Dipole moment and tautomeric form of 3(5)-nitropyrazole in dioxane solution

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The dipole moments of 3(5)-nitropyrazole, its methyl-substituted derivatives, and H-complexes with dioxane were measured experimentally and estimated by *ab initio* calculations (6-31G* basis set). Comparison of the experimental and calculated dipole moments suggests a shift of the tautomeric equilibrium toward the 3-nitroisomer.

Key words: nitropyrazoles, tautomer, dipole moment, quantum-chemical calculation.

Based on analysis of the UV and NMR spectra, pK_{BH^+} value, and regiochemistry of *N*-methylation of 3(5)-nitropyrazole, the authors of Refs. 1—4 suggested that the 3-nitrotautomer predominates in media with a sufficiently high dielectric constant (H_2O, Me_2SO, MeOH, Me_2CO, and EtOH). Solvatochromism of the long-wave absorption band in the UV spectra of this compound was studied[5] for a wide series of aprotic and amphiprotic solvents. According to the data obtained,[5] the tautomeric equilibrium, regardless of the medium polarity, is strongly shifted toward the 3-nitroisomer. However, this conclusion is based on indirect results and, hence, needs confirmation by another independent method. Under several conditions, this confirmation can be obtained by measuring the dipole moment (μ) of 3(5)-nitropyrazole in low-polarity solvents.[6] In this work, we chose dioxane as a low-polarity medium, 3(5)-nitropyrazole is not soluble in benzene or CCl_4 in concentrations sufficient for measuring the dipole moment, and in octane its molecules associate.

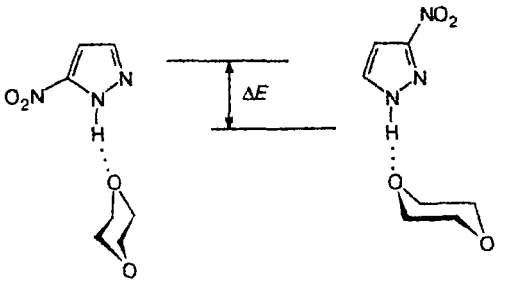
Experimental

Dielectric constants of solutions were measured on an Epsilon instrument (Angarsk) at a frequency of 1 MHz. Dipole moments were calculated by the Higasi formula.

Free molecules of pyrazoles and nitropyrazoles were calculated within the AM1 semiempirical approximation and by the *ab initio* quantum-chemical method in the 6-31G* basis set using the GAUSSIAN 94 program package.[7] *Ab initio* calculations for H-complexes of nitropyrazoles containing one dioxane molecule were also performed.

Results and Discussion

Dissolution of the azole under study in dioxane results in the formation of a complex with a hydrogen bond (H-complex).[5] Therefore, the "dioxane" effect should be taken into account. It can be seen from the experimental value of the dipole moments of the model five-membered heterocycles (compounds **1**, **5**—**9**) presented in Table 1 that μ varies ($\Delta\mu$ = −0.1 to 0.8 D) and depends on the structure of the donor of the hydrogen bond. Therefore, the "dioxane" effects for 3- and 5-nitropyrazoles were estimated by *ab initio* calculations of dipole moments of free molecules and their 1 : 1 H-complexes with dioxane.



The difference between the energies (ΔE) obtained for these complexes is 1.1 kcal mol^{-1}.

Calculations show that the dipole moments of the molecule and corresponding H complexes slightly differ (−0.2 D). The results of *ab initio* and semiempirical calculations indicate that the dipole moments of 5-nitro- and 3-nitroisomers differ nearly threefold, and the polarity of the latter is very high. This fact allows one to use the μ value for the solution of the problem under discussion.

The parameters of the H-complex of the tautomeric compound under study and the *N*-methylated analog of one of the tautomers can also be compared.[6] This follows from the theoretical data (see Table 1), according to which the μ values of the H-complex of

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Table 1. Measured at 25 °C (μ_{exp}/D) and calculated (μ_{calc}/D) dipole moments of 3-nitropyrazole and model compounds

Compound	μ_{calc}		μ_{exp}		
	AM1	6-31G*	Benzole	Dioxane	$\Delta\mu$
Pyrazole (**1**)	2.11	2.42 2.51[a]	2.06[a]	2.33[a]	0.27
1-Methylpyrazole (**2**)	2.35		2.28[a]		
3-Nitropyrazole (**3**)	6.78	6.90	[b]		
H-Complex of 3-nitropyrazole with dioxane (**4**)		7.12		6.19	
1-Methyl-3-nitropyrazole (**5**)	7.32	7.26	6.26	6.20	−0.06
3,5-Dimethyl-4-nitropyrazole (**6**)	5.08[a]	4.85	4.18 3.88[a]		
H-Complex of 3,5-dimethyl-4-nitropyrazole with dioxane (**7**)		5.80		4.96	0.78
1,3,5-Trimethyl-4-nitropyrazole (**8**)	5.79[a]		4.63	4.89	0.26
2-Nitropyrrole (**9**)	5.07	4.90	4.33[a]	4.57[a]	0.24
1-Methyl-2-nitropyrrole (**10**)	5.16		4.67[a]		
5-Nitropyrazole (**11**)	2.86	2.41			
H-Complex of 5-nitropyrazole with dioxane (**12**)		2.22			

[a] Refs. 8—10 and literature cited therein.
[b] Insoluble in concentrations sufficient for experiments.

3-nitropyrazole and free 1-methyl-3-nitropyrazole almost coincide, whereas the difference between the dipole moments of free tautomers reaches 4 D. Thus, if the equilibrium in the solution is shifted toward one side, the problem is reduced to the establishment of a specific form of the tautomer from the experimental μ value.

Comparison of the dipole moments of the model compounds (see Table 1, compounds **1**, **2**, **5**, **6**, and **8—10**) measured in benzene with the calculated values demonstrates that the theoretical μ values agree with the experimental ones. In addition, *ab initio* calculations indicate that the increase in the dipole moment on going from NH- to NMe-pyrazoles is equal to 0.36 D. According to the experiments for model pyrazoles and pyrroles (see Table 1), the effect of *N*-methylation is ~0.34 D. Therefore, direct comparison of the dipole moments observed for 3(5)-nitropyrazole and 1-methyl-3-nitropyrazole answers, in this case, the question about the position of tautomeric equilibrium. All the data obtained evidently indicate the shift of the equilibrium in dioxane toward the 3-nitroisomer.

In the gas phase, as follows from the previous *ab initio* calculations in the 6-31G* basis set,[5] the 3-nitrotautomer is also more stable (the difference in energies is ~0.85 kcal mol^{-1}). The complex of 3-nitropyrazole with one dioxane molecule is more stable than a similar complex of the 5-nitro-substituted derivative by 1.1 kcal mol^{-1}.

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