Investigation of the Molecular Geometry of Donor-Acceptor Complexes by the NDDO Method

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The molecular geometries of simple electron donor-acceptor complexes have been obtained from NDDO semi-empirical calculations. The results are in agreement with earlier observations based on experimental evidence concerning the characteristic geometrical variations in the donor and acceptor parts upon the complexation as compared with the free uncomplexed molecules. While the direction of the geometrical changes can be unambiguously predicted for the acceptor, these changes cannot be predicted for the donor as they are the results of opposing effects. It is generally observed that an increase in the bond angles is accompanied by bond shortening and vice versa. In order to interpret the results, calculated quantities from the energy partitioning have been attributed to electron pair repulsions and non-bonded atom-atom repulsions in a qualitative model.

The semiempirical all-valence-electron NDDO (Neglect of Diatomic Differencial Overlap) method [1–4] has not been widely used, though it has proved to be superior to the CNDO/2 method in several cases in predicting molecular geometries [5–7]. The NDDO method has not yet been applied to electron donor-acceptor complexes.

This paper presents an application of the NDDO method to the study of the geometries of donor-acceptor complexes. The geometries of the donor and acceptor parts of the DY_3AX_3 complexes show characteristic changes upon complex formation, as compared with the structures of the respective free uncomplexed molecules [8–10]. The geometrical consequences of the complex formation are unambiguous in the acceptor part as the electron pair repulsion from the new complex linkage and the new non-bonded atom-atom interactions (D...X, Y...X) all tend to decrease the X–A–X bond angles and to lengthen the A–X bonds. On the other hand, the diminishing electron pair repulsion from the donor lone pair allows an opening of the Y–D–Y bond angles and a shortening of the D–Y bonds while the new atom-atom interactions (A...Y, X...Y) tend to close the angles and lengthen the bonds. Thus they have opposing effects on the geometrical changes. The outcome depends on the relative magnitude of the two effects and cannot be reliably predicted. It is a general observation, however, that in any case an increased bond angle occurs together with shorter bonds and vice versa. The partitioning of the calculated total energy is considered in the present work in order to interpret the changes in the donor geometries.

The simplest representatives of the NY_3BX_3 type (X and Y = H, F) were chosen for the calculations. Complete experimental geometries are not available for these complexes, only for some of their derivatives [8–12].

Method of Calculation

The NDDO program as developed by Köhler et al. [3, 4] and further improved by us [7] was applied. For all the three complexes considered, viz. NH_3BH_3, NH_3BF_3, and NF_3BH_3, the staggered forms were first studied [cf. 13]. The geometry optimization was started from experimental data

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when available. Both the bond lengths and the bond angles have been optimized. The optimization procedure was performed for each parameter in turn. The bond distances and bond angles were changed by 2–5 pm and 2–3°, respectively, and the total energy was determined. A parabola was fitted using five data points, and its minimum was determined analytically. The optimization was finished when the changes in the optimized bond lengths and bond angles became less than 1 pm or 1°, respectively.

In addition, the rotation barriers were determined in the complexes using the optimized geometries. In each case the total energy minimum was obtained for the staggered and the maximum for the eclipsed forms. These findings are in agreement with the experimental results obtained for other boron-nitrogen complexes [13].

Results and Discussion

The experimental and NDDO-optimized geometries are collected in Table 1. Table 2 contains the N–B distances as calculated by different methods. Both the CNDO/2 [14] and the NDDO methods produce results in accordance with the experimental data while the ab initio calculations [15] show larger deviation from experiment. Neither in the CNDO, nor in the ab initio calculations were performed complete geometry optimizations.

Table 1. Experimental and NDDO optimized geometries (bond lengths in pm, bond angles in degrees).

Molecule	NDDO	Experimental [8–10]
NH_3BH_3		
N–B	154	156
N–H	106	
B–H	119	
N–B–H	108.0	
B–N–H	109.0	
NH_3BF_3		
N–B	155	160
N–H	106	
B–F	148	138
N–B–F	108.0	107.0
B–N–H	109.0	
NF_3BH_3		
N–B	158	
N–F	126	
B–H	119	
N–B–H	106.0	
B–N–F	114.0	

Table 2. Experimental and calculated N–B bond distances (pm).

Molecule	NDDO	CNDO/2 [14]	ab initio [15]	Experimental [8–10]
NH_3BH_3	154	157	168	156
NH_3BF_3	155	160	167	160
NF_3BH_3	158	158	—	—

Now the changes upon the complex formation in the calculated geometries of the donor and acceptor parts are considered. Compared to the trigonal planar geometries of the free acceptors, the geometries of the complexed acceptor parts are indeed characterized by smaller X–B–X bond angles and a longer B–F bond (in BF_3 it is 131.1–131.6 pm [8]; the geometry of the BH_3 molecule is not known).

Table 3 shows the interatomic distances and bond angles of the free and complexed NH_3 and NF_3. The calculated values of NH_3 and NH_3BH_3, as well as those of NF_3 and NF_3BH_3 are compared, lacking complete experimental geometries. It is seen that the bond lengths increase and the bond angles decrease in the complexes which means that the new atom-atom repulsions are dominating according to the calculations.

A total energy partitioning was performed [3, 16] in order to attribute calculated quantities to the two types of repulsions (electron pair and atom-atom). The sum of the one-center repulsion and exchange energy terms of the nitrogen atom (E_N) is considered here as corresponding to the lone-pair repulsion. The two-center total energy terms of the new bonded (E_{NB}) and non-bonded (E_{XY}) atom pairs in the complex are taken for the new atom-atom repulsions. As can be seen from Table 4, the

Table 3. Structural data characteristic of the donors (bond lengths in pm, bond angles in degrees).

Molecule	r(N–Y)		r(Y … Y)		∢ Y–N–Y	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
NH_3	104	102	175	165	114.5	108.0
NH_3BH_3	106	—	174	—	109.9	—
NF_3	124	137	204	213	111.3	102.0
NF_3BH_3	126	—	199	—	104.6	—
NF_3O	—	143	—	220	—	100.5

Table 4. Partitioned energy terms (a.u.).

Molecule	E_N	ΔE_N	$E_{NB} + \sum E_{XY}$
NH_3	7.81500		
NH_3BH_3	6.96311	− 0.85189	− 1.02160
NF_3	6.39475		
NF_3BH_3	5.76757	− 0.62718	− 0.88739

E_N values in both cases are smaller in the complex than in the free donor molecules. In both complexes the new atom-atom repulsions are larger than the respective differences of the nitrogen lone-pair repulsions between the free and complexed donors. This result is in agreement with the calculated changes in the geometries.

The influence of the atom-atom repulsions can also be demonstrated by the changes in the respective H...H and F...F distances of the donors being shorter in the complexes (Table 3). The decrease of the negative charge on the fluorine atoms in NF_3BH_3 as compared with NF_3 is in accordance with the change in F...F distance (Table 5). In NH_3BH_3, however, a slight decrease of the H...H distances is accompanied by an increase of the positive charge on the hydrogen atoms. In this case the change of sign of the charge on the nitrogen atom upon complexation is remarkable (Table 5).

Table 5. Net atomic charges.

Molecule	q_N	q_Y	q_B	q_X
BH_3	—	—	0.192	− 0.064
NH_3	− 0.179	0.060	—	—
NH_3BH_3	0.138	0.153	− 0.228	− 0.122
NF_3	0.297	− 0.099	—	—
NF_3BH_3	0.561	− 0.047	− 0.190	− 0.077

The calculated dipole moment of NH_3BH_3 supports the reliability of the calculated charges. The NDDO result is 21.7, the experimental 16.3 [17], and the ab initio value 18.6 [18] in 10^{-30} Cm units. No experimental data are available for the other complex.

In order to have experimental support to the calculated geometry changes, the NF_3O molecule was considered. The structure of NF_3O [19] is characterized by the short N=O bond presumably causing large repulsion. At the same time the O...F repulsions also seem to be important since the oxygen and fluorine atoms in NF_3O have nearly tetrahedral arrangement. As can be seen from Table 3, the N–F bond distances are increasing parallel with the decrease of the F–N–F bond angles, as compared with the NF_3 molecule. The decrease in the bond angles is relatively small and, accordingly, there is some increase in the F...F distances.

The determination of the complete experimental geometries of the complexes considered here would be desirable in order to check the reliability of the conclusions drawn from the calculations.

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