

# The vibrational spectra of the boron halides and their molecular complexes Part 10. The complexes of boron trifluoride with ammonia and its methyl derivatives. An *ab initio* study

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## Abstract

*Ab initio* calculations, at the level of second order Møller–Plesset perturbation theory, and using a triple-zeta Gaussian basis set with polarization and diffuse functions on all atoms, have been carried out on the donor–acceptor complexes of boron trifluoride with ammonia and its mono-, di- and trimethyl derivatives. The structures, interaction energies and vibrational spectra of the complexes have been determined. An eclipsed and a staggered conformer have been examined for each complex, and the preferred conformer was found to be the staggered species in each case. The computed data have been compared with those for some similar complexes containing boron trifluoride and a series of oxygen and sulphur electron donors (water, hydrogen sulphide, methanol, methanethiol, dimethyl ether and dimethyl sulphide) and the effect of successive methyl substitution in all three series has been investigated.

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## 1. Introduction

We have reported a series of *ab initio* calculations of the properties of some electron donor–acceptor (EDA) complexes of boron trifluoride with the series of oxygen and sulphur bases  $\text{H}_2\text{O}$  [1,2],  $\text{CH}_3\text{OH}$  [3],  $(\text{CH}_3)_2\text{O}$  [4,5],  $\text{H}_2\text{S}$  [2],  $\text{CH}_3\text{SH}$  [3] and  $(\text{CH}_3)_2\text{S}$  [4,5]. In the cases of  $\text{H}_2\text{O}$  [1],  $(\text{CH}_3)_2\text{O}$  and  $(\text{CH}_3)_2\text{S}$  [5,6], we complemented the theoretical studies with experimental measurements of the infrared spectra of the components co-condensed in nitrogen and argon matrices at cryogenic temperatures. We have confirmed [3] a clear dependence of the interaction energies on the gas phase basicities [7] of the electron donors, paralleling the increasing degree of methylation [3]. Other structural and vibrational spectroscopic properties of the complexes were also found to show a monotonic dependence on the number of substituted methyl groups and, for the same number of substituted methyl groups, the oxygen donor

was invariably more strongly bound than the sulphur analogue. We now extend this investigation to the series of methylated ammonia derivatives  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$ , in an effort to determine whether the generalizations apparent in the complexes with the oxygen and sulphur base series are also applicable to the corresponding nitrogen species.

Our earlier theoretical studies of complexes of boron trifluoride have included those with the linear nitrogen bases  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{FCN}$ ,  $\text{C}_2\text{N}_2$  and  $\text{HC}_3\text{N}$  [8,9], and with  $\text{NH}_3$  [10] and  $\text{NF}_3$  [11]. The complex of  $\text{BF}_3$  with  $\text{NH}_3$  has received a great deal of attention from other theoretical chemists [12–35]. Most of these reports have concentrated mainly on the interaction energies and the intermolecular geometries, and only one [21] addressed the vibrational spectrum. The complex with  $(\text{CH}_3)_3\text{N}$  has also been the subject of a number of reports [15,17,19,20,30–32,36–39]. On the other hand, the  $\text{CH}_3\text{NH}_2$  and  $(\text{CH}_3)_2\text{NH}$  complexes with  $\text{BF}_3$  have not enjoyed such popularity.

In the case of the adduct with  $\text{NH}_3$ , we have also carried out matrix isolation infrared spectroscopic studies of the complexes trapped in argon and nitrogen [10]. Other experimental studies of the complex of  $\text{BF}_3$  with  $\text{NH}_3$  have been carried

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out by means of infrared [40–42], Raman [41], photoelectron [12] and microwave [23,43] spectroscopy. The  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$  adduct has been the subject of infrared [40,44,45], NMR [46], microwave [47], electron diffraction [48,49] and photoelectron spectroscopic [37] examination, while infrared studies have been performed on the  $\text{CH}_3\text{NH}_2$  and  $(\text{CH}_3)_2\text{NH}$  complexes [40,45]. Only in a few cases was the range of bases sufficient to enable trends to be observed in the positions of some of the intramolecular vibrational modes; the symmetric  $\text{BF}_3$  stretching mode wavenumber decreased monotonically as the base was changed from  $\text{NH}_3$  to  $(\text{CH}_3)_3\text{N}$  and the corresponding antisymmetric mode from  $\text{CH}_3\text{NH}_2$  to  $(\text{CH}_3)_3\text{N}$ , while the antisymmetric NH stretching mode wavenumbers decreased regularly from  $\text{NH}_3$  to  $(\text{CH}_3)_2\text{NH}$  [40]. In this study we examine the changes in the properties of the complexes as methyl groups are successively substituted for the hydrogen atoms of ammonia.

## 2. Computational details

The calculations were carried out using the Gaussian-98 program [50], at the second order level of Møller–Plesset perturbation theory (MP2) [51], with the 6-311++G(d,p) basis set [52,53]. Geometry optimizations were performed at the VERYTIGHT convergence level, under  $C_{3v}$  ( $\text{BF}_3 \cdot \text{NH}_3$  and  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$ ) or  $C_s$  ( $\text{BF}_3 \cdot \text{CH}_3\text{NH}_2$  and  $\text{BF}_3 \cdot (\text{CH}_3)_2\text{NH}$ ) symmetry. Interaction energies were computed from the minimized energies of the complexes and monomers, and were corrected for basis set superposition error (BSSE) [54], using the Boys–Bernardi full counterpoise method [55], and for zero-point energy differences. Harmonic vibrational analyses were done using analytical derivatives.

## 3. Results and discussion

### 3.1. Structural properties

All four complexes optimized preferentially in the staggered conformation, as shown in Fig. 1. The eclipsed conformers were uniformly found to be first order saddle points. The optimized geometrical parameters of the complexes are reported in Table 1, along with the changes in the values of the monomer structural parameters which take place on complexation. The changes of the BF bond lengths of the electron acceptor are all positive, indicating a general weakening of the intramolecular BF bonds accompanying the formation of the intermolecular B···N bonds. The mean BF bond length increases change regularly from 5.95 pm to 6.52 pm going from the  $\text{NH}_3$  to the  $(\text{CH}_3)_3\text{N}$  complexes, consistent with decreasing strength of the BF bonds on successive methylation. The gradual lengthening of the BF bonds is accompanied by a consistent reduction in the values of the FBF angles, associated with an increasing trend to greater pyramidalization around the boron atoms. The mean decreases of the FBF angles on complexation vary monotonically from  $5.79^\circ$  for  $\text{BF}_3 \cdot \text{NH}_3$  to  $6.79^\circ$  for  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$ , tracking with the changes in the BF bond lengths.

Table 2 shows the values of the intermolecular separations and the intermolecular bond angles. In keeping with

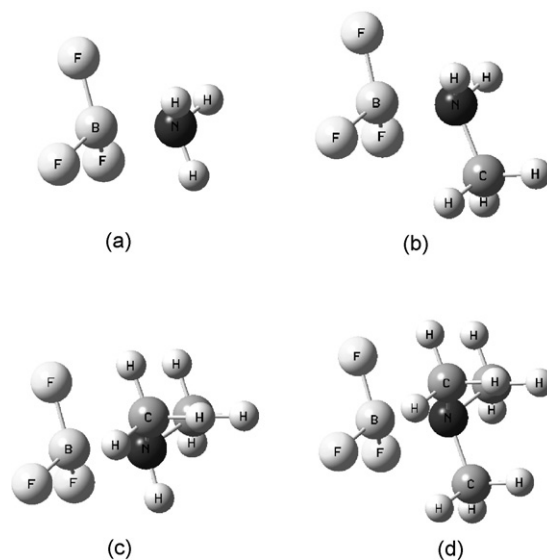


Fig. 1. The optimized structures of the complexes of  $\text{BF}_3$  with (a)  $\text{NH}_3$ , (b)  $\text{CH}_3\text{NH}_2$ , (c)  $(\text{CH}_3)_2\text{NH}$ , (d)  $(\text{CH}_3)_3\text{N}$ .

the changes of the intramolecular  $\text{BF}_3$  parameters, the intermolecular structural data also show a more or less regular variation with the number of substituted methyl groups. The B···N separation decreases from  $\text{BF}_3 \cdot \text{NH}_3$  (166.87 pm) to  $\text{BF}_3 \cdot (\text{CH}_3)_2\text{NH}$  (165.16 pm), but then increases slightly to 165.86 pm at  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$ , probably due to increased steric crowding. The mean FBF···N angle, however, increases monotonically from  $104.17^\circ$  to  $105.41^\circ$ , consistent with the change from an angle of  $90^\circ$  for a hypothetical non-interacting system to approach a more pyramidal coordination. Earlier reports of the intermolecular separation of  $\text{BF}_3 \cdot \text{NH}_3$  vary in the range 160 pm [13] to 177 pm [14], but these were among the two earliest studies, which were performed at low levels of theory. More recent values cluster around 168.4 pm, compared with our 166.87 pm. The experimental gas phase distance is 167.3 pm [23]. Similarly, the B···N distance in  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$  varies from 163.1 pm [15] to 168.6 pm [30]. Our value lies between these two extremes, and may be compared with the experimental value of 167.4 pm [47].

The rotational constants are listed in Table 3. Only in the case of  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$  has an experimental rotational constant value been reported. Iijima and Shibata's average value for B (1756.17 MHz) [49] is in remarkably good agreement with our datum.

### 3.2. Dipole moments

Our computed dipole moments are 6.58, 6.76, 6.75 and 6.64 D,<sup>1</sup> respectively, in increasing order of methyl substitution. Values reported for  $\text{BF}_3 \cdot \text{NH}_3$  by other workers vary between 6.14 D [19,20] and 6.17 D [32] (experimental 5.9027 D [31]), and for  $\text{BF}_3 \cdot (\text{CH}_3)_3\text{N}$  between 6.09 D [19] and 6.11 D [31], compared with the experimental value of 6.0157 D [31].

<sup>1</sup> 1 D =  $3.33564 \times 10^{-30}$  C m.

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