ELECTRONIC AND PHOTOELECTRON SPECTRA OF AMINO-1-METHYLNITROPYRAZOLES AND THEIR QUANTUM-CHEMICAL INTERPRETATION

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The electronic and photoelectron spectra of isomeric vic-aminonitro-1-methylpyrazoles were interpreted by means of the data from PPP and MNDO quantum-chemical calculations.

In [1], on the basis of the similarity of the electronic absorption (EA) spectra of o-nitroaniline and amino-1-methylnitropyrazoles with the vicinal arrangement of the amino and nitro groups we made a preliminary assignment of the long-wave band in the spectra of these compounds to the $CT_{NH_2}^{NO_2}$ band and of the band in the region of 270 nm to the $CT_C^{NO_2}$ band, and we tried to relate the position and intensity of the long-wave band to the characte istics of the electron density distribution in the pyrazole ring.

In a continuation of the spectral investigations we undertook a quantum-chemical calculation for the molecules of 5-amino-1-methyl-4-, 3-amino-1-methyl-4-, 4-amino-1-methyl-3-, and 4-amino-1-methyl-5-nitropyrazoles (I-IV) and also pyrazole (V), 1-methylpyrazole (VI), and 1-methyl-4-nitropyrazole (VII). A planar arrangement of the amino and nitro groups was adopted for the molecules of (I-IV); this must be assisted by the existence of an intramolecular hydrogen bond between these substituents [1, 2].

The charges at the atoms and the bond orders, obtained during calculation of the unsubstituted pyrazole molecule with the same parametrization of the $N_{(1)}$ atom as for the nitrogen atom of the amino group in aniline, agree well with the published data [3, 4]. The use of the parameters of the nitrogen atom in N-methylaniline [5] for the $N_{(1)}$ atom during calculation of the (VI) molecule (and its aminonitro derivatives) led, in contrast to compound (V), to equalization of the $C_{(3)}-C_{(4)}$ and $C_{(4)}-C_{(5)}$ bond orders (Table 1).

The data from the calculation predict the position of the long-wave band in the EA spectrum of the aminonitropyrazoles (I-IV) satisfactorily (Table 2). The principal contribution to the electronic transition corresponding to this band comes from the singly excited configuration Φ_{6-7} (c_i 0.98-0.99, according to the usual numbering of the molecular orbitals of aminonitropyrazoles, MO_6 is the HOMO, and MO_7 is the LUMO). Here there is a large increase in the π charge at the atoms of the nitro group ($\Delta q = -0.692 - 0.733$) and an appreciable decrease at the nitrogen atom of the amino group ($\Delta q = 0.290 - 0.345$) (Table 1), and this makes it possible to assign the long-wave band to the $CT_{NH_2}^{NO_2}$ bands. The prerequisites for their appearance in the EA spectra of compounds (I-IV) lie in the ground state of the molecules; in the formation of the HOMO a large contribution comes from the AO of the amino group with insignificant participation of the AO of the nitro group, and for the LUMO the contribution from the AO of the nitro group is the largest (Table 3).

For the isomers (I-IV) the calculation gives similar values for the oscillator forces of the electronic transitions responsible for the $CT_{NH_2}^{NO_2}$ bands (f = 0.258-0.298) (Table 2). At the same time, the intensity of these bands with identical half-width $\Delta\nu_{1/2}$ in the EA spectra of 4,5- and 5,4-aminonitropyrazoles (IV) and (I) is 1.5 times higher than in the spectra of the 3,4 and 4,3 isomers (II) and (III). We interpreted this [1] as resulting from the greater double-bond character of the $C_{(4)}-C_{(5)}$ bond in the molecules of (I) and (IV) compared with the $C_{(3)}-C_{(4)}$ bond in the aminonitropyrazoles (II) and (III). In view of the fact that in the molecule of (V), in contrast to the derivative (VI), the calculated π orders of the bonds differ significantly (Table 1) while N-methylation of substituted pyrazoles has little effect on the position of the characteristic band in the EA spectra [6], we calcu-

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TABLE 1. Calculated Values of the π Charges and π Orders in the Molecules of (I-VI) in the Ground State (A by the PPP method, B by the MNDO method)

Compound	Method	Charges on atoms and groups							Bond orders						
		$N_{(1)}$	$N_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	NH_2	NO_2	$N_{(1)}-N_{(2)}$	$N_{(2)}-C_{(3)}$	$C_{(3)}-C_{(4)}$	$C_{(4)}-C_{(5)}$	$C_{(5)}-N_{(1)}$	$C-NH_2$	$C-NO_2$
V	A	0,448	−0,339	0,047	−0,107	−0,049	—	—	0,447	0,730	0,609	0,728	0,578	—	—
VI	A	0,581	−0,381	0,022	−0,120	−0,102	—	—	0,493	0,683	0,635	0,698	0,639	—	—
	B	0,411	−0,255	0,000	−0,123	−0,043	—	—	0,447	0,783	0,542	0,779	0,516	—	—
I	A	0,528	−0,379	0,080	−0,210	−0,028	0,192	−0,183	0,417	0,737	0,566	0,543	0,632	0,426	0,375
	B	0,391	−0,291	0,083	−0,372	0,107	0,156	−0,074	0,357	0,812	0,507	0,622	0,570	0,413	0,251
I*	A	0,402	−0,347	0,095	−0,207	0,025	0,216	−0,178	0,373	0,772	0,536	0,574	0,570	0,464	0,375
II	A	0,600	−0,462	0,076	−0,205	−0,041	0,221	−0,188	0,424	0,639	0,513	0,587	0,703	0,479	0,378
	B	0,453	−0,376	0,106	−0,341	0,066	0,154	−0,062	0,368	0,728	0,482	0,668	0,633	0,412	0,242
II*	A	0,465	−0,431	0,082	−0,187	0,021	0,219	−0,168	0,383	0,672	0,483	0,642	0,639	0,480	0,364
III	A	0,621	−0,359	−0,090	−0,038	−0,175	0,190	−0,149	0,555	0,596	0,561	0,627	0,609	0,417	0,349
	B	0,460	−0,208	−0,169	−0,026	−0,141	0,127	−0,043	0,510	0,704	0,534	0,709	0,515	0,350	0,213
III*	A	0,482	−0,309	−0,062	−0,039	−0,039	0,185	−0,126	0,506	0,649	0,534	0,664	0,553	0,412	0,329
IV	A	0,571	−0,314	−0,044	−0,030	−0,201	0,207	−0,179	0,545	0,680	0,595	0,565	0,529	0,432	0,366
	B	0,426	−0,187	−0,067	0,013	−0,265	0,146	−0,066	0,495	0,758	0,540	0,673	0,454	0,380	0,248
IV*	A	0,431	−0,270	−0,008	−0,012	−0,166	0,217	−0,181	0,485	0,738	0,545	0,605	0,477	0,446	0,370

*The model molecules of the 1H analogs with changed parametrization for the $N_{(1)}$ atom.

TABLE 2. Calculated and Experimental Values of the Energy Characteristics for Compounds (I-VII) (A by the PPP method, B by the MNDO method)

Compound	Method	Calculated data					Experimental data				
		$-E_{LUMO}$, eV	$-E_{HOMO}$, eV	$-E_{2OMO}$, eV	$\Delta E_{NH_2}^{NO_2}$, eV	f	IP_1, eV	IP_2, eV	$\Delta E_{NH_2}^{NO_2}$, eV (ε)		$\Delta E_C^{NO_2}$, eV (ε), ethanol
									benzene	ethanol	
V	A	—	10,27	10,91	—	—	9,15	9,88	—	—	—
	B	—	10,17	9,74	—	—					
VI	A	—	10,04	10,62	—	—	9,05	9,60	—	—	—
	B	—	9,54	9,77	—	—					
VII	A	2,88	10,86	11,19	—	—	9,88	10,52	—	—	—
	B	—	10,85	11,16							
I	A	2,56	9,65	10,74	3,78	0,290	8,91	9,80	3,66	3,76	4,61
	B	—	9,72	10,93					(5910)	(6400)	(3600)
I*	A	—	9,74	11,22	3,79	0,329					
II	A	2,59	9,44	10,74	3,63	0,298	8,62	9,65	3,54	3,59	4,46
	B	—	9,50	10,74	—	—			(3800)	(4040)	(4820)
II*	A	2,78	9,64	10,81	3,60	0,234					
III	A	2,78	8,99	11,03	3,12	0,268	8,60	9,80	3,15	3,35	4,44
	B								(3300)	(3230)	(5220)
	φ=0°	—	8,97	11,03	—	—					
	φ=45°	—	9,23	11,10	—	—					
	φ=60°	—	9,45	11,14	—	—					
III*	A	2,98	9,08	11,26	2,99	0,225					
IV	A	3,07	9,08	11,11	2,97	0,258	8,52	9,78	3,04	3,16	4,32
	B	—	9,13	10,98	—	—			(3940)	(5210)	(4300)
IV*	A	3,12	9,30	11,34	3,16	0,349					

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*Model molecules of the 1H analogs with changed parametrization for the $N_{(1)}$ atom.

TABLE 3. Contributions from the Atomic Orbitals to the Molecular Orbitals Calculated for Compounds (I-VII) by the MNDO Method

Compound	MO	Coefficients at AOs								
		$N_{(1)}$	$N_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$\ddot{N}$	N	O	O
V	2OMO	0,571	−0,368	−0,622	−0,290	0,260	—	—	—	—
	HOMO	0,225	0,488	−0,014	−0,639	−0,550	—	—	—	—
VI	2OMO	−0,445	0,485	0,560	0,009	−0,459	—	—	—	—
	HOMO	0,398	0,301	−0,239	−0,696	−0,429	—	—	—	—
VII	HOMO	0,260	0,478	−0,016	−0,666	−0,446	—	0,024	0,141	0,168
	LUMO	0,279	−0,067	−0,154	0,266	−0,526	—	0,489	−0,385	−0,388
I	2OMO	−0,600	0,088	0,480	0,538	−0,027	0,102	−0,022	−0,153	−0,105
	HOMO	0,154	−0,490	−0,189	0,507	0,312	−0,560	0,014	−0,102	−0,138
	LUMO	0,195	0,032	−0,194	0,171	−0,456	0,187	0,550	−0,423	−0,406
II	2OMO	0,232	0,510	0,026	−0,653	−0,449	−0,007	0,018	0,144	0,163
	HOMO	−0,350	0,435	0,256	0,309	−0,187	−0,683	0,012	−0,060	−0,086
	LUMO	−0,307	0,106	0,125	−0,234	0,536	−0,057	−0,486	0,373	0,386
III	2OMO	−0,413	0,464	0,572	−0,027	−0,453	−0,087	−0,029	−0,095	−0,165
	HOMO	−0,269	−0,288	0,264	0,370	0,458	−0,642	0,013	−0,051	−0,077
	LUMO	−0,282	0,437	−0,284	0,147	0,175	−0,067	−0,505	0,391	0,418
IV	2OMO	0,353	−0,509	−0,536	0,013	0,517	0,001	−0,011	−0,139	−0,100
	HOMO	−0,384	−0,172	0,316	0,357	0,411	−0,620	0,032	−0,092	−0,120
	LUMO	−0,270	0,313	−0,105	−0,347	−0,235	0,166	0,523	−0,408	−0,411

lated the model molecules of aminonitro-1H-pyrazoles by the PPP method in order to establish the effect of the orders of the C—C bonds on the characteristics of the $CT_{NH_2}^{NO_2}$ bands in the EA spectra of (I-IV).

The calculated values of the oscillator force for the electronic transition corresponding to the long-wave band for the model compounds agree well with the intensity ratio of the long-wave bands in the EA spectra of the amino-1-methylnitropyrazoles (Table 2). However, with the planar arrangement of the substituents the calculation predicts the most long-wave absorption in 4-amino-3-nitropyrazole, and this contradicts the spectral data for compound (III) (Table 2).

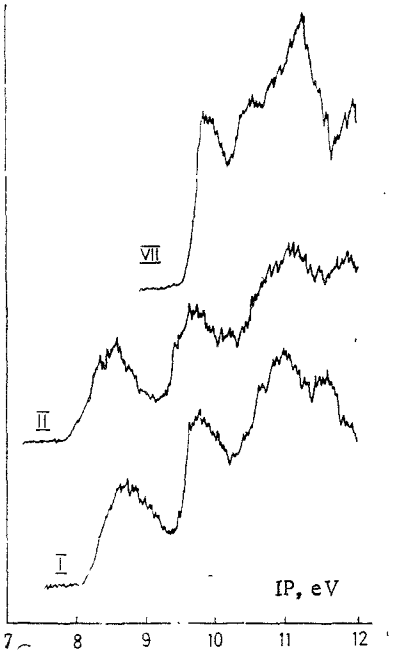

Fig. 1

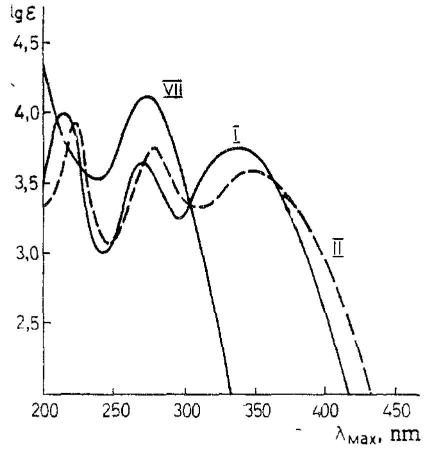

Fig. 2

Fig. 1. Photoelectron spectra of compounds (I, II, VII).

Fig. 2. Electronic absorption spectra (in ethanol) of compounds (I, II, VII).

As follows from the results of the calculation for the molecules of compounds (I-IV) and their nonmethylated analogs, the position of the $\text{CT}_{\text{NH}_2}^{\text{NO}_2}$ bands [$\Delta E_{\text{NH}_2}^{\text{NO}_2}$ (eV) = 1239.8/λ (nm)] is determined by the difference in the energies of the HOMO and LUMO: $\Delta E_{\text{NH}_2}^{\text{NO}_2} = 0.75\ (E_{\text{LUMO}} - E_{\text{HOMO}}) - 1.53$ (regression coefficient r = 0.99), and N-methylation does not affect the order of the values for the energies of the HOMO in the isomers (Table 2).

For the experimental determination of the energy of the HOMO, according to Koopman's theorem [7], it is possible to use the first vertical ionization potentials (IP_1), obtained from the photoelectron (PE) spectra. The PE spectra of the aminonitropyrazoles (I-IV) and also of compounds (VI) and (VII) were measured for the first time (Fig. 1, Table 2), and the molecules of these compounds and of pyrazole were calculated by the MNDO method used for the determination of the ionization potential [8].

The assignment of the ionization potential of the pyrazole was made in [9] by the ab initio method. The appearance of the first two ionization potentials is due to the ionization of an electron from the π-MOs formed in the following way: The HOMO of $N_{(1)}N_{(2)}-C_{(2)}C_{(3)}$ and the second occupied MO (2OMO) of $N_{(2)}C_{(3)}C_{(4)}-N_{(1)}C_{(5)}$. However, the coefficients at the AOs were not given in [9].

The results from the calculations on the molecule of (V), made by the PPP and MNDO methods, agree well with the data from the PE spectra and give the same qualitative pattern for the formation of the HOMO and the 2OMO as in [9], indicating a minimal contribution from the AO of $C_{(3)}$ to the HOMO. The MNDO method confirms the conclusion in [9] (in contrast to [10]) that the IP_1 and IP_2 of pyrazole are due to the ionization of the π electrons and only the third band in the PE spectrum is due to the ionization of an electron of the $N_{(2)}$ atom. N-Methylation of pyrazole gives rise to a decrease in the ionization potential, but the change in IP_2 (Δ 0.28) is larger than in IP_1 (Δ 0.10 eV), since the contribution from the AO of $N_{(1)}$ to the 2OMO exceeds the contribution from this orbital to the HOMO of pyrazole.

In the PE spectra of amino-1-methylnitropyrazoles (I-IV) IP_1 and IP_2 (Table 2) correspond to the ionization of electrons from the π-MO and are close in value to the analogous ionization potentials of nitroanilines [11]. The IP_1 values for compounds (I-IV) decrease in the order I > II ≈ III > IV, which according to Koopmans' theorem ($\text{IP}_1 \approx E_{\text{HOMO}}$) makes it possible to consider that $E_{\text{HOMO}} \approx E_{\text{HOMO}}(\text{III})$. However, this is not fulfilled for the energies of the HOMO obtained by the PPP method for compounds (II) and (III) and their 1H analogs.

Calculation of the amino-1-methylnitropyrazoles (I-IV) by the MNDO methods (Tables 1-3) with the planar arrangement of the amino and nitro groups gives the same pattern for the formation of the HOMO of the isomers as calculation by the PPP method with optimization of the geometry of the molecules.

A large contribution to the HOMO of the molecules of (I-IV) comes from the π-electron-donating nitrogen atom of the amino group, during destruction of the conjugation of which with the π-electron system of the heterocycle there must be an increase in IP_1 compared with the value of IP_1 for the planar molecule. In the series of isomers (I-IV) 4-amino-1-methyl-3-nitropyrazole (III) has the weakest intramolecular hydrogen bond between the amino and nitro groups [1]. This is due, according to the data from calculation by the MNDO method, to the minimal total (σ + π)-charge at the atoms of the amino group (q + +0.032) compared with the other isomers (q = +0.048-0.059). Therefore, compound (III) evidently has the greatest susceptibility for removal of the steric ortho hindrances through rotation of the amino group.

Calculation of the molecule of (III) by the MNDO method gives the following values for the energies of the HOMO for various angles of rotation (φ) of the amino group in relation to the plane ofthe pyrazole ring [−8.97 (φ = 0°), −9.09 (30°), −9.23 (45°), and −9.44 eV (60°)], whereas the values for the energies of the 2OMO and the LUMO, for which the contribution from the AO of the nitrogen in the amino group is close to zero, remain practically unchanged. With correction of the $-E_{HOMO}$ value for 4-amino-3-nitropyrazole (III) (9.2-9.4 eV) there is satisfactory agreement between the $-E_{HOMO}$ values and the experimental IP_1 values and also $|E_{HOMO} - E_{2HOMO}|$ and $IP_2 - IP_1$ in the series of aminonitropyrazoles (I-IV), which is often considered a test for the adequacy of the experimental and calculated energy characteristics of molecules [12].

The foregoing makes it possible to consider that $-E_{HOMO}$ for the model molecule of 4-amino-3-nitro-1H-pyrazole must in fact approximate to $-E_{HOMO}$ for 3-amino-4-nitro-1H-pyrazole and amount to approximately 9.5 eV. In this case, by means of the relationship $\Delta E_{NH_2}^{NO_2} = 0.75\,(E_{LUMO} - E_{HOMO}) - 1.53$ it is possible to determine the position of the $CT_{NH_2}^{NO_2}$ band in the EA spectrum of 4-amino-3-nitropyrazole. Calculation shows that with such an approximation $\Delta E_{NH_2}^{NO_2}$ will be equal to 3.32 eV (λ_{max} 373 nm) and coincides with the experimental data for compound (III) (Table 2).

Analysis of the PE spectra shows that the IP_2 values ($-E_{2OMO}$) of the aminonitropyrazoles (I-IV) differ little from the IP_1 values of the nitropyrazoles (VII) and (VIII). As follows from the results of calculation of these compounds by the MNDO method, the reasons for such agreement are the characteristics of the investigated MOs, namely, the participation of mainly the AO of the pyrazole ring in their formation (Table 3).

The observed relationship in the PE spectra of nitro- and aminonitropyrazoles clearly gives rise to the agreement of the band in the region of 270 nm in the EA spectrum of the aminonitropyrazoles with the long-wave $CT_C^{NO_2}$ band in the spectrum of the nitropyrazoles (Fig. 2).

The postions of the $CT_{NH_2}^{NO_2}$ and $CT_C^{NO_2}$ bands ($\Delta E_{NH_2}^{NO_2}$ and $\Delta E_C^{NO_2}$ in Table 2) in the EA spectra of amino-1-methylnitropyrazoles (I-IV) are determined by the values of (E_{LUMO} + IP_1) and (E_{LUMO} + IP_2), respectively, and this indicates a relationship between the EA spectra and PE spectra of these compounds. Since the main contribution to the LUMO comes from the AOs of the nitro group, competing participation of this group [13] evidently arises in the electronic transitions responsible for the $CT_{NH_2}^{NO_2}$ and $CT_C^{NO_2}$ bands. This conclusion is confirmed by the change in the intensity ratio of these bands in the transition from the EA spectra of 5,4- and 4,5-aminonitropyrazoles (I) and (IV) to the spectra of the isomers (II) and (III).

EXPERIMENTAL

The electronic absorption spectra were measured on a Specord UV-vis spectrophotometer for concentrations of 10^{-4} M in benzene and ethanol. The photoelectron spectra were recorded on a Perkin–Elmer PES-18 spectrophotometer and were calibrated with reference to the $^2p_{1/2}$, $^2p_{3/2}$ Xe lines at 12.13 and 13.43 eV. The quantum-chemical calculation for the ground and first excited states of the molecules was made by the PPP method [16] in the variable β approximation [17] with the additional introduction of optimization of the internuclear separations in the ground state by the minimum atomization energy using a program which realizes the Dewar algorithm [18] and also by the MNDO method [8] with fixed geometry for the pyrazole ring [19].

The aminonitropyrazoles (I-IV) and the nitropyrazoles (VII, VIII) were synthesized by the previously described methods [14, 15].

LITERATURE CITED

1. V. P. Perevalov, L. I. Baryshnenkova, G. P. Sennikov, I. B. Savina, Sh. G. Isaev, M. A. Andreeva, and B. I. Stepanov, Khim. Geterotsikl. Soedin., No. 5, 657 (1985).
2. J. R. Holder, Acta Cryst., 22, 545 (1965).
3. M. Kagime, Bull. Chem. Soc. Jpn., 43, 3344 (1970).
4. R. E. Burton and I. L. Finar, J. Chem. Soc., B, No. 9, 1692 (1970).
5. T. L. Kunil and H. Kuroga, Theoret. Chim. Acta (Berlin), 11, 97 (1968).
6. I. I. Grandberg, Zh. Obshch. Khim., 33, 519 (1963).
7. V. I. Vovna and F. I. Vilesov, Usp. Fotoniki, LGU, Leningrad, No. 5, 3 (1975).
8. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977).
9. S. Cradock, R. H. Findlay, and M. H. Palmer, Tetrahedron, 29, 2173 (1973).
10. A. Baker and D. Betteridge, Photoelectron Spectroscopy [Russian translation], Mir, Moscow (1975), p. 89.
11. O. S. Khalil, J. L. Meeks, and S. P. McGlynn, J. Am. Chem. Soc., 95, 5876 (1973).
12. T. Kobayashi, Bull. Chem. Soc. Jpn., 56, 3224 (1983).
13. A. E. Lutskii and N. I. Gorokhova, Opt. Spektr., 27, 917 (1969).
14. V. P. Perevalov, L. I. Baryshnenkova, M. A. Andreeva, Yu. A. Manaev, I. A. Denisova, B. I. Stepanov, and V. I. Seraya, Khim. Geterotsikl. Soedin., No. 12, 1672 (1983).
15. V. P. Perevalov, M. A. Andreeva, L. I. Baryshnenkova, Yu. A. Manaev, G. S. Yamburg, B. I. Stepanov, and V. A. Dubrovskaya, No. 12, 1676 (1983).
16. P. Pariser and R. Parr, J. Chem. Phys., 23, 711 (1955).
17. V. P. Zvolinskii, Author's Abstract of Candidate's Dissertation, Chemical Sciences, Moscow (1970).
18. M. J. S. Dewar, Molecular Orbital Theory for Organic Chemists, McGraw-Hill, New York (1969).
19. La Cour and S. F. Rasmussen, Acta Chem. Scand., 27, 1845 (1973).