Heat capacity data for aqueous sodium bisulfate were also calculated as a function of temperature from the heat capacity of aqueous bisulfuric acid and the difference in the heat capacity of aqueous sodium ion and aqueous hydrogen ion[5]

$$\bar{C}_p{}^\circ{}_{NaHSO_4}(t) = \bar{C}_p{}^\circ{}_{H\cdot HSO_4}(t) + \bar{C}_p{}^\circ{}_{Na^+}(t) - \bar{C}_p{}^\circ{}_{H^+}(t) \qquad (19)$$

These data are summarized in Table VI and Figure 4.

The Thermodynamic Functions of the Bisulfate Ion

Since the thermodynamic functions of the aqueous sulfate ion are well established,[32] it is now possible to derive similar functions for the bisulfate ion from eq 7 and the data of Tables III, IV, and VI. The revised values for the standard heat and free energy of formation at 25° are −213.20 and −180.68 kcal mol^{-1}, respectively. The standard entropy and heat capacity at 25° are 27.7 and 14.6 cal mol^{-1} deg^{-1}, respectively. The heat of formation and entropy are considerably different from the previously accepted values,[31] but, as discussed, the previous values were based on much less extensive data than in the present analysis.

Acknowledgment.—The authors are indebted to Dr. Eugene C. Jekel for his determination of the heats of solution of sodium sulfate in aqueous hydrochloric acid solutions at 95.00°.

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[32] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., Jan 1968.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND MATERIALS RESEARCH CENTER,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

Nature of the Donor–Acceptor Bond in Acetonitrile–Boron Trihalides. The Structures of the Boron Trifluoride and Boron Trichloride Complexes of Acetonitrile

BY BASIL SWANSON,[1] D. F. SHRIVER,[2] AND JAMES A. IBERS

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The crystal and molecular structure of the boron trichloride complex of acetonitrile has been determined and that of the boron trifluoride complex redetermined. Least-squares refinement of three-dimensional X-ray data led to a conventional R factor on F of 3.9% for the BCl_3 complex (441 nonzero reflections) and 5.6% for the BF_3 complex (382 nonzero reflections). Both complexes crystallize in the space group $D_{2h}{}^{16}$-Pnma of the orthorhombic system with four molecules in unit cells of dimensions $a = 8.67$ (1), $b = 7.32$ (1), and $c = 10.19$ (1) Å for Cl_3BNCCH_3 and $a = 7.784$ (3), $b = 7.177$ (3), and $c = 8.360$ (3) Å for F_3BNCCH_3. The calculated densities of 1.65 g/cm^3 for Cl_3BNCCH_3 and 1.55 g/cm^3 for F_3BNCCH_3 are in reasonable agreement with previously measured densities of 1.60 and 1.59 g/cm^3, respectively. The molecules are required to have symmetry m. The configuration about the boron in each complex is nearly tetrahedral. The B–N bond length in the BCl_3 complex (1.562 (8) Å) is significantly shorter than the B–N bond length in the BF_3 complex (1.630 (4) Å). The X_1–B–N and X_2–B–N bond angles are, respectively, 105.3 (3) and 105.8 (2)° where X = F and 106.9 (3) and 106.7 (4)° where X = Cl. These results are rationalized in terms of a model for donor–boron halide interaction in which the acceptor strength of a boron halide increases with increasing distortion of the BX_3 group. This model also is consistent with thermochemical and spectroscopic data on boron halide complexes.

Introduction

The enthalpy for the reaction of boron halides with Lewis bases is in the order $BF_3 > BCl_3 \gtrsim BBr_3$ (*i.e.*, the BF_3 reaction is the least exothermic).[3] This is the reverse of the order expected from consideration of the inductive effects of the halogens, and the explanation generally offered is that inductive effects are less important than the energy necessary to reorganize the planar free boron halide to the pyramidal form required for complex formation.[3,4] That is, the relative order of ΔH_5 for a series of boron halides with one reference donor, D, is thought to be dominated by ΔH_1 in the thermochemical cycle

$$\begin{tikzcd}
\underset{\text{pyramidal}}{BX_3(g)} + D(g) \arrow[rr, "\Delta H_3"] & & X_3BD(g) \arrow[d, "\Delta H_4"] \\
\underset{\text{planar}}{BX_3(g)} \arrow[u, "\Delta H_1"] + D(l) \arrow[u, "\Delta H_2"'] \arrow[rr, "\Delta H_5"] & & X_3BD(\text{s or soln})
\end{tikzcd}$$

where X = F, Cl, or Br. If published estimates of ΔH_1 are employed[4] and ΔH_4 is assumed to be constant for the series of boron halides with one donor, then one finds that the heat of donor–acceptor bond formation, ΔH_3, follows the trend expected from electronegativities. That is, the calculated B–N bond strength decreases from the BF_3 through the BBr_3 complexes.

In addition to the thermochemical work, many spectroscopic studies have been performed on boron halide complexes. These include studies of the

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[1] NDEA Fellow, 1968.

[2] Alfred P. Sloan Fellow, 1967–1969.

[3] This order has been found for: (a) acetonitrile: A. W. Laubengayer and D. S. Sears, *J. Am. Chem. Soc.*, **67**, 164 (1945); J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **43**, 1873 (1965); (b) nitrobenzene and pyridine: H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

[4] F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959), and references therein.

influence of BX_3 on C=O stretching frequencies, electronic spectra of $Fe(phen)_2(CN)_2 \cdot 2BX_3$ (phen = 1,10-phenanthroline),[5] and nmr chemical shifts of X_3BNCCH_3 and similar systems.[6] In these studies it is observed that the spectrum of the parent compound is perturbed most by BBr_3 and least by BF_3, and the interpretation generally offered is that the donor–boron bond strength increases from BF_3 through BBr_3. Miller and Onyszchuk[6a] were the first to point out the discrepancy between this inference of bond strengths with those deduced from published reorganization energies and thermochemical data.

Neither the estimates of reorganization energies nor the current inferences from spectroscopy afford a firm basis for a discussion of bonding. With the thought that accurate bond lengths and angles would provide more precise insight into the bonding in the boron halide complexes, we have investigated the structures of acetonitrile–boron trifluoride and acetonitrile–boron trichloride. The choice of these particular compounds for study was based on several considerations: (1) linearity of the acetonitrile group reduces problems of nonbonded atom repulsions, (2) a greater difference in properties is observed between BF_3 and BCl_3 complexes than between the analogous BCl_3 and BBr_3 complexes, and (3) comparison of the molecular parameters might be facilitated by suggested similarities in the crystal structures.[7] The crystal structure of F_3BNCCH_3 has been determined previously;[8] however, it was necessary to collect a new data set in order to attain the accuracy required for a detailed comparison with the Cl_3BNCCH_3 structure.

Unit Cells and Space Group

Because of the rapid hydrolysis of F_3BNCCH_3 and Cl_3BNCCH_3, both complexes were prepared on a high-vacuum line[9] and transferred by sublimation to 0.3-mm quartz capillaries which were subsequently sealed under vacuum. Crystals of both complexes were grown slowly in the evacuated capillaries by sublimation in a small thermal gradient. In the case of the highly volatile BF_3 complex, nitrogen was subsequently introduced into the capillary to suppress sublimation of the crystal during the data collection. A great many crystals had to be investigated optically and with precession photography until suitable ones were found. Precession photographs (Mo $K\alpha$) show the crystals to be orthorhombic. The unit cell parameters for Cl_3BNCCH_3 are a = 8.67 (1), b = 7.32 (1), and c = 10.19 (1) Å and for F_3BNCCH_3 are a = 7.784 (3), b = 7.177 (3), and c = 8.360 (3) Å. These unit cell parameters were determined at 25° for each complex by a least-squares refinement of the setting angles of 20 reflections which had been accurately centered on a Picker four-circle automatic diffractometer, as previously described.[10] The calculated densities for the two complexes, assuming four molecules per unit cell (ρ = 1.647 g/cm^3 for Cl_3BNCCH_3, ρ = 1.547 g/cm^3 for F_3BNCCH_3), agree with the densities measured by Laubengayer and Sears[3a] ($\rho = 1.60 \pm 0.05$ g/cm^3 for Cl_3BNCCH_3, $\rho = 1.59 \pm 0.05$ g/cm^3 for F_3BNCCH_3). Precession photographs of the $h0l$, hll, $0kl$, and $1kl$ layers of each compound exhibited Laue symmetry mmm with systematic absences characteristic of the centric space group Pnma and the noncentric space group $Pn2_1a$. In view of the absence of a pyroelectric effect for F_3BNCCH_3,[8] the space group D_{2h}^{16}-Pnma was tentatively assumed, and this choice was subsequently verified by the refinements. This space group requires the molecules to have a mirror plane of symmetry.

Collection and Reduction of Data

Cl_3BNCCH_3.—A set of intensity data was collected at room temperature with a four-circle Picker automatic diffractometer from a single crystal of dimensions 0.1 × 0.2 × 0.22 mm oriented in the $(\bar{2}11)$ direction on a eucentric goniometer head. Procedures previously described[10] were followed. Mosaicity of the crystal was checked by ω scans on several reflections using a takeoff angle of 0.5°; peak widths at half-height never exceeded 0.1°. Mo $K\alpha$ radiation ($\lambda(K\alpha_1)$ 0.7093 Å) was used for data collection. A takeoff angle of 1.0° was employed. The diffracted beam was filtered through 4.5-mil Zr foil (50% attenuation of the $K\alpha$ and 98% attenuation of the $K\beta$ peaks). Intensities were gathered by the θ–2θ scan technique using a scan range 0.8° on the low-angle side of the centered 2θ position to 1.0° on the high-angle side, and a scan rate of 1.0°/min. Stationary counter, stationary crystal background counts of 10 sec were taken at each end of the scan range. The pulse height analyzer was set to admit about 90% of the Mo $K\alpha$ peak and the scintillation counter was placed 30 cm from the crystal with an aperture of 4 × 4 mm. Cu foils with an attenuation factor of about 2.2 were inserted in the diffracted beam when the counting rate exceeded 7000 counts/sec.

A unique set of reflections having $2\theta \leq 55°$ was generated and arranged in efficient order to minimize slewing time. Three intense reflections in diverse regions of reciprocal space were monitored after every 100 reflections were recorded; none of these reflections showed any systematic change during the course of data collection. There were very few intense reflections between 50 and 55°, and so data collection was terminated at 55° in 2θ.

Lorentz and polarization factors were applied to reduce the raw intensities of F^2 values. A value of p = 0.04[10] was used in the calculation of $\sigma(F_o^2)$. Of the 808 independent reflections, 441 had $F^2 > 3\sigma(F^2)$. While absorption was not a major problem in this crystal (μ(Mo $K\alpha$) = 12.2 cm^{-1}, where μ is the linear

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(5) D. F. Shriver and J. Posner, *J. Am. Chem. Soc.*, **88**, 1672 (1966).

(6) Some representative references include: (a) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **44**, 899 (1966); (b) R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Am. Chem. Soc.*, **89**, 2391 (1967).

(7) S. Geller and O. N. Salmon, *Acta Cryst.*, **4**, 379 (1951).

(8) J. L. Hoard, T. B. Owen, A. Buzzell, and O. N. Salmon, *ibid.*, **3**, 130 (1950).

(9) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

absorption coefficient), its effects are not negligible and a correction was made. The resulting transmission factors[11] ranged from 0.70 to 0.78.

F_3BNCCH_3.—Owing to the small cell dimensions and the lack of significant absorption problems, we felt that the maximum number of reliable data could be collected by using Cu Kα (λ(Kα_1) 1.54056 Å) radiation rather than Mo Kα radiation.

The orientation of a crystal of dimensions 0.6 × 0.45 × 0.12 mm was determined by accurately centering 20 reflections as before. The crystal was oriented approximately in the [010] direction. Alignment of the crystal so that one of the symmetry axes is nearly coaxial (0.3° between b and φ) with the diffractometer axis, φ, may give rise to coincidence of reflections. However, this problem is minimized by the small size of the unit cell. Reflections were collected to 110° in 2θ in the bisecting geometry; reflections in the range $110° < 2\theta < 150°$ were collected with the diffractometer in the parallel geometry. Here χ was fixed at 90° and orientation was achieved with the use of ω and φ. The orientation of the crystal was initially determined in the bisecting geometry, but this orientation was refined again when the high-angle data were collected. Again the mosaicity of the crystal was checked by means of narrow-source open-aperture ω scans; the width at half-height never exceeded 0.11°. The takeoff angle during data collection was 1.1°. The intensities were gathered by a θ–2θ scan technique using an unsymmetric scan range of 1.0° on the low-angle side to 1.3° on the high-angle side of the centered 2θ position for the parallel geometry and a symmetric scan range of 1.0° on either side of the centered position for the bisecting geometry. The reflections were scanned at 0.5°/min, and 20-sec stationary counter, stationary crystal background counts were taken at each end of the scan range. The pulse height analyzer and the scintillation counter were adjusted as before. Cu foils with an attenuation factor of about 2.3 were inserted in the beam when the count rate exceeded 7000 counts/sec. The diffracted beams were filtered through 1.5 mils of Ni foil.

A unique set of reflections, 282 in the bisecting geometry having $2\theta \leq 110°$ and 188 in the parallel geometry having $110° < 2\theta < 150°$, were generated. Because of the geometrical limitations, 24 reflections in the bisecting geometry and 64 reflections in the parallel geometry could not be observed. During data collection standard reflections in diverse regions of reciprocal space were monitored. No systematic variation in intensity was noted.

The same scale factor was applied to each set during the refinement. (The intensities of three reflections, common to both data sets, were in excellent agreement after correction for absorption.) Lorentz and polarization factors were applied to both data sets to yield values of F^2. A value of p of 0.04 was used in the calculation of $\sigma(F_o^2)$. Of the 414 independent observations, 382 had $F^2 > 3.0\sigma(F^2)$. Because of the size of the crystal, an absorption correction was applied; the transmission factors ranged from 0.49 to 0.74.

Solution and Refinement of the Structures

Cl_3BNCCH_3.—A three-dimensional Patterson function was computed and trial atomic parameters for the three chlorine atoms were obtained on the assumption that the space group is Pnma. This trial solution was refined by least-squares techniques to give $R_1 = 0.26$ and $R_2 = 0.42$, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$. The function minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor, w, was taken as $4F_o^2/\sigma(F^2)$. Unless otherwise stated refinements were made on the 441 reflections with $F_o^2 > 3\sigma$. The neutral Cl, C, B, and N scattering factors were taken from the usual tabulation,[12] while the anomalous contributions of the Cl scattering factor were obtained from Cromer's[13a] tabulation and were included in the calculated structure factors.[13b] The H scattering factors were those given by Stewart, *et al.*[14]

A difference Fourier map after the initial refinement exhibited four peaks which were attributed to the remaining nonhydrogen atoms. These atoms were included in a succeeding refinement with isotropic thermal parameters to give $R_1 = 0.085$ and $R_2 = 0.105$. Subsequently, a refinement allowing all atom anisotropic thermal parameters led to $R_1 = 0.046$ and $R_2 = 0.061$. A difference Fourier map showed peaks of equal electron density (5% of the methyl group carbon atom) about 0.9 Å from the carbon atom of the methyl group in staggered and eclipsed conformations with respect to the chlorine atoms. A refinement was made by assuming α% staggered molecules and $(100 - \alpha)$% eclipsed molecules in the unit cell with α taken as a variable. This refinement was based on an idealized methyl geometry with a C–H bond length of 0.904 Å and tetrahedral C–C–H angles; the thermal parameter of H was fixed at 5.0 Å^2. This refinement led to a 53 (7)% distribution of the staggered conformation and to $R_1 = 0.039$ and $R_2 = 0.046$. A subsequent refinement assuming the $-CH_3$ group to be a free rotor led to $R_1 = 0.040$ and $R_2 = 0.047$. If one assumes that there are only random errors in the data, then the difference between R_2 for the two models significantly favors the model with H atoms occupying two conformations. Of more importance, the heavy-atom positions are insignificantly affected by the change in model.

The error in an observation of unit weight is 1.41. An analysis of this function as a function of $|F_o|$ and $\lambda^{-1} \sin \theta$ revealed no significant trends. Thus, the relative weights appear to be essentially correct while the absolute weights are about 2 times too high. As

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[11] Our version of Hamilton's GONO absorption program was used for this calculation. Other computer programs used included local versions of Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE bond distance and angle program, and Johnson's ORTEP plotting program.

[12] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[13] (a) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965); (b) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES OF Cl_3BNCCH_3 ON THE LEFT ($\times$5 IN ELECTRONS) AND F_3BNCCH_3 ON THE RIGHT ($\times$25 IN ELECTRONS)

K	L	FO	FC
***** H = 0 *****			
0	4	595	607
0	6	99	103
0	8	182	187
0	10	36	32
1	1	251	245
1	3	33	41
1	5	106	104
1	9	58	62
2	0	160	162
2	2	781	809
2	4	91	92
2	6	259	262
2	8	31	26
2	10	64	62
3	1	232	230
3	3	303	297
3	5	133	138
3	7	112	118
3	11	40	40
4	0	416	420
4	2	88	85
4	4	187	189
4	8	69	67
5	1	228	232
5	3	133	134
5	5	140	139
5	7	74	71
5	9	66	66
6	0	139	139
6	2	85	84
6	4	61	62
6	8	37	38
7	1	85	85
7	3	104	104
7	5	61	59
7	7	45	45
8	2	84	79
8	6	44	43
9	1	39	36
9	3	29	16
***** H = 1 *****			
0	1	220	205
0	2	133	128
0	3	92	93
0	4	52	54
0	5	131	132
0	6	78	79
0	7	80	82
0	8	35	34
0	9	86	91
0	10	60	57
0	11	56	53
0	13	47	39
1	1	79	77
1	2	196	192
1	3	78	79
1	4	67	67
1	5	134	136
1	6	40	46
1	7	91	93
1	9	72	72
2	1	96	91
2	3	113	108
2	4	73	70
2	5	95	92
2	6	50	50
2	7	102	108
2	8	63	66
2	9	54	56
2	11	46	43
2	12	28	21
3	1	45	54
3	2	59	58
3	3	90	93
3	4	107	106
3	5	40	47
3	6	44	42
3	7	112	112
3	8	58	58
3	10	33	34
3	11	40	34
4	1	89	90
4	2	36	31
4	4	40	23
4	5	43	49
4	6	30	29
4	9	41	39
4	11	32	22
5	1	65	48
5	2	71	72
5	5	70	74
5	6	56	57
5	8	39	38
5	9	55	52
5	10	35	35
7	4	37	40
7	7	42	39
7	8	35	32
***** H = 2 *****			
0	1	457	434
0	2	530	528
0	3	487	483
0	4	65	65
0	5	113	114
0	6	229	232
0	7	159	163
0	9	79	81
0	10	77	78
1	0	244	239
1	1	127	115
1	2	74	68
1	4	87	87
1	7	50	52
1	8	62	65
1	10	27	13
1	11	33	33
2	0	398	403
2	1	352	349
2	2	58	58
2	3	164	165
2	4	305	306
2	5	252	254
2	6	43	40
2	7	63	64
2	8	106	106
2	9	32	34
2	12	35	30
3	0	177	175
3	1	94	93
3	2	214	215
3	3	125	122
3	4	145	144
3	5	83	86
3	6	132	135
3	8	33	32
3	9	43	44
3	10	34	33
4	0	54	52
4	1	93	95
4	2	176	178
4	3	120	120
4	4	72	76
4	6	99	100
4	7	55	50
4	9	32	22
4	10	32	36
5	0	176	184
5	1	104	103
5	2	137	147
5	3	66	66
5	4	120	122
5	5	43	47
5	6	67	64
5	7	55	52
5	8	69	68
5	10	28	26
5	11	32	24
6	0	50	49
6	2	61	64
6	4	55	56
6	5	26	18
6	6	48	45
6	9	27	17
7	0	69	71
7	1	37	38
7	2	78	76
7	3	47	44
7	4	65	62
7	5	30	35
7	6	52	50
8	0	41	39
8	1	37	33
8	4	35	42
8	5	38	39
9	0	31	27
***** H = 3 *****			
0	1	101	95
0	2	62	64
0	3	116	115
0	4	191	188
0	5	112	114
0	6	53	51
0	7	70	67
0	8	93	96
0	9	54	53
0	10	75	77
0	11	30	26
0	12	46	46
1	1	221	212
1	2	55	53
1	3	218	211
1	4	52	54
1	5	56	57
1	6	39	38
1	7	37	32
1	11	35	36
2	1	81	80
2	2	74	71
2	3	107	104
2	4	23	23
2	5	82	83
2	6	141	144
2	7	67	68
2	8	74	73
2	9	41	40
2	10	47	45
2	11	32	27
2	12	36	29
3	1	149	151
3	2	22	22
3	3	85	84
3	4	40	39
3	5	111	113
3	7	41	48
3	9	54	50
4	1	52	55
4	3	61	59
4	4	80	84
4	5	52	57
4	7	42	41
4	8	38	39
4	9	31	31
4	10	39	34
5	1	49	50
5	3	99	108
5	7	52	50
5	9	33	36
6	1	32	29
6	5	35	30
6	6	33	31
7	5	52	46
7	7	36	34
***** H = 4 *****			
0	0	133	129
0	1	334	315
0	2	256	250
0	3	227	226
0	5	132	134
0	6	166	164
0	7	98	98
0	9	80	79
0	10	57	57
0	11	29	14
1	0	49	46
1	1	47	45
1	2	196	190
1	3	58	56
1	6	31	36
1	7	50	48
1	8	30	38
2	0	182	183
2	1	189	189
2	2	38	40
2	3	177	178
2	4	181	183
2	5	143	143
2	7	79	76
2	8	85	83
3	0	227	229
3	1	87	88
3	2	52	53
3	3	68	70
3	4	161	165
3	5	79	81
3	6	74	77
3	8	35	35
3	9	34	35
4	1	81	87
4	2	87	92
4	3	53	58
4	4	35	32
4	5	34	27
4	6	68	68
4	10	30	25
5	0	85	85
5	1	72	77
5	2	155	160
5	3	67	66
5	4	55	59
5	6	64	64
5	7	46	44
5	8	46	51
6	1	25	12
6	2	33	32
6	4	32	26
7	0	74	76
7	1	40	35
7	2	39	39
7	3	37	31
7	4	64	62
7	5	36	30
7	6	37	36
8	4	29	28
8	5	32	24
***** H = 5 *****			
0	1	70	68
0	3	194	192
0	4	59	58
0	5	51	50
0	7	141	147
0	10	39	49
0	11	70	69
1	1	121	121
1	2	46	47
1	3	57	62
1	5	55	56
1	7	42	41
2	1	92	92
2	3	70	68
2	5	156	163
2	6	41	38
2	8	47	43
2	9	91	92
3	1	75	79
3	3	52	60
3	4	40	38
3	5	29	25
3	6	46	48
3	7	46	51
4	1	40	37
4	3	97	98
4	4	32	27
4	5	37	42
4	7	74	74
4	10	34	27
5	1	50	51
5	4	30	28
5	5	39	37
5	6	32	26
5	8	34	35
6	1	27	26
6	3	33	36
6	5	45	45
7	4	31	20
***** H = 6 *****			
0	0	281	280
0	2	136	134
0	4	157	154
0	6	75	76
0	8	78	76
1	0	61	64
1	1	99	99
1	2	58	60
1	3	40	34
1	4	45	47
1	5	66	71
1	6	46	46
1	8	31	35
2	0	76	77
2	2	175	177
2	4	95	100
2	6	94	91
2	10	28	21
3	0	56	58
3	1	67	72
3	2	36	39
3	3	143	151
3	4	36	39
3	5	46	43
3	6	30	33
3	7	69	65
4	0	104	107
4	4	49	42
5	0	32	26
5	1	116	116
5	2	29	28
5	3	48	48
5	5	79	78
5	7	34	30
7	1	43	37
7	3	62	59
***** H = 7 *****			
0	1	168	169
0	3	60	62
0	5	89	91
0	6	38	37
0	9	56	51
0	10	39	40
1	1	41	45
1	2	30	34
1	3	30	28
1	5	36	35
1	7	25	16
2	1	126	129
2	3	98	102
2	7	68	70
2	8	33	39
3	1	31	30
3	3	40	38
3	7	32	33
3	8	35	25
4	1	96	98
4	3	36	40
4	5	55	50
5	5	28	29
6	1	50	50
6	3	35	31
***** H = 8 *****			
0	0	76	79
0	1	104	103
0	2	41	36
0	3	72	74
0	4	28	30
0	5	60	56
0	7	35	31
0	9	41	33
1	0	57	58
1	4	57	58
1	6	49	41
1	8	53	55
2	1	64	64
2	2	44	45
2	3	63	67
2	4	38	36
2	5	52	48
2	6	31	24
2	7	32	33
3	2	71	74
3	3	32	31
3	6	75	73
4	0	37	38
4	1	33	33
5	0	61	64
5	1	32	31
5	2	34	34
5	4	54	52
***** H = 9 *****			
0	1	69	67
0	3	60	57
0	4	59	60
0	5	51	46
0	8	36	33
1	3	30	26
2	1	53	56
2	2	26	21
2	3	56	57
2	6	52	53
4	1	39	39
4	3	33	36
***** H = 10 *****			
0	0	48	46
0	1	46	43
0	3	52	52
0	4	39	35
1	2	55	55
1	4	36	33
2	1	37	33
2	2	29	35
2	5	48	47
3	0	52	53
3	4	58	52

K	L	FC	FC
***** H = 0 *****			
0	2	180	152
0	4	1028	1021
0	6	97	107
0	8	171	153
0	10	88	76
1	1	1049	913
1	3	338	342
1	5	483	485
1	7	107	92
1	9	101	89
2	0	1582	1776
2	2	1658	1532
2	4	14	15
2	6	212	212
2	8	48	48
2	10	52	76
3	1	979	907
3	3	820	785
3	5	200	209
3	7	217	216
4	0	356	358
4	2	986	906
4	4	203	192
4	6	185	201
5	1	123	130
5	5	26	29
6	2	69	69
***** H = 1 *****			
0	1	746	768
0	2	1095	1122
0	3	97	107
0	4	30	31
0	5	428	418
0	6	241	252
0	7	72	78
0	8	47	38
0	10	121	113
1	1	52	94
1	2	858	857
1	3	52	48
1	4	65	57
1	5	204	194
1	6	83	87
1	8	25	18
1	9	17	11
1	10	62	60
2	1	443	441
2	2	462	487
2	3	416	392
2	4	325	308
2	5	41	45
2	6	22	20
2	7	103	95
2	8	120	121
2	9	77	74
2	10	65	72
3	1	228	215
3	2	196	212
3	3	133	127
3	4	319	300
3	5	127	127
3	6	140	134
3	7	98	101
3	8	110	114
3	9	43	47
4	1	230	232
4	2	167	165
4	3	194	189
4	4	175	151
4	5	17	15
4	6	51	59
4	7	64	65
4	8	75	77
4	9	56	56
5	1	115	101
5	2	200	193
5	3	122	119
5	6	21	26
6	1	139	138
6	4	33	40
***** H = 2 *****			
0	0	353	330
0	1	1023	1086
0	2	846	883
0	3	990	1019
0	4	94	99
0	5	271	286
0	6	216	210
0	7	77	74
0	9	88	68
0	10	36	36
1	0	1030	1064
1	1	318	308
1	2	909	934
1	3	116	110
1	4	148	129
1	5	55	43
1	6	128	128
1	7	22	13
1	8	154	142
1	9	65	60
1	10	13	10
2	0	587	597
2	1	464	476
2	2	279	278
2	3	103	106
2	4	276	277
2	5	186	185
2	6	41	42
2	7	72	65
2	8	42	47
2	9	32	23
3	0	738	733
3	1	121	135
3	2	407	425
3	3	249	246
3	4	661	675
3	5	88	79
3	6	135	139
3	7	88	93
3	8	38	37
3	9	25	24
4	0	257	268
4	1	396	407
4	2	29	27
4	3	212	216
4	4	152	151
4	5	206	215
4	6	21	7
4	7	79	83
4	8	37	45
5	0	70	77
5	1	77	77
5	2	180	186
5	3	50	54
5	4	161	152
5	5	40	53
5	8	50	46
6	0	32	36
6	2	80	91
6	7	22	21
***** H = 3 *****			
0	1	356	339
0	2	141	135
0	3	178	161
0	4	691	668
0	5	341	337
0	6	266	255
0	7	19	32
0	8	212	220
1	1	651	641
1	2	352	331
1	3	572	549
1	4	168	167
1	6	103	97
1	7	23	19
1	8	72	76
1	9	44	45
2	1	160	149
2	2	129	112
2	3	303	306
2	4	273	267
2	5	119	99
2	6	406	395
2	7	56	67
2	8	80	82
2	9	26	24
3	1	371	380
3	2	34	37
3	3	122	119
3	4	57	63
3	5	173	164
3	6	197	214
3	7	144	141
3	9	29	29
4	1	40	51
4	2	51	52
4	3	172	164
4	4	141	132
4	5	30	35
4	6	236	235
4	7	46	58
4	8	46	45
5	1	50	70
5	2	66	74
5	3	136	139
5	4	51	56
5	5	35	32
5	7	19	9
5	8	34	27
***** H = 4 *****			
0	0	671	639
0	1	375	359
0	2	803	831
0	3	539	536
0	4	100	91
0	5	167	174
0	6	156	153
0	7	261	275
0	8	64	76
0	9	29	33
1	0	64	54
1	1	241	230
1	2	373	370
1	3	348	355
1	4	45	36
1	6	55	51
1	7	21	20
1	8	52	45
1	9	32	30
2	0	165	154
2	1	115	124
2	2	60	64
2	3	94	96
2	4	368	365
2	5	338	344
2	7	141	138
2	8	40	40
2	9	71	57
3	0	384	388
3	1	389	397
3	2	119	113
3	3	194	195
3	4	187	186
3	5	171	167
3	6	120	114
3	7	65	65
3	8	30	29
4	0	142	139
4	1	104	120
4	2	105	108
4	4	255	266
4	5	256	244
4	6	33	36
4	7	65	71
4	8	17	27
5	1	51	44
5	2	50	58
5	3	31	27
5	7	29	35
6	0	195	189
6	[illegible]	80	80
6	6	30	23
***** H = 5 *****			
0	1	132	131
0	2	202	202
0	3	251	260
0	4	102	107
0	6	36	24
0	7	68	71
0	8	37	42
1	1	154	154
1	2	257	262
1	3	45	42
1	5	54	61
1	6	52	63
1	7	49	47
1	8	41	34
2	1	130	141
2	2	99	99
2	3	147	142
2	5	121	121
2	6	67	76
2	7	40	38
3	1	101	98
3	2	97	95
3	3	79	89
3	4	146	159
3	6	47	45
3	8	111	124
4	1	31	46
4	2	62	58
4	3	82	71
4	4	64	67
4	5	70	72
4	7	39	31
5	2	125	117
5	3	43	52
5	4	23	27
5	6	46	48
6	5	20	16
***** H = 6 *****			
0	0	484	489
0	1	147	144
0	3	221	221
0	4	235	237
0	5	40	46
0	6	56	46
0	7	48	44
0	8	23	26
1	0	278	263
1	1	278	277
1	2	77	76
1	3	111	126
1	4	60	58
1	5	143	148
1	6	19	22
1	7	50	54
1	8	41	56
2	0	141	138
2	1	83	85
2	2	212	220
2	3	50	43
2	4	20	31
2	5	95	90
2	6	55	55
2	7	24	29
3	0	33	36
3	1	22	24
3	2	156	153
3	3	270	265
3	4	114	116
3	5	34	21
3	6	34	17
3	7	119	104
4	0	32	20
4	1	73	79
4	2	136	142
4	3	18	10
4	5	79	68
4	6	62	55
5	0	147	137
5	1	93	80
5	5	25	35
6	4	53	35
***** H = 7 *****			
0	1	329	347
0	2	132	140
0	3	170	168
0	4	44	47
0	5	34	37
0	6	14	30
0	7	55	54
1	1	181	183
1	2	30	31
1	4	66	71
1	5	67	57
1	6	65	76
1	7	41	60
2	1	263	298
2	2	61	59
2	3	112	119
2	4	20	25
2	5	45	53
2	6	57	48
3	1	103	93
3	3	41	47
3	5	16	22
3	6	80	77
4	2	37	20
4	3	49	56
4	5	42	40
5	2	13	17
5	3	16	12
6	1	66	81
***** H = 8 *****			
0	0	50	56
0	1	167	165
0	2	60	81
0	4	91	73
0	5	29	31
1	0	58	57
1	1	22	27
1	2	48	41
1	4	46	45
2	1	39	40
2	2	42	41
2	3	91	78
2	4	101	82
2	5	55	59
3	0	61	78
3	1	24	26
3	2	40	35
3	3	16	8
3	4	66	59
4	0	30	37
4	1	14	4
4	2	38	32
4	3	70	70
5	0	10	12
5	1	10	16
***** H = 9 *****			
0	1	93	88
0	2	62	61
0	3	22	25
1	1	86	82
1	2	45	37
1	3	126	116
2	1	64	60
2	2	47	37
3	1	64	46

secondary extinction was not a problem in this crystal, no extinction correction was made.

In order to check the correctness of those data omitted ($F_o^2 \leq 3\sigma$) from the refinement, a final structure factor calculation was made for all reflections. This calculation, which gave $R_1 = 0.061$ and $R_2 = 0.080$, showed that there were no large disparities between $|F_o|$ and $|F_c|$. A difference map based on this structure factor calculation was essentially flat, the highest residual being 0.29 $e^-/Å^3$ or about 3% of the methyl group carbon peak. Values for $5|F_o|$ and $5|F_c|$ (in electrons) for the 441 reflections used in the refinement appear in Table I. The 367 reflections not used in this refinement all have $5|F_o| < 24.0$ where $5F_{000} = 3164$. The final bond lengths and angles are given in Table II. Fractional coordinates and thermal parameters are given in Table III. Root-mean-square amplitudes of vibrations are given in Table IV and a plot of the thermal ellipsoids is shown in Figure 1. The β_{22} components of the ellipsoids (normal to the mirror plane) are not excessively large and this is further support for the choice of space group Pnma.

F_3BNCCH_3.—An attempt was made to refine the Weissenberg data collected on acetonitrile–boron trifluoride by Hoard, *et al.*;[8] however, the resulting errors on parameters were too large for a precise comparison of the structures. (The R factor was 0.26.) Therefore, a new data set was obtained on the diffractometer.

TABLE II

X_3BNCCH_3 INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)

Distances			Angles		
	X			X	
Atoms[a]	F	Cl	Atoms	F	Cl
X_1–B	1.334 (5)	1.826 (7)	X_2–B–X_1	113.5 (2)	111.9 (2)
X_2–B	1.353 (3)	1.825 (4)	X_2–B–X_2	112.0 (2)	112.0 (2)
B–N	1.630 (4)	1.562 (8)	X_2–B–N	105.8 (2)	106.7 (4)
N–C_1	1.135 (5)	1.122 (7)	X_1–B–N	105.3 (3)	106.9 (3)
C_1–C_2	1.439 (5)	1.437 (8)	B–N–C_1	179.0 (3)	178.4 (6)
			N–C_1–C_2	179.3 (4)	179.7 (6)

[a] In this and subsequent tables, the standard deviation in the last significant figure is given in parentheses. C_1 is the carbon atom in the cyanide group, while C_2 is in the methyl group. X_1 and X_2 are the special- and general-position halogen atoms, respectively.

The atomic parameters for F, B, N, and C reported by Hoard, *et al.*,[8] were used as a trial structure in a least-squares refinement of the 382 reflections above background ($F^2 > 3.0\sigma(F^2)$). The scattering factors were from the sources mentioned above. No anomalous dispersion terms were included. All atoms were allowed anisotropic thermal parameters, to give $R_1 = 0.087$ and $R_2 = 0.125$. At this point it was apparent that secondary extinction was important and a refinement was made by including a variable extinction parameter in addition to the other parameters; this led to $R_1 = 0.068$ and $R_2 = 0.117$. A difference Fourier map again showed peaks disposed about the methyl

Table III

Positional and Thermal Parameters for Cl_3BNCCH_3

Atom[a]	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Cl_2	0.4156 (2)	0.0433 (2)	0.2651 (1)	17.0 (2)	21.9 (2)	11.5 (1)	−0.4 (2)	−0.8 (1)	−2.6 (2)
Cl_1	0.2781 (2)	$^1/_4$	0.4939 (2)	12.5 (2)	28.7 (4)	12.2 (2)	0	3.1 (2)	0
B	0.4242 (8)	$^1/_4$	0.3648 (6)	8.7 (8)	18.6 (15)	7.8 (6)	0	0.3 (10)	0
N	0.5842 (6)	$^1/_4$	0.4351 (4)	8.8 (7)	21.6 (12)	8.7 (5)	0	0.2 (6)	0
C_1	0.6975 (7)	$^1/_4$	0.4882 (6)	10.1 (8)	18.7 (13)	8.4 (6)	0	0.4 (7)	0
C_2	0.8431 (8)	$^1/_4$	0.5556 (6)	10.0 (9)	29.7 (18)	11.0 (7)	0	−1.2 (7)	0
H_1[b]	0.921	$^1/_4$	0.494						
H_2	0.852	0.149	0.605						
H_3	0.829	$^1/_4$	0.642						
H_4	0.898	0.149	0.531						

[a] x, y, and z are fractional orthorhombic coordinates. Thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$. [b] H_1 and H_2 are the staggered special- and general-position hydrogen atoms, respectively; and H_3 and H_4 are the eclipsed special- and general-position hydrogen atoms, respectively.

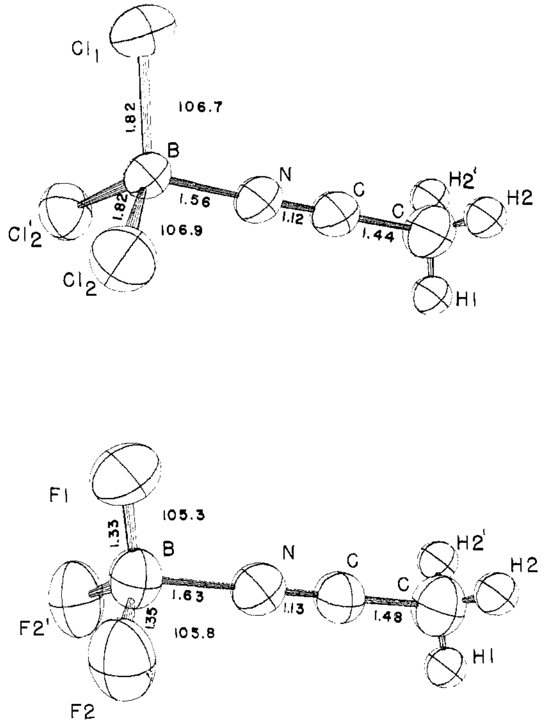

Figure 1.—Perspective views of Cl_3BNCCH_3 and F_3BNCCH_3. The atoms are displayed as 50% thermal vibration ellipsoids with the exception of hydrogen atoms which have been made artificially small for the sake of clarity. Only the staggered configurations are shown.

Table IV

Root-Mean-Square Amplitudes of Vibration (Å)

F_3BNCCH_3

Atom	Min	Intermed	Max
F_1	0.199 (3)	0.282 (3)	0.431 (5)
F_2	0.221 (3)	0.260 (3)	0.331 (2)
B	0.204 (4)	0.241 (4)	0.271 (7)
N	0.208 (4)	0.223 (3)	0.246 (6)
C_1	0.200 (4)	0.215 (4)	0.248 (6)
C_2	0.201 (5)	0.264 (5)	0.281 (7)

Cl_3BNCCH_3

Atom	Min	Intermed	Max
Cl_1	0.199 (2)	0.269 (2)	0.279 (2)
Cl_2	0.222 (2)	0.255 (2)	0.266 (2)
B	0.182 (9)	0.203 (9)	0.225 (9)
N	0.183 (7)	0.214 (7)	0.242 (7)
C_1	0.195 (8)	0.212 (8)	0.226 (8)
C_2	0.192 (9)	0.244 (8)	0.284 (9)

carbon atom in staggered and eclipsed conformations with respect to the fluorine atoms. A refinement was made for the eclipsed and staggered conformations of the CH_3 group by the procedure outlined above. This led to 50 (6)% distribution of each conformation and to $R_1 = 0.059$ and $R_2 = 0.114$. A refinement was made assuming the $-CH_3$ group to be a free rotor, and, again, on the basis of R_1 and R_2 for the two refinements, the model with H atoms occupying two conformations is preferred. An analysis of the error in an observation of unit weight showed a marked dependence on $|F_o|$. (Values varied from 2.2 to 8.6 and there was a sharp peak at $|F_o| = 2.0$ e^-.) The weighting scheme was modified in order to reduce the dependence of this function on $|F_o|$ to a value of about 1.0 for the entire range of $|F_o|$. This weighting scheme resulted in an average error in an observation of unit weight of 1.11 with values ranging from 0.85 to 1.5. A refinement using this weighting function led to values of $R_1 = 0.056$ and $R_2 = 0.088$ and to values of the parameters that differed by no more than one standard deviation from the previous ones, with the exception of the scale factor, which changed from 34.3 (5) to 35.3 (4).

A structure factor calculation for all 414 observed reflections showed no unexpected disparity between $|F_o|$ and $|F_c|$ and led to values of $R_1 = 0.062$ and $R_2 = 0.092$ and to a difference Fourier map which was relatively flat with a maximum residual of 0.23 $e^-/Å^3$, about 3% of the methyl carbon atom peak height.

Values of $25|F_o|$ and $25|F_c|$ (in electrons) for all 382 reflections used in the refinement appear in Table I. The 32 reflections not used in the refinement all have $25|F_o| < 10.75$, with $25F_{000} = 10{,}880$. The final bond distances and angles are given in Table II. Positional and thermal parameters are given in Table V. A sketch of the thermal ellipsoids appears in Figure 1 and root-mean-square amplitudes of vibration are presented in Table IV.

Description of the Structure

The crystal structures consist of discrete X_3BNCCH_3 molecules packed in an alternating fashion at $y = {}^1/_4$ and $y = {}^3/_4$. The molecules are well separated with the nearest approach of H and X on neighboring mole-

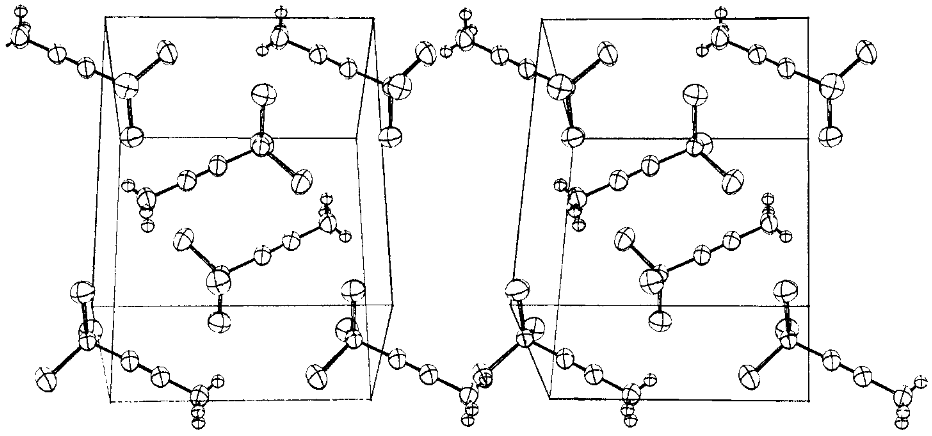

Figure 2.—A stereoscopic view of the Cl_3BNCCH_3 unit cell, where *a* points from left to right and *c* points from bottom to top.

TABLE V
POSITIONAL AND THERMAL PARAMETERS FOR F_3BNCCH_3[a]

Atom	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
F_2	0.3971 (2)	0.0937 (3)	0.2695 (2)	27.9 (4)	23.5 (8)	22.3 (4)	−0.4 (3)	−7.9 (3)	−3.7 (3)
F_1	0.2702 (3)	$^1/_4$	0.4704 (3)	13.8 (5)	71.2 (16)	21.6 (5)	0	3.1 (3)	0
B	0.3941 (5)	$^1/_4$	0.3601 (5)	15.0 (6)	28.0 (15)	15.1 (5)	0	−2.2 (4)	0
N	0.5737 (4)	$^1/_4$	0.4603 (3)	14.2 (5)	23.3 (10)	13.9 (4)	0	0.4 (3)	0
C_1	0.7000 (4)	$^1/_4$	0.5280 (4)	13.7 (6)	23.5 (12)	12.4 (6)	0	−0.8 (4)	0
C_2	0.8591 (5)	$^1/_4$	0.6156 (5)	14.9 (6)	30.3 (14)	18.1 (6)	0	−3.4 (5)	0
H_1	0.949	$^1/_4$	0.547						
H_2	0.864	0.146	0.679						
H_3	0.836	$^1/_4$	0.723						
H_4	0.921	0.146	0.591						

[a] See the footnotes to Table III for definitions of symbols.

cules in the unit cell being 2.99 Å for Cl_3BNCCH_3 and 2.64 Å for F_3BNCCH_3. A stereoscopic view of the packing is presented in Figure 2.

In both complexes the X_3BNCCH_3 molecule lies on a mirror plane at $y = {}^1/_4$ with X_1 on the mirror plane and the two X_2 atoms in general positions related by the mirror operation. The disordered hydrogen atoms assume both eclipsed and staggered conformations with respect to the BX_3 moiety and these are present in about equal amounts in both complexes. Bond lengths for the boron trifluoride complex are equal to those previously given, within the limits of error quoted in the original work.[8,15] The bond lengths between the general- and the special-position halogen atoms and the boron atom are equal in the BCl_3 complex (B–Cl_2 = 1.825 (4) Å, B–Cl_1 = 1.826 (6) Å), and the dihedral angle between the planes containing Cl_3–B–N and Cl_1–B–N is 119.9 (3)°. (For the BF_3 complex the corresponding angle is 120.5 (2)°.) Thus, the Cl_3BNCCH_3 molecule possesses C_{3v} symmetry. The usual refinement, which does not include a correction for thermal motion, yields a surprisingly large difference between the B–F_1 and B–F_2 bond lengths (1.334 (5) and 1.353 (3) Å, respectively). By contrast, correction for thermal motion using the riding model[16] yields bond lengths which agree to within two standard deviations (1.387 (5) and 1.376 (3) Å for B–F_1 and B–F_2, respectively). It is not possible to justify a large distortion from packing considerations, and a comparison of results of the two refinements indicates that the apparent B–F bond distance distortions may be due, at least in part, to peculiarities in the thermal motion.[16a]

Discussion

Comparison of bond lengths for the two compounds (Table II) reveals that the B–N distance is 0.068 (9) Å shorter for the BCl_3 complex. This very significant difference is unaffected by corrections of the B–N distances for various models of thermal motion. We conclude that the donor–acceptor bond is stronger in Cl_3BNCCH_3 than in F_3BNCCH_3. This finding puts on firm ground the inference from previous spectroscopic data that BCl_3 is the stronger electron-pair acceptor. From two different bond length–bond energy correlations for the isoelectronic C–C single bond,[17,18] we estimate the difference in B–N bond energy between the two complexes to be 8 or 16 kcal/mol. Obviously, these estimates give only an order of magnitude indication of the differences in B–N bond energies.

The extent to which the donor and acceptor reorganize upon bond formation is also apparent from the data in Table II. From the small variation in

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[15] J. L. Hoard, S. Geller, and T. B. Owen, *Acta Cryst.*, **4**, 405 (1951).

[16] W. R. Busing and H. A. Levy, *ibid.*, **17**, 142 (1964).

[16a] NOTE ADDED IN PROOF.—A recent broad-line nmr study by B. A. Dunell, C. A. Fyfe, C. A. McDowell, and J. Ripmeester, *Trans. Faraday Soc.*, **65**, 1153 (1969), indicates that methyl groups are rotating to the lowest temperature studied (77°K), and the onset of BF_3 reorientation occurs around 130°K, for F_3BNCCH_3.

[17] J. E. Bloor and S. Gartside, *Nature*, **184**, 1313 (1959).

[18] M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962, p 66.

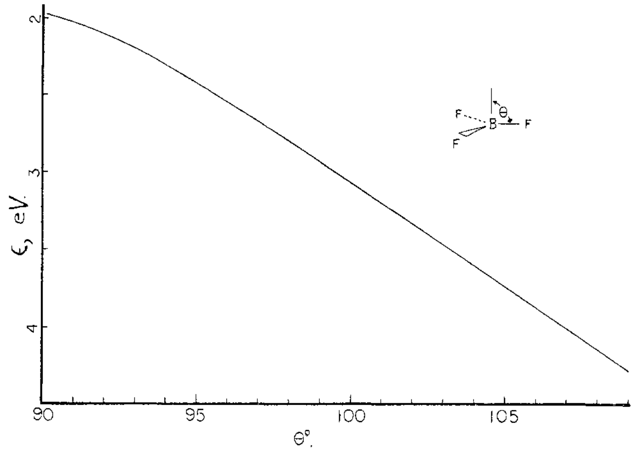

Figure 3.—Calculated energy of lowest unfilled molecular orbital of BF_3 as a function of distortion angle θ. In these calculations the B–F bond distance was assumed to be a linear function of θ between 1.295 Å for $\theta = 90°$ (BF_3) and 1.40 Å for $\theta = 109°$ (BF_4^-).

C≡N bond lengths in a variety of compounds[19] and from Hoard's classic studies on donor–acceptor compounds,[15] little reorganization is expected for the acetonitrile moiety. The C≡N distance (r_s) in acetonitrile is 1.157 Å,[20] and by comparison with the carbon–nitrogen bond lengths in Table II it is clear that a small apparently significant C≡N bond shortening (*ca.* 0.02 Å) has occurred upon formation of F_3BNCCH_3.[21] This indicates that the C≡N bond strength is slightly increased by donor–acceptor bond formation. This observation is relevant to the origin of the increase in C≡N stretching frequency which occurs when nitriles serve as electron donors.[22] We conclude that the increase in frequency is at least in part due to an increase in the C≡N stretching force constant.[23] There is a small decrease (0.013 Å) in the C≡N bond length from the BF_3 complex to the BCl_3 complex; however, this difference is less than twice the standard error and it may not be significant. The C–C bond distances 1.439 (5) and 1.437 (8) Å are identical in the two complexes. Interestingly, this C–C distance of 1.438 Å is 0.02 Å shorter than in the free molecule.[20]

To consider reorganization of the boron halides it is helpful to compare symmetry-related B–X bonds in the two compounds because of their low site symmetry. First, we compare the degree to which the boron halides have been distorted from the planar configuration of the free molecules. Interestingly, the Cl_1–B–N angle is 1.6 (4)° larger than the F_1–B–N angle, despite the fact that steric crowding should be more severe for chlorine than fluorine atoms. Similarly, the Cl_2–B–N angle is 0.9 (4)° larger than the F_2–B–N angle. These bond-angle differences are, respectively, three and two times the standard deviation. Whether these differences are significant is difficult to assess, owing to differences in the thermal motions of the atoms in the two complexes.

The B–F bond-length increase upon complex formation is evident from a comparison of the value for the free molecule, 1.309 (1) Å,[24] with the B–F_1 and B–F_2 distances in Table II. For B–F_1 the increase in distance, Δr, is 0.025 (5) Å and for B–F_2 it is 0.044 (4) Å. Unfortunately, the accuracy of the B–Cl distances determined for free BCl_3 in the solid state is not high—1.75 (2) Å.[25] However, the bond lengthening, 0.07–0.08 Å, appears to be significant. Comparison of these values with those of the BF_3 complex suggests that upon complex formation boron–halogen bond stretching may be more extensive for BCl_3 than for BF_3.

These structural comparisons show that the B–N donor–acceptor bond is shorter in the BCl_3 complex than in the BF_3 complex. The results also indicate, but do not prove, that upon complex formation the BCl_3 group is subject to a greater angular and bond-lengthening distortion than is BF_3. These observations conform to the postulate that partial reorganization of the BX_3 group plays an important role in determining the acceptor strength of the boron halides.[26] According to this model the most easily distorted acid (in the present case BCl_3[27]) will undergo the greatest distortion and this in turn leads to enhanced acceptor strength.[28]

A graphic and more exact illustration of the influence of reorganization is presented in Figure 3, where the results of a semiempirical valence-orbital basis-set LCAO–MO–SCF calculation are presented for BF_3 with progressive degrees of distortion.[29] The important feature of this diagram is the decrease in energy (increase in electron affinity) of the acceptor orbital upon reorganization of the BF_3 molecule. To the extent that we can talk of localized bond energies, the increase in donor–acceptor bond energy upon distortion of the BX_3 group must be balanced against the energy neces-

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(19) D. Britton in "Perspectives in Structural Chemistry," Vol. 1, J. D. Dunitz and J. A. Ibers, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 109.

(20) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). From a similar analysis of microwave data, Costain showed that the r_s value is 0.002 Å larger than r_e for HCN and he also concluded that this is the disparity generally expected; therefore, the equilibrium value in acetonitrile is probably close to 1.155 Å.

(21) This C≡N bond shortening is indicated but not proven by the earlier structural data[15] where the standard deviations are relatively large.

(22) (a) H. J. Coever and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958); (b) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960).

(23) This conclusion is in agreement with partial vibrational analyses of acetonitrile complexes: (a) I. R. Beattie and T. Gilson, *ibid.*, 2292 (1964); (b) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966).

(24) S. G. W. Ginn, J. K. Kenney, and J. Overend, *J. Chem. Phys.*, **48**, 1571 (1968).

(25) M. Atoji and W. N. Lipscomb, *ibid.*, **27**, 195 (1957).

(26) The postulate that BCl_3 is more extensively reorganized and is therefore a stronger electron-pair acceptor than BF_3 was proposed by J. J. Rupp and D. F. Shriver, *Inorg. Chem.*, **6**, 755 (1967), and by D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Am. Chem. Soc.*, **90**, 5706 (1968), to explain spectroscopic and thermal data for boron halide adducts.

(27) Out-of-plane bending force constants and molecular orbital estimates show that BCl_3 is more easily distorted than BF_3 (see ref 4).

(28) The increase in acceptor strength is expected because of the increased s character in the acceptor orbital and the decrease in B–X π bonding, which occur upon progressive distortion of BX_3 from a planar to a pyramidal geometry.

(29) The calculation was performed using a modified CNDO model described by P. M. Kuznesof and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 1079 (1968). In the notation of this reference, input data are: $\beta°_B = -13$, $\beta°_F = 21$, $U_{ss}(B) = 32.08$, $U_{pp}(B) = 25.528$, $U_{ss}(F) = 140.888$, and $U_{pp}(F) = 123.508$ eV.

sary to bring about the distortion. Thus, the most easily distorted molecule may turn out to form the strongest donor–acceptor bond.

To explain the thermodynamic data we note that for easily distorted Lewis acids, such as BCl_3, ΔH_1 has a smaller positive value and ΔH_3 has a larger negative value than for a less easily distorted molecule such as BF_3. The net effect is to make the donor–acceptor reaction enthalpy, ΔH_5, more negative (exothermic) for the more easily distorted acid. Similarly, most spectroscopic studies and the present structural results indicate the more easily distorted acid forms the stronger donor–acceptor bond. In summary, the model of partial reorganization, which is suggested by the structural results, affords a straightforward explanation of both spectral and thermodynamic data for a series of boron halides interacting with a common donor.

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CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.,
MURRAY HILL, NEW JERSEY 07974

Dianionic Rhenium Carbonyl Halides

BY M. J. HAWKES AND A. P. GINSBERG

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The dinegative rhenium carbonyl halide anions $Re(CO)_3X_3^{2-}$ (X = Cl, Br, I) and $Re_2(CO)_6X_4^{2-}$ (X = Cl, Br) have been obtained as their tetraethylammonium salts from the reaction of $[(C_2H_5)_4N][Re_2(CO)_6L_3]$ (L = H, C_2H_5O, *i*-C_3H_7O) with the hydrohalic acids. With the exception of the dimeric bromo complex, they can also be prepared by the action of halide ions on the appropriate halogenopentacarbonylrhenium. An isothiocyanato complex, $Re(CO)_3(NCS)_3^{2-}$, results from treating any of the dianions with SCN^-. Infrared spectra were determined, and the CO and ReX stretching frequencies were identified. The results are consistent with *cis* (C_{3v}) octahedral geometry for $Re(CO)_3X_3^{2-}$ and with a doubly halogen-bridged dimeric arrangement for $Re_2(CO)_6X_4^{2-}$. The ReX stretching frequencies of $Re(CO)_5X$ (X = Cl, Br, I), $Re(CO)_4X_2^-$ (X = Br, I), $Re_2(CO)_8X_2$ (X = Cl, Br, I), and $Re_2(CO)_7X_3^-$ (X = Cl, Br) are also reported and used to indicate probable structures.

Introduction

Rhenium forms a series of monomeric and also a series of dimeric carbonyl halide complexes. The monomer series is comprised of the pentacarbonyl halides,[1,2] $Re(CO)_5X$, the dihalogenotetracarbonyl anions,[3] $Re(CO)_4XY^-$ (X and Y = Cl, Br, or I), and the triiodotricarbonyl dianion,[3] $Re(CO)_3I_3^{2-}$. The dimer series consists of the dihalogenooctacarbonyldirhenates,[4] $Re_2(CO)_8X_2$ (X = Cl, Br, I), and the trihalogenoheptacarbonyldirhenate anions,[3] $Re_2(CO)_7X_2Y^-$ (X and Y = Cl or Br). In the present paper we report two members of a new class of complex belonging to the dimer series, the tetrahalogenohexacarbonyldirhenate dianions, $Re_2(CO)_6X_4^{2-}$ (X = Cl, Br) and also three new members of the known class of monomeric dianions, $Re(CO)_3X_3^{2-}$ (X = Cl, Br, NCS). These dinegative rhenium carbonyl halide anions were obtained as their tetraethylammonium salts from the reaction of tri-μ-hydrido- and tri-μ-alkoxy-hexacarbonyldirhenate(I),[5] $[(C_2H_5)_4N][Re_2(CO)_6L_3]$ (L = H, C_2H_5O, *i*-C_3H_7O), with the hydrohalic acids. With the exception of the dimeric bromo complex, they have also been prepared by the action of halide ions on the appropriate halogenopentacarbonylrhenium.

In order to characterize the $Re(CO)_3X_3^{2-}$ and $Re_2(CO)_6X_4^{2-}$ complexes it was necessary to study their far-infrared spectra in the metal–halogen stretching region and to compare the results with the spectra of the other rhenium carbonyl halides. The far-infrared spectra of the pentacarbonyl halides have been reported,[6] but none of the other compounds appears to have been examined in this region. We therefore determined the infrared spectra in the metal–halogen stretching region of most of the known rhenium carbonyl halide complexes and interpreted the results in terms of probable structures.

Experimental Section

Far-infrared spectra were recorded on a Beckman IR 11 spectrophotometer over the range 400–80 cm^{-1}, for samples in CsI disks and Nujol mulls mounted between polyethylene plates. The instrument was calibrated by reference to part of the rotational spectrum of water vapor. The correction to the chart-read frequencies was within ±1 cm^{-1} over the whole range. The frequencies quoted should be accurate to ±2 cm^{-1}. Infrared spectra in the range 4000–300 cm^{-1} were recorded on Perkin-Elmer 337 and 457 spectrophotometers, calibrated by reference to the spectrum of a polystyrene film. In the CO stretching region the frequencies quoted should be accurate to ±2 cm^{-1}. Conductivities were measured at 25.0 ± 0.1° on a Serfass con-

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