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Hydrogen Bonding Properties of the Complexes of Formaldehyde and its Derivatives with HF and HCl

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Summary. The complexes of formaldehyde and some of its derivatives with HF and HCl were investigated at HF/6-311 + +G** and MP2/6-311 + +G** levels of theory. Interaction energies were corrected for the basis set superposition error (BSSE). The full optimizations of dimers and monomers were performed during calculations. The *Bader* theory of atoms-in-molecules (AIM) was also applied for the localization of bond critical points (BCP) and for the calculation the electron densities and their *Laplacians* at these points. The relationships between H-bond energy and parameters obtained from calculations were also studied.

Keywords. *Ab initio* calculations; *Bader* theory; Formaldehyde; H-Bond energy; Corrections for BSSE.

Introduction

The prediction of the properties of hydrogen bonds has frequently been the subject of investigations since such interactions play important roles in many chemical, physical, and biological processes [1–3]. For example, hydrogen bonds belong to the relatively strong and directional intermolecular interactions and are hence responsible for crystal packing [4, 5]. Computational chemistry methods are very useful for the analysis of H-bonded complexes, yielding information about their geometries and energies as well as about their vibrational and NMR spectra [3].

The purpose of this paper is to analyse the above mentioned properties of $H_2C{=}O\cdots HX$ ($X = F$, Cl) dimers and of related complexes. The complexes were chosen because of their simplicity and because of their molecular structures, allowing to study not only the properties of HF and HCl proton donating bonds, but also those of the C=O acceptor. Besides, such systems have often been the subject of studies, and many results of calculations are available [3, 6–8]. However, in many cases the results are incomplete, and the calculations for $H_2C{=}O\cdots HX$ and related complexes were performed at different levels of theory.

The proton-accepting properties of the carbonyl group have been theoretically investigated for a complex between formaldehyde and water, but a variety of fairly

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small basis sets have been used [9]. A small stretch of both the O–H donating covalent bond and the C=O bond has been detected which is in line with results from neutron diffraction studies on O–H···O=C systems. The correlation between C=O bond length and H···O distance suggested that the C=O bond length might be used as a measure of the H-bond strength [10].

The aim of the present work was to study C=O···H–*X* systems within Y_2C=O···H*X* dimers (*Y* = H, F, Cl; *X* = F, Cl) at the same levels of theory. The optimized geometries, H-bond energies, calculated IR spectra, and topological parameters will be discussed.

Results and Discussion

Geometries and energies

The complexes of formaldehyde and some of its derivatives with hydrogen fluoride and hydrogen chloride as proton donating molecules were analyzed.

$$\begin{matrix} Y^1 \\ \diagdown \\ \quad C{=}O\cdots H{-}X \\ \diagup \\ Y^2 \end{matrix} \quad (Y^1, Y^2 = \text{H, F, Cl; } X = \text{F, Cl})$$

The geometries of the dimers optimized using MP2/6-311 + +G** and HF/6-311 + +G** levels of theory are presented in Table 1. The results show that for the same accepting molecules the H···O distances are shorter for complexes with HF than for those with HCl and are in line with previous investigations concerning HFCO···H*X* and HClCO···H*X* (*X* = F, Cl) dimers optimized at the MP2/6-311G(2d,2p) level of theory [7]. Table 1 shows that HF is a stronger *Lewis* acid than HCl as reflected by the fact that the H-bond energies for C=O···H–F systems are higher than those for the corresponding C=O···H–Cl ones.

The results for H_2O···HF and H_2O···HCl complexes are also given in Table 1 for comparison. Again HF turns out to be a stronger *Lewis* acid than HCl (−7.54 *vs.* −4.68 kcal/mol at the MP2/6-311 + +G** level). The corresponding H-bond energies for dimers with formaldehyde and its derivatives are smaller, indicating that the carbonyl group is a much weaker *Lewis* base centre than H_2O.

The elongation of the proton donating bond also confirms that HF is a stronger *Lewis* acid than HCl. The elongation is measured as described by Eq. (1) where r_{HX} is the length of the proton donating bond (HF or HCl) in the considered complex and r^0_{HX} is the corresponding bond length for the isolated HF or HCl molecule. Optimized HF and MP2 geometrical parameters for monomers are given in Table 2.

$$\delta_{HX} = (r_{HX} - r^0_{HX})/r^0_{HX} \tag{1}$$

The measure of elongation given by Eq. (1) may be also treated as a measure of the H-bond strength [14]. Figure 1 presents the relationship between H-bond energy and δ_{HX} for MP2/6-311 + +G** and HF/6-311 + +G** levels of theory. The linear correlation coefficients for MP2 and HF results amount to 0.997 and

Table 1. Geometrical parameters for the complexes of formaldehyde derivatives with HF or HCl (Å, °); the values for the corresponding complexes with H_2O are also given; H-bond energy (E_{HB}) in kcal/mol (corrected for BSSE); all results were obtained from MP2/6-311 + +G** optimizations (HF results are given in parentheses)

	H···O	HF (HCl)	F(Cl)–H···O	C=O	E_{HB}
$H_2O\cdots HF$	1.731	0.917	178.6		−7.543
	(1.731)	(0.932)	(178.6)		(−7.653)
$H_2CO\cdots HF$	1.869	0.923	179.8	1.214	−5.423
	(1.898)	(0.904)	(179.7)	(1.182)	(−6.161)
$HFCO\cdots HF$	1.927	0.921	176.1	1.188	−4.002
	(1.956)	(0.902)	(176.5)	(1.161)	(−4.741)
$F_2CO\cdots HF$	1.962	0.920	179.8	1.180	−3.215
	(2.001)	(0.901)	(179.8)	(1.154)	(−3.759)
$Cl_2CO\cdots HF$	1.933	0.921	179.7	1.190	−3.367
	(2.004)	(0.901)	(179.8)	(1.158)	(−3.600)
$H_2O\cdots HCl$	1.904	1.287	178.7		−4.677
	(2.028)	(1.279)	(180.0)		(−4.601)
$H_2CO\cdots HCl$	2.057	1.279	179.8	1.214	−3.519
	(2.136)	(1.275)	(179.9)	(1.182)	(−3.652)
$HFCO\cdots HCl$	2.136	1.277	166.3	1.187	−2.398
	(2.213)	(1.273)	(176.9)	(1.160)	(−2.731)
$F_2CO\cdots HCl$	2.161	1.276	179.7	1.179	−2.004
	(2.270)	(1.272)	(179.8)	(1.153)	(−2.091)
$Cl_2CO\cdots HCl$	2.133	1.276	179.7	1.190	−2.179
	(2.275)	(1.272)	(179.8)	(1.156)	(−1.988)

Table 2. Proton donating (HF or HCl) or proton accepting (C=O) bond lengths (Å) for monomeric free molecules (6-311 + +G** basis set)

	MP2	HF
HF	0.917	0.897
HCl	1.273	1.270
H_2CO	1.213	1.180
HFCO	1.185	1.158
F_2CO	1.177	1.150
Cl_2CO	1.186	1.152

0.999, respectively. Equations (2) and (3) illustrate these dependencies (y: H-bond energy in kcal/mol; x: δ_{HX} parameter).

$$y = -680.63x - 0.4656 \quad (\text{MP2}) \tag{2}$$

$$y = -773.92x - 0.6379 \quad (\text{HF}) \tag{3}$$

Figure 1 presents the above mentioned relationships, Fig. 2 shows the dependence between C=O bond length and H-bond energy for MP2 results; obviously, there is no correlation in such a case in spite of the same accepting centre, and the length of

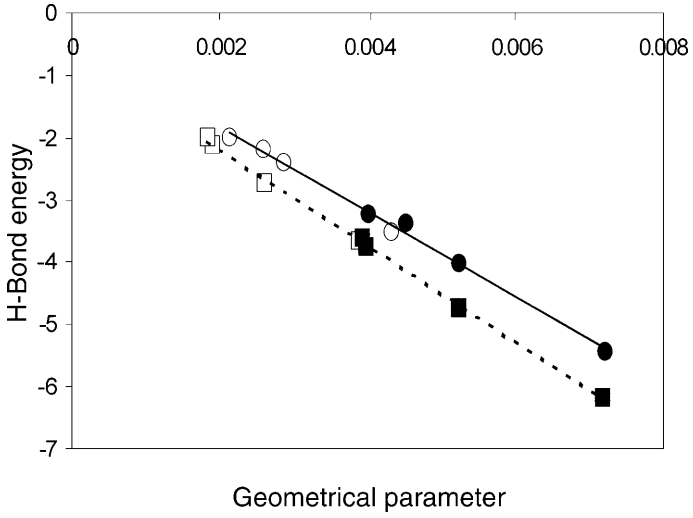

Fig. 1. Correlation between geometrical parameter as defined by Eq. (1) and H-bond energy (kcal/mol); ◯: MP2/6-311 + +G**, □: HF/6-311 + +G**; open circles and squares represent complexes with HCl, full symbols correspond to those with HF

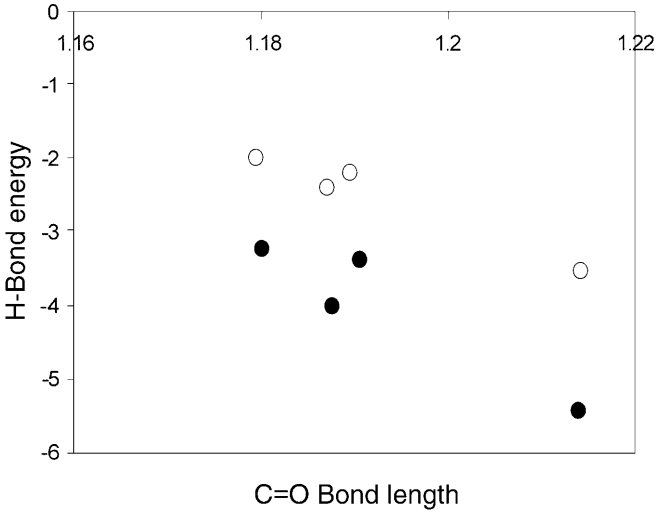

Fig. 2. Relationship between the length of the C=O bond (Å) and H-bond energy (kcal/mol); ●: complexes of HF, ◯: complexes of HCl (MP2/6-311 + +G** level of theory)

the C=O bond is not a good measure of H-bond strength for the sample investigated here. A normalization of the C=O bond length according to Eq. (1) did not improve the correlation.

Bader theory

The topological parameters obtained from the atoms-in-molecules (AIM) theory of *Bader* [13] are often used for the description of the properties of hydrogen bonding. *Koch* and *Popelier* have proposed eight criteria based on AIM properties to

characterize both inter- and intramolecular H-bonds [15]. One of the criteria is connected with the electron density at the $H \cdots Y$ (*Y*: hydrogen accepting centre) bond critical point ($\rho_{H \ldots Y}$). This criterion states that the value of $\rho_{H \ldots Y}$ should lie within the range of 0.002 and 0.04 au in the case of an existing hydrogen bond. This topological parameter is also frequently used as a measure of H-bond strength. A lot of correlations between $\rho_{H \ldots Y}$ and H-bond energy can be found in the literature [16–18]. However, it seems that such correlations may be fulfilled only for related complexes. It is difficult to say if the sample of complexes considered in this paper is homogeneous. There is the same kind of proton acceptor (C=O bond) and the same kind of intermolecular contact ($H \cdots O$); however, there are two different proton donors: HF and HCl. Additionally, the properties of the C=O bond are strongly affected by Cl and F substituents for HFCO, Cl_2CO, and F_2CO molecules. Figure 3 shows a good correlation between $\rho_{H \ldots Y}$ and H-bond energy in spite of the possible heterogeneity of the sample above mentioned. The correlation coefficients amount to 0.973 and 0.991 for MP2 and HF results respectively; Eqs. (4) and (5) (*y*: H-bond energy; *x*: $\rho_{H \ldots O}$) illustrate these linear correlations.

$$y = -355.24x + 2.5509 \quad (\text{MP2}) \tag{4}$$

$$y = -432.94x + 1.989 \quad (\text{HF}) \tag{5}$$

Table 3 presents the topological parameters for the complexes considered in this paper: the properties of bond critical points for the proton donating bonds, the $H \cdots Y$ contacts, and the C=O bonds. The electron densities and their *Laplacians* for these bonds are shown. The topological parameters for $H_2O \cdots HX$ (X = F, Cl) complexes are also given for comparison. It has been pointed out that for stronger hydrogen bonding a greater elongation of the proton donating bond [19, 20] and a decrease of ρ_{HX} (electron density at BCP of proton donating bond) [18, 21]

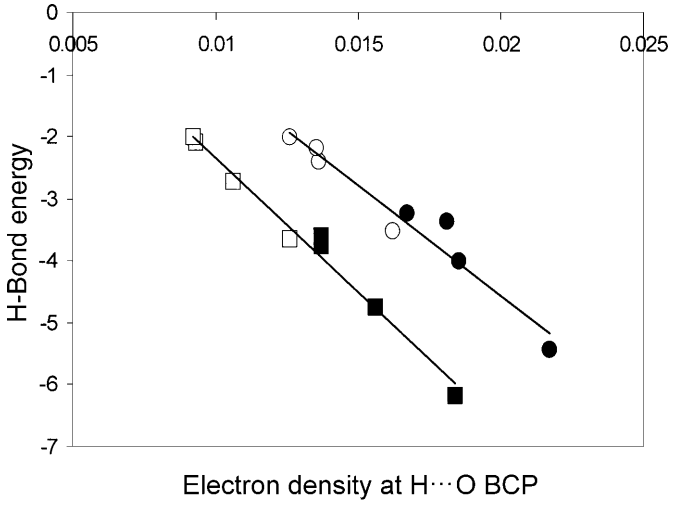

Fig. 3. Correlation between the electron density at $H \cdots O$ bond critical point (au) and H-bond energy (kcal/mol); ◯: MP2/6-311 + +G**, □: HF/6-311 + +G**; open circles and squares represent complexes with HCl, full symbols correspond to those with HF

Table 3. Topological parameters (au) of proton donating bonds, H···O contacts, and proton accepting C=O bonds; electron densities at bond critical points (ρ) and their *Laplacians* ($\nabla^2\rho$) are given; the results were obtained from MP2/6-311 + +G** wave functions (in parentheses: results from HF/6-311 + +G** wave functions)

	$\rho_{HF(Cl)}$	$\nabla^2\rho_{HF(Cl)}$	$\rho_{H\cdots O}$	$\nabla^2\rho_{H\cdots O}$	$\rho_{C=O}$	$\nabla^2\rho_{C=O}$
$H_2O\cdots HF$	0.3466	−2.650	0.0366	0.1414	–	–
	(0.3746)	(−3.364)	(0.0267)	(0.1299)		
$H_2CO\cdots HF$	0.3590	−2.789	0.0217	0.1073	0.3924	0.2142
	(0.3821)	(−3.429)	(0.0184)	(0.1056)	(0.4267)	(0.5525)
$HFCO\cdots HF$	0.3620	−2.808	0.0185	0.0935	0.4241	0.1799
	(0.3855)	(−3.442)	(0.0156)	(0.0908)	(0.4587)	(0.4041)
$F_2CO\cdots HF$	0.3639	−2.819	0.0167	0.0855	0.4366	0.1134
	(0.3879)	(−3.448)	(0.0137)	(0.0804)	(0.4738)	(0.2765)
$Cl_2CO\cdots HF$	0.3631	−2.813	0.0181	0.0920	0.4197	0.2214
	(0.3879)	(−3.448)	(0.0137)	(0.0800)	(0.4611)	(0.5164)
$H_2O\cdots HCl$	0.2415	−0.7101	0.0267	0.0960	–	–
	(0.2506)	(−0.8165)	(0.0185)	(0.0753)		
$H_2CO\cdots HCl$	0.2462	−0.7220	0.0162	0.0683	0.3938	0.1864
	(0.2532)	(−0.8186)	(0.0126)	(0.0567)	(0.4292)	(0.5287)
$HFCO\cdots HCl$	0.2472	−0.7203	0.0136	0.0562	0.4260	0.1656
	(0.2542)	(−0.8158)	(0.0106)	(0.0459)	(0.4609)	(0.4078)
$F_2CO\cdots HCl$	0.2478	−0.7199	0.0126	0.0520	0.4383	0.1071
	(0.2546)	(−0.8112)	(0.0093)	(0.0390)	(0.4761)	(0.2831)
$Cl_2CO\cdots HCl$	0.2474	−0.7188	0.0135	0.0560	0.4217	0.2146
	(0.2547)	(−0.8126)	(0.0092)	(0.0386)	(0.4642)	(0.5208)

Table 4. Proton donating (HF or HCl) and proton accepting (C=O) topological parameters (au) for monomeric free molecules (6-311 + +G** basis set)

	ρ(MP2)	$\nabla^2\rho$(MP2)	ρ(HF)	$\nabla^2\rho$(HF)
HF	0.3704	−2.836	0.3961	−3.427
HCl	0.2487	−0.7105	0.2556	−0.7982
HCOH	0.3976	0.1541	0.4336	0.5285
HCOF	0.4302	0.1644	0.4656	0.4255
FCOF	0.4417	0.1136	0.4803	0.3107
ClCOCl	0.4264	0.2274	0.4692	0.5645

is observed. The same dependence can be seen here (Table 3): for $H_2O\cdots HF$, $H_2CO\cdots HF$, $HFCO\cdots HF$, $Cl_2CO\cdots HF$, and $F_2CO\cdots HF$ complexes, the values of ρ_{HF} amount to 0.3466, 0.3590, 0.3620, 0.3631, and 0.3639 au respectively (MP2). The H-bond energies for the same sequence of complexes are −7.54, −5.42, −4.00, −3.37, and −3.22 kcal/mol, respectively (Table 1). The same results are obtained for complexes with hydrogen chloride and for the HF method. Table 4 shows the MP2 and HF topological parameters for C=O, HF, and HCl bonds of monomers.

Table 5. Shift in frequency (cm^{-1}) and intensity (ratio of intensity in the complex/isolated subunit) of HF(Cl) and C=O bond stretch caused by complexation

	$\Delta\nu$ (HF or HCl)	I/I_0	$\Delta\nu$ (C=O)	I/I_0
$H_2O\cdots HF$	−349	5.65	–	–
$H_2CO\cdots HF$	−135	4.79	12	1.38
$HFCO\cdots HF$	−94	4.00	2	1.27
$F_2CO\cdots HF$	−70	3.56	−1	1.22
$Cl_2CO\cdots HF$	−83	4.60	−9	1.29
$H_2O\cdots HCl$	−188	15.55	–	–
$H_2CO\cdots HCl$	−57	7.91	4	1.38
$HFCO\cdots HCl$	−34	6.46	−3	1.27
$F_2CO\cdots HCl$	−22	5.74	−4	1.25
$Cl_2CO\cdots HCl$	−30	7.63	−11	1.31

Vibrational spectra

Table 5 presents the shift in the frequencies for HF, HCl, and C=O bonds of the complexes considered here. It is well known that the frequency associated with H–*X* is red-shifted its intensity is enhanced upon formation of a H-bond. This red-shift is usually valuable in a quantitative sense, as it is correlated with the strength of the H-bond as well as with its length [22]. The results of Table 5 are in agreement with this dependence. The greatest shifts are observed for the complexes with water. The H-bond formation is connected not only with an elongation of the proton donating bond, but often also with an elongation of the accepting bond. Such elongations have been observed from neutron diffraction measurements on crystals containing $C{=}O\cdots H{-}O$ systems [10]. Tables 1 and 2 show that H-bond formation causes only a slight elongation of the C=O bond. From Table 5 it can be seen that the C=O stretching frequency is slightly shifted for the complexes considered in this paper, be it to the red or the blue side. It has been pointed out that the C=O frequency for the $H_2CO\cdots HX$ complexes is slightly red-shifted [3]. A linear relationship has been found between the H-bond energy and the C=O frequency shift for the same complex [8]. In that case, the theoretical frequency values were obtained for a fixed set of $H\cdots O$ intermolecular distances; all remaining parameters were optimized. We did not observe such a dependence for the complexes considered here because of their variety and the small range of C=O bond elongation.

Conclusions

Theoretical calculations on formaldehyde and its derivatives with HF and HCl show that there are relationships between geometrical, energetic, and topological parameters. The results confirm conclusions made on other systems, *i.e.* that the parameters describing the proton donating bond within H-bonded systems serve as the best measures of the H-bond strength [14, 18]. Correlations between the H-bond energy and the elongation of the H*X* bond, the frequency shift, and other parameters were found. It was shown that HF is a stronger *Lewis* acid than HCl within H-bonded dimers; the carbonyl group is a weaker *Lewis* base than the oxygen atom of water.

Experimental

Calculations were carried out using the Gaussian 98 program [11]. The geometries of complexes and of monomers were fully optimized with the 6-311 + +G** basis set at HF and MP2 levels of theory. The interaction energies were corrected for the inherent basis set superposition error (BSSE) by using the full counterpoise method [12]. To investigate the bonding features of the dimers and monomers, the atoms-in-molecules (AIM) theory of *Bader* was used [13]. The bond critical points (BCP) have been located since the values of the charge density and its *Laplacian* at these points give useful information regarding the strength of the linkages.

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