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Electronic Structure of π Systems: XX.[1] Electronic Structure and Keto–Enol Tautomerism of Dihydrofuro[2,3-*h*]-coumarin-9-ones by Photoelectron Spectroscopy

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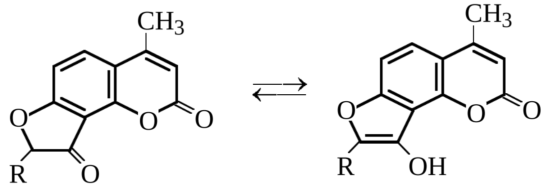
Abstract—Photoelectron spectroscopy and semiempirical quantum-chemical calculations were used to study the electronic structure and keto–enol tautomerism of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one and its 8-substituted derivatives. Analysis of the electronic structure of 8,8-dibromo-4-methyldihydrofuro[2,3-*h*]-coumarin-9-one (fixed keto form) and 9-acetoxy-4-methylangelicin (fixed enol form) allowed to reveal ionization ranges for the corres ponding tautomeric forms. All dihydrofuro[2,3-*h*]coumarin-9-ones studied were found to exist in the gas phase exclusively in the keto form.

Photoelectron (PE) spectra are widely used for studying the electronic structure of molecules. At the same time, tautomeric transformations have rarely been studied by this method [2, 3]. For example, the PE spectra of acetylacetone and 3,3-dimethylacetylacetone have been studied [4]. The spectrum of acetylacetone was assigned relying on MINDO/2 calculations, and bands due to both the keto and the enol forms were revealed. The PE spectra of 2-hydroxypyridine and its *N*- and *O*-methylated analogs have been reported [5, 6]. On the basis of quantum-chemical calculations by the AM1 method the first band in the spectrum of 2-hydroxypyridine has been assigned to the keto form, and the second, to the HOMO enol tautomer. We have studied the PE spectrum of 3-acetyl-4-hydroxycoumarin and found in it bands from both the tautomeric forms [7].

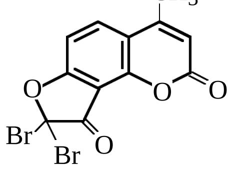
In the present work we performed a PE spectral and quantum-chemical study of the electronic structure and keto–enol tautomerism of dihydrofuro[2,3-*h*]-coumarin-9-ones. These compounds are intresting in that they proved synthons for preparing furocoumarin derivatives which are widely applied in medicine [8]. Earlier we studied [1] the keto–enol tautomerism of dihydrofuro[2,3-*h*]coumarin-9-ones by electronic spectroscopy and semiempirical and nonempirical calculations. It was found that 4-methyldihydrofuro-[2,3-*h*]coumarin-9-one (**Ia**) in solution exists in tautomeric equilibrium with 9-hydroxy-4-methylangelicin (**Ib**).



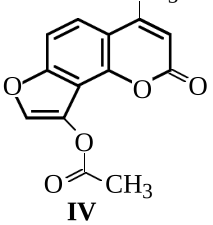
(a) (b)

R = H (**I**), Cl (**II**).

The same tautomeric equilibrium is observed in solution, when an electron-acceptor substituent is present in the 8 position. In a polar solvent (methanol), the enol form is prevailing, whereas in a nonpolar solvent (carbon tetrachloride), the keto form. With electron-donor substituents in the 8 position, no tautomeric transformations are observed. We measured the PE spectra of a series of 4-methyldihydrofuro[2,3-*h*]-coumarin-9-one derivatives: 4-methyldihydrofuro-[2,3-*h*]coumarin-9-one (**Ia**), 8-chloro-4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**IIa**), 8,8-dibromo-4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**III**), and 9-acetoxy-4-methylangelicin (**IV**).



III



IV

Compound **III** is a fixed keto form of compounds

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[1] For communication XIX, see [1].

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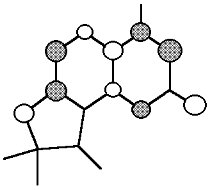
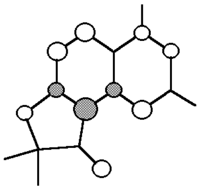
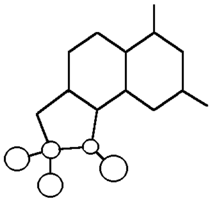


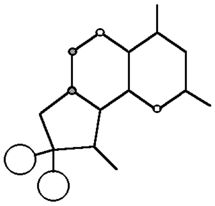
π_9 9.07 eV



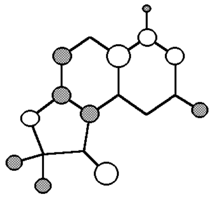
π_8 9.92 eV



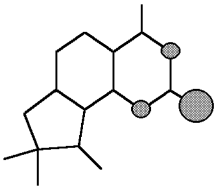
$\sigma_{n(O)+n(Br)}$ 10.46 eV



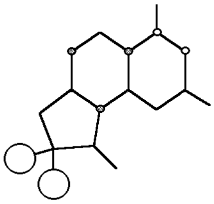
$\sigma_{n(Br)}$ 10.55 eV



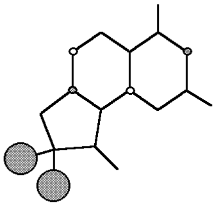
π_7 10.80 eV



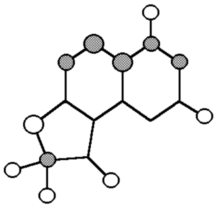
$\sigma_{n(O)}$ 11.02 eV



$\sigma_{n(Br)}$ 11.09 eV



$\sigma_{n(Br)}$ 11.47 eV



π_6 11.82 eV

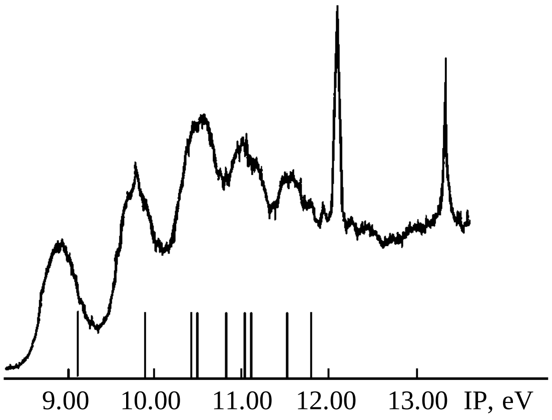


Fig. 1. PE spectrum of compound **III**. Here and in Fig. 2, solid lines show AM1 ionization potentials.

I and **II**, and compound **IV**, a fixed enol form of compounds **I** and **II**. Therefore, analysis of the tautomeric transformations of dihydrofuro[2,3-*h*]coumarin-9-ones we started from the PE spectra of compounds **III** and **IV**.

The PE spectrum of compound **III** (Fig. 1) contains five bands assigned to the orbitals depicted above. Comparison of the results of AM1 quantum-chemical calculations in terms of the Koopmans theorem [9] with the experimental ionization potentials allowed the first band at 8.91 eV to be assigned to a π orbital localized on the coumarin fragment of the molecule. Apparently, the AM1 method overestimates the contribution of the two bromine atoms in HOMO and overestimates by 0.16 eV the first ionization potential. The same relates to the second ionization potential which is overestimated by 0.12 eV. The second ionization band is formed by ionization of a π orbital localized on the benzene ring. The third band at 10.50–10.70 eV has a complicated pattern and is formed by ionization from three orbitals. The first of them, like in **IIa**, is contributed by the dibromofuranone carbonyl oxygen and its neighboring atoms (48%), as well as by the bromine atoms (37%). The following orbital is mostly contributed by the unshared electron pairs of the bromine atoms (90%). The third is a π orbital delocalized over the entire molecule. The fourth band at 11.05–11.20 eV, too, has a complicated pattern and is formed by ionization from two orbitals. The first of them is localized on the *n*(O) orbital of the lactone carbonyl oxygen. The contribution of the latter together with atoms α to the carbonyl group into this molecular orbital is 83%. The second orbital is localized on the unshared electron pairs of the bromine atoms (86%). The fifth band has two peaks, at 11.56 and 11.72 eV. The first of them is associated with an orbital localized by 90% on the unshared electron pairs of the bromine atoms. The second potential relates to a π orbital delocaized over the entire molecule.

The PE spectrum of 9-acetoxy-4-methylangelicin (**IV**) (Fig. 2) is much different from those of **Ia** and **IIa**. The reason is that compound **IV** is a fixed enol form whose furan fragment has a conjugated planar aromatic six-electron π system. The PE spectrum of compound **IV** contains three bands. The first broad band has two peaks at 8.35 and 8.80 eV. The first relates to electron expulsion from the π-type HOMO localized mostly (91%) on the benzofuran fragment. The second potential relates to a π orbital delocalized

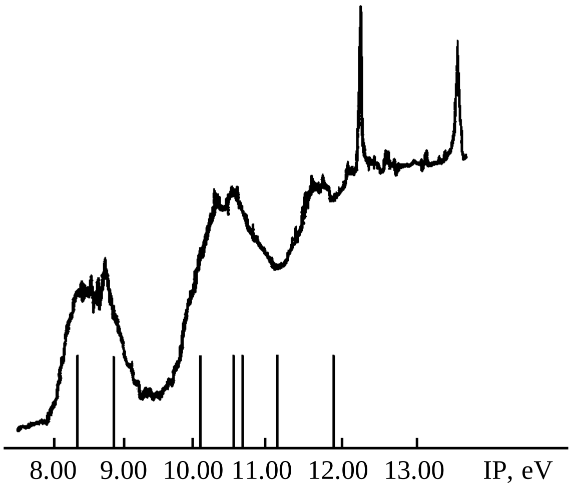


Fig. 2. PE spectrum of compound **IV**.

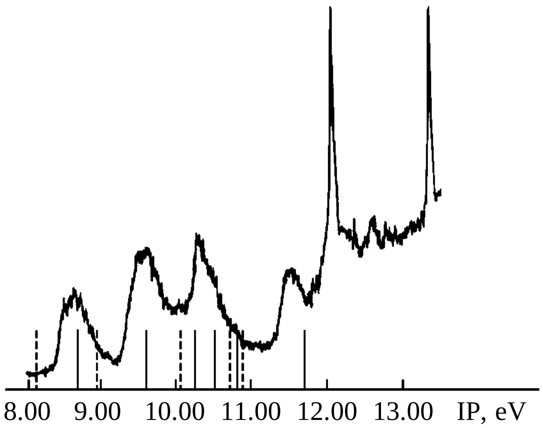
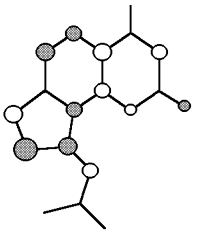
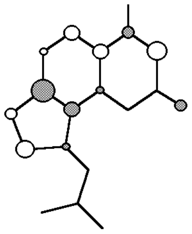


Fig. 3. PE spectrum of compound **I**. Here and in Fig. 4, solid lines show the AM1 ionization potentials of the keto forms, and dashed lines, those of the enol form.

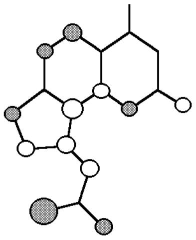
over the entire molecule. The second broad band at 10.15 and 10.40–10.70 eV is formed by ionization from three orbitals. The first of them is a π orbital localized on the benzofuran fragment, including the acetoxy group. The second is localized on the *n*(O) orbital of the unshared electron pair of the lactone carbonyl oxygen. The contribution of the latter and its neighboring atoms into this molecular orbital is 83%. Thus, all the compounds, regardless of substitution in the furan ring, give the *n*(O) ionization band. The third orbital is contributed by the *n*(O) orbital of the acetyl carbonyl oxygen and two neighboring atoms (total contribution 85%).



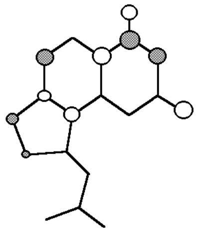
π_{10} 8.35 eV



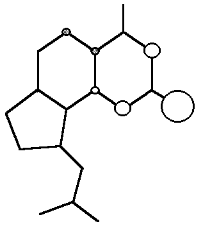
π_9 8.85 eV



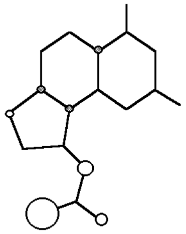
π_8 10.05 eV



π_7 10.59 eV

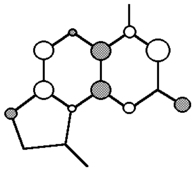


$\sigma_{n(O)}$ 10.68 eV

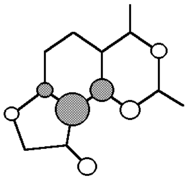


$\sigma_{n(O)}$ 11.08 eV

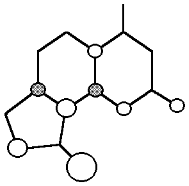
The PE spectrum of compound **I** (Fig. 3) contains four bands in the range 8–12 eV. Comparing the AM1 results with the experimental ionization potentials in terms of the Koopmans theorem we can conclude with confidence that the molecule of 4-methyldihydrofuro[2,3-*h*]coumarin-9-one in the gas phase exists exclusively in the keto form. This conclusin follows from the fact that the spectrum lacks bands due to the enol form both in the range 8.3–8.4 eV and in other parts of the spectrum. Moreover, the calculated ionization potentials of the keto form of compound **I** are nicely consistent with spectral data. The first band in the PE spectrum at 8.75 eV is associated, according to AM1 calculations, with the π-type HOMO delocalized over the coumarin fragment of the molecule. The contribution of the dihydrofuran fragment in HOMO is as low as 2%. Thus, the disturbance of the conjugation in the furan ring results in a considerable (by 0.4 eV) increase in the first ionization potential. The second band at 9.66 eV, too, is associated with ionization of a π orbital. The orbital coefficients shows that this orbital is localized on the benzene ring (79%). The



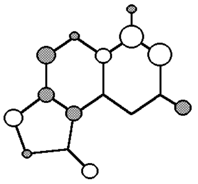
π_8 8.79 eV



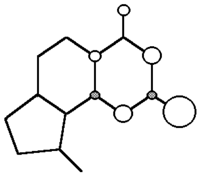
π_7 9.64 eV



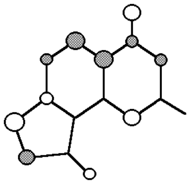
$\sigma_{n(O)}$ 10.38 eV



π_6 10.55 eV



$\sigma_{n(O)}$ 10.81 eV

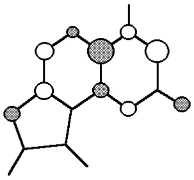


π_5 11.92 eV

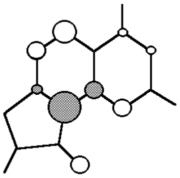
Experimental (IP_{exp}, PE spectroscopy) and AM1 (IP_{calc}) ionization potentials of dihydrofuro[2,3-*h*]coumatin-9-one derivatives (eV)

Comp. no.	IP_{exp}	IP_{calc}
Ia	8.75	8.79
	9.66	9.64
	10.35–10.65	10.38, 10.55, 10.81
	11.74	11.92
Ib		8.33
		8.95
		10.08
		10.71
		10.91
IIa	8.83	8.97
	9.80	9.81
	10.36	10.41
	10.55–10.70	10.74, 10.94
	11.60–11.90	11.59, 12.04
IIb		8.27
		8.99
		10.16
		10.77
		10.99
		11.63
III	8.91	9.07
	9.80	9.92
	10.50–10.70	10.46, 10.55, 10.80
	11.05–11.20	11.02, 11.09
	11.56	11.47
	11.72	11.82
IV	8.35	8.35
	8.80	8.85
	10.15	10.05
	10.40–10.70	10.59, 10.68
	11.60	11.08

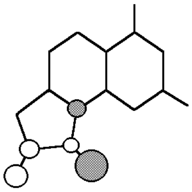
third band at 10.35–10.65 eV has a complicated pattern and is a superposition of three bands. According to the calculation results, the band at 10.38 eV is associated with the *n*(O) orbital of the dibenzofuran carbonyl oxygen and two neighboring atoms (total contribution 81%). The band at 10.55 eV is assignable to a π orbital delocalized over the entire molecule. The following band at 10.81 eV is formed by ionization of the molecular orbital contributed by the *n*(O) orbital localized on the lactone carbonyl oxygen and its neighboring atoms (total contribution 82%). The large difference between the experimental and calculated ionization potentials of this orbital can be explained by the known tendency of semiempirical methods to overestimate the energies of *n*(O) orbitals [10]. The fourth band in the spectrum of compound **I** at 11.74 eV is associated with a π orbital localized on the benzodihydrofuran fragment of the molecule. We also recorded variable-temperature PE spectra of compound **I**. Increased temperature had no effect on the PE spectrum, implying that at high temperatures, too, the keto form is prevailing.



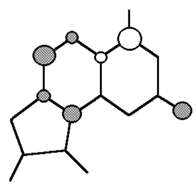
π_8 8.97 eV



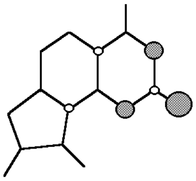
π_7 9.81 eV



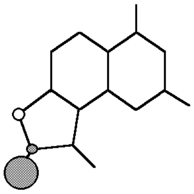
$\sigma_{n(O)+n(Cl)}$ 10.41 eV



π_6 10.74 eV



$\sigma_{n(O)}$ 10.94 eV



$\sigma_{n(Cl)}$ 11.59 eV

The spectrum of 8-chloro-4-methyldihydrofuro[2,3-*h*]coumarin-9-one (**II**) (Fig. 4), like that of **I**, belongs exclusively to one of the tautomeric forms. According to quantum-chemical calculations, this is keto form **IIa**. This conclusion follows from the fact that the spectrum lacks band near 8.3 eV, where, according to the calculations, the ionization band of the HOMO of enol form **IIb** should appear, as well as other bands of this form, in the range 8.8–12 eV (Fig. 4). The PE spectrum of compound **IIa**, too, contains four bands at 8–12 eV. The first two bands are the same in nature as those of compound **Ia**, i.e., the ionization band of HOMO at 8.83 eV is associated with a π orbital localized on the coumarin fragment of the molecule. The second band at 9.80 eV, too, is associated with a π orbital localized mostly on the benzene ring (79%). The reason for such an inconsiderable effect of chlorine substitution is that its position contributes almost nothing into the above two orbitals. The third band at 10.36, 10.55–10.70 eV has a complicated pattern. It is formed by ionization of three orbitals. The peak at 10.36 eV is associated with a σ orbital. This orbital is contributed by 60% by the *n*(O) orbital of the dihydrofuranone carbonyl oxygen and its neighboring atoms and by 20% by one of the unshared electron pairs of the chlorine atom. The band at 10.55–10.70 eV is formed by ionization of two orbitals. The first is a π orbital and the second, the orbital of the unshared electron pair of the lactone carbonyl oxygen and its neighboring atoms. The total contribution of the mentioned atoms into the latter orbital is 83%.

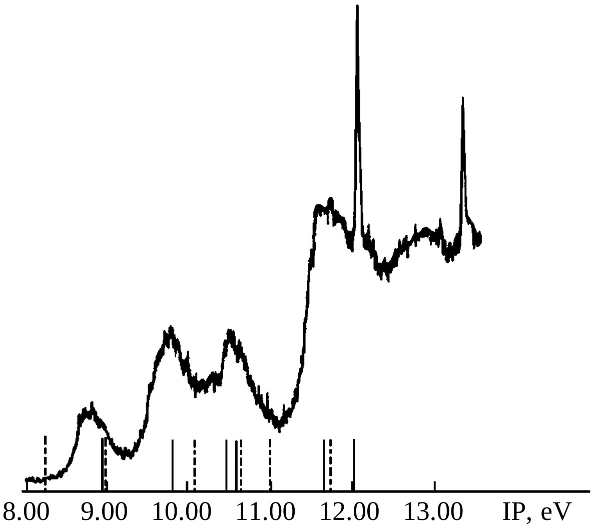


Fig. 4. PE spectrum of compound **II**.

The fourth band at 11.60–11.90 eV, too, has a complicated pattern. The band is formed by ionization of two orbitals. They both are localized on the chlorine atom, the first by 76% and the second, by 66%. On attempted recording the spectrum at a higher temperature compound **II** thermolyzed. Thus, when the temperature in the chamber was raised from 155 to 175°C, the ionization bands slightly decreased in intensity and smoothened, and a strong doubled peak appeared (12.75 and 12.83 eV), corresponding, according to [11], to ionization of the $^2P_{3/2}$ (12.748 eV) and $^2P_{1/2}$ (12.828 eV) orbitals of hydrogen chloride.

Thus, unlike our previous results for solution, in the present PE spectral and AM1 quantum-chemical study we established that in the gas phase compounds **I** and **II** exist exclusively in the keto form and found no evidence for the enol form.

EXPERIMENTAL

The PE spectra were measured on a Perkin–Elmer PS-18 spectrometer and calibrated against the $^2P_{1/2}$ and $^2P_{3/2}$ lines of xenon at 12.13 and 13.43 eV at a residual pressure of 2×10^{-5} mm.

The AM1 quantum-chemical calculations were performed using the MOPAC package [12]. Preliminary geometry optimization was performed by the MM+ molecular mechanics method.

Dihydrofuro[2,3-*h*]coumarin-9-ones were prepared and purified as described in [13].

REFERENCES

1. Safronova, O.B., Kravchenko, D.V., Senchenya, I.N., and Traven', V.F., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 4, pp. 588–595.
2. Ghosh, P.K., *Introduction to Photoelectron Spectroscopy*, New York: Willey, 1983.
3. Traven, V.F., *Frontier Orbitals and Properties of Organic Molecules*, Chichester: Horwood, 1992.
4. Schweing, A., Vermeer, H., and Weidner, U., *Chem. Phys. Lett.*, 1976, vol. 26, pp. 229–234.
5. Guimon, G., *Tetrahedron Lett.*, 1979, vol. 28, p. 2585.
6. Turchaninov, V.K., Danovich, D.K., Ermikov, A.F., and Andriyanenkov, M.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1992, no. 4, pp. 872–878.
7. Traven', V.F., Manaev, A.V., Safronova, O.B., Chibisova, T.A., Lysenko, K.A., and Antipin, M.Yu., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 5, pp. 853–864.
8. Traven, V.F., Kravtchenko, D.V., Chibisova, T.A., Shorshnev, S.V., Eliason, R., and Wakefield, D.H., *Heterocycl. Commun.*, 1996, vol. 2, no. 4, pp. 345–354.
9. Koopmans, T., *Physica*, 1934, vol. 1, pp. 104–113.
10. Traven', V.F., Safronov, A.I., and Chibisova, T.A., *Zh. Obshch. Khim.*, 1991, vol. 61, no. 3, pp. 697–705.
11. Vovna, V.I. and Vilesov, F.I., *Usp. Fotoniki*, 1975, no. 5, pp. 3–149.
12. Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc.*, 1985, vol. 107, no. 13, pp. 3902–3909.
13. Kravtchenko, D.V., Chibisova, T.A., and Traven, V.F., *Heterocycl. Commun.*, 1997, vol. 3, no. 4, pp. 331–338.