Density Functional Theory Studies of Bonding in Complexes $H_3N\cdots XY$ of Ammonia and Dihalogen Molecules: A Comparison with Experimental Results from Rotational Spectroscopy

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The electron density and nuclear quadrupole coupling constants (NQCC) of the $H_3N\cdots XY$ (n aσ type in Mulliken notation) complexes, (X, Y = F, Cl, Br and I), are analyzed with the aid of density functional calculations. To demonstrate the quality of the calculations, various bond lengths and NQCCs obtained by using the hybrid Becke-Lee-Perdew-Yang functional are compared with the corresponding experimental values determined from rotational spectroscopy. An analysis of the NQCC values and various quantities derived from the natural bond orbital approach reveals that the molecular interaction is mainly electrostatic, with probably only a small extent of intermolecular electric charge redistribution on complex formation.

Key words: DFT; Quadrupole Coupling Constants; n aσ complexes.

1. Introduction

Halogens X_2 and interhalogens XY form electron donor-acceptor complexes $B\cdots X_2$ and $B\cdots XY$ for a wide range of Lewis bases B. In his classification of donor-acceptor complexes, Mulliken [1, 2] distinguished two main types: outer (weak) complexes $B\cdots XY$ having only a minor electric charge rearrangement on complex formation and inner (strong) complexes $[BX]^+\cdots Y^-$ in which there is significant charge transfer. The formation of the latter is generally viewed as a mark of a strong donor-acceptor interaction and favored relative to the outer complex by, e. g., a polar solvent. The consensus of evidence [3] is that the order of the the relative electron acceptor strengths of the halogens with respect to a given Lewis base B in forming $B\cdots XY$ is ICl > BrCl > I_2 > Br_2 > Cl_2. A question of some importance concerns the change in nature of the $B\cdots XY$ interaction in the gas phase as XY is varied. Is this order of electron acceptor strength maintained for such complexes when isolated in the gas phase and, if so, is there any evidence of a substantial increase in the extent of charge transfer in the stronger complexes?

Rotational spectroscopy is a powerful and precise method of determining molecular properties in the gas phase. Traditionally, it has been the source of geometries, force fields, electric dipole moments and electric field gradients near certain nuclei. Since the advent of supersonic jets, produced when mixtures of two components B and A, diluted in argon are expanded through a pinhole into a vacuum, the rotational spectra of large numbers of weakly bound complexes $B\cdots A$ have been observed [4]. Recently, the use of the so-called fast-mixing nozzle [5] has allowed pre-chemical intermediates $B\cdots A$ to be isolated and characterized in mixtures of B and A that would under normal conditions be chemically reactive. This has been particularly useful when A is a dihalogen molecule that would otherwise undergo a chemical reaction with the Lewis base B when the two are mixed under normal conditions. The spectroscopic, and as a consequence molecular, properties obtained from rotational spectra when observed in this way refer to the molecule in isolation and are therefore

more appropriate for comparison with the results of ab initio calculations.

Simple systems for the investigation this type of interaction are those involving NH_3 with one of five dihalogen molecules based on F, Cl, Br, and I, namely Cl_2, ClF, BrCl, Br_2 or ICl. Complexes $H_3N\cdots XY$ are described according to the classification due to Mulliken as being of the n aσ type, since the electron is formally donated from the non-bonding orbital on N into the aσ (anti-bonding) orbital of XY. In addition to the inherent simplicity of these complexes and to the simplicity of on their spectra because the molecules are of the symmetric-top type, there are two further advantages to be gained by their investigation. The first advantage lies in the important position occupied by NH_3 in the series of hydrogen-bonded complexes B···HCl that has been systematically investigated by rotational spectroscopy [4]. Recently, it has been established that there exists a strict parallelism of the properties of B···HCl and B···Cl_2 (and indeed for other series B···HX and B···XY) [6], for a wide range of Lewis bases B. This parallelism is so striking that it was possible to postulate the existence of a halogen bond in complexes B···XY that is the analogue of the more familiar hydrogen bond in complexes B···HX [6]. The Legon-Millen rules [7], which were originally developed for predicting the angular geometries of hydrogen-bonded complexes B···HX, are essentially electrostatic in origin. The parallelism noted earlier also extends to the angular geometries of the B···HX and B···XY series in the gas phase. This result indicates that the angular geometries of the halogen-bonded complexes B···XY are also determined largely through the electrostatic component of the interaction [6]. Moreover, relationships that apply to the intermolecular stretching force constants for B···HX [8] also apply to B···XY. In view of these conclusions about the series of halogen- and hydrogen-bonded complexes, it seems important to investigate the nature of the former interaction theoretically.

The second advantage of investigating $H_3N\cdots XY$, where X and Y are F, Cl, Br or I, is that Cl, Br and I have non-zero nuclear electric quadrupole moments, and therefore the rotational spectra of such species exhibit nuclear quadrupole hyperfine structure. Analysis of hyperfine structure leads to the electric field gradient (EFG) at each halogen nucleus and, via a comparison of the EFG in the complex and the free halogen, to the changes in the extent of electric charge redistribution that accompanies complex formation. In fact, values of the fractional intermolecular electron transfers $\delta(B\rightarrow X)e$ and $\delta(X\rightarrow Y)e$ have been obtained experimentally by application of the simple Townes-Dailey model to the observed nuclear quadrupole coupling constants (NQCC) [9]. A conclusion about the type of complex (inner or outer) is then possible once these quantities are known.

Table 1. Calculated (B3LYP)[a] and experimental bond lengths (Å) for dihalogens XY and their complexes $H_3N\cdots XY$ with NH_3.

Molecule	Experimental values		Calculated values		
	R(N···X) Å	R(X-Y) Å	R(N···X)/Å (6-311G**)	R(X-Y)/Å 6-31G**	6-311G**
Cl_2		1.992		2.009	2.022
ClF		1.632		1.634	1.645
Br_2		2.284		2.294	2.301
BrCl		2.139		2.156	2.162
ICl		2.323		2.364	
NH_3	1.016			1.007	1.006
$H_3N\cdots Cl_2$	2.730	2.00	2.533		2.071
$H_3N\cdots ClF$	2.376		2.363		1.695
$H_3N\cdots Br_2$	2.720		2.586		2.353
$H_3N\cdots BrCl$	2.627	2.186	2.511		2.224
$H_3N\cdots ICl$	2.711		2.481		2.441

[a] For molecules containing an iodine atom, the 3-21G** basis set was used.

2. Computational Details

The calculations were carried out using the GAUSSIAN'98W [10] program package on a personal computer. The geometry optimizations were carried out using the density functional theory (BHandHLYP functional) [11] in conjunction with such extended standard basis set as 3-21G** (for iodine only), 6-31G**, 6-311G**, cc-pVTZ and aug-cc-pVTZ. The quadrupole coupling constants for Cl, Br, I and N nuclei were calculated on the basis of the eigenvalues of the EFG tensor. We have used the natural bond orbital approach (NBO) [12] for the analysis of the bonding situation in the complexes.

3. Results

A comparison of the N···X and X-Y bond lengths calculated at the BHandHLYP/6-311G**, BHandHLYP/6-31G** and BHandHLYP/aug-cc-pVTZ levels of theory with the experimental data is given in Tables 1 and 2. We note from these tables that the bond lengths R(X-Y) and R(N-X) have been overestimated when the basis set BHandHLYP/6-31G**is used.

Table 2. The bond length R (N···X) and R (X-Y) and the nuclear quadrupole coupling constants of $H_3N\cdots XY$ type complexes n aσ complexes calculated at the BHandHLYP/aug-cc-pVTZ level of theory. The bond length R(N···X) and R(X-Y) and the nuclear quadrupole coupling constants of $H_3N\cdots XY$ type complexes n aσ complexes calculated at the BHandHLYP/aug-cc-pVTZ level of theory.

Molecule	Experimental values				Calculated values			
	R(X-Y) Å	R(N···X) Å	χ(N) MHz	χ(Cl/Br) MHz	R(X-Y) Å	R(N···X) Å	χ(N) MHz	χ(Cl/Br) MHz
Cl_2	1.992			111.79	1.996			110.96
ClF	1.632			145.87	1.615			143.40
Br_2	2.284			810.00	2.286			808.2
BrCl	2.139			102.5, 875.3	2.141			101.02, 878.5
HCl	1.274			66.62	1.273			64.51
NH_3	1.016		4.090		1.003		4.34	
$H_3N\cdots Cl_2$	2.00	2.730		115.78, 101.79	2.024	2.685	3.97	116.52, 100.00
$H_3N\cdots ClF$		2.376	2.95	145.88	1.690	2.338	3.26	146.95
$H_3N\cdots BrCl$	2.186	2.627		915.55, 86.05	2.191	2.579	3.59	932.4, 84.2
$H_3N\cdots Br_2$		2.720		852.5, 695.3	2.326	2.670	3.74	863.0, 690.6
$H_3N\cdots HCl$			3.61	52.9	1.320	1.789	3.88	46.97

Table 3. Calculated (BHandHLYP) and experimental nuclear quadrupole coupling constants XY and their complexes $H_3N\cdots XY$ with ammonia.

Molecule	Experimental values				Calculated values						
	χ(Cl) MHz	χ(Br) MHz	χ(I) MHz	χ(N) MHz	χ(Cl)/MHz 6-31G**	χ(Cl)/MHz 6-311G**	χ(Br)/MHz 6-31G**	χ(Br)/MHz 6-311G**	χ(N)/MHz 6-31G**	χ(N)/MHz 6-311G**	χ(I)/MHz 3-21G*
Cl_2	111.79				106.9	112.8					
ClF	145.87				138.7	139.5					
Br_2		810					749	885			
BrCl	102.45	875.31			98.7	102.3	806	965			
ICl	85.89		2928		79.5						2490
HCl	66.62					64.5					
NH_3				4.090					4.52	5.20	
$H_3N\cdots Cl_2$	115.78(inner)					119.9(inner)				4.15	
	101.79(outer)					96.6(outer)					
$H_3N\cdots ClF$	145.88			2.95		141.8				3.75	
$H_3N\cdots Br_2$								946(inner)		3.99	
								726(outer)			
$H_3N\cdots BrCl$	86.05	915.55				82.3		1018		3.77	
$H_3N\cdots ICl$	68.93		3073	2.99	56.7					3.10	2670
$H_3N\cdots HCl$	52.9			3.61		45.24				4.17	

However, for calculations at the BHandHLYP/6-311G** level the intermolecular bond length R(N-X) is smaller than the experimental value in general. On the other hand, the results of using the BHandHLYP/aug-cc-pVTZ level of theory were in better agreement with the experimental data. Analysis of the results obtained at the BHandHLYP/aug-ccpVTZ level leads to the following correlation between the calculated and experimental N-X and X-Y bond lengths [R(cal.) and R(exp.), respectively] for the complexes studied (see Fig. 1):

$$R(\text{cal.})/\text{Å} = 0.11 + 0.95\ R(\text{exp.})/\text{Å}, \quad (1)$$
$$r = 0.998;\ s = 0.02;\ n = 10,$$

where r is the correlation coefficient, s is the standard deviation and n is the number of the compounds. The factor preceding R(exp.) is close to unity, which indicates the high reliability of the calculations with the aug-cc-pVTZ basis set.

These results encouraged us to perform the calculations of the NQCCs associated with the chlorine and bromine atoms for the complexes investigated. For these calculations, the preferred level of theory was BHandHLYP/aug-cc-pVTZ (Table 3). We note that a good correlation exists between the experimental [13 - 19] and calculated NQCC values [χ(exp.) and χ(cal.), respectively], as seen graphically by the

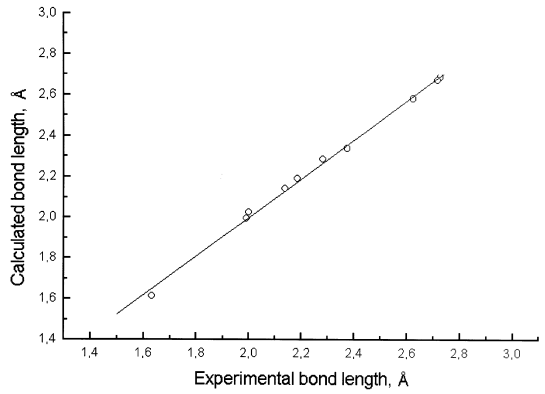

Fig. 1. The correlation between the bond lengths of various $H_3N\cdots XY$ calculated at the BHandHLYP/aug-cc-pVTZ level and the experimental values from rotational spectroscopy.

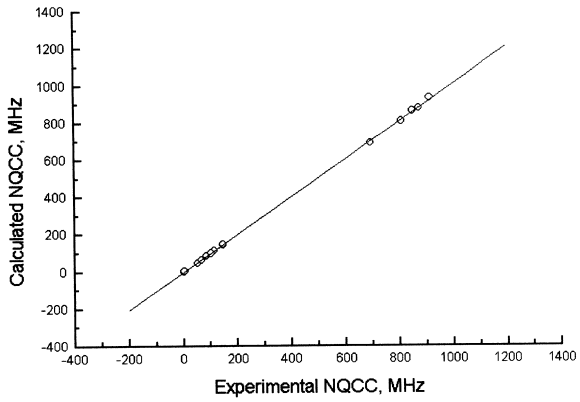

Fig. 2. The correlation between the NQCC values calculated at the BHandHLYP/aug-cc-pVTZ level and the experimental values from rotational spectroscopy for ^{14}N, ^{35}Cl and ^{79}Br nuclei of the $H_3N\cdots XY$ n aσ complexes.

straight line in Fig. 2 and as described numerically by the equation:

$$[\chi(\text{cal.})/\text{MHz}] = -2.1 + 1.01\,[\chi(\text{exp.})/\text{MHz}], \quad (2)$$
$$r = 0.9999;\ s = 4.6;\ n = 17.$$

It should be pointed out that the correlation of the experimental and theoretical values indicated by (2) was obtained by using the results for all three coupling nuclei, *i.e.* NQCC for ^{14}N, ^{35}Cl and ^{79}Br from experiment (rotational spectroscopy) and from the calculations reported here.

Table 4 gives the energies calculated at the BHandHLYP/6-311G** level of theory at the optimized geometries of the $H_3N\cdots XY$ complexes. The bond dissociation energies for the halogen-bonded complexes with NH_3 are smaller than those involving Lewis acids such as $SbCl_5$, for example [20]. The calculated bond dissociation energies (D_e) for these complexes are strongly correlated with the extent of electron transfer from ammonia to the inner halogen atom, $\delta(N\rightarrow X)e$ (the electron transfer was calculated by proceeding from the atomic charges q_X) (Fig. 3):

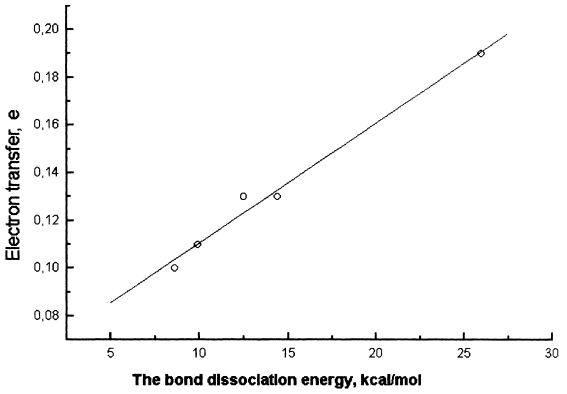

Fig. 3. The relationship between the intramolecular electron transfer in XY on formation of the complexes $H_3N\cdots XY$ and the energy of complex formation calculated at the BHandHLYP/6-311G** level.

$$\delta(N\rightarrow X) = 0.06 + 0.005(D_e/\text{kcal mol}^{-1}) \quad (3)$$
$$r = 0.993;\ s = 0.005;\ n = 5.$$

It is of interest to draw attention to the fact that such a correlation encompasses all complexes studied, despite the use of a different basis set (3-21G*) for the iodine atom. This correlation between the fraction $\delta(N\rightarrow X)$ of an electronic charge donated from N to X and the calculated dissociation energies for halogen-bonded complexes contrasts with the different situation found for the main group and transition metal complexes [21].

The quantity $\delta(X\text{-}Y)$ has also been measured experimentally for several $H_3N\cdots XY$ complexes by a method based on the changes in the nuclear quadrupole coupling constants of the halogen molecules when subsumed into the complex and discussed in detail in [9]. The values are 0.009, 0.066, 0.069 and 0.15 for XY = Cl_2, Br_2, BrCl and ICl, respectively. (The method described in [9] cannot be applied to $H_3N\cdots ClF$ because it depends on each halogen nucleus having a non-zero electric quadrupole moment and this is not the case for F). These val-

Table 4. List of principal NBOs for representative halogens (BHandHLYP/6-311G** level), showing the stabilization energy of the complexes, NBO charges, occupancies (e), and composition ($c_X h_X + c_Y h_Y$) in terms of hydrids (h_X, h_Y) and polarization coefficients (c_X, c_Y) on each atom.

Molecule	D_e/kcal mol^{-1}	q_{Cl}/e	$q_{Br,F,I}/e$	$W_{N\cdots X}$	q_N/e	q_H/e	NBO type	Occupation (e)	Composition ($c_X h_X + c_Y h_Y$)
Cl_2		0					σ(Cl-Cl)	2.0000	$0.707(sp^{14.9})_{Cl}$ +$0.707(sp^{14.9})_{Cl}$
							n_{Cl}	1.9999	$sp^{0.07}$
								1.9966	p
								1.9966	p
Br_2			0				σ(Br-Br)	2.0000	$0.707(sp^{18.2})_{Br}$ + $0.707(sp^{18.2})_{Br}$
							n_{Br}	1.9999	$sp^{0.05}$
								1.9972	p
								1.9972	p
ClF		0.335	–0.335				σ(Cl-F)	2.0000	$0.574(sp^{16.4})_{Cl}$ + $0.819(sp^{10.4})_{F}$
							n_{Cl}	1.9999	p
								1.9972	p
								1.9972	$sp^{0.05}$
							n_F	1.9999	$sp^{0.01}$
								1.9969	p
								1.9969	p
BrCl		–0.092	0.092				σ(Br-Cl)	2.0000	$0.740(sp^{15.2})_{Cl}$ + $0.672(sp^{17.6})_{Br}$
							n_{Cl}	2.0000	$sp^{0.07}$
								1.9960	p
								1.9960	p
							n_{Br}	1.9999	$sp^{0.05}$
								1.9977	p
								1.9977	p
ICl		–0.251	0.251				σ(I-Cl)	2.0000	$0.610(sp^{20.0})_{I}$ + $0.792(sp^{13.4})_{Cl}$
							n_I	1.9998	$sp^{0.04}$
								1.9998	p
								1.9998	p
							n_{Cl}	2.0000	$sp^{0.07}$
								1.9961	p
								1.9961	p
NH_3					–1.022	0.341	σ(N-H)	1.9992	$0.820(sp^{2.7})_{N}$ + $0.572(s)_{H}$
							n_N	1.9951	$sp^{3.9}$
$H_3N\cdots Cl_2$	8.6	0.020		0.110	–0.989	0.362	σ(N-H)	1.9991	$0.826(sp^{2.8})_{N}$ + $0.564(s)_{H}$
		–0.117					σ(Cl-Cl)	1.9983	$0.681(sp^{27.3})_{Cl}$ + $0.732(sp^{13.5})_{Cl}$
							n_N	1.8949	$sp^{3.6}$
							n_{Cl}	1.9995	$sp^{0.04}$
								1.9959	p
								1.9958	p
								1.9958	p
								2.0000	$sp^{0.04}$
								1.9973	p

ues of δ(X-Y) are all smaller than the corresponding quantities calculated here by the DFT approach, but by a nearly constant amount. Hence, the plot of experimental values δ(X-Y) against the formation energy D_e is parallel to, but displaced from, the line Fig. 3, which involves the theoretical values of δ(X-Y). It is of interest to mention here that the DFT calculation seems to systematically overestimate this type of charge transfer.

In Table 4 we give the calculated values of the Wiberg indices ($W_{N\cdots X}$) of the weak N···X bond. Note that these are considerably smaller than those of the proper covalent bond of the donor-acceptor type [21]. At the same time, we did not define of the co-ordinating N···X bonds hybridization by the NBO approach. In each case the model depicts it as consisting of one σ, one nitrogen electron lone pair and three halogen electron lone pairs. This results in considerable mixing of halogen s and p atomic orbitals in the formation of the molecular orbitals; the σ MO, ideally an sp hybrid, is characterized as sp^x (x = 15-60), corresponding to 2-6% s and 98-94%

Table 4 (continued).

Molecule	D_e/kcal mol^{-1}	q_{Cl}/e	$q_{Br,F,I}/e$	$W_{N\cdots X}$	q_N/e	q_H/e	NBO type	Occupation (e)	Composition ($c_X h_X + c_Y h_Y$)
$H_3N\cdots ClF$	14.4	0.303	–0.431	0.186	–0.983	0.371	σ(N-H)	1.9993	$0.829(sp^{2.8})_N + 0.560(s)_H$
							σ(Cl-Cl)	1.9989	$0.548(sp^{31.9})_{Cl} + 0.837(sp^{9.3})_F$
							n_N	1.8623	$sp^{3.6}$
							n_{Cl}	1.9993	$sp^{0.03}$
								1.9978	p
								1.9976	p
							n_F	1.9997	$sp^{0.11}$
								1.9973	p
								1.9973	p
$H_3N\cdots Br_2$	9.9		0.029	0.122	–0.996	0.368	σ(N-H)	1.9992	$0.828(sp^{2.8})_N + 0.561(s)_H$
			–0.136				σ(Br-Br)	1.9980	$0.675(sp^{37.0})_{Br} + 0.738(sp^{15.8})_{Br}$
							n_N	1.8852	$sp^{3.6}$
							n_{Br}	1.9996	$sp^{0.03}$
								1.9968	p
								1.9967	p
								1.9999	$sp^{0.06}$
								1.9976	p
								1.9976	p
$H_3N\cdots BrCl$	12.5	–0.236	0.109	0.157	–0.986	0.371	σ(N-H)	1.9993	$0.829(sp^{2.8})_N + 0.560(s)_H$
							σ(Br-Cl)	1.9980	$0.637(sp^{38.5})_{Br} + 0.771(sp^{13.2})_{Cl}$
							n_N	1.8643	$sp^{3.6}$
							n_{Br}	1.9995	$sp^{0.02}$
								1.9966	p
								1.9966	p
							n_{Cl}	1.9999	$sp^{0.08}$
								1.9968	p
								1.9968	p
$H_3N\cdots ICl$	26.0	–0.429	0.242	0.250	–1.045	0.410	σ(N-H)	1.9994	$0.840(sp^{2.77})_N + 0.542(s)_H$
							σ(I-Cl)	1.9987	$0.556(sp^{62.0})_I + 0.831(sp^{11.0})_{Cl}$
							n_N	1.8079	$sp^{3.9}$
							n_I	1.9988	$sp^{2.94}$
								1.9984	$sp^{13.0}$
								1.9979	$sp^{0.5}$
							n_{Cl}	1.9998	$sp^{0.09}$
								1.9964	p
								1.9964	p

$q_N = -1.059$, $q_H = 0.353$ for NH_3 molecule calculated in 3-21G** basis set.

p character. A detailed analysis of the X-Y bonding (σ_{X-Y}) and lone electron pairs of the nitrogen (n_N) and halogen atoms (n_X) in $H_3N\cdots XY$ complexes has demonstrated that the extent of any charge reorganisation in general, and intermolecular charge transfer in particular, is small. The polarization of X-Y bonds (polarization coefficients on the halogen atoms c_X and c_Y) by NH_3 increases as the interaction strength increases, as might be expected. The dissociation energies, electron transfer (Fig. 3) and Wiberg indices of the complexes (Table 4) investigated here indicate that the relative acceptor strengths of the halogens have the same trend as shown by the NQCC of a given halogen and a similar trend as that described by the intermolecular stretching force constant [9].

The conclusions of the calculations reported here are consistent with a picture of the interaction in $H_3N\cdots XY$ that is predominantly electrostatic in origin and agree well with those derived experimentally from rotational spectroscopy. All of the above results indicate that the complexes formed between NH_3 and XY are of the outer type. This is not surprising if the interaction is mainly electrostatic.

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