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MOLECULAR STRUCTURES OF DONOR-ACCEPTOR COMPLEXES OF BORON TRIFLUORIDE WITH TRIMETHYLAMINE AND DIMETHYLETHER

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The molecular structures of $(CH_3)_3N \cdot BF_3$ and $(CH_3)_2O \cdot BF_3$ were determined by electron diffraction. Both molecules were found to have a staggered form with $r_g(N—B) = 1.673 \pm 0.006$ Å, $r_g(O—B) = 1.719 \pm 0.023$ Å. The other molecular parameters for the complexes were compared with those for their donors and acceptor.

The Lewis complexes trimethylamine-boron trifluoride $(CH_3)_3N \cdot BF_3$ and dimethylether-boron trifluoride $(CH_3)_2O \cdot BF_3$ are considerably stable in the gaseous state.[1,2] The molecular structures of gaseous $(CH_3)_3N \cdot BF_3$ and $(CH_3)_2O \cdot BF_3$ were already studied by microwave spectra[3] and electron diffraction,[4] respectively. However, the microwave spectroscopic study gave only the N—B distance in spite of the interesting result that it is very different from that by X-ray diffraction.[5] On the other

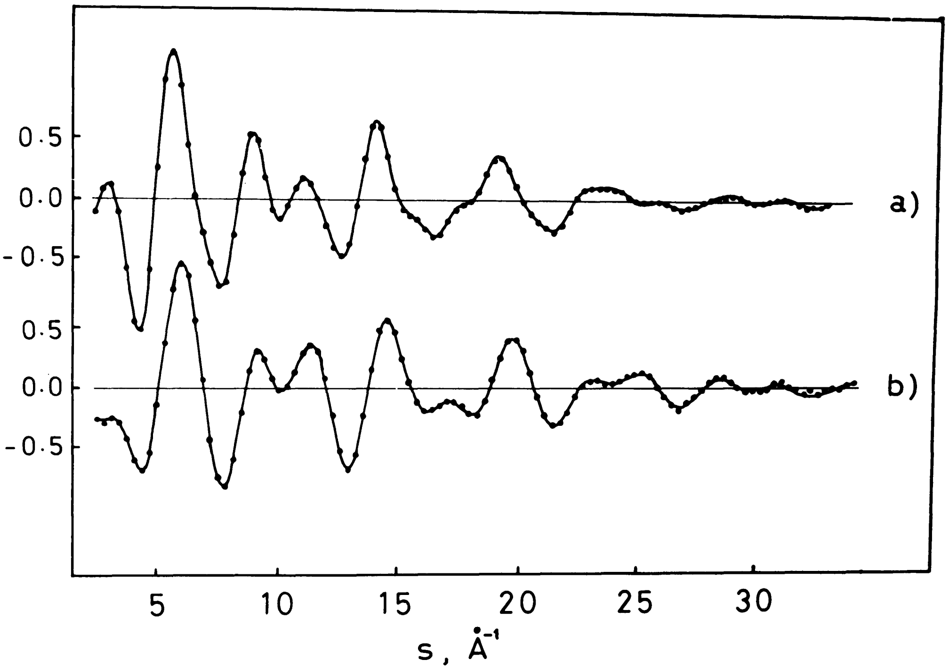

Fig. 1. Molecular intensities of $(CH_3)_3N \cdot BF_3$ and $(CH_3)_2O \cdot BF_3$
a) : $(CH_3)_3N \cdot BF_3$ b) : $(CH_3)_2O \cdot BF_3$
The dots are the observed intensities, and the curves are the calculated intensity variations.

hand, the diffraction study was carried out by a visual method with many assumptions on the geometry of the molecule. Therefore, more accurate determinations of the structures of both molecules were carried out using a sector-microphotometer method.6)

The 1:1 complexes $(CH_3)_3N\cdot BF_3$ and $(CH_3)_2O\cdot BF_3$ were prepared by mixing the donor and acceptor components, and were purified by sublimation and vacuum distillation, respectively.

Electron diffraction experiments were performed using high voltage of 40 kV, an r^3-sector, and camera distances of 144 and 294 mm. The sample of $(CH_3)_3N\cdot BF_3$ was vaporized at 130°C by means of a high-temperature nozzle, but the sample of $(CH_3)_2O\cdot BF_3$ was directly injected to a diffraction chamber at 16°C through a nozzle from a flask. The average intensities shown in Fig. 1 were obtained from densitometries for four short and three long distance photographs for $(CH_3)_3N\cdot BF_3$ and three plates for each distance for $(CH_3)_2O\cdot BF_3$. Least-squares method7,8) were applied to intensity data in the s ranges of 2.5 – 33.0 $Å^{-1}$ for $(CH_3)_3N\cdot BF_3$ and 2.5 – 34.2 $Å^{-1}$ for $(CH_3)_2O\cdot BF_3$. In the analysis of $(CH_3)_3N\cdot BF_3$, C_{3v} symmetry with a staggered form was assumed. An assumption of an eclipsed form could not yield good convergence in the calculations. C_s symmetry was assumed for $(CH_3)_2O\cdot BF_3$ with C_{2v} for $(CH_3)_2O$ and C_{3v} for BF_3. Table 1 lists the structure parameters obtained for both complexes. In the analysis of $(CH_3)_2O\cdot BF_3$ the degree of dissociation was taken as one of parameters varied. The bond distances and bond angles are quite different from those by Bauer et al.4) The planar form suggested by them was excluded, and a staggered form was concluded.

When the donor $(CH_3)_3N$9) or $(CH_3)_2O$10) and the acceptor $BF_3$11) form a complex molecule, main changes in the molecular structures are the increases in the B–F

TABLE 1. MOLECULAR STRUCTURES OF $(CH_3)_3N\cdot BF_3$ AND $(CH_3)_2O\cdot BF_3$ IN THE GAS PHASE

	$(CH_3)_3N\cdot BF_3$		$(CH_3)_2O\cdot BF_3$	
	r_g	l	r_g	l
X–B a) (Å)	1.673 (6) b)	0.082 (11)	1.719 (23)	0.133 (32)
X–C (Å)	1.485 (3)	0.056 (4)	1.425 (10)	0.060 c)
B–F (Å)	1.374 (2)	0.052 (3)	1.358 (7)	0.064 (6)
F–F (Å)	2.291 (3)	0.068 (2)	2.324 (20)	0.089 (9)
C–H (Å)	1.100 (4)	0.075 (3)	1.117 (13)	0.080 (9)
C–C (Å)	2.428 (5)	0.062 c)	2.311 (42)	0.075 c)
∠FBF (°)	112.9 (3)		117.6 (19)	
∠CXC (°)	109.6 (5)		108.4 (31)	
∠BXC (°)	109.3 (5)		119.2 (32)	
form	staggered		staggered	

a) X = N or O . b) This means error for 99 % confidence.
c) assumed values.

TABLE 2. COMPARISON OF THE STRUCTURAL DATA FOR $(CH_3)_3N$, BF_3, AND $(CH_3)_3N \cdot BF_3$

	$(CH_3)_3N$,[a] BF_3[b] (gas)	$(CH_3)_3N \cdot BF_3$[c] (gas)	$(CH_3)_3N \cdot BF_3$[d] (solid)
N – B		1.673 Å	1.585 Å
B – F	1.313 Å	1.374 Å	1.39 Å
N – C	1.454 Å	1.485 Å	1.50 Å
∠FBF	120.0°	112.9°	107°
∠CNC	110.6°	109.6°	114°

a) Ref. 9. b) Ref. 11. c) present data. d) Ref. 5.

distance, 0.06 and 0.04 Å, and the decreases in the FBF angle, 7.1 and 2.4°, for $(CH_3)_3N \cdot BF_3$ and $(CH_3)_2O \cdot BF_3$, respectively. That a planar structure of the free BF_3 molecule[11] changes to a pyramidal structure is, of course, due to the donor-acceptor σ-bond formation. The comparison of the present data of $(CH_3)_3N \cdot BF_3$ with the X-ray data[5] shows a considerable increase of the N–B distance with an increase of the FBF angle, as seen from Table 2. This suggests that the donor-acceptor bond enhanced in the solid state. The N–B distance (1.636 ± 0.004 Å) determined from the microwave spectroscopy[3] was greater than that determined from the X-ray analysis. This also indicates a change between the gas and the solid. However the N–B distance from the present study is still longer than that from the above spectroscopic study. Therefore it appears that the N–B bond is lengthened as the temperature is raised from room temperature to high temperature (130 – 140°C) because the donor-acceptor bond is remarkably weak.

The complex of $(CH_3)_2O \cdot BF_3$ is less stable than that of $(CH_3)_3N \cdot BF_3$. For example, the heats of formation of both complexes were estimated to be 13.65[2] and 26.6[12] kcal/mol, respectively. The finding that the O–B distance (1.719 Å) is pretty larger than the N–B distance (1.673 Å) is compatible with these facts. The least-square analysis for $(CH_3)_2O \cdot BF_3$ yielded the dissociation of 47 % at 16°C. This value is in good agreement with that from thermochemical data.[2]

The present results indicate two general features in donor-acceptor complex formation: The molecular structure of a donor remains almost unchanged and the nitrogen is more active as a donor atom than the oxygen.

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