

794. *Boron-Nitrogen Compounds. Part V.¹ Aminoborines.
An Infrared Spectroscopic Study of Organo-substituted Aminoborines.*

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Comparison of the infrared spectra of organo-substituted aminoborines and their hydrolysis products has been found to be a useful and reliable method for identifying the B-N infrared stretching frequency of aminoborines. The bond character and hydrolytic stability of aminoborines is largely dependent upon the nature of the substituents. Reduction of double-bond character and great sensitivity towards hydrolysis seem to be typical for the *N*-aryl derivatives. A semiquantitative comparison of the double-bond character has been made for typical *N*-aryl- and *N*-alkyl-aminoborines.

REPORTED B-N stretching frequencies in symmetrically substituted aminoborines vary from 1194 cm^{-1} for *NN*-dimethylaminoborine² to 1530 cm^{-1} for dimethyl(dimethylamino)borane.³ Since the frequency of absorption of a stretching vibration in the infrared region is very sensitive to changes in the force constant of the linkage, this strongly suggests that the introduction of different substituents on the =B-N= group of aminoborines produces a variation in the degree of double-bond character between the boron and the nitrogen.⁴

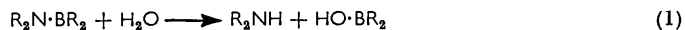
¹ Part IV, *Chem. Ber.*, 1961, **94**, 671.

² Price, Fraser, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

³ Becher and Goubeau, *Z. anorg. Chem.*, 1952, **268**, 133.

⁴ Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 553.

Generally the 1250—1600 cm^{-1} region of the infrared spectra of organic substituted aminoborines shows a number of strong absorptions, one of which should definitely belong to the B-N stretching frequency. It appeared logical to study the hydrolysis of aminoborines as a means of identifying the B-N absorption, since during hydrolysis the B-N linkage is ruptured according to eqn. (1). Under mild conditions, the secondary amine that is formed does not decompose, whereas the borinic acid is likely to disproportionate and/or dehydrate. Thus the only new bonds formed on hydrolysis of aminoborines other than those leading to amine-borine systems are N-H and B-O linkages. Since N-H stretching frequencies are known to occur near 3400 cm^{-1} , they should not cause interference. The N-H bending frequencies of secondary amines are usually relatively weak and they occur at slightly higher frequencies (1490—1580 cm^{-1})⁵ than the range



reported for most B-N absorptions. The formation of B-O bonds is known to give rise to a strong, broad absorption band (B-O stretching) at 1310—1350 cm^{-1} .⁶ This would present a problem only in the event that none of the bands of the aminoborine was to disappear on hydrolysis (which would indicate a B-N stretching band obscured by the B-O band); fortunately this was not the case.

Unsymmetrically substituted aminoborines⁷ were studied in more detail through infrared spectroscopy, in order further to elucidate the nature of the B-N bond and its relation to chemical reactivity. Methyl-(*N*-methylanilino)phenylborine, $\text{NPhMe}\cdot\text{BPhMe}$, was selected as the prototype of unsymmetrical substitution for this investigation.

It is reasonably certain that methyl-(*N*-methylanilino)phenylborine exists in at least two modifications at room temperature.⁷ This has led to the tentative conclusion that *cis-trans*-isomerism might occur in the aminoborines. More recently, Ryschkewitsch and his co-workers⁸ found evidence by proton resonance spectroscopy for hindered rotation about the boron-nitrogen bond in dimethyl-(*N*-methylanilino)borine, leading to *cis-trans*-configurations. However, their estimate of the energy barrier between the two isomers (*ca.* 15 kcal./mole) is likely to be too low to permit the existence of isolable isomers at room temperature.

So far the two modifications of methyl-(*N*-methylanilino)phenylborine have not been separated. One of the difficulties in handling this compound arises from its extreme sensitivity towards hydrolysis, giving an oil,⁹ which showed a strong N-H band near 3400 cm^{-1} in the infrared spectrum and a strong broad absorption band in the 1300—1350 cm^{-1} region. The latter is typical for a B-O grouping as found in organoboric acids,⁶ thereby confirming the hydrolysis of the B-N bond of the original aminoborine. Two strong bands (at 1381 and 1120 cm^{-1}) that were originally present in the starting material could not be detected in the hydrolysis product.

The hydrolysis of methyl-(*N*-methylanilino)phenylborine gives *N*-methylaniline, which has been isolated and identified, and methylphenylborinic acid. The latter appears to undergo rapid decomposition. Phenylboronic acid is probably formed first, as one of the products and may in turn dehydrate to yield tri-*B*-phenylboroxine. This course seems probable since a 1 : 3 molar mixture of tri-*B*-phenylboroxine and *N*-methylaniline exhibited an infrared spectrum similar to that of the hydrolysis product of methyl-(*N*-methylanilino)-phenylborine. Since one of the B-C bonds is broken, the absorption band at 1120 cm^{-1} can in all probability be assigned to the asymmetric stretching vibration of the C-B-C

⁵ Jones and Sandorfy, "Chemical Applications of Spectroscopy," Interscience Publishers Inc., New York, 1956, pp. 510—521.

⁶ Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

⁷ Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1960, **82**, 4223.

⁸ Ryschkewitsch, Brey, jun., and Saji, *J. Amer. Chem. Soc.*, 1961, **83**, 1010.

⁹ Fortunately it was possible to obtain infrared spectra of the solid by covering it with a suitable mulling medium (paraffin oil or hexachlorobutadiene) and thus keeping it from contact with moisture.

grouping, in accordance with a similar assignment by Becher.¹⁰ The band at 1381 cm.⁻¹ can then be assigned with reasonable certainty to the B-N stretching frequency. The validity of this assignment is further substantiated since all bands within the range 1250—1600 cm.⁻¹ could then be assigned in agreement with other work⁶ on related systems. (These assignments are combined in Table 1.)

TABLE 1.

Methyl-(*N*-methylanilino)phenylborine: Infrared absorption bands and their assignments in the 1250—1600 cm.⁻¹ region, measured with the solid as a mull in Nujol or hexachlorobutadiene, as appropriate.

| | | | | | | | |
|--------------------------------------|------|------|------|------|------|------|------|
| Frequency (cm. ⁻¹) | 1600 | 1496 | 1462 | 1430 | 1381 | 1302 | 1259 |
| Assignment..... | Ph | Ph | B-Me | B-Ph | B-N | B-Me | B-Ph |

Similar observations were made with ethyl-(*N*-ethylanilino)phenylborine. This compound likewise shows a strong absorption band at 1383 cm.⁻¹, which disappears on hydrolysis and which may consequently be assigned as the B-N stretching frequency, and a band at 1120 cm.⁻¹ which exhibited similar behaviour to the corresponding band of the methyl analogue and was, therefore, assigned to the C-B-C asymmetric stretching frequency.

The rates of hydrolysis of several aminoborines have been roughly compared by infrared spectroscopy. Typical *N*-monoaryl compounds are completely hydrolyzed within two minutes. The rate of hydrolysis of (diarylamino)borines appears to be still more enhanced, whereas *N*-alkyl derivatives generally require considerably longer exposure to moisture to produce the same degree of hydrolysis as (arylamino)borines. When the samples were kept in a laboratory atmosphere for about one hour, the original B-N frequency of (alkylamino)borines could no longer be observed in the infrared spectra.

The B-N stretching frequencies of some aminoborines are listed in Table 2. For the compounds studied in this work, the bands were assigned by comparison of the original compounds with their respective hydrolysis products.

The B-N bond in aminoborines may have considerable double-bond character, resulting primarily from resonance $\text{>B-N}^{\ddagger} \rightleftharpoons \text{>B}^{\ddagger}=\text{N}^{\ddagger}$. These observations indicate that the introduction of an *N*-phenyl group brings about a considerable lowering of the double-bond character of the B-N linkage by resonance interaction of the unshared electron pair of the nitrogen atom with the adjacent phenyl group. Since such interaction results in

TABLE 2.

B-N stretching bands of aminoborines.

| Substituents | | | Frequency (cm. ⁻¹) | Substituents | | Frequency (cm. ⁻¹) |
|--|--|------------|-----------------------------------|--|--------|-----------------------------------|
| <i>N</i> - | <i>B</i> - | <i>N</i> - | | <i>B</i> - | | |
| 2Me | 2H | Ph, Me | 1194 ^a | 2Me | 2Me | 1388 |
| Ph, H | 2Me | 2Me | 1332 ^b | 2 <i>p</i> -Me·C ₆ H ₄ | Ph, Et | 1410 ^c |
| 2 <i>p</i> -Me·C ₆ H ₄ | 2Ph | Me, Bu | 1361 ^c | Ph, Et | Ph, Me | 1412 |
| 2Ph | 2Ph | 2Me | 1372 ^c | 2Et | 2Et | 1417 |
| Ph, Me | Ph, Me | 2Et | 1381 | Me, H | 2Me | 1490 |
| Ph, Et | Ph, Et | 2Me | 1383 | 2Me | 2Me | 1525 ^d |
| 2Ph | 2 <i>p</i> -Me·C ₆ H ₄ | | 1385 ^c | | | 1530 ^d |

^a Ref. 2. This compound was probably a dimer. ^b Ref. 10. ^c Coates and Livingstone, *J.*, 1961, 1000. ^d Ref. 3.

increased electron deficiency at the boron atom, the latter is more subject to nucleophilic attack (*e.g.*, hydrolysis).

¹⁰ Becher, *Z. anorg. Chem.*, 1957, **289**, 262.

The effect of *B*-aryl groups seems less pronounced, although here again a tendency toward lower frequencies is apparent (cf. Table 2). Resonance interaction is again possible (since the phenyl group is "amphoteric" in this respect) leading to increased double-bond character for the *B*-phenyl bond and a corresponding decrease in the double-bond character for the B-N link. It should be noted, however, that the electron density around the boron atom is not diminished and, consequently, increased reactivity toward nucleophilic attack is not to be expected.

The wide range of B-N stretching frequencies shown in Table 2 is a good indication of a considerable variation in the bond orders of the B-N bonds in these compounds. While, in general, the bond order (or double-bond character) increases as the B-N stretching frequency shifts to higher frequencies, an exact determination of the bond orders will have to await the availability of further infrared data (mainly on aminoborines) and the determination of the B-N bond distances for some of the aminoborines. However, on the basis of a rough, semi-quantitative calculation, following Gordy's equations¹¹ (neighbouring-group mass effects and coupling between the B-N and the adjacent B-C and N-C stretching modes being neglected) and the best available estimates for the B-N bond distances being used, a range of 1.30—1.60 is obtained for the bond orders (corresponding to 30—60% double-bond character) for the aminoborines listed in Table 2, which appears to be consistent with their chemical behaviour.

EXPERIMENTAL

Preparative techniques have been described elsewhere.^{4,7} When methyl-(*N*-methylanilino)-phenylborine is distilled without the benefit of a condenser it can be obtained liquid; crystallization can be promoted by seeding, and is spontaneous, highly exothermic, and never complete. The solid is always contaminated with a small amount of liquid and the melting range of 35—58° indicates the inhomogeneity. Purification was attempted by washing the compound in a dry box under nitrogen with inert anhydrous solvents. However, the washed crystals spontaneously partly liquefied.

On one occasion the material was distilled directly into a solvent and the infrared spectrum of the solution measured. No difference between such a spectrum and those obtained by normal procedures was observed. Furthermore, in no case could a dilution effect on the infrared spectrum be observed, thereby strongly suggesting the absence of a higher aggregated species as one of the modifications. Repeated determinations of molecular weight by the cryoscopic method and through isothermal distillation confirm the existence of the monomer only.

All infrared spectra were recorded with a Perkin-Elmer model 21 double-beam spectrophotometer, sodium chloride optics being used. Spectra of solutions were observed in carbon tetrachloride. The spectra of solids were determined as mulls in paraffin oil, Kel-F polymer oil, or hexachlorobutadiene.

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¹¹ Gordy, *J. Chem. Phys.*, 1946, **14**, 305.