862. *Nuclear Magnetic Resonance of Borazole Compounds.*

(Mrs.) I. M. Butcher, W. Gerrard, J. B. Leane, and E. F. Mooney.

The proton magnetic resonance spectra of a series of *B*-trimethylborazoles [$(MeBNR)_3$; R = Me, Et, Ph, and *o*-, *m*-, and *p*-tolyl] and *N*-trimethylborazoles [$(MeNBX)_3$; X = Me, Et, Cl, Br, Ph, and *o*-, *m*-, and *p*-tolyl] have been recorded at 40 Mc./sec. The screening of the *B*- and *N*-methyl groups by the induced magnetic moment of the phenyl rings has been calculated. and, from the agreement between the experimental and calculated screening, it is shown that the planes of the phenyl groups are perpendicular to the plane of the borazole nucleus.

Preliminary studies [1] have shown that the *B*-methyl resonance of *N*-triaryl-*B*-trimethylborazoles, $(MeBNAr)_3$, occurs to high field of tetramethylsilane, and this has been ascribed to the shielding from the *N*-aryl nucleus. This shielding suggests that the methyl groups are situated above the plane of the aromatic rings (analogous to the shielding found for the methylene groups of 1,4-polymethylenebenzenes [2]), which implies that the plane of each of the three aryl groups must be essentially perpendicular to the plane of the borazole ring.

The screening which would result from the perpendicular *B*- and *N*-aryl groups on the *N*- and *B*-methyl groups, respectively, has been calculated, and, although a number of

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[1] Mooney, *Spectrochim. Acta*, 1962, **18**, 1355.

[2] Waugh and Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846.

assumptions have been made, there is fairly good agreement between the calculated and observed values.

Calculation of Shielding in B-*Trimethyl*-N-*triphenylborazole*.—The following assumptions have been made. (i) That there are three orientations of the borazole molecule in the magnetic field to be considered, namely, where H_0 (the applied field) is perpendicular to the plane of one aryl ring, where H_0 is in the plane of one aryl ring, and, lastly, where H_0 is perpendicular to the borazole ring. (ii) That the times the molecule spends in each of the three orientations are equal. (iii) That the aryl rings are rigid and remain fixed perpendicular to the borazole ring. In practice this is not the case and the aryl nucleus will oscillate about the N–C_1–C_4 axis. However, it is significant that in the *B*-trimethyl-*N*-tri-*o*-tolylborazole, where the *o*-methyl group would sterically restrict the oscillation, the shielding observed is closer to the calculated value. (iv) That the three hydrogen atoms of the methyl group are equivalent and that the centre of the arc of rotation of the H_3 group is taken as the average position of the three protons for the purposes of calculating the distance of these protons from the centre of the aromatic nuclei. (v) That the ring current in the borazole nucleus is constant and is small compared to that of the aromatic ring. (vi) For calculating the geometry of the molecules bond lengths given in Tables [3] have been used.

In calculating the shielding, each of the three orientations has been considered in turn, and the magnetic field experienced at the methyl protons, as a result of the ring current, has been calculated following a procedure similar to that of Pople, Schneider, and Bernstein.[4] Thus, the field experienced at the *B*-methyl protons is: with H_0 perpendicular to the plane of one aromatic nucleus, $2{\cdot}18M \times 10^{22}$; with H_0 in the plane of one aromatic nucleus, $0{\cdot}77M \times 10^{22}$; with H_0 perpendicular to the borazole ring, 0; *i.e.*, the total field arising from ring current $= \frac{1}{3} \times 2{\cdot}95M \times 10^{22}$, where M is the induced magnetic dipole at the centre of the aromatic nucleus and is equal to $3a^2e^2H_0/2mc^2$. Thus, the shielding experienced by the methyl protons is given by $\Delta\sigma = \dfrac{\Delta H}{H_0} = \dfrac{2{\cdot}95}{3H_0} \cdot \dfrac{3a^2e^2H_0}{2mc^2} \times 10^{22}$. The value of $e^2a^2/2mc^2$ was calculated from the shielding value for benzene,[4] and by substitution in the above equation it was shown that $\Delta\sigma = 1{\cdot}11 \times 10^{-6}$, *i.e.*, the *B*-methyl protons are shielded (*i.e.*, moved to high field) by 1·1 p.p.m.

For the isomeric *B*-triaryl-*N*-trimethylborazoles, similar calculations have been made, and the field experienced by the *N*-methyl protons, due to the induced magnetic dipole of the aryl rings, is: with H_0 perpendicular to the plane of one aromatic nucleus, $2{\cdot}21M \times 10^{22}$; with H_0 in the plane of one aromatic nucleus, $0{\cdot}50M \times 10^{22}$; with H_0 perpendicular to the borazole ring, 0; *i.e.*, the total field arising from ring current $= \frac{1}{3} \times 2{\cdot}71M \times 10^{22}$. Consequently, a value for the shielding of the *N*-methyl group is found as above, and $\Delta\sigma = 0{\cdot}93 \times 10^{-6}$, *i.e.*, the *N*-methyl protons are shielded by 0·93 p.p.m.

DISCUSSION

The chemical shifts of a series of *B*-methyl- and *N*-methylborazoles are shown in Tables 1 and 2. Table 1 demonstrates that when an *N*-aryl group is present the *B*-methyl resonance occurs to high field of tetramethylsilane. If the average value (9·54 τ) of the *B*-methyl resonance of the *N*-methyl- and *N*-ethyl-borazoles is taken as being characteristic of this resonance in the absence of shielding, then it is seen that the shielding is 0·69 ± 0·01 p.p.m. when phenyl or *p*- or *m*-tolyl groups are present, and 0·80 p.p.m. when *o*-tolyl groups are present. Considering the assumptions made, this latter value is in favourable agreement with the calculated shielding of 1·1 p.p.m., especially as it would be expected that even in the *N*-*o*-tolyl compounds there would still be some rocking of the aryl groups.

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[3] "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

[4] Pople, Schneider, and Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, London, 1959, p. 182.

The value to be taken as characteristic of the *N*-methyl groups in the absence of shielding is a little more difficult, as is shown in Table 2, where, for four borazoles with non-aromatic *B*-substituents, the value for the *N*-methyl resonance varies from 6·73 to 7·13 τ. If, however, the average value of 6·9 τ is taken (the *N*-methyl resonance of *N*-trimethylborazole has been reported at 6·90 τ [5]) then the shielding for *B*-phenyl and *B*-*m*- and *B*-*p*-tolyl derivatives is about 0·63 p.p.m. and increases to 0·67 p.p.m. in the *B*-*o*-tolyl compound; these values are in reasonable agreement with the calculated value of 0·93 p.p.m.

TABLE 1.

Proton chemical shifts of *B*-trimethylborazoles, $(MeBNR)_3$.

R	Solvent	τ(*B*-CH_3)	τ(Aryl)	τ(*Ar*-CH_3)
Me	$CDCl_3$	9·53	—	—
Et	CCl_4	9·55	—	—
Ph	CS_2	10·22	2·5—3·4	—
p-Me·C_6H_4	CS_2	10·24	2·8—3·5 *	7·70
m-Me·C_6H_4	CS_2	10·23	2·8—3·5	7·69
o-Me·C_6H_4	CS_2	10·34	2·7—3·3	7·91

* Gives an A_2B_2 spectrum.

TABLE 2.

Proton chemical shifts of *N*-trimethylborazoles, $(RBNMe)_3$.

R	Solvent	τ(*N*-CH_3)	τ(Aryl)	τ(*Ar*-CH·)
Cl	CS_2	6·89	—	—
Br	CS_2	6·73	—	—
Me	$CDCl_3$	7·13 *	—	—
Et	CCl_4	7·06 †	—	—
Ph	CS_2	7·51	2·87	—
p-Me·C_6H_4	CS_2	7·54	3·01	7·70
m-Me·C_6H_4	CS_2	7·52	3·02	7·68
o-Me·C_6H_4	CS_2	7·57	2·89	7·77

* *B*-CH_3 resonance at 9·53. † *B*-C_2H_5 resonance at 9·01; the CH_2 and CH_3 resonances are coincident.

It is significant that the measured shielding is greater in the *o*-substituted phenylborazoles, which clearly indicates that oscillation is occurring about the N–C_1–C_4 axis and that with *o*-substituents this rotation is becoming restricted.

It is thus now apparent that the plane of each aromatic group is perpendicular to the plane of the borazole nucleus, and aryl-substituted borazoles could be referred to as " paddle-wheel " molecules.

EXPERIMENTAL

The proton resonance spectra were recorded on a Perkin-Elmer n.m.r. spectrometer operating at 40 Mc./sec., using tetramethylsilane as an internal standard.

TABLE 3.

Hexa-alkylborazoles, $(RBNR')_3$.

			Found					Required				
R	R′	B. p. (m. p.)	C (%)	H (%)	B (%)	N (%)	*M*	C (%)	H (%)	B (%)	N (%)	*M*
Me	Me	(97°)	43·6	11·2	19·6	25·4	175	43·7	11·0	19·7	25·5	165
Me	Et	63°/0·1 mm.	52·2	11·6	15·4	20·2	215	52·3	11·7	15·7	20·3	207
Et	Me	73°/0·05 mm.	52·1	11·6	15·6	20·1	215	,,	,,	,,	,,	,,
Et	Et	98°/0·2 mm. (88°)	57·9	12·3	12·7	16·7	250	57·9	12·2	13·0	16·9	248

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[5] Phillips, Powell, and Semlyen, *J.*, 1963, 1202.

The borazoles $(MeNBCl)_3$ and $(MeNBBr)_3$,[6] $(PhBNMe)_3$,[7] $(MeBNPh)_3$,[8] $(MeBNTol)_3$, and $(TolBNMe)_3$,[9] were prepared as previously described. The ***hexa-alkylborazoles*** (Table **3**) were prepared by a modification of a procedure used for the preparation of $(EtBNMe)_3$.[10]

We gratefully acknowledge a grant from the D.S.I.R. to purchase the n.m.r. spectrometer.

NORTHERN POLYTECHNIC, HOLLOWAY, LONDON N.7. [*Received, January 8th*, 1964.]

[6] Butcher, Gerrard, Mooney, Rothenbury, and Willis, *Spectrochim. Acta*, 1962, **18**, 1487.
[7] Burch, Gerrard, and Mooney, *J.*, 1962, 2200.
[8] Groszos and Stafiej, *J. Amer. Chem. Soc.*, 1958, **80**, 1357.
[9] Gerrard, Mooney, and Pratt, *J. Appl. Chem.*, 1963, **13**, 127; Gerrard, Howarth, Mooney, and Pratt, *J.*, 1963, 1582.
[10] Ryschkeiwitsch, Harris, and Sisler, *J. Amer. Chem. Soc.*, 1958, **80**, 4515.