of 98 % HNO_3 and 5 mL of 20 % oleum at −20÷−25° C. The mixture was stirred at the same temperature for 2 h, then poured on 50 g ice. The product was extracted by ethyl acetate (3×30 mL); the extract was washed with water (2×20 mL), dried over $MgSO_4$ and evoporated *in vacuo*. The residue was recrystallizated from an isopropanol : water mixture (5 : 1) to give compound **2**.

2a, yield 42 %, m.p. 152—154 °C. IR (ν/cm^{-1}): 3410, 3170 (NH), 1700 (C=O), 1622, 1546, 1522, 1296 (N—NO_2). ^{1}H NMR (DMSO-d_6, δ, ppm): 3.34 (s, 3 H, Me), 5.13 (d, 2 H, CH_2, ^3J = 5.4 Hz), 7.8 (br. s, 1 H, NH—NO_2), 8.56 (t, 1 H, C—NH—C). ^{13}C NMR (CD_3COCD_3, δ, ppm): 38.8 (CH_3), 56.9 (CH_2), 151.2 (C=O). ^{14}N NMR (DMSO-d_6, δ, ppm): −35.0 ($\underline{N}O_2$—NH), -28.2 ($\underline{N}O_2$—N—CH_3).

2b, yield 44 %, m.p. 126—127 °C. IR (ν/cm^{-1}): 3420, 3180 (NH), 1698 (C=O), 1632, 1520, 1288 (N—NO_2). ^{1}H NMR (CD_3COCD_3, δ, ppm): 1.14 (t, 3 H, Me), 3.9 (q., 2 H, CH_2—C), 5.23 (d, 2 H, N—CH_2—N).

2c, yield 28 %, m.p. 113—115 °C. IR (ν/cm^{-1}): 3400, 3160 (NH), 1706 (C=O), 1624, 1550, 13 (N—NO_2). ^{1}H NMR (CD_3COCD_3, δ, ppm): 1.20 (d, 6 H, 2 Me), 4.57 (m, 1 H, CH), 5.20 (d, 2 H, CH_2).

References

1. A. S. Ermakov, S. A. Serkov, V. A. Tartakovsky, T. S. Novikova, and L. I. Khmel'nitskii, *Khimiya Geterotsikli-cheskikh Soedinenii*, 1994, 1129 [*Chem. Heterocycl. Compds.*, 1994, No. 8 (Engl. Transl.)].
2. B. R. Iohn and N. I. Verona, US Pat. 2 310 038 (*Chem. Abstr.*, 1943, **37**, 4077).
3. G. G. Martin, Us Pat. 2 369 439 (*Chem. Abstr.*, 1945, **39**, 5368).

Received June 28, 1994

X-Ray photoelectron spectra and electronic structure of pyrazolanthrone and its derivatives

T. M. Ivanova, R. V. Linko, A. M. Galushko, and B. E. Zaitsev*

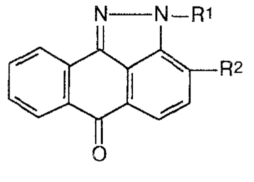
Research Institute of Organic Dyestuffs and Intermediates,
1/4 B. Sadovaya ul., 103787 Moscow, Russian Federation.
Fax: +7 (095) 254 1200

X-ray photoelectron spectroscopy (XPS) was used to investigate the electronic structures of pyrazolanthrone and its derivatives on the basis of quantum-chemical data. The high mobility of hydrogen atoms adjacent to the pyrrole atom as well as the existence of an intermolecular hydrogen bond were hypothesized. The considerable influence of the carbonyl group on redistribution of electronic density in a pyrazole fragment was observed.

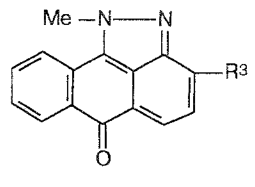
Key words: pyrazolanthrone, X-ray photoelectron spectroscopy, N1s level, binding energy, electronic density.

Pyrazolanthrone and its derivatives are of practical significance and used as vat dyes. However, the chemical properties and electronic structure of this class of compounds have not been adequately investigated.

In this work the electronic structures of pyrazolanthrone and its derivatives were studied by X-ray photoelectron spectroscopy (XPS) using data from quantum-chemical calculations. The class of pyrazolanthrone derivatives under consideration consists of compounds with the following structures:



1—7



8—9

1: R^1 = R^2 = H; **2**: R^1 = H, R^2 = Me; **3**: R^1 = H, R^2 = Bu^t;
4: R^1 = Me , R^2 = H; **5**: R^1 = R^2 = Me;
6: R^1 = C(O)Ph, R^2 = H; **7**: R^1 = $CH_3C_6H_4SO_2$, R^2 = H;
8: R^3 = H; **9**: R^3 = Me.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2043—2045, November, 1994.

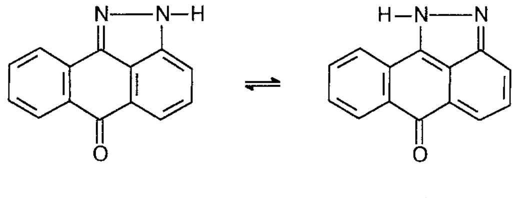
Experimental

Measurements were carried out on a Kratos ES-100 XPS spectrometer. For electron excitation the K_α-band of Mg ($h\nu$ = 1253.6 eV) was used. Samples were prepared by pressing into a brass netting. Chromatographically pure substances were used for the analysis. C1s-line of diffusive oil vapors, the energy of which equals 285 eV, was accepted as a standard. All measurements were performed no less than three times at −20 °C *in vacuo* (10^{-7} Torr). The reproducibility of energy values was ±0.1 eV. No effect of radiation on the samples was observed. Deconvolution of X-ray spectra was carried out on a PDP-11/03 computer using a program of Gaussian peaks synthesis.

Quantum-chemical calculations of electronic structures of pyrazolanthrone and its derivatives were performed by the Parizer-Parr-Pople method with "varied β" approximation.

Results and Discussion

Pyrazolanthrone can exist in two tautomeric forms: paraquinoid (***a***) and anaquinoid (***b***).[1]



a ***b***

Table 1. XPS characteristics of nitrogen N1s level for pyrazolanthrone and its derivatives

Compound	R^1	R^2	R^3	E_b/eV	ΔE_b/eV	δ/eV
1	H	H	—	400.1	—	2.2
2	H	Me	—	399.9	—	2.3
3	H	Bu^t	—	399.9	—	2.2
4	Me	H	—	400.8		
				399.5	1.3	1.4
5	Me	Me	—	400.8		
				399.4	1.4	1.4
6	C(O)Ph	H	—	401.2		
				399.8	1.4	1.4
7	$SO_2C_6H_4CH_3$	H	—	401.4		
				399.6	1.5	1.5
8	—	—	H	401.3		
				399.3	2.0	1.5
9	—	—	Me	401.4		
				399.2	2.2	1.5
10*	2-Amino-anthraquinone	—	—	399.4	—	1.5

* 2-Aminoanthraquinone is used as a model for comparison.

XPS spectral data of pyrazolanthrone and its *N*-methyl-fixed tautomeric forms, as well as some derivatives are given in Table 1. One broad symmetrical band with binding energy (E_b) equal to 400.1 eV and total bandwidth at a halfheight (δ) equal to 2.2 eV (Fig.1, curve *1*) is observed for nitrogen atoms in the pyrazolanthrone molecule and its derivatives (Table 1, compounds **1—3**). Moreover, the N1s-band in 2-aminoanthraquinone having one type of nitrogen atoms is characterized by a δ value equal to 1.5 eV (compound **10**). Presented XPS spectral parameters for N1s level may be accounted for by the strong intermolecular hydrogen bond N...H—N between the tautomers ***a*** and ***b***. This is confirmed by frequencies of the NH-group stretching vibrations of compound **1** in a crystal state, which are observed in the regions of 2500—3000 and 3100—3300 cm^{-1}.[1] Observed displacement by 900—500 cm^{-1} as compared to the frequency of the free group ν(NH) 3475 cm^{-1} suggests the existence of a very strong hydrogen bond. This results in equalizing the electronic density at the amine and imine atoms of pyrazolanthrone.

For the compounds with fixed paraquinoid structure (compounds **4**, **5**), in which the hydrogen atom is substituted by a methyl group (in the pyrazole fragment), there are two insufficiently resolved peaks (Fig. 1, curve *2*). Deconvolution of these spectra resulted in lines with E_b 400.8 and 399.5 eV, suggesting the presence of two types[2] of N atoms (amine and imine) in the molecule. The resolution of nitrogen N1s lines for the fixed form is caused, in particular, by the absence of a hydrogen bond. As one would expect, the substitution of the methyl group in compound **4** by electron-withdrawing groups, such as benzoyl (compound **6**) and tolylsulphonyl (compound **7**), leads to a decrease in electronic density, at both the imine and amine atoms, and to an increase in E_b of both atoms. In this case the difference in binding energy (ΔE_b) for these two N atoms practically did not change. For compounds **4—7**, ΔE_b are in the range of 1.3—1.5 eV.

The compounds with anaquinoid structure (compounds **8** and **9**) have an almost completely resolved spectrum of nitrogen N1s level (Fig. 1, curve *3*). It should be noted that ΔE_b has considerably increased and is equal to 2.0—2.2 eV.

The energy E_b of N1s level corresponding to the amine type in anaquinoid form is 0.6 eV greater than that in the paraquinoid one. This essential difference in N1s energies of para- and anaquinoid forms can be accounted for by the stronger electron-accepting influence of the C=O group on electronic density of the amine nitrogen atom in the anaquinoid structure.

An oxygen O1s line was recorded for all compounds, and had E_b = 531.1—531.3 eV and δ equal to 1.6 eV, corresponding to that of the carbonyl oxygen atom.[3]

The results obtained may be compared with the XPS data of Clark *et al.*[4] for pyrazole. In this study, two lines of nitrogen N1s level for the pyrazole molecule with ΔE_b equal to 1.3 eV are given. According to the calculations, this difference should be 2.7 eV. For *N*-methyl-pyrazole, the authors obtained two peaks with ΔE_b = 2.3 eV. The

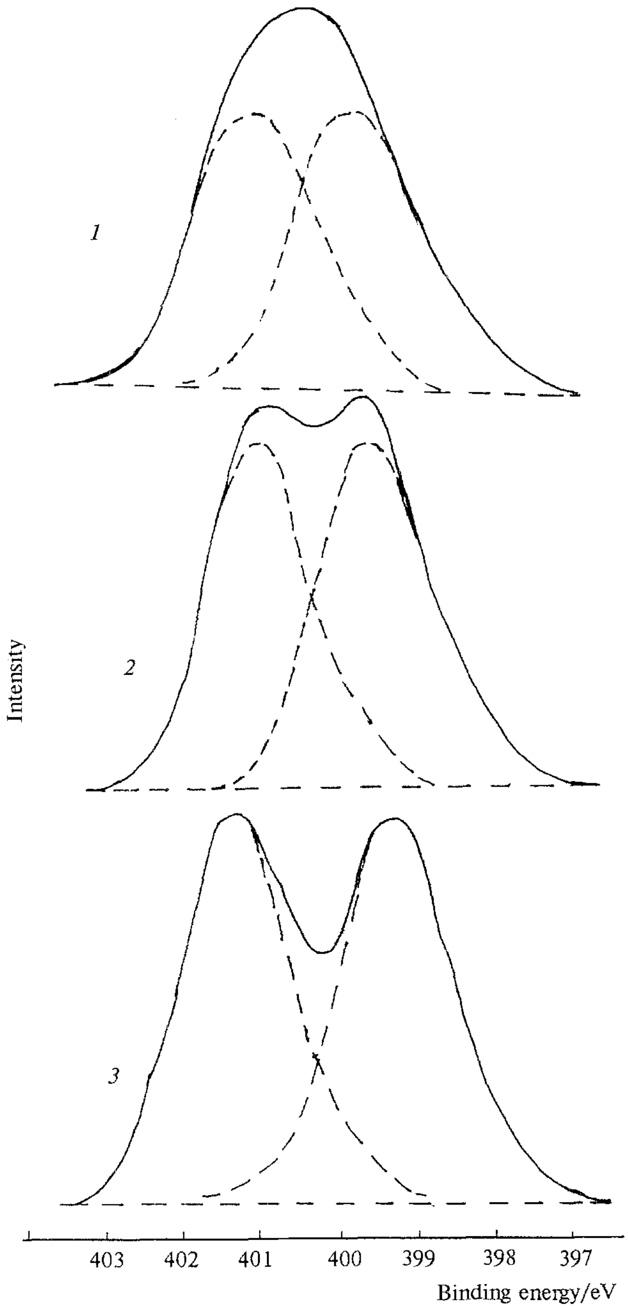


Fig. 1. XPS spectra of nitrogen N1s line in the compounds of pyrazolanthrone **1** (1) and its derivatives **4** (2) and **8** (3).

substitution of hydrogen at the nitrogen atom for the methyl group practically has no influence on the binding energy of N1s level, and eliminates the possibility of formation of an intermolecular hydrogen bond. On this basis, the study concluded the existence of a strong intermolecular H-bond, which contributes to the considerable convergence in binding energies of nitrogen N1s levels in the pyrazole crystal.

Another work[5] presents the results of XPS investigation of substituted pyrazoles. The considerable difference in E_b (1.8 eV) for the two nitrogen atoms in *N*-methyl substituted pyrazoles was accounted for by the discrepancy in participation of nitrogen atoms in the formation of an aromatic π-sextet. Hence, the authors offer no explanation of the drastic decrease in ΔE_b equal to 1.0 eV in the case of hydrogen linked to the nitrogen atom of pyrazole.

Therefore, one can assume that, as in pyrazole, similar effects will be observed in pyrazolanthrone, namely:

— high mobility of hydrogen linked to the pyrrole N atom, which leads to delocalization of the electron density at nitrogen atoms of the pyrazole fragment;

— capacity of pyrazolanthrone to form an intermolecular H-bond;

— possible existence of pyrazolantrone in two tautomeric forms ***a*** and ***b***.

Assuming that pyrazolanthrone exists in the form of tautomers and substitution of hydrogen by methyl group at the pyrrole N atom does not significantly affect its binding energy, the XPS spectrum of pyrazolanthrone should be similar to those of compounds **4** or **8** (Fig. 1, curve *2*, *3*). In the case of the simultaneous existence of both tautomers in the absence of a strong H-bond, the overall spectrum of compounds **4** or **8** should be observed. This supposition correlates well with quantum-chemical data indicating that for imine nitrogen the charges are equal to −0.282 and −0.339, whereas for amine the nitrogen atom these values are equal to 0.422 and 0.500, respectively. The XPS spectra of compounds **4** and **8** correspond to the obtained values of π-electronic density at the nitrogen atoms. However, the spectrum of N1s level of pyrazolanthrone does not coincide with those of compounds **4** and **8**, although it exhibits the mean value E_b. Moreover, the high mobility of hydrogen and its capacity to form an intermolecular H-bond should result in equalizing the electronic density at both nitrogen atoms in the pyrazolanthrone molecule. As a result, the peaks should converge in XPS spectra of N1s bands, as seen in the spectrum of compound **1** (Fig. 1, curve *1*).

The special effect of the carbonyl group as a strong electron acceptor on distribution of electron density in pyrazolanthrone molecule was noted in Ref. 6. According to XPS data the displacement of the electronic density from amine nitrogen atom leads to an increase in E_b of this atom in the compounds with anaquinoid structure (compounds **8** and **9**). The higher E_b may be explained by closer localization of the carbon group to the nitrogen atom with lone electron pair as compared to compounds **4** and **5** with paraquinoid structure. In other words, the amine nitrogen is directly conjugated with the electron-withdrawing carbonyl group.

The authors thank Dr. S. I. Popov (NIOPiC) for discussion of the results.

This investigation was carried out with financial support of the International Scientific Foundation (Grant MA 2000).

References

1. A. M. Galushko, Ph.D.Thesis, NIOPiK (RIODI), Moscow, 1984 (in Russian).
2. A. Katreb, F. G. Baddar, N. R. El-Rayges, and F. H. Al-Hajjar, *J. Mol. Struct.*, 1980, **60**, 193.
3. T. Yoshida and S. Sawada, *Bull. Chem. Soc. Japan*, 1976, **49**, 3319.
4. D. T. Clark and D. M. J. Lilley, *Chem. Phys. Lett.*, 1971, **9**, 234.
5. A. Katreb, N. R. El-Rayges, and F. M. Al-Kharafi, *J. Electron Spectrosc. Relat. Phenom.*, 1983, **31**, 317.
6. W. Bradley and K. W. Geddes, *J. Chem. Soc.*, 1953, **47**, 1130.

Received July 11, 1994