Inramolecular hypervalent O→Cl interaction in the chloronium cations: an *ab initio* study

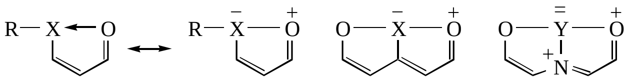
Ruslan M. Minyaev* and Vladimir I. Minkin

Institute of Physical and Organic Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation. Fax: +7 8632 28 5667; e-mail: minyaev@ipoc.rsu.ru

10.1070/MC2000v010n05ABEH001366

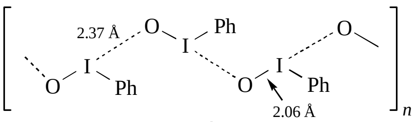
The *ab initio* [MP2(fu)/6-31G**] and DFT (B3LYP/6-31+G**) calculations predict that the strong hypervalent O→Cl interaction stabilises the cyclic and bicyclic heteropentalene structures of chloronium cations.

Attractive inter- and intramolecular interactions of the hypervalent type play an important role in the stabilization of sterically hindered conformations of organoelement compounds[1] and are responsible for secondary and tertiary structures of proteins, which are crucial for recognition processes.[2,3] In the last decade, both experimental and theoretical works have been devoted to the elucidation of the nature of the intramolecular hypervalent O→X(Y) interactions in compounds **1**–**3**, where X and Y are chalcogens (X = S, Se, Te; R = H, Me, Cl)[1,4] or pnictogens (Y = = N, P, As, Sb, Bi).[5,6]



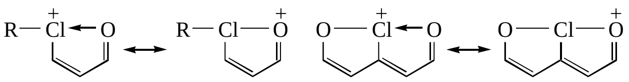
1a **1b** **2** **3**

The energy of these hypervalent interactions was found to strongly depend on the electronegativity of chalcogen atoms X and substituents R.[4,6] Similar hypervalent interactions were also observed in organoelement compounds.[7–9] At the same time, weak attractive intermolecular interactions between chalcogens (O, S) and chlorine were experimentally observed in the bimolecular complexes $H_2O\cdots ClF$,[10] $SO_2\cdots ClF$[11] and $H_2S\cdots ClF$.[12] The noncovalent O···I contact length observed in a crystal of PhIO **4** with the T-shaped geometry around the iodine centres is considerably shorter than the sum of the van der Waals radii of O and I (3.32 Å).[13]

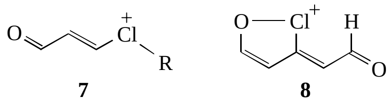


4

Therefore, it may be expected that similar intramolecular attractive O→Hal hypervalent interactions also exist in halogen-containing organic compounds **5** and **6** (X = Hal$^+$ and R = H, Me, Ph, F, Cl), isoelectronic to **1** or **2**. Here, we report on the *ab initio* [MP2(fu)/6-31G**][14] and DFT (B3LYP/6-31+G**)[14] calculations of chloronium cations **5** (R = H, F) and **6**, which evidenced for rather strong attractive O→Cl interactions in these cations.



5a **5b** **6a** **6b**



7 **8**

To estimate the energy of the O→Cl interaction, cations **5** (R = = H, F) and **6** were compared with their *trans-trans*-isomers **7** (R = H, F) and **8**, which are free of the O→Cl interaction.

According to the calculations, all structures of **5**–**8** correspond to genuine minima (λ = 0, hereafter λ designates the number of hessian negative eigenvalues at a given stationary point) on the corresponding potential-energy surfaces (PES). Figures 1 and 2 and Table 1 demonstrate the calculated molecular structures, geometries and energy parameters of cations **5**–**8**.

Table 1 *Ab initio* [MP2(fu)/6-31G**] and DFT (B3LYP/6-31+G**) data for cations **5**–**8**.[a]

Structure	Method	E_{tot}	ΔE	ZPE	ΔE_{ZPE}	ΔH	ω_1
5, C_s	MP2	–650.638323	0	0.063294	0	0	142
R = H	DFT	–651.763734	0	0.061428	0	0	148
5, C_s	MP2	–749.583135	0	0.057537	0	0	163
R = F	DFT	–750.939596	0	0.056113	0	0	162
6, C_{2v}	MP2	–801.638849	0	0.082396	0	0	179
	DFT	–803.171914	0	0.080209	0	0	194
7, C_1	MP2	–650.627010	7.1	0.061814	6.2	6.6	100
R = H	DFT	–651.754787	5.6	0.059694	4.5	5.0	91
7, C_1	MP2	–749.550728	20.3	0.055466	19.0	19.4	62
R = F	DFT	–750.908761	19.3	0.053964	18.0	18.8	56
8, C_s	MP2	–801.584553	34.1	0.078684	31.7	31.9	72
	DFT[b]	–803.098488	46.1				

[a]E_{tot} (a.u.) and ΔE (kcal mol^{-1}) are the total and relative energies (1 a.u. = = 627.5095 kcal mol^{-1}); ZPE (a.u.) is the harmonic zero-point correction; ΔE_{ZPE} (kcal mol^{-1}) is the relative energy including the harmonic zero-point correction; ΔH (kcal mol^{-1}) is the relative enthalpy under standard conditions P = 1 atm and T = 298.1 K; ω_1 (cm^{-1}) is the smallest harmonic vibration frequency. [b]Single-point calculations at the MP2 geometry.

All of the calculated bond lengths and angles are consistent with the available experimental data on chloronium cations (see ref. 15). As can be seen in Table 1 and Figure 1, the *cis-cis* forms of compounds **5** (R = H or F) are stabilised by the O→Cl interaction, whose energy substantially depends on the substituent at the chlorine. For compound **5** with an electropositive substituent R = H, the O→Cl interaction energy was predicted to be 7.1 (MP2) and 5.6 (DFT) kcal mol^{-1}, whereas, in the case of an electronegative substituent R = F, this energy increases up to 20.3 (MP2) and 19.3 (DFT) kcal mol^{-1}. The nonbonded O···Cl dis-

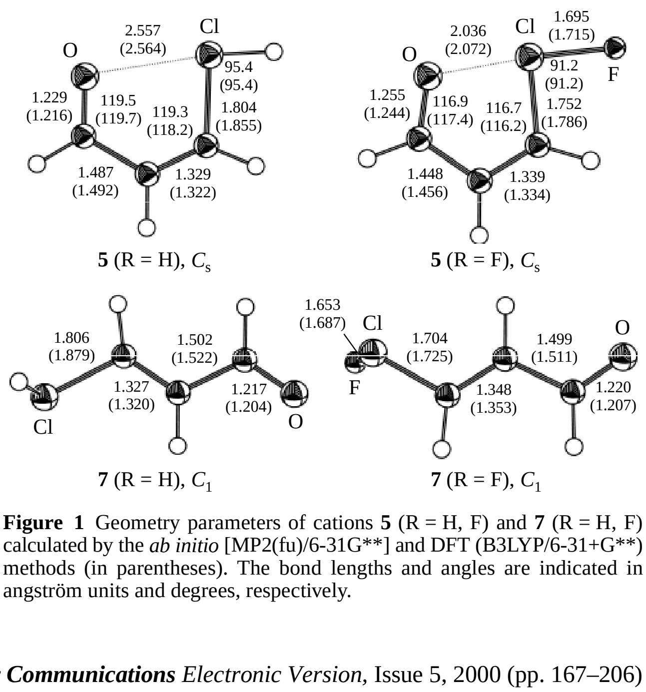
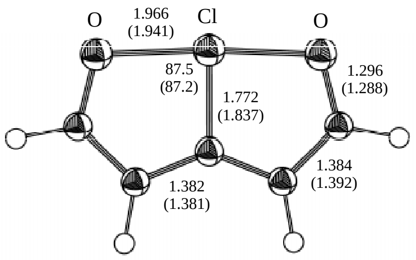
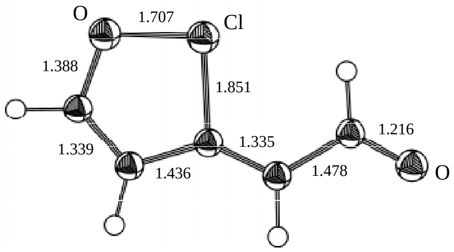


Figure 1 Geometry parameters of cations **5** (R = H, F) and **7** (R = H, F) calculated by the *ab initio* [MP2(fu)/6-31G**] and DFT (B3LYP/6-31+G**) methods (in parentheses). The bond lengths and angles are indicated in angström units and degrees, respectively.



6, C_{2v}



8, C_s

Figure 2 Geometry parameters of cations **6** and **8** calculated by the *ab initio* [MP2(fu)/6-31G**] and DFT (B3LYP/6-31+G**) methods (in parentheses). The bond lengths and angles are given in angström units and degrees, respectively.

tance in **5** (R = F) is ~0.5 Å shorter than that in **5** (R = H). The C–C lengths calculated for **5** (R = H or F) indicate that the structure of **5** (R = F) is also more delocalised than that of **5** with R = H. Note that the degree of equalization of C–C bonds in **5** (R = H or F) is higher than that in unstrained *trans–trans* conformers **7** (R = H or F) (Figure 1). This fact is indicative of the partially aromatic character of five-membered pseudo-heterocycles **5**. The structures of **7** (R = H or F) have C_1 symmetry since the substituent at the chlorine is out of the molecular plane. The corresponding planar *trans–trans* structures of C_s symmetry are transition states for the internal rotation of the substituent R around the Cl–C bond. The energy barriers for this rotation were found to be about 8 kcal mol^{-1}.

The heteropentalene system of **6**, in which the effects of both the 10π-electronic stabilization and the hypervalent O→Cl interaction act cooperatively, may exhibit a stronger hypervalent bonding than that of compounds **5**. Indeed, according to the calculations, chloronium cation **6** corresponds to a minimum ($\lambda = 0$, the smallest harmonic frequency is $\omega_1 = 179$ cm^{-1}, see Table 1) on the PES of $C_5H_4O_2Cl^+$. The structure of **8**, in which no effects of the 10π-electronic stabilization and the hypervalent O→Cl bonding are present, is predicted to be 34.1 (MP2) or 46.1 (DFT) kcal mol^{-1} thermodynamically less stable than that of **6**. Note that DFT calculations do not reveal a minimum corresponding to a stable structure like **8**. To estimate the energy difference between the structures of **6** and **8**, the latter was calculated by DFT in a single point with the MP2 optimised geometry.

In conclusion, we found that the strong attractive hypervalent O→Cl interaction exists in chloronium cations **5** and **6**. It may be expected that this interaction will increase in similar bromonium and iodonium cations.

This work was supported by the Russian Foundation for Basic Research (grant nos. 98-03-33169a and 00-15-97320) and by the Ministry of Education (grant no. 97-9.1-288).

References

1 V. I. Minkin, *Ross. Khim. Zh.*, 1999, **43**, 10 (in Russian).
2 A. C. Legon and D. J. Millen, in *Principles of Molecular Recognition*, eds. A. D. Buckingham, A. C. Legon and S. M. Roberts, Blackie Academic and Professional, London, 1993, pp. 16–42.
3 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
4 R. M. Minyaev and V. I. Minkin, *Can. J. Chem*., 1998, **76**, 766.
5 A. J. Arduengo, III and C. A. Stewart, *Chem. Rev.*, 1994, **94**, 1215.
6 E. G. Nesterova, T. N. Gribanova. R. M. Minyaev and V. I. Minkin, *Izv. Akad. Nauk, Ser. Khim.*, in press.
7 R. R. Holmes, *Chem. Rev.*, 1996, **96**, 927.
8 J. G. Vercade, *Acc. Chem. Res*., 1993, **26**, 483.
9 V. Pestunovich, V. Sidorkin and M. Voronkov, in *Progress in Organosilicon Chemistry*, eds. B. Marcinies and J. Chojnowski, Gordon and Breach Science Publishers, New York, 1994, ch. 5, p. 69.
10 S. A. Cooke, G. Cotti, C. M. Evans, J. H. Holloway and A. C. Legon, *Chem. Commun*., 1996, 2327.
11 G. Cotti, J. H. Holloway and A. C. Legon, *Chem. Phys. Lett*., 1996, **255**, 401.
12 H. I. Bloemink, K. Hinds, J. H. Holloway and A. C. Legon, *Chem. Phys. Lett*., 1995, **242**, 113.
13 P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123.
14 M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian-94, Revision B.3*, Gaussian, Inc., Pittsburgh PA, USA, 1995.
15 C. H. Reynolds, *J. Am. Chem. Soc*., 1992, **114**, 8676.

Received: 26th June 2000; Com. 00/1692