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THE FAR-INFRARED SPECTRA OF *B*-TRIHALOBORAZINES

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INTRODUCTION

Despite the extensive studies on the vibrational spectra of borazine derivatives (see *e.g.* ref. 1), there appear to have been no detailed investigations in the low frequency region. Following a preliminary report concerning some cyclic boron-nitrogen compounds[2], we have studied the far-infrared spectra of a series of borazines $(XBNR)_3$ [X = Cl, Br; R = H, Me, Et, n-Pr, n-Bu) in solution in cyclohexane and/or benzene, as part of a programme on the spectroscopy of organoboron compounds.

RESULTS AND DISCUSSION

Watanabe, Narisada, Nakagawa, and Kubo[3] have carried out an S.V.F.F. analysis of *B*-trichloroborazine. They calculated that only three fundamentals should appear in the infrared region below 500 cm^{-1}, namely at 368 cm^{-1} [ν_{16} (E'); 24.2 % B–Cl stretching, 67.4 % ring distortion], 118 cm^{-1} [ν_{10} (A_2''); 28.1 % B–Cl out-of-plane bending, 71.7 % ring torsion], and 106 cm^{-1} [ν_{17} (E'); 94.3 % B–Cl in-plane bending]. Although instrumental limitations did not permit direct observation, it was suggested that the frequency corresponding to ν_{16} was 326 cm^{-1}, on the basis of assignment of a postulated overtone and combination of this mode. In the present work (Fig. 1) we have observed a prominent band in the spectrum of *B*-trichloroborazine at 373 cm^{-1}, which is clearly assignable to ν_{16} on account of its close agreement with the estimated value of 368 cm^{-1}. The calculated[3] potential energy distribution of the planar fundamental ν_{16} suggests a vibration of the type shown in Fig. 2. If the form of this vibration is maintained on symmetrical substitution of other groups about the borazine ring, the frequency might be expected to decrease in a regular manner both on substituting bromine instead of chlorine, and by increasing the mass of the groups on nitrogen. These effects are clearly demonstrated in Figs. 3 and 4, which add further support to the band assignments.

The splitting of ν_{16} into a doublet in each of the *N*-triethylborazines is interesting. That this is an intramolecular effect is evident from the invariance in frequencies and relative intensities on dilution in both cyclohexane and benzene solutions. A possible explanation is that ν_4 (A'), a Raman-active fundamental of similar vibrational nature to ν_{16} (calculated to occur at 347 cm^{-1} in *B*-trichloroborazine[3]), is activated in the infrared even in solution by non-planarity of the *B*-substituents and borazine ring. A similar situation is believed to occur in *N*- in contrast to *B*-triarylborazines, a splitting of ν(B–H) but not of ν(N–H) being observed[4]. However, in the compounds

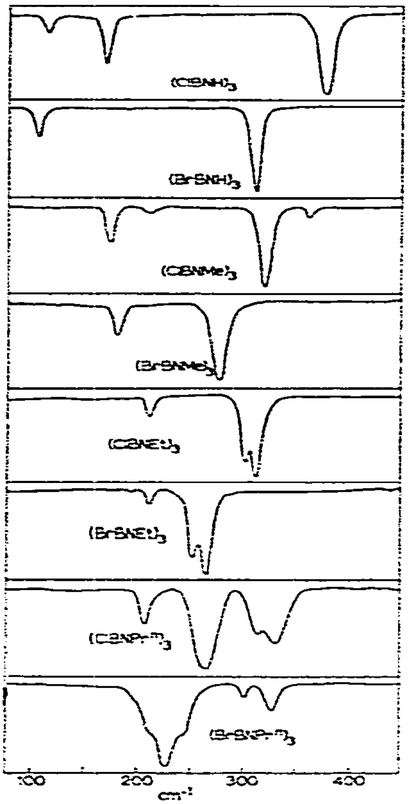

Fig. 1

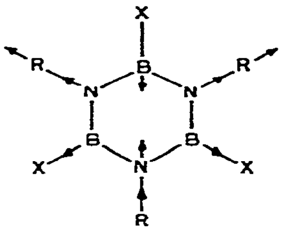

Fig. 2

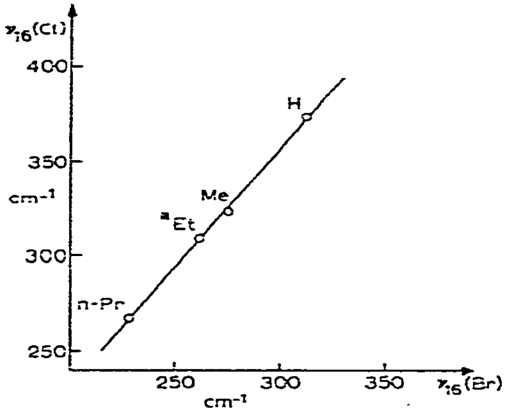

Fig. 3

Fig. 1. Far infrared spectra (450–80 cm^{-1}) of *B*-trihaloborazines.

Fig. 2. Suggested form of ν_{16} in *B*-trihaloborazines.

Fig. 3. Variation of ν_{16} in $(XBNR)_3$ with X. (*Mean values – see text.)

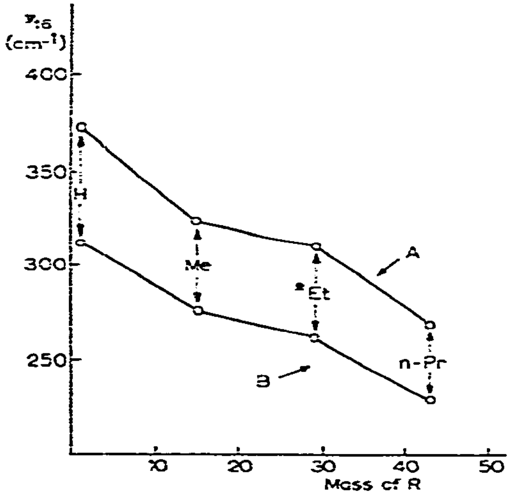

Fig. 4. Variation of ν_{16} in $(XBNR)_3$ with R; A: X = Cl, B: X = Br. (*Mean values – see text.)

at present studied there appears to be no reason why such non-planarity should occur only in the *N*-triethylborazines. A more likely explanation is that there is steric hindrance to rotation about the N–C bonds, giving rise to two conformers and hence splitting of ν_{16} (Fig. 5). The presence of restriction in rotation of the *N*-ethyl groups is readily demonstrated by molecular models. In agreement with this, we find that the spectra of the *N*-tri-n-propyl and *N*-tri-n-butylborazines are considerably more complex and the bands are generally broader; indeed in the *N*-tri-n-butylborazines the complexity of absorption prevents unambiguous assignments, so that details of these spectra are not reported herein.

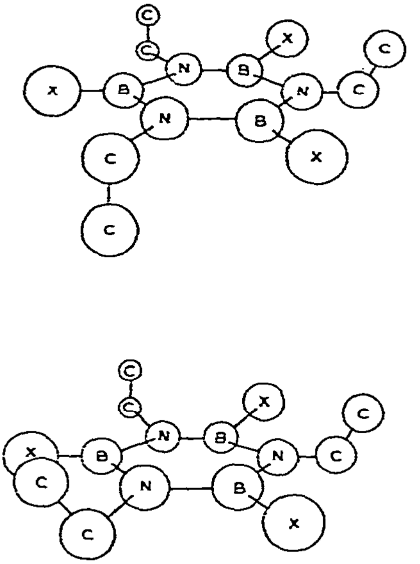

Fig. 5. Conformers of *B*-trihalo-*N*-triethylborazines.

The two other bands predicted[3] in this spectral region for *B*-trichloroborazine have now been found at 170 cm^{-1} and 117 cm^{-1} (Fig. 1), but present evidence does not permit unequivocal identification of each observed absorption with the corresponding fundamental. Both these bands either shift out of the accessible region or are of considerably reduced intensity in the spectra of the other compounds.

The other bands observed in the spectra of the *N*-trialkylborazines are probably associated with methyl torsional or alkyl skeletal vibrations (Table 1).

EXPERIMENTAL

The preparation of the borazines has been described[5]. The spectra were obtained on a Research and Industrial Instruments Company FS-520 interferometer, the calculations being carried out on the University of London ATLAS computer over the frequency range 450–80 cm^{-1}. The final computer output consists of a graphical plot of the ratio of the spectral intensity of sample to that of the background at each frequency output, on a linear percentage transmission/linear frequency scale. The resolution was 5 cm^{-1} and the frequencies are considered accurate to better than $\pm$ 2 cm^{-1} for sharp absorptions. Splitting arising from ^{10}B and ^{11}B isotopes (*c.* 1:4

TABLE 1

FAR-INFRARED (450–80 cm^{-1}) ABSORPTION BANDS OF THE BORAZINES $(XBNR)_3$

R =	*H*		*Me*		*Et*		*n-Pr*		*Assignment*
X =	*Cl*	*Br*	*Cl*	*Br*	*Cl*	*Br*	*Cl*	*Br*	
			365 w						
							336 m	328 m	R skeletal
							317 w	303 w	
								245 sh	
					314 vs	267 vs			ν_{16} (*E'*)
	373 vs	312 vs	323 vs	275 vs			268 vs	228 s	
					304 s	254 s			
			212 vw						
					216 m–w	215 w	210 m	212 sh	R skeletal
			178 m	180 m					Me torsion
	170 s	108 m							ν_{17} (*E'*) and ν_{20} (A_2'')
	117 w								

natural abundance) was in no case observed, since the four possible ways in which the different isotopes of boron can be combined in a given borazine ring, together with the presence of ^{35}Cl and ^{37}Cl isotopes, simply results in band broadening. Bands of less than 5 % absorption under the experimental conditions are often irreproducible and are therefore not reported. The samples were studied in solution (1–10 % w/v) in dry cyclohexane and/or benzene at path-lengths 1–4 mm using Rigidex windows. All operations were carried out under anhydrous conditions.

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SUMMARY

The infrared spectra of a series of *B*-trihaloborazines $(XBNR)_3$ [X = Cl, Br; R = H, Me, Et, n-Pr, n-Bu] in cyclohexane and/or benzene solution have been recorded over the frequency range 450–80 cm^{-1}, and assignments made for all but the n-butyl compounds. The nature of the vibrations has been deduced by comparing the spectra of borazines having the same *B*- but different *N*-substituent groups, and *vice versa*; sensitivity to both groups is observed. The presence of restricted rotation about the N–C bonds in the *B*-trihalo-*N*-triethylborazines and higher homologues is suggested on the basis of band splitting.

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