AM1 study of photoelectronic spectra
8.* Direct calculations of ionization in the study of conformations of some methoxy-substituted benzenes

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Ionization energies of four model compounds with known conformations, *i.e.*, benzo-1,3-dioxole, 2-methoxyphenol, benzo-1,3-dioxole-5-carbaldehyde (piperonal), and 4-hydroxy-3-methoxybenzaldehyde, have been calculated by the *ab initio* AM1 method, using the formalized scheme of configuration interactions. It has been demonstrated that this method is adequate for the study of photoelectronic spectra of methoxy(hydroxy)-substituted benzenes. The ionization energies of 1,2-dimethoxybenzene, 3,4-dimethoxybenzaldehyde, and 4-hydroxy-3,5-dimethoxybenzaldehyde have been calculated for various orientations of the *o*-methoxy(hydroxy) groups. It has been revealed that three first ionization potentials corresponding to the states with vacancies on the π-MO depend on the torsion angle. It has been established by comparison of calculated and experimental ionization potentials that in gas the compounds with adjacent methoxy groups have one O—Me bond parallel with the plane of the benzene ring, while another group is nearly perpendicular to this plane. Conformations of the heavy-atom framework are planar for gaseous molecules with adjacent methoxy and hydroxy groups.

Key words: molecular conformation, photoelectronic spectroscopy, *ab initio* quantum-chemical calculations, methoxy(hydroxy)-substituted benzenes and benzaldehydes.

Presently, conformations of polysubstituted benzenes containing *o*-methoxy(hydroxy) groups are under intensive experimental and theoretical study,[2—12] because the conformations depend on both the chemical structure of a compound and its phase state. For example, according to the data of photoelectron spectroscopy (PES), 1,2-dimethoxybenzene is nonplanar in the gas phase.[2] Nonempirical calculations in the OST-3GF basis performed with partial optimization of the geometry of this molecule give qualitatively the same result.[2] However, a planar conformation of the heavy-atom framework of 1,2-dimethoxybenzene was obtained for the complete geometric optimization in the same basis.[3]

According to ^{13}C NMR spectroscopy, this molecule is planar in solution.[4,5] On the contrary, the ^{17}O NMR spectra indicate nonplanar equilibrium conformations of *o*-methoxybenzenes.[6,7] The values of dipole moments of 1,2-dimethoxybenzene[8] and parameters of its IR and Raman spectra in solution[9] are consistent with the existence of a mixture of planar and nonplanar conformers.

The planar structure was realized for the overwhelming majority of crystalline *o*-dimethoxybenzenes by XDA.[10] However, it follows from IR and Raman spectra of 1,2-dimethoxybenzene that a mixture of its planar and nonplanar conformers exists in the solid phase.[9] 1,2,3-Trimethoxybenzenes in solution[5,7,8] and in crystalline state[10] are characterized by the planar arrangement of 1- and 3-MeO groups and orthogonal position of the 2-MeO group. However, crystalline compounds containing two MeO fragments separated by the OH group (syringic subunits of lignin) have planar conformations.[11]

Several dimethoxy(methoxyhydroxy)benzenes that are abundant in plant objects have been studied by the *ab initio* quantum-chemical AM1 method and PES.[12] The data obtained indicate the planar structures of the heavy-atom framework of 2-methoxyphenol (guaiacol) and 4-hydroxy-3-methoxybenzaldehyde (vanillin) molecules in gaseous phase. 1,2-Dimethoxybenzene (veratrole) and 3,4-dimethoxybenzaldehyde (veratraldehyde) exist in nonplanar conformations. The data on the forms of trimethoxy(dimethoxyhydroxy)-substituted benzenes in the gas phase are lacking.

The aim of this work is to reinvestigate dimethoxy(hydroxymethoxy)-substituted derivatives and to study the conformational structure of 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) with three torsional degrees of freedom for methoxy(hydroxy) groups. The theoretically established functional correlation of energy gaps between conformationally dependent π-MO

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with the bias angle of methoxy(hydroxy) groups from the benzene ring plane has been previously[12] used for estimation of mean torsion angles. The more strict approach based on direct calculation of ionization potentials is used in the present work.

Calculation procedure

Quantum-chemical calculations of ionization potentials of the compounds studied were performed by the AM1 method,[13] using the formalism of the configuration interaction (CI) scheme. At first all geometric parameters of a neutral molecule, except its torsion angles, were optimized. Then parameters of the ground and excited states of radical cations were calculated by the CI method. In order to fulfill the conditions of vertical transition, the geometry of an ion was assumed identical to that of the molecule.

The first ionization potential was determined as the difference between the heats of formation of a molecule and a radical cation. The subsequent potentials were calculated as the sum of the first ionization potential and relative energies of excited (predominantly, Koopmans') states of a cation. This resulted in the theoretical photoelectronic spectrum of the compound with constant values of torsion angles. For comparison with the experiment, further calculation of spectra was performed, varying these angles with an increment of 15°. Spectra of planar analogs of the molecules studied were obtained with the complete geometry optimization.

Results and Discussion

It has been shown previously[12] that the energies of three higher occupied π-MO of the aforementioned compounds are conformationally dependent. Therefore, it was necessary to elucidate whether the direct calculation of ionization potentials reproduces the mutual arrangement and energies of ionic π-states. It is evident that photoelectronic spectra of compounds with known or fixed conformations should be used for checking the adequacy of the AM1 (CI) method.

For this purpose, planar analogs of the compounds under study were chosen: 2-methoxyphenol (guaiacol) and 4-hydroxy-3-methoxybenzaldehyde (vanillin). In addition, the photoelectronic spectra of benzo-1,3-dioxole and benzo-1,3-dioxole-5-carbaldehyde (piperonal) were calculated. The latter contain the five-membered cycle annelated with the benzene ring and with two oxygen atoms linked through a methylene bridge. They also can be used as model compounds.

Table 1. Ionization potentials

Compound	Method	Ionization potentials of π-states/eV		
2-Methoxyphenol	PES[14]	8.13	9.03	11.12
	AM1 (CI)	8.05	8.91	11.11
4-Hydroxy-3-methoxybenzaldehyde	PES[12]	8.42	9.32	11.14
	PES[15]	8.51	9.43	11.21
	PES[16]	8.49	9.45	11.28
	PES (m)	8.5	9.4	11.2
	AM1 (CI)	8.37	9.15	11.44
Benzo-1,3-dioxole	PES[2]	8.21	9.15	11.09
	AM1 (CI)	8.21	9.17	10.79
Benzo-1,3-dioxole-5-carbaldehyde	PES[15]	8.43	9.53	11.21
	AM1 (CI)	8.53	9.50	11.11

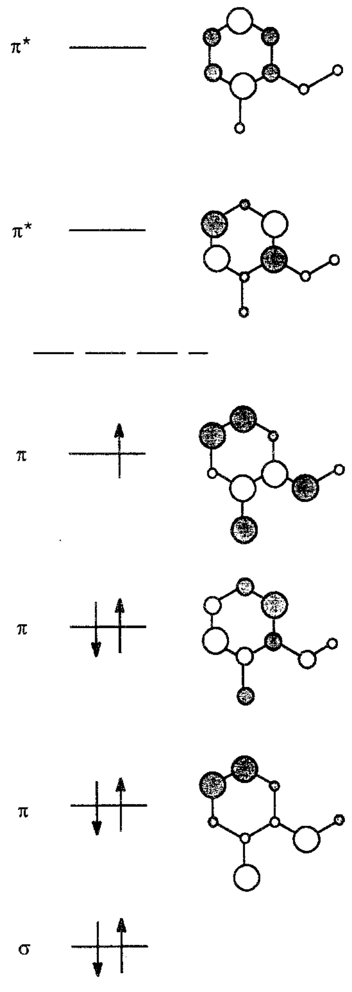

Fig. 1. Scheme of MO of 2-methoxyphenol according to the data of the AM1 method.

It turned out that the ionization potentials (Table 1) calculated by imposition of 100 Koopman and non-Koopman ionic configurations manifested for six MO (two unoccupied, one partially occupied, and three completely populated MO, as shown in Fig. 1) are the closest to the experimental values. Under these conditions, theoretical (EP_i) and experimental (IP_i) values of ionization potentials are related by the correlation: $EP_i = (0.99\pm0.03)IP_i + (0.08\pm0.28)$; $n = 12$, $r = 0.996$. The mean square deviation of the calculated values from the experimental ones is 0.13 eV, which is close to the error of experimental determination of the difference in ionization potentials. These data allow one to consider this

Table 2. Theoretical and experimental ionization potentials of nonplanar conformations of benzene derivatives

Compound	φ_1	φ_2	AM1		AM1 (CI)		PES,
	/deg		MO	$-\varepsilon_i$ /eV	Predominant conformation	EP_i /eV	IP_i /eV
1,2-Dimethoxybenzene[a]	0	90	π_5	8.97	0.98 π_5	8.29	8.17[b], 8.19[c]
			π_4	9.70	0.98 π_4	9.12	8.94[b], 9.15[c]
			π_3	10.74	0.96 π_3	10.11	10.06[b], 10.18[c]
3,4-Dimethoxybenzaldehyde[d]	0	90	π_6	9.31	0.98 π_6	8.63	8.25[e], 8.47[f], 8.38[c]
			π_5	10.05	0.98 π_5	9.47	9.28[e], 9.35[f], 9.18[c]
			n_0	10.66	0.91 n_0; 0.29 π_4	10.25	~9.25[e], —, 9.40[c]
			π_4	11.13	0.92 π_4; 0.27 n_0	10.11	10.36[e], 10.37[f], 10.36[c]
4-Hydroxy-3,5-dimethoxybenzaldehyde[g]	0	0	π_6	9.03	0.98 π_6	8.22	8.28[f]
			π_5	9.31	0.96 π_5	8.69	8.73[f]
			n_0	10.79	0.93 n_0[h]	10.35	9.43[f]
			π_4	11.62	0.86 π_4[h]	10.89	10.58[f]

[a] σ = 0.10 eV. [b] See Ref. 2. [c] See Ref. 16. [d] σ = 0.30 eV. [e] See Ref. 12. [f] See Ref. 15. [g] σ = 0.23 eV. [h] Mixing with single and double excitation in the valent shell of the radical cation.

method adequate and to use it for estimations of ionization potentials of rotation isomers of nonplanar methoxy-substituted benzenes.

1,2-Dimethoxybenzene is the simplest compound of this type for which ionization potentials of all rotation isomers, whose torsion angles (φ_1, φ_2) differ by the specified value, are calculated. The dispersion map with the increment of 15° is built, and the region of angles in which the mean square deviation (σ) of theoretical potentials from experimental ones is minimum and does not exceed 0.13 eV, is determined. This corresponds to the conformational isomer in which one O—Me bond is declined from the benzene ring plane by no more than 15°, and another bond is almost perpendicular to the ring ($\varphi_2 = 90 \pm 15°$).

The structure with $\varphi_1 = 30°$ and $\varphi_2 = 90°$ also satisfies the condition of $\sigma < 0.13$ eV. This result agrees well with that obtained previously[12]: $\varphi_1 \approx 0°$ and $\varphi_2 = 80 \pm 10°$. No region of dispersions comparable with the experimental error was found for 3,4-dimethoxybenzaldehyde: the minimum σ value determined for ionic π-states was 0.30 eV. This value of σ corresponds to the structure in which one O—Me bond is arranged in the plane with the ring, while another bond is declined from it by $\varphi_2 \approx 90°$.

One of the torsion angles of 3,4-dimethoxybenzaldehyde estimated previously[12] is considerably smaller: $\varphi_1 \approx 0°$ and $\varphi_2 = 55 \pm 5°$. The quantitative mismatch of the two approaches is explained by the partially non-monoelectronic nature of the transition to the state with the vacancy on one of the π-MO (Table 2). Therefore, the corresponding ionization potential is less sensitive to the changes in torsion angles than the orbital energy. Thus, the use of the difference in calculated energies of π-MO in estimation of torsion angles results in the qualitatively correct, but not quite quantitatively exact result.

Two dispersion maps are built for 4-hydroxy-3,5-dimethoxybenzaldehyde: one for the structures with the planar C=COH moiety and another for the forms in which the OH bond is perpendicular to the benzene ring plane. In this case, no dispersions close to 0.1 eV were found either. The minimum σ value calculated for the ionic π-states of 4-hydroxy-3,5-dimethoxybenzaldehyde is equal to 0.23 eV and corresponds to the rotation isomer with the planar arrangement of the OH bond and heavy atoms of the both MeO groups. Therefore, the conformational structure of gaseous syringaldehyde and crystalline syringic subunits of lignin[11] are similar.

The bands corresponding to the ionization of MO of the antibonding electron pair of the oxygen atom of the carbonyl group[12,15] are observed in the photoelectronic spectra of 3,4-dimethoxybenzaldehyde and 4-hydroxy-3,5-dimethoxybenzaldehyde (veratraldehyde and syringaldehyde) (see Table 2). The values of these ionization potentials calculated by the AM1 (CI) method do not coincide with the measured values. Most likely, the reason is in the underestimation of the correlation energy in the calculations in the AM1 (CI) approximation. It is likely that the use of the multi-configuration second-order perturbation theory is needed for taking into account correlation corrections in full measure.

Thus, the approach developed made it possible to establish that in free molecules containing *o*-methoxyl groups one O—Me bond lies in the benzene ring plane, while another group is perpendicular to it. Compounds with adjacent methoxyl and hydroxyl groups have planar conformations of the heavy-atom framework in the gaseous phase.

References

1. V. K. Turchaninov and Yu. R. Mirskova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 55 [*Russ. Chem. Bull.*, 1995, **44**, 49 (Engl. Transl.)].
2. G. M. Anderson, P. A. Kollman, L. N. Domelsmith, and K. N. Houk, *J. Am. Chem. Soc.*, 1979, **101**, 2344.
3. H. Konschin, *J. Mol. Struct. (TEOCHEM)*, 1988, **168**, 293.
4. T. Schaefer, R. Sebastian, A. Lemire, and G. H. Penner, *Can. J. Chem.*, 1990, **68**, 1393.
5. A. Makriyannis and S. Fesik, *J. Am. Chem. Soc.*, 1982, **104**, 6462.
6. J. C. Facelli, *THEOCHEM*, 1992, **95**, 307.
7. M. A. Wysocki, P. W. Jardon, G. J. Mains, E. J. Eisenbraun, and D. W. Boykin, *Magn. Reson. Chem.*, 1987, **25**, 331.
8. O. Exner and V. Jehlicka, *Collect. Czech. Chem. Commun.*, 1983, **48**, 1030.
9. V. P. Novikov, F. V. Yarkov, A. F. Solotnov, and O. A. Raevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1047 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 952 (Engl. Transl.)].
10. W. Hummel, K. Huml, and H.-B. Burgi, *Helv. Chim. Acta*, 1988, **71**, 1291.
11. R. Stomberg, M. Hauteville, and K. Lundquist, *Acta Chem. Scand.*, 1988, **B42**, 69.
12. A. I. Vokin, Yu. L. Frolov, S. A. Medvedeva, and S. G. D'yachkova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1757 [*Russ. Chem. Bull.*, 1993, **42**, 1680 (Engl. Transl.)].
13. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
14. L. Klasinc, B. Ruscic, A. Sabljic, and N. Trinajstic, *J. Am. Chem. Soc.*, 1979, **101**, 7477.
15. L. Pasa Tolic, B. Kovac, L. Klasinc, and S. M. Shevchenko, *Croat. Chem. Acta*, 1990, **63**, 37.
16. M. V. Kleimenov, D. A. Sukhov, V. I. Kleimenov, and V. A. Andreev, *Khimiya derevesiny* [*Chemistry of Wood*], 1992, 49 (in Russian).

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