ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 966–969. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.P. Feshin, E.V. Feshina, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 6, pp. 1010–1013.

An ab initio Study of the *p*,π Interaction: III.[1] Interaction of an Ether Oxygen Atom with a Double Bond

V. P. Feshin and E. V. Feshina

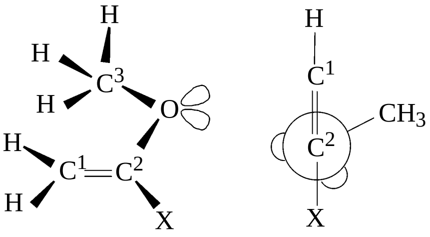
*Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences,
ul. Lenina 13, Perm, 614990 Russia*

Received May 12, 2005

Abstract—RHF/6-311G(d) calculations were performed for the $H_2C=CHOCH_3$ and $H_2C=CClOCH_3$ molecules 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 first molecule has one energy minimum and one transition state, and the second molecule, two minima. 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 conjugation between the lone electron pairs of the oxygen atoms and π electrons of the C=C bonds.

DOI: 10.1134/S107036320606020X

According to the existing views, the ether oxygen atom can participate in the *p*,π conjugation with the π-electron system of the adjacent double bond (see, e.g., [2, 3]). At the same time, this atom has a tetrahedral structure (see, e.g., [4]), and the orientation of two its lone electron pairs is quite unfavorable for conjugation (see scheme):



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

Such an orientation does not allow appreciable overlap between the orbitals of the oxygen lone electron pairs and π orbitals of the olefinic carbon atoms. The results of RHF/6-31G(d) calculations of the $ClCH_2OCH_3$ molecule at various angles of rotation of the methoxy group about the C–O bond and other geometric parameters of the molecule optimized [5] are consistent with the tetrahedral structure of the ether oxygen atom and the specific effect of its lone electron pairs on the electon distribution in the molecule. According to these calculations, in the most energetically favorable conformation (ClCOC dihedral angle 73.28°) one of the oxygen lone electron pairs is in the *trans* position relative to the C–Cl bond and polarizes this bond directly through the field. The angle between the two lone electron pairs of the ether oxygen atom is 146.57° [5]. To examine the possibility of their participation in the *p*,π conjugation with the π-electron system of the adjacent double bond, we performed RHF/6-311G(d) calculations of the $H_2C=CHOCH_3$ (**I**) and $H_2C=CClOCH3$ (**II**) molecules (see scheme) with full optimization of their geometries, and also at different fixed angles of rotation (φ) of the methoxy group about the C^2–O bond (at 15° step) and other geometric parameters optimized. Molecule **II** was studied for the comparison with $ClCH_2OCH_3$ [5]. In the calculation of **I**, the C^1 nucleus was chosen as the origin, and the z axis was oriented along the C^1–C^2 bond; in the calculation of **II**, the Cl nucleus was chosen as the origin, and the *z* axis coincided with the Cl–C^2 bond. The calculations were performed with the GAUSSIAN-94W program [6].

Presumably, calculations including electron correlation effects will furnish the most reliable data on the capability of the oxygen lone electron pairs to participate in the *p*,π conjugation with the π-electron system of the adjacent double bond. However, the RHF/6-311G(d) and MP2/6-311G(d) calculations of $XCH=CH_2$ [7] and $XCOCH_3$ [1] molecules showed that consideration of the electron correlation did not principally affect the estimated electron distribution in the molecules. The natural bond orbital (NBO) analysis may also be useful for studying the *p*,π conjugation. However, in this method it is assumed that

---

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

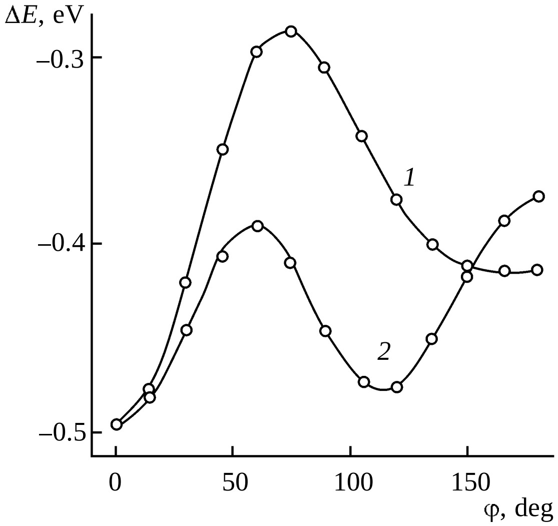


Fig. 1. Total energy of the molecules of (*1*) **I** ($E = 5223.0 + \Delta E$, eV) and (*2*) **II** ($E = 17711.0 + \Delta E$, eV) as a function of the dihedral angle $C^1C^2OC^3$ (φ).

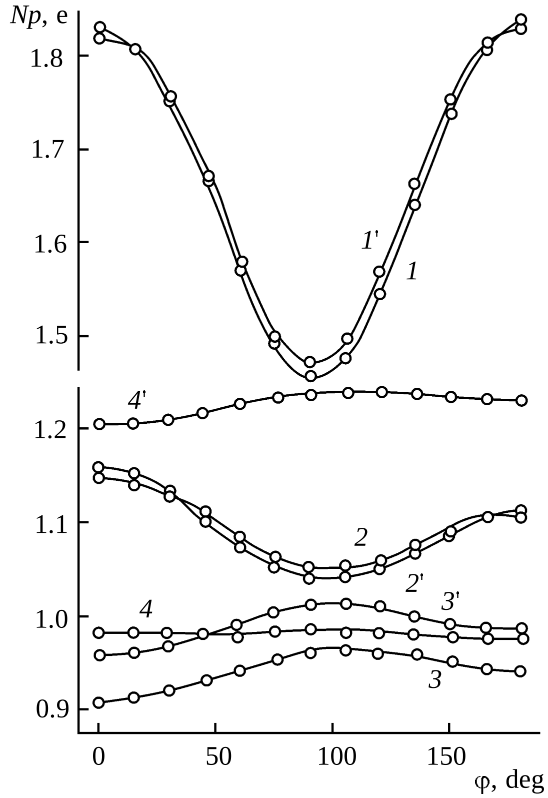


Fig. 2. Variation of the populations (*Np*) of the p_y orbitals of the (*1, 1'*) O, (*2, 2'*) C^1, and (*3, 3'*) C^2 atoms in the molecules of (*1–3*) **I** and (*1'–3'*) **II**, and of the p_z orbitals of the (*4*) C^1 atom in **I** and (*4'*) Cl atom in **II** with the dihedral anhgle $C^1C^2OC^3$ (φ).

the two lone electron pairs of the ether oxygen atom are nonequivalent: One of them occupies a hybrid orbital, and the other, a pure *p* orbital (see, e.g., [8]). According to our calculations using NBO analysis, in **I** one of the lone electron pairs has 38.13% s character, and the other occupies a pure *p* orbital. However, experimental data on the geometries of oxygen-containing molecules and the results of optimizing the geometry of **I** show that in these molecules two lone electron pairs of the ether oxygen atom are equivalent. Therefore, it is not appropriate to apply NBO analysis to studying p,π conjugation.

According to the calculations, the molecule of **I** has a global energy minimum at the dihedral angle φ ($C^1C^2OC^3$) –0.05° (Fig. 1), i.e., when both lone electron pairs of the oxygen atom are oriented virtually symmetrically toward different sides of the molecular plane in the *trans* position to the C=C bond. At φ ~75°, when one of the lone electron pairs lies in the molecular plane in the *trans* position to the C=C bond, the molecular energy is maximal. The angle φ ~105°, when the other lone electron pair of the oxygen atom lies in the molecular plane but in the *cis* position relative to the C=C bond, does not correspond to any characteristic point in the energy curve. At φ 179.96°, when both lone electron pairs of the oxygen atom are oriented toward different sides of the molecular plane in the *cis* position relative to the C=C bond, there is a stationary point corresponding to a transition state (at this angle, there is one imaginary vibration frequency). The energy difference between the transition state and energy maximum is 2.91 kcal mol^{-1}. The molecule of **II** has two energy minima: at φ –0.01° (dihedral angle ClC^2OC^3 179.99°) and φ 113.09° (dihedral angle ClC^2OC^3 –66.91°). In these points, there are no imaginary vibration frequencies. The height of the barrier separating these minima is 2.52 kcal mol^{-1}. The second minimum lies higher than the first minimum by 0.51 kcal mol^{-1}. The conformation with φ 180.00° (dihedral angle ClC^2OC^3 0.00°) is the least energetically favorable. Its energy is 2.38 kcal mol^{-1} higher than the energy of the second minimum (Fig. 1). The dihedral angle ClC^2OC^3 (see above) corresponding to the second minimum in **II** is close to the ClCOC angle in the molecule of $ClCH_2OCH_3$ in its energetically most favorable conformation [5]. As in the latter molecule, in the molecule of **II** in this conformation the population of the valence p_z orbital of the chlorine atom (Fig. 2), the fractional negative charge on the Cl atom (–0.117 e), and the C–Cl bond length are maximal. The molecular geometries of **I** and **II** at the two angles corresponding to the energy minima are given in the table.

Bond lengths (Å) and bond angles (deg) in the molecules of **I** and **II** at two values of dihedral angles φ corresponding to the potential wells

Bond, angle	**I**		**II**	
	φ –0.015°	φ 179.96°	φ –0.01°	φ 113.09°
$C^1–C^2$	1.320	1.316	1.317	1.311
$C^2–O$	1.338	1.344	1.325	1.330
$O–C^3$	1.398	1.398	1.405	1.412
$Cl–C^2$	–	–	1.737	1.758
C^1C^2O	128.67	123.01	129.25	124.29
C^2OC^3	118.41	116.49	118.23	117.41
HC^1H	117.22	118.58	118.02	119.28
HC^2O	110.07	115.48	–	–
ClC^2O	–	–	109.75	114.73

The dependences of the populations of the p_y orbitals of the respective atoms C^1, C^2, and O in the molecules of **I** and **II** on the angle of rotation of the methoxy group about the $C^2–O$ bond are similar. For the C^1 atoms, they virtually coincide, as well as for the O atoms (Fig. 2). The Cl atom decreases the population of the p_y orbital of the C^2 atom in **II**, compared to **I**, by approximately the same value at any φ. If the oxygen lone electron pairs were involved in the p,π conjugation with the π electrons of the C atoms, the changes in the populations of the p_y orbitals of the C^1, C^2, and O atoms should be dependent on the orientation of the oxygen lone electron pairs relative to the double bond. However, such a dependence is lacking. The populations of the p_y orbitals of the oxygen atoms of both molecules appreciably decrease as φ is increased from 0° to 90° and then increase as φ is further increased to 180°. The populations of the p_y orbitals of the C^1 atoms also decrease as φ is increased to 105° (angle at which one of the oxygen lone electron pairs is in the molecular plane in the cis position relative to the C=C bond) and then decrease. On the contrary, the populations of the p_y orbitals of the C^2 atoms first slightly increase as φ is increased to 105° and then decrease. In each molecule, the populations of the p_y orbitals of the C^1 and C^2 atoms vary in opposite directions and to a considerably lesser extent than do the populations of the p_y orbitals of the O atoms (Fig. 2). Our results show that changes in the populations of the valence p_y orbitals of the C^1, C^2, and O atoms, occurring upon variation of φ, cannot be attributed to the participation of these orbitals in the p,π conjugation. The populations of the p_y orbitals of the O atoms essentially depend on the position of the methyl groups relative to the C=C bonds. The population of the p_z orbital of the C^1 atom in **I** is virtually independent of φ, and that of the chlorine p_z orbital in **II** varies insignificantly, increasing with an increase in φ, passing through a maximum at φ 113° (ClC^2OC^3 angle −66.91°), and then slightly decreasing. Similar trend is observed with the population of the lest diffuse component of the valence p_z orbital of the Cl atom in $ClCH_2OCH_3$ [5].

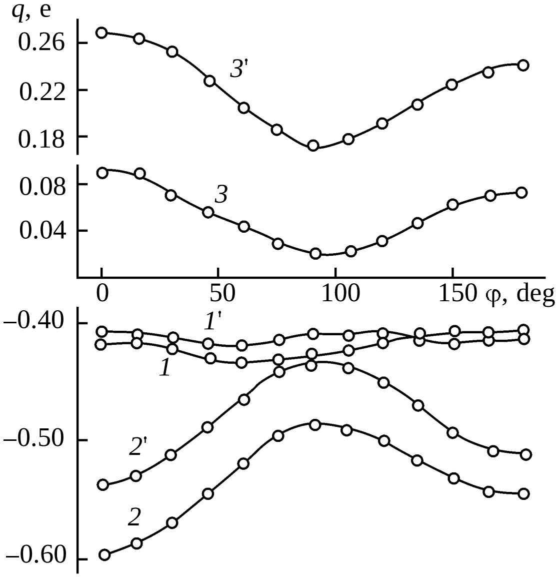


Fig. 3. Fractional charge *q* on the (*1, 1'*) O, (*2, 2'*) C^1, and (*3, 3'*) C^2 atoms as a function of the dihedral angle $C^1C^2OC^3$ (φ) in the molecules of (*1–3*) **I** and (*1'–3'*) **II**.

On the contrary, the charges on the C^1 and C^2 atoms vary with φ to an appreciably greater extent than the charges on the O atoms in both molecules. A slight increase in the fractional negative charges on the O atoms with an increase in φ to ~70° is accompanied by a noticeable decrease in the negative charges on the C^1 atoms and by a decrease in the fractional positive charges on the C^2 atoms (up to φ 90°). With a further increase in φ, the charges on these atoms vary in the opposite directions, except for the O atom in **II**, whose charge varies insignificantly, showing no definite trend. The fractional negative charges on the C^1 atoms and the positive charges on the C^2 atoms of both molecules vary in the opposite directions (Fig. 3). These results are inconsistent with the concept of the p,π conjugation between the lone electron pair of the O atom and the π-electron system of the adjacent double bond in the molecules of **I** and **II**. Variations in the charges on the C^1 and C^2 atoms in both molecules at varying φ are associated essentially with the position of the methyl groups, rather than with the orientation of the oxygen lone electron pairs relative to the C=C bonds.

REFERENCES

1. Feshin, V.P., Feshina, E.V., and Zhizhina, L.I., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 5, p. 776.
2. Dneprovskii, A.S. and Temnikova, T.I., *Teoreticheskie osnovy organicheskoi khimii* (Theoretical Principles of Organic Chemistry), Leningrad: Khimiya, 1991.
3. Feshin, V.P., *Elektronnye effekty v organicheskikh i elementoorganicheskikh molekulakh* (Electronic Effects in Organic and Organometallic Molecules), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1997.
4. Yanovskaya, L.A., *Sovremennye teoreticheskie osnovy organicheskoi khimii* (Modern Theoretical Principles of Organic Chemistry), Moscow: Khimiya, 1978.
5. Feshin, V.P. and Feshina, E.V., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 11, p. 1895.
6. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Gill, P.M.W., Johnson, B.G., Robb, M.A., Cheeseman, J.R., Keith, T., Petersson, G.A., Montgomery, J.A., Raghavachari, K., Al-Laham, M.A., Zakrzewski, V.G., Ortiz, J.V., Foresman, J.B., Cioslowski, J., Stefanov, B.B., Nanayakkara, A., Challacombe, M., Peng, C.Y., Ayala, P.Y., Chen, W., Wong, M.W., Andres, J.L., Replogle, E.S., Gomperts, R., Martin, R.L., Fox, D.J., Binkley, J.S., Defrees, D.J., Baker, J., Stewart, J.P., Head-Gordon, M., Gonzalez, C., and Pople, J.A., *GAUSSIAN-94, Rev. E.3,* Pittsburgh: Gaussian, 1995.
7. Feshin, V.P., Feshina, E.V., and Zhizhina, L.I., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 5, p. 770.
8. Bzhezovskii, V.M., Kapustin, E.G., Chura, M.B., and Shermolovich, Yu.G., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 11, p. 1823.