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Solvatochromism of Heteroaromatic Compounds: XV.[1] 3-Nitro-1,2,4-triazol-5-ones

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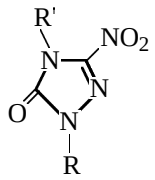
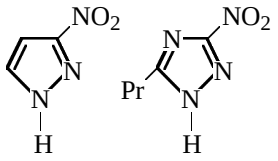
Abstract — Effect of the medium on the parameters of the long-wave absorption band in the electronic spectra of H complexes formed by 3-nitro-1,2,4-triazol-5-one and its *N*-methyl derivatives with aprotic protophilic solvents was described on a quantitative level using Kamlet–Taft solvatochromic parameters. A weak nonadditivity was revealed in the influence of two kinds of intermolecular hydrogen bonds.

Quantitative analysis of solvatochromic properties of 3- and 4-nitroanilines in aprotic protophilic media, which was performed with the aid of Kamlet–Taft empirical solvent parameters, led us to conclude that the specific solvatochromic effect arising from intermolecular hydrogen bonding is not a strictly additive quantity [1]. On replacement of one hydrogen atom in the NH_2 group by an alkyl radical, this effect changes more or less than twofold (as the additivity principle requires). Although deviations from additivity were not always large and were revealed only when the spectrum was sufficiently sensitive to specific solvation, they were systematic. In the present work we studied a different kind of compounds whose solvatochromic properties are governed by specific interactions with the medium, namely 3-nitro-1,2,4-triazol-5-ones **I**–**III**:



I, R = Me, R' = H; **II**, R = R' = H; **III**, R = H, R' = Me.

Molecules **I**–**III** have a law dipole moment in the ground state (μ_g ~1.5 D in dioxane); therefore, the position of the long-wave absorption band in their electronic spectra is determined mainly by specific rather than nonspecific solvation [2]. For comparison, we used 3-nitropyrazole (**IV**) and 3-nitro-5-propyl-1,2,4-triazole (**V**) whose molecules in the ground state are characterized by a high dipole moment (6–7 D; in dioxane [3] and our present data).



IV **V**

Table 1 contains the solvatochromic parameters of 3-nitro-1,2,4-triazol-5-ones **I** and **II** and triazole **V** in aprotic protophilic solvents; the corresponding data for compounds **III** and **IV** were reported in [2] and [4], respectively. Quantitative analysis was performed using two general (β, π^*) and two group (ξ, δ) Kamlet–Taft parameters according to the following linear regression equation:

$$\nu_{max} = \nu_0 + b\beta + s\pi^* + e\xi + d\delta.$$

Here, $\nu_0 = \nu_{max}$ at $\beta = \pi^* = \xi = \delta = 0$; β is the proton-acceptor power of the solvent in H complex with the solute; π^* is a solvent parameter characterizing its ability to stabilize dipolar molecules or ions (nonspecific solvation); ξ is an approximate measure of covalent character of the coordination bond; and δ is a parameter characterizing polarizability of the solvent [5, 6]. The coefficients and free terms of the above equation are given in Table 2. It should be noted that for the series of 3-nitro-1,2,4-triazol-5-ones there is no need of describing the effects of aromatic and aliphatic solvents separately.

Before considering solvatochromic properties of the compounds under study, it is reasonable to speak about the tautomeric equilibrium of 3-nitro-1,2,4-tri-

[1] For communication XIV, see [1].

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Table 1. Solvatochromism of 3-nitro-1,2,4-triazol-5-ones **I** and **II** and triazole **V** in aprotic protophilic media

Solvent	Kamlet–Taft parameters[a]				ν_{max}, cm^{-1}		
	β	π^*	ξ	δ	**I**	**II**	**V**
Dibutyl ether	0.46	0.24	0.2	0.0	29350	30100	40650
Diethyl ether	0.47	0.27	0.2	0.0	29250[b]	30000	40400
1,2-Dimethoxyethane	0.41	0.53	0.2	0.0	29150	30000	39450
Dioxane	0.37	0.55	0.2	0.0	29100	30100	39600
Ethyl acetate	0.45	0.55	0.0	0.0	29250	30300	39400[c]
Anisole	0.22	0.73	0.2	1.0	29050	30400	[d]
Cyclohexanone	0.53	0.76	0.0	0.0	28900	–	–
Propylene carbonate	0.40	0.83	0.0	0.0	29050	30300	38400
Tetramethylurea	0.80	0.83	0.0	0.0	28600	29300	[d]
Pyridine	0.64	0.87	0.6	1.0	28200	28650	[d]
HMPA	1.05	0.87	–0.2	0.0	28400	29200	38100
DMF	0.69	0.88	0.0	0.0	28650	29500	[d]
Benzonitrile	0.37	0.90	0.1	1.0	28900	30250	[d]
1-Methyl-2-pyrrolidone	0.77	0.92	0.0	0.0	28500	29300	37800
DMSO	0.76	1.00	0.0	0.0	28500	29250	[d]

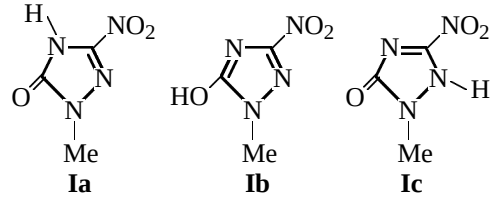
[a] The parameters were taken from [4, 5]. [b] In diisopropyl ether (β = 0.49, π^* = 0.27, ξ = 0.20, δ = 0.0): ν_{max} = 29300 cm^{-1}. [c] In tetrahydrofuran (β = 0.55, π^* = 0.58, ξ = 0.20, δ = 0.0). [d] Obscured by the solvent.

Table 2. Quantitative description of solvatochromic properties of azoles **I**–**V** in aprotic protophilic media and dipole moments of their H complexes with dioxane

Comp. no.	μ_g,[a] D	ν_0, cm^{-1}	–*b*, cm^{-1}	–*s*, cm^{-1}	–*e*, cm^{-1}	–*d*, cm^{-1}	*R*	*s*	*n*
I	1.40	30220 ± 40	1070 ± 60	950 ± 50	860 ± 70	–	0.987	40	16
II	1.40	31680 ± 60	2240 ± 90	680 ± 90	2030 ± 110	–180 ± 50	0.991	50	14
III[b]	1.59	31120 ± 40	1320 ± 40	850 ± 40	890 ± 40	–	0.991	40	18
IV[c]	6.19[d]	42290 ± 90	1460 ± 120	3380 ± 140	1700 ± 110	–	0.993	70	11
V	7.26	41610 ± 90	200 ± 150	3760 ± 150	–	–	0.991	90	9

[a] In dioxane at 25°C. [b] Data of [2]. [c] Experimental data from [4]. [d] Data of [7].

azol-5-ones in aprotic solvents. According to published data (see [2] and references therein) the most stable tautomers of compounds **II** and **III** are 1*H*/4*H* and 1*H*, respectively. Triazolone **I** gives rise to three possible tautomers:

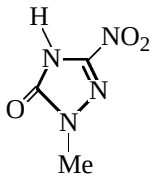
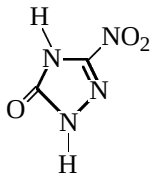
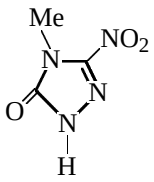


Ia **Ib** **Ic**

In keeping with the AM1(CI) calculations of electronic absorption spectra, tautomers **Ia**–**Ic** show a much stronger difference in the energies of the long-wave electronic transition, as compared to tautomeric forms of compound **III** [2].

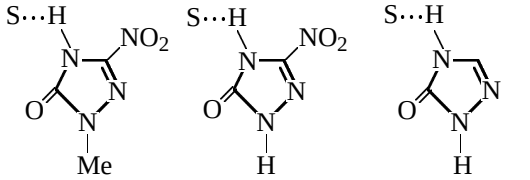
Tautomer	**Ia**	**Ib**	**Ic**
ν, cm^{-1} [AM1(CI)]	31900	36400	28100

Therefore, tautomers **Ia**–**Ic** can readily be distinguished by the position of absorption maximum in a completely inert solvent (see ν_0 values in Table 2):

Predominant tautomer			
ν, cm^{-1} [AM1(CI)]	31900	32200	32800
ν_0, cm^{-1}	30220	31680	31120
$\Delta\nu$, cm^{-1}	~1700	~500	~1700

An additional support to the greater stability of tautomer **Ia** follows from a comparison of the calculated dipole moment of **Ia** with the experimental dipole moment of the H complex of **I** with dioxane: μ(HF/6-31G*) = 1.49 D, μ(dioxane) = 1.40 D.

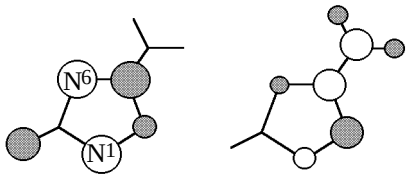
The specific solvatochromic effect for related solvents (ξ = const, δ = const) is defined as $\Delta\nu_N = b\beta$, where *b* is a parameter of the solute, and β is the solvent parameter (average value for a set of reference compounds). The coefficient *b* in the solvatochromic equations for compounds **I**–**III** has a negative sign. This means that hydrogen bonding with a protophilic solvent leads to displacement of the long-wave absorption maximum to lower frequencies. Hence, in all cases the intermolecular hydrogen bond becomes stronger in going to the Franck–Condon excited state. Among compounds with a single NH bond, the lowest $\Delta\nu_H$ value was found for triazolone **I** (Table 2), which, however, is the strongest acid in water: pK_a(**I**) = 3.65, pK_a(**III**) = 6.50 [8]. In dimethyl sulfoxide (β = 0.76, ξ = δ = 0), stabilization of its excited state relative to the ground state through H bonding is estimated at 2.4 kcal/mol. The corresponding value for compound **III** in the same solvent is $\Delta\nu_H$ = 2.9 kcal/mol. This may be due to formation of a weaker H complex between protophilic solvents and 1-methyl-3-nitro-1,2,4-triazol-5-one in the ground state. However, this assumption disagrees with the results of nonempirical calculations (HF/6-31G*) of the energy of formation of 1 : 1 solvate complexes of compounds **I**–**III** and 1,2,4-triazol-5-one with dioxane (S). Below are given the ΔE_H(BSSE) values in kcal/mol:



9.10 (1.29) 9.27 (1.26) 8.37

8.41 (1.17) 8.25 (1.18) 7.30

Insofar as vertical electron transitions are not accompanied by change of geometric parameters of H-complexes, their strength in the nonequilibrial excited state is likely to increase as a result of variation of electronic parameters. According to the AM1(CI) semiempirical calculations, the long-wave absorption band in the spectrum of 3-nitro-1,2,4-triazol-5-ones corresponds to $\pi \rightarrow \pi^*$ single-electron transfer between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO):

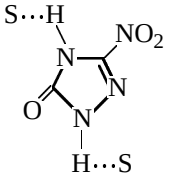


HOMO LUMO

Taking into account that the contributions of the N^1 and N^4 atoms to the HOMO are greater than to the LUMO, the transition into the Franck–Condon state should be accompanied by reduction of the orbital electron density on these atoms. As a result, additional polarization of the N−H bond should occur, and electrostatic interactions between the components in the H complex in the excited state should also change. Therefore, in the first approximation the degree of polarization of the NH fragment (which is involved in H bonding) can be regarded as an electric parameter on the molecular level. In terms of the above stated, the origin of specific solvatochromic effect may be purely electrostatic, and it may be related to nonspecific solvatochromic effect. The latter appears due to interaction between the H complex and its solvation shell. Such interactions are referred to as universal, and their overall effect on absorption spectrum is described (in the most general form) by the theory of solvatochromism, developed by Bakhshiev [9] on the basis of the Onsager–Betcher model. In particular, this effect depends on the dipole moment ratio of the ground (μ_g) and excited states (μ_e). For the series of compounds **I**–**V** we observed a distinct tendency for *s* values (which reflect nonspecific solvatochromic effect) to increase as the polarity of molecules rises (Table 2; see also [10, 11]). Such relation is possible when $\mu_e/\mu_g \approx$ const, i.e., when the degree of charge transfer on absorption of a quantum of light changes in accordance to properties of the ground state. Here, we shall not consider the relation between *b* and *s*. However, it should be noted that empirical solution of this problem requires thorough selection of compounds with similar distributions of the orbital electron density.

As in the case of 3(4)-nitroanilines, the formation by heteroaromatic systems **I**–**III** of two hydrogen bonds with solvent leads to deviation from the additivity (Table 2). First of all, this may be explained in terms of some mutual influence of intermolecular hydrogen bonds in the ground and Franck–Condon

excited states. As applied to the ground state, such assumption can readily be verified by calculating the energy of formation of the 1 : 2 H complex. According to HF/6-31G* nonempirical calculations, the ΔE_H value for the solvate complex of 3-nitro-1,2,4-triazol-5-one with dioxane (see below) is 17.28 kcal/mol. It differs from the total energy of formation of 1 : 1 complexes by only 0.4 kcal/mol. Within the indefiniteness intrinsic to the basis set superposition error (BSSE) it is admissible to assume that the nonadditivity in the ground state is weak, if any. The nonequilibrial excited state is likely to be characterized by a greater degree of nonadditivity.



EXPERIMENTAL

The electronic absorption spectra of azoles **I**–**V** were measured on a Specord UV-Vis spectrophotometer at 22–25°C. The dielectric constants of solutions were determined on an Sh2-5 instrument (Angarsk, Experimental Design Office of Automation Joint-Stock Company) at a frequency of 1 MHz. The dipole moments were calculated by the Higasi formula. Quantum-chemical calculations of the electronic transition energies were performed in terms of the AM1 approximation with allowance for configurational interactions (total of 200 configurations arising from electron excitation from six occupied molecular orbitals to six vacant molecular orbitals were considered). Nonempirical calculations of the energy parameters and dipole moments of 1,2,4-triazol-5-ones and their H complexes with dioxane (HF/6-31G*) were performed using GAUSSIAN 94 [12].

The procedures for synthesizing compounds **I** and **III** were reported in [13, 14]. These products melted with decomposition at 227–228 and 177–179°C, respectively. They were purified by recrystallization from water and ethanol. Compound **II** was obtained by the procedure described in [15], mp 266–268°C (decomp.), and was purified by recrystallization from water and then from 3 : 1 ethyl acetate–ethanol. The purity was checked by physical methods.

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