Absence of p,π-conjugation in the Cl₂C=CHOMe molecule from data of *ab initio* calculations

V. P. Feshin* and M. Yu. Kon'shin

*Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences,
13 ul. Lenina, 614000 Perm', Russian Federation.
Fax: +7 (342 2) 325 018*

ab initio Calculation of the Cl_2C=CHOMe molecule has been carried out with geometrical optimization in the split valence basis set in the RHF/6-31G*//RHF/6-31G* approximation. An analysis of the populations of the p-orbitals of the Cl atoms implies the absence of p,π-conjugation between the unshared electron pairs of these atoms and the π-bond. The asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei, calculated from the 3p-orbital populations of the Cl atoms, practically coincide with the experimental values.

Key words: *ab initio* calculations, Cl_2C=CHOMe, p,π-conjugation, populations of p-orbitals.

Unusual geometry (determined experimentally or by quantum-chemical calculations) and reactivity of a molecule, as well as the composition of individual MO's, NMR data, *etc.*, are often regarded as evidence of the existence of p,π-conjugation between the unshared electron pair of a heteroatom and the π-electrons of the neighboring double bond or aromatic ring in this molecule (see, for example, Refs. 1—5). However, all these properties do not directly characterize p,π-conjugation and can neither prove nor disprove its existence. A promising direction in these studies is joint analysis of NQR data (especially for the nuclei of halogen atoms) and results of the corresponding quantum-chemical calculations. This provides a better understanding of experimental facts and, *vice versa*, makes it possible to use these facts for checking the reliability of quantum-chemical calculation schemes.

The most direct experimental information concerning p,π-conjugation is provided by the asymmetry parameters (η) of the electric field gradient (EFG) at the nucleus of an indicator atom (for example, Cl); these parameters characterize the deviation of the electron distribution from the axially symmetrical distribution (see, for example, Refs. 6—8). The η values of the *trans*-chlorine atoms in the compounds Cl_2C=CHOR are equal or close to zero.[7-10] This unambiguously indicates that the electron distribution around these Cl atoms is nearly axially symmetrical, *i.e.*, their p_x- and p_y-orbitals (the Z axis is directed along the C—Cl bond) are virtually equally populated. In conformity with the concepts of p,π-conjugation, one of the above-mentioned orbitals should participate in the conjugation, while the other one, lying in the plane of the molecule, is incapable of this participation.

Thus, the most direct experimental data indicate that no p,π-conjugation exists in the Cl—C=C (or X—C=C) group. In agreement with this conclusion are the results of quantum-chemical calculations (in the MNDO approximation) for XCH=CH_2 molecules with variable C—X bond length and also for XCH=CH_2—HF and $[XCH$=$CH_2]^+$—HF systems with the distance between their components being optimized.[10,11]

Unfortunately, the asymmetry parameters of the EFG at the ^{35}Cl nuclei found by semiempirical quantum-chemical methods are always much lower than the experimental values and do not correlate with them in any manner (see, for example, Refs. 10—12). This casts some doubt upon the validity of the semiempirical evaluation of the populations of the p-orbitals of atoms in molecules in the studies of p,π-conjugation. Nonempirical quantum-chemical approaches that take into account the variations of the atomic orbitals under the action of various factors are more promising for these purposes. Ethylene derivatives have been studied by these methods many times, however, in our opinion, the conclusions drawn from these studies regarding the existence of the p,π-conjugation are unconvincing (see above).

We carried out *ab initio* calculations for the molecule
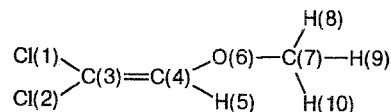
and compared the results with those obtained previously[7-9] by ^{35}Cl NQR. We used the "Gaussian-92 for Windows" (Gaussian, Inc.)[13] program and optimization of the molecular geometry by the RHF/6-31G*//RHF/6-31G* method, according to

Table 1. Lengths of chemical bonds (d), angles between them (α), and torsional angles (β) in the $Cl_2C=CHOMe$ molecule

Bond	d/Å	Angle	α/deg	Angle	β/deg
Cl(1)—C(3)	1.721	Cl(1)C(3)C(4)	123.2	Cl(1)C(3)C(4)O(6)	−1.5
Cl(2)—C(3)	1.730	Cl(2)C(3)C(4)	120.8	Cl(2)C(3)C(4)O(6)	177.8
C(3)—C(4)	1.318	C(3)C(4)H(5)	119.7	Cl(2)C(3)C(4)H(5)	−0.8
C(4)—H(5)	1.076	C(3)C(4)O(6)	122.8	C(3)C(4)O(6)C(7)	162.5
C(4)—O(6)	1.333	C(4)O(6)C(7)	116.3	C(4)O(6)C(7)H(8)	58.1
O(6)—C(7)	1.407	O(6)C(7)H(8)	110.9	C(4)O(6)C(7)H(9)	177.0
C(7)—H(8)	1.085	O(6)C(7)H(9)	106.5	C(4)O(6)C(7)H(10)	296.0
C(7)—H(9)	1.079	O(6)C(7)H(10)	111.0		
C(7)—H(10)	1.084				

which each valence AO is represented as a combination of two basis orbitals of different sizes. Besides, the basis set is supplemented by the polarization functions. This makes it possible to take into account the variations of the AO of heavy atoms under the action of various factors.

The optimized geometrical parameters of the $Cl_2C=CHOMe$ molecule are presented in Table 1, and Mulliken charges of its atoms are given below.

Atom	Cl(1)	Cl(2)	C(3)	C(4)	H(5)
q	0.05	0.03	−0.33	0.26	0.22

Atom	O(6)	C(7)	H(8)	H(9)	H(10)
q	−0.58	−0.19	0.16	0.02	0.17

The p-orbital populations of the Cl atoms are listed in Table 2. Along with the overall populations, we also present the populations of both constituents of the valence p-AO of Cl atoms in the split basis set, namely, the less diffuse (3p) and the more diffuse (4p) constituent.

Results and Discussion

According to the calculation, the skeleton of the $Cl_2C=CHOMe$ molecule is almost planar. The C atom of the methyl group deviates from this plane by ~17°, *i.e.*, the C(3)C(4)O(6)C(7) dihedral angle is 162.5° (see Table 1). This geometry of the molecule is favorable for the Cl atoms to be involved in p,π-conjugation: their p_x-orbitals are virtually perpendicular to the plane of the $Cl_2C=CHO$ moiety. The lengths of both C—Cl bonds are nearly identical (the C—Cl *cis*-bond is only slightly shorter than the *trans*-bond). The orbitals of the unshared electron pairs of the O atom are not prone to participate in p,π-conjugation, since they are directed away from the π-bond. The total energy of this molecule $E = -1109.7026$ eV.

The charges on both Cl atoms are positive and close to zero (see above). In view of this fact, together with the positive charge on the H(5) atom and the substantial negative charge on the O atom, one might expect that the Cl(2)C(3)C(4) angle would be larger than the

Table 2. Electron populations of the p-orbitals (N), their sum (Σ), and calculated (η_{calc}) and experimental (η_{exp})[8] asymmetry parameters of the EFG at the ^{35}Cl nuclei in the $Cl_2C=CHOMe$ molecule

Atom	Orbital	N_x	N_y	N_z	η_{calc}(%)	η_{exp}(%)
Cl(1)	3p	1.311	1.329	0.917	6.6	7.3±1.5
	4p	0.645	0.626	0.172		
	Σ	1.956	1.955	1.089		
Cl(2)	3p	1.318	1.320	0.920	1.1	0.0±0.5
	4p	0.647	0.636	0.177		
	Σ	1.965	1.956	1.097		

Cl(1)C(3)C(4) angle. However, this does not agree with the results of calculations. Of notice is the appreciable difference between the charges on the C(3) and C(4) atoms: the carbon atom bound to the Cl atoms bears a large negative charge, while that attached to the O atom bears a substantial positive charge. This may be caused by both the higher electron-withdrawing properties of the O atom compared to the Cl atoms and polarization of the C=C bond under the action of the negatively charged O atom. Similar polarization (through the action of the charge of the neighboring atom) can be observed in any nonlinear triatomic group, in particular, in Cl—C—O (see, for example, Refs. 9 and 14).

Although in the $Cl_2C=CHOMe$ molecule, favorable conditions exist for the participation of both Cl atoms in p,π-conjugation with the π-electron system, no conjugation is manifested in the populations of the p-orbitals of these Cl atoms. In studying the p,π-conjugation, the populations of the less diffuse 3p-orbitals of the *trans*-Cl atom are the most interesting. This atom is less affected by the substituents at the C(4) atom (direct through-space effect) than the *cis*-Cl atom. According to the calculations, the populations of the $3p_x$- and $3p_y$-orbitals of the *trans*-Cl atom are virtually identical. If this atom were involved in the p,π-conjugation, its p_x-orbital would be less populated than the p_y-orbital. However, the population of the more diffuse p_x-orbital perpendicular to the plane of the molecule is even somewhat

higher than that of the p_y-orbital lying in this plane. Accordingly, the overall population of the $3p_x$- and $4p_x$-orbitals of the *trans*-Cl atom in the Cl₂C=CHOMe molecule is somewhat higher than that of the $3p_y$- and $4p_y$-orbitals.

The less diffuse valence p_x-orbital of the *cis*-Cl atom in the split basis set is substantially less populated than the p_y-orbital. Conversely, the population of the more diffuse $4p_x$-orbital is larger than that of the $4p_y$-orbital. The overall populations of the valence p_x- and p_y-AO of the *cis*-Cl atom are identical. The redistribution of the electron density between the 3p- and 4p-constituents of the p_x- and p_y-AO of the *cis*-Cl atom is apparently due to the fact that this Cl atom is subjected to direct through-space effect of the OMe group and primarily its O atom. The fact that the overall populations of the valence p_x- and p_y-AO of both Cl atoms are nearly identical does not agree with the assumption that one of them is involved in the p,π-conjugation with the π-bond in the Cl₂C=CHOMe molecule.

The results of the quantum-chemical calculation of the Cl₂C=CHOMe molecule can be juxtaposed with experimental NQR data. In the Cl₂C=CHOMe molecule, as in the case of other Cl₂C=CHOR molecules, the asymmetry parameter of the EFG at the ³⁵Cl nucleus is equal to zero for the *trans*-Cl atom and is noticeably greater than zero for the *cis*-Cl atom.[7—10] The calculated η values almost coincide with the experimental values (see Table 2). These parameters were calculated using the p-orbital populations of the Cl atoms, in conformity with the Townes and Daily theory (see, for example, Ref. 12). Only the populations of the 3p-orbitals of the Cl atoms were taken into account, since the 4p-orbitals contribute slightly to the EFG at the site where the nucleus of the Cl atom is located, because they are much less populated and more diffuse than the 3p-orbitals.

The EFG is known (see, for example, Ref. 15) to be inversely proportional to the cubed distances to the electrons creating it. The η values calculated from the sum of the populations of the 3p- and 4p-orbitals of the Cl atoms without regard for their sizes are close to zero, like those calculated in the MNDO approximation in the valence sp-basis set with optimization of the molecule geometry (Table 3). Thus, the p-orbital populations of the Cl atoms in the Cl₂C=CHOMe molecule found by *ab initio* and MNDO calculations indicate that there is no p,π-conjugation involving these atoms in the molecule.

Table 3. Electron populations (N) of the 3p-AO in the Cl₂C=CHOMe molecule (MNDO calculations) and the corresponding asymmetry parameters (η) of the EFG at the ³⁵Cl nuclei

Atom	N_x	N_y	N_z	η(%)
Cl(1)	1.976	1.984	1.107	1.41
Cl(2)	1.979	1.987	1.130	1.37

Previously we believed that the lower ³⁵Cl NQR frequencies of the *cis*-Cl atoms compared to those of the *trans*-atoms in compounds ClCH=CHOR and Cl₂C=CHOR are due to the polarization of the *cis*-C—Cl bond due to a direct through-space effect of the negatively charged oxygen atom.[7,8,16,17] Similar polarization (under the action of the O atom) of the orbitals of the unshared electron pairs of the *cis*-Cl atom accounts for its η value differing from zero (see, for example, Refs. 7 and 8). However, an evaluation of the populations of the p-AO of the Cl atoms in these compounds from their experimental ³⁵Cl NQR frequencies and asymmetry parameters of the EFG at the ³⁵Cl nuclei implies that the decrease in the ³⁵Cl NQR frequency and the increase in the η value of the *cis*-Cl atom (compared to the *trans*-atom) are mostly due to the deviation of its electron distribution from axial symmetry.[12] In fact, the ³⁵Cl NQR frequency of the *cis*-Cl atom in Cl₂C=CHOMe is lower than that of the *trans*-atom, whereas the population of the p_z-AO of the latter calculated from experimental data (at $N_y = 2$) is much higher ($N_z = 1.32$ against $N_z = 1.31$).

A similar difference between the populations of the p_z-AO of the *cis*- and *trans*-Cl atoms in the Cl₂C=CHOMe molecule has been obtained by MNDO (see Table 3) and *ab initio* (see Table 2) calculations, however, in the latter case, the difference is smaller than that evaluated from experimental data. Nevertheless, *ab initio* calculations confirm that the major contribution to the decrease in the ³⁵Cl NQR frequency of the *cis*-Cl atom in the Cl₂C=CHOR molecules (compared to the *trans*-atom) is made by the appreciable asymmetry of its electron distribution caused by polarization of the orbitals of its unshared electron pairs due to direct through-space effect of the negatively charged O atom.

Thus, the populations of the p-orbitals of the Cl atoms in the Cl₂C=CHOMe molecule calculated *ab initio* are in agreement with the conclusion that there is no p,π-conjugation between their unshared electron pairs and the π-bond, which was drawn based on the experimental asymmetry parameters of the EFG at the ³⁵Cl nuclei in compounds Cl₂C=CHOR. The asymmetry parameters calculated using the populations of less diffuse constituents of the p-AO of the Cl atoms virtually coincide with the experimental values. The *ab initio* calculations confirm that the lower ³⁵Cl NQR frequencies of the *cis*-Cl atoms (compared to those of the *trans*-atoms) are caused by the asymmetry of the electron distribution around their nuclei in the Cl₂C=CHOR molecules.

References

1. A. S. Dneprovskii and T. I. Temnikova, *Teoreticheskie osnovy organicheskoi khimii* [*Theoretical Fundamentals of*

Organic Chemistry], Khimiya, Leningrad, 1991, 560 pp. (in Russian).

2. J. March, *Advanced Organic Chemistry*, Wiley, New York, 1985, **1**, 380 pp.

3. G. Frenking, *J. Am. Chem. Soc.*, 1991, **113**, 2476.

4. R. Kimmelma, *Acta Chem. Scand.*, 1988, **42**, 592.

5. L. B. Krivdin, G. A. Kalabin, and B. A. Trofimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 570 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].

6. E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, London, 1969.

7. V. P. Feshin, *Mendeleev Commun.*, 1992, **1**, 18.

8. V. P. Feshin, G. V. Dolgushin, M. G. Voronkov, T. I. Bychkova, A. V. Kalabina, Yu. E. Sapozhnikov, and Ya. B. Yasman, *Teor. Eksp. Khim.*, 1982, **18**, 378 [*Theor. Exp. Chem.*, 1982, **18** (Engl. Transl.)].

9. V. P. Feshin and M. G. Voronkov, *Z. Naturforsch.*, 1990, **45a**, 213.

10. V. P. Feshin and M. Yu. Konshin, *J. Mol. Struct.*, 1994, **319**, 183.

11. V. P. Feshin and M. Yu. Kon'shin, *Zh. Obshch. Khim.*, 1994, **65**, 125 [*J. Gen. Chem.*, 1994, **65** (Engl. Transl.)].

12. V. P. Feshin and M. Yu. Konshin, *J. Mol. Struct.*, 1995, **345**, 83.

13. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *Gaussian-92, Revision E.I*, Gaussian, Inc., Pittsburgh PA, 1992.

14. V. P. Feshin and M. G. Voronkov, *J. Mol. Struct.*, 1982, **83**, 317.

15. C. P. Slichter, *Principles of Magnetic Resonance*, Springer-Verlag, Berlin, Heidelberg, New York, 1980, 448 pp.

16. V. P. Feshin, P. A. Nikitin, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, 1978, **240**, 381 [*Dokl. Chem.*, 1978, **240** (Engl. Transl.)].

17. V. P. Feshin, M. G. Voronkov, G. V. Dolgushin, T. I. Bychkova, and A. V. Kalabina, *Dokl. Akad. Nauk SSSR*, 1980, **253**, 192 [*Dokl. Chem.*, 1980, **253** (Engl. Transl.)].