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An ab initio Study of the *p*,π Interaction: IV.[1] Interaction of an Ether Oxygen Atom with a Carbonyl Group

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Abstract—RHF/6-311G(d) calculations were performed for the H_3COCOH molecule with full geometry optimization and at varied angles of rotation of the methoxy group about the C–O bond, with all the other geometric parameters optimized. The molecule can exist in two stable conformations with the dihedral angle $O^1C^1O^2C^2$ of 0.00° and 179.99°. The influence of the rotation angle on the population of the p_y orbital of the carbonyl oxygen atom in compounds with different types of the adjacent bond is essentially similar. The results obtained are inconsistent with the concept of the *p*,π conjugation involving the p_y orbitals of the planar molecular fragment (orbitals whose symmetry axes are perpendicular to this fragment).

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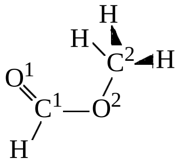
It is commonly believed (see, e.g., [2, 3]) that the lone electron pair of the alkoxyl oxygen atom participates in the *p*,π conjugation with the adjacent π-electron system of the molecule. At the same time, it is known (see, e.g., [4]) that two bonds and two hybridized lone electron pairs of the oxygen atom are oriented toward vertices of a tetrahedron. In this case, any conjugation is impossible, because the orbitals of the lone electron pairs cannot overlap with the π-electron system of the molecule. In the $H_2C{=}CHOCH_3$ and $H_2C{=}CClOCH_3$ molecules, changes in the populations of the p_y orbitals of the olefinic carbon and oxygen atoms (orbitals whose symmetry axes are perpendicular to the molecular plane) and in the fractional charges on these carbon atoms, occurring upon rotation of the methoxy groups about the C–O bonds, cannot be attributed to changes in the extent of the *p*,π interaction between the oxygen lone electron pairs and π electrons of the C=C bonds [1]. Changes in the populations of the p_y orbitals of halogen and carbon atoms in CH_3COX molecules, occurring in going from X = F to X = Cl and Br, also cannot be attributed to changes in the extent of the *p*,π interaction between the lone electron pairs of the halogen atom and π-electron system of the carbonyl group. The binding molecular orbitals involving these atomic p_y orbitals of acetyl halides do not originate from such interaction [5]. In this study we examined by quantum-chemical calculations the structurally related molecule, H_3COCOH (**I**), with the aim to find whether the *p*,π conjugation between the lone electron pairs of alkoxyl oxygen atom and the π-electron system of the carbonyl group will be manifested in compounds of the series ROCOX. The RHF/6-311G(d) calculations of **I** (GAUSSIAN-94W program [6]) were performed at different angles of rotation of the methoxy group about the C^1–O^2 bond (at 15° step), with all the other geometric parameters optimized, and with full optimization of the molecular geometry in states of the lowest energy. The O^1 nucleus was chosen as the origin, the *z* axis coincided with the O^1–C^1 bond, and the *y* axis was perpendicular to the molecular plane.



I

Methods including electron correlation effects will presumably be more adequate as applied to studying the *p*,π conjugation. However, we showed previously [5, 7] that RHF/6-311G(d) and MP2/6-311G(d) calculations of molecules of the $XCH{=}CH_2$ and CH_3COX series give essentially similar results for the populations of the valence orbitals of atoms, for the energies, shapes, and compositions of the molecular orbitals, and for the coefficients at the atomic orbitals forming these molecular orbitals. That is, inclusion of electron correlation does not noticeably

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

alter the parameters in question and hence the conclusions about the p,π interaction. Therefore, in this study we used the RHF/6-311G(d) method. Our calculations showed that the molecule of **I** can exist in two stable states: at the dihedral angle $O^1C^1O^2C^2$ (φ) equal to 0.00° and 179.99° (Fig. 1). At these angles, the molecule of **I** has no imaginary vibration frequencies. The first state lies lower than the second state by 6.01 kcal mol^{-1} and is separated from the second state by a 12.44 kcal mol^{-1} barrier. In both states the molecule is planar.

To examine the p,π ionteraction in **I**, we used the Mulliken population analysis of atomic orbitals, which described the electron distribution in molecules most adequately. This is confirmed, for example, by the consistency between the experimental NQR parameters of a large set of halogen-containing organic and organometallic compounds and the parameters calculated from the Mulliken populations of the least diffuse components of the valence p orbitals of the halogen atoms, found by ab initio calculations (see, e.g., [2]). In the natural bond orbital (NBO) analysis, sometimes used in studies of electronic effects, two lone electron pairs of the ether or ester oxygen atom are assumed to be nonequivalent (see, e.g., [1, 8]), which is inconsistent with the experimental data (molecular geometry, NQR spectra, etc.). Therefore, the NBO method seems to be unsuitable in our case.

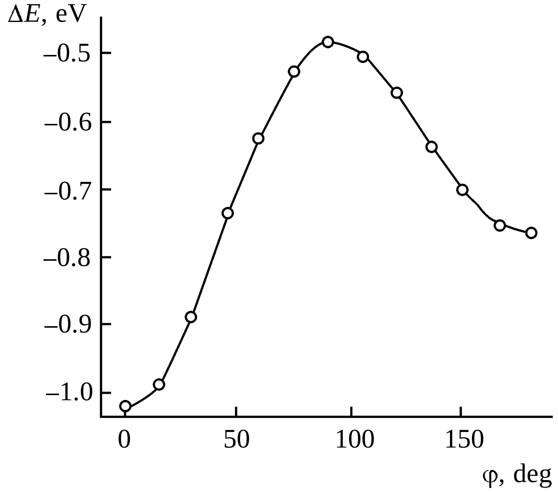

Fig. 1. Total energy of the molecule of **I** ($-E = -6199.0 - \Delta E$, eV) as a function of the dihedral angle $O^1C^1O^2C^2$ (φ).

According to our calculations of **I**, the p_y orbitals of its atoms (orbitals whose symmetry axes are perpendicular to the molecular plane) form three molecular orbitals in each stable state (see table). The molecular orbital with the lowest energy is bonding. As judged from the coefficients at the atomic orbitals, the major contribution to this orbital is made by the p_y orbitals of the oxygen and methoxyl carbon atoms. These molecular orbitals do not originate from the conjugation of the lone electron pair of the methoxyl oxygen atom with π electrons of the carbonyl group. In these stable states, the population of the p_y orbital of the ester oxygen atom is maximal (Fig. 2). It is close to 1.8 e, like the population of the nonhybridized p_x orbital of the carbonyl oxygen atom, occupied by one of its lone electron pairs. The population of the latter orbital is only slightly dependent on φ [1.810 e at φ 90° (maximum), 1.807 e at 0°, and 1.800 e at 180°]. As the angle φ is increased from 0° to 90°, the population of the p_y orbital of the ester oxygen atom sharply decreases, and with a further increase in φ to 180° it increases again. With the variation of φ, the population of this orbital of the ester oxygen atom varies similarly to the $H_2C{=}CHOCH_3$ and $H_2C{=}CCl\cdot OCH_3$ molecules [1]. The range of variation of its population in all the three molecules is also similar. The trends observed are independent of the nature of the double bond (C=O or C=C). Furthermore, the similar trends are observed even when the adjacent bond is single. For example, the RHF/6-311G(d) calculations of the $ClC^1H^2OC^2H^3$ molecule at different angles of rotation (φ) of the methoxy group about the C^1–O bond {previously we calculated this molecule by the RHF/6-31G(d) method} showed that the dependence of the population of the p_y orbital of the ether oxygen atom on φ is essentially similar to that observed in $H_2C{=}CHOCH_3$, $H_2C{=}CClOCH_3$ [1], and $HOCOCH_3$ (Fig. 2). The dependences on φ of the populations of the p_y orbitals of the carbonyl oxygen atom in **I** (atom located in the geminal position relative to ester oxygen) and the related olefinic carbon atoms in the $H_2C{=}CHOCH_3$ and $H_2C{=}CClOCH_3$ molecules [1] are also essentially similar. As φ is

Energies (–E) of particular molecular orbitals involving atomic p_y orbitals and coefficients k at these atomic orbitals in two stable states (φ 0.00° and 179.99°) of the molecule of **I**, according to RHF/6-311G(d) calculations

φ, deg	–E, eV	k			
		O^1	C^1	O^2	C^2
0	18.602	0.262	0.310	0.709	0.437
	15.258	0.606	0.440	0.212	–0.537
	12.735	–0.683	–0.156	0.876	–0.276
179.99	18.737	0.210	0.280	0.690	0.482
	15.611	0.592	0.454	0.301	–0.372
	12.611	–0.695	–0.203	0.871	–0.258

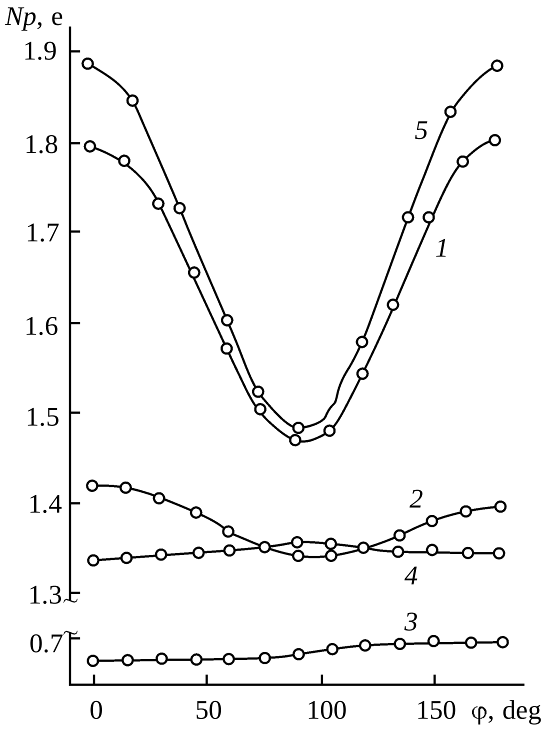

Fig. 2. Populations *Np* of the (*1*–*3*) p_y orbitals of (*1*) O^2, (*2*) O^1, and (*3*) C^1 atoms in **I**, (*4*) p_z orbital of the O^1 atom in **I**, and (*5*) p_y orbital of the O atom in $ClCH_2 \cdot OCH_3$ as functions of the dihedral angle $O^1C^1O^2C^2$ (φ).

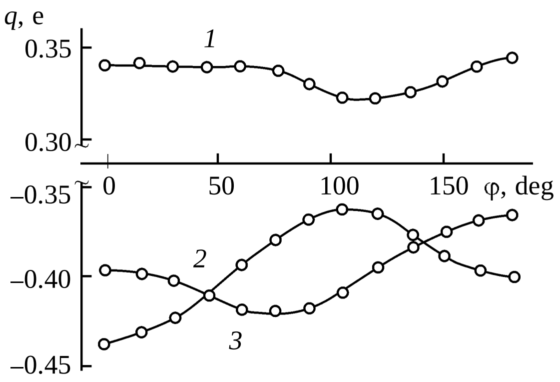

Fig. 3. Fractional charge on the (*1*) C^1, (*2*) O^1, and (*3*) O^2 atoms in **I** as a function of the dihedral angle $O^1C^1O^2C^2$ (φ).

increased from 0° to 90°, the populations of the p_y orbitals of the ester and carbonyl oxygen atoms decrease; at φ 90° and 105°, they pass through a minimum and then increase with further increase in φ. The population of the p_y orbital of the C^1 atom in **I** is virtually independent of φ (Fig. 2). These data are inconsistent with the concept of the *p*,π conjugation involving the p_y orbitals of atoms of the planar fragment of **I**.

The dependence on φ of the population of the p_z orbital of the O^1 atom in **I** (Fig. 2) is simliar to those observed for the C^1 atoms in the $H_2C^1{=}C^2HOCH_3$ and $H_2C^1{=}C^2ClOCH_3$ molecules [1].

The populations of the *p* orbitals of the C and O atoms of the planar fragment of **I** vary within a somewhat narrower range than those of the respective p orbitals of atoms in the $H_2C^1{=}C^2HOCH_3$ and $H_2C^1{=}C^2ClOCH_3$ molecules, occupying the similar positions relative to the ether oxygen atom [1]. This fact is consistent with the lower polarizability of these orbitals in **I** because of the presence of a strongly electronegative carbonyl oxygen atom.

The dependences on φ of the charge on the carbonyl oxygen atom in **I** (Fig. 3) and on the C^1 atoms in the geminal position to the ether oxygen atom in the $H_2C^1{=}C^2HOCH_3$ and $H_2C^1{=}C^2ClOCH_3$ molecules [1] are similar. The fractional negative charge on this atom in **I** is minimal at φ ~105°, when one of the lone electron pairs of the ester oxygen atom lies in the molecular plane in the *cis* position relative to the carbonyl oxygen atom. At this φ, the fractional positive charge on the carbonyl carbon atom is also minimal. The fractional charges on the carbonyl carbon and oxygen atoms vary with φ in opposite directions. These variations are caused by polarization of the O^1–C^1 bond with the variation of φ. The dependences on φ of the charges on the carbon atoms adjacent to the ester (ether) oxygen atoms in the molecules of **I** and $H_2C^1{=}C^2HOCH_3$ are also essentially similar. The fractional negative charge on the ester oxygen atom in **I** is maximal at φ ~75°, when one of its lone electron pairs lies in the molecular plane in the *trans* position to the carbonyl oxygen atom.

Similar dependences on φ of the populations of the valence *p* orbitals of atoms in the planar fragments of molecules of **I**, $H_2C^1{=}C^2HOCH_3$, and $H_2C^1{=}C^2Cl \cdot OCH_3$, and also of the fractional charges on these atoms suggest essentially similar pattern of atomic interactions in these molecules.

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