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Structural Aspects of Donor−Acceptor Interactions

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Quantum chemical calculations at the MP2(FC)/6-311+G(2df,p) level have been performed for the donor−acceptor complexes BH_3NH_3, BCl_3NH_3, AlH_3NH_3, $AlCl_3NH_3$, and $GaCl_3NH_3$. Variations of the potential energy, total charge transfer, and geometrical parameters have been investigated along the d_{AN} (A = B, Al, Ga) donor−acceptor distance from a compressed (1.5 Å) arrangement up to dissociation. Among the well-known geometrical consequences of complex formation (lengthening of the A−L and N−H bonds, increase of the L−A−N and H−N−A bond angles), those in the AL_3 acceptors are well pronounced whereas those in NH_3 are rather small. The geometrical effects show a gradual decrease with increasing d_{AN}, but most of them can still be recognized at considerable elongation (by 2 Å) from the equilibrium donor−acceptor distance. Among the investigated properties, the potential energy and the L−A−N angle are the most sensitive indicators of the interaction.

Introduction

Molecular geometry is a fundamental property of chemical compounds. Besides a unique characterization of the molecular species, the three-dimensional geometry plays an important role in the mechanism of chemical reactions, in molecular recognition, as well as in biological function. The geometrical parameters are sensitive to intra- and intermolecular interactions; hence they can indicate and characterize these processes.

The equilibrium geometry is associated with the minimum position on the potential energy surface of the molecule. It is obtainable from quantum chemical geometry optimizations and can be elucidated, in limited cases, from gas-phase experimental studies. The equilibrium geometry is altered upon intermolecular interactions, which occur in liquids and especially in solids. The magnitude of changes gives information on the forces arising in these systems if the energy cost of the change of the particular internal coordinate is known. Recently, we have estimated the energy required for the change of some fundamental internal coordinates, viz. the C−C single bond, the C−C−C bond angle, and the C−C−C−C torsional distortion in alkanes using quantum chemical calculations.[1]

In the present study we have extended these investigations to donor−acceptor complexes. In conjunction with the NH_3 donor, the following acceptors were selected: BH_3, BCl_3, AlH_3, $AlCl_3$, and $GaCl_3$. They cover both central atoms from the first to third row of the periodic system and ligands of electropositive (H) and electronegative (Cl) nature. Emphasis was made on the following properties as a function of the d_{AN} donor−acceptor distance:

- potential energy
- intermolecular charge transfer
- A−L and N−H bond distances
- L−A−N and H−N−A bond angles

There is a wealth of references (see, e.g., refs 2−6) to quantum chemical calculations of these and similar complexes in the literature. However, our literature search has found only two papers with goals related to the present study. Ghosh[7] has investigated the change of the kinetic interference energy and the charge distribution as a function of the donor−acceptor distance in BH_3NH_3, whereas Harabaev et al.[8] have analyzed the change of the H−N−B and H−N−Al angles in BH_3NH_3 and AlH_3NH_3 complexes along the B−N and Al−N distances from 1 to 3 Å. Both studies have been performed by means of semiempirical quantum chemical calculations (CNDO, MNDO). These low level computations could not provide reliable quantitative data.

Computational Details

The crucial consideration in the selection of the computational method is its reliability. Although numerous theoretical studies of simple donor−acceptor complexes have appeared in the last two decades, reliable calculations have been carried out only on the equilibrium structures.[9−11] The performance of standard quantum chemical methods for geometries at nonequilibrium donor−acceptor distances is less known. A proper treatment of electron correlation and large diffuse basis sets are basic requirements for such calculations. The latter is especially important for elongated donor−acceptor distances, where the dispersion forces gain considerable importance. Thus, Hartree−Fock and density functional theories may be inadequate, the latter one because of its deficiency for dispersion energy.[12] On

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TABLE 1: Comparison of Different Theoretical Levels for the Equilibrium Geometry of BH_3NH_3[a]

	6-311+G(2df,p)			aug-cc-pVTZ			
	MP2(fc)	MP2(full)	QCISD	MP2(fc)	MP2(full)	QCISD	exp[b]
B−N	1.650	1.646	1.654	1.651	1.645	1.656	1.6576(16)
B−H	1.208	1.207	1.212	1.207	1.202	1.210	1.2160(17)
N−H	1.017	1.016	1.017	1.014	1.012	1.014	1.0140(20)
H−N−H	108.0	108.0	108.0	107.9	108.0	108.0	108.65(14)
H−B−H	113.6	113.6	113.6	113.7	113.7	113.7	113.80(11)

[a] Bond distances are given in angstroms, bond angles in degrees. [b] r_s structure from ref 17.

the other hand, there are molecules with third-row atoms (Ga, Cl) among the target complexes, and this has limited our choice for a consistently large basis set. The above considerations have prompted us to select the MP2(fc) theory[13] in conjunction with the 6-311+G(2df,p) basis set for the overall energetic and structural characterization of the donor−acceptor interactions. Besides its sufficient flexibility, this basis is also affordable for the large series of calculations performed in this study.

The calculations along the d_{AN} coordinate have been carried out at geometries with constrained d_{AN} distances at (ca. 30) selected values between 1.5 and 10 Å and with all the other geometrical parameters allowed to relax. Analysis of the charge distribution and charge-transfer processes was performed using the NBO partitioning scheme.[14] The natural charges obtained from the NBO analysis were shown to be sufficiently reliable and stable to computational parameters.[14] The second-order perturbation energies ($E^{(2)}$ donor → acceptor) were obtained from HF/6-311+G(2df,p) single-point calculations on the MP2(fc)/6-311+G(2df,p) geometries. In all the calculations, the Gaussian 98 program[15] extended by the NBO 5.0 code[16] was used.

Results and Discussion

1. Performance Test. To assess the reliability of the MP2(fc)/6-311+G(2df,p) level, we performed first a series of comparative test calculations on BH_3NH_3. The effect of the frozen-core approximation was investigated by MP2(full) calculations, whereas the QCISD level served as the reference method for electron correlation. The quality of the 6-311+G(2df,p) basis set was assessed by comparison with the aug-cc-pVTZ basis. The equilibrium geometries are given in Table 1, and Figure 1 compares the potential energy function and the changes of the B−H and N−H bond distances along d_{BN}.

The equilibrium geometrical parameters of BH_3NH_3 computed at different levels of theory are close to each other and approximate well the experimental (r_s) geometry[17] (cf. Table 1).[18] As expected, the best results were obtained at the QCISD level, but the performance of MP2(fc) theory is also satisfactory, whereas the largest deviations were produced by the MP2(full) computations. The excellent quality of the 6-311+G(2df,p) basis set for the equilibrium structure is manifested in the marginal differences from the data obtained using the aug-cc-pVTZ basis.

The curves in Figure 1 demonstrate the good and similar performance of the MP2(fc)/6-311+G(2df,p) and MP2(fc)/aug-cc-pVTZ levels along the d_{BN} coordinate. The deviation of the dissociation energies obtained from the 6-311+G(2df,p) basis from that from the aug-cc-pVTZ basis is small (2 kJ/mol, cf. the MP2(fc) and QCISD results). The small overestimation of the former values is in agreement with a slightly larger BSSE affecting the 6-311+G(2df,p) results. Concerning the theories, the MP2(full) calculations give larger deviations from QCISD than the frozen-core approximation.

The performance of the MP2(fc)/6-311+G(2df,p) level with respect to QCISD/aug-cc-pVTZ along the d_{BN} coordinate can be summarized in the following:

- energy, dissociation energy higher by 10 kJ/mol
- Δ(N−H), larger elongation upon complex formation by 0.002 Å
- Δ(B−H), agreement within 0.0003 Å
- Δ(B−N−H), agreement within 0.2°
- Δ(N−B−H), agreement within 0.1°

2. Equilibrium Structures. Table 2 compiles the equilibrium geometrical parameters for all five complexes. Among these compounds, gas-phase experimental data have been reported for $AlCl_3NH_3$[19] and $GaCl_3NH_3$.[20] For the BCl_3NH_3 complex only X-ray crystallographic data are available,[21] and our literature search did not find any information on the existence of AlH_3NH_3.

The data in Table 2 demonstrate as good performance of the MP2(fc)/6-311+G(2df,p) level for the heavier complexes of $AlCl_3NH_3$ and $GaCl_3NH_3$ as was found for BH_3NH_3 (vide supra). The H−N−H angle could not be determined reliably in $AlCl_3NH_3$ and $GaCl_3NH_3$ from experiment. The only noteworthy deviation between computations and experiment appeared for the Al−Cl bond distance, which is overestimated in the calculations by 0.01 Å. The experimental data are r_g parameters from ED investigations[19,20] and the equilibrium value should not be the same; the r_e distance is expected to be smaller rather than larger than the r_g value.[22] Overestimation seems to be a systematic error of the computations observed often for halogen-containing compounds.[23−25]

Several trends can be deduced from the data in Table 2. The geometrical variations are consistent with our earlier observations.[26,27] We note here the decrease of the equilibrium donor−acceptor (d_e) distance when the hydrogen on the acceptor is substituted by chlorine. This marked strengthening of the donor−acceptor interaction can be attributed to two factors: (i) The electronegative chlorines gain electron density at the cost of the central atom, which becomes more positive (cf. the atomic charges in Table 2). At the same time, the negative charge of N in the ACl_3NH_3 complexes is largely due to a slightly increased charge separation in the NH_3 moiety. The enhanced partial charges on the donor and acceptor atoms lead to a stronger electrostatic attraction in the chloride complexes. This is especially true for the boron acceptor, in which the small negative charge in BH_3NH_3[28] turns into a positive one in BCl_3NH_3. (ii) The second factor in strengthening the donor−acceptor bond is the enhanced charge transfer (by ca. 0.01 e) from N to A in the chloride derivatives.

According to the computations, the N−H bond distances and the H−N−A bond angles are only marginally dependent on the nature of L (H or Cl). This is, again, in agreement with our earlier observations about competing effects in shaping the donor geometry in these donor−acceptor complexes.[26,27] The barrier to internal rotation (ΔE_{rot}) is strongly related to the A−N distance, which determines the steric interactions between the

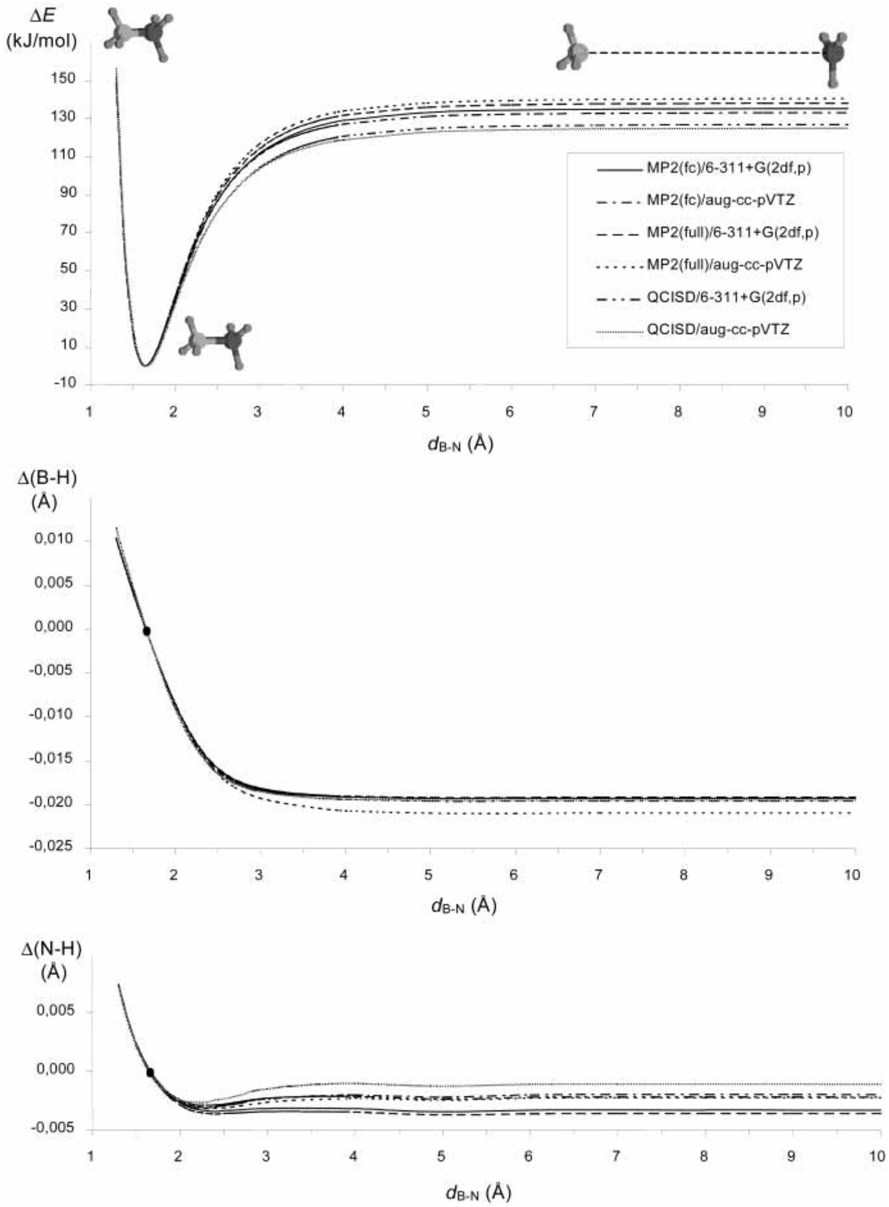

Figure 1. Comparison of different theoretical levels for the dissociation of BH_3NH_3.

ligands L and H. We note the flat torsional potential curve of $GaCl_3NH_3$. The slight minimum at the staggered arrangement ($\Delta E = 0.6$ kJ/mol) corresponds to essentially free rotation under ambient conditions.

Finally, we comment on the charge-transfer processes in the equilibrium complexes, the most important contributions of which are included in Table 2. The largest intermolecular charge transfer is found in the B−N complexes (0.37 e) and can be attributed to the extensive overlap of the lone pair of N (n_N) with the empty p_z orbital of B (cf. the second-order perturbation energies, $E^{(2)}$). The analogous donation to Al and Ga is considerably weaker. Minor contributions include the $n_N \rightarrow \sigma^*_{AL}$, as well as the anti-positioned $\sigma_{AL} \rightarrow \sigma^*_{NH}$ and $\sigma_{NH} \rightarrow \sigma^*_{AL}$ hyperconjugations.

3. Changes along the d_{AN} Coordinate. Figure 2 demonstrates the changes of the potential energy and total charge transfer along the d_{AN} internal coordinate. The Morse-type curve for ΔE and the gradually decreasing trend for Δq is in agreement with the expectations. The increase of the potential energy (and the parallel decrease of the charge transfer) is steep within an elongation of about 1 Å. Beyond this change, the slope of the curves diminishes, but there is still considerable intermolecular interaction, as witnessed by the potential energy for about another 2 Å. The curve of Δq levels off sooner, indicating that the interaction at larger intermolecular distances has little charge-transfer component (hence donor−acceptor character). The dissociation energies (D_0) are listed in Table 2. We note the large dissociation energy of $AlCl_3NH_3$ parallel with the strongest Coulomb interaction between Al and N found in this complex (cf. the atomic charges in Table 2).

At distances $d_{AN} < d_e$, Figure 2 shows the expected steep energy increase in the complexes due to increased repulsive interactions. The behavior of the total charge-transfer curve is noteworthy in this range. This curve reaches a maximum and starts to decrease upon further compression. The location of the maximum of Δq is somewhat farther away from d_e for the AH_3NH_3 complexes than for the ACl_3NH_3 ones. Analysis of the atomic charges at distances $d_{AN} < d_e$ revealed marginal changes on the ligands, but a considerable increase of the positive charge of A and the negative charge of N. All this points to a decreasing $n_N \rightarrow p_{zA}$ charge transfer at the compressed distances. On the other hand, the energy contribution of the n_N

TABLE 2: Computed Molecular Properties of AL_3NH_3 (A = B, Al, Ga; L = H, Cl) Complexes

parameter[a]	BH_3NH_3	BCl_3NH_3[b]	AlH_3NH_3	$AlCl_3NH_3$[c]	$GaCl_3NH_3$[d]
A−L	1.208	1.826	1.596	2.114	2.149
A−N (d_e)	1.650	1.615	2.069	1.999	2.054
N−H	1.017	1.021	1.017	1.019	1.019
H−N−H	108.0	109.0	107.6	107.8	108.1
L−A−L	113.6	113.5	117.5	116.5	116.7
ΔE_{rot}	9.2	11.5	2.8	2.0	0.6
Δq	0.363	0.370	0.172	0.187	0.209
q_A	−0.134	0.291	1.029	1.369	1.215
q_N	−0.823	−0.892	−1.021	−1.053	−1.024
Δq	0.363	0.370	0.172	0.187	0.209
$\Delta E^{(2)}n_N \rightarrow p_{zA}$	1697.3	1813.5	556.7	600.0	567.9
$\Delta E^{(2)}n_N \rightarrow \sigma^*_{AL}$	18.7	38.4	48.7	40.6	66.1
$\Delta E^{(2)}\sigma_{AL} \rightarrow \sigma^*_{NH}$[e]	30.3	22.5	7.5	3.3	2.7
$\Delta E^{(2)}\sigma_{NH} \rightarrow \sigma^*_{AL}$[e]	5.1	21.6	2.4	6.3	6.3
$D_{0,BSSE}$	132.9	115.6	122.6	166.5	132.1

[a] Computed at the MP2(fc)/6-311+G(2df,p) level. The parameters include: bond distances (Å); bond angles (deg); rotational barrier (ΔE_{rot}, kJ/mol); charge-transfer N → A (Δq, e), atomic charges (e). The second-order perturbation energies ($E^{(2)}$ donor → acceptor, kJ/mol) were obtained from HF/6-311+G(2df,p) single-point calculations on the MP2(FC)/6-311+G(2df,p) geometries. The dissociation energies ($D_{0,BSSE}$, kJ/mol) are corrected for zero-point vibrational energy and basis set superposition error. [b] The X-ray molecular structure of BCl_3NH_3 is characterized by B−N, 1.579(4) Å; B−Cl(mean), 1.837 Å.[21] [c] The experimental geometrical parameters (bond distances are r_g, bond angles are r_a) for $AlCl_3NH_3$: Al−Cl, 2.102(5) Å; Al−N, 1.998(19) Å; Cl−Al−Cl, 116.35(40)°; H−N−H, 114.3(12).[19] The r_g parameters have been calculated from r_a distances using the vibrational amplitudes from ref 31. [d] The experimental geometrical parameters (bond distances are r_g, bond angles are r_a) for $GaCl_3NH_3$: Ga−Cl, 2.144(5) Å; Ga−N, 2.059(11) Å; N−H, 1.029(12) Å; Cl−Ga−Cl, 116.4(3)°; H−N−H, 116.4(3)°.[20] The r_g parameters have been calculated from r_a distances using the vibrational amplitudes from ref 31. [e] Contributions from the equivalent n_{Cl}, σ_{NH}, and σ^*_{NH} orbitals in the individual complexes are summed up.

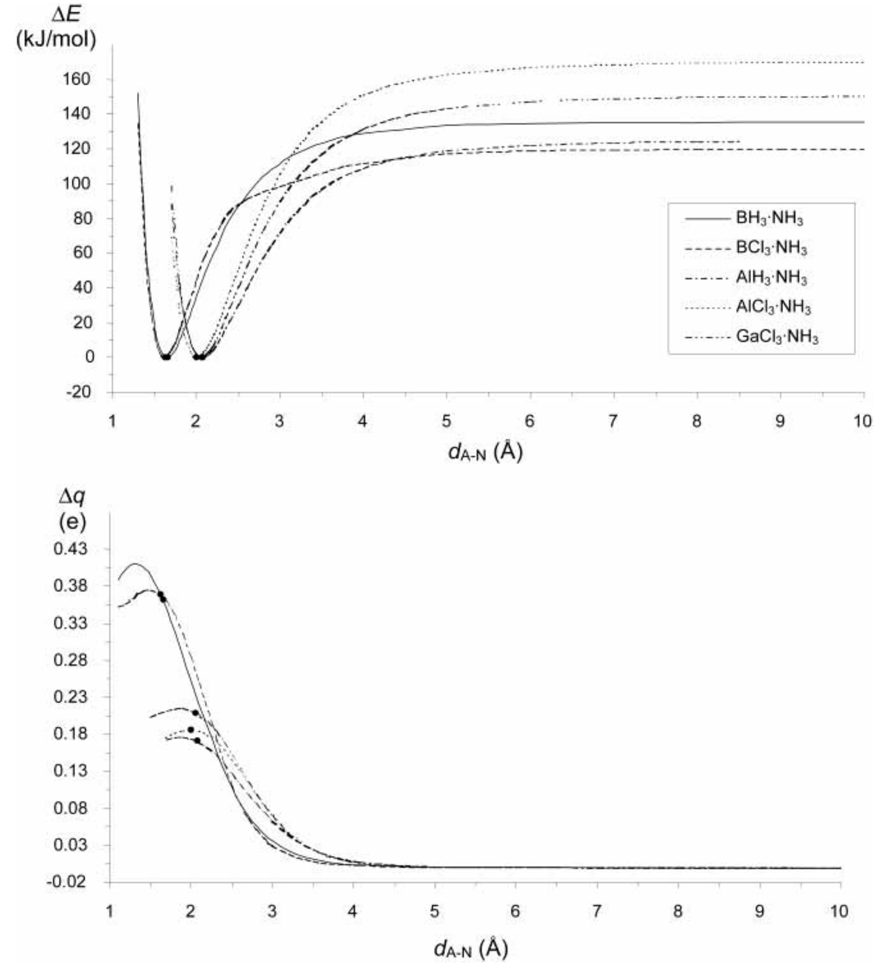

Figure 2. Variation of the uncorrected potential energy (top) and intermolecular charge transfer (bottom) along the donor−acceptor distance.

→ p_{zA} interaction, $\Delta E^{(2)}n_N \rightarrow p_{zA}$, was found to increase (although in a declining manner) in this range.

The variations of the A−L and N−H bond lengths and those of the L−A−N and H−N−A bond angles along d_{AN} are depicted in Figures 3 and 4, respectively. The curves demonstrate the gradual changes (decrease of the bond lengths and the L−A−N angle and a Morse-type curve for the H−N−A angle) when the donor and acceptor moieties move away from

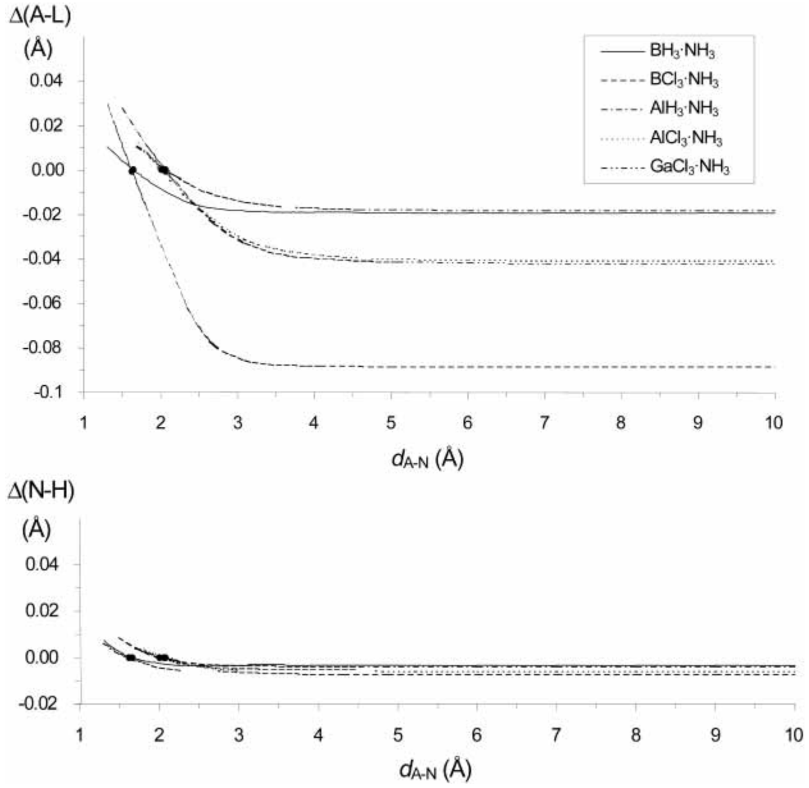

Figure 3. Variation of the A−L (top) and N−H (bottom) bond lengths along the donor−acceptor distance.

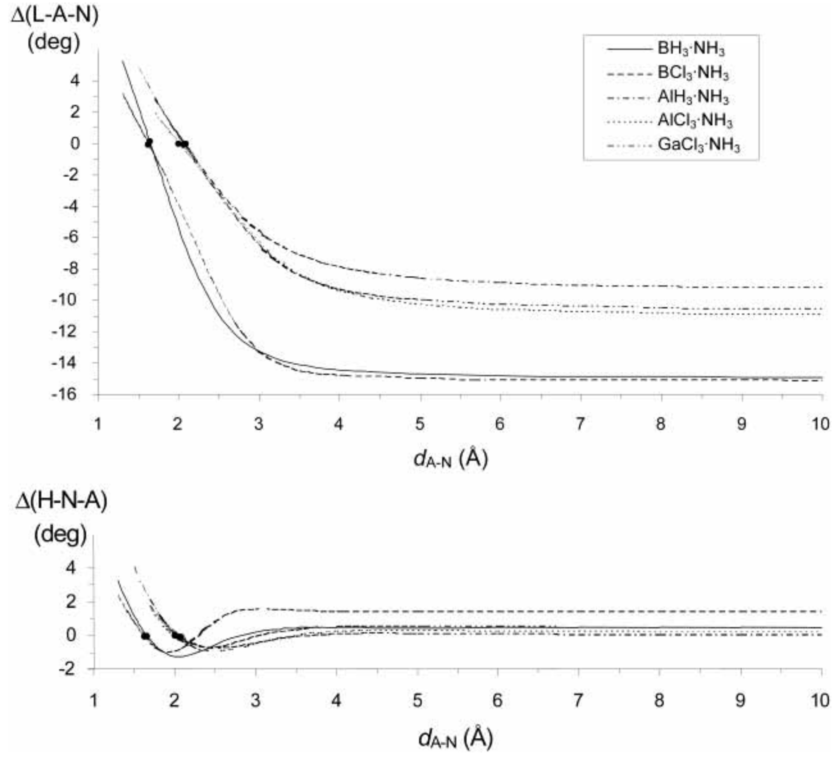

Figure 4. Variation of the L−A−N (top) and H−N−A (bottom) bond angles along the donor−acceptor distance.

each other. The values at sufficiently large d_{AN} distances represent the geometrical differences of the free moieties with respect to the equilibrium complexes.

There are substantial geometrical changes upon complex formation in the acceptor moiety, whereas only marginal ones in NH_3. We have already commented upon our results being consistent with earlier interpretations of geometrical variations.[26,27] Whereas both electron pair repulsions and atom−atom nonbonded interactions point to the planar to pyramidal transition for the acceptor part, the changes in the NH_3 part are the result of the two effects competing with each other. The pyramidalization of the AL_3 geometry is straightforward to interpret with the VSEPR model.[29,30] This change (measured by the variation of the L−A−N angles) is most pronounced in BH_3 and BCl_3, whose acceptors form the shortest donor−acceptor distance with NH_3. The magnitudes of the L−A−N angles in the equilibrium complexes correlate with the $n_N \rightarrow p_{zA}$ donation according to the data listed in Table 2. They demonstrate the important role of the donated electron density in the formation of the tetrahedral arrangement around A. Because of the staggered orientation of AL_3 and NH_3 in the complexes (favored along the whole d_{AN} coordinate), steric interactions between the two moieties for this property are probably less important.

The pronounced elongation of the A−L bonds upon complex formation originates partly from increased hyperconjugation effects between the n_N and σ^*_{AL} as well as the σ_{NH} and σ^*_{AL} orbitals (cf. Table 2) and from A−L/A−L repulsion in the more crowded pyramidal arrangement of AL_3. Thus the largest elongation, 0.09 Å, is observed in the BCl_3 moiety (Figure 3), where the largest deformation from planarity was found (Figure 4). The A−H bonds lengthen much less (<0.02 Å), in agreement with the small size (and the consequently minor steric interactions) of the hydrogen ligands.

In contrast to AL_3, the geometrical parameters of the NH_3 moiety are only marginally changed in the complexes as compared to those in the free NH_3 molecule, in keeping with the two competing effects on the NH_3 geometry in the complex formation.[26,27] The increase of the N−H bond lengths upon complex formation is below 0.01 Å and the largest change of the H−N−A angle (in BCl_3NH_3) is only 1°. The peculiarity of the H−N−A curves showing a small minimum (cf. Figure 4) indicates that at some point the effect lessening the pyramidal character of NH_3 prevails. As the donor and acceptor moieties start to move away from each other, the steric repulsion from the A−L bonds reduces to return at larger separations in the form of the steric effect of the reestablished lone pair of N.

Conclusions

In the present study, the variations of geometrical and electronic characteristics along a broad range (1.5−10.0 Å) of the donor−acceptor distance have been analyzed at the MP2(fc)/6-311+G(2df,p) level. The reliability of both the MP2(fc) theory and the 6-311+G(2df,p) basis for the long-range interactions were justified by sophisticated calculations using QCISD theory and the aug-cc-pVTZ basis set. Selected properties of five complexes (BH_3NH_3, BCl_3NH_3, AlH_3NH_3, $AlCl_3NH_3$, $GaCl_3NH_3$), viz., potential energy, total charge transfer, the A−L and N−H bond lengths, and the L−A−N and H−N−A bond angles were computed.

The geometrical consequences of complex formation are the lengthening of the A−L and N−H bonds as well as the increase of the L−A−N and H−N−A bond angles. Among them, most pronounced are the changes in the ACl_3 acceptors, up to 0.09 Å in the B−Cl bond length and 14° in the Cl−B−N angle. The geometrical changes in the AH_3 acceptors are somewhat smaller, and those in the NH_3 donor are marginal. Except for the H−N−A angle, the geometrical characteristics show a gradual decrease upon moving the two moieties away from each other. The effects of the donor−acceptor interactions on the molecular properties can be well recognized within the range of $d_e + 2$ Å. Among the investigated properties the potential energy and the L−A−N angle are the most sensitive indicators of the interaction.

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(28) The negative atomic charges of B and N in BH_3NH_3 do not necessarily mean that they repel each other. It has been found in several donor−acceptor complexes that despite the small positive or negative atomic charges the local charge distribution can show electron concentration or depletion, respectively, on the side facing the counterpart atom. See, e.g.: Timoshin, A. Y.; Frenking, G. *J. Am. Chem. Soc.* **2002**, *124*, 7240.

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