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Charge-Transfer Complexes between Dihalogen Compounds and Electron Donors

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A theoretical study of the charge-transfer complexes formed by dihalogen compounds (F_2, Cl_2, Br_2, FBr, FCl, and ClBr) and electron donors (FH, OH_2, NH_3, CO, NCH, and C_2H_2) has been carried out. The geometries, energies, and electronic and spectroscopic properties of these complexes have been compared with the corresponding properties of the hydrogen bonded complexes of FH with the same electron donors. The hybrid HF-DFT, B3LYP, and second-order Møllet−Plesset perturbation, MP2, methods have been used. The properties analyzed include geometry, energy, electron distribution using the atoms in molecules (AIM) methodology, and spectroscopic constants of the complexes and monomers. Similarities in the variations of the geometries, in the trends in the interaction energetic, and in the topological electron density characteristics between the properties of the HB complexes and the dihalogen charge-transfer systems are pointed out. The main differences correspond to the variation trend of the atomic properties and the NMR shielding when going from the monomers to the complexes.

Introduction

The charge-transfer complexes, as defined by Mulliken[1] in 1969, include a number of situations as the hydrogen bonds (HBs) and complexes where a halogen atom acts as an electron acceptor (named in this article as halogen bonded (HalB) complexes in homology to the HB ones). These interactions have been shown to be important in different molecular recognition processes such as crystal packing.[2,3]

While much effort has been devoted to the study of HB complexes, extending the possible electron donor (carbenes,[4,5] isocyanides,[6] radicals,[7,8] π-systems,[9] and metal hydrides[10,11]) and electron acceptor groups (C−H moiety[12,13]), experimental studies of charge-transfer HalB complexes have been limited, for experimental reasons, mostly to complexes with iodine. More recently, the development of new methods for interrupting the vigorous reaction of hydrogen compounds with halogens has allowed characterization of a number of pre-reactive HalB complexes, using Fourier transform microwave spectroscopy, where the interacting halogen atom includes bromine, chlorine, and fluorine.[14,15]

A number of theoretical studies have focused their attention on these kinds of interactions. Thus, in 1950 Mulliken theoretically and experimentally examined the complexes between halogen molecules and aromatic and oxygenated solvents.[16] The experimental description of the "anti-hydrogen bonded" complexes of FH with dihalogen molecules in the 1980s produced a theoretical study of the relative stability of the HB and HalB complexes of these molecules.[17] More recently, the complex formed by $BrONO_2\cdots H_2O$ was shown to be a nearly linear O−Br···O configuration, as the authors note "like in conventional HBs".[18] The natural bond orbital (NBO) analysis indicates a charge transfer from the acetylene to the FCl molecule and a $\pi_{C-C} \rightarrow \sigma^*_{ClF}$ donor−acceptor interaction as the source of the charge transfer for the acetylene−chlorine monofluoride ($C_2H_2\cdots ClF$) system.[19] Finally, calculations performed on the I_2−pyridine[20] systems show a binding energy of about 9 kcal/mol and a charge transfer between 0.2 and 0.3 *e*.

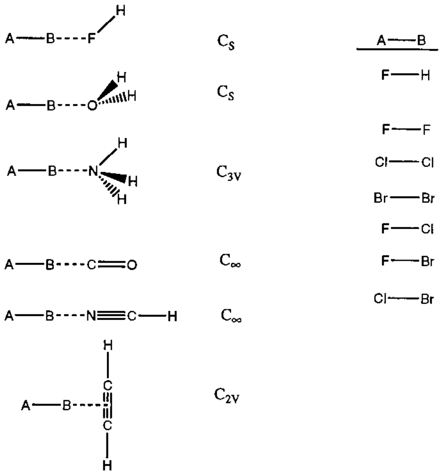

Figure 1. Schematic representation of the complexes studied.

In the present article, the complexes formed by six dihalogen molecules (FF, ClCl, BrBr, FCl, FBr, and ClBr) with six electron donor molecules (FH, OH_2, NH_3, CO, NCH, and C_2H_2) have been studied using hybrid HF-DFT (B3LYP) and MP2 methods. A comparative analysis of the properties of the present complexes with the parallel HB series formed by F−H and the six electron donor monomers has been carried out.

Methods

The charge-transfer complexes formed by six dihalogen molecules (FF, ClCl, BrBr, FCl, FBr, and ClBr) with six electron donor molecules (FH, OH_2, NH_3, CO, NCH, and C_2H_2) have been studied as shown in Figure 1. The less electronegative atom of the dihalogen molecule has been pointed toward the electron rich center of the electron donor molecules in order to generate a favorable dipole−dipole interaction.

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TABLE 1: Calculated and Experimental Intermolecular Distances (Å) and the Experimental Intermolecular Stretching Constants, *k* (N/m)

	B3LYP/6-31G*	B3LYP/6-311++G**	MP2/6-311++G**	expt	*k*	exptl data taken from given ref
FH···FH			1.874			
FH···OH_2			1.730			
FH···NH_3			1.703			
FH···CO			2.132			
FH···NCH			1.887			
FH···HCCH			2.186			
FF···FH	2.422	2.666	2.713			
FF···OH_2	2.387	2.356	2.641	2.719	3.6	32
FF···NH_3	2.214	1.986	2.594	2.708	4.69	33
FF···CO	2.701	2.765	3.005			
FF···NCH	2.680	2.668	2.805	2.803	2.61	34
FF···HCCH	2.596	2.481	2.901			
ClCl···FH	2.658	2.875	2.917	2.960	4.5	35
ClCl···OH_2	2.578	2.667	2.780			
ClCl···NH_3	2.384	2.448	2.621	2.730	12.71	36
ClCl···CO	2.913	3.048	3.180	3.134	3.7	37
ClCl···NCH	2.812	2.860	2.920	2.917	6.5	38
ClCl···HCCH	2.927	3.031	3.173	3.163	5.6	37
BrBr···FH	2.731	2.964	3.161			
BrBr···OH_2	2.629	2.733	2.823			
BrBr···NH_3	2.492	2.551	2.624	2.720	18.5	39
BrBr···CO	2.881	3.090	3.208			
BrBr···NCH	2.850	2.900	2.939			
BrBr···HCCH	2.944	3.093	3.193			
FCl···FH	2.531	2.668	2.777	2.760	7.23	40
FCl···OH_2	2.454	2.457	2.588	2.575	14.2	41
FCl···NH_3	2.337	2.277	2.312	2.370	34.3	42
FCl···CO	2.640	2.597	2.937	2.770	7.03	43
FCl···NCH	2.631	2.559	2.698	2.639	12.25	44
FCl···HCCH	2.754	2.787	2.958	2.869	9.98	45
FBr···FH	2.547	2.713	2.816			
FBr···OH_2	2.487	2.501	2.572			
FBr···NH_3	2.385	2.361	2.358			
FBr···CO	2.388	2.317	2.759			
FBr···NCH	2.540	2.505	2.625			
FBr···HCCH	2.749	2.740	2.878			
ClBr···FH	2.635	2.884	2.961			
ClBr···OH_2	2.576	2.655	2.765			
ClBr···NH_3	2.431	2.490	2.570	2.672	26.7	46
ClBr···CO	2.748	2.927	3.136	3.004	6.18	46
ClBr···NCH	2.749	2.794	2.874	2.834	11.2	47
ClBr···HCCH	2.867	2.996	3.134	3.059	9.4	46

The geometries of the monomers and the complexes have been fully optimized with the program Gaussian-94[21] using the standard 6-31G*[22] and 6-311++G**[23] basis sets and the hybrid Hartree−Fock-density functional method (Becke3LYP).[24] Post-Hartree−Fock calculations have been carried out at the second-order Møller−Plesset (MP2) level[25] with the largest basis set.

In addition, the HB complexes formed by FH and the six electron donor molecules previously mentioned have been optimized at the B3LYP/6-311++G** and MP2/6-311++G** levels of theory.

The selected level of calculation allows for comparison of the B3LYP method with the MP2 one. The latter method in conjunction with an extended basis set that includes diffuse and polarization functions in all of the atoms, as the 6-311++G**, is considered adequate for the study of HB interactions[26] and provides results in agreement with experimental data for some HalB complexes.[19]

The nature of the monomers and complexes as a potential energy minimum has been established at the B3LYP/6-31G* and MP2/6-311++G** levels in all cases by verifying that the corresponding frequencies are all positive. The interaction energies, $E_I(AB)$, have been calculated as the difference between the energy of the complex and the sum of the energies of the monomers (eq 1), where $E(AB)_{AB}$ represents the energy of the complex and $E(A)_A$ the energy of the isolated monomer A calculated with its corresponding basis set.

$$E_I(AB) = E(AB)_{AB} - [E(A)_A + E(B)_B] \qquad (1)$$

In addition, a corrected interaction energy (E_{I+BSSE}) excluding the inherent basis set superposition error (BSSE) has been evaluated. The BSSE has been calculated using the Boys−Bernardi counterpoise technique[27] and eq 2, where $E(A)_{AB}$

$$E_{BSSE}\,(AB) = E(A)_A - E(A)_{AB} + E(B)_B - E(B)_{AB} \qquad (2)$$

represents the energy calculated for monomer A using its geometry in the complex and the complete set of basis functions used to described the dimer and $E(A)_A$ the energy for monomer A using its geometry in the complex and its basis set.

The corrected interaction energies have been calculated with eq 3.

$$E_{I+BSSE}(AB) = E_I(AB) + E_{BSSE}(AB) \qquad (3)$$

The topological properties of the electronic charge density and the atomic charges have been characterized using the atoms in molecules methodology (AIM)[28] with the AIMPAC program package[29] at the MP2/6-311++G** level. The AIM methodology self-consistently partitioned any system and its properties into its atomic fragments by considering the gradient vector field of its electron density distribution. A 0.001 e/au^3 electron density has been used to define the atomic volume.

Nuclear magnetic resonance (NMR) spectroscopic shieldings of the isolated molecules and complexes have been calculated using the gauge-independent atomic orbital (GIAO) perturbation method[30] as implemented in the Gaussian-94 program. This perturbation method, as suggested by London, proposes local gauge origins to define the vector potential of the external electric field.[31]

Results and Discussion

Geometry. The calculated and experimentally available intermolecular distances have been gathered in Table 1. The hybrid HF-DFT (B3LYP/6-31G* and B3LYP/6-311++G**) methods used here provide the shortest distances when compared to the MP2/6-311++G** results or to the experimental ones. The results obtained with the latter methods are the closest to the experimental ones with an average absolute error of 0.066 Å, while the corresponding error for the hybrid HF-DFT methods is 0.200 Å for B3LYP/6-31G* and 0.160 Å for B3LYP/6-311++G**.[32−47]

The largest error obtained for the hybrid HF-DFT methods corresponds to the complexes formed between homodihalogen compounds and the electron donors. Those errors can reach values of 0.494 at B3LYP/6-31G*and 0.722 Å at B3LYP/6-311++G** for the $F_2\cdots NH_3$. The largest error at the MP2/6-311++G** level is 0.167 Å in the $FCl\cdots CO$ complex.

The longest interacting distances always correspond to those complexes where the electron donors have the smallest dipole moments and at the same time are the weakest bases, CO and HCCH. The shortest distances correspond to the complexes with OH_2 and NH_3. The same tendencies are observed in the HBs reported in Table 1.

The calculated bond angles in the HalBs, as well as in the HBs, defined as $X-Y\cdots Z$ (where XY is the dihalogen molecule in the HalB systems and Z the electron donor group; in the case of HCCH the center of the molecule has been considered) are almost linear in all cases. For example, the largest deviation from linearity in the $X-Y\cdots Z$ angle corresponds to the $Cl_2\cdots FH$ and $FH\cdots FH$ systems with values of 177 and 172°, respectively.

The formation of the HalB complexes produces an elongation of the dihalogen bond. This effect is generally very small in the weakest complexes, although, it can reach values of 0.065 Å in cases such as the strong $FBr\cdots NH_3$ complex. Something similar occurs in the HB complexes. For example, the FH bond elongates by 0.03 Å on the $FH\cdots NH_3$ complex. In contrast, the geometrical perturbation on the electron donor groups is always very small, for instance in the two strong complexes mentioned above, where only a lengthening of 0.002 Å is produced in the NH bonds.

Energy. The interaction energy, BSSE correction, and corrected interaction energy have been collected in Table 2. These methods that provide the shortest distances, B3LYP/6-31G* and B3LYP/6-311++G**, are those that provide the largest interaction energies for each complex studied.

As expected, the dihalogen molecules with the largest dipole moments (FBr > FCl > ClBr), or in the case of homodihalogen those which are most polarizable ($Br_2 > Cl_2 > F_2$), have the largest interaction energies. Regarding the electron donor atoms, the strongest complexes are those formed with NH_3. They are approximately two times stronger than those of OH_2 and NCH. The weakest complexes correspond to those with FH, CO, and HCCH. The same trend is observed in the case of the HBs calculated here. The BSSE correction is especially important for these calculations with the 6-31G* basis set where it can represent, in some cases, over 75% of the uncorrected interaction energy. The smallest effects of this correction correspond to the B3LYP/6-311++G** calculations, which are not greater than 1.0 kcal/mol.

A Free−Wilson model[48] of the corrected interaction energy, $E_{\mathrm{I+BSSE}}$, at the MP2/6-311++G** level, as a function of the different monomers involved in the complexes, can be established:

$$E_{\mathrm{I+BSSE}} = \sum X_i Y_i$$

where the coefficients X_i are 1 if the monomer i is present and 0 if not and Y_i indicates the contribution of that monomer to $E_{\mathrm{I+BSSE}}$. To avoid the singularity of the matrix, the correlation should be carried out with respect to a reference monomer which by definition has a Y_i coefficient equal to 0.0. In this case the reference monomer chosen is FH. The corresponding coefficients for the rest of the monomers are gathered in Table 3, and the correlation coefficient obtained is $r^2 = 0.926$ for the 36 cases studied. The values of the coefficients agree with the previous analysis of the $E_{\mathrm{I+BSSE}}$ as a function of the monomers involved. In addition, the coefficients of the electron donors follow the same tendency as the experimental proton affinities.[49]

A set of good linear correlations between the energy of the complexes for each electron donor and those obtained in the corresponding HB complexes with HF (Figure 2) is obtained:

$$E_{\mathrm{I+BSSE}}(\text{HalB complexes with } F_2) = -0.053 + 0.093E_{\mathrm{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.957$$

$$E_{\mathrm{I+BSSE}}(\text{HalB complexes with } Cl_2) = 0.198 + 0.325E_{\mathrm{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.964$$

$$E_{\mathrm{I+BSSE}}(\text{HalB complexes with } Br_2) = 0.352 + 0.505E_{\mathrm{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.949$$

$$E_{\mathrm{I+BSSE}}(\text{HalB complexes with FCl}) = 0.789 + 0.806E_{\mathrm{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.951$$

$$E_{\mathrm{I+BSSE}}(\text{HalB complexes with FBr}) = 0.939 + 1.164E_{\mathrm{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.927$$

$$E_{\mathrm{I+BSSE}}(\text{HalB complexes with ClBr}) = 0.447 + 0.619E_{\mathrm{I+BSSE}}(\text{HB complexes with FH}), \quad r^2 = 0.952$$

This indicates a direct relation between the ability of the electron donor to form charge-transfer complexes and their basicity in the gas phase denoted by the strength of their HB. A related experimental correlation has been described in the literature between the free energy of I_2 complexation in a series of sulfur compounds and their corresponding proton affinities in the gas phase.[50]

An acceptable linear correlation is obtained between the corrected interaction energies at the MP2 level and the experimental intermolecular stretching constants, k, of these

TABLE 2: Calculated Interaction Energy, E_I, BSSE Correction, and Corrected Interaction Energy, E_{I+BSSE} (kcal/mol)

	E_I			BSSE			E_{I+BSSE}		
	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**	B3LYP/ 6-31G*	B3LYP/ 6-311++G**	MP2/ 6-311++G**
FH···FH			−4.75			0.97			−3.78
FH···OH_2			−9.73			2.19			−7.54
FH···NH_3			−13.37			2.20			−11.17
FH···CO			−3.58			0.57			−3.01
FH···NCH			−7.27			0.76			−6.51
FH···HCCH			−4.40			1.26			−3.14
FF···FH	−2.36	−0.56	−1.01	2.09	0.30	0.67	−0.27	−0.26	−0.34
FF···OH_2	−3.13	−2.29	−2.11	1.87	0.75	1.44	−1.26	−1.54	−0.67
FF···NH_3	−5.02	−8.71	−2.54	1.65	1.00	1.44	−3.37	−7.71	−1.10
FF···CO	−1.24	−0.73	−0.85	0.98	0.28	0.52	−0.26	−0.45	−0.33
FF···NCH	−1.25	−1.01	−1.31	0.71	0.25	0.57	−0.54	−0.76	−0.74
FF···HCCH	−2.11	−1.92	−1.63	1.39	0.44	1.24	−0.72	−1.48	−0.39
ClCl···FH	−4.20	−1.24	−1.56	3.16	0.26	0.73	−1.04	−0.98	−0.83
ClCl···OH_2	−6.22	−3.52	−3.41	2.20	0.61	1.40	−4.02	−2.91	−2.01
ClCl···NH_3	−11.19	−8.39	−5.39	1.25	0.78	1.78	−9.94	−7.61	−3.61
ClCl···CO	−2.11	−1.11	−1.48	1.04	0.28	0.63	−1.07	−0.83	−0.85
ClCl···NCH	−2.69	−2.11	−2.68	0.72	0.28	0.81	−1.97	−1.83	−1.87
ClCl···HCCH	−3.02	−1.81	−2.35	0.88	0.31	1.27	−2.14	−1.50	−1.08
BrBr···FH	−5.72	−1.56	−1.87	4.39	0.17	0.63	−1.33	−1.39	−1.24
BrBr···OH_2	−8.08	−4.21	−4.25	3.64	0.49	1.28	−4.44	−3.72	−2.97
BrBr···NH_3	−12.86	−9.41	−7.47	3.22	0.63	1.83	−9.64	−8.78	−5.64
BrBr···CO	−3.83	−1.25	−1.78	2.58	0.09	0.49	−1.25	−1.16	−1.29
BrBr···NCH	−4.40	−2.70	−3.59	1.91	0.17	0.79	−2.49	−2.53	−2.80
BrBr···HCCH	−5.07	−2.13	−2.82	2.57	0.14	1.12	−2.50	−1.99	−1.70
FCl···FH	−5.77	−2.73	−2.72	3.34	0.46	0.74	−2.43	−2.27	−1.98
FCl···OH_2	−8.85	−7.13	−6.06	2.27	0.86	1.63	−6.58	−6.27	−4.43
FCl···NH_3	−14.68	−15.15	−11.28	1.46	0.95	2.42	−13.22	−14.20	−8.86
FCl···CO	−3.85	−3.21	−2.53	1.42	0.37	0.56	−2.43	−2.84	−1.97
FCl···NCH	−4.88	−5.17	−4.85	0.90	0.35	0.74	−3.98	−4.82	−4.11
FCl···HCCH	−4.74	−4.26	−3.62	1.19	0.41	1.37	−3.55	−3.85	−2.25
FBr···FH	−8.05	−3.58	−3.42	4.82	0.36	0.67	−3.23	−3.22	−2.75
FBr···OH_2	−11.90	−9.13	−8.02	4.31	0.87	1.67	−7.59	−8.26	−6.35
FBr···NH_3	−18.57	−18.13	−15.56	3.99	0.87	2.40	−14.58	−17.26	−13.16
FBr···CO	−8.04	−6.01	−3.96	4.20	0.48	0.73	−3.84	−5.53	−3.23
FBr···NCH	−7.89	−7.53	−7.03	2.61	0.45	0.89	−5.28	−7.08	−6.14
FBr···HCCH	−8.22	−5.98	−5.11	3.25	0.36	1.45	−4.97	−5.62	−3.66
ClBr···FH	−6.57	−2.10	−2.26	4.34	0.24	0.70	−2.23	−1.86	−1.56
ClBr···OH_2	−9.49	−5.43	−5.08	3.60	0.64	1.46	−5.89	−4.79	−3.62
ClBr···NH_3	−15.47	−11.58	−9.00	3.36	0.84	2.09	−12.11	−10.74	−6.91
ClBr···CO	−4.76	−2.01	−2.33	2.73	0.28	0.72	−2.03	−1.73	−1.61
ClBr···NCH	−5.46	−3.80	−4.37	1.93	0.33	0.97	−3.53	−3.47	−3.40
ClBr···HCCH	−6.18	−3.00	−3.39	2.63	0.32	1.40	−3.55	−2.68	−1.99

TABLE 3: Coefficients of the Free−Wilson Model of the Corrected Interaction Energy, E_{I+BSSE} (MP2/6-311++G), as a Function of the Monomers, and the Proton Affinity of the Electron Donor Moieties**

monomer	Y_i coeff (kcal/mol)	monomer	Y_i coeff (kcal/mol)	exptl[49] proton affinity (kcal/mol)
FF	0.9	FH	0.0[a]	117.0
ClCl	−0.2	OH_2	−1.9	166.5
BrBr	−1.1	NH_3	−5.1	204.0
FCl	−2.4	CO	−0.1	141.7
FBr	−4.3	NCH	−1.7	171.0
ClBr	−1.6	HCCH	−0.4	153.3

[a] By definition.

complexes, as shown in Figure 3. The following equation for the 19 cases experimentally available was obtained, with a good correlation coefficient and a small standard deviation:

$$E_{I+BSSE} = -(0.270 \pm 0.007)k; \quad r^2 = 0.989; \quad SD = 0.4; \quad N = 19$$

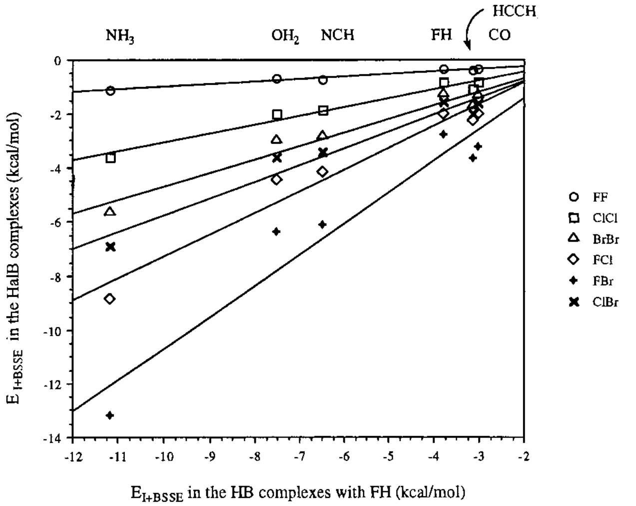

Figure 2. Linear correlation between the interaction energies of each series of HalB complexes and the corresponding HB ones.

Electronic Properties. One of the most characteristic properties of these complexes is the charge transfer between the interacting monomers, as has been calculated using the AIM methodology (Table 4). The expected electron transfer from the electron donor to the electron acceptor is observed for most of the complexes. The exceptions are those where FH acts as electron donor. In two of these cases (FH···FH and F_2···FH) it acts as electron donor, with very small electronic loss, but it

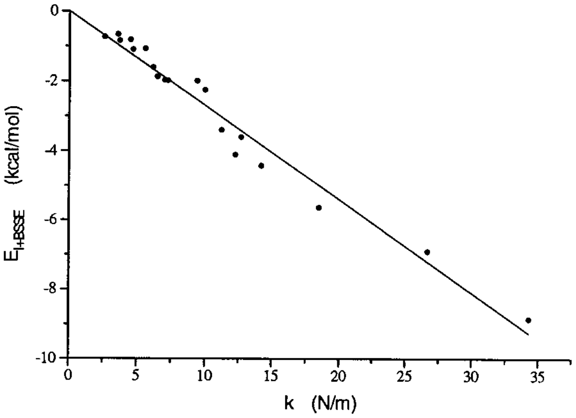

Figure 3. Calculated corrected interaction energy, E_{I+BSSE}, at the MP2/6-311++G** level vs experimental intermolecular stretching force constant, *k*.

TABLE 4: Charge Transfer (*e*), within the AIM Methodology, and Dipole Moment (D) of the Calculated Monomers and Complexes at the MP2/6-311++G Level**

system	charge transfer	dipole moment	system	charge transfer	dipole moment
FF		0.00	ClCl···CO	−0.009	0.63
ClCl		0.00	ClCl···NCH	−0.010	3.73
BrBr		0.00	ClCl···HCCH	−0.022	0.45
FCl		1.35	BrBr···FH	0.005	2.31
FBr		1.83	BrBr···OH_2	−0.012	3.06
ClBr		0.52	BrBr···NH_3	−0.088	4.43
FH		1.97	BrBr···CO	−0.010	0.85
OH_2		2.19	BrBr···NCH	−0.012	4.13
NH_3		1.74	BrBr···HCCH	−0.026	0.76
CO		0.28	FCl···FH	0.000	3.33
HCN		3.00	FCl···OH_2	−0.027	4.06
HCCH		0.00	FCl···NH_3	−0.157	5.92
FH···FH	−0.008	3.68	FCl···CO	−0.019	2.20
FH···OH_2	−0.034	4.49	FCl···NCH	−0.023	5.33
FH···NH_3	−0.064	4.80	FCl···HCCH	−0.040	2.07
FH···CO	−0.023	2.84	FBr···FH	0.001	3.86
FH···NCH	−0.030	5.86	FBr···OH_2	−0.025	5.33
FH···HCCH	−0.033	2.53	FBr···NH_3	−0.163	6.95
FF···FH	−0.003	2.02	FBr···CO	−0.043	3.19
FF···OH_2	−0.012	2.24	FBr···NCH	−0.039	6.38
FF···NH_3	−0.038	2.13	FBr···HCCH	−0.061	3.08
FF···CO	−0.011	0.40	ClBr···FH	0.004	2.73
FF···NCH	−0.011	3.21	ClBr···OH_2	−0.016	3.54
FF···HCCH	−0.025	0.16	ClBr···NH_3	−0.100	5.02
ClCl···FH	0.003	2.23	ClBr···CO	−0.018	1.41
ClCl···OH_2	−0.011	2.74	ClBr···NCH	−0.015	4.69
ClCl···NH_3	−0.069	3.47	ClBr···HCCH	−0.031	1.32

is clearly "harder" than the rest of the electron donors treated here. In the rest of the cases, the acceptor fluorine atom gains small amounts of electronic population, more so when it interacts with the more polarizable and less polar dihalogen. These results are in agreement with the experimental data that indicate that the FH complexes are a borderline case, forming in some cases only HB complexes (F_2···HF, Br_2···HF, and FBr··· HF), a mixture with HalB complexes (Cl_2···FH and Cl_2···HF), or mainly a HalB complex (FCl···FH).[51]

The charge transferred, especially in the complexes with NH_3, is very large (0.16 *e* in the complexes with FCl and FBr), indicating the formation of a highly dipolar complex. This effect is clearly confirmed by the large dipole moment of those complexes (Table 4). In fact, several of the complexes of NH_3 with different dihalogen molecules (Cl_2, Br_2, ClBr, FBr, and ClBr) possess a dipole moment that is more than twice the value of the sum of the isolated monomers. This is an indication of a strong polarization of the systems.

TABLE 5: Electron Density (*e*/au^3), ρ_{bcp}, Laplacian (*e*/au^5), $\nabla^2\rho_{bcp}$, at the Bond Critical Points and Distance from That Point to the Atoms Involved in the Interaction (Å) at the MP2/6-311++G Level**

syst (X−Y···Z)	ρ_{bcp}	$\nabla^2\rho_{bcp}$	$r_{Y\cdots bcp}$	$r_{bcp\cdots Z}$
FH···FH	0.0206	0.0990	0.657	1.220
FH···OH_2	0.0366	0.1415	0.560	1.171
FH···NH_3	0.0501	0.1196	0.519	1.184
FH···CO	0.0177	0.0609	0.710	1.422
FH···NCH	0.0270	0.1012	0.620	1.267
FH···HCCH	0.0158	0.0529	0.747	1.562
FF···FH	0.0073	0.0389	1.295	1.421
FF···OH_2	0.0221	0.0534	1.221	1.421
FF···NH_3	0.0164	0.0695	1.165	1.430
FF···CO	0.0062	0.0268	1.351	1.653
FF···NCH	0.0082	0.0381	1.286	1.519
FF···HCCH	0.0081	0.0333	1.314	1.700
ClCl···FH	0.0089	0.0430	1.535	1.383
ClCl···OH_2	0.0155	0.0626	1.423	1.359
ClCl···NH_3	0.0273	0.0899	1.306	1.316
ClCl···CO	0.0082	0.0322	1.581	1.599
ClCl···NCH	0.0122	0.0503	1.480	1.440
ClCl···HCCH	0.0087	0.0322	1.587	1.699
BrBr···FH	0.0089	0.0393	1.613	1.400
BrBr···OH_2	0.0168	0.0617	1.472	1.352
BrBr···NH_3	0.0318	0.0907	1.329	1.295
BrBr···CO	0.0094	0.0332	1.630	1.578
BrBr···NCH	0.0141	0.0525	1.519	1.420
BrBr···HCCH	0.0100	0.0339	1.634	1.673
FCl···FH	0.0115	0.0541	1.438	1.342
FCl···OH_2	0.0221	0.0888	1.304	1.285
FCl···NH_3	0.0508	0.1423	1.138	1.174
FCl···CO	0.0127	0.0488	1.442	1.495
FCl···NCH	0.0184	0.0752	1.346	1.352
FCl···HCCH	0.0124	0.0464	1.466	1.611
FBr···FH	0.0125	0.0549	1.482	1.337
FBr···OH_2	0.0245	0.1003	1.295	1.277
FBr···NH_3	0.0526	0.1285	1.170	1.188
FBr···CO	0.0217	0.0722	1.381	1.378
FBr···NCH	0.0252	0.0929	1.329	1.296
FBr···HCCH	0.0172	0.0584	1.458	1.545
ClBr···FH	0.0097	0.0427	1.579	1.384
ClBr···OH_2	0.0186	0.0684	1.435	1.331
ClBr···NH_3	0.0350	0.0979	1.296	1.274
ClBr···CO	0.0106	0.0376	1.587	1.549
ClBr···NCH	0.0157	0.0589	1.478	1.396
ClBr···HCCH	0.0110	0.0374	1.599	1.651

The values of the electron density at the bond critical points, ρ_{bcp}, as well as the Laplacian, $\nabla^2\rho$ (Table 5), indicate that these complexes correspond to open shell interactions. The ρ_{bcp} obtained for the complexes with heterodihalogen are similar to the ones corresponding to the HBs formed by FH with the different electron donors. The complexes with homodihalogen show the smallest values of ρ_{bcp}; however, they are still in the range of weak HBs (for instance 0.0093 *e*/au^3 for the FH··· benzene complex).

Another characteristic that has been compared between the HB and the HalB is the topology of the electron density. Except in cases where the electron donor is HCCH, the bond path connecting the two interacting atoms is almost linear. The position of the bcp between the two interacting atoms moves closer to the electron donor atom as the polarity of the electron acceptor increases. Thus, the position of the bcp is closer to the electron donor atoms in the FH complexes followed by FBr, FCl, and ClBr, and the farthest correspond to the homodihalogen complexes.

In the complexes with HCCH, the topology of the HBs has been described as a catastrophic configuration[9] and the same is observed here for the HalB (as example, the FBr···HCCH complex is represented in Figure 4). This configuration presents

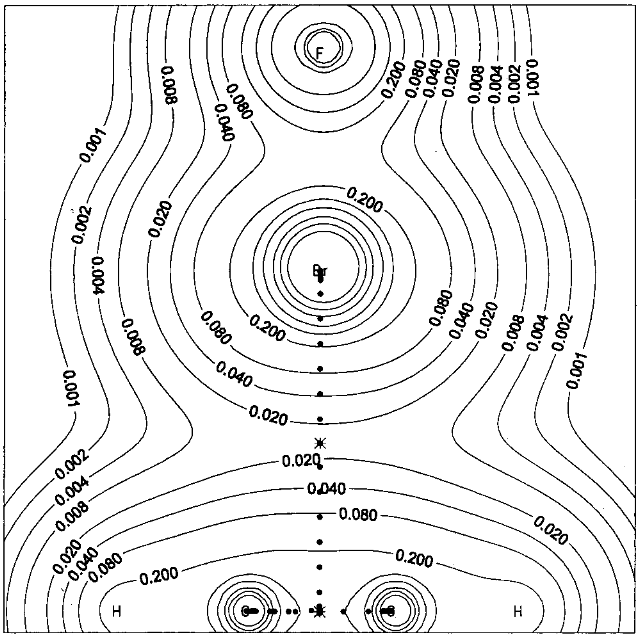

Figure 4. Electron density (e/au^3) map of the FBr···HCCH complex. The asterisks represent the position of the bond critical points and the dots the bond path.

a unique bond critical point and partially the same bond path for the two carbon atom···halogen interactions (or carbon···hydrogen in the HB systems). As shown elsewhere,[9,27] a minimal distortion of the symmetry of these systems breaks this situation, giving place to individual bond paths for each interaction.

Using the AIM methodology, the properties of the atoms involved in the HBs have been used to characterize these interactions.[52] However, several of the properties used in the original study have shown exceptions,[8] even though they can be useful on an initial analysis of these interactions. Regarding the charge variation of the hydrogens involved in HB, a loss of atomic charge occurred in most of the cases, as expected, except in the case of the complex with HCCH. A similar charge reduction is observed in the electron acceptor halogen of the HalB complexes (Table 6) with the exceptions of all the FX···Y complexes (where X is F, Cl, and Br and Y is NH_3, CO, and HCCH). The latter indicates an important electronic withdrawal of the fluorine atom, that is in the extreme position, from its partner.

A reduction of the hydrogen atom's volume in HBs has been generally observed,[52] with exceptions in cases with weak long-distance interactions. In the case of HalB complexes, an increase of the atomic volume of the interacting halogen is observed in the three F_2 complexes with CO, NCH, and HCCH (Table 6). Although these complexes, with long HalB distances, are in general weaker than the rest, it is not clear if there is a general rule for these exceptions.

An atomic energy destabilization is observed in the hydrogen involved in HBs.[9,52] The HalBs studied here do not follow this tendency. Only in three cases (complexes of F_2 with FH, OH_2, and NH_3) is an energy destabilization observed, while in the rest an atomic stabilization is obtained (Table 6).

There are three cases where the variation of the atomic dipolar polarization is positive (complexes FF···CO, FF···HCCH, and FBr···HCCH). In the remaining cases the variation is negative following the same tendency as that in the HBs (Table 6).

Spectroscopic Properties. The variation of two spectroscopic properties from the monomers to the HB and HalB complexes have been studied. The first corresponds to the IR stretching band of the dihalogen bond (X−H bond in the case of the HB complexes), and the second corresponds to the NMR shielding of the halogen (hydrogen in the HB complexes) involved in the interaction.

TABLE 6: Atomic Properties (au) of the Interacting Halogen Atom in the HalB Complex (Hydrogen in the HB Cases) Calculated within the AIM Framework of the Monomers and Their Variation in the Complexes at the MP2/6-311++G Level**

	net charge	vol	energy	dipolar polarizn
FH	0.7116	15.82	−0.2957	0.1264
FF	0.0000	103.33	−99.6350	0.2487
ClCl	0.0000	219.41	−459.7386	0.3383
BrBr	0.0000	264.92	−2575.1245	0.2552
FCl	0.3552	207.30	−459.6304	0.6738
FBr	0.4364	251.73	−2572.1547	0.7756
ClBr	0.1161	263.64	−2574.9770	0.4395

	Δ (net charge)	Δ (vol)	Δ (energy)	Δ (dipolar polarizn)
FH···FH	0.0197	−5.93	0.0090	−0.0262
FH···OH_2	0.0198	−7.61	0.0146	−0.0311
FH···NH_3	0.0119	−9.08	0.0131	−0.0336
FH···CO	0.0051	−4.82	0.0055	−0.0132
FH···NCH	0.0152	−6.45	0.0140	−0.0232
FH···HCCH	−0.0017	−5.09	0.0033	−0.0080
FF···FH	0.0063	−0.39	0.0182	−0.0155
FF···OH_2	0.0058	−1.79	0.0090	−0.0188
FF···NH_3	−0.0046	−2.53	0.0047	−0.0182
FF···CO	−0.0026	1.19	−0.0268	0.0038
FF···NCH	0.0044	0.08	−0.0563	−0.0098
FF···HCCH	−0.0149	1.14	−0.0429	0.0096
ClCl···FH	0.0241	−5.01	−0.0189	−0.0663
ClCl···OH_2	0.0327	−8.16	−0.0178	−0.0934
ClCl···NH_3	0.0270	−11.68	−0.0083	−0.1152
ClCl···CO	0.0093	−1.74	−0.0864	−0.0252
ClCl···NCH	0.0290	−6.20	−0.1113	−0.0693
ClCl···HCCH	0.0011	−2.75	−0.0855	−0.0265
BrBr···FH	0.0306	−3.69	−0.2699	−0.0829
BrBr···OH_2	0.0457	−8.38	−0.2983	−0.1237
BrBr···NH_3	0.0476	−12.98	−1.1572	−0.1501
BrBr···CO	0.0167	−1.43	−0.3265	−0.0419
BrBr···NCH	0.0424	−7.48	−0.3988	−0.1014
BrBr···HCCH	0.0075	−2.67	−0.2848	−0.0435
FCl···FH	0.0143	−5.42	−0.0319	−0.0784
FCl···OH_2	0.0047	−9.06	−0.0464	−0.1253
FCl···NH_3	−0.0728	−9.91	−0.0613	−0.2423
FCl···CO	−0.0044	−3.20	−0.1352	−0.0429
FCl···NCH	0.0058	−6.58	−0.1827	−0.1043
FCl···HCCH	−0.0236	−3.47	−0.1413	−0.0466
FBr···FH	0.0183	−6.45	−3.0022	−0.1022
FBr···OH_2	0.1072	−15.43	−2.4583	−0.1044
FBr···NH_3	−0.0641	−9.63	−0.9856	−0.2762
FBr···CO	−0.0116	−4.89	−3.2459	−0.0972
FBr···NCH	0.0059	−10.29	−3.3398	−0.1667
FBr···HCCH	−0.0323	−8.22	−0.1682	−0.0753
ClBr···FH	0.0280	−7.74	−1.4924	−0.0922
ClBr···OH_2	0.0381	−11.16	−1.4910	−0.1403
ClBr···NH_3	0.0230	−16.48	−0.0343	−0.1919
ClBr···CO	0.0081	−5.29	−1.6083	−0.0641
ClBr···NCH	0.0355	−8.78	−0.2025	−0.1179
ClBr···HCCH	0.0006	−5.93	−1.5872	−0.0536

The formation of an HB produces a reorganization of the electron density in the surroundings of the hydrogen atom with a subsequent loss of electron density in the covalent bond in favor of the HB. This effect produces a weakening of the covalent bond in the complex and thus a decrease in the corresponding stretching frequency (Table 7). The observed frequency shifts due to the formation of the complex are dependent on the nature of both the electron acceptor and donor molecules. However, some generalizations can be made. The

TABLE 7: Dihalogen Bond (X−H Bond in the HB Complexes) Harmonic Stretching Frequencies (cm^{-1}) in the Isolated Monomers and Complexes Calculated at the MP2/6-311++G Level, the Variation Observed, Δ, with Respect to the Isolated Monomers, and the Percent Variation Weighted to the Absolute Value of the Monomer Frequency, % Variation**

monomers	stretching freq	monomers	stretching freq
FH	4197	FCl	733
FF	899	FBr	636
ClCl	546	ClBr	444
BrBr	330		

complexes	stretching freq	Δ	% variation
FH···FH	4104	−93	−2.2
FH···OH_2	3851	−346	−8.2
FH···NH_3	3481	−716	−17.1
FH···CO	4068	−129	−3.1
FH···NCH	3958	−239	−5.7
FH···HCCH	4041	−156	−3.7
FF···FH	891	−8	−0.8
FF···OH_2	874	−25	−2.7
FF···NH_3	812	−87	−9.6
FF···CO	886	−13	−1.4
FF···NCH	879	−20	−2.2
FF···HCCH	864	−35	−3.9
ClCl···FH	543	−3	−0.6
ClCl···OH_2	532	−14	−2.5
ClCl···NH_3	480	−65	−12.0
ClCl···CO	540	−6	−1.0
ClCl···NCH	534	−12	−2.2
ClCl···HCCH	532	−13	−2.5
BrBr···FH	329	−1	−0.3
BrBr···OH_2	322	−8	−2.3
BrBr···NH_3	290	−39	−12.0
BrBr···CO	326	−4	−1.2
BrBr···NCH	323	−7	−2.1
BrBr···HCCH	320	−10	−2.9
FCl···FH	727	−6	−0.9
FCl···OH_2	703	−30	−4.1
FCl···NH_3	589	−145	−19.7
FCl···CO	715	−19	−2.6
FCl···NCH	705	−28	−3.9
FCl···HCCH	698	−35	−4.8
FBr···FH	632	−4	−0.6
FBr···OH_2	613	−23	−3.7
FBr···NH_3	552	−85	−13.3
FBr···CO	615	−21	−3.3
FBr···NCH	613	−23	−3.6
FBr···HCCH	604	−32	−5.0
ClBr···FH	442	−2	−0.5
ClBr···OH_2	432	−12	−2.7
ClBr···NH_3	390	−54	−12.1
ClBr···CO	438	−6	−1.4
ClBr···NCH	433	−11	−2.5
ClBr···HCCH	431	−13	−3.0

TABLE 8: Absolute NMR Shieldings (ppm) of the Atom in the Electron Acceptor Monomers Involved in the Interaction (in Italics) Calculated Using the GIAO Perturbation Theory at the B3LYP/6-311++G Level**

σ monomers	NMR shielding	σ monomers	NMR shielding
F*H*	30.2	F*Cl*	−726.5
F*F*	−247.3	F*Br*	−1908.5
Cl*Cl*	449.5	Cl*Br*	793.0
Br*Br*	1502.9		

σ complexes	NMR shielding	$\Delta\sigma$	σ complexes	NMR shielding	$\Delta\sigma$
F*H*···FH	28.1	2.2	Br*Br*···CO	1546.1	−43.1
F*H*···OH_2	25.4	4.8	Br*Br*···NCH	1427.5	75.5
F*H*···NH_3	22.8	7.4	Br*Br*···HCCH	1654.3	−151.4
F*H*···CO	29.2	1.1	F*Cl*···FH	−682.0	−44.4
F*H*···NCH	27.7	2.6	F*Cl*···OH_2	−507.6	−218.9
F*H*···HCCH	28.1	2.1	F*Cl*···NH_3	−135.3	−591.1
F*F*···FH	−253.9	6.6	F*Cl*···CO	−440.6	−285.9
F*F*···OH_2	−285.6	38.3	F*Cl*···NCH	−575.8	−150.7
F*F*···NH_3	−193.2	−54.1	F*Cl*···HCCH	−411.8	−314.7
F*F*···CO	−261.1	13.8	F*Br*···FH	−1587.9	−320.6
F*F*···NCH	−298.8	51.5	F*Br*···OH_2	−909.6	−998.9
F*F*···HCCH	−214.2	−33.2	F*Br*···NH_3	124.2	−2032.7
Cl*Cl*···FH	424.3	25.2	F*Br*···CO	331.6	−2240.1
Cl*Cl*···OH_2	428.7	20.8	F*Br*···NCH	−787.5	−1121.0
Cl*Cl*···NH_3	483.5	−34.0	F*Br*···HCCH	−454.9	−1453.6
Cl*Cl*···CO	448.0	1.5	Cl*Br*···FH	767.9	25.1
Cl*Cl*···NCH	399.1	50.4	Cl*Br*···OH_2	889.5	−96.5
Cl*Cl*···HCCH	484.5	−35.0	Cl*Br*···NH_3	1235.1	−442.1
Br*Br*···FH	1440.3	62.6	Cl*Br*···CO	974.4	−181.5
Br*Br*···OH_2	1474.9	28.0	Cl*Br*···NCH	834.1	−41.1
Br*Br*···NH_3	1647.4	−144.5	Cl*Br*···HCCH	1093.6	−300.6

largest variations are observed when the electron donor is NH_3 > C_2H_2 > OH_2 > NCH > CO > FH. This tendency holds for all the HalB complexes studied. In the case of the HB complexes, the same tendency is observed except for the C_2H_2 case, whose effect is smaller than that of NCH.

The numerical analysis of these variations with respect to the absolute value of the stretching frequency in the monomers (given as a percentage in Table 7) shows striking similarities for each electron donor through the HalB series studied. Thus, the variations observed are in the following ranges: 0.9−0.3 (FH as electron donor), 3.3−1.0 (CO), 3.9−2.1 (NCH), 4.1−2.3 (OH_2), 5.0−2.5 (C_2H_2), and 19.7−9.6% (NH_3). The upper limit corresponds to a complex with a heterodihalogen and the lower one to a complex with a homodihalogen.

The absolute NMR shieldings of the HB and HalB complexes are gathered in Table 8. In contrast to the uniform shift of the signals to lower fields observed in the hydrogen involved in the HBs, the halogens of the HalB complexes only follow this tendency in some homodihalogens. The reverse is observed for all the heterodihalogen complexes, except for ClBr···FH in which an important reverse charge transfer is observed, as mentioned before. In addition, while in the HBs the observed effect follows the trend of the interaction energy, where stronger complexes provide larger changes in shielding, in the HalB there is not such relationship; even though, in general, the largest negative effect corresponds to the complexes with NH_3 and the smallest to those with FH.

Conclusions

The geometric, electronic (including the AIM analysis), and spectroscopic properties of a series of charge-transfer complexes formed between dihalogen compounds (F_2, Cl_2, Br_2, FBr, FCl, and ClBr) and electron donors groups (FH, OH_2, NH_3, CO, NCH, and C_2H_2), as well as the HB complexes of FH with the same electron donors, have been calculated. The comparison of these two sets of charge-transfer complexes (HB and HalB complexes) shows some similarities and differences.

The similarities found between HalBs and HBs include to geometrical variation of the monomers in the formation of the complexes, the trend in interaction energy with respect to the electron donor molecule, the electronic properties of the bcp (ρ_{bcp} and $\nabla^2\rho_{bcp}$), the topology of the electron density, and the changes in the IR signal corresponding to the bond stretching of the dihalogen bond in the HalB complexes and the X−H bond in the HB ones.

The differences observed are the lack of regularities in the variation of the atomic properties calculated for the interacting halogen within the AIM methodology (charge, volume, energy, dipolar polarization) in contrast to the ones observed for the HB complexes. In addition, the changes in the NMR shieldings of the interacting atom in the HalB are not dependent on the strength of the complexes.

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