X-ray photoelectron spectra and structure of 2-(2-phenylhydrazono)acetoacetanilide

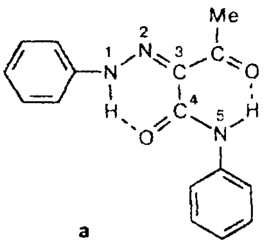
T. M. Ivanova, B. E. Zaitsev, R. V. Linko, M. A. Ryabov, and K. M. Dyumaev*

*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: tiva@ionchran.rinet.ru*

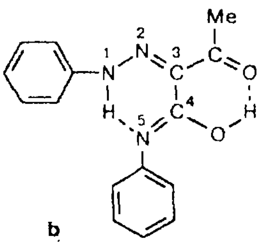
2-(2-Phenylhydrazono)acetoacetanilide, its *N*-methyl derivatives, and model compounds were studied by X-ray photoelectron spectroscopy. The chemical shifts were obtained from the ^{13}C NMR spectra. A correlation between the calculated charges, the binding energies on N atoms, and the ^{13}C NMR chemical shifts was found. The analysis of the XPS data and the ^{13}C NMR chemical shifts led to the conclusion that crystalline 2-(2-phenylhydrazono)acetoacetanilide exists mainly in the oxo hydrazone form.

Key words: 2'-(2-phenylhydrazono)acetoacetanilide, X-ray photoelectron and ^{13}C NMR spectra, binding energies, chemical shifts.

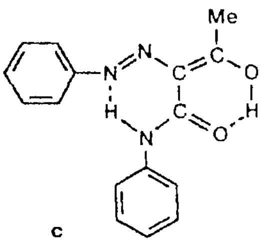
2-(2-Phenylhydrazono)acetoacetanilide (**1**) is the basis for a number of important dyes.[1] The properties of the dyes are determined by structural features and electronic structures of their molecules. Compound **1** can exist, in principle, as several tautomeric forms (**a**—**e**).



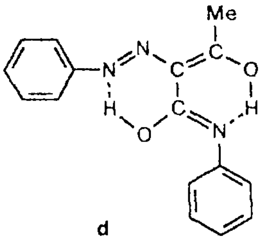
a



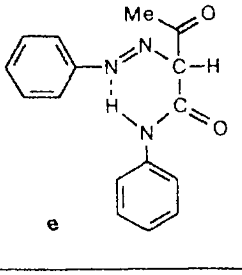
b



c



d



e

These tautomers can be divided into two groups: structures (**a**, **b**) containing a hydrazo group (—NH—N=) and structures with an —N=N— group (**c**—**e**). There is no common opinion among researchers on what particular species reflects the actual structure of molecule **1**. Direct experimental data on its electronic structure are absent in the literature. Structures **1c**—**e** are at variance with some known facts. According to X-ray diffraction analysis,[2] the molecule of *p*-chloro-2-(2-phenylhydrazono)acetoacetanilide in the crystalline state contains an —NH—N= bond rather than an —N=N— bond. The polarographic half-wave potential $E_{1/2}$ corresponds[3] to molecules with hydrazone structures, **1a** and **1b**. Analysis of frequencies and intensities of the ν(C=O) and ν(N—H) stretching bands in the IR spectra of these compounds attests in favor of hydrazone structures.[4] However, mass spectrometric study with ^{15}N labels showed[5] that in the gas phase, compound **1** exists in hydrazone and azo forms. According to the data of ^{1}H and ^{15}N NMR spectroscopy,[6] compound **1** in organic solvents occurs mainly in a hydrazone form, but the presence of an azo form (up to 10%) also cannot be ruled out.[6] Structure **1e** is inconsistent with the data of IR and UV spectra.[4,7] To interpret the spectral characteristics of the tautomers of **1** (IR and UV-VIS spectra), derivatives of the hydrazone form of 2-(2-phenylhydrazono)acetoacetanilide were synthesized.[8,9] The data of IR and UV-VIS spectra and calculation of these molecules by the Pariser—Parr—Pople (PPP) method led to some qualitative conclusions concerning their electronic structures.[4] To study the electronic structure of **1** in more detail, *i.e.*, to choose between species **1a** and **1b**, in this work we used X-ray photoelectron spectroscopy (XPS) and quantum-chemical calculations in the all-valence (σ—π) approximation (INDO/S), and also ^{13}C NMR spectroscopy.

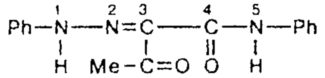
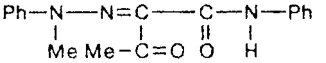
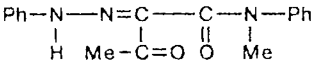
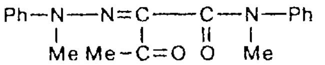
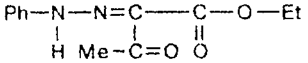
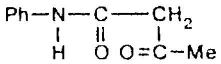
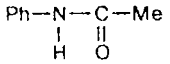
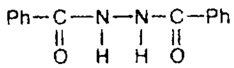
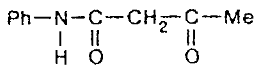
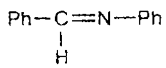
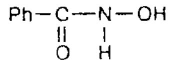
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 488—491, March, 1999.

1066-5285/99/4803-0484 $22.00 © 1999 Kluwer Academic/Plenum Publishers

Experimental

Measurements were carried out on an ES-100 Kratos X-ray electron spectrometer using Al-Kα radiation ($h\nu$ = 1486.6 eV). Samples were prepared by pressing into a copper grid. Analyses were carried out with analytically pure substances. The C1s line from diffusion oil vapor with an energy of 285 eV was used as the standard. All measurements were repeated at least three times both at room temperature and at −20 °C *in vacuo* (10^{-7} Torr). The energy values were reproducible to within ±0.1 eV. An effect of irradiation on the samples was not observed. The X-ray photoelectron spectra were processed on a PDP-11/03 PC using the program for Gaussian peak synthesis. ^{13}C NMR spectra were run on XL-100-15 (25.16 MHz) and CFT Varian (20 MHz) spectrometers in the pulse accumulation mode with Fourier transform in $CDCl_3$ (~10%) solutions.

Table 1. Binding energies (E_b) for the 1s levels for the N and O atoms

Compound		E_b/eV	
		N1s (FWHM)[a]	O1s
 $\mathrm{Ph{-}\underset{H}{\overset{1}{N}}{-}\overset{2}{N}{=}\underset{Me-C=O}{\overset{3}{C}}{-}\underset{O}{\overset{4}{C}}{-}\underset{H}{\overset{5}{N}}{-}Ph}$	**(1a)**	400.6 (1.8)	532.0
 $\mathrm{Ph{-}\underset{Me}{N}{-}N{=}\underset{Me-C=O}{C}{-}\underset{O}{C}{-}\underset{H}{N}{-}Ph}$	(**2**)	400.5 (1.9)	532.2
 $\mathrm{Ph{-}\underset{H}{N}{-}N{=}\underset{Me-C=O}{C}{-}\underset{O}{C}{-}\underset{Me}{N}{-}Ph}$	(**3**)	400.9 (1.8)	532.0
 $\mathrm{Ph{-}\underset{Me}{N}{-}N{=}\underset{Me-C=O}{C}{-}\underset{O}{C}{-}\underset{Me}{N}{-}Ph}$	(**4**)	400.7 (1.8)	531.9
 $\mathrm{Ph{-}\underset{H}{N}{-}N{=}\underset{Me-C=O}{C}{-}\underset{O}{C}{-}O{-}Et}$	(**5**)	400.6 (1.9)	532.3, 533.7
 $\mathrm{Ph{-}\underset{H}{N}{-}\underset{O}{C}{-}\underset{O=C-Me}{CH_2}}$	(**6**)	400.5 (1.8)	532.3
 $\mathrm{Ph{-}\underset{H}{N}{-}\underset{O}{C}{-}Me}$	(**7**)[b]	400.7 (1.9)	531.7
 $\mathrm{Ph{-}\underset{O}{C}{-}\underset{H}{N}{-}\underset{H}{N}{-}\underset{O}{C}{-}Ph}$	(**8**)[c]	400.7 (1.9)	—
 $\mathrm{Ph{-}\underset{H}{N}{-}\underset{O}{C}{-}CH_2{-}\underset{O}{C}{-}Me}$	(**9**)	400.5 (1.8)	531.8
 $\mathrm{Ph{-}\underset{H}{C}{=}N{-}Ph}$	(**10**)	399.4 (1.8)	
 $\mathrm{Ph{-}\underset{O}{C}{-}\underset{H}{N}{-}OH}$	(**11**)[d]	401.4 (1.9)	531.8, 533.8

[a] Full width at the half maximum height.

[b] See Ref. 14.

[c] See Ref. 13.

[d] See Ref. 15.

Results and Discussion

In order to determine the type of the hydrazone structure (**1a** or **1b**), X-ray photoelectron spectra of 2-(2-phenylhydrazono)acetoacetanilide and its mono- and disubstituted derivatives (**2**—**4**) and also model compounds (**5**—**11**), containing various fragments of molecule **1**, were studied. The results are summarized in Table 1. Structures **1a** and **1b** can be divided conventionally into the "left" and "right" parts (at the C(3) and C(4) atoms). The "left" parts of both molecules are identical.

Comparison of the positions of lines corresponding to the N1s level (Fig. 1) and the full width measured at the half maximum height (FWHM) (see Table 1) for structure **1a** and its "left" (**5**) and "right" parts (**6**—**9**) shows that the N atoms in compound **1a** in the crystalline state are energetically equivalent and bear approximately equal charges. This conclusion is consistent[2,10] with the nearly planar structure of the system of bonds of the two chelate rings in **1a**. Mono- (**2** and **3**) and difixed (**4**) species are characterized by close binding energies (E_b) for the N1s level and close FWHM, indicating that their structures are identical to that of molecule **1a**. By comparing the data on the binding energies for the N1s levels in compounds **1a** and **4**, we find that the presence of an intramolecular hydrogen bond does not significantly influence[4,7] the energy state of the N atoms. The measured binding energies for the O1s level

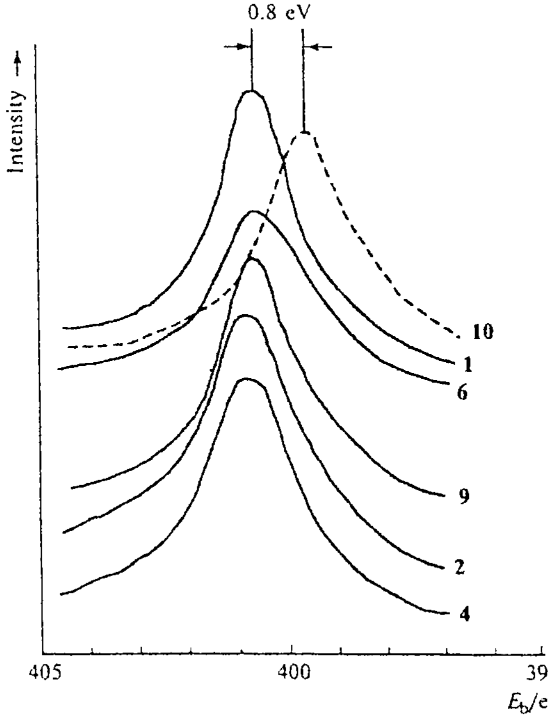


Fig. 1. N1s lines in the X-ray photoelectron spectra of 2-(2-phenylhydrazono)acetoacetanilide (**1**), its mono- and disubstituted derivatives (**2**, **4**), and model compounds (**6**, **9**, **10**).

in compound **1a** and the corresponding mono- and difixed structures lie in the 531.8—532.3 eV range, which corresponds to the normal values for an O atom in a carbonyl group rather than in a hydroxy group, for which E_b > 533 eV (see Table 1, compound **11**).

Since the "left" parts of molecules **1a** and **1b** are identical, let us consider the position of the N1s peak for the "right" part of molecule **1b**, whose fragment is represented by compound **10**. In this case, E_b for N1s is 399.4 eV. Compound **10** does not contain an —O— fragment, and the shifting increment of a directly attached atom in the presence of —O— is[11] 0.4 eV; therefore, it can be expected that the E_b value for the N1s level for the N atom located in the β-position in relation to the —O— fragment would increase by 0.2—0.3 eV (due to the withdrawal of the electron cloud away from the C atom by the O atom). Therefore, the E_b value for the N1s level for —COH=N— should not exceed 400 eV, and the peak shown as a dotted line in Fig. 1 may be expected to appear in the spectrum. Peaks of this type can be either resolved or substantially broadened. Superposition of the spectra of N1s for compounds **5** and **10** (Fig. 2) implies that if compound **1** contains a —COH=N— fragment, the N1s line should be considerably broadened (FWHM is 2.4 eV). In the case where the "right" part of the compound under study is represented by an amide group, as shown by structure **1a**, then, taking into account the E_b value for N1s in model compound **6**, the E_b(N1s) values for both parts of molecule **1a** would coincide and the FWHM would correspond to an energetically uniform N atom.

As has been shown previously,[5,6] 2-(2-phenylhydrazono)acetoacetanilide can exist as several tautomers both in the gas phase and in a solution. ^{13}C NMR spectroscopy can be used most efficiently to analyze the structures of the tautomers. By this method, one can identify the structure of the carbon skeleton of the molecule and, when fixed forms are present, draw conclusions about the type of tautomerism. ^{13}C NMR spectra were recorded for compounds with both unfixed (**1a**, **5**, **9**) and fixed (**2**—**4**) structures. All of the spectra exhibit a signal with δ 194—203. According to the published data,[12] this δ value can be unambiguously assigned to one C atom in an oxo group. Thus, it can be concluded that both unfixed (**1a**, **5**, **9**) and mono- and dimethylated (**2**—**4**) molecules contain an oxo rather than an enol group. The chemical shifts observed in the δ 161—167 range can be assigned to the ^{13}C nucleus in an amide[12] (>NC=O) rather than in an azomethine (>C=N—) fragment. Thus, the presence of signals characteristic of C atoms in oxo and amide groups in the spectra of compounds **1a**, **2**—**5**, and **9** permits one to reject all the hypothetical structures except for **1a**.

This conclusion is in agreement with the results of PPP and INDO/S calculations for structures **1a** and **1b**. The quantum-chemical calculations show that structure **1a** is energetically more favorable than **1b**, because the energy of atomization for molecule **1a** is 179.54 eV, while that for **1b** is 178.70 eV. The change in the electronic structure of the molecule on passing from structure **1a** to **1b** is significant. The electron density at the N(5) atom in molecule **1b** is much greater (5.35 e) than in **1a** (5.16 e), in which it is close to the electron densities at the N(1) and N(2) atoms. This finding suggests that "abstraction" of an electron from N(5) for structure **1b** is markedly facilitated compared to that from the N(1) and N(2) atoms; this is consistent with the assumed resolution of the N1s line in E_b or broadening of this band for compound **1b**.

The set of data considered here attests that the compound in question is more likely to occur as species **1a**.

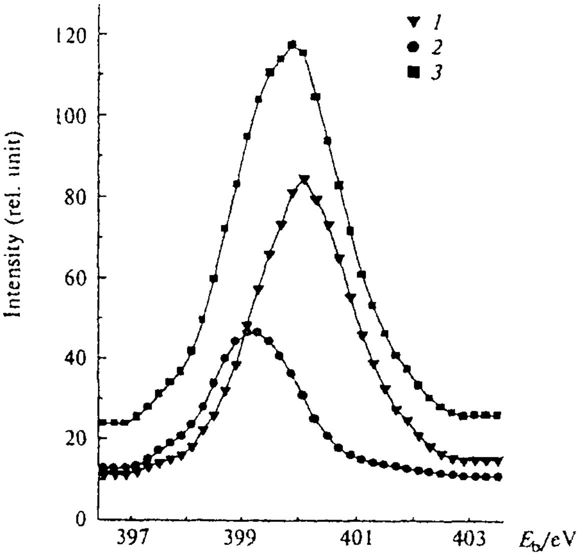


Fig. 2. N1s lines in the X-ray photoelectron spectra for compounds **5** (*1*) and **10** (*2*) and their superposition (*3*).

The authors wish to thank O. A. Tambieva for providing samples for the study.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-15-97388).

References

1. B. I. Stepanov, *Vvedenie v khimiyu i tekhnologiyu krasitelei* [*Introduction to Dye Chemistry and Technology*], Khimiya, Moscow, 1984, 317 pp. (in Russian)
2. H. C. Mes, *Ber. Bunsen. Phys. Chem.*, 1968, **72**, 389.
3. O. S. Zhdamarov, B. E. Zaitsev, O. A. Tambieva, E. S. Lisitsyna, and K. M. Dyumaev, *Zh. Obshch. Khim*, 1978, **12**, 2741 [*J. Gen. Chem. USSR*, 1978, **12** (Engl. Transl.)].
4. Zh. B. Sheban, B. E. Zaitsev, O. A. Tambieva, E. S. Lisitsyna, and K. M. Dyumaev, *Zh. Prikl. Spektr.*, 1978, **29**, 1478 [*J. Appl. Spectr. USSR*, 1978, **29** (Engl. Transl.)].
5. A. Kettrup, M. Grote, and J. Hartman, *Monatsh. Chem.*, 1976, **107**, 1391.

6. N. M. Neplyuev, U. N. Usenko, P. G. Dubenko, and P. S. Palkis, *Zh. Org. Khim.*, 1970, 801 [*J. Org. Chem. USSR*, 1970 (Engl. Transl.)].
7. Y. Yagi, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 487.
8. K. M. Dyumaev, B. E. Zaitsev, O. A. Tambieva, and E. S. Lisitsyna, *Zh. Org. Khim.*, 1978, 562 [*J. Org. Chem. USSR*, 1978 (Engl. Transl.)].
9. K. M. Dyumaev, O. A. Tambieva, and E. S. Lisitsyna, *Zh. Org. Khim.*, 1979, 1586 [*J. Org. Chem. USSR*, 1979 (Engl. Transl.)].
10. A. Whitaker, *Z. Kristallogr.*, 1984, **166**, 177.
11. V. I. Nefedov, *Primenenie RES v khimii. Struktura molekul i khimicheskaya svyaz'* [*Application of XPS in Chemistry. Molecular Structure and Chemical Bond*], dep. in VINITI, Moscow, 1973, p. 4 (in Russian).
12. G. Levi and G. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley-Interscience, New York, 1972.
13. V. I. Nefedov, M. A. Porai-Koshits, I. A. Zakharova, and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, 1972, **3**, 605 [*Dokl. Chem.*, 1972 (Engl. Transl.)].
14. B. J. Lindberg and K. Hamrin, *Acta Chem. Scand.*, 1970, **24**, 3661.
15. B. J. Lindberg, A. Berndtsson, R. Nilsson, and R. Nyholm, *Acta Chem. Scand.*, 1978, **32A**, 353.

Received July 2, 1998;
in revised form October 28, 1998