Solvation of 4-nitropyrazoles according to UV spectroscopy data

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The dependence of the energies of intramolecular charge-transfer electron transitions in 1,3,5-trimethyl-4-nitropyrazole, 4-nitropyrazole, and its anion on the dielectric and acid-base properties of solvents was analyzed. The dipole moments of these species in the excited state are larger than those in the ground state. The nonspecific solvation is accomplished through dipole-dipole interactions. 4-Nitropyrazole, which possesses acidic properties, is also solvated by the mechanism of hydrogen bonding with the solvent, which acts as a base. The strength of the hydrogen bond increases on going from the ground to the electron-excited state. The 4-nitropyrazole anion is a base, and its hydrogen bonds with the solvent are stronger in the ground state. The mechanism of specific solvation of the molecule and the anion of 4-nitropyrazole during electronic excitation is discussed.

Key words: solvation, hydrogen bond, UV spectra, 4-nitropyrazoles.

The majority of studies[1—8] devoted to the UV spectra of nitropyrazoles contain no data on the effect of the medium on the energies of electron transitions. However, the long-wavelength absorption band of these compounds caused by $\pi\rightarrow\pi^*$-transitions with transfer of charge from the ring to the nitro group[7,8] undergoes substantial shifts induced by the solvent.[9] In addition, mononitropyrazoles are relatively strong acids ($pK_a = 8-11$)[3] and, therefore, they can be specifically solvated by solvents possessing basic properties. The anions of these compounds can be solvated as conjugated bases owing to the formation of hydrogen bonds with donors of protons. Therefore, the study of the effects of the dielectric and acid-base properties of the medium on the UV spectra of molecules and anions of nitropyrazoles can provide information on the mechanism of their solvation. The purpose of this work was to study the UV spectra of some nitropyrazoles in various solvents. We have chosen 4-nitropyrazole (**1**), which is a fairly strong acid ($pK_a = 9.67$),[3] anion **1**$^-$, *viz.*, the base conjugated with this acid, and neutral 1,3,5-trimethyl-4-nitropyrazole (**2**) as the objects of the investigation. The properties of solvents were described using the Kamlet—Taft empirical solvatochrome parameters.[10]

Experimental

The UV spectra of nitropyrazoles were recorded on a Specord UV-VIS spectrophotometer at 22—25 °C. The UV spectra of the 4-nitropyrazole anion were obtained in polar solvents by the addition of 10^{-2} *M* MeONa. Compound **1** was synthesized by isomerization of 1-nitropyrazole prepared by nitration of pyrazole.[11] 1,3,5-Trimethyl-4-nitropyrazole (**2**) was obtained by the known procedure.[12] The compounds were purified by recrystallization from organic solvents followed by repeated vacuum sublimation.

Results and Discussion

To evaluate quantitatively the effect of the properties of the solvent on the position of the absorption maximum corresponding to intramolecular charge transfer (ν_{max}) in the compounds under study, we used a three-parameter equation that relates ν_{max} to the Kamlet—Taft parameters of solvents:

$$\nu_{max} = \nu^0_{max} + a\alpha + b\beta + c\pi^*.$$

Here, ν^0_{max} is the statistical magnitude of ν_{max} in an inert solvent, α and β are parameters characterizing the ability of a solvent to release or to add a proton in the formation of a hydrogen bond with the solute, π^* is a parameter determined by the ability of the solvent to stabilize a charge or a dipole. From the set of solvents for which the Kamlet—Taft parameters are known, we have chosen solvents that do not absorb in the spectral region of 40000—30000 cm^{-1}, that belong to various classes of chemical compounds, and that differ substantially in at least one of these parameters (Table 1).

In the case of compound **2**, the following equation was obtained:

$$\nu_{max} = (36310\pm80) + (180\pm90)\alpha + (60\pm130)\beta - (2040\pm120)\pi^*,\ r = 0.975,\ s = 100,\ N = 10.$$

The coefficient at the parameter π^*, which characterizes the capacity of the medium for nonspecific solva-

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tion, is the greatest. In this case, the effect of the acid-base properties of the solvent is statistically insignificant. The classical solvation of a molecule by a dipolar solvent is mostly determined by the dipole moment of the molecule. Only the dipole moment of 3,5-dimethyl-4-nitropyrazole (3.88 D at 25 °C in benzene) can be found in the literature.[13] The dipole moment that we calculated for this compound in the semiempirical AM1 approximation amounted to 5.09 D. Thus, the AM1 method overestimates the dipole moments for 4-nitropyrazoles by approximately 1 D. The calculated dipole moments for **2**, **1**, and **1**$^-$ were 5.79, 5.39, and 1.38 D, respectively. Thus, the dipole moments for noncharged species are fairly large. Therefore, the changes in the dipole moments caused by electron excitation are reflected in the fact that the charge-transfer band shifts substantially on going from nonpolar solvents to polar solvents (see Table 1). The sign of the coefficient at the parameter π^* indicates that the energy of a transition accompanied by charge transfer decreases as the charge decreases. Hence, the dipole moment of **2** in the excited state is larger than that in the ground state.

The dependence of ν_{max} of this compound on the Kirkwood parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ is characterized by a low correlation coefficient (0.751), which increases to 0.934 only when dioxane and ethanol are excluded from consideration. If we take into account the polarizability of the solvent by using the equation

$$\nu_{max} = \nu^0_{max} + A(\varepsilon - 1)/(2\varepsilon + 1) + B(n^2 - 1)/(2n^2 + 1),$$

the correlation coefficient virtually does not change in both cases. Thus, in the first approximation, the solvation of **2** is determined by the dipole-dipole interactions.

The basic properties of the medium become significant in the case of 4-nitropyrazole, which is indicated by the magnitude of the coefficient at the parameter β:

$$\nu_{max} = (38900\pm120) + (360\pm140)\alpha - (1100\pm200)\beta - \\ - (2360\pm190)\pi^*,\ r = 0.972,\ s = 150,\ N = 10.$$

The sign and the magnitude of the coefficient at the parameter π^* implies that, as in the case of the N-methyl-derivative, the dipole moment of **1** increases in the excited state. The additional red shift of the charge-transfer band of this compound is due to solvation through the formation of hydrogen bonds between the molecules of the solute and the solvent, the latter acting as a base. The sign of the coefficient at the parameter β indicates that this bond becomes stronger on going to the electron-excited state.

For anion **1**$^-$, the following equation was obtained:

$$\nu_{max} = (30500\pm280) + (1410\pm90)\alpha + (230\pm200)\beta - \\ - (830\pm230)\pi^*,\ r = 0.987,\ s = 90,\ N = 5.$$

The fact that this dependence of ν_{max} on the π^* parameter is less pronounced than those for neutral molecules is due to the fact that the difference between the solvations of the anion in the ground and excited states caused by the dielectric properties of the solvent, is smaller. Since the anion is highly symmetrical (C_{2v}), the negative charge is highly delocalized, and the dipole moment of the anion should be markedly smaller than that of the initial molecule. Nevertheless, it does change following electron excitation as indicated by the relatively large coefficient at the parameter π^*. The coefficient at the parameter α characterizing the acidic properties of the solvents is also significant in the dependence under consideration. It is positive, which accounts for the blue shifts of the charge-transfer band following an increase in the acidity of the solvent. Thus, in this case, the hydrogen bond is stronger in the ground state.

Table 1. Energies of $\pi\rightarrow\pi^*$-transitions with charge transfer in the UV spectra of 4-nitropyrazoles and the Kamlet—Taft parameters of the solvents

Solvent	α	β	π^*	**2**	**1**	**1**$^-$
					ν_{max}/cm^{-1}	
cyclo-C_6H_{12}	0.00	0.00	0.00	36200	38900	—
Et_2O	0.00	0.47	0.27	35800	37500	—
$CHCl_3$	0.44	0.00	0.58	35200	37800	—
Dioxane	0.00	0.37	0.55	35300	37200	—
THF	0.00	0.55	0.58	35300	37000	—
EtOH	0.83	0.77	0.54	35400	37200	31400
MeCN	0.19	0.31	0.75	34900	37000	30200
H_2O	1.17	0.18	1.09	34300	36400	31300
DMF	0.00	0.69	0.88	34500	36000	30000
DMSO	0.00	0.76	1.00	34200	35700	29800

The results obtained make it possible to explain the mechanism of specific solvation of compound **1** and its anion in the context of a unified approach. The electron excitation is accompanied by transfer of charge from the pyrazole ring to the nitro group. In the case of the neutral molecule, the hydrogen atom of the N—H bond thus acquires an additional positive charge; hence, the acidity of **1** in the excited state is higher and, therefore, the hydrogen bond with the solvent is stronger than that in the ground state. In the case of anion **1**$^-$, the "decrease" in the negative charge of the π-system can cause an increase in the energies of binding of the lone-pair electrons with the nuclei of the nitrogen atoms of the ring. Therefore, after electron excitation, their ability to participate in the formation of hydrogen bonds with the solvent decreases. This hypothesis has been completely confirmed by experiments. Therefore, the intramolecular charge transfer in the π-system of 4-nitropyrazoles has a substantial effect on the solvation accomplished by the mechanism of hydrogen bond formation and occurring in the σ-system of these compounds. According to the AM1 data, molecule **1** and anion **1**$^-$ are planar. Thus, the two mutually orthogonal electronic systems (π,σ) in these species exert a considerable effect on each other.

References

1. C. L. Habraken, P. C. M. Van Woerkom, H. W. De Wind, and C. G. M. Kallenberg, *Rec. Trav. Chim.*, 1966, **85**, 1191.
2. C. L. Habraken, C. I. M. Beenakker, and J. Brussee, *J. Heterocycl. Chem.*, 1972, **9**, 939.
3. J. W. A. M. Janssen, C. G. Kruse, H. J. Koeners, and C. L. Habraken, *J. Heterocycl. Chem.*, 1973, **10**, 1055.
4. D. Dumanovic, J. Ciric, A. Muk, and V. Nicolic, *Talanta*, 1975, **22**, 819.
5. M. A. Andreeva, M. I. Bolotov, Sh. G. Isaev, R. Ya. Mushii, V. P. Perevalov, V. I. Seraya, and B. I. Stepanov, *Zh. Obshch. Khim.*, 1980, **50**, 2116 [*J. Gen. Chem. USSR*, 1980, **50** (Engl. Transl.)].
6. V. P. Perevalov, L. I. Baryshenkova, G. P. Sennikov, I. B. Savina, Sh. G. Isaev, M. A. Andreeva, and B. I. Stepanov, *Khim. Geterotsikl.. Soedin.*, 1985, 657 [*Chem. Heterocycl. Compd.*, 1985 (Engl. Transl.)].
7. V. P. Perevalov, V. V. Redchenko, G. V. Shelban, A. B. Kostitsyn, L. I. Baryshnenkova, and B. I. Stepanov, *Khimiya Geterotsikl. Soedin.*, 1986, 1629 [*Chem. Heterocycl. Compd.*, 1986 (Engl. Transl.)].
8. A. I. Vokin, T. N. Komarova, L. I. Larina, V. A. Lopyrev, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 310 [*Russ. Chem. Bull.*, 1996, **46**, No. 2 (Engl. Transl.)].
9. K. Reichard, *Rastvoriteli i effekty sredy v organicheskoi khimii* [*Solvents and Medium Effects in Organic Chemistry*], Mir, Moscow, 1991, 763 pp. (Russ. Transl.).
10. M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
11. R. Huttel and F. Buchele, *Chem. Ber.*, 1955, **88**, 1586.
12. L. Knorr, *Lieb. Ann. Chem.*, 1894, **279**, 234.
13. S. A. Giller, I. B. Mazheika, I. I. Grandberg, and L. I. Gorbacheva, *Khim. Geterotsikl. Soedin.*, 1967, 130 [*Chem. Heterocycl. Compd.*, 1967 (Engl. Transl.)].

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ESR study of radical adducts of dialkoxyphosphoryl radicals with $(\eta^2\text{-}C_{60})IrH(CO)(PPh_3)_2$ and $(\eta^2\text{-}C_{60})IrH(C_8H_{12})(PPh_3)$

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The reaction of phosphoryl radicals with $(\eta^2\text{-}C_{60})IrH(CO)(PPh_3)_2$ and $(\eta^2\text{-}C_{60})IrH(C_8H_{12})(PPh_3)$ was shown (ESR) to result in the formation of isomers differing in the constants of hyperfine interaction (HFI) with ^{31}P nuclei, g-factors, and linewidths. It is likely that the addition of phosphoryl radicals at a distance of two-three bond lengths from the metallofragment is predominant.

Key words: ESR, phosphoryl radical, fullerenyl radical, metallocomplex, isomers.

Insertion of metallocomplexes or a methylene fragment in fullerenes causes a drastic decrease in the polyhedron symmetry and the appearance of several groups of nonequivalent carbon atoms. Distortion of the fullerene polyhedron occurs simultaneously. In this connection, there arises a question of the effect of different groups bonded to fullerene C_{60} on the reactivity of the atoms of the distorted fullerene sphere.

It was shown previously[1] that the addition of dialkylphosphoryl radicals to metallocomplexes $C_{60}M(PPh_3)_2$ (M = Pt, Pd) results in the formation of at least five isomers that differ in the constants of hyperfine interaction (HFI) with the nucleus of the phosphorus atom of the phosphoryl residue and g-factors. However, these data did not make it possible to decide which of the isomers corresponded to the addition of the phosphoryl radical in the vicinity of the metal atom. In studies of reactions of the phosphoryl radicals with $C_{60}C(C_6H_4OMe)_2$, the most stable of the seven isomers formed was shown to result from the addition of the phosphoryl radical in the vicinity of the methylene group.[2]

In this work, the ESR spectra of radical adducts of the phosphoryl radicals with the octahedral hydride

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