Investigation of UV spectra of isomeric nitropyrazoles by the semiempirical AM1 (CI) method

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The absorption bands in the UV spectra of isomeric nitropyrazoles were assigned by the calculations in the semiempirical AM1 (CI) approximation. The long-wave absorption of nitropyrazoles is caused by $\pi\rightarrow\pi^*$ and $n_0\rightarrow\pi^*$ transitions. The charge-transfer band is the most intense. The $\pi\rightarrow\pi^*$ transitions undergo a considerable bathochromic shift in the deprotonation. The first ionization potential (PI) of the 4-nitropyrazole anion was estimated from the empirical dependence of the energy of the excited π-state on PI of alkyl-substituted 4-nitropyrazoles. The PI of the 4-nitropyrazole anion is 3 eV lower than that of a neutral molecule. This is evidence for a substantial destabilization of the boundary π-orbital in the heterolytic cleavage of the N—H bond. The analysis of the UV and NMR spectra of 3(5)-nitropyrazole confirms the viewpoint that the 3-nitro tautomer predominates in solution.

Key word: nitropyrazoles; UV spectra, semiempirical quantum-chemical calculations; tautomerism.

The study of UV spectra of nitro derivatives of pyrazole[1—7] has revealed a substantial effect of substituents, medium, and ionization processes on the position of the absorption band in the near UV region. For example, in neutral media, this band is observed within 250 to 290 nm; in sulfuric acid, it is shifted by ~30 nm to the short-wave region;[4] and in solutions of NaOH, it is shifted by ~40 nm to the long-wave region.[3] These shifts are caused by protonation and deprotonation of nitropyrazoles. The existence of these shifts made it possible to determine spectrophotometrically the pK_a and pK_{BH+} values of the compounds studied.[3,4] The spectra of *C*-substituted nitropyrazoles (R = Aryl or NO_2) contain a shoulder on the long-wave side of the band detected,[4] while the spectra of amino-substituted nitropyrazoles exhibit two bands of approximately equal intensities with maxima in the regions of 260—290 and 340—410 nm.[6] By analogy with the spectra of *o*-nitroaniline, both bands are assigned to $\pi\rightarrow\pi^*$ transitions, which agrees with the data of quantum-chemical calculations in the PPP approximation.[7] According to the results obtained, the one-configurational electron transition corresponding to the band observed results in an increase in the π-charge on the nitro group and a decrease on the nitrogen atom of the amino group. The bathochromic shift of the maximum of this band (~20 nm) on going to a polar solvent (benzene → ethanol) also indicates that it is a charge-transfer band.[6,7] The spectral data and the fact that nitropyrazoles have boundary and near-boundary π-orbitals close-in-energy[8] indicate that two close in energy or quasi-degenerate charge-transfer $\pi\rightarrow\pi^*$ transitions can appear in the range of $\lambda > 250$ nm. The considerable bathochromic shift of the observed bands of the anions relative to those of the molecules and the dependence of the position of their maxima on the existence of "spectroscopically" inert alkyl substituents[3] do not contradict this viewpoint. UV spectra of nitropyrazoles can contain not only $\pi\rightarrow\pi^*$ transitions but also $n_\pi\rightarrow\pi^*$ transitions. Their spectral parameters were not discussed in the literature. Among the substituted pyrazole derivatives, $n_0\rightarrow\pi^*$ transitions were observed for 4-nitropyrazoles.[2] Their bands do not overlap those for $\pi\rightarrow\pi^*$ transitions, and they have low extinction coefficients and undergo a hypsochromic shift as the polarity of the solvent increases (benzene → methanol). The position of the $n_N\rightarrow\pi^*$ transition was estimated only theoretically in terms of the semiempirical CNDO/S method for nonsubstituted pyrazole,[9] because its energy is close to those of two $\pi\rightarrow\pi^*$ transitions and is not detected experimentally.[10] Since transitions of both types are possible for pyrazoles, the probability of their detection increases. However, in the majority of cases, available experimental data were obtained in the majority of cases under different conditions, which makes their interpretation difficult.

In the present work, we present the results of studying isomeric nitropyrazoles and their anions by UV spectroscopy under similar conditions using quantum-chemical calculations in the semiempirical AM1 (CI) approximation.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 310—314, February, 1997.

1066-5285/97/4602-0297 $18.00

Experimental

UV spectra of nitropyrazoles were recorded on a Specord UV-VIS spectrophotometer at 22—25 °C. ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer in DMSO-d_6. Chemical shifts from ^{13}C signals were measured relative to DMSO-d_6 (39.6 ppm).

Quantum-chemical calculations of energies of electron transitions were performed by the AM1 method in terms of the formalism of configurational interactions. Two hundred configurations appearing in the excitation of electrons from six occupied MO to six vacant MO were used. Moments of $\pi\rightarrow\pi^*$ transitions were calculated by the CNDO/S method. Ten configurations lower in energy appearing in the one-electron excitation were taken into account.

3(5)-Nitropyrazole was synthesized from 1-nitropyrazole,[11] which was obtained by the nitration of pyrazole.[12] 4-Nitropyrazole was synthesized by two methods: nitration of pyrazole[12] and isomerization of 1-nitropyrazole.[12] 4-Nitro-1,3,5-trimethylpyrazole was obtained by nitration according to a known procedure.[13] All substances were purified by recrystallization from organic solvents followed by double vacuum sublimation. The position of the maxima of low-intensity bands at the boundary of the UV and visible regions and their half-widths were determined by graphic numerical differentiation.[14] The UV spectrum of the 4-nitropyrazole anion was obtained after MeONa (10^{-2} mol L^{-1}) was added to an ethanol solution of 4-nitropyrazole.

Results and Discussion

The UV spectrum of 4-nitropyrazole in ethanol in the range of energies lower than 47000 cm^{-1} consists of a band with a maximum at 37200 cm^{-1}, which has a pronounced shoulder on the short-wave side and a low-intensity shoulder on the long-wave side (Fig. 1). The theoretical UV spectrum of this compound was obtained by two methods: CNDO/S and AM1 (CI). According to the AM1 (CI) data, four $\pi\rightarrow\pi^*$ transitions occur in the energy range considered: two transitions near the maximum of the main band and two transitions in the range of its short-wave shoulder (see Fig. 1). According to the CNDO/S calculations, three $\pi\rightarrow\pi^*$ transitions, which are strongly shifted to the short-wave region from the maximum observed, fall in this spectral range (see Fig. 1). Thus, AM1 (CI) (unlike CNDO/S) reproduces satisfactorily the position of the most intense bands in the UV spectrum of 4-nitropyrazole. On this basis, this method was used for interpretation of UV spectra of the other nitropyrazoles. The low-intensity shoulder on the long-wave wing of the main band in the UV spectrum of 4-nitropyrazole cannot be assigned to an admixture, because the value of its relative intensity remains unchanged when different methods of the synthesis are used (see Experimental) and when the samples were thoroughly purified. This shoulder cannot be assigned to the absorption of the 4-nitropyrazole anion, because it is retained when nonpolar and weakly polar solvents (*e.g.*, benzene, dioxane, and chloroform) are used. Moreover, the AM1 (CI) data testify that two $n_0\rightarrow\pi^*$ transitions should manifest themselves in this energy range (Table 1). The adequacy of the AM1 (CI) method for the reproduction of the $n\rightarrow\pi^*$ transitions was checked by the calculation of the UV spectrum of 4-nitropyrazole, whose $n_0\rightarrow\pi^*$ transition has a maximum at 15000 cm^{-1}.[2] According to the calculated data, its energy is equal to 16900 cm^{-1}, which agrees satisfactorily with the experiment. Therefore, the weak absorption in the range of 30000—32000 cm^{-1} is caused by the $n_0\rightarrow\pi^*$ transitions, and the AM1 (CI) method reproduces not only the energies of the $\pi\rightarrow\pi^*$ transitions, but also those of the $n\rightarrow\pi^*$ transitions. This conclusion was confirmed when the theoretical and experimental values of the energies of the $n\rightarrow\pi^*$ transitions of substituted and isomeric nitropyrazoles were compared. Thus, according to the data of the calculations in the AM1 (CI) approximation, the hypsochromic shift of both $n\rightarrow\pi^*$ transitions occurs in the series 4-nitropyrazole, 1,3,5-trimethyl-4-nitropyrazole, and 1-nitropyrazole (see Table 1) (for 1-nitropyrazole, the band caused by the $n\rightarrow\pi^*$ transition is not manifested against the background of a more intense band of the $\pi\rightarrow\pi^*$ transition due to their substantial overlapping). For this series, the sequence of the calculated energies of the $\pi\rightarrow\pi^*$ transition is different: 1-NO_2 > 4-NO_2 > 1,3,5-Me_3-4-NO_2. It completely corresponds to the experimental data (see Table 1). In this series, the maximum of the main absorption band of 1-nitropyrazole has the highest energy.

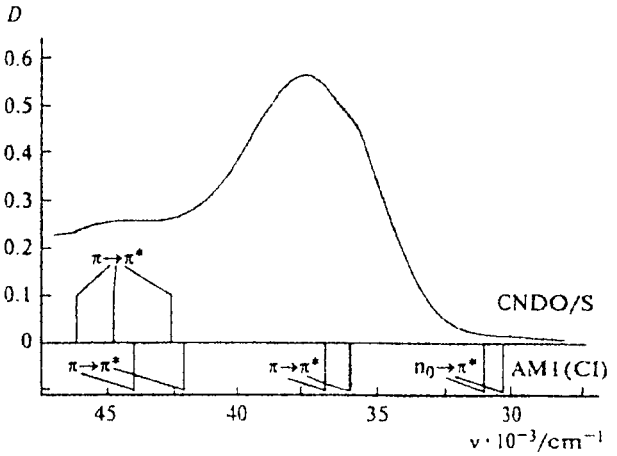
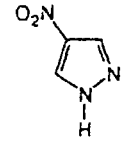
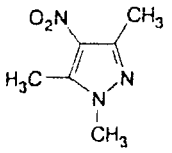
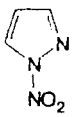
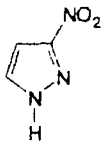
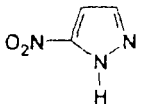
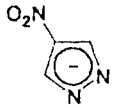


Fig. 1. UV spectrum of 4-nitropyrazole.

According to the AM1 (CI) data, the two low-energy $\pi\rightarrow\pi^*$ transitions are predominantly two-configurational. They correspond to the excitation of electrons from the boundary and near-boundary occupied π-MO to two lower free π-type MO. The analysis of the electron density distribution over these orbitals (Fig. 2) shows that these transitions result in its increase on the nitro group. This suggests the existence of the transfer of the π-charge in the electron excitation. For the uniform series of compounds with charge-transfer $\pi\rightarrow\pi^*$ transitions, the energies of these transitions should correlate

Table 1. UV spectral parameters (ν/cm^{-1}) of nitropyrazoles

Compound	Experiment (EtOH)		Method AM1 (CI)		Moment of transition (CNDO/S)
	ν_{max}	$\Delta\nu_{1/2}$	ν_{max}	transition	
	~31500	~5400	30400	$n_0\rightarrow\pi^*$	
	37200	5000*	31100	$n_0\rightarrow\pi^*$	
			35900	$\pi\rightarrow\pi^*$	0.14
			36400	$\pi\rightarrow\pi^*$	0.42
	~33000	~6600	32300	$n_0\rightarrow\pi^*$	
	35400	4800*	32900	$n_0\rightarrow\pi^*$	
			33700	$\pi\rightarrow\pi^*$	0.27
			34800	$\pi\rightarrow\pi^*$	0.50
			34000	$n_0\rightarrow\pi^*$	
	**		39500	$n_0\rightarrow\pi^*$	
	37600	4800*	36600	$\pi\rightarrow\pi^*$	0.35
			37500	$\pi\rightarrow\pi^*$	0.41
			31100	$n_0\rightarrow\pi^*$	
	~31000	~5500	32100	$n_0\rightarrow\pi^*$	
	39300	6800*	34600	$\pi\rightarrow\pi^*$	0.21
			38300	$\pi\rightarrow\pi^*$	0.61
			29900	$n_0\rightarrow\pi^*$	
			31100	$n_0\rightarrow\pi^*$	
			34000	$\pi\rightarrow\pi^*$	0.69
			36500	$\pi\rightarrow\pi^*$	0.51
	**		31700	$n_0\rightarrow\pi^*$	
	31400	4600*	30100	$\pi\rightarrow\pi^*$	0.90
			33500	$\pi\rightarrow\pi^*$	0.24

* The half-width was determined for the long-wave wing of the band. ** Not detected.

with the first ionization potential (IP). IP of alkyl-substituted derivatives of 4-nitropyrazole obtained by photoelectron spectroscopy[8] can be used for studying this correlation. Unfortunately, the work published previously (Ref. 8) contains no data on the PI of nonsubstituted 4-nitropyrazole, whose parameters are necessary to extend the range of a change in spectral parameters. For this purpose, the PI value calculated in the AM1 (OVGF) approximation was used, which would require only a small correction by the value of the average deviation (0.25 eV) of the values calculated by this method from the experimental values of the first ionization potential in the series of 4-nitropyrazole derivatives. It is determined that the dependence of the energy of the main absorption band in the UV spectra of the compounds discussed on their PI (Fig. 3) is described with a high accuracy by a linear function

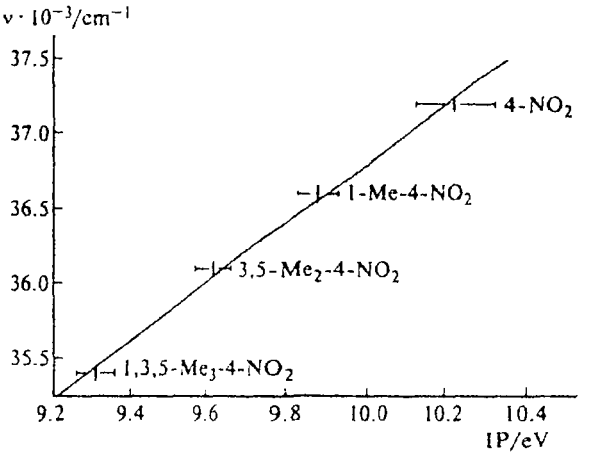


Fig. 2. Dependences of the energies of the maximum (ν_{max}) of the main band in the UV spectra of 4-nitropyrazoles on the first ionization potential (IP).

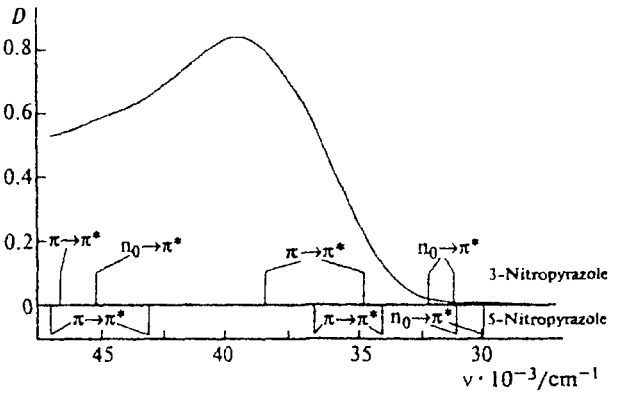


Fig. 3. UV spectrum of 3(5)-nitropyrazole.

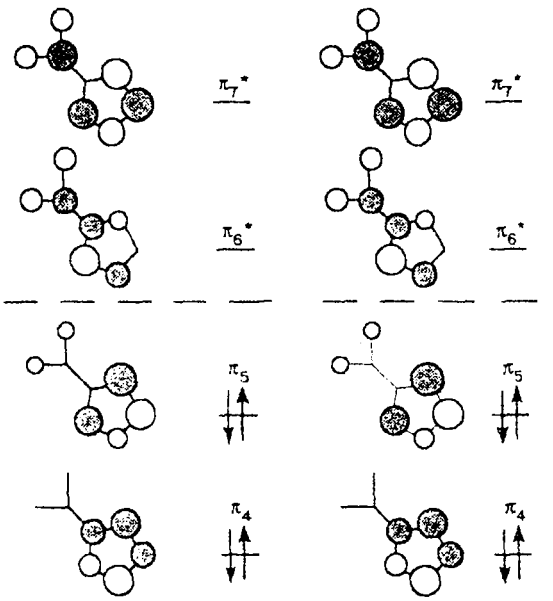
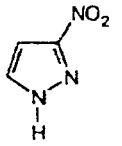
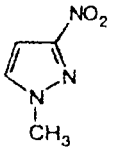
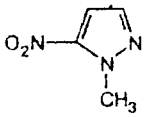


Table 2. Data of ^{13}C NMR spectroscopy of derivatives of 3- and 5-nitropyrazoles

Compound	δ ^{13}C ($J_{^1H-^{13}C}$/Hz)			Solvent	Reference
	C(3)	C(4)	C(5)		
	156.6	101.7	133.1	DMSO-d_6	17
		102.4 (^1J = 186.8, ^2J = 8.5)	132.8 (^1J = 192.2, ^2J = 7.3)	Acetone-d_6	18
		102.4 (^1J = 187.6, ^2J = 8.8)	132.8 (^1J = 193.4, ^2J = 7.3)	CD_3OD	This work
	154.9	102.7 (^1J = 187.2, ^2J = 9.9)	134.5 (^1J = 195)	DMSO-d_6	19
	137.6	106.3	145.8	DMSO-d_6	19

(r = 0.998), *i.e.*, the main band observed in the UV spectra of nitropyrazoles is a charge-transfer band. This conclusion is also confirmed by a considerable bathochromic shift of the maximum observed in the deprotonation (see Table 1, $\Delta\nu$ = 5800 cm^{-1}). The dependence obtained can be used for the estimation of PI values of 4-nitropyrazoles. In particular, for the 4-nitropyrazole anion, its value is equal to 7.2—7.3 eV, which is approximately 3 eV lower than that of a neutral molecule. This is evidence for a substantial destabilization of the boundary π-MO in the heterolytic cleavage of the N—H bond of pyrazoles.

Unlike the UV spectrum of 4-nitropyrazole, the spectrum of 3(5)-nitropyrazole is characterized by a greater relative intensity of the short-wave shoulder, the hypsochromic shift of the global maximum, and a substantial broadening of the main band (see Fig. 3, Table 1, the half-width of the most intense band was estimated by its long-wave wing to exclude the effect of the short-wave absorption). Analysis of the theoretical data on the energies of the transitions in the UV spectra of 3-, 4-, and 5-nitropyrazoles makes it possible to draw the following conclusions. A change from 4-nitro- to 3-nitropyrazole should be accompanied by the shift of one of the π→π* transitions to a short-wave region, and the second transition should be shifted to a long-wave region, *i.e.*, this results in the resolution of the corresponding bands. As compared to 4-nitropyrazole, the bathochromic shift of one π→π* transition and the retention of the energy of another transition can be predicted for the 5-nitro derivative. In this case, the global maximum of the main band should undergo either the bathochromic shift or remain unchanged. The hypsochromic shift is observed experimentally, but the bands are not resolved. This can be caused by either a smaller (compared to that predicted by the calculation) energy gap between the π→π* transitions or by their different intensities. In the latter case, the maximum only of the more intense band is detected. Since the AM1 (CI) method gives no information on the intensity of the transitions, the CNDO/S method was used for this purpose. For the transitions discussed, whose configurational composition is approximately retained in both methods, the moments of transitions were calculated in terms of CNDO/S. This additional information (see Table 1) makes it possible to assert that the observed UV spectrum of 3(5)-nitropyrazole in a solution is mainly caused by the absorption of the 3-nitro tautomer, whose most intense transition is shifted to a shorter-wave region compared to the corresponding transition of 4-nitropyrazole. Thus, the absence of the resolution of the "π"-bands is explained by a smaller moment of the transition corresponding to one of the bands. The broadening of the main band of 3-nitropyrazole indicates the possibility of the existence of two π→π* transitions in this energy range. The predominance of the 3-nitro tautomer in the solution, which follows from the analysis of the UV spectra, is in accordance with the conclusion based on the pK_{BH^+} values of isomeric nitropyrazoles.[4] This value for 3(5)-nitropyrazole (−4.66) is close to the pK_{BH^+} value of 1-methyl-3-nitropyrazole (−4.64) and differs sharply from the corresponding value for 1-methyl-5-nitropyrazole (−2.38). The methylation of 3(5)-nitropyrazole mainly results in the formation of 1-methyl-3-nitropyrazole,[15] which also testifies that the 3-nitro tautomer predominates in the solution.

The ^1H (Ref. 16) and ^{13}C NMR data (Table 2) also show that 3(5)-nitropyrazole exists in the form of the 3-nitro tautomer. As can be seen from Table 2, the

Table 3. Predominant tautomers of 3(5)-substituted pyrazoles from the data of semiempirical quantum-chemical methods and ^{13}C NMR spectroscopy

Substituent	$\Delta_fH°(3) - \Delta_fH°(5)$ /kcal mol^{-1}			^{13}C NMR	
	MNDO	AM1	PM3	Predominant tautomer	References
NO_2	−0.37	1.31	1.88	3-NO_2	16, 19, this work
CH_3	0	0.95	0.99	1 : 1	20, 21, this work
NH_2	−0.95	0.56	−0.33	3-NH_2	22

values of the chemical shifts of ^{13}C and spin-spin coupling constants ($J_{^1H-^{13}C}$) of 3-nitropyrazoles and their 1-methyl-substituted derivative are almost equal.

Data on the prevailing tautomer of the pyrazoles studied can be obtained by the comparison of the heats of formation of 3- and 5-tautomers. The application of the AM1 method for this purpose showed that the results of this method do not agree with the data of the NMR spectra of the solutions (Table 3). Among the other semiempirical methods, a qualitative agreement between the theory and experiment is achieved only by the MNDO method (see Table 3).

Thus, the use of the semiempirical AM1 (CI) method made it possible to assign the bands in the UV spectra of isomeric nitropyrazoles to the $\pi\rightarrow\pi^*$ and $n_0\rightarrow\pi^*$ transitions and to indicate that the 3-nitro tautomer predominates in the solution. The most intense band in the UV spectra of the compounds studied is a charge-transfer band. The value of the first ionization potential of the deprotonated form of 4-nitropyrazole was estimated.

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Received May 14, 1996