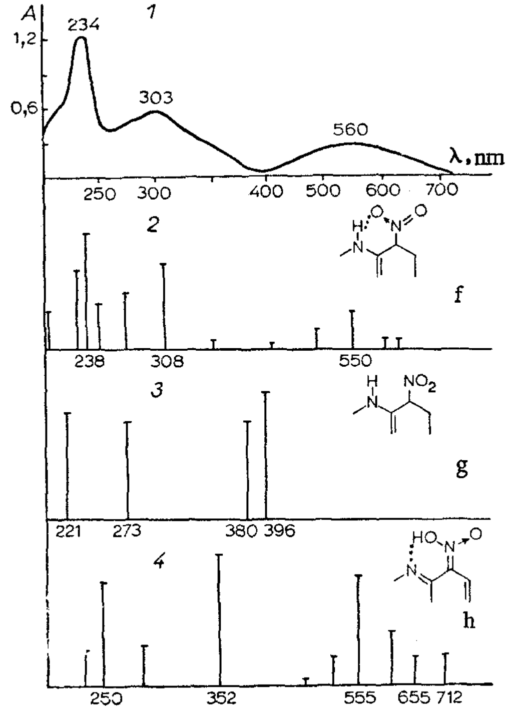

Fig. 1. Electronic spectra of IIb: 1) experimental spectrum; 2) theoretical spectrum of structure f; 3) theoretical spectrum of structure g; 4) theoretical spectrum of structure h.

of compounds [1]. The deepening of the color in this case can be associated with the formation of a hydrogen bond between the nitro group in the 1 position and the N—H fragment of the six-membered ring, which promotes an increase in the coplanarity of the molecule and reinforcement of the conjugation in the system.

To confirm this assumption we made a quantum-chemical calculation of the electronic spectrum of the IIb molecule by the Pariser—Parr—Pople (PPP) method with application of the procedure and computational parameters used for nitroformazans [4, 5] and with allowance for 15 singly excited configurations. In order to arrive at a more accurate estimate of the contribution of the nitro group the computation procedure was modified in accordance with [6], in which the fractional values of the integral charges of the σ framework of the molecules were used instead of their standard values. The valence angles and interatomic distances characteristic for related azine compounds [7] were used in the calculation. The dihedral angle between the planes of the phenyl rings was assumed to be 120°C. According to these parameters, one of the oxygen atoms of the nitro group and the hydrogen atom of the N—H group are separated by a distance of ~1.7 Å; this should promote the formation of a hydrogen bond.

Three structures of the IIb molecule were calculated. A comparison of the experimental and theoretical spectra showed that when the hydrogen bond is disregarded (Fig. 1, structure g), long-wave absorption at 400-500 nm is completely absent, and the short-wave transitions differ significantly from the experimental transitions with respect to their energies and intensities. The theoretical spectrum of structure h (Fig. 1) with a nitro group in the acid form is characterized by the appearance of a number of long-wave transitions at 600-700 nm, which are absent in the real spectrum. On the other hand, the theoretical spectrum of structure f is in very good agreement with the experimental spectrum; this makes it possible to assign this variant of the structure to the IIb molecule.

A considerable decrease in the frequency of the stretching vibrations of the N—H bond for dihydrophenazines IIa-e as compared with Ia-e has been demonstrated [1].

To compare the polarities of the N—H bond in a number of dihydrophenazines Ia-e and IIa-e we calculated the integral intensities of the corresponding IR bands with allowance

TABLE 1. Integral Intensities of the Stretching Vibration of the N—H Bond in Substituted 5,10-Dihydrophenazines

Compound	A, liter·mole^{-1}·cm^2
Ia	4610±50
Ib	6540
Ic	6580
Id	6590
Ie	7060
IIa	3750
IIb	5070
IIc	5060
IId	6000

for their asymmetry [7] (Table 1). A comparison of these values shows that in the series of 5-acyl derivatives Ib-d the integral intensities increase; this is associated with a change in the dipole moment of the N—H bond under the influence of increasing electronegativity of the substituent in the 5 position.

A considerable decrease in the intensity of the band of the stretching vibration of the N—H bond is observed on passing to compounds with a nitro group in the 1 position (IIa-c); i.e., the N—H bond is depolarized due to charge transfer from the oxygen atom of the nitro group to the nitrogen atom through a hydrogen bridge [8]. The depolarization of the N—H bond promotes its homolytic cleavage during oxidation of the corresponding dihydrophenazines with lead dioxide [1, 2].

The increase in the integral intensity of the band of the N—H bond in the IIa-e series is explained by an increase in the electron-acceptor properties of the substituent in the 5 position (Table 1).

Thus the results of a comparison of the integral intensities of the bands of the stretching vibrations of the N—H bond and the results of the quantum-chemical calculations confirm the previous assumption of the formation of an intramolecular hydrogen bond in substituted 1-nitro-5,10-dihydrophenazines.

EXPERIMENTAL

The electronic spectra of ethanol solutions of the compounds C_2H_5OH ($c = 2 \cdot 10^{-5}$ mole/liter) were measured with a Perkin—Elmer 402 spectrophotometer at a layer thickness of 1 cm.

The bands of the stretching vibrations of the N—H bond at 3000-3600 cm^{-1} of solutions of the compounds in chloroform ($c = 2 \cdot 10^{-3}$ mole/liter) were recorded with a UR-20 spectrometer with a 0.4-cm thick cuvette.

LITERATURE CITED

1. Z. V. Pushkareva, I. N. Noskova, and V. F. Gryazev, Khim. Geterotsikl. Soedin., No. 10, 1428 (1970).
2. I. N. Borukhova, V. F. Gryazev, Z. V. Pushkareva, and V. I. Koryakov, Khim. Geterotsikl. Soedin., No. 4, 521 (1977).
3. P. C. Taunk, R. P. Gupta, and R. L. Mital, J. Ann. Soc. Scient. Brux., 85, 291 (1971).
4. A. P. Zeif, G. N. Lipunova, N. P. Bednyagina, L. N. Shchegoleva, and L. I. Chernyavskii, Zh. Org. Khim., 6, 2590 (1970).
5. G. N. Lipunova, N. N. Gulemina, A. P. Zeif, and N. P. Bednyagina, Khim. Geterotsikl. Soedin., No. 4, 493 (1974).
6. M. D. Gordon and J. F. Neumer, J. Phys. Chem., 78, 1868 (1974).
7. Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 18, London (1965).
8. A. V. Iogansen and B. V. Rassadin, Zh. Prirodn. Soedin., 11, 828 (1969).