J. Chem. Soc. (A), 1968

Nuclear Magnetic Resonance Studies of π -Bonding in Aminoboranes. Part I. Ambient Temperature Spectra

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The ¹H n.m.r. spectra at ambient temperatures of a number of aminoboranes with general formula ArB(X¹)NMe₂ (I) or PhB(X²)N(R¹)R² (II) are reported both for pure liquids and for a variety of solutions. Positive evidence is presented for restricted rotation about the boron-nitrogen bond for the compounds (a) of type (I) with Ar = Ph, $X^1 = Br$, Cl, NCO, Me or with $Ar = \rho$ -MeOC₆H₄, X = Cl and (b) of type (II) with $X^2 = Cl$, R = Et, R² = Me or with $X^2 = CI$, $R^1 = Pr^i$, $R^2 = Me$. The effects of varying the boron-substituent and the solvent upon chemical shifts are considered.

REFERENCE to the possibility of back-donation of electrons to a three-co-ordinate boron centre has frequently been made and, in the case of open-chain aminoboranes and cyclic borazines, the evidence for back-donation of the nitrogen lone-pair towards the boron atom, *i.e.* the creation of $(p \longrightarrow p) \pi$ -bonding, has previously been summarised.¹ One consequence of the existence of such bonding is a high degree of restriction to interconversion between minimum energy conformations by 180° rotation about the boron-nitrogen bond. Restrictions of this kind are reflected in the observation of a temperature-dependence of the high resolution nuclear magnetic resonance spectra;² at low interconversion rates, distinct absorption from individual rotational isomers is evident, while at the other extreme of rapid interconversion timeaveraging occurs; in intermediate situations, the spectra are more complex. As has been shown previously,³⁻⁸ the barrier to rotation in certain aminoboranes is sufficiently high to permit the observation of separate absorption

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¹ M. F. Lappert in 'Developments in Inorganic Polymer Chemistry,' ed. M. F. Lappert and G. J. Leigh, Elsevier, New York, 1962, p. 44.

² J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, London, 1965, vol. 1, ch. 9.

³ P. A. Barfield, M. F. Lappert, and J. Lee, Proc. Chem. Soc., 1961, 421.

⁴ G. E. Ryschkewitsch, W. S. Brey, and A. Saji, J. Amer. Chem. Soc., 1961, 83, 1010.

⁵ W. S. Brey, M. E. Fuller, G. E. Ryschkewitsch, and A. S. Marshall, 'Boron-Nitrogen Chemistry, Advances in Chemistry Series, No. 42,' American Chemical Society, 1964, p. 100.

from rotational isomers (rotamers) at ambient temperatures. The present paper extends the range of aminoboranes studied and describes nuclear magnetic spectral observations at these temperatures. A subsequent paper ⁹ will be devoted to studies at higher temperatures and the evaluation of kinetic parameters for the internal rotational process.

EXPERIMENTAL

Starting Materials.—All the compounds studied in the present work were prepared from appropriate aryldihalogenoboranes. Aryldichloroboranes were obtained by the transmetalation of boron trichloride by tetra-aryltins.¹⁰⁻¹² Dibromophenylborane was obtained through interaction of boron tribromide and triphenylboroxine.13 Ethylmethylamine (not commercially available) was prepared by reduction of the condensation product of ethylamine and

⁶ H. Watanabe, K. Nagasawa, T. Totani, T. Yoshizaki, T. Nakagawa, O. Ohashi, and M. Kubo, 'Boron-Nitrogen Chemistry, Advances in Chemistry Series, No. 42,' American Chemical

Society, 1964, p. 108. ⁷ H. Baechle, H. J. Becher, H. Beyer, W. S. Brey, J. W. ⁸ Niedenzu Inorg. Chem., 1963, 2, Dawson, M. E. Fuller, and K. Niedenzu, Inorg. Chem., 1963, 2, 1065

⁸ T. Totani, H. Watanabe, and M. Kubo, 'Nuclear Magnetic Resonance and Relaxation in Solids,' Proc. XIIIth Colloque Ampère, 1965, 366.

P. A. Barfield, M. F. Lappert, and J. Lee, to be published. ¹⁰ F. E. Brinckman and F. G. A. Stone, Chem. and Ind., 1959,

78, 254. ¹¹ F. E. Brinckman and F. G. A. Stone, J. Amer. Chem. Soc., 1960, **82**, 6218.

¹² J. E. Burch, W. Gerrard, M. Howarth, and E. F. Mooney,

J. Chem. Soc., 1960, 4916. ¹³ E. W. Abel, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 1957, 5051.

formaldehyde.¹⁴ Isopropylmethylamine was a gift from Imperial Chemical Industries Ltd.

Aminochloroboranes.— Chloro(dimethylamino)phenylborane PhB(Cl)NMe₂, p-methoxyphenylchlorodimethylaminop-MeOC₆H₄B(Cl)NMe₂, chloro(ethylmethylamino)borane phenylborane PhB(Cl)N(Me)Et, chloro(methylisopropyl-PhB(Cl)N(Me)Prⁱ, amino)phenylborane chloro(methylphenylamino)phenylborane PhB(Cl)N(Me)Ph, and t-butylaminochlorophenylborane PhB(Cl)N(H)But were obtained by dehydrohalogenation of the appropriate amine-aryldichloroborane adduct,¹⁵ or by a disproportionation procedure analogous to that used for the preparation of chloroalkoxyboranes.16

Bis(amino)arylboranes.---Bis(dimethylamino)phenylborane PhB(NMe₂)₂, p-methoxyphenylbis(dimethylamino)borane p-MeOC₄H₄B(NMe₂)₂, bis(methylphenylamino)phenylborane PhB[N(Me)Ph]₂, bis(methylamino)phenylborane PhB(NHMe)2, and bis(t-butylamino)phenylborane PhB[N(H)Bu^t], were obtained by the dropwise addition of dichloroarylborane (1 mol.), in light petroleum to a solution of the appropriate amine (4 mol.), in light petroleum at -78°.12 (Dimethylamino)methylphenylborane

to -78° and dry methyl alcohol (1.49 g., 1 mol.) was slowly added. The mixture was set aside to attain room temperature and then gently warmed, dimethylamine (2.1 g., 100%)being evolved. Distillation of the residue gave (dimethylamino)methoxyphenylborane (5.9 g., 78%). This compound was also prepared by the dropwise addition of chloro-(methoxy)phenylborane (16.4 g., 1 mol.), in light petroleum (50 ml.), to dimethylamine (9.6 g., 2 mol.), in the same solvent (80 ml.) at -78° . The mixture was set aside for 3 hr., dimethylammonium chloride (8.4 g., 96%) was filtered off, and the solvent was distilled off under reduced pressure. Further distillation then gave (dimethylamino)methoxyphenylborane (12.0 g., 69%).

Dimethylamino(fluoro)phenylborane, $PhB(F)NMe_2$.— Chloro(dimethylamino)phenylborane (4.3 g., 3 mol.) and antimony(III) fluoride (1.6 g., 1 mol.) were mixed together at room temperature; an increase in temperature was noted. After 2 hr., the mixture was distilled to give dimethylamino(fluoro)phenylborane (3.5 g., 88%) and an undistillable residue.

The purity of all compounds was checked by elemental microanalysis and by infrared spectrometry, using Perkin-

TABLE	1
TUDFF	1

Elemental analyses an	nd physical	properties of new	compounds
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					Found	d		Calc.					
Compound	B. p. (°/torr)	n_{20}^{D}	ć	н	В	Halogen	N	ć	н	В	Halogen	N	
PhB(F)NMe	62/3.0	1.5058	63.1	7.1	ь	Ь	9.5	63.7	7.3	$7 \cdot 2$	12.6	9.3	
PbB(Cl)NMeEt	82/0·2	1.5284	60-2	6.7	5.8	19.4	7.7	60.0	6.7	6.0	19.6	7.8	
PbB(Cl)NMePr ⁴	90/0-2	1.5193	62.0	7.6	5.4	18.1	7.2	61.5	7.7	5.5	18.2	$7 \cdot 2$	
PhB(Br)NMe	63/0-8	1.5554	45.4	$5 \cdot 1$	5.0	37.8	6.5	45.3	$5 \cdot 2$	5.1	37.8	6.6	
PhB(Br)NMePh	123/0.3 •	1.5990	59.7	4 ∙5	3.9	29.2	$5 \cdot 1$	60.0	4 ∙8	4 ∙0	$29 \cdot 2$	$5 \cdot 1$	
p-MeOC, H, B(Cl)NMe,	95/0-4	1.5438	54·1	6·4	5·4	17.9	$7 \cdot 1$	54.7	6.6	5.5	18.0	7.1	
p-MeOC H B(NMe)	82/0.3	1.5256	63 ·8	8.9	$5 \cdot 2$		13.4	64.1	9.2	5.3		13.6	
PhB(OMe)NMe	70/4.5	1.4966	66.5	8.7	6.2		8.5	66.3	8 ∙6	6.7		8.6	
PhB(NMePh)	155/0.05	Ь	79 ·7	6.9	3.5		9 ·2	80 ∙0	7 ·0	3.7		9.3	

^a Molecular weight by mass spectrometry and by cryoscopy in benzene = 151; cf. calculated value of 150.9. ^b Not determined. • Supercools, m. p. ca. 88°.

PhB(Me)NMe₂, was prepared by reaction of a benzene solution of chloro(dimethylamino)phenylborane with an ethereal solution of methylmagnesium iodide.¹⁵ 1,2-Bis(dimethylamino)-1,2-diphenyldiboron 17,18 was prepared by treatment of chloro(dimethylamino)phenylborane in dry xylene with sodium.

Pseudohalogenoboranes.--Samples of two pseudohalogenoboranes $PhB(X)NMe_{e}$ with X = NCS or NCO were provided by Dr. H. Pyszora.19, 20

Aminobromoboranes.—(i) Bromo(dimethylamino)phenylborane, PhB(Br)NMe. Dibromophenylborane (7.5 g., 1 mol.) and bis(dimethylamino)phenylborane (5.3 g., 1 mol.) were mixed together and set aside for $2\frac{1}{2}$ hr. The mixture was then distilled under reduced pressure to give bromo-(dimethylamino)phenylborane (11.2 g., 87%).

(ii) Bromo(methylphenylamino)phenylborane

PhB(Br)N(Me)Ph. The method was entirely analogous to (i), the second reactant being bis(methylphenylamino)phenylborane (9.0 g.).

(Dimethylamino)methoxyphenylborane, PhB(OMe)NMe2.---Bis(dimethylamino)phenylborane (8.2 g., 1 mol.) was cooled Elmer models 21 (sodium chloride and calcium fluoride optics) and 137 (potassium bromide optics) spectrometers. Elemental analyses for compounds not previously documented are compared with calculated values in Table 1, which also presents boiling points and refractive indices (sodium D-line at 20°).

Nuclear Magnetic Resonance Measurements.—¹H n.m.r. spectra were recorded at ambient temperature on the following instruments: a Varian V 4300B (40 MHz) spectrometer belonging to Imperial Chemical Industries, Dyestuffs Division, Blackley; a Varian A 60 (60 MHz) spectrometer in the Faculty of Science of this University, a Varian HR 100 (100 MHz) spectrometer at the University of Salford, and an Associated Electrical Industries R.S.2 (60 MHz) spectrometer in this department. Materials were examined both as neat liquids and in 10% (w/w) solutions in carbon tetrachloride, methylene dichloride, and nitrobenzene. Tetramethylsilane was universally employed as internal standard. Separations from the standard and internal separations were determined by the usual audio side-band method. Chemical shifts are given on the τ scale.

¹⁷ R. J. Brotherton, H. M. Manasevit, and A. L. McCloskey, Inorg. Chem., 1962, 1, 749. ¹⁶ H. Nöth and W. Meister, Chem. Ber., 1961, **94**, 509

- ¹⁹ M. F. Lappert and H. Pyszora, Proc. Chem. Soc., 1960, 350.
- ²⁰ M. F. Lappert and H. Pyszora, J. Chem. Soc., 1963, 1744.

¹⁴ J. Graymore, J. Chem. Soc., 1931, 1490.

¹⁵ K. Niedenzu and J. W. Dawson, J. Amer. Chem. Soc., 1960, 82, 4223.

¹⁰ S. H. Dandegaonker, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 1957, 2872.

RESULTS AND DISCUSSION

Studies have been based upon the two molecular systems, (I) and (II) $[X^1 = F, Cl, Br, OMe, NMe_2, Me,$ NCO, NCS, or $Ph(NMe_2)B$; $X^2 = Cl$, Br, NHMe, N(Me)Ph, or $N(H)Bu^{t}$; $R^{1} = Me$, Et, Pr^{i} , Bu^{t} , or Ph; $R^2 = H \text{ or } Me; Ar = Ph \text{ or } p\text{-MeOC}_6H_4].$



In system (I), two N-methyl groups occupy two chemically distinct but equally abundant electronic environments; transfer of a particular methyl group between environments occurs by rotation through 180° about the BN bond. In system (II), the two rotamers are not, in general, of equal stability and each R^1 (or R^2) group has two environments with correspondingly unequal abundance. Spectral analysis, both at ambient and at other temperatures,⁹ was facilitated by careful choice of nitrogen substituents. By this expedient,



¹H spectrum of chlorodimethylaminophenylborane, FIGURE 1 $PhB(Cl)NMe_2$, at 100 MHz in 10% (w/w) solution of carbon tetrachloride. The sweep rate was increased between the two main absorption regions

unnecessary complication due to spin-spin interaction was minimised. It is assumed that the bonds around boron are planar disposed. If there were considerable delocalisation of the nitrogen lone-pair into the B-N bond, the same could well be true for the bonds about nitrogen. However, if this is not the case, *i.e.*, if the bond disposition is pyramidal, no spectroscopic complication would arise. Nitrogen inversion would merely cause transfer of an alkyl group to an electronically equivalent environment in an enantiomorphic structure. To all intents and purposes, then, we can assume molecular planarity about the B-N bond.

(a) Compounds of Type (I).-Except in cases where the X substituent contains hydrogen atoms and where, therefore, the spectrum will have corresponding additional absorption, spectra are typified by the particular example of chlorodimethylaminophenylborane, PhB(Cl)NMe₂. The 100 MHz spectrum of a 10% (w/w) solution in carbon tetrachloride is presented in Figure 1. The complex low field absorption, centred upon τ 2.67, is assigned to the B-phenyl substituent. The two bands centred upon τ 7.03 were separated by 15.0 Hz, but this decreased to 9.0 Hz at a radiofrequency of 60 MHz, an

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observation typical of the existence of an internal chemical shift. The bands were assigned to the Nmethyl groups, significant differential shielding probably arising from the large diamagnetic anisotropy of the vicinal phenyl substituent,4,5 although a non-equivalence has recently been observed ²¹ in the absence of this group. The observation of differential shielding in chlorodimethylaminophenylborane is indicative of restricted internal rotation about the B-N bond. On the basis of the general theory for the collapse of an internal chemical shift due to exchange between two equally abundant chemical sites,9,22 the rate of exchange of methyl groups between the two minimum energy positions is less than 30 sec.⁻¹; excess of this rate would produce a single maximum in the absorption system, *i.e.*, coalescence. Detailed consideration of the rotational kinetics will be described in a subsequent paper.⁹

The essential features which characterise the spectrum of chlorodimethylaminophenylborane are also exhibited by several other compounds of type (I). Table 2 summarises the results of 60 MHz measurements, both for neat liquids (where these exist at ambient temperatures) and for solutions in carbon tetrachloride, methylene dichloride, and nitrobenzene. Noteworthy exceptions to the pattern described above are when X = NCS(CCl₄ solution), F, and NMe₂; in these cases, the methyl absorption is represented by a single band, due apparently to a large rate of rotamer interconversion. In fact, this structure persists even at temperatures as low as 223°K.

(b) Compounds of Type (II).-60 MHz Spectral results are summarised in Table 3. As in the case of compounds of type (I), data for any ¹H absorption due to the substituent X² is not tabulated. Chemical shifts for N-methyl groups are, in general, similar to those found in type (I) molecules. A significant difference occurs for molecules with a N-phenyl substituent. A low-field shift in these cases is presumably associated with the participation of nitrogen lone-pair electrons in the aromatic π structure, *i.e.*, a negative mesomeric effect from the phenyl group. As with type (I) compounds, no spinspin splitting was ever observed for the N-methyl absorption (excluding ¹³C satellite formation); this is compatible with the zero moment of ¹²C and rapid quadrupolar relaxation of ¹⁴N, ¹⁰B, and ¹¹B nuclei.

For the neat liquid chloro(ethylmethylamino)phenylborane, PhB(Cl)N(Me)Et, at 60 MHz and ambient temperature, the methyl absorption comprises two bands with a mean τ 7.24 and of approximately equal integrated intensity (and width), thus implying near equality in the populations of the two methyl environments. This approximation has been accepted in the analysis of variable temperature results.⁷ Absorptions from the ethyl group occurred at mean τ values of 6.90 for methylene and 9.02 for methyl, and both consisted of overlapping systems. In the former case, two overlapping 1:3:3:1 quartets gave an observed

H. Nöth, personal communication.
H. M. McConnell, J. Chem. Phys., 1958, 28, 430.

1:3:4:4:3:1 sextet, whilst in the latter, overlap of 1:2:1 triplets yielded an observed 1:3:3:1 quartet. In dilute carbon tetrachloride solution, not only were there shifts in the absorption centroids but there were differences in the splitting patterns (Figure 2). The methylene absorption became a 1:3:3:2:3:3:1 septet and the triplets from the two methyl environments were distinctly separated (there was also a slight change in the ratio of integrated intensities of the N-Me bands).

to restricted rotation about the B-N bond and the consequent isomerism. Contributions were proposed from structures (III) and (IV), it being assumed that the structure with spatially proximate alkyl groups could be eliminated on steric grounds. The ¹H magnetic resonance spectrum of bis(methylamino)phenylborane at ambient temperature comprised two main regions of absorption, one associated with phenyl at $\tau 2.66$ and the other with the remaining hydrogens at τ 7.42. These

TABLE 2	
Chemical shifts (on the τ -scale) of compounds of type (I), ArB(X ¹)NI	$4e_2$

				-	_					
		Pure liq	uid	10% (w	/w) solution	in CCl4	10% solu CH ₂	ution in Cl ₂	10% solu PhN	ition in 10 ₂
X1	Ar	$\tau (\text{NMe}_2)$	$\Delta \tau^{a}$	-; (Ar) i	τ (NH)	$\Delta \tau^{a}$	$\tau (\text{NMe}_2)$	$\Delta \tau^{a}$	$\tau (\mathrm{NMe}_2)$	$\Delta \tau^{a}$
Br	Ph	7.18	0.298	2.67	7.03	0.233	7.04	0.233	7.05	0.225
CI	\mathbf{Ph}	7.26	0.214	2.67	7.03	0.120	7.04	0.142	7.09	0.120
NCS	Ph	Soli	d	2.65	7.07	f	*	*	*	*
NCO	\mathbf{Ph}	Soli	d	2.65	7.15	0.092	*	*	*	*
Me *	Ph	7.32	0.070	2.60	7.18	0.125	7.18	0.134	7.24	0.075
F	\mathbf{Ph}	7.35	f		Insoluble		7.20	f	$7 \cdot 25$	f
OMe ^j	Ph	7·47 {	0·026 ^b 0·290 c	2.73	7.35	g	7.35	d	7.36	d
NMe.	Ph	7.49	f	2.73	7.35	f	7.36	f	7.36	f
Cl	p-MeOC _e H	7.24	0.149	2·86 *	7.06	0.105	*	*	*	*
NMe.	p-MeOC H	7.51	f	3.00 y	7.40	f	*	*	*	*
$Ph(\tilde{NMe}_2)B$	Ph **	Soli	d	2.85	7.11	f	*	*	*	*
				* No	ot studied.					

^a Modulus of internal chemical shift (p.p.m.) for two Me environments (± 0.004 p.p.m. except where otherwise stated). ^b ± 0.01 p.p.m. ^c At 253°x. ^d Single band, several Hz wide. ^e Mean value. ^f Single band; width at half-height <1.0 Hz. ^e Single band; width at half-height = 13.0 ± 0.5 Hz. ^b τ (OMe) = 6.26 in both cases. ^f Centroid of complex absorption. ^f τ (OMe) in CCl₄ = 6.62. $k \tau$ (Me) in CCl₄ = 9.48.

TABLE 3

Chemical shifts (on the τ -scale) of compounds of type (11) PhB(A)	$^{2})N(R^{1})R^{2}$	
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				Pure liquid	1		10% (w/w)solution in CCl ₄					
\mathbf{X}^{2}	R1	R²	T NR ²	Δτ α		T NR1 b	$\overline{\tau \text{ (BPh) }^{d}}$	τ (NR ¹) b	Δτ *		τ (NR) »	
Cl	Et	Ме	7.24	0.189	{	CH ₂ 6·90 CH ₃ 9·02	2.70	7.05	0.117	{	CH ₂ 6·83 CH ₃ 8·80	
Cl	Pr^i	Me	7.27	0.193		CH ₃ 9.01	2.70	7.19	0.142		CH ₃ 8.80 °	
Cl	\mathbf{Ph}	Me		Solid		0	2.85	6.58	е		° f	
Br	\mathbf{Ph}	Me		Soliđ			2.70	6.50	е		f	
N(Me)Ph	\mathbf{Ph}	Me		Solid			3.00	7.05	e		f	
N(H)Me	н	Me	*			*	2.66	7.42	е		7.4 h, i	
CI	н	But	*	r		*	2.50	8.57	е		g	
$N(H)Bu^t$	Н	$\mathbf{Bu^t}$	*	:		*	2.80	8.84	е		7.3×	

* Not studied.

The spectrum of chloro(methylisopropylamino)phenylborane, PhB(Cl)N(Me)Prⁱ, follows the general pattern outlined above. The NMe absorption consisted of two bands, with relative intensities 1.00:1.33 at ambient temperatures both in the pure liquid and in carbon tetrachloride solutions. As in the previous case, solution in carbon tetrachloride assisted resolution of the bands associated with the larger alkyl group.

The bis(alkylamino)phenylboranes, PhB(NHR)2, have interesting spectral features. With one exception, the infrared spectra 12 show two NH stretching bands, separated by about 23 cm^{-1} ; the exception is the tertiary butyl compound $(R = Bu^t)$ where only a single band at 3428 cm.⁻¹, is observed. These results were attributed

^a Modulus of internal chemical shift (p.p.m.) for two NMe or NBu^t environments (±0.004 p.p.m.). ^b Mean values. ^c CH absorption barely distinguishable above noise level; $\tau 5.5$. ⁴ Centroid of complex absorption. ⁴ Single band. ⁴ Not distinguished from BPh. ⁹ Not observed, probably very broad. ⁴ Very broad. ⁴ Overlaps partially with NMe absorption.

> figures were derived from the spectrum of a 10% solution of the material in carbon tetrachloride at 60 MHz; the observed spectrum was substantially the same as an



early 40 MHz recording. In these spectra, only a single band for the non-phenyl hydrogens was clearly observed. The relative areas of the two regions were 1.0: 1.5 (low field : high field); this may be compared with expectations of 1.0: 1.6 for overlapping NH and NMe, and 1.0:1.2 if the absorption at τ 7.42 is entirely due to NMe. At 100 MHz, however, the high-field system separated clearly into two components of relative intensities 1.0 and 1.5 and separated by 0.53 ± 0.05 Hz (Figure 3). In addition, a very broad absorption



FIGURE 2 ¹H-alkyl spectrum of chloro(ethylmethylamino)phenylborane, PhB(Cl)NMeEt, at 60 MHz in 10% (w/w) solution of carbon tetrachloride



FIGURE 3 ¹H NHMe spectrum of bis(methylamino)phenylborane, PhBN(NHMe)₂, at 100 MHz in 10% (w/w) solution of carbon tetrachloride. The bands marked with asterisks are markers with 20.00 Hz spacing

occurred on the high-field side of the two bands. This is associated with NH, the broadening being distinctive and probably of quadrupolar origin. Integration of the parts of the high-field system supported the latter assignment. The interpretation of the two sharper bands in terms of isomer abundance is, unfortunately, not unambiguous. If the two methyl environments in (III) are similar to one another but distinct from the single environment in (IV), an isomer abundance ratio [(III) : (IV) or its inverse] of *ca.* 1.5 is indicated. If, on

²³ K. Nakanishi, 'Infrared Absorption Spectroscopy,' Holden-Day, San Francisco, 1962, Appendix 1/NMR, p. 223.

the other hand, one of the environments in (III) is similar to that in (IV) and these are distinct from the remaining environment in (III), an abundance ratio of ca. 4.0 is indicated. The latter situation seems the more likely, but in either case, (IV) is probably the more abundant species on steric grounds. No doubling of bands was observed for the corresponding t-butylamino-derivative; this may be due to (i) a lower barrier to rotation, implying the unimportance of a steric factor, or (ii) the stabilisation of a single isomer, *e.g.*, (IV), or (iii) a small internal chemical shift for different rotameric forms.

Both in the neat liquids and in the various solutions, chemical shifts for N-methyl in the compounds of type (I) studied here are intermediate between values ²³ for

MeN= ($\tau \simeq 7.7$) and MeN= ($\tau \simeq 6.7$). The shifts reported in the present work are in harmony with other published data.⁴⁻⁸

For a common, inert medium—as we might expect to be the case for dilute solutions in carbon tetrachloridethe NMe₂ chemical shift may be expected to reflect the extent of participation of the nitrogen lone-pair in B-N π -bonding. Increased positive charge on the nitrogen, occasioned by such an effect, would presumably diminish the electronic shielding of the methyl hydrogen nuclei and thereby decrease the τ value. If donation of π or lone-pair electrons could arise also from the non-aminoboron substituents, this would diminish the necessity of nitrogen lone-pair donation for satisfaction of the boron deficiency.' For all except two of the compounds of type (I) two of the boron substituents remain invariant as phenyl and dimethylamino, only the third being varied. For such cases, one might expect τ (NMe₂) to increase as the mesomeric effect (+M) of the variable substituent increased. On this basis, Table 2 indicates an order of +M as follows: Br < Cl < NCS < NCO <Me < F < OMe, NMe_2 ; $Ph(NMe_2)B$ is not included in the list. Although spectral studies both in other solvents and for neat liquids have been less extensive, the order seems to be preserved in these cases. The two pmethoxyphenyl compounds also conform to expectation on the basis of the above order of mesomeric effect. With the possible exception of Me, the substituent order seems to be in accord with traditional arguments based upon the reactivity of organic molecules and also with the Lewis acid behaviour of three-co-ordinate boron compounds.

Two significant effects were observed (see Tables 2 and 3) in the ¹H absorption of compounds having an Nmethyl group, when these were dissolved in *any* of the three solvents used in this investigation. (a) The separation of the rotameric doublet, $\Delta \tau$, where this was observed, decreased; the only exception was (dimethylamino)methylphenylborane. A similar observation ^{24,25} has been reported for amides. (b) τ (NMe) Is significantly decreased. With the possible exception of

²⁴ J. C. Woodbrey and M. T. Rogers, *J. Amer. Chem. Soc.*, 1962, 84, 13.

²⁵ J. V. Hatton and R. E. Richards, Mol. Phys., 1960, 3, 253.

(dimethylamino)methylphenylborane, the three solvents have essentially the same effect on compounds of type (I). The choice of solvents was based upon the following. (a) They offer a range of dielectric constants; the values are: 26 CCl₄ 2.238/20°, CH₂Cl₂ 9.08/20°, and PhNO₂ $34 \cdot 8/25^{\circ}$. (b) Neither hydrogen-containing solvent absorbs between τ 6.5 and τ 8.0, the absorption region for N-methyl. (c) They were all apparently inert towards the solutes, despite the fact that nitrobenzene behaves as a Lewis base towards haloboranes.²⁷ Had this been the case in the present study, a significant shift of the N-methyl resonance to high field would have been expected for the nitrobenzene solutions in comparison with corresponding solutions in carbon tetrachloride. Reference to Table 2 shows that this is not the case.

The difference in behaviour between pure liquids and solutions is probably due to significant interaction between molecules in the former case. The various effects of the medium upon shielding coefficients have been presented previously.28 Here, increased shielding of N-methyl on increasing the proximity of identical molecules would occur if the negatively charged boron caused repulsion of electronic charge along the nitrogencarbon bond (as it would do if the atom were very close to the positively charged nitrogen). The electrostatic field (E) of the neighbouring molecule would not have to be too large, otherwise an opposing deshielding effect ²⁸

26 'Table of Dielectric Constants of Pure Liquids, Circular 514,' National Bureau of Standards, Washington, 1951, pp. 5, 18.

 (∞E^2) would predominate. (Two other effects which would probably deshield the hydrogen nuclei are, (a) intermolecular co-ordination of nitrogen lone-pair electrons into a B-N 'bond,' and (b) increased intramolecular co-ordination by the electrostatic field of an adjacent dipolar molecule.) Molecular attraction might also lead to an increase in shielding from the diamagnetic anisotropy in a phenyl group of an adjacent molecule.28 This could also be responsible for the effect upon $\Delta \tau$ if the methyl groups are, on the average, differently spaced and differently orientated to the phenyl plane. The absence of such effects in the nitrobenzene solvent is then perhaps anomalous, but may possibly be rationalised in terms of a different solute-solvent intermolecular attraction.

The authors thank Dr. J. K. Becconsall (Imperial Chemical Industries Ltd.) for early spectrograms, Mr. R. F. Warren (Faculty of Science in this University) for spectra recorded on the A60 Spectrometer, Dr. H. Pyszora for the provision of two of the compounds studied, Mr. V. Manohin and Mr. P. Woodbridge for performance of microanalyses. Gifts of tetraphenyltin from Pure Chemicals Ltd., and financial support from the Air Research and Development Command of the U.S. Air Force (European Office) are also gratefully acknowledged.

[7/1063 Received, August 14th, 1967]

27 H. C. Brown and R. R. Holmes, J. Amer. Chem. Soc., 1956,

78, 2173.
²⁸ A. D. Buckingham, T. Schaefer, and W. G. Schneider, J.
²⁹ A. D. Buckingham, T. Schaefer, and W. G. Schneider, J.