

193. *Monomeric Dimethylaminoboron Dihalides.*

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The four dimethylaminoboron dihalides Me_2NBX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$) have been prepared by an improved method and their vapour-phase infrared spectra recorded in the range $400\text{--}4000\text{ cm.}^{-1}$. There is a monomer-dimer equilibrium in the gaseous difluoride but the other compounds are exclusively monomeric in the gas phase. A detailed assignment of the spectra has been carried out on the basis of a planar $\text{C}_2\text{N-BX}_2$ skeleton. The solid difluoride and dibromide have been shown to be dimeric like the dichloride; the diiodide, which is a new compound, has been obtained as a relatively involatile monomeric liquid and no dimeric modification has been identified.

As part of a study of the factors affecting the polymerization of compounds containing B-N bonds, the four monomeric dimethylaminoboron dihalides have been prepared and their infrared spectra studied in the gas phase. The di-iodide is a new compound and its synthesis has enabled the first systematic study of a complete series of boron-halogen compounds outside the boron trihalides themselves. Indeed, apart from the boron trihalides, the only compounds containing the B-I bond for which physical measurements relative to structure have been reported are Pr^n_2BI ,¹ $(\text{Ph}_2\text{PBI}_2)_2$,² and $(\text{Et}_2\text{PBI}_2)_3$.³

Dimethylaminoboron difluoride, dichloride, and dibromide have been described in the literature. The colourless compound of empirical formula Me_2NBF_2 was shown by Burg and Banus⁴ to be monomeric in the vapour phase and in ether solution; in the solid it was thought to be monomeric although previously⁵ it had been considered to be dimeric by comparison with the solid chloride, $(\text{Me}_2\text{NBCl}_2)_2$. At room temperature dimethylaminoboron dichloride and dibromide are both reactive liquids which slowly deposit colourless crystals, stable to air and water. The degree of association of the bromide in the liquid and solid states has not previously been determined, although in the liquid it had been assumed to be monomeric and in the solid dimeric by analogy with the chloride.

The four dimethylaminoboron dihalides were prepared by reaction of trisdimethylaminoborane, $\text{B}(\text{NMe}_2)_3$, with the appropriate boron trihalide:⁶



¹ Long and Wallbridge, *J.*, 1963, 2181.

² Gee, Shaw, Smith, and Bullen, *Proc. Chem. Soc.*, 1961, 432.

³ Biddulph, Brown, M. P., Cass, Long, and Silver, *J.*, 1961, 1822.

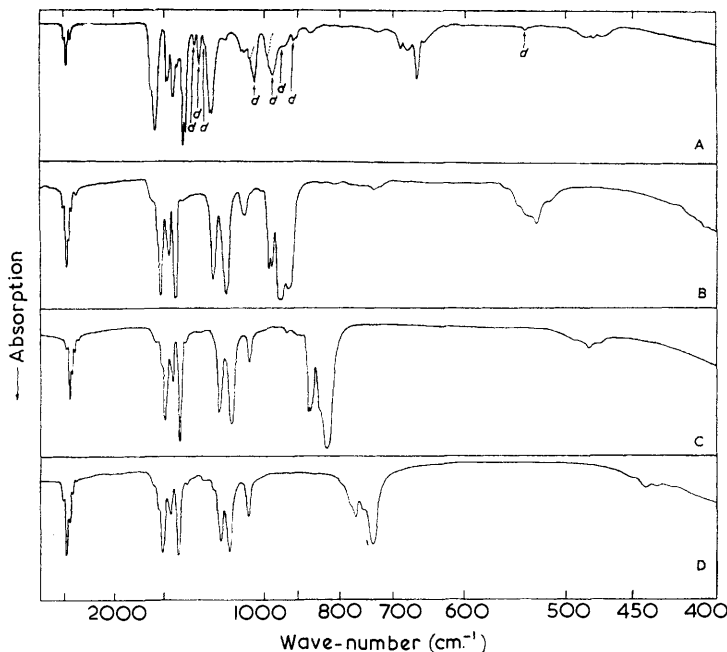
⁴ Burg and Banus, *J. Amer. Chem. Soc.*, 1954, **76**, 3903.

⁵ Brown, J. F., *J. Amer. Chem. Soc.*, 1952, **74**, 1219.

⁶ Goubeau, Rahtz, and Becker, *Z. anorg. Chem.*, 1954, **275**, 161.

This method, which had previously been applied only to the dichloride, gave good yields (70—85%) and was found to be superior to other published methods. The difluoride was precipitated immediately during the preparation and was purified by vacuum sublimation at 30° or by recrystallization from benzene. The dichloride and dibromide were obtained initially as colourless liquid monomers which deposited the solid dimer during several

Infrared spectra of gaseous monomeric dimethylaminoboron dihalides.



A, Me_2NBF_2 (d = dimer bands). B, Me_2NBCl_2 . C, Me_2NBBr_2 . D, Me_2NBI_2 .

(Wave-numbers in cm^{-1}).

Me_2NBF_2	Me_2NBCl_2	Me_2NBBr_2	Me_2NBI_2	Assignment			
3000	3030	3027	3017	CH ₃ stretch			
2947	2953	2932	2943				
2911	2891	2853	2882				
2827	2815	2814	2804				
1595	1548	1543	1538	¹⁰ B-N stretch			
1562	1527	1517	1508	¹¹ B-N stretch			
1473	1467	1466	1453	CH ₃ antisym. deform.			
1433	1414	1412	1391	CH ₃ sym. deform.			
1398 PR	978 PR	876 PR	762 PR	¹⁰ B-X ₂ antisym. stretch			
1359 PR	946	833	730	¹¹ B-X ₂ antisym. stretch			
1209	1199	1189	1167	CH ₃ rock			
—	1143	1136	1129	N-C ₂ antisym. stretch			
1078	1068	1063	1050	CH ₃ rock			
—	—	852	762	¹⁰ B-X ₂ sym. stretch			
1035	923	833	730	¹¹ B-X ₂ sym. stretch			
985		906	—	N-C ₂ sym. stretch			
688 Q	540	—	—	¹⁰ B-X ₂ out-of-plane deform.			
675 R	532 R	495 R	454 R	¹¹ B-X ₂ out-of-plane deform.			
663 Q					525 Q	485 Q	443 Q
651 P					513 P	476 P	432 P
490	*	*	*	¹⁰ B-X ₂ in-plane deform.			
486 R	*	*	*	¹¹ B-X ₂ in-plane deform.			
478 Q							
470 P							

* Expected to fall below 400 cm^{-1} .

days. The monomeric di-iodide was obtained as a colourless oil by vacuum distillation at 100° of the yellow powder formed initially during the preparation at -10° . The di-iodide is extremely reactive and is explosively hydrolysed by water.

The problem of whether the solid difluoride is monomeric⁴ or dimeric⁵ has been resolved by X-ray crystal studies in this laboratory.⁷ These studies have shown that the solid is, in fact, dimeric like the solid dichloride,^{7,8,9} the molecular unit being comprised of a planar four-membered (B-N)₂ ring with substituents on the boron and nitrogen atoms both above and below the plane of the ring. This conclusion has been confirmed by the infrared spectrum of the dimer both as a solid (KBr disc) and in non-polar solvents such as carbon disulphide, carbon tetrachloride, and benzene. The infrared spectrum of the monomeric difluoride was obtained by placing a small amount of the solid dimer in the side-arm of a gas-cell, mounting the windows, evacuating, and then heating the cell in a stream of warm air. A complex spectrum was obtained [see Figure (A)] which could be analysed on the basis of a monomer-dimer equilibrium in the vapour. By subtracting the lines known to be due to the dimer, the spectrum of the monomer was obtained as recorded in the Table.

Monomeric dimethylaminoboron dichloride and dibromide were obtained by heating the solid dimeric compounds for 30 min. under a vacuum at their melting points (142° ⁹ and 152° ¹⁰ respectively), and then condensing the more volatile monomer into the side-arm of a gas-cell; the spectra were then recorded at various pressures by heating the gas-cell [see Figure (B and C) and Table]. The monomeric di-iodide was distilled directly into the gas-cell at 100° under reduced pressure, and a vapour-phase spectrum of adequate intensity [Figure (D)] was obtained at $60-70^\circ$; a freshly distilled sample of monomer was used for each spectrum since the compound slowly decomposed above 60° under these conditions.

The spectra of the gaseous dimethylaminoboron dihalides can be analysed in terms of a planar C₂N-BX₂ skeleton with three hydrogen atoms orientated in the normal tetrahedral arrangement around each of the carbon atoms. This structure has thirty fundamental modes of which twenty-five are active in the infrared spectrum. The C₂N-BX₂ skeleton itself has C_{2v} symmetry with eleven infrared-active fundamentals: five of species A₁, four of species B₁, and two of species B₂. Since the remaining fundamentals are concerned with CH₃ modes which are well characterized, it is possible to assign all the fundamentals which occur above 400 cm.⁻¹, with reasonable certainty. The shape of the band contours is of considerable help in deducing the assignments. Furthermore, the bands associated with the NBX₂ group can often be recognized by the presence of a subsidiary band due to the ¹⁰B isotope.

DISCUSSION

Two difficulties arise in attempting to assign group frequencies to molecules of intermediate complexity. The first concerns the mixing of modes; thus it is not possible to assign the individual absorption bands of small molecules (3-8 atoms) to specific group frequencies since each mode of vibration involves all the atoms in the molecule. This difficulty diminishes as the complexity of the molecule increases, but mixing still occurs in 12-atomic molecules, such as the monomeric dimethylaminoboron dihalides, if two groups are close together and have similar group frequencies. The second difficulty arises from the kinematic or mass effect of other substituents on the group frequency considered. Both difficulties obtrude in the assignment of the BX₂ and NC₂ group frequencies of Me₂NBX₂ and related molecules. In particular, it is misleading to use the assignments made for the mixed dihalides YBX₂^{11,12} in which the "symmetric BX₂ mode"

⁷ Hazell, unpublished work.

⁸ Clarke and Powell, personal communication.

⁹ Brown, C. A., and Osthoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2340.

¹⁰ Wiberg, Bolz, and Bucheit, *Z. anorg. Chem.*, 1948, **256**, 285.

¹¹ Lindemann and Wilson, *J. Chem. Phys.*, 1956, **24**, 242.

¹² Butcher, Gerrard, Howarth, Mooney, and Willis, *Spectrochim. Acta*, 1963, **19**, 905.

frequently occurs at approximately half the value of the "antisymmetric BX_2 mode." Nor is it possible to adopt, without modification, the suggestion¹² that if the group X is lighter than Y then the symmetric and antisymmetric BX_2 stretching modes are relatively close together, whereas if X is heavier than Y the two frequencies differ by nearly a factor of two. For example, this mass relationship would predict widely separated frequencies for the two modes in the compounds Me_2NBBr_2 and $Me_2NB I_2$, although this is not observed. In the present analysis, the two modes are found to be very close together, except for the difluoride which is considered in more detail below.

Dimethylaminoboron Difluoride.—The most difficult region of the spectrum to assign is that near 1000 cm.^{-1} where dimer bands almost completely overlap two of the monomer bands and so make it impossible to observe the true band shapes or intensities. The two vibrations expected in this region of the spectrum are the symmetric BF_2 and NC_2 stretching modes which belong to the same symmetry class. Thus, additional coupling of these modes is probable, and it is preferable to assign the bands at 1035 and 985 cm.^{-1} jointly to these two modes rather than to assign each band individually. Both, however, are well removed from the BF_2 antisymmetric stretching frequency which occurs at 1359 cm.^{-1} .

The only other band which is difficult to assign occurs at 478 cm.^{-1} . This band has an incipient PQR envelope which suggests a type A band of an asymmetric-top molecule. It is assigned to the BF_2 in-plane bending vibration, rather than to the analogous NC_2 bending motion, on the following evidence. There is some indication of a side-band at 490 cm.^{-1} due to the $^{10}BX_2$ group. Moreover, if the absorption at 478 cm.^{-1} were due to the NC_2 bending mode, then a similar band would be expected in this region for the other dihalides. No band occurs between 450 and 500 cm.^{-1} for the dichloride and di-iodide; the dibromide absorbs at 485 cm.^{-1} but this is due to the BBr_2 out-of-plane deformation. Furthermore, the Raman spectrum of $Me_2NB Cl_2$ has a strong band at 393 cm.^{-1} which has been assigned⁶ to the NC_2 deformation, and in the Raman spectrum of dimethylamine the NC_2 bending mode occurs at 397 cm.^{-1} . Finally, the infrared spectrum of dimethylaminoboron dichloride, shown in the Figure (B), indicates that there is a peak just below 400 cm.^{-1} which could be assigned to the NC_2 bending mode.

Dimethylaminoboron Dichloride.—The dimethylaminoboron dihalides are expected, from symmetry considerations, to be asymmetric-top molecules. Calculations of the moments of inertia confirm this, except for dimethylaminoboron dichloride. This has two moments which are approximately equal and so the monomer chloride can be treated as a symmetric-top molecule. Two different types of band shape are thus predicted: (a) fundamentals belonging to the symmetry classes A_1 and B_1 , which appear as perpendicular bands (calculated PR separation, *ca.* 11 cm.^{-1}); and (b) fundamentals of class B_2 , which appear as parallel bands with a prominent Q branch (calculated PR separation, *ca.* 17 cm.^{-1}). The values for the PR separations were calculated by the usual method.¹³

The 900 — 1000 cm.^{-1} region of the spectrum is complicated by the fact that several overlapping bands are present. The $^{11}BCl_2$ antisymmetric stretching mode is identified at 946 cm.^{-1} , being the strongest band in the spectrum, and also by the presence of the ^{10}B isotope band at a slightly higher wave-number (978 cm.^{-1}). The PR separation of the ^{10}B isotope band is *ca.* 10 cm.^{-1} , in good agreement with the calculated value. The band at 923 cm.^{-1} is assigned to the $^{11}BX_2$ symmetric stretch, the ^{10}B component being masked by the band at 946 cm.^{-1} . An alternative assignment proposed by Goubeau *et al.*⁶ for the Raman spectrum of the dichloride was the placing of the BX_2 symmetric stretching mode at 530 cm.^{-1} . This band was very close to a band at 511 cm.^{-1} which was tentatively assigned to the BX_2 out-of-plane deformation. The vapour-phase infrared spectrum [see Figure (B)] shows a band with a prominent Q branch at 525 cm.^{-1} and a small

¹³ Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.

shoulder at approximately 540 cm^{-1} . Since a prominent Q branch is characteristic of a parallel band of a symmetric-top molecule, we prefer to assign the two bands to the isotope doubling of the BX_2 out-of-plane deformation. Goubeau *et al.*⁶ assigned the extra band at 924 cm^{-1} , in the monomer dichloride, to the NC_2 symmetric stretch. However, PhBCl_2 ,¹² MeOBCl_2 ,¹⁴ and $\text{Bu}^t\text{NH}\cdot\text{BCl}_2$ ¹⁵ all have an extra band associated with the antisymmetric BX_2 stretch in this region, and these compounds contain no NC_2 group. The NC_2 symmetric and antisymmetric stretching bands are also expected to have a PR separation of 10 cm^{-1} , but only the NC_2 antisymmetric stretch can be assigned with any certainty. This appears as a PQR band at 1143 cm^{-1} (PR separation, 9 cm^{-1}). The symmetric NC_2 stretch is expected to occur in the $900\text{--}1000\text{ cm}^{-1}$ region where it is probably overlapped by other bands. The vibration is also likely to be coupled with the symmetric BCl_2 stretching vibration. The BN stretching mode, which is expected to be in the region of 1500 cm^{-1} owing to the double-bond character of the B-N bond,^{16,17} can easily be identified at 1527 cm^{-1} because of the ^{10}B isotope side-band at 1548 cm^{-1} .

Dimethylaminoboron Dibromide.—The assignments for the spectrum of the monomeric dibromide are very similar to those for the monomeric dichloride except that the NBBr_2 bands move to lower wave-numbers, owing to the mass effect of the bromine atoms and the change in double-bond character of the B-N bond. Thus the frequency of the $^{11}\text{B-N}$ stretching mode diminishes with increasing atomic number of the halogen atom: 1562 (F); 1527 (Cl); 1517 (Br); and 1508 cm^{-1} (I) (the corresponding values for $^{10}\text{B-N}$ are: 1595 ; 1548 ; 1543 ; and 1538 cm^{-1}). The particularly high value for the difluoride may also indicate some coupling with the symmetric BF_2 mode.

Goubeau *et al.*⁶ assigned the band at 485 cm^{-1} to the BBr_2 symmetric stretching vibration. However, the Figure (C) indicates that this band exhibits PQR structure with a strong Q branch and a PR separation of 18 cm^{-1} , *i.e.*, a typical type C band for an asymmetric-top molecule. The calculated separation for a type C band¹⁸ for Me_2NBBr_2 is 15 cm^{-1} and this confirms the assignment of the 485 cm^{-1} band as the BBr_2 out-of-plane deformation. This implies that the BBr_2 symmetric stretch is either below 400 cm^{-1} or near 833 cm^{-1} , the position of the BBr_2 antisymmetric stretching band. Our results favour the latter interpretation. This is supported by the Raman data of Becher¹⁹ which show that there are no suitable bands just below 400 cm^{-1} for this particular mode of vibration. As the mass of the halogen atom increases from chlorine to bromine, the $^{11}\text{BX}_2$ symmetric and antisymmetric modes become virtually coincident and only a shoulder on the high-frequency side of this intense, broad band can be distinguished. This shoulder is assigned to the $^{10}\text{BBr}_2$ symmetric mode. The $^{10}\text{BBr}_2$ antisymmetric stretch is clearly observed at 876 cm^{-1} . The weak band at 906 cm^{-1} is attributed to the NC_2 symmetric stretch.

Dimethylaminoboron Di-iodide.—The vapour-phase spectrum of the monomeric di-iodide shows a strong doublet at $730, 762\text{ cm}^{-1}$. By a continuation of the trend observed for the dichloride and the dibromide, it is to be expected that the BI_2 symmetric and antisymmetric stretching modes will be completely superimposed and hence only two of the expected bands will be observed, corresponding to $^{11}\text{BI}_2$ and $^{10}\text{BI}_2$. Although this appears to be the case, the interpretation is complicated by the presence of two weak impurity bands at 752 and 780 cm^{-1} . The impurity is probably a decomposition product of the monomer di-iodide since it appears in increasing concentration after the latter has been warmed for a few minutes in the gas-cell.

The weak PQR band at 443 cm^{-1} is assigned to the NBI_2 out-of-plane deformation.

¹⁴ Lehmann, Onak, and Shapiro, *J. Chem. Phys.*, 1959, **30**, 1219.

¹⁵ Turner, personal communication.

¹⁶ Wyman, Niedenzu, and Dawson, *J.*, 1962, 4068.

¹⁷ Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1960, **82**, 4223.

¹⁸ Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

¹⁹ Becher, *Spectrochim. Acta*, 1963, **19**, 575.

The only band which was not observed for the di-iodide was the NC_2 symmetric stretching mode, which was expected to occur at about 900 cm^{-1} .

EXPERIMENTAL

Compounds were handled in dry, nitrogen-filled glove-boxes and in conventional vacuum lines.

Dimethylaminoboron Difluoride, Me_2NBF_2 .—A solution of trisdimethylaminoborane (4.1 g., 0.03 mole) in dry pentane (200 ml.) was placed in a flask equipped with a gas-bubbler, magnetic stirrer, and outlet tube which terminated in a mercury seal. A mixture of boron trifluoride and nitrogen was bubbled into the solution; a white powder was immediately precipitated and the flow of gas was continued until precipitation ceased. The solvent was removed by distillation and the product (6.6 g., 0.07 mole, 82%) was purified either by vacuum sublimation at 30° (96% recovery) or by recrystallization from benzene (90% recovery). It crystallized as well-formed, elongated needles (Found: B, 11.6; F, 42.0; N, 15.3. Calc. for $\text{C}_2\text{H}_6\text{BF}_2\text{N}$: B, 11.7; F, 42.1; N, 15.1%).

Dimethylaminoboron Dichloride, Me_2NBCl_2 .—(a) Boron trichloride replaced boron trifluoride in the preceding preparation; after removal of the solvent, the residue was a colourless liquid which deposited crystals at room temperature during 5 days. The crystals (68%) were filtered off and washed with dry pentane (Found: B, 8.5; Cl, 56.7; N, 11.0. Calc. for $\text{C}_2\text{H}_6\text{BCl}_2\text{N}$: B, 8.6; Cl, 56.5; N, 11.1%).

(b) The dichloro-compound was also prepared (62%) by adding triethylamine to a slurry of dimethylamine-boron trichloride ($\text{Me}_2\text{NH}\cdot\text{BCl}_3$) in benzene.⁵

Dimethylaminoboron Dibromide, Me_2NBBr_2 .—Boron tribromide (14.4 g., 0.06 mole) was added slowly to a pentane solution of trisdimethylaminoborane (4.1 g., 0.03 mole). The solvent was removed under a vacuum, leaving a colourless liquid. This was sealed under a vacuum in an ampoule and heated at 65° for seven days. The large crystals which had formed were filtered off and dried under a vacuum. Very little more solid was obtained when the filtrate was heated at 65° for a further 14 days (total yield 63%) (Found: B, 6.4; Br, 74.2; N, 4.9. Calc. for $\text{C}_2\text{H}_6\text{BBr}_2\text{N}$: B, 6.5; Br, 74.5; N, 5.0%).

Dimethylaminoboron Di-iodide, Me_2NBI_2 .—A solution of boron tri-iodide (12.6 g., 0.03 mole) in dry pentane (250 ml.) was immersed in an ice-salt bath at -10° and trisdimethylaminoborane (4.8 g., 0.03 mole.) was added slowly, with shaking, from a syringe; immediate precipitation occurred. The solvent was decanted in the glove-box and the yellow, oily residue was purified by washing with pentane to give a yellow powder, stable indefinitely under a vacuum at 0° (14.8 g., 85%) (Found: B, 3.5; I, 76.0; N, 4.6%). At higher temperatures, or with different molar proportions, the reaction gave dark brown residues. The yellow powder, on being warmed to 20° under a vacuum, gave a viscous brown mixture. At (a) 20° , (b) 30° , and (c) 100° , the most volatile fractions were condensed at -196° and afforded small quantities of (a) methyl iodide, identified by its infrared and mass spectra, (b) an unidentified colourless oil, and (c) a colourless oil which distilled very slowly. A small quantity of the latter oil was distilled into a weighed glass ampoule for analysis. After re-weighing, the ampoule was broken under a large volume of water and the solution analysed for boron (by mannitol titration), for iodine (as silver iodide), and for nitrogen (Kjeldahl) (Found: B, 3.5; I, 81.9; N, 4.4. $\text{C}_2\text{H}_6\text{BI}_2\text{N}$ requires B, 3.5; I, 82.2; N, 4.5%).

The vapour-phase infrared spectra were recorded on a Grubb-Parsons GS 2 spectrometer, with sodium chloride optics, and on Perkin-Elmer 137 spectrometers with sodium chloride or potassium bromide optics. The 10-cm. gas-cell was equipped with a 3-cm. side-arm.

We thank W. A. Campbell for help with analyses, and Borax Consolidated Ltd. for a gift of trisdimethylaminoborane. We also thank King's College (now The University), Newcastle upon Tyne, for a Fellowship (to B. P. S.), and the D.S.I.R. for a Senior Research Associateship (to A. J. B.) and a Maintenance Grant (to J. W.).