Properties of the Halogen−Hydride Interaction: An ab Initio and "Atoms in Molecules" Analysis

Paweł Lipkowski,[†,‡] Sławomir J. Grabowski,*[,†,§] and Jerzy Leszczynski[†]

Computational Center for Molecular Structure and Interactions, Department of Chemistry, Jackson State University, Jackson, Mississippi 39217, Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland, and Department of Physics and Chemistry, University of Łódź, 90-236 Łódź, ul. Pomorska 149/153, Poland

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X−Cl···H−Y interactions are analyzed by applying ab initio methods as well as the Bader theory. All calculations were performed using Pople's basis sets (6-311++G(2df,2pd) and 6-311++G(3df,3pd)) as well as the Dunning-type bases (aug-cc-pVDZ and aug-cc-pVTZ) within the MP2 method. For the complexes analyzed here, X−Cl and H−Y may be treated as a Lewis acid and a Lewis base, respectively. The Cl···H interactions are rather weak or at most moderate since, for the strongest interaction of the $F_3CCl\cdots HLi$ complex, the binding energy calculated at the MP2/6-311++G(3df,3pd) level of approximation amounts to −3.4 kcal/mol, and the H···Cl distance is equal to 2.65 Å, less than the corresponding sum of van der Waals radii. These interactions may be classified as halogen−hydride interactions. However, some of the complexes analyzed, especially $F_3SiCl\cdots HBeF$ and $F_3SiCl\cdots HBeF$, are very weakly bound, probably by typical van der Waals interactions.

Introduction

There are different types of intermolecular interactions influencing the arrangement of molecules in crystals. It seems that hydrogen bonds are mainly responsible for the crystal structure architecture.[1,2] There are numerous studies where different kinds of hydrogen bonds in crystals are considered. Among those various H-bonds the so-called dihydrogen bond (DHB) was described as being in nature related to the hydrogen bond. It was designated as X−H···H−E, where X−H is the typical proton-donating bond (such as O−H or N−H), while E is a metal or boron.[3] In early studies of DHBs it was pointed out that one of the H-atoms possesses an excess negative charge; hence, its connection with metal is needed. However, further studies indicate various X−H···H−Y interactions as DHBs, even C−H···H−C interactions.[4] Generally, $X-H^{\delta+}$ acts as a Lewis acid, while $H^{\delta-}-Y$ acts as a Lewis base, which is similar to typical X−H···Y hydrogen bonds, where Y as an accepting center is a Lewis base.

Rozas et al. explained that there is also the so-called inverse $X-H^{\delta-}\cdots Y$ bond where, opposite to the typical H-bond, the excess negative charge is on the hydrogen atom.[5] However, the term "inverse" was also used for "blue-shifting" hydrogen bonding, and the term "hydride bonding" was proposed recently[6] for $X-H^{\delta-}\cdots Y$ interactions. It is worth mentioning that the $B-H\cdots Na^+$ hydride bond was found by Cotton et al. in the crystal structure of the diniobium tetragonal lantern compound.[7] This type of interaction was investigated theoretically at the MP2/6-311++G(d,p) level of theory, and the following connections were analyzed: B−H···Li, Be−H···Li, and Li−H···Li.[5] It was found that there is a transfer of the electron charge from the hydrogen atom to its electropositive acceptor, contrary to typical H-bonds where such a transfer is from an acceptor of the proton to the proton-donating part of the system. All interactions mentioned above may be classified as Lewis acid−Lewis base interactions, and there is an electron transfer from the Lewis base to the Lewis acid for all of them. This is in line with the earlier statements concerning hydrogen bonding; it was pointed out that there is an electron charge transfer from the proton-accepting part (Lewis base) to the proton-donating bond (Lewis acid).[8]

There is another interesting kind of nonbonded interaction, the halogen bond, which may be briefly defined as the interaction of a halogen atom acting as a Lewis acid with a lone-pair-possessing atom, i.e., a Lewis base.[9] It is often detected that a halogen atom connected with a carbon atom (C−Hal) has strong directional preference to act as a Lewis acid, and hence, C−Hal···Y linear systems (Y = O, N, etc.) are mainly observed.[10,11] This is connected with the anisotropy of the electron charge distribution of the covalently bonded halogen atom which occupies ellipsoidal volume space.[12] This implies that the electrostatic interaction energy which is repulsive for the Hal···Y interaction is least repulsive for linear C−Hal···Y systems.[11,12b] In other words, the C−Hal bond acts as a Lewis acid in its direction, while the halogen atom acts as a Lewis base in the direction perpendicular to the C−Hal bond.

There are recent numerous studies of halogen bonds, among them those connected with the analyses of crystal structures. For example, C−Br···N interactions as stabilizing structural motifs in crystal structures of triazoles have been analyzed recently, and ab initio calculations have also been performed on such interactions.[13] There are other computational studies of halogen bonds. For example, Hal···Y interactions were analyzed if CH_3Hal (Hal = Cl, Br, I) are Lewis acids and NH_3 is a Lewis base, and it was found that the range of energy of such interactions is 2−6 kcal/mol.[14] For $CF_3I\cdots NH_3$, it is equal to 5.8 kcal/mol (MP2 method applied and DZVP basis set).[15] Other studies were connected with the CF_3Cl, CF_3Br, and SiF_3-

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* To whom correspondence should be addressed. E-mail: slagra@ccmsi.us.
[†] Jackson State University.
[‡] Wrocław University of Technology.
[§] University of Łódź.

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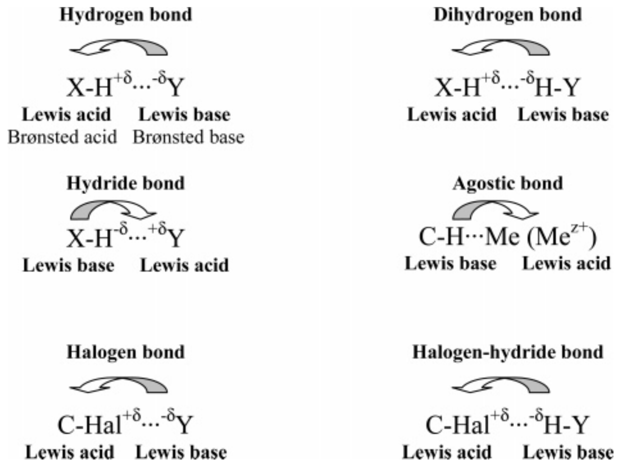

Figure 1. Different interactions which may be classified as Lewis acid−Lewis base interactions.

Cl Lewis acids and the NH_3, H_2O, or Br^- Lewis bases. The calculations were performed at the MP2/6-311++G(d,p) level of approximation, and it was detected that, for almost all of the considered complexes, the C−Hal bond may be treated as a blue-shifting bond since its shortening is observed as an effect of complexation.[16]

One can observe that various interactions existing in crystal structures and influencing the arrangement of molecules may be described as Lewis acid−Lewis base interactions and that the H-bond is the most important bond, especially if its influence on the crystal architecture is considered. The aim of this study is to investigate an interesting interaction that is, to our knowledge, not described yet. It is the C(Si)−Hal···$H^{\delta-}$−Y interaction which may be treated as a halogen bond on one hand and as a hydride bond on the other hand. The halogen atom acts here as a Lewis acid center and an H-atom with an excess negative charge like a Lewis base. In our study it is called a halogen−hydride interaction. However, for such an interaction, one would expect the reverse situation where the halogen atom, being electronegative, acts as a Lewis base and the H-atom as an acid for typical H-bonds.

It is worth mentioning that the C(Si)−Hal···$H^{\delta-}$−Y interaction probably rarely exists in crystal structures since the Cambridge Structural Database (CSD)[17] was searched here for all C−Cl···$H^{\delta-}$−Me (Me = metal) connections; four such interactions were found with Cl···H distances in the range of 2.7−3.0 Å, slightly less than the corresponding sum of van der Waals radii. The following transition metals are connected with H-atoms for these systems: Ir, Ag, Re, and Ru. This is in line with the early findings on DHBs where a H-atom connected with a transition metal and possessing the excess negative charge was expected to act as the Lewis base center. Further studies indicated the existence of the broader spectrum of DHB interactions. These four findings, where probably $Cl^{\delta+}\cdots H^{\delta-}$ interactions exist, are based on X-ray diffraction measurements where the positions of H-atoms are not determined accurately. Hence, these geometrical experimental results do not support evidently the existence of that type of interaction. To have more precise positions of H-atoms, neutron diffraction measurements are needed. However, the neutron diffraction measurements constitute less than 0.3% of all crystal structures collected in the CSD; the remaining are X-ray measurements.

Figure 1 is also presented here to classify roughly all kinds of interactions mentioned here and to place C(Si)−Hal···$H^{\delta-}$−Y among them. The arrows show the transfer of electron charge from the first molecule to the second molecule, and it is always the transfer from the Lewis base to the Lewis acid.

Computational Details

The calculations have been performed using the Gaussian 98[18] and Gaussian 03[19] programs. Complexes where the C(Si)−Hal···$H^{\delta-}$−Y interaction exists were taken into account, with LiH, BeH_2, and HBeF as Lewis bases and F_3CCl, F_3SiCl, and F_2NCl as Lewis acids. For the chosen Lewis base centers the H-atom is connected with Li or Be; such species—BeH_2 and LiH and their relatives—are often chosen in calculations as the simple and model ones to mimic the Lewis base H-atom properties. One should also mention that the choice of Lewis acids is connected with the expected anisotropy of chlorine charge distribution. It is known that for C−Cl bonds the longest axis of the ellipse of charge distribution is often perpendicular to this bond or nearly so; the shortest axis is in the same direction as the C−Cl bond. Hence, the formation of linear C−Cl···Y (Y = electronegative atom) is possible since, in such a case, C−Cl acts as a Lewic acid.

The calculations were performed here using the second-order perturbation Møller−Plesset method (MP2).[20] The Pople-type basis sets were used (6-311++G(2df,2pd) and 6-311++G(3df,3pd))[21] and also the Dunning basis sets (aug-cc-pVDZ and aug-cc-pVTZ).[22] The supermolecular approach was applied to calculate the binding energies. This indicates that the interaction energy of the two systems A and B is calculated as the difference between the energy of the dimer, E_{AB}, and the energies of the monomers, E_A and E_B, each calculated for a given nuclear configuration.[23]

To deepen the nature of the investigated interactions, the variation-perturbation approach, which allows the interaction energy to be decomposed, was applied.[24] The decomposition of the interaction energy was implemented[25] in the GAMESS program.[26] In this approach, the starting wave functions of the subsystems are obtained in the dimer-centered basis set (DCBS).[27] This is why the total interaction energy as well as its components is free of basis set superposition error (BSSE) due to the full counterpoise correction.

The interaction energy within the variation-perturbation scheme mentioned above is decomposed as follows: the energy at the all-electron MP2 level is decomposed into a Hartree−Fock (SCF) contribution and a correlation term:

$$\Delta E^{\mathrm{MP2}} = \Delta E^{\mathrm{HF}} + \Delta E^{\mathrm{CORR}} \qquad (1)$$

The Hartree−Fock term consists of

$$\Delta E^{\mathrm{HF}} = E_{\mathrm{EL}}{}^{(1)} + E_{\mathrm{EX}}{}^{(1)} + E_{\mathrm{DEL}}{}^{(\mathrm{R})} \qquad (2)$$

where $E_{\mathrm{EL}}{}^{(1)}$ is the first-order electrostatic interaction energy term, $E_{\mathrm{EX}}{}^{(1)}$ is the first-order Heitler−London exchange term, and $E_{\mathrm{DEL}}{}^{(\mathrm{R})}$ corresponds to a higher order delocalization term. The sum of the first-order terms constitutes the Heitler−London energy term ΔE^{HL}:

$$\Delta E^{\mathrm{HL}} = E_{\mathrm{EL}}{}^{(1)} + E_{\mathrm{EX}}{}^{(1)} \qquad (3)$$

The Bader theory, "atoms in molecules" (AIM),[28] was also applied here. The critical points were analyzed in terms of electron densities and their Laplacians; additionally, the energetic characteristics of critical points were taken into account. The AIM calculations were performed with the use of the AIM2000 program.[29]

TABLE 1: Geometrical Parameters of the Systems Analyzed Here: Cl···H Lewis Acid−Lewis Base Contacts (Å) and the Increments of X−Cl and H−Y Distances as a Result of Complexation (Å)[a]

	X−Cl incr	H−Y incr	Cl···H	X−Cl incr	H−Y incr	Cl···H
		$F_3CCl\cdots HLi$			$F_3SiCl\cdots HLi$	
A	−0.61	−0.08	2.715	−0.48	−0.01	3.059
B	−0.50	0.02	2.650	−0.47	0.05	2.965
C	−0.51	−0.25	2.698	−0.44	−0.20	2.973
D	−0.55	0.02	2.664	−0.47	0.08	3.032
		$F_3CCl\cdots HBeH$			$F_3SiCl\cdots HBeH$	
A	−0.15	0.01	2.949	−0.07	0.04	3.167
B	−0.10	0.03	2.798	−0.18	0.02	2.993
C	−0.13	0.01	2.887	−0.09	0.03	3.073
D	−0.14	0.04	2.855	−0.10	0.04	3.070
		$F_3CCl\cdots HBeF$			$F_3SiCl\cdots HBeF$	
A	−0.09	−0.01	2.975	−0.03	0.02	3.187
B	−0.04	−0.02	2.792	−0.01	−0.01	2.969
C	−0.07	−0.05	2.898	−0.04	−0.03	3.060
D	−0.08	0.02	2.867	−0.05	0.03	3.067
		$F_2NCl\cdots HBeH$			$F_2NCl\cdots HBeF$	
A	−0.10	0.05	2.654	−0.03	−0.02	2.704
B	−0.07	0.11	2.589	−0.02	0.02	2.606
C	−0.20	0.09	2.666	−0.12	0.03	2.710
D	−0.16	0.11	2.629	−0.08	0.07	2.662

[a] Key: (A) MP2/6-311++G(2df,2pd), (B) MP2/6-311++G(3df,3pd), (C) MP2/aug-cc-pVDZ, (D) MP2/aug-cc-pVTZ.

Results and Discussion

Energetic and Geometrical Results. Table 1 presents some of the geometrical characteristics of the analyzed systems. These geometrical parameters correspond to minima since the complexes were fully optimized and since no imaginary frequencies were found. The Cl···H intermolecular distances as well as the changes of the X(C,Si,N)−Cl and H−Me(Li,Be) bond lengths as a result of complexation are collected. These changes are calculated as increments of bond lengths related to bonds not involved in any intermolecular interactions. In other words, these are $100(r - r_0)/r_0$, where r corresponds to the bond length considered while r_0 corresponds to the reference bond not involved in the interaction and obtained as a result of full geometry optimization of the monomeric system.

The H···Cl distance is smaller than the sum of the corresponding van der Waals radii of chlorine and hydrogen (∼3 Å)[30] for complexes with F_3CCl and F_2NCl Lewis acids, and it is close to that sum for complexes with a F_3SiCl Lewis acid. If one assumes that the Cl···H intermolecular distance roughly corresponds to the strength of the interaction, then systems with F_3SiCl are weakly bound, and the Cl···H interaction is not halogen−hydride bonding but rather is a weak van der Waals interaction. Systems with F_3CCl are more strongly bound. One can conclude that the strength of the Lewis acid properties increases according to $F_3SiCl < F_3CCl < F_2NCl$, while the Lewis base strength increases according to HBeF < HBeH < LiH. It should be related to the charges on the interacting H-atoms. Really the shortest Cl···H distances are for the $F_2NCl\cdots HBeH$, $F_2NCl\cdots HBeF$, and $F_3CCl\cdots HLi$ complexes.

The increments of bond lengths do not correspond to the H···Cl distances. It is known that the evidence of H-bond formation, for such typical interactions as O−H···O or N−H···O, is connected with the elongation of the proton-donating bond. For the systems considered here there is a shortening of the X−Cl bond for all systems analyzed. Such a shortening occurs for all levels of approximations applied. The greatest shortenings are for the $F_3CCl\cdots HLi$ and $F_3SiCl\cdots HLi$ complexes. For $H^{\delta-}$−Y bonds the changes of lengths as an effect of complexation are meaningless, and they are sometimes connected with elongation, sometimes with shortening. All results collected in Table 1 were obtained using the MP2 method and applying different basis sets. However, one can observe that the quality differences between the analyzed complexes are the same for different basis sets.

Since all X−Cl and H−Y increments are meaningless (only for the LiH Lewis base and X−Cl bonds they are about 0.5%, and the remaining are much smaller), the deformation energy as a result of complexation is not taken into account here. Table 2 presents the binding energies calculated within the supermolecular approach without the inclusion of the deformation energies. The components derived from the decomposition scheme are also presented. As was mentioned in the previous section, the energy components collected are free of BSSE due to the full counterpoise correction. However, these results are not in line with the geometrical parameters (Table 1) since the greatest binding energies are for systems with a LiH molecule as a Lewis base and the next greatest are for the $F_2NCl\cdots HBeH$ complex. Such an order corresponds to the shortening of the X−Cl bond but not to the shortening of the Cl···H distance. Thus, the latter distance does not correspond to the strength of the Cl···H interaction. There are very low binding energies for the $F_3CCl\cdots HBeH$ and $F_3CCl\cdots HBeF$ complexes and also for the $F_3SiCl\cdots HBeH$ and $F_3SiCl\cdots HBeF$ species. The low binding energies correspond to the long H···Cl distances of these systems, which are close to the sum of van der Waals radii. Similarly, such a long distance is observed for the $F_3SiCl\cdots HLi$ complex. However, in the latter case there is a meaningful binding energy. The results derived from the decomposition of the interaction energy are very interesting. Almost for all of the systems, the first-order attractive electrostatic interaction energy term is balanced by the exchange repulsive interaction energy; hence, the first-order Heitler−London energy term is close to zero. Sometimes (with the F_2NCl Lewis acid) the exchange outweighs the electrostatic energy significantly, and the system is stable due to the other attractive energy terms: delocalization and dispersion. The latter term is the main attractive component of the correlation energy. For two complexes, $F_3SiCl\cdots HBeH$ and $F_3SiCl\cdots HBeF$, the correlation and electrostatic energies are comparable. This may confirm the suggestion mentioned above that these complexes are bound through van der Waals interactions and not through halogen−hydride interaction since the dispersion energy is very important here. There is a similar situation for $F_3CCl\cdots HBeH$ and $F_3CCl\cdots HBeF$ complexes where the binding energies are greater since F_3CCl is a stronger Lewis acid than F_3SiCl.

Figure 2 shows the dependence between the Cl···H distance and the interaction energy components. Closed symbols correspond to systems with HBeH and HBeF Lewis bases, and open symbols correspond to systems with a LiH Lewis base. If the X−Cl···H−Li complexes are excluded from consideration, then one can observe the monotonic changes of energy components with a decrease of the Cl···H distance.

The geometrical and energetic results presented above are generally very similar for all levels of approximation applied, and the changes of these parameters do not depend systematically on the basis set used (all results were obtained within the MP2 method). For example, for the $F_3CCl\cdots HLi$ complex, the Cl···H distances are close to each other for the 6-311++G(3df,3pd) and aug-cc-pVTZ basis sets (2.65 and 2.66 Å, respectively), and this is very close for the 6-311++G(2df,2pd) and aug-cc-pVDZ basis sets (2.72 and 2.70 Å, respectively). For complexes with HBeH and HBeF Lewis bases,

TABLE 2: MP2 Binding Energies (kcal/mol) and the Results of the Decomposition of Interaction Energies (kcal/mol)[a]

	$E_{EL}^{(1)}$	$E_{EX}^{(1)}$	$E_{DEL}^{(R)}$	E_{CORR}	ΔE_{MP2}	$E_{EL}^{(1)}$	$E_{EX}^{(1)}$	$E_{DEL}^{(R)}$	E_{CORR}	ΔE_{MP2}
			$F_3CCl\cdots HLi$					$F_3SiCl\cdots HLi$		
A	−6.44	6.92	−2.12	−1.44	−3.08	−2.99	2.94	−0.83	−0.96	−1.84
B	−7.14	8.25	−2.51	−1.99	−3.39	−3.55	3.83	−1.03	−1.35	−2.10
C	−6.77	7.25	−2.26	−1.61	−3.39	−3.84	3.74	−1.05	−1.18	−2.33
D	−6.88	7.94	−2.41	−2.19	−3.54	−3.30	3.60	−1.00	−1.46	−2.16
			$F_3CCl\cdots HBeH$					$F_3SiCl\cdots HBeH$		
A	−1.18	1.38	−0.28	−0.68	−0.76	−0.60	0.79	−0.11	−0.54	−0.46
B	−1.59	2.27	−0.46	−1.07	−0.85	−0.89	1.43	−0.20	−0.86	−0.52
C	−1.40	1.71	−0.36	−0.84	−0.89	−0.83	1.08	−0.17	−0.68	−0.60
D	−1.40	1.89	−0.38	−1.06	−0.95	−0.72	1.09	−0.15	−0.81	−0.59
			$F_3CCl\cdots HBeF$					$F_3SiCl\cdots HBeF$		
A	−0.83	1.16	−0.22	−0.69	−0.58	−0.41	0.68	−0.08	−0.53	−0.34
B	−1.26	2.15	−0.41	−1.12	−0.64	−0.71	1.41	−0.18	−0.89	−0.37
C	−0.99	1.50	−0.29	−0.87	−0.65	−0.59	1.02	−0.14	−0.72	−0.43
D	−1.05	1.67	−0.32	−1.06	−0.76	−0.54	1.02	−0.13	−0.82	−0.47
			$F_2NCl\cdots HBeH$					$F_2NCl\cdots HBeF$		
A	−2.48	3.33	−0.98	−1.08	−1.21	−1.71	2.61	−0.74	−1.06	−0.90
B	−2.84	4.12	−1.20	−1.44	−1.36	−2.15	3.61	−1.01	−1.46	−1.01
C	−2.46	3.24	−0.98	−1.13	−1.33	−1.65	2.55	−0.73	−1.14	−0.97
D	−2.59	3.62	−1.06	−1.47	−1.50	−1.88	3.01	−0.84	−1.45	−1.16

[a] The MP2 method and different basis sets were applied: (A) MP2/6-311++G(2df,2pd), (B) MP2/6-311++G(3df,3pd), (C) MP2/aug-cc-pVDZ, (D) MP2/aug-cc-pVTZ.

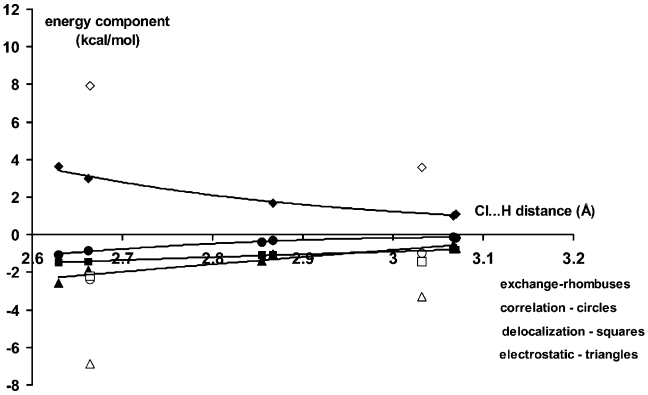

Figure 2. Correlation between the Cl···H distance (Å) and the components of the interaction energy (kcal/mol): electrostatic interaction energy, triangles; first-order Heitler−London exchange energy, tilted squares; higher order delocalization energy, squares; correlation energy, circles. The empty figures correspond to LiH complexes, full ones to the remaining species. The figure is based on MP2/aug-cc-pVTZ results.

the Cl···H distances obtained at the MP2/6-311++G(2df,2pd) level differ from the remaining distances, which are very similar to each other. Similarly, Table 2 shows that the energetic results are usually different for the 6-311++G(2df,2dp) basis set; however, this is not the rule, and generally the differences are not systematic.

Table 3 presents some results based on the Mulliken population analysis. The dipole moments of the monomers and complexes are presented; also the enhancements of dipole moments as a result of complexation are included. This means that the dipole moment of the complex is compared with the vector sum of the monomers' dipole moments. One can see that the enhancement is the most meaningful for complexes with LiH species. It is partly connected with the transfer of electron charge between two interacting species within the complex. There are also complexes with the meaningful decrease of the dipole moment within the complex as compared with monomers. This is because the dipole vectors of monomers connected have opposite directions; such a situation occurs for HBeF species. Table 3 also presents the transfer of electrons from X−Cl to H−Y species. This is not in line with the idea of acid−base interaction. However, these results are based on the Mulliken population analysis, and they may be incredible.[31] The more reliable results of charges, based on AIM theory, are discussed in the next section.

TABLE 3: Dipole Moments of Isolated Monomers and of the Corresponding Complexes (D), Enhancements of Dipole Moments (Δ*μ*, D) as a Result of Complexation, and Transfer of Charge from the Lewis Base to the Lewis Acid (Δ, au)[a]

	dipole moment				
A···B	A	B	complex	$\Delta\mu$	Δ
$F_3CCl\cdots HLi$	0.6016	6.0263	7.7103	1.0824	0.0143
$F_3SiCl\cdots HLi$	0.7104	6.0263	7.5873	0.8506	−0.0090
$F_3CCl\cdots HBeH$	0.6016	0.0010	0.8050	0.2024	0.0175
$F_3SiCl\cdots HBeH$	0.7104	0.0010	0.8839	0.1725	0.0180
$F_3CCl\cdots HBeF$	0.6016	0.8990	0.0159	−1.4847	0.0131
$F_3SiCl\cdots HBeF$	0.7104	0.8990	0.1027	−1.5067	0.0156
$F_2NCl\cdots HBeH$	1.0470	0.0010	1.5245	0.4765	0.0103
$F_2NCl\cdots HBeF$	1.0470	0.8990	0.6136	−1.3297	0.0582

[a] All results correspond to the MP2/aug-cc-pVTZ level of approximation.

TABLE 4: AIM Charges (au) of Cl and H Atoms (Those Which Constitute Cl···H Contacts)[a]

	Q_{Cl}	Q_H	Δ	Q_{Cl}	Q_H	Δ
		$F_3CCl\cdots Hli$			$F_3SiCl\cdots Hli$	
A	−0.0840	−0.8771	−0.0356	−0.7537	−0.9020	−0.0091
B	−0.0958	−0.8834	−0.0296	−0.7485	−0.8999	−0.0113
C	−0.0848	−0.8762	−0.0405	−0.7328	−0.8953	−0.0197
D	−0.0944	−0.8730	−0.0399	−0.7782	−0.8977	−0.0133
		$F_3CCl\cdots HBeH$			$F_3SiCl\cdots HBeH$	
A	−0.1154	−0.8524	−0.0099	−0.7547	−0.8541	−0.0073
B	−0.1267	−0.8458	−0.0122	−0.7483	−0.8489	−0.0082
C	−0.1170	−0.8485	−0.0094	−0.7321	−0.8510	−0.0086
D	−0.1249	−0.8492	−0.0111	−0.7765	−0.8499	−0.0056
		$F_3CCl\cdots HBeF$			$F_3SiCl\cdots HBeF$	
A	−0.1193	−0.8287	−0.0058	−0.7554	−0.8297	−0.0034
B	−0.1305	−0.8249	−0.0082	−0.7489	−0.8272	−0.0056
C	−0.1215	−0.8295	−0.0085	−0.7327	−0.8313	−0.0064
D	−0.1287	−0.8236	−0.0069	−0.7784	−0.8252	−0.0046
		$F_2NCl\cdots HBeH$			$F_2NCl\cdots HBeF$	
A	0.1137	−0.8465	−0.0157	0.1096	−0.8250	−0.0115
B	0.1227	−0.8390	−0.0199	0.1190	−0.8199	−0.0159
C	0.1208	−0.8420	−0.0188	0.1163	−0.8250	−0.0136
D	0.1037	−0.8428	−0.0194	0.0997	−0.8192	−0.0134

[a] Δ designates the charge transferred from the Lewis base to the Lewis acid (au). Key: (A) MP2/6-311++G(2df,2pd), (B) MP2/6-311++G(3df,3pd), (C) MP2/aug-cc-pVDZ, (D) MP2/aug-cc-pVTZ.

Topological Parameters. Table 4 presents the integrated AIM charges of the Cl and H interacting atoms. The Δ values representing the amount of charge transferred from the Lewis

TABLE 5: Topological Parameters Concerning Cl···H Contacts: Electron Densities (au) at H···Y BCPs, Their Laplacians (au), and the Energetic Parameters (au) of BCPs (*G*, Kinetic Energy Electron Density at BCP; *V*, Potential Electron Energy Density)[a]

	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	G	V	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	G	V
		$F_3CCl\cdots HLi$				$F_3SiCl\cdots HLi$		
A	0.0105	0.0310	0.0066	−0.0055	0.0057	0.0177	0.0035	−0.0025
B	0.0122	0.0340	0.0076	−0.0068	0.0070	0.0207	0.0042	−0.0033
C	0.0111	0.0310	0.0067	−0.0057	0.0069	0.0197	0.0040	−0.0030
D	0.0121	0.0324	0.0074	−0.0066	0.0068	0.0193	0.0040	−0.0032
		$F_3CCl\cdots HBeH$				$F_3SiCl\cdots HBeH$		
A	0.0052	0.0192	0.0037	−0.0025	0.0036	0.0129	0.0024	−0.0016
B	0.0074	0.0250	0.0051	−0.0040	0.0053	0.0181	0.0035	−0.0026
C	0.0063	0.0210	0.0043	−0.0033	0.0046	0.0151	0.0030	−0.0022
D	0.0066	0.0224	0.0045	−0.0035	0.0045	0.0156	0.0030	−0.0020
		$F_3CCl\cdots HBeF$				$F_3SiCl\cdots HBeF$		
A	0.0048	0.0119	0.0034	−0.0023	0.0033	0.0122	0.0022	−0.0014
B	0.0073	0.0249	0.0051	−0.0040	0.0054	0.0185	0.0036	−0.0026
C	0.0060	0.0202	0.0042	−0.0033	0.0047	0.0153	0.0031	−0.0023
D	0.0063	0.0216	0.0043	−0.0033	0.0045	0.0152	0.0029	−0.0021
		$F_2NCl\cdots HBeH$				$F_2NCl\cdots HBeF$		
A	0.0095	0.0331	0.0068	−0.0053	0.0083	0.0298	0.0060	−0.0046
B	0.0112	0.0367	0.0079	−0.0066	0.0106	0.0352	0.0075	−0.0062
C	0.0098	0.0308	0.0067	−0.0058	0.0088	0.0280	0.0061	−0.0052
D	0.0104	0.0336	0.0073	−0.0061	0.0095	0.0314	0.0067	−0.0055

[a] Key: (A) MP2/6-311++G(2df,2pd), (B) MP2/6-311++G(3df,3pd), (C) MP2/aug-cc-pVDZ, (D) MP2/aug-cc-pVTZ.

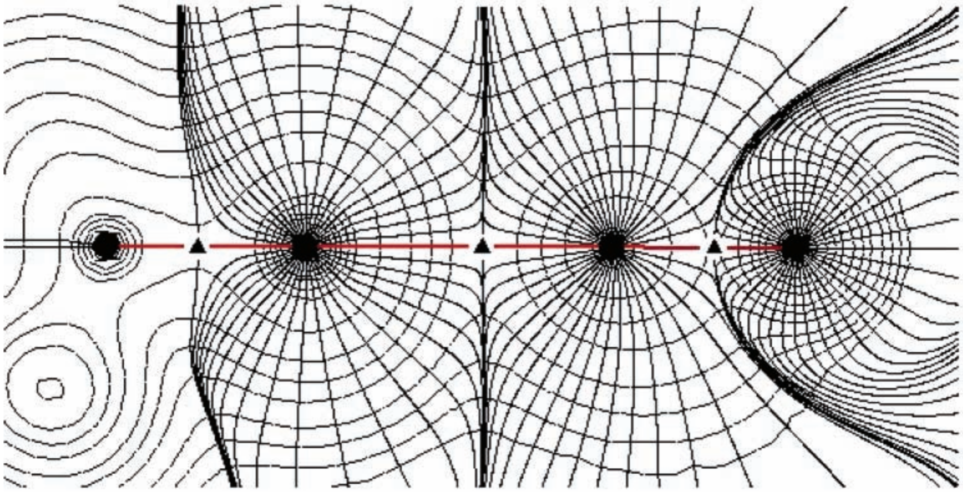

Figure 3. Contour map of the electron density for the $F_3CCl\cdots HLi$ complex: attractors C, Cl, H, and Li from the left side of the figure. The figure is based on MP2/aug-cc-pVTZ results.

base to the Lewis acid as a result of complexation are also included. There is the greatest transfer for the $F_3CCl\cdots HLi$ complex. It is in the range of 30−40 millielectrons (from LiH to F_3CCl); this depends on the level of approximation. It is worth mentioning that for the trans-linear dimer of water the transfer from the proton acceptor to the donor is equal to 23 millielectrons.[32] However, this value was obtained at the MP2/6-311++G(d,p) level of approximation and from the Mulliken population analysis. For the $F_2NCl\cdots HBeH$ system there is a transfer of 16−20 millielectrons from BeH_2 to the Lewis acid. For the $F_2NCl\cdots HBeF$ complex such a transfer amounts to 12−16 millielectrons. For the remaining complexes the transfer is less than 10 millielectrons.

The AIM charge of the electron-donating H-atom is equal from −0.87 to −0.90 for the LiH molecule and from −0.82 to −0.85 for the remaining H(Be)-atoms. The diversity of the Cl charges is even greater. For F_2NCl the chlorine is positive, while for the remaining Lewis acids it is negative. Despite that fact, the latter interactions are attractive, confirming the idea that the Lewis acidity of chlorine is sometimes connected with the anisotropy of the electron charge distribution.

The other topological parameters derived from the Bader theory[28] are also analyzed here. Table 5 presents the topological parameters of the complexes investigated; the electron density at the Cl···H bond critical point (BCP) $\rho(\mathbf{r})$, its Laplacian $\nabla^2\rho(\mathbf{r})$, and the energetic topological parameters G and V are included. G represents the electron kinetic energy density, while V is the potential electron energy density. Figure 3 presents a contour map of the electron density for the $F_3CCl\cdots HLi$ complex. One can observe the slight anisotropy of the electron density for the chlorine atom; such anisotropy is in line with the findings for halogen bonds that are well-known in the literature[11] where the Hal···Y (Y is a Lewis base center such as O, N, etc.) interactions are usually stronger than the interactions considered here. Also the anisotropies of halogen atoms are more meaningful.

There is poor correlation between the Cl···H distance and the electron density at the corresponding BCP. For the MP2/6-311++G(3df,3pd) level of approximation, the linear correlation coefficient for this dependence amounts to 0.93. There are similar results for the other levels. However, it is better than for the relationship between the Cl···H distance and the binding energy where no correlation is observed as was mentioned above. The other topological parameters confirm that the Cl···H interactions are rather weak. The Laplacians $\nabla^2\rho(\mathbf{r})$ are positive for interactions between closed-shell systems, and the

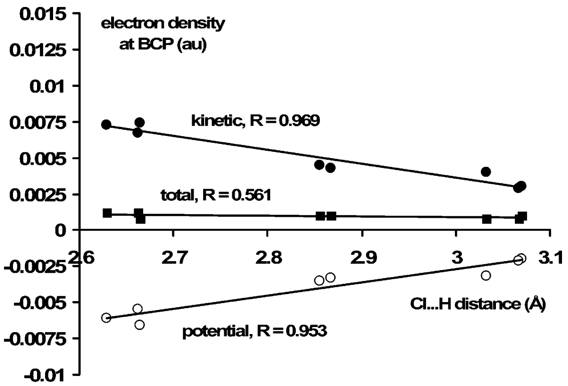

Figure 4. Dependencies between the Cl···H distance (Å) and topological energetic parameters (au): total electron energy density at BCP, H (■); kinetic electron energy density at BCP, G (●); potential electron energy density at BCP, V (○). The figure is based on MP2/aug-cc-pVTZ results.

H values are positive. H designates the total electron energy density. It is claimed in the literature from time to time that if the Laplacian value is negative for any interaction which is not covalent, then such an interaction is covalent in nature. This was found for some very strong hydrogen bonds.[33] G is always positive, and V is negative. Since $^1/_4\nabla^2\rho(\mathbf{r}) = 2G + V$ and $H = G + V$, and if $\nabla^2\rho(\mathbf{r})$ is positive and H is negative, then the interaction may be treated as not weak but at least as medium in strength and as partly covalent in nature.[34] Figure 4 presents the dependencies between the Cl···H distance and the energetic topological parameters H, V, and G for the complexes analyzed here. One can see that the changes of these parameters are monotonic; G increases, V decreases, and H practically does not change if the Cl···O distance decreases.

Summary

A new type of interaction, halogen−hydride, is not described yet and is analyzed here. It may be designated as C(Si)−Hal···$H^{\delta-}$−Y, where C(Si)−Hal is the Lewis acid and H−Y is the Lewis base. It was found that there is a transfer of electron charge from the base to the acid as a result of the formation of the complex. The systems analyzed here are at most medium in strength since for the strongest halogen−hydride contact the binding energy is about 3.5 kcal/mol.

Some of the systems investigated here may be classified as those where halogen−hydride bonding exists, but some of complexes are weakly bound and hence may be attributed to van der Waals interactions.

It seems that the halogen−hydride bond described here is a rare phenomenon since only four cases of similar interactions were found in the Cambridge Structural Database. Besides, the latter interactions from the CSD were not investigated in detail and only hardly may be classified as halogen−hydride interactions. The latter crystal structures' findings show that halogen−hydride weak interaction is not competitive for stronger interactions such as hydrogen bonds, halogen bonds, dihydrogen bonds, and hydride bonds.

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