Theor Chem Acc (2003) 110:1–9
DOI 10.1007/s00214-003-0448-0

Theoretical
Chemistry Accounts

Feature article

The intermolecular interaction in the charge-transfer complexes between amines and halogens: A theoretical characterization of the trends in halogen bonding

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Received: 11 February 2003 / Accepted: 15 April 2003 /

Abstract. The trends in the properties of prereactive or charge-transfer complexes formed between the simple amines NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ and the halogens F_2, ClF, Cl_2, BrF, BrCl, and Br_2 were investigated by the ab initio restricted Hartree–Fock approach, the Møller–Plesset second-order method, and with several density functional theory variants using extended polarized basis sets. The most important structural parameters, the stabilization energies, the dipole moments, and other quantities characterizing the intermolecular halogen bond in these complexes are monitored, discussed, and compared. A wide range of interaction strengths is spanned in these series. Successive methyl substitution of the amine as well as increasing polarities and polarizabilities of the halogen molecules both systematically enhance the signature of charge-transfer interaction. These trends in halogen bonds of varying strength, in many aspects, parallel the features of hydrogen bonding.

Keywords: Intermolecular interaction – Charge-transfer complexes – Amines and halogens – Møller–Plesset second-order method – Density functional theory

Introduction

Charge-transfer (CT) complexes formed between halogens and Lewis bases constitute an interesting and important class of intermolecular compounds. At least in principle, CT complexes, often also termed electron donor–acceptor complexes or Lewis acid–base complexes, are suitable objects for systematic theoretical studies of some basic features of intermolecular interactions. Experimental investigation of these complexes in the gas phase is, however, a difficult task. Owing to the high reactivity of halogens with amines, resulting in different halogenated amines as reaction products, the complexes are extremely short-lived. Only with the aid of pulsed-nozzle, Fourier transform microwave spectroscopy can these complexes be analyzed in a collision-free environment. In his pioneering rotational spectroscopic investigations, Legon [1, 2] succeeded in preparing and structurally analyzing a large number of these prereactive complexes between halogens XY and different Lewis bases.

The complexes formed between the first members of aliphatic amines, $(CH_3)_nNH_{3-n}$, and halogens are also generally considered to fall into the class of CT complexes. These dimers may be viewed as being held together by the formation of a halogen bond, reminiscent of the well-known case of hydrogen bonding. The close analogy of many structural and spectroscopic trends between hydrogen-bonded systems and CT complexes with halogens has already been pointed out by Legon [1, 2] and Alkorta et al. [3]. The terms halogen bond and chlorine bond have been used to stress that the intermolecular interaction in hydrogen-bonded dimers has much in common with that in CT complexes. The most characteristic features of hydrogen bonding in a complex $A\text{–H}\cdots B$ have been summarized and amply discussed in the literature [4, 5].

In this overview, the $(CH_3)_nNH_{3-n}\text{–}XY$ complexes are dealt with systematically. We shall restrict X and Y to F, Cl, and Br. From this subgroup, the rotational spectra of the complexes of NH_3 with the halogens F_2 [6], ClF [7], Cl_2 [8], BrCl [9], and Br_2 [10] and of $(CH_3)_3N$ with F_2 [11] and ClF [12] have been studied by Legon and coworkers. From the gas-phase investigations of Legon and coworkers, the complexes of the halogens with NH_3 were characterized either as weak intermolecular complexes or as complexes with only a small contribution of an ionic valence-bond structure. The structure of the $(CH_3)_3N\text{–ClF}$ complex was described as being dominated by a significant contribution of an ionic $[(CH_3)_3NCl]^+\text{—}F^-$ valence-bond structure. Even stronger tendencies towards an $[(CH_3)_3NF]^+\text{—}F^-$ ionic structure were found for the $(CH_3)_3N\text{–}F_2$ complex. For the complexes of NH_3 with BrF, of trimethylamine with Cl_2, BrF, BrCl, and Br_2, and for the complexes of methylamine and dimethylamine with the six halogens no experimental gas-phase data are available so far. Experimental binding energies or gas-phase vibrational spectroscopic results are not available for any of these halogen–amine complexes.

Theoretical studies of amine–halogen complexes have been performed already. The term CT complex was coined by Mulliken [13] in a theoretical study of the interaction of benzene with I_2. Mulliken classified the CT complexes as "outer" and "inner" CT complexes, the outer CT complexes showing only small signs of CT, while the inner complexes have substantial CT. The relative importance of CT contributions versus classic electrostatic, i.e. Coulomb and polarization interactions, was actually strongly under debate [14, 15, 16]. Early ab initio restricted Hartree–Fock (RHF) calculations [17] and RHF energy partitioning studies [18, 19] led to the classification that the NH_3–F_2 and NH_3–Cl_2 complexes are weak electrostatic CT complexes [18], while NH_3–ClF was characterized as an intermediate electrostatic complex. With the aid of improved ab initio studies including electron correlation, and therefore also including the important contribution of the intermolecular dispersion energy, and with density functional theory (DFT) calculations [3, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35] the complexes of ammonia with the halogens XY, $X, Y \in \{\mathrm{F, Cl, Br}\}$, have been extensively studied. Corresponding theoretical studies on the complexes of halogens with methylated amines are much scarcer [22, 23, 28, 29, 33, 36, 37].

In this survey, new results for the complexes of the three amines CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ with the halogens Cl_2, BrF, BrCl, and Br_2, and of NH_3 with BrF, BrCl, and Br_2 are presented and compared to already published data for the NH_3–F_2 [29, 30, 31], NH_3–ClF [31], and NH_3–Cl_2 [31] complexes and the corresponding methylated amine complexes with F_2 [29] and ClF [33]. In some cases it turned out to be necessary to perform a few additional calculations for the two latter series as well. All calculations were done with the Gaussian 98 suite of programs [38]. The calculations were carried out at the RHF and Møller–Plesset second-order (MP2) [39] level, and with three DFT variants (B3LYP [40, 41, 42, 43], PW91PW91 [44], and BH&HLYP as implemented in Gaussian 98) using the extended, polarized 6-311++G(3df,2p) [45, 46, 47, 48, 49, 50] basis set. Complete structure optimizations including explicitly [51] the counterpoise correction to the basis set superposition error [52] were done at RHF, MP2, and DFT.

This overview aims at a coherent description of the binding energies and equilibrium structures of amine–halogen complexes. The striking similarity between the properties of halogen bonds and hydrogen bonds is discussed in detail. Therefore, emphasis is laid on a thorough description of the trends in equilibrium structures and stabilization energies. As main CT indicators, the calculated dipole moments, the dipole moment increases relative to the sum of monomer dipole moments, and atoms-in-molecule (AIM) [53] derived charges are used. Finally, other important and interesting properties, such as the trends in calculated nuclear quadrupole coupling constants (NQCC) and in selected vibrational frequencies and IR intensities are also discussed. More detailed results on the individual complexes including also post-MP2 results will be published separately.

CT complexes and hydrogen-bonded complexes

Quite similar to the more familiar case of hydrogen-bonded dimers, where the most interesting structural parameters are directly connected to the A–H···B hydrogen-bond geometry, the most important geometrical parameters in the amine–XY complexes are the two distances $R(\mathrm{N}\cdots X)$ and $R(X–Y)$ in the N···X–Y substructure. One prominent structural property of hydrogen bonds is the short intermolecular A···B distance. In most hydrogen-bonded complexes, this distance is well below the sum of the van der Waals radii of A and B, despite the presence of the H atom between A and B. Exceptions are only the very weakest, nonpolar hydrogen bonds. The intermolecular distance between the N atom of the amine and the inner halogen atom X is also considerably shorter than the sum of the van der Waals radii of N and X. Assuming accepted values of van der Waals radii of 1.6 Å for N, and of 1.5, 1.8, and 1.9 Å for F, Cl, and Br, respectively, one arrives at 3.1, 3.4, and 3.5 Å for the van der Waals distances in N···F_2, N···Cl–Y, and N···Br–Y. Experimental as well as calculated N···X distances are much shorter than these values, already for the weaker complexes with ammonia.

As with the stretching of the A–H bond upon formation of the hydrogen bond, the X–Y bond is lengthened upon forming the CT complex. This intramolecular structural relaxation leads to one of the most important spectroscopic means of detecting hydrogen bonds: the redshift of the A–H stretching frequency and the intensity increase observed in IR vibrational spectroscopy. Quite analogous features connected with the stretching and the increasing polarity of the X–Y bond of the halogen are expected to occur in CT complexes as well. So far, they could not be observed experimentally in the gas phase.

In the overwhelming majority of cases, isolated hydrogen bonds in the gas phase are nearly linear. In the complexes of halogens with amines, the N···X–Y moiety is also always close to linear. The structural relaxations in the amines taking place upon forming the CT complex are usually close to negligible, with the sole exception of the pyramidalization angle at the nitrogen atom, which is distorted from a near tetrahedral arrangement in the free amine in the direction toward a more planar structure of the amine in the CT complex. This widening of the R–N–R bond angles is proportional to the strength of the interaction and may, for example, amount to about 6° in the case of the strongly bound $(CH_3)_3N–F_2$ complex [29].

Increasing the strength of the hydrogen bond results in shorter intermolecular $H\cdots B$ distances and in even stronger A–H bond stretchings, leading eventually to strong, ionic and nearly symmetric hydrogen bonds (FHF^-, $H_5O_2^+$, hydrogen bonds in ionic solids, etc.) with binding energies close to those of chemical bonds. These strong hydrogen-bonded systems cannot be treated as intermolecular problems anymore. Increasing the strength of the CT interaction results in shorter $N\cdots X$ distances and further lengthenings of the $X–Y$ bond, and can thus lead to the case of "inner"-type CT complexes with strong ionic character, either nearly symmetric $N\cdot\cdot X\cdot\cdot Y$ arrangements or even $[N–X]^+—Y^-$ gas-phase ion pairs, and with large binding energies. For these strong CT complexes the intermolecular character is essentially lost. Experimental and theoretical structure determinations and the evaluation of binding energies are, therefore, the main sources for the characterization of CT complexes as "outer", "inner", or intermediate cases, with the obvious problem that a sharp categorization is necessarily arbitrary.

In the language of intermolecular perturbation theory, increasing the strength of the intermolecular interaction also results in enhanced mutual polarization and in stronger intermolecular CT, in both cases, hydrogen bonding and CT. As measures of both effects and as further descriptors, the dipole moment of the complexes, the enhancement relative to the monomer dipole moments, and the amount of intermolecular CT based either on integrations of the electron density or calculated with the aid of one of the population analysis schemes may be chosen. Of particular significance for the comparison with rotational spectroscopic results is the calculation of NQCC derived from electric field gradients at the nuclei. These are very sensitive to small changes in molecular structures. The variation of all the previously mentioned properties and the trends in the series of amine–halogen CT complexes are discussed in the following.

Equilibrium structures and stabilization energies

The calculated $R(N\cdots X)$ and $R(X–Y)$ distances compiled in Tables 1 and 2 and the stabilization energies reported in Table 3 illustrate the structural and energetic trends in the series of amine–XY complexes and shed light on the performance of the different calculation methods and their ability to describe this particular kind of intermolecular interaction. The increases of the calculated intramolecular $R(X–Y)$ distances are displayed graphically in Fig. 1.

Let us first turn to the results of the RHF method. While it is, generally, well known that the RHF approach is insufficient for accurate calculations of intermolecular interaction, it appears worthwhile to have a closer look at what goes wrong and by how much. At this level of approximation the electrostatic interaction, in the given case dominated by the dipole moment of the amine and the quadrupole moment of the halogens X_2 or the dipole moment of halogens XY, is expected to be approximately taken account of. Similarly, the polarization interaction, involving mainly the leading electrostatic moment of one partner and the dipole polarizability of the other, is usually acceptably well described in the case of hydrogen-bonded systems, although electron correlation contributions to the electrostatic moments and the polarizabilities of the monomers are clearly not negligible. Comparison of the RHF results in Tables 1, 2 and 3 with the available

Table 1. Calculated $R(N\cdots X)$ distances of amine–XY charge-transfer complexes as obtained with restricted Hartree–Fock (*RHF*), Møller–Plesset second-order perturbation theory (*MP2*), and density functional theory (*DFT*) methods using the 6-311++G(3df,2p) basis set (Å)

Halogen	Amine	RHF	MP2	B3LYP	BH&HLYP	PW91PW91	Experimental
F_2	NH_3	3.39	2.69	2.09	2.73	1.93	2.71 [6]
	CH_3NH_2	3.48	1.83	1.91	2.67	1.87	
	$(CH_3)_2NH$	3.48	1.84	1.84	2.60	1.84	
	$(CH_3)_3N$	3.46	1.85	1.80	2.55	1.82	~1.7 [54]
ClF	NH_3	2.70	2.27	2.27	2.34	2.20	2.37 [7]
	CH_3NH_2	2.60	2.14	2.20	2.24	2.15	
	$(CH_3)_2NH$	2.54	2.08	2.17	2.19	2.13	
	$(CH_3)_3N$	2.53	2.06	2.16	2.17	2.14	2.09 [12]
Cl_2	NH_3	3.11	2.71	2.54	2.70	2.39	2.73 [8]
	CH_3NH_2	3.06	2.51	2.42	2.59	2.32	
	$(CH_3)_2NH$	3.03	2.30	2.36	2.50	2.28	
	$(CH_3)_3N$	3.02	2.20	2.35	2.43	2.27	
BrF	NH_3	2.57	2.34	2.36	2.38	2.31	
	CH_3NH_2	2.49	2.26	2.31	2.31	2.27	
	$(CH_3)_2NH$	2.44	2.22	2.29	2.28	2.26	
	$(CH_3)_3N$	2.44	2.21	2.30	2.27	2.27	
BrCl	NH_3	2.93	2.57	2.52	2.60	2.44	2.63 [9]
	CH_3NH_2	2.85	2.42	2.45	2.49	2.38	
	$(CH_3)_2NH$	2.81	2.34	2.41	2.45	2.36	
	$(CH_3)_3N$	2.81	2.30	2.41	2.44	2.37	
Br_2	NH_3	3.05	2.66	2.58	2.68	2.48	2.72 [10]
	CH_3NH_2	2.98	2.49	2.50	2.57	2.42	
	$(CH_3)_2NH$	2.94	2.39	2.47	2.52	2.42	
	$(CH_3)_3N$	2.94	2.34	2.46	2.50	2.41	

Table 2. Calculated *R*(*X*–*Y*) distances of amine–*XY* charge-transfer complexes as obtained with RHF, MP2, and DFT methods using the 6-311++G(3df,2p) basis set (Å)

Halogen	Amine	RHF	MP2	B3LYP	BH&HLYP	PW91PW91	Experimental
F_2	NH_3	1.326	1.409	1.527	1.366	1.641	
	CH_3NH_2	1.326	1.734	1.634	1.367	1.703	
	$(CH_3)_2NH$	1.326	1.763	1.696	1.374	1.740	
	$(CH_3)_3N$	1.326	1.774	1.735	1.379	1.766	~1.9 [54]
ClF	NH_3	1.603	1.703	1.727	1.663	1.763	
	CH_3NH_2	1.608	1.743	1.752	1.684	1.787	
	$(CH_3)_2NH$	1.612	1.769	1.768	1.700	1.800	
	$(CH_3)_3N$	1.614	1.787	1.774	1.706	1.805	
Cl_2	NH_3	1.981	2.010	2.072	2.010	2.107	2.00 [8]
	CH_3NH_2	1.982	2.037	2.106	2.025	2.142	
	$(CH_3)_2NH$	1.983	2.093	2.133	2.040	2.166	
	$(CH_3)_3N$	1.982	2.138	2.143	2.055	2.174	
BrF	NH_3	1.753	1.837	1.854	1.805	1.881	
	CH_3NH_2	1.763	1.859	1.872	1.821	1.899	
	$(CH_3)_2NH$	1.770	1.874	1.882	1.831	1.908	
	$(CH_3)_3N$	1.771	1.881	1.885	1.833	1.911	
BrCl	NH_3	2.140	2.184	2.238	2.181	2.258	2.186 [9]
	CH_3NH_2	2.145	2.218	2.262	2.203	2.283	
	$(CH_3)_2NH$	2.148	2.248	2.280	2.217	2.298	
	$(CH_3)_3N$	2.148	2.263	2.286	2.221	2.302	
Br_2	NH_3	2.284	2.320	2.380	2.322	2.400	2.335 [10]
	CH_3NH_2	2.287	2.353	2.406	2.341	2.427	
	$(CH_3)_2NH$	2.289	2.384	2.422	2.355	2.439	
	$(CH_3)_3N$	2.289	2.403	2.430	2.358	2.456	

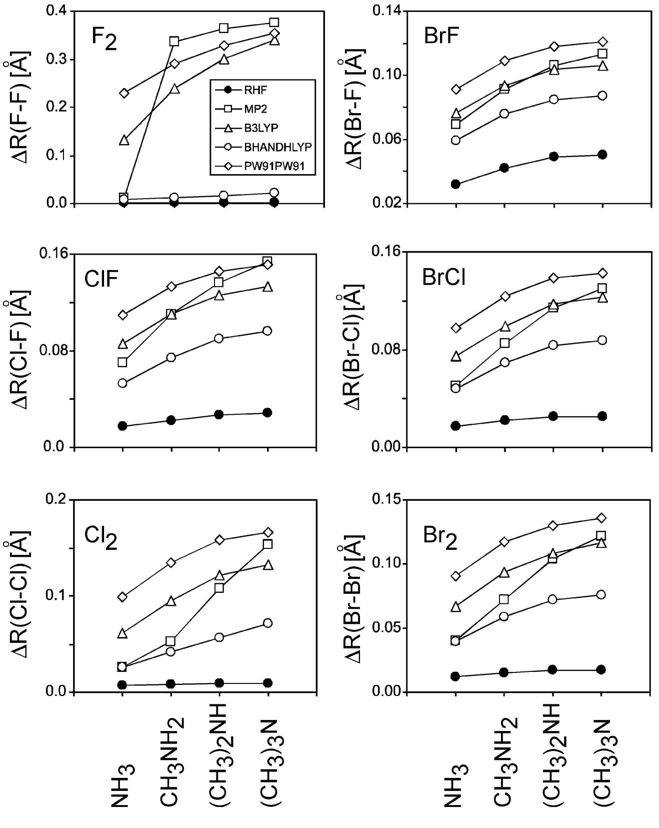

Fig. 1. Calculated lengthenings of the intramolecular *R*(*X*–*Y*) distances in amine–*XY* charge-transfer (*CT*) complexes

experimental data and with the MP2 and DFT results demonstrates, however, conclusively that the interaction between the halogens and the four amines cannot be satisfactorily described at the RHF level. The errors are much larger than in conventional hydrogen-bonded systems. Although, the RHF-calculated *R*(N···*X*) values (Table 1) are in most cases indeed shorter than the sum of the van der Waals radii, they are still considerably longer by about 0.3–0.5 Å than the available experimental results. The discrepancy is even much larger in the case of the amine–F_2 complexes, where the calculated values exceed the sum of the van der Waals radii (3.1 Å). What is at least qualitatively correctly described is the reduction of the calculated *R*(N···*X*) distances upon successive methylation of the amine, again with the exception of the complexes with F_2.

Parallel with the too long intermolecular distance, the increase of the intramolecular distance Δ*R*(*X*–*Y*) is calculated much too small at the RHF level in all six cases. This is particularly well visible in Fig. 1. This failure is already present in the NH_3–*XY* complexes and becomes progressively larger for the methylated amines. Furthermore, this failure is largest in the amine–X_2 complexes. To a certain degree this shortcoming is already buried in the too large harmonic force constant and therefore too high vibrational frequency obtained at the RHF level for the halogens, in particular for F_2.

The calculated RHF stabilization energies (Table 3) are much too small in absolute value. Most strikingly, however, there is no appreciable change of the RHF stabilization energies upon going from the ammonia to the trimethylamine complexes. The lack of the dispersion energy contribution to the intermolecular interaction and the too stiff intramolecular potential of the halogens are thus responsible for the incorrect description of CT complexes at the RHF level.

The MP2 and DFT results in these series show a completely different pattern. Where a systematic comparison to experimental quantities is possible, i.e., in the case of the complexes with ammonia, MP2- and

Table 3. Calculated stabilization energies, ΔE, of amine–XY charge-transfer complexes as obtained with RHF, MP2, and DFT methods using the 6-311++G(3df,2p) basis set (kcal mol^{-1})

Halogen	Amine	RHF	MP2	B3LYP	BH&HLYP	PW91PW91
F_2	NH_3	−0.32	−1.60	−4.61	−1.19	−14.56
	CH_3NH_2	−0.30	−7.16	−9.24	−1.38	−21.32
	$(CH_3)_2NH$	−0.29	−14.66	−13.59	−1.50	−26.20
	$(CH_3)_3N$	−0.26	−20.06	−16.50	−1.61	−28.93
ClF	NH_3	−4.80	−10.33	−12.55	−9.69	−17.93
	CH_3NH_2	−5.36	−14.73	−15.84	−12.05	−22.15
	$(CH_3)_2NH$	−5.61	−18.62	−17.82	−13.65	−24.56
	$(CH_3)_3N$	−5.51	−21.32	−18.31	−14.20	−25.11
Cl_2	NH_3	−1.95	−4.49	−5.61	−4.10	−9.49
	CH_3NH_2	−2.06	−6.20	−7.71	−5.02	−12.77
	$(CH_3)_2NH$	−2.04	−8.40	−9.11	−5.69	−14.80
	$(CH_3)_3N$	−1.94	−10.70	−9.56	−6.02	−15.37
BrF	NH_3	−8.04	−14.43	−15.55	−13.59	−20.30
	CH_3NH_2	−9.22	−18.81	−18.63	−16.16	−24.13
	$(CH_3)_2NH$	−9.72	−22.25	−20.10	−17.51	−25.96
	$(CH_3)_3N$	−9.43	−24.29	−20.04	−17.61	−25.99
BrCl	NH_3	−3.81	−7.82	−9.06	−7.29	−13.03
	CH_3NH_2	−4.19	−10.83	−11.46	−8.92	−16.27
	$(CH_3)_2NH$	−4.26	−13.70	−12.70	−9.83	−17.96
	$(CH_3)_3N$	−4.05	−15.78	−12.74	−9.97	−18.08
Br_2	NH_3	−2.84	−6.35	−7.42	−5.78	−11.32
	CH_3NH_2	−3.09	−8.95	−9.65	−7.19	−14.45
	$(CH_3)_2NH$	−3.12	−11.61	−10.97	−8.04	−16.15
	$(CH_3)_3N$	−2.95	−13.68	−11.01	−8.21	−16.29

BH&HLYP-calculated $R(N\cdots X)$ distances agree best. This is particularly so for the NH_3–X_2 complexes. There, B3LYP and much more so PW91PW91 exaggerate the intermolecular interaction considerably. In the case of the NH_3–XY complexes, MP2 and B3LYP results are closer to each other. The BH&HLYP-calculated $R(N\cdots X)$ values match the experimental numbers even better. The close agreement between MP2 and BH&HLYP structures is also clearly visible when inspecting the intramolecular $R(X–Y)$ distances of the NH_3–X_2 complexes and the relative elongations $\Delta R(X–Y)$ (Table 2, Fig. 1). From the few available post-MP2 investigations on these systems (CCSD(T) calculations on NH_3–F_2, NH_3–ClF, and NH_3–Cl_2, and amine–ClF [30, 31, 33]) it is known that, as in other cases of intermolecular interaction, MP2 overshoots slightly. Thus, among the DFT approaches probed, BH&HLYP performs best for the NH_3–X_2 and NH_3–XY complexes. Similar conclusions have already been drawn by others [26, 27, 32, 33, 34, 35]. This does, however, not imply that the dispersion energy is appropriately taken account of with BH&HLYP. The argon dimer, Ar_2, for example, is unbound with BH&HLYP.

For all the methods including correlation energy contributions successive methylation of the amine has a profound effect on the structures and stabilization energies. The only exception is the amine–F_2 case, when treated at the BH&HLYP level. This catastrophic failure is most probably again a consequence of a too stiff intramolecular F_2 potential calculated with BH&HLYP. With increasing number of methyl groups, thus when increasing the gas phase basicities, the intermolecular $R(N\cdots X)$ distances are contracted, the intramolecular $R(X–Y)$ distances are lengthened, and the intermolecular binding energies are enhanced. Most of the discrepancies among the DFT methods occur already at the stage of the ammonia complexes. The trends obtained within the series are quite similar. MP2, on the other hand, behaves somewhat differently, showing a steeper change of $R(N\cdots X)$, $R(X–Y)$, and ΔE, with the consequence that the MP2 results for $(CH_3)_3N$–XY are, in general, closer to the B3LYP and PW91PW91 data. The only published small basis set CCSD(T) calculations for amine–ClF [33] and preliminary results for the other halogen–amine complexes again point in the direction that MP2 tends to overshoot progressively in this series. The strongest bound $(CH_3)_3N$–XY complexes are, as expected, those with dipole molecules ClF and BrF and with F_2, with MP2 binding energies in the range from −20 to −25 kcal mol^{-1}.

The calculated $\Delta R(X–Y)$ bond length elongations of Fig. 1 do not exceed 0.18 Å, even for the $(CH_3)_3N$–XY complexes, with the exception of the methylated amine–F_2 complexes. In that case the elongation extends to almost 0.4 Å. This finding, in combination with the known difficulties to produce an acceptable potential curve for the dissociation of F_2, also gives a hint that MP2 is expected to exaggerate the intermolecular interaction in that case. However, B3LYP and PW91PW91 also produce $R(X–Y)$ elongations larger than 0.3 Å for $(CH_3)_3N$–F_2. In general, the variation of structural features and binding energies is perfectly smooth upon going from the NH_3–XY to the $(CH_3)_3N$–XY complexes. The only abrupt change is predicted for the step from the NH_3–F_2 to the CH_3NH_2–F_2 complex.

In the case of hydrogen-bonded systems A–H$\cdots B$ of varying strength, the intimate correlation between intermolecular $A\cdots B$ distances and intramolecular A–H distances for a given atom pair A,B is well documented. That this relation is also valid for amine–halogen dimers is shown in Fig. 2, where MP2 optimized $R(N\cdots X)$

distances are plotted versus the corresponding $\Delta R(X\text{–}Y)$ values for all 24 complexes.

Dipole moments and CT

As measures of CT, the MP2-calculated electric dipole moments, the increase of the dipole moments relative to the sum of monomer dipole moments, the intermolecular CT based on AIM charges and the AIM atomic charges on the two halogen atoms are shown in Table 4. Intermolecular CT calculated from charges derived from natural population analysis or even from conventional Mulliken populations displays similar trends and could have been equally well used. With the exception of an estimate of the dipole moment of $(CH_3)_3N\text{–}F_2$ (10.4 D [11]), there are no experimental values for the dipole moments of the complexes available, nor are there any direct determinations of CT.

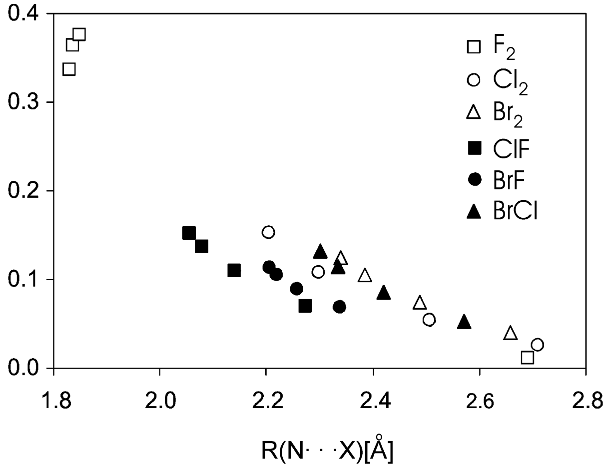

Fig. 2. MP2/6-311++G(3df,2p) optimized intermolecular $R(\text{N}\cdots X)$ distances versus lengthenings of the intramolecular $R(X\text{–}Y)$ distances in amine–XY CT complexes

Not surprisingly, the trends visible in the dipole moments and dipole moment enhancements are also mirrored in the calculated CT. There is, obviously, no direct linear correlation between the dipole moment enhancements and the AIM intermolecular CT for all 24 complexes. For a given amine–halogen series the trends are, however, very similar to those observed for structures and stabilization energies. A plot of AIM-derived CT versus the dipole moment increases is shown in Fig. 3. Clearly, the shorter the intermolecular distance $R(\text{N}\cdots\text{X})$ becomes, the more arbitrary is the determination of CT by either of the population analyses. It appears, therefore, preferable to use the dipole moment for the characterization of the charge distribution in CT complexes. Table 4 and Fig. 3 suggest that the best candidates for "inner" CT complexes are the amine–F_2 complexes, with $(CH_3)_3N\text{–}F_2$ displaying the strongest CT and the largest dipole moment. The calculated AIM charges on the halogen atoms also reveal that, in case of the strong complexes with F_2, the polarization within the halogen is radically different from the other cases. For the methylated amine–F_2 complexes the inner F atom carries the more negative charge. For all other complexes, the more negative charge is located at the outer halogen, whereas with a few exceptions the inner halogen still has a positive net charge.

Nuclear quadrupole coupling constants

Very important quantities for the comparison with the results of rotational spectroscopy are the NQCC

Table 4. MP2/6-311++G(3df,2p) calculated dipole moments, the intermolecular charge transfer based on atoms-in-molecules (*AIM*) charges and AIM atomic charges of amine–XY charge-transfer complexes

Halogen	Amine	Dipole moment (D)	Dipole moment increase (D)[a]	Intermolecular charge transfer	$q(X)$	$q(Y)$
F_2	NH_3	1.91	0.45	0.03	−0.004	−0.026
	CH_3NH_2	7.20	5.83	0.61	−0.368	−0.243
	$(CH_3)_2NH$	7.73	6.61	0.68	−0.419	−0.260
	$(CH_3)_3N$	7.98	7.30	0.71	−0.444	−0.270
ClF	NH_3	5.46	3.00	0.17	0.305	−0.478
	CH_3NH_2	6.63	4.35	0.26	0.250	−0.508
	$(CH_3)_2NH$	7.26	5.26	0.31	0.215	−0.527
	$(CH_3)_3N$	7.52	5.92	0.34	0.194	−0.536
Cl_2	NH_3	3.03	1.48	0.06	0.021	−0.077
	CH_3NH_2	3.79	2.42	0.11	0.016	−0.121
	$(CH_3)_2NH$	5.30	4.21	0.20	−0.002	−0.200
	$(CH_3)_3N$	6.36	5.68	0.27	−0.022	−0.252
BrF	NH_3	6.41	3.45	0.17	0.408	−0.577
	CH_3NH_2	7.15	4.37	0.22	0.378	−0.594
	$(CH_3)_2NH$	7.54	5.05	0.25	0.358	−0.604
	$(CH_3)_3N$	7.61	5.52	0.26	0.346	−0.608
BrCl	NH_3	4.73	2.70	0.10	0.163	−0.264
	CH_3NH_2	5.87	4.03	0.16	0.150	−0.311
	$(CH_3)_2NH$	6.69	5.13	0.21	0.135	−0.344
	$(CH_3)_3N$	7.02	5.86	0.24	0.123	−0.360
Br_2	NH_3	4.05	2.50	0.08	0.043	−0.125
	CH_3NH_2	5.19	3.82	0.14	0.043	−0.184
	$(CH_3)_2NH$	6.14	5.05	0.19	0.037	−0.231
	$(CH_3)_3N$	6.56	5.88	0.23	0.029	−0.255

[a] Increase relative to the sum of monomer dipole moments

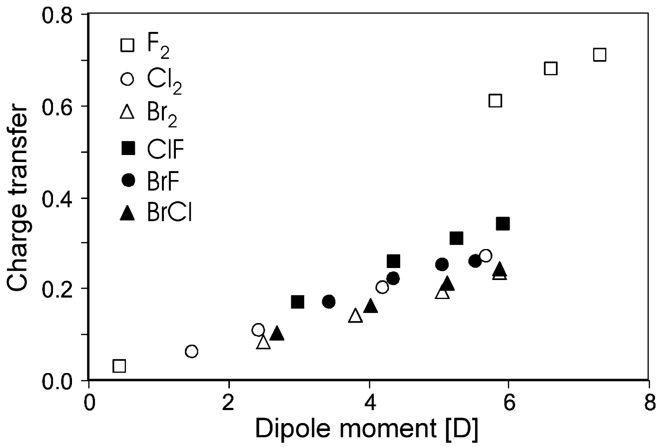

Fig. 3. Atoms-in-molecules charges derived intermolecular CT versus the dipole moment increase of amine–*XY* complexes as obtained at the MP2/6-311++G(3df,2p) level

of the nuclei $\chi(^{14}N)$, $\chi(^{35}Cl)$, and $\chi(^{79}Br)$. The MP2/6-311++G(3df,2p) calculated NQCC for the halogens, for ammonia and trimethylamine, and for the complexes of NH_3 and $(CH_3)_3N$ with the six halogens are collected in Table 5 and are compared with available experimental data. A similar set of BH&HLYP-calculated data for the NH_3–*XY* complexes has been reported very recently [35]. Although caution is necessary in a direct comparison of experimental and calculated NQCC (vibrational averaging, relativistic effects in case of Br, etc.) the trends appear to be well described. Both for NH_3 and $(CH_3)_3N$ complexes, the calculated $\chi(^{14}N)$ values are shifted to lower values with increasing strength of the interaction. The shifts are larger in case of the $(CH_3)_3N$ complexes. The trends in $\chi(^{35}Cl)$ and $\chi(^{79}Br)$ are also well described in the series of NH_3–Cl*Y* and NH_3–Br*Y* complexes, although the calculated values for $\chi(^{79}Br)$ are all significantly too low, a consequence of the neglect of relativistic effects [56].

Intramolecular and intermolecular stretching vibrations

The complete vibrational spectra of the complexes are not discussed here. Only the B3LYP/6-311++G(3df,2p) (MP2 in case of NH_3–F_2) calculated harmonic vibrational frequencies and IR intensities pertinent to the N···*X*–*Y* moiety of the NH_3–*XY* and $(CH_3)_3N$–*XY* complexes are reported in Table 6. The frequencies of the intermolecular modes, $\nu(N\cdots X)$, increase within the series of NH_3 and $(CH_3)_3N$ complexes with increasing interaction strength. The decrease of $\nu(N\cdots X)$ upon going from the NH_3 to the $(CH_3)_3N$ complex for a given halogen (F_2 is an exception), despite the stronger interaction and shorter $R(N\cdots X)$, is simply a mass effect. The increasing redshift of $\nu(X–Y)$, when going from the NH_3–*XY* to the $(CH_3)_3N$–*XY* complex, accompanied by an increase of the IR intensity, is just the behavior reminiscent of that known from countless investigations on the vibrational spectra of hydrogen-bonded systems. The calculated redshift (shift to lower frequencies) is particularly dramatic for $(CH_3)_3N$–F_2, where it amounts to more than 600 cm^{-1}. At the same time the corresponding IR intensity is enhanced by about a factor of 50 if compared to the weakly bound intermolecular case of NH_3–F_2.

Summary and conclusions

The change of a variety of ground-state properties of amine–halogen complexes taking place either upon exchanging the halogen molecule or upon successive methylation of the amine has been described and discussed. These CT complexes formed via a halogen bond have indeed much in common with the properties of hydrogen-bonded systems. Practically all the features known from spectroscopic and theoretical investigations on hydrogen-bonded dimers are encountered in amine–halogen complexes as well. The

Table 5. MP2/6-311++G(3df,2p) calculated nuclear quadrupole coupling constants (MHz) $\chi(^{14}N)$,$\chi(^{35}Cl)$, and$\chi(^{79}Br)$ of NH_3, $(CH_3)_3N$, the halogens *XY*, and of amine–*XY* charge-transfer complexes. χs were converted from electric field gradients by multiplication with 0.234965*Q*, where *Q* is the nuclear quadrupole moment in barn. *Q* values taken from Ref. [55] (20.44, −81.65, and 313 for ^{14}N,^{35}Cl, and ^{79}Br, respectively)

Molecule	$\chi(^{14}N)$	$\chi(^{35}Cl)$	$\chi(^{79}Br)$
ClF	–	−136 (−145.9)[a]	–
Cl_2	–	−103 (−115)	–
BrF	–	–	1053(1087)
BrCl	–	94 (103)	836(875)
Br_2	–	–	769(810)
NH_3	−3.98 (−4.08)	–	–
$(CH_3)_3N$	−5.29 (−5.50)	–	–
NH_3–F_2	−3.90 (−2.96)	–	–
$(CH_3)_3N$–F_2	−0.81 (−1.73)	–	–
NH_3–ClF	−2.92	−135 (−145.9)	–
$(CH_3)_3N$–ClF	−2.49 (−3.095)	−123 (−136.3)	–
NH_3–Cl_2	−3.79	−108/−94 (−115.8/−101.8)[b]	–
$(CH_3)_3N$–Cl_2	−3.17	−106/−73	–
NH_3–BrF	−2.76	–	1033
$(CH_3)_3N$–BrF	−2.79	–	959
NH_3–BrCl	−3.32	−79 (−86.05)	875 (916)
$(CH_3)_3N$–BrCl	−3.17	−66	839
NH_3–Br_2	−3.44	–	810/664 (852/695)
$(CH_3)_3N$–Br_2	−3.31	–	787/548

[a] Experimental values as observed or quoted in Refs. [6,7, 8,9, 10,11, 12,56] in parentheses

[b] In the cases of X_2 the notation inner/outer is used

Table 6. B3LYP/6-311++G(3df,2p) calculated harmonic stretching frequencies and IR intensities of the N···*X*–*Y* moiety of NH_3–*XY* and $(CH_3)_3N$–*XY* charge-transfer complexes. Frequencies and frequency shifts relative to the *X*–*Y* monomers (in *brackets*) (cm^{-1}), IR intensities (in *parentheses*) (km mol^{-1})

Halogen	NH_3		$(CH_3)_3N$	
	$\nu(N\cdots X)$	$\nu(X–Y)$	$\nu(N\cdots X)$	$\nu(X–Y)$
F_2[a]	101 (3)	907 (13) [−82]	242 (29)	415 (673) [−626]
ClF	254 (66)	601 (250) [−185]	205 (21)	529 (371) [−257]
Cl_2	171 (56)	539 (90) [−102]	149 (40)	365 (298) [−176]
BrF	255 (52)	550 (162) [−123]	178 (15)	507 (205) [−166]
BrCl	191 (66)	362 (55) [−71]	142 (30)	321 (156) [−112]
Br_2	175 (63)	268 (29) [−47]	128 (25)	239 (94) [−79]

[a] MP2/6-311++G(3df,2p) results for NH_3–F_2

N···*X*–*Y* moiety is close to linear. Shorter *R*(N···*X*) intermolecular distances than distances based on pure van der Waals radii of N and *X*, and substantial lengthenings of halogen *R*(*X*–*Y*) bond lengths were observed and calculated. With increasing strength of the interaction, achieved via a larger dipole moment of the halogen (BrF > ClF > BrCl), a larger dipole polarizability of the halogen ($Br_2 > Cl_2 > F_2$), or by increasing the gas-phase basicity of the amine [$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$], the *R*(N···*X*) intermolecular distance is further contracted and the *R*(*X*–*Y*) intramolecular distance is widened. The calculated stabilization energies span a wide range from about −1.6 kcal mol^{-1} in NH_3–F_2 to less than –20 kcal mol^{-1} in some of the $(CH_3)_3N$–*XY* complexes. The trends in other properties, such as dipole moment enhancements, intermolecular CT, NQCC modifications, and vibrational frequencies and their intensities, are all fully compatible with the notion of a halogen bond with properties quite analogous to that of a hydrogen bond.

All complexes of NH_3 with the six halogens can be described as "outer"-type complexes, with intermolecular N···F, N···Cl, and N···Br distances much larger than standard intramolecular N–F (1.38 Å), N–Cl (1.71 Å), and N–Br (1.85 Å) single-bond distances. The complexes of $(CH_3)_3N$ with the halogens are mostly intermediate cases, or at the border of "inner"-type complexes, showing substantial dipole moments and considerably contracted *R*(N···*X*) distances. They are, however, also still far from the gas-phase ion pairs $[(CH_3)_3NX]^+—Y^-$, for which the short *R*(N–*X*) distances of $(CH_3)_3NX^+$ cations might serve as orientation. For *X* = F, Cl, and Br, these are calculated as 1.39, 1.74, and 1.92 Å. The hitherto unobserved complexes CH_3NH_2–*XY* and $(CH_3)_2NH$–*XY* fit in each case and for each of the properties considered vary regularly between those of the corresponding ammonia and trimethylamine complexes. Among the complexes investigated, the $(CH_3)_3N$–F_2 complex is closest to Mulliken's "inner"-type CT complex.

Acknowledgements. The calculations were performed on the Linux-Cluster SCHRÖDINGER I at the computer center of the University of Vienna. The author is grateful for ample supply of computer time at this installation.

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