

SPECTROSCOPIC STUDIES OF LEWIS ACID–BASE COMPLEXES. IV. AN INFRARED STUDY OF ORIENTED SINGLE CRYSTALS AND NORMAL COORDINATE ANALYSES OF TRIMETHYLAMINE–BORON HALIDE ADDUCTS

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ABSTRACT

A total of 19 isotopic species of various $(\text{CH}_3)_3\text{NBX}_3$ complexes have been prepared and their IR spectra studied in the solid state in the region $40\text{--}4000\text{ cm}^{-1}$. The isotopes involved are deuterium, boron-10, boron-11, and nitrogen-15 with $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I . C_{3v} symmetry has been preserved in all cases. Symmetry classifications of the fundamental molecular frequencies have been derived from polarized IR measurements on oriented single crystals in the range $250\text{--}4000\text{ cm}^{-1}$. Errors and inconsistencies in previous studies have been resolved and revised vibrational assignments are proposed on the basis of the new data. Normal coordinate analyses have been carried out utilizing symmetry compliance constants without the assumption of point mass methyl groups. A common potential function containing 22 parameters for the A_1 class and 26 for the E class was utilized. The results support the proposed frequency assignments. B–N force constants obtained by inversion of the compliance matrices vary systematically from the chloro to the iodo complex. However, the B–N force constant for the fluoro complex falls between that for the chloro and bromo species; no systematic trend appears for the B–N compliance constants.

INTRODUCTION

The problems encountered in vibrational studies and normal coordinate analyses of relatively large molecules are well known to spectroscopists and the situation has been well summarized by Califano [1]. On the experimental side, one is troubled by accidental degeneracies and usually it is either not feasible to obtain spectra of the vapor or it is impossible to distinguish band contours satisfactorily because of band overlapping. Vital symmetry information as well as auxiliary data such as Coriolis constants are therefore difficult to obtain. In carrying out a normal coordinate analysis, vexatious problems include the inability to arrive at a satisfactory and unequivocal frequency assignment, a lack of sufficient data to determine the force constants, the absence of accurate values for molecular parameters and the fact that many force constants are insensitive to vibrational frequencies and

hence are poorly determined by frequency data alone. Despite these and other difficulties, the determination of vibrational potential functions of relatively large molecules continues to be of considerable interest to chemists. If the limitations and constraints involved are kept in mind, the results can be of significant value, particularly when the spectra of a series of related molecules can be analyzed by a uniform and consistent procedure.

A number of favorable circumstances in the present work has allowed some of the difficulties cited above to be avoided or minimized. In particular, prior determinations of the crystal structures [2-4] of the compounds have not only provided accurate values of the molecular parameters but have made it possible to establish unequivocal symmetry assignments from the spectra of oriented single crystals. Extensive isotopic substitution has aided in establishing descriptive assignments in addition to providing a large number of vibrational data for the normal coordinate analyses. The latter were formulated in terms of compliance constants rather than force constants in order to compare the advantages and disadvantages of this approach for molecules of the size involved.

The first extensive spectroscopic investigation of $(\text{CH}_3)_3\text{NBX}_3$ complexes was that of Amster and Taylor [5] who studied the IR and Raman spectra of the fluoro, chloro and bromo complexes prepared from materials enriched in boron-10 as well as from natural boron. Vibrational assignments were proposed on the basis of the boron-10 isotopic shifts plus correlations with frequencies and assignments of related molecules available in the literature. Work prior to Amster's is summarized in ref. 5. Sawodny and Goubeau [6] included the trimethylamine-boron halide complexes in an extensive series of force constant calculations on R_3NBX_3 type molecules. However, no new isotopic data were presented and in their calculations, the methyl groups were treated as point masses. Unfortunately, the point mass methyl group approximation is not always a good one, and this is particularly so in the case of large molecules having skeletal modes with frequencies in the neighborhood of methyl rocking and deformation frequencies.

From a chemical point of view, the study of the trimethylamine-boron halide complexes has a number of interesting aspects. Chief among these is the extent to which a correlation exists among force (or compliance) constants, dative bond lengths, and chemical properties such as the variation in acid strength of the boron halides. A variety of physical and chemical data now exist [7-11] indicating that the order of acid strength of these halides deduced from electronegativity arguments is not correct and that the correct sequence is $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$, although the position of BI_3 in this sequence is not well established. In discussions of molecular energetics, attention has been called to the fact that the reorganisation energy needed to distort a boron halide from a planar to a pyramidal form is greatest for BF_3 and progressively less for the other halides [12, 13]. One might therefore expect progressively greater dative bond strengths with the heavier halides if there is to be agreement with the chemical data and this has been borne out by

studies of acetonitrile-boron halide complexes [13]. Further corroboration appears desirable, however.

EXPERIMENTAL

Preparation and Purification

Boron trifluoride was prepared by the thermal decomposition of isotopically enriched potassium fluoborate (99.4 atom percent boron-11 or 92 atom percent boron-10) in vacuum at 700–750 °C. Boron trichloride and tribromide were made by halogen exchange from isotopically enriched KBF_4 and the appropriate aluminum halide [14]. The products were purified before use by trap to trap distillation and the completeness of the halogen exchange was checked by IR and vapor pressure measurements. Boron triiodide (K & K Laboratories) containing natural boron was purified before use by dissolving the crystals in benzene and shaking the solution with mercury to remove free iodine. Isotopically enriched samples of the iodide were prepared by halogen exchange using lithium iodide and the appropriate enriched boron tribromide [15].

Trimethylamine was obtained by the addition of NaOH to the hydrochloride salt. The amine was passed through BaO to remove water and further purified by trap to trap distillation. Trimethylamine- d_9 was obtained from Merck, Sharpe and Dohme, Ltd. Trimethylamine enriched to 95 atom percent in nitrogen-15 was prepared by the reaction of paraformaldehyde and NH_4Cl at 130 °C. The amine was freed by the addition of excess NaOH and purified by distillation after passage through BaO and Ascarite*.

The boron trifluoride, trichloride and tribromide adducts were made simply and successfully by direct combination of equimolar amounts of the acid and base in the vacuum line at -196°C . Each complex formed as a white powder when the mixture warmed. The triiodide was prepared similarly except that the BI_3 was dissolved in benzene and the solution frozen before the addition of the amine. Excess reagents (and solvent in the iodo case) were removed by pumping. Purification of the complexes was achieved by sublimation and the iodo compound was further purified by passing its solution through activated charcoal after which it was crystallized from chloroform. Since the iodide complex slowly decomposed upon exposure to air, spectra were obtained immediately after purification. Complexes prepared from the boron-enriched iodide gave satisfactory elemental analyses but the IR spectra showed two extraneous frequencies which were attributed to a small amount of bromide contamination since the frequencies were absent in the samples prepared from the commercial BI_3 .

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Spectroscopic Equipment and Procedures

Infrared spectra were taken with a Beckman IR-12 spectrophotometer in the range $200\text{--}4000\text{ cm}^{-1}$. The instrument had been calibrated with standard substances throughout its range and found to be well within specifications. Spectra of all compounds were obtained from samples in KBr discs at room temperature, and most samples were also examined at liquid nitrogen temperatures. Polarized IR spectra of thin oriented crystals were recorded from $250\text{ to }4000\text{ cm}^{-1}$ using a Beckman mirror beam condenser and micro sample holder in conjunction with a gold wire polarizer on an AgBr substrate. The polarizer was mounted immediately before the exit slit in the monochromator compartment. No attempt was made to measure the dichroic ratios accurately since the intensity difference for a given band between the two modes of polarization was such that a qualitative inspection sufficed for symmetry determination. Far-infrared spectra of the samples in the form of mulls in the range $50\text{ to }600\text{ cm}^{-1}$ were obtained through the courtesy of Dr. Howard Sloane and the Beckman Instrument Co., and Dr. William Potts and the Dow Chemical Co.

Raman spectra of the $(\text{CD}_3)_3\text{NBrCl}_3$ and $(\text{CD}_3)_3\text{NBrBr}_3$ complexes were obtained photographically from pressed discs of the pure substances using the equipment and procedures described by Amster [5]. Halation from the exciting line prevented observations below about 600 cm^{-1} . Raman spectra of the normal chloro and bromo complexes dissolved in acetone and dimethylsulfoxide were obtained using a Toronto arc source primarily to check on the polarization characteristics of certain lines. However, the low concentrations of the saturated solutions and resultant long exposure times made the procedure useful for only the more intense lines.

Infrared Polarization Measurements

Single crystal X-ray studies have shown that the fluoride complex belongs to the $R\bar{3}m$ space group [4] with one molecule per unit cell. The molecular three-fold axes are aligned parallel to the direction of the crystallographic three-fold axis. The chloro, bromo and iodo complexes are not isomorphous with the fluoride but crystallize in the $P2_1/m$ space group with two molecules per unit cell [2]. The molecular axes deviate from 5° to 14° from the direction of the crystallographic a axis. In all four crystals, the molecular axes are parallel making it relatively simple to distinguish the A_1 and E molecular modes by experiments with polarized IR radiation.

Single crystals of the complexes were grown by slow evaporation from chloroform solutions. The most suitable specimens were the thin plates which grew up the sides of the container. X-ray diffraction photographs of fragments of the specimens were taken to confirm their crystallographic orientation. The fluoro crystals grew with the prominent direction of growth parallel to the direction of the unique 3-fold crystallographic axis;

the chloro and bromo compounds grew in thin, elongated plates which possessed prominent crystallographic ac (010) planes with the most rapid growth parallel to the a axis. The iodo complex grew in rectangular, striated sections which had prominent ab planes or well-developed bc planes. Thin crystals of the compounds were aligned with the molecular 3-fold axis of each approximately parallel to the exit slit of the monochromator. The polarizer rather than the crystals was rotated in order to keep the sample area in the beam as large as possible.

The crystals of the fluoro complex and, to a slight extent, the chloro, sublimed in the heat of the beam condenser; it was necessary to direct a stream of cold, dry nitrogen onto the fluoro sample while its spectrum was being obtained to preserve the specimen. Some difficulty was met with the iodo complex in obtaining large enough crystals with an appropriate and uniform thickness. As a result, the spectra of this compound were of somewhat poorer quality than those of the others.

RESULTS AND ASSIGNMENTS

Selected IR spectra of species whose spectra have not been previously published are shown in Figs. 1 and 2 while a typical polarized spectrum is illustrated in Fig. 3. Complete tables of observed frequencies for all isotopic species investigated, since they are quite extensive, have not been included here but are available elsewhere [16]. Instead, the assigned fundamental frequencies are compiled in Tables 1–4 for the series of complexes. Good agreement with previously reported frequency values was found, differences generally being less than experimental error. As a result of the high dichroic ratio for the IR spectra, it was possible to identify and measure the frequencies of several fundamentals whose location previously had had to be inferred because they were involved in accidental degeneracies. The present data, therefore, are more complete and possess smaller experimental errors by virtue of the improved instrumentation and better resolution. Uncertainties in sharp, well-resolved bands are estimated to be of the order of 1 cm^{-1} .

The site group and factor group analyses for these compounds have been discussed elsewhere [16] but the experimental results do not appear to require this level of interpretation. Instead, a simple "oriented gas" model appeared entirely adequate for the interpretation of the spectra. Factors justifying this simplification include the high degree of coincidence of the Raman and IR frequencies, the high dichroic ratios observed, the virtual absence of appreciable splittings in sharp bands and the fact that there were few bands that could not be satisfactorily accounted for by a straightforward assignment to A_1 and E molecular modes. In the following discussion, therefore, the vibrational assignments will be discussed in terms of a C_{3v} model having 10 A_1 , 5 A_2 and 15 E modes. The numbering scheme and a simplified description of the various normal modes are given in Table 5.

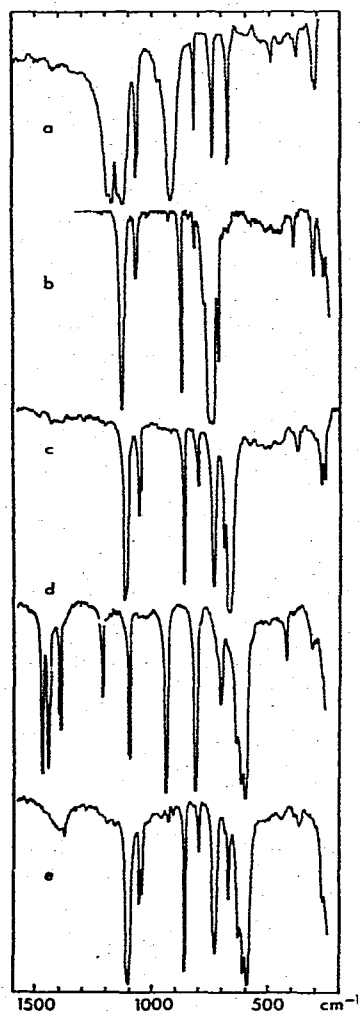


Fig. 1. Infrared spectra of various trimethylamine—boron halide complexes in KBr discs. (a) TMA- d_3 : $^{11}\text{BF}_3$; (b) TMA- d_3 : $^{11}\text{BCl}_3$; (c) TMA- d_3 : $^{11}\text{BBr}_3$; (d) TMA: $^{10}\text{BI}_3$ and (e) TMA- d_3 : $^{10}\text{BI}_3$; (n refers to the natural isotopic composition of boron).

Bands above 250 cm^{-1} were classified as to symmetry primarily on the basis of the IR polarization results. Bands falling below the limit of the IR polarizer were classified on the basis of trends in frequencies in the series of adducts plus the polarization results from the Raman spectra of solutions of the chloro and bromo complexes. Product rule calculations were made for the two active symmetry classes as an additional verification of the assignments; the results shown in Table 6 are well within the limits expected from the harmonic approximation and provide additional substantiation. Since attempts to sort out and assign the C—H and C—D stretching modes were not pursued, the product rule calculations were based on the fundamentals appearing below 1600 cm^{-1} . The theoretical ratios were evaluated from the

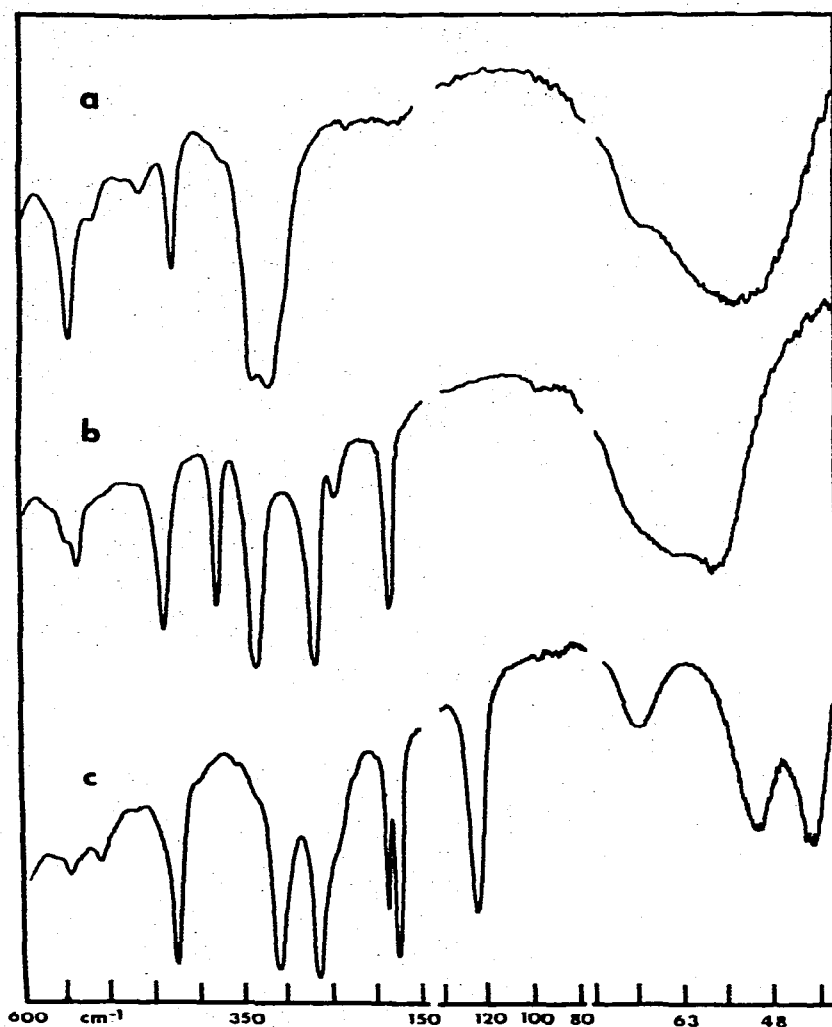


Fig. 2. Far infrared spectra of some trimethylamine-boron halide complexes as Nujol mulls. (a) $(\text{CH}_3)_3\text{N}^+\text{BF}_3^-$; (b) $(\text{CH}_3)_3\text{N}^+\text{BCl}_3^-$ and (c) $(\text{CH}_3)_3\text{N}^+\text{BBr}_3^-$.

determinants of the reduced G matrices which were calculated from the X-ray parameters.

Assignments of bands to specific vibrational modes were made on the basis of the isotope shifts which indicated whether a particular equivalent set of atoms was contributing to a specific normal mode. It was observed that frequencies associated with the amine half of the complexes varied relatively little with change in halogen. Also, relatively little change in the geometry of trimethylamine occurs upon complex formation and consequently comparisons with the frequencies and assignments of free trimethylamine [16, 17] were helpful in establishing assignments for this portion of the complexes. Although the symmetry characteristics of the C-H and C-D stretching bands were determined from the polarization measurements,

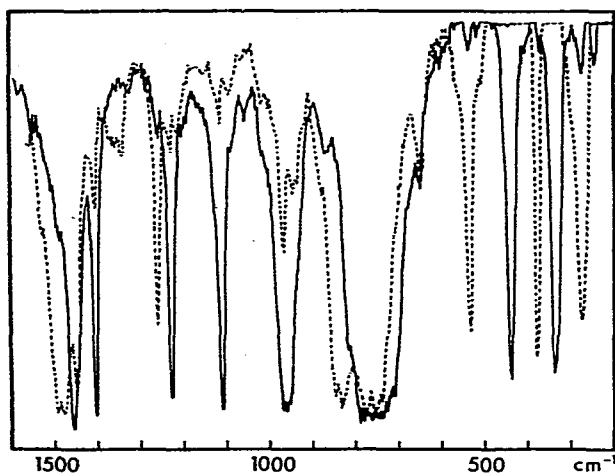


Fig. 3. Polarized infrared spectra of single crystal $(\text{CH}_3)_3\text{NBF}_3$ (natural boron). --- Electric vector parallel to molecular C_3 axis; — Electric vector perpendicular to molecular C_3 axis.

TABLE 1

Observed fundamental frequencies below 1500 cm^{-1} and differences between observed and calculated values for five isotopic varieties of $(\text{CH}_3)_3\text{NBF}_3$ (cm^{-1})

	$(\text{CH}_3)_3\text{N}^{10}\text{BF}_3$		$(\text{CH}_3)_3\text{N}^{11}\text{BF}_3$		$(\text{CH}_3)_3^{15}\text{N}^{11}\text{BF}_3$		$(\text{CD}_3)_3\text{N}^{10}\text{BF}_3$		$(\text{CD}_3)_3\text{N}^{11}\text{BF}_3$	
	Exptl ^a	Diff ^b	Exptl	Diff	Exptl	Diff	Exptl	Diff	Exptl	Diff
A_1										
ν_3	1487	1	1486	1	1485	2	1054	-2	1054	-2
ν_4	1454	2	1453	1	1453	2	1069	-2	1069	-2
ν_5	1272	1	1271	1	1258	2	1180	2	1171	-6
ν_6	845	2	843	0	836	0	745	-2	745	0
ν_7	700	1	694	1	693	0	682	-2	677	-1
ν_8	(330)	0	330	0	(330)	1	303	0	302	-1
ν_9	960	2	929	0	930	1	946	-3	922	0
ν_{10}	550	1	550	2	542	-1	492	-1	492	-1
E										
ν_{19}	1480	-4	1478	-5	1479	-4	1050	1	1050	5
ν_{20}	1470	1	1469	1	1648	0	1059	1	1059	1
ν_{21}	1412	-1	1412	-1	1412	3	1069	-1	1069	0
ν_{22}	1258	3	1255	3	1242	0	1200	-2	1186	-1
ν_{23}	1111	-5	1105	0	1103	-1	878	1	878	2
ν_{24}	991	-2	990	0	981	3	823	-1	823	-1
ν_{25}	1176	5	1144	1	1144	1	1149	-4	1127	-3
ν_{26}	432	1	432	1	429	-1	383	0	383	0
ν_{27}	343	-1	343	-1	342	-2	300	2	300	2
ν_{28}	300	2	300	2	300	2	210	-2	210	-2
ν_{29}	520	-1	520	1	(520)	1	505	-1	505	1
ν_{30}	323	0	323	0	325	2	313	-2	313	-2

^aUnobserved or obscured frequencies given by (). ^bDiff = (experimental-calculated).

TABLE 2

Observed fundamental frequencies below 1500 cm^{-1} and differences between observed and calculated values for five isotopic varieties of $(\text{CH}_3)_3\text{NBCl}_3$ (cm^{-1})

	$(\text{CH}_3)_3\text{N}^{10}\text{BCl}_3$		$(\text{CH}_3)_3\text{N}^{11}\text{BCl}_3$		$(\text{CH}_3)_3^{15}\text{N}^{11}\text{BCl}_3$		$(\text{CD}_3)_3\text{N}^{10}\text{BCl}_3$		$(\text{CD}_3)_3\text{N}^{11}\text{BCl}_3$	
	Exptl ^a	Diff ^b	Exptl	Diff	Exptl	Diff	Exptl	Diff	Exptl	Diff
A_1										
ν_3	1487	1	1486	0	1485	0	1070	0	1070	0
ν_4	1452	0	1452	1	1452	1	1055	-1	1055	-1
ν_5	1267	0	1266	0	1255	2	1134	0	1132	-1
ν_6	838	1	833	-1	825	0	(760)	-2	(760)	1
ν_7	770	1	748	0	(748)	1	(740)	0	716	-1
ν_8	540	-2	535	0	534	2	477	-1	475	1
ν_9	382	0	381	-1	382	1	368	0	368	0
ν_{10}	272	-1	272	-1	274	2	266	0	266	0
E										
ν_{19}	1466	-5	1466	-5	1465	-6	1064	6	1064	6
ν_{20}	1458	-2	1458	-2	(1458)	-2	1030	1	1030	2
ν_{21}	1410	-4	1410	-4	1410	0	1071	2	1071	2
ν_{22}	1234	-1	1234	0	1222	-7	1131	1	1131	4
ν_{23}	1116	-2	1116	-2	1115	0	878	3	877	2
ν_{24}	966	-4	966	-2	955	2	817	2	816	1
ν_{25}	784	-2	756	-1	756	0	776	2	747	1
ν_{26}	443	0	443	1	441	-1	391	0	391	0
ν_{27}	341	0	341	0	339	-1	306	0	306	0
ν_{28}	(275)	-5	(275)	-5	(275)	-5	196	0	196	0
ν_{29}	250	2	246	-2	(246)	-2	249	0	249	0
ν_{30}	190	1	187	-2	(187)	-2	183	1	182	0

^aUnobserved or obscured frequencies given by (). ^bDiff = (experimental—calculated).

detailed assignments were not made since these frequencies were of less interest for the normal coordinate analysis and the situation was complicated by Fermi resonances involving overtones of the deformation modes.

A detailed discussion of the evidence and reasoning leading to the assignments summarized in Tables 1–4 will not be given here; interested readers should see ref. 16. Most of the assignments are consistent with those proposed previously [5, 6] although there are some interesting exceptions. One instance to which attention should be called involves the symmetric NC_3 deformation, the amine skeleton umbrella mode, which has previously been assigned at a frequency in the vicinity of 320 to 340 cm^{-1} and lower than the asymmetric mode. The polarized IR results of the present work show clearly, however, that, with the exception of the fluoro complex, the bands in this region have E symmetry and not A_1 . The assignment of the symmetric NC_3 deformation was made, therefore, to the A_1 bands at 540 , 520 and 510 cm^{-1} , respectively, in the spectra of the chloro, bromo and iodo complexes and the assignment was confirmed by the normal coordinate

TABLE 3

Observed fundamental frequencies below 1500 cm^{-1} and differences between observed and calculated values for five isotopic varieties of $(\text{CH}_3)_3\text{NBBBr}_3$ (cm^{-1})

	$(\text{CH}_3)_3\text{N}^{10}\text{BBBr}_3$			$(\text{CH}_3)_3\text{N}^{11}\text{BBBr}_3$		$(\text{CH}_3)_3^{15}\text{N}^{11}\text{BBBr}_3$		$(\text{CD}_3)_3\text{N}^{10}\text{BBBr}_3$		$(\text{CD}_3)_3\text{N}^{11}\text{BBBr}_3$	
	Exptl ^a	Diff ^b		Exptl	Diff	Exptl	Diff	Exptl	Diff	Exptl	Diff
A_1											
ν_3	1485	-2		1485	-2	1483	-4	1055	3	(1055)	3
ν_4	1449	-2		1449	-2	1448	-3	1065	2	1065	3
ν_5	1262	-2		1262	-2	1250	-2	1125	3	1125	3
ν_6	833	-1		830	-3	820	0	761	2	746	1
ν_7	754	-4		734	0	733	1	715	3	700	0
ν_8	520	-2		517	-1	517	0	475	-1	475	3
ν_9	275	-1		275	0	274	-1	267	1	267	1
ν_{10}	196	-1		196	0	(196)	0	192	0	192	1
E											
ν_{19}	1463	-3		1463	-3	1463	-3	1058	3	1058	3
ν_{20}	1449	-1		1449	-1	1448	-2	1020	1	1020	2
ν_{21}	1408	-2		1408	-2	1408	0	1068	2	1068	2
ν_{22}	1228	0		1228	0	1216	-6	1121	1	1121	2
ν_{23}	1114	0		1114	0	1112	0	873	2	872	1
ν_{24}	960	-2		960	-2	947	1	812	0	812	0
ν_{25}	709	0		678	-2	678	-2	700	1	674	3
ν_{26}	434	1		434	1	432	0	380	-1	380	-1
ν_{27}	321	1		321	2	319	0	281	-2	281	-1
ν_{28}	265	2		265	2	(265)	2	(190)	-7	(190)	1
ν_{29}	184	-1		184	-1	(184)	-1	180	2	180	2
ν_{30}	129	0		128	-1	(128)	-1	127	1	127	1

^aUnobserved or obscured frequencies given by (). ^bDiff = (experimental—calculated).

calculations. In the fluoro case, the calculations showed the two A_1 bands at 550 and 330 cm^{-1} to be strongly mixed with large components of both the BF_3 and NC_3 deformations.

NORMAL COORDINATE CALCULATIONS

At the present time, most normal coordinate analyses employ the GF formalism of Wilson to calculate force constants. However, Decius [18] has pointed out that there are certain advantages in using compliance constants together with the kinetic energy matrix, K , as an alternative basis for analysis. The practicalities of this method, at least for molecules with sizeable numbers of atoms, have not been explored to any extent and clearly deserve attention. Also, the usefulness of compliance constants as a basis for correlation with other chemical and physical properties can only be judged after an appreciable number of data have been accumulated. The present investigation has therefore utilized the compliance constant basis for the normal coordinate analyses as part of a more general study.

TABLE 4

Observed fundamental frequencies below 1500 cm^{-1} and differences between observed and calculated values for four isotopic varieties of $(\text{CH}_3)_3\text{NBI}_3$ (cm^{-1})

	$(\text{CH}_3)_3\text{N}^{10}\text{BI}_3$		$(\text{CH}_3)_3\text{N}^{11}\text{BI}_3$		$(\text{CD}_3)_3\text{N}^{10}\text{BI}_3$		$(\text{CD}_3)_3\text{N}^{11}\text{BI}_3$	
	Exptl ^a	Diff ^b	Exptl	Diff	Exptl	Diff	Exptl	Diff
A_1								
ν_3	1482	1	1482	1	1057	-1	1057	-1
ν_4	1448	1	1448	1	1065	-1	1065	-1
ν_5	1255	1	1255	1	1118	-2	1118	0
ν_6	824	1	824	1	745	0	739	-1
ν_7	728	-6	715	6	697	-3	681	2
ν_8	510	-2	510	3	460	-2	460	1
ν_9	239	1	238	0	223	0	223	0
ν_{10}	150	0	150	0	144	0	143	-1
E								
ν_{19}	1458	-4	1458	-4	1050	3	1050	3
ν_{20}	1448	10	1448	10	1020	-6	1020	-6
ν_{21}	1405	-1	1405	-1	1062	1	1062	1
ν_{22}	1223	-4	1223	-4	1110	0	1110	0
ν_{23}	1110	1	1110	1	868	-1	868	-1
ν_{24}	950	-1	950	0	808	0	808	2
ν_{25}	640	0	616	3	632	-2	607	-1
ν_{26}	431	-3	429	-4	375	3	375	3
ν_{27}	316	1	316	2	275	-1	274	-2
ν_{28}	260	4	260	4	182	-3	182	-3
ν_{29}	142	0	142	0	(142)	5	(142)	5
ν_{30}	97	-1	97	-1	96	1	96	1

^aUnobserved or obscured frequencies given by (). ^bDiff = (experimental-calculated).

In the present treatment, the secular equation was written as $|\text{CK} - \phi\text{I}| = 0$ and solved in the form $\text{CK} \cdot \text{L} = \text{L} \cdot \Phi$, where C is the matrix of compliance constants ($\text{C} = \text{F}^{-1}$), K is the kinetic energy matrix ($\text{K} = \text{G}^{-1}$) and Φ is a diagonal matrix whose elements, ϕ_i , are the reciprocal λ_i values. The L matrix is identical with the L matrix in the more commonly used equation, $\text{GF} \cdot \text{L} = \text{L} \cdot \Lambda$. The computer program used has been described previously [19]. Briefly, the secular equation is symmetrized by the method of Aldous and Mills [20] and the compliance constants adjusted by a standard iterative least squares procedure based on the Jacobian of frequencies with respect to compliance constants. Data for all isotopic species of the same symmetry were treated at one time, all frequencies being fitted simultaneously. Weights were taken proportional to the frequencies to the fourth power [19]. Symmetry coordinates and symmetry compliance constants formed the basis of the calculations.

Although methods for calculating the elements of the kinetic energy matrix have been given by Taylor and Pitzer [21], it proved somewhat more

TABLE 5

Numbering scheme and descriptive designation of vibrational modes of $(\text{CH}_3)_3\text{NBX}_3$ molecules

Class		Class	
A_1		E	
ν_1	C—H asymmetric ^a stretch	ν_{16}	C—H asymmetric stretch
ν_2	C—H symmetric stretch	ν_{17}	C—H asymmetric stretch
ν_3	CH_3 asymmetric deformation	ν_{18}	C—H symmetric stretch
ν_4	CH_3 symmetric deformation	ν_{19}	CH_3 asymmetric deformation
ν_5	CH_3 rock	ν_{20}	CH_3 asymmetric deformation
ν_6	C—N symmetric stretch	ν_{21}	CH_3 symmetric deformation
ν_7	B—N stretch	ν_{22}	C—N asymmetric stretch
ν_8	NC_3 symmetric deformation	ν_{23}	CH_3 rock
ν_9	B—X symmetric stretch	ν_{24}	CH_3 wag
ν_{10}	BX_3 symmetric deformation	ν_{25}	B—X asymmetric stretch
A_2		ν_{26}	NC_3 asymmetric deformation
ν_{11}	C—H asymmetric stretch	ν_{27}	NC_3 rock
ν_{12}	CH_3 asymmetric deformation	ν_{28}	CH_3 torsion
ν_{13}	CH_3 rock	ν_{29}	BX_3 asymmetric deformation
ν_{14}	CH_3 torsion	ν_{30}	BX_3 rock
ν_{15}	B—N torsion		

^aThe use of symmetric and asymmetric in the methyl group modes refers to the local symmetry of the CH_3 group, not the overall molecular symmetry.

TABLE 6

Hydrogen—Deuterium product rule ratios for frequencies below 1500 cm^{-1} of $(\text{CH}_3)_3\text{NBX}_3$ molecules

Compound	Class	Theoret. ^a	Exptl.	% Dev.
TMA: BF_3	A_1	2.903	2.965	+2.1
	E	8.102	8.211	+1.3
TMA: BCl_3	A_1	2.930	2.918	−0.4
	E	8.236	7.680	−6.8
TMA: BBr_3	A_1	2.962	2.868	−3.2
	E	8.415	8.080	−4.0
TMA: BI_3	A_1	2.975	3.109	+4.5
	E	8.532	8.349	−2.1

^aCalculated from the ratios of the determinants of the reduced G matrices.

convenient to calculate the G matrix elements by standard methods and then invert the symmetry G matrices. The geometrical parameters employed in calculating the G matrix elements were taken from the X-ray studies of Clippard et al. [2] and Geller and Hoard [4]. The 50×50 g matrices assembled in terms of the internal valence coordinates were block diagonalized by computer using the similarity transformation $G = U \cdot g \cdot \bar{U}$, where U is the full transformation matrix defining all symmetry coordinates (including redundant coordinates) in terms of the internal valence coordinates $S = U \cdot r$. A complete set of symmetry coordinates for C_{3v} molecules of the general formula $(CH_3)_3MXY_3$ apparently has not been published but two papers were found [22, 23] listing symmetry coordinates for related molecules with the general formula $(CH_3)_3MX$. The coordinates used in the present work agreed with the set given by Shimizu and Murata [22] but not with those of Kuroda and Kimura [23]. Symmetry coordinates S_{16} , S_{21} and S_{23} of the latter authors, while not erroneous, appear to belong to the second set of E class symmetry coordinates and consequently their inclusion in the first set does not properly block diagonalize the G matrix. With the set employed in the present work, all elements of the off-diagonal blocks of the symmetry G matrices were computed to be zero within round-off error confirming that the sets used were correctly selected. Since the full set of coordinates is rather lengthy, it is not reproduced here but is available elsewhere [24]. The symmetrized G matrices factored into one 10×10 A_1 block, one 5×5 A_2 block and two 15×15 E blocks. Since the C—H stretching frequencies were of marginal interest, the rows and columns of the K matrices associated with the C—H coordinates were deleted [25] reducing the dimensions of the A_1 and E classes to 8×8 and 12×12 , respectively. The A_2 class was not considered since fundamentals belonging to this class are inactive.

The total numbers of independent symmetry compliance constants in the reduced A_1 and E classes are 36 and 78, respectively. However, it is not practicable to attempt to work with potential functions this large and consequently the number of compliance constants actually used in the analysis was reduced appreciably by the following considerations. Past experience and physical arguments indicate that interactions between coordinates having no common atoms (non-adjacent coordinates) are usually quite small and most of the corresponding off-diagonal terms in the potential energy can be constrained to zero without introducing significant error into a vibrational analysis. (The neglect of such terms is implicit in certain specialized potential functions such as the hybrid orbital force field of Mills [26].) In addition, it is well known that some of the potential constants of a molecule are often quite insensitive to vibrational frequency data alone and that such constants can be constrained to zero without affecting the frequency fit significantly. Actually, the removal of such constants from the fitting process may prove beneficial to the numerical computations since their inclusion is usually the cause of the normal equations in the least squares adjustment procedure being ill-conditioned.

The alternative to constraining constants, namely, transformation to a space in which redefined constants are orthogonal (parameterization), appeared unattractive because of the complexity involved.

In the present work, compliance constants which did not contribute to the fitting process were identified in the early stages on the basis of the above arguments or by their high dispersions and were constrained [27]. The remaining constants actually needed in fitting the observed frequencies comprised 22 in the A_1 class and 26 in the E class. The same constants were retained in the analysis of all four complexes giving a common potential function. Average deviations between observed and calculated frequencies were satisfactorily low, ranging from 0.12 % to 0.21 % in the A_1 classes and from 0.24 % to 0.46 % in the E . The deviations between experimental and calculated frequency values are listed in Tables 1–4 while the symmetry compliance constants and their dispersions are given in Tables 7 and 8. Symmetry force constant matrices were obtained by inversion of the corresponding compliance matrices. In general, these force constant matrices were less sparse than the compliance matrices, entries appearing in most positions. However, many of the off-diagonal values were quite small and for practical purposes may be regarded as being zero. The symmetry force constants having significant magnitudes are also listed in Tables 7 and 8. Valence constants may be obtained from the symmetry constants utilizing the definitions of the symmetry coordinates expressed in the transformation matrix, U . Values for stretching constants of the skeletal bonds are listed in Table 9 and afford the best basis for comparison with previous literature values.

An important result of a normal coordinate analysis is the information provided on the atom motions and the characterization of the various normal modes. Although the L matrix is often used to delineate the vibrational amplitudes of the atoms, the characterization of the nature of a vibration appears more satisfactorily performed via the potential energy distribution. In Tables 10 and 11 are given the potential energy distributions in symmetry coordinate space. Only terms contributing ten percent or more to the total have been included and (+) and (–) signs have been added to indicate the relative phases of the symmetry coordinates, as given by the elements of the L matrix. As can be seen by inspection of the tables, very few of the skeletal frequencies below about 1200 cm^{-1} approach being pure vibrations. In particular, only in the Br and I complexes can one say there is a dative bond frequency (at 754 and 728 cm^{-1} , respectively). In the complexes of the two lighter halides, the B–N stretching motion does not dominate any of the frequencies although it is substantially represented in the two A_1 bands in the $700\text{--}770\text{ cm}^{-1}$ region. The C–N stretching motion can be clearly identified with the A_1 bands between 850 and 820 cm^{-1} for all four complexes and is distinct. The corresponding NC_3 umbrella deformation, as was mentioned earlier, can be easily assigned to the bands in the vicinity of $520\text{--}540\text{ cm}^{-1}$ for the chloro and bromo complexes but is less unequivocally identified

in the fluoro and iodo cases. The B—X stretching and BX_3 deformation motions, though mixed to a greater or lesser extent, can also be assigned without difficulty in both the A_1 and E classes of all four complexes.

DISCUSSION

The results of the normal coordinate analysis present a satisfying interpretation of the vibrational spectra of these four complexes. The use of compliance constants rather than force constants appeared to reduce numerical problems associated with ill-conditioning although the extent to which this was true was difficult to evaluate. It was noted that the calculations converged relatively rapidly for the BF_3 complex but the process was significantly slower and a fit was more difficult to obtain for the BI_3 case. The other two halides were intermediate in this respect. The indications were that low frequencies (large ϕ_i values) are dealt with less satisfactorily in the compliance constant basis. Moreover, the dispersions for the BI_3 compliance constants were the largest of the four complexes, the magnitudes being appreciably smaller for the lighter halides.

The parameters associated with the B—N dative bond are the most important in seeking correlations between molecular properties and chemical properties such as adduct stability and acid strength. The length of the B—N bond in the series shows only a very small contraction (less than experimental uncertainty) from chloride to iodide [2]. The B—N distance in the fluoride is not well determined; the original X-ray value of 1.58 Å is quite old [4], is based on a limited number of reflections and carries an estimated uncertainty of 0.03 Å. A modern microwave value of 1.636 Å has been reported [28] for $(CH_3)_3NBF_3$ which is consistent with the values for the other halides (1.610, 1.603 and 1.584 Å, respectively) but there is a residual uncertainty due to the difference in phase. In any case, there is no marked variation in the B—N distance in these complexes, a fact which is not too surprising since these molecules are very crowded sterically.

The compliance constants and the derived force constants, however, do show significant variations which are not as regular as the bond distances. The least compliant (stiffest) B—N bond is found in the fluoride with a value of 0.37 Å mdyn⁻¹ appreciably less than the values of 0.55, 0.47 and 0.51 Å mdyn⁻¹ for the other three halides. The variation in the latter three values is just within the range of the dispersions and therefore may not be significant. Judging from the compliance data, the B—N bond in the fluoride clearly is stronger than the B—N bond in the other three complexes. If one examines the force constants for the four complexes obtained by the inversion of the compliance matrices, however, the distinctive position of the fluoride does not occur. The B—N force constants in the chloride, bromide and iodide complexes exhibit a regular increase of 3.10, 3.98 and 4.32 mdyn Å⁻¹ while the value of the B—N force constant for the fluoride (3.59 mdyn Å⁻¹) falls between the chloride and bromide values. This difference in the relative

TABLE 7

Symmetry compliance constants and symmetry force constants for the A_1 class of the four halogen-substituted complexes, $(CH_3)_3NBX_3$

Indices	TMA:BF ₃		TMA:BCl ₃		TMA:BBr ₃		TMA:BI ₃	
	C_{ij}	F_{ij}	C_{ij}	F_{ij}	C_{ij}	F_{ij}	C_{ij}	F_{ij}
3,3	1.876(1) ^a	0.53	1.820(42)	0.55	1.832(38)	0.55	1.856(333)	0.54
4,4	1.769(2)	0.70	1.865(6)	0.71	1.975(31)	0.72	1.839(639)	0.69
5,5	1.276(7)	0.78	1.228(30)	0.82	1.174(12)	0.91	1.489(435)	0.73
6,6	0.255(3)	4.83	0.273(5)	5.24	0.389(7)	4.43	0.384(185)	4.29
7,7	0.372(4)	3.59	0.546(54)	3.10	0.474(26)	3.98	0.510(172)	4.32
8,8	0.657(3)	1.63	0.656(10)	2.04	0.568(10)	2.06	1.262(554)	0.90
9,9	0.185(1)	6.65	0.506(44)	2.69	0.508(39)	2.69	0.292(108)	3.83
10,10	1.128(26)	1.13	0.823(96)	1.66	1.042(115)	1.28	0.956(281)	2.03
3,5	^b	0	-0.039(44)	0	-0.102(25)	0.05	0.042(307)	0
3,6	0.009(1)	-0.02	—	0.02	—	-0.02	0.062(119)	-0.13
3,7	—	0	—	0	—	-0.01	—	-0.06
4,5	—	0	—	0.03	—	0.07	—	0.09
4,6	0.292(1)	-0.80	0.338(4)	-0.95	0.434(17)	-0.79	0.338(376)	-0.79
4,7	—	-0.01	—	-0.19	—	-0.43	—	-0.36
4,8	—	-0.02	—	0.03	—	-0.11	—	-0.04
4,9	—	-0.01	—	-0.09	—	-0.13	—	-0.09
4,10	—	0	—	0.02	—	0.08	—	0.14
5,6	—	0	0.042(10)	-0.17	0.072(11)	-0.33	0.170(291)	-0.47
5,7	—	0.01	—	-0.06	—	-0.23	—	-0.23
5,8	-0.023(5)	0.03	0.037(2)	-0.06	0.132(6)	-0.26	-0.094(283)	0.03
5,9	—	0	—	-0.02	—	-0.07	—	-0.05
5,10	—	0	—	0.03	—	0.05	—	0.11
6,7	-0.003(2)	0.08	-0.087(5)	1.04	-0.141(11)	1.95	-0.137(78)	1.95
6,8	-0.012(4)	0.10	0.058(2)	-0.16	0.006(6)	0.51	-0.097(21)	0.23
6,9	—	0.03	—	0.47	—	0.59	—	0.48
6,10	—	-0.01	—	-0.10	—	-0.38	—	-0.76
7,8	-0.110(1)	0.60	-0.162(9)	0.93	-0.136(7)	1.01	-0.086(507)	-0.06
7,9	-0.092(1)	1.21	-0.247(46)	1.24	-0.209(39)	1.21	-0.115(67)	0.99
7,10	0.252(4)	-0.62	0.200(9)	-0.72	0.286(59)	-0.78	0.438(412)	-1.88
8,9	—	0.20	—	0.17	—	0.29	—	0.11
8,10	—	-0.10	0.229(23)	-0.75	0.012(42)	-0.22	-0.328(665)	0.35
9,10	-0.168(4)	0.72	-0.192(16)	0.28	-0.283(28)	0.40	-0.110(30)	0.02

^aNumbers in brackets represent dispersions of the compliance constants.

^bA "—" indicates that the compliance constant was constrained to zero; compliance constants for which no indices are listed likewise were constrained to zero.

TABLE 8

Symmetry compliance constants and symmetry force constants for the *E* class of the four halogen-substituted complexes, $(\text{CH}_3)_3\text{NBX}_3$

Indices	TMA:BF ₃		TMA:BCl ₃		TMA:BBr ₃		TMA:BI ₃	
	<i>C</i> _{ij}	<i>F</i> _{ij}	<i>C</i> _{ij}	<i>F</i> _{ij}	<i>C</i> _{ij}	<i>F</i> _{ij}	<i>C</i> _{ij}	<i>F</i> _{ij}
19,19	1.886(47)	0.53	1.871(8)	0.53	1.889(24)	0.53	1.906(18)	0.52
20,20	2.098(51)	0.48	2.211(21)	0.45	2.257(64)	0.44	2.191(27)	0.46
21,21	1.951(146)	0.62	1.911(25)	0.62	1.844(236)	0.62	1.794(19)	0.61
22,22	0.312(19)	5.28	0.403(49)	3.64	0.396(81)	3.59	0.368(29)	3.03
23,23	1.141(16)	0.88	1.273(19)	0.79	1.261(36)	0.79	1.232(19)	0.81
24,24	1.864(109)	0.72	1.333(72)	0.97	1.393(102)	0.98	1.158(24)	0.87
25,25	0.313(22)	3.90	0.808(57)	2.01	0.904(145)	2.12	0.916(269)	1.38
26,26	0.901(107)	1.13	1.321(116)	0.97	1.236(419)	1.06	0.667(35)	1.50
27,27	0.573(34)	2.26	0.702(101)	2.45	0.814(122)	2.29	1.122(243)	1.64
28,28	4.574(48)	0.22	5.296(165)	0.19	6.067(273)	0.17	6.494(333)	0.15
29,29	0.831(54)	1.27	0.639(31)	1.56	0.650(113)	1.52	0.958(680)	1.69
30,30	0.812(90)	1.82	1.138(99)	2.15	1.248(132)	2.55	1.104(644)	1.98
19,24	-0.014(31)	0.01	—	0	—	0	—	0
21,22	0.321(68)	-0.68	0.336(23)	-0.56	0.293(163)	-0.50	0.247(27)	-0.42
21,24	0.400(129)	0.00	0.212(55)	0.02	0.160(108)	0.04	—	0.02
21,27	—	-0.13	—	0.12	—	0.08	—	0
21,30	—	0.05	—	-0.06	—	-0.05	—	0
22,24	0.369(38)	-0.90	0.297(24)	-0.73	0.305(31)	-0.78	0.067(20)	-0.18
22,25	—	-0.14	—	0.07	—	0.02	—	0
22,26	—	0.08	—	-0.04	—	-0.20	—	0
22,27	-0.094(27)	1.03	—	-0.67	0.072(99)	-0.48	—	0
22,29	—	-0.07	—	0	—	0.21	—	0
22,30	—	-0.36	—	0.31	—	0	—	0
23,24	-0.104(24)	0.07	—	0	—	0	—	0
24,25	—	0.02	—	0.05	—	0.10	—	0
24,26	—	-0.01	-0.313(96)	0.24	-0.353(86)	0.33	—	0
24,27	—	-0.18	—	0.01	—	0	—	0
24,30	—	0.06	—	0.07	—	0.13	—	0
25,26	—	-0.03	—	0.26	—	0.38	—	0
25,27	-0.028(24)	-0.32	-0.179(61)	-0.39	-0.264(93)	-0.49	-0.174(640)	0.52
25,29	—	0.21	—	0	—	0	-0.277(537)	0.64
25,30	-0.205(36)	1.12	-0.569(36)	1.22	-0.693(125)	1.52	—	-0.54
26,27	-0.073(28)	0.18	0.167(57)	-0.52	—	-0.35	—	0
26,30	—	-0.06	-0.215(48)	0.53	-0.283(96)	0.63	—	0
27,29	—	-0.15	—	0	—	0	—	0.68
27,30	0.246(54)	-0.79	0.480(136)	-1.33	0.633(152)	-1.51	0.629(543)	-1.19

TABLE 9

Valence stretching compliance and force constants for trimethylamine-boron halide complexes (in mdyn Å⁻¹)

Constant	Fluoride		Chloride		Bromide		Iodide	
	<i>C</i>	<i>F</i>	<i>C</i>	<i>F</i>	<i>C</i>	<i>F</i>	<i>C</i>	<i>F</i>
C—N	0.29	5.13	0.36	4.17	0.39	3.87	0.37	3.45
C—N, C—N	−0.02	−0.15	−0.04	0.53	0.00	0.28	0.01	0.42
B—X	0.27	4.82	0.71	2.24	0.77	2.31	0.71	2.20
B—X, B—X	−0.04	0.92	−0.10	0.23	−0.13	0.19	−0.21	0.81
B—N	0.37	3.59	0.55	3.10	0.47	3.98	0.51	4.32

magnitudes of these B—N bond parameters depending on whether compliance constants or force constants are considered is unexpected and the explanation is not entirely clear. It can be noted, however, that values obtained for compliance constants tend to be more specific to a given coordinate and less dependent on the rest of the potential function than in the case of force constants [28]. Consequently, the compliance values may provide a more accurate assessment of the B—N bond strength than the force constants.

Considering the force constants themselves, the values derived from the compliance matrices appear quite reasonable and do not differ markedly from the more approximate values in the literature [6]. If further discussion is restricted to force constants on the basis that insufficient compliance constant data are available in the literature to be useful, an interesting comparison can be made with the results of a recent study of acetonitrile-boron halide complexes [13]. In the CH₃CN:BF₃ complex, the B—N bond distance was found to be 1.63 Å with a force constant of 2.54 mdyn Å⁻¹. In the chloro complex, the B—N bond shortens to 1.56 Å and the force constant increases to 3.40 mdyn Å⁻¹. The force constant found in the present study for (CH₃)₃NBF₃ (3.59 mdyn Å⁻¹) indicates that the B—N distance in the solid is likely to be the short X-ray distance (1.58 Å) and if this is correct, the force constant and bond length data for both series of complexes can be explained quite satisfactorily in a qualitative sense by the following simple assumptions. Firstly, trimethylamine is a significantly better electron donor than acetonitrile and will form a stronger bond (larger force constant) with a given acid if other effects are absent. Secondly, the electron acceptor abilities of the boron halides progressively increase from the fluoride to the iodide and progressively shorter and stronger dative bonds are formed with a given donor, again in the absence of other effects. The latter behavior is shown clearly by the acetonitrile complexes. However, because the trimethylamine-boron halide complexes are very crowded sterically, it is not possible for the acid and base to approach each other as closely as they otherwise might. Boron trifluoride, which is the least bulky of the four acids, can approach most closely and thus can form a stronger bond which is somewhat

TABLE 10

Potential energy distribution (PED) among A_1 class symmetry coordinates for $(CH_3)_3NBX_3$ complexes^a

Complex	Frequency and PED									
$(CH_3)_3NBF_3$	1487	1454	1272	960	845	700	550	330		
	0.61 + S_3	0.18 - S_3	0.16 + S_3	0.62 + S_9	0.19 - S_5	0.19 + S_9	0.21 - S_6	0.26 + S_7		
	0.18 + S_4	0.82 + S_4	0.52 + S_5	0.23 - S_7	0.18 - S_9	0.31 + S_6	0.30 + S_{10}	0.32 - S_{10}		
	0.19 - S_5		0.08 - S_7	0.11 - S_{10}	0.45 + S_6	0.23 + S_7	0.37 + S_8	0.41 + S_8		
			0.17 + S_8		0.14 - S_7	0.27 + S_{10}				
$(CH_3)_3NBrCl_3$	1487	1452	1267	838	770	540	382	272		
	0.86 + S_3	1.00 + S_4	0.11 + S_3	0.14 - S_3	0.36 + S_6	0.10 - S_6	0.10 + S_7	0.35 + S_7		
	0.14 - S_5		0.65 + S_5	0.56 + S_6	0.36 + S_7	0.60 + S_8	0.11 + S_8	0.15 + S_9		
			0.20 + S_8	0.11 - S_7	0.28 + S_{10}	0.12 - S_9	0.76 + S_9	0.50 + S_{10}		
				0.14 + S_8						
$(CH_3)_3NBrF_3$	1485	1449	1262	833	754	520	275	196		
	0.50 + S_3	0.40 + S_3	0.76 + S_5	0.11 - S_5	0.18 + S_6	0.49 - S_6	0.78 + S_9	0.21 + S_9		
	0.42 - S_4	0.61 + S_4	0.13 + S_8	0.39 + S_6	0.79 + S_7	0.33 + S_8	0.11 - S_{10}	0.69 + S_{10}		
				0.45 + S_8		0.12 + S_{10}				
$(CH_3)_3NBI_3$	1482	1448	1225	824	728	510	239	150		
	0.87 + S_3	1.00 + S_4	0.56 + S_5	0.15 + S_5	0.16 + S_6	0.35 - S_6	0.21 + S_7	0.15 - S_8		
	0.12 - S_5		0.18 - S_7	0.55 + S_6	0.66 + S_7	0.12 + S_8	0.35 + S_8	0.13 + S_9		
			0.18 + S_8	0.12 - S_7	0.18 - S_9	0.24 - S_9	0.43 + S_9	0.73 + S_{10}		
				0.17 + S_8		0.30 + S_{10}				

^a A "+" or "-" sign preceding coordinate indicates phase of displacements as given by L matrix.

TABLE 11

Potential energy distribution among *E* class symmetry coordinates for $(\text{CH}_3)_3\text{NBX}_3$ complexes^a

Complex	Frequency and PED														
$(\text{CH}_3)_3\text{NBF}_3$	1480	1470	1412	1258	1176	1111	991	520	432	343	323	300			
	0.49 + S_{19}	0.34 + S_{19}	0.91 + S_{11}	0.48 + S_{22}	0.11 + S_{14}	0.11 + S_{19}	0.11 + S_{22}	0.14 + S_{22}	0.29 + S_{26}	0.36 - S_{26}	0.26 - S_{29}	0.13 + S_{30}			
	0.30 - S_{20}	0.47 + S_{20}		0.11 - S_{23}	0.49 + S_{25}	0.67 + S_{23}	0.48 + S_{24}	0.30 + S_{25}	0.12 + S_{27}	0.56 + S_{27}	0.66 + S_{30}	0.68 + S_{28}			
	0.11 - S_{23}			0.18 - S_{24}	0.14 - S_{17}		0.19 - S_{26}	0.16 + S_{29}	0.33 - S_{29}						
$(\text{CH}_3)_3\text{NBrCl}_3$	1466	1458	1410	1234	1116	986	784	443	339	275	246	187			
	0.86 + S_{19}	0.64 + S_{20}	0.92 + S_{21}	0.26 - S_{22}	0.61 + S_{23}	0.35 + S_{22}	0.54 + S_{25}	0.52 + S_{26}	0.16 + S_{22}	0.55 + S_{28}	0.23 + S_{25}	0.17 - S_{26}			
		0.21 + S_{24}		0.40 + S_{24}	0.18 - S_{24}	0.21 + S_{23}	0.12 - S_{27}	0.31 + S_{30}	0.19 + S_{25}	0.14 - S_{29}	0.21 - S_{26}	0.16 - S_{29}			
						0.18 + S_{24}	0.33 - S_{29}		0.48 + S_{27}		0.13 - S_{27}	0.73 + S_{30}			
$(\text{CH}_3)_3\text{NBrF}_3$	1463	1449	1408	1228	1114	960	709	434	321	265	184	129			
	0.83 + S_{19}	0.60 + S_{20}	0.99 + S_{21}	0.20 - S_{20}	0.68 + S_{23}	0.36 + S_{22}	0.56 + S_{25}	0.13 + S_{22}	0.14 + S_{22}	0.11 + S_{20}	0.19 + S_{25}	0.12 - S_{25}			
	0.11 - S_{24}	0.25 + S_{24}		0.28 - S_{22}	0.15 - S_{24}	0.14 + S_{23}	0.16 - S_{27}	0.56 + S_{26}	0.14 + S_{25}	0.69 + S_{28}	0.20 - S_{26}	0.43 - S_{29}			
				0.33 + S_{24}		0.25 + S_{24}	0.28 - S_{30}	0.26 + S_{30}	0.59 + S_{27}		0.17 + S_{29}	0.45 + S_{30}			
$(\text{CH}_3)_3\text{NBI}_3$	1458	1448	1405	1223	1110	950	640	431	316	260	142	97			
	0.85 + S_{19}	0.71 + S_{20}	1.00 + S_{21}	0.16 - S_{20}	0.11 + S_{19}	0.63 + S_{22}	0.69 + S_{25}	0.14 + S_{22}	0.10 + S_{25}	0.13 - S_{27}	0.57 + S_{29}	0.26 + S_{25}			
	0.13 - S_{23}	0.20 + S_{24}		0.58 + S_{24}	0.78 + S_{23}	0.11 - S_{24}	0.32 - S_{30}	0.74 + S_{26}	0.83 + S_{27}	0.71 + S_{28}	0.43 - S_{30}	0.42 + S_{29}			
				0.10 - S_{26}								0.30 + S_{30}			

^aA "+ " or "- " sign preceding coordinate indicates phase of displacements as given by L matrix.

atypical of the series. In the other three halides, steric repulsion results in essentially the same B—N bond distances but the progressively stronger electron attraction down the series shifts electron density into the dative bond and results in progressively larger force constants. The two opposing effects result in a minimum force constant at the chloride complex. As evidence of the inductive effect, it can be pointed out that the C—N force constants regularly decrease in magnitude from the fluoride through the iodide.

As a concluding remark, it can be noted that the results found in the present study are not concordant with the thermodynamic results nor with the recent mass spectral data [29] which indicate that the B—N bond in the fluoride complex is weaker than that for the other three halides. However, the force or compliance constant is a property of the bond as it exists in the molecule whereas the thermodynamic and mass spectral data involve bond dissociation energies. Customarily, force constants and dissociation energies are assumed to be more or less proportional, but this is true only if the shape of the potential function is reasonably invariant.

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REFERENCES

- 1 S. Califano, *Pure Appl. Chem.*, 18 (1969) 353.
- 2 P. H. Clippard, J. C. Hanson and R. C. Taylor, *J. Cryst. Mol. Struct.*, 1 (1971) 363.
- 3 H. Hess, *Acta Crystallogr.*, 25 (1969) 2338.
- 4 S. Geller and J. L. Hoard, *Acta Crystallogr.*, 4 (1951) 399.
- 5 R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 20 (1964) 1487. (Paper I in the present series).
- 6 W. Sawodny and J. Goubeau, *Z. Phys. Chem. Frankfurt am Main*, 44 (1965) 227.
- 7 H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, 78 (1956) 2173.
- 8 C. M. Bax, A. R. Katritzky and L. E. Sutton, *J. Chem. Soc.*, (1958) 1258.
- 9 M. F. Lappert, *J. Chem. Soc.*, (1962) 542.
- 10 J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, 42 (1964) 1518.
- 11 G. F. Lanthier and J. M. Miller, *J. Chem. Soc. A*, (1971) 346.
- 12 C. T. Mortimer, *Reaction Heats and Bond Strengths*, Pergamon, New York, N.Y., 1962, p. 111 ff.
- 13 D. F. Shriver and B. Swanson, *Inorg. Chem.*, 10 (1971) 1354.
- 14 E. O. Gamble, *Inorganic Syntheses*, Vol. III, McGraw-Hill, New York, N.Y., 1950, p. 27.
- 15 T. Wentink, Jr. and V. H. Tiensuu, *J. Chem. Phys.*, 28 (1958) 826; *Diss. Abstr.*, 23 (1962) 1535.
- 16 P. H. Clippard, Ph.D. Dissertation, University of Michigan, 1969; University Microfilms (Ann Arbor) No. 69-17983, *Diss. Abstr. Int. B*, 30 (1969) 2107.

- 17 P. H. Clippard and R. C. Taylor, *J. Chem. Phys.*, 50 (1969) 1472.
- 18 J. C. Decius, *J. Chem. Phys.*, 38 (1963) 241.
- 19 R. C. Taylor, R. W. Rudolph, R. J. Wyma and V. D. Dunning, *J. Raman Spectrosc.*, 2 (1974) 175.
- 20 J. Aldous and I. M. Mills, *Spectrochim. Acta*, 18 (1962) 1073.
- 21 W. J. Taylor and K. S. Pitzer, *J. Res. Nat. Bur. Stand.*, 38 (1947) 1.
- 22 K. Shimizu and H. Murata, *J. Mol. Spectrosc.*, 4 (1960) 201.
- 23 Y. Kuroda and M. Kimura, *Spectrochim. Acta*, 22 (1966) 47.
- 24 The full set of coordinates is given in Ref. 16 and is also available from the authors.
- 25 E. B. Wilson, Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, N.Y., 1955, p. 74.
- 26 I. M. Mills, *Spectrochim. Acta*, 19 (1963) 1585.
- 27 J. N. Gayles, W. T. King and J. H. Schachtschneider, *Spectrochim. Acta*, Part A, 23 (1967) 703.
- 28 L. H. Jones and R. R. Ryan, *J. Chem. Phys.*, 52 (1970) 2003.
- 29 G. F. Lanthier and J. M. Miller, *J. Chem. Soc. A*, (1971) 346.