Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

DERIVATIVES OF TETRAZABOROL-2-INE (CYCLOTETRAZENOBORANE) V*. PREPARATION AND PROPERTIES OF *B*-ALKYL, *B*-ARYL AND *B*-VINYL DERIVATIVES

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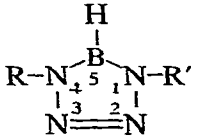
(Received February 12th, 1968)

SUMMARY

Two routes for the preparation of *B*-substituted tetrazaborol-2-ines have been developed. The action of Grignard reagents on derivatives of the type R_2N_4BH produces compounds R_2N_4BR'' in high yield, through the intermediate formation of magnesium-containing complexes. Thermal degradation of a diorganoboron azide in the presence of an organic azide also produces boron-substituted tetrazaborol-2-ines. The UV, IR and NMR spectra of the compounds have been studied.

INTRODUCTION

It is only recently that the novel heterocyclic system tetrazaborol-2-ine (I) has been described[2,3], and little of its chemistry is known. Some doubt has existed on the nature and polarity of the B–H bond, since the B–H stretching frequency in these compounds occurs at very high wavenumbers[2,3,4], and a study of the effect of solvent on the B–H stretching frequency[5] failed to resolve the problem. Furthermore, attempts to hydroborate ethylene and 1-butene failed.



(I)

RESULTS AND DISCUSSION

We have found that in common with borazines[6], the hydrogen attached to boron can be replaced by organic groups by means of Grignard reagents, and the reaction proceeds through the formation of a magnesium-containing intermediate.

$$R_2N_4BH + R''MgX \xrightarrow[\text{or THF}]{Et_2O} R_2N_4BH\cdot R''MgX \ ?$$

$$R_2N_4BH\cdot R''MgX \ ? \xrightarrow[NH_4Cl]{\text{Sat. aq.}} R_2N_4BR''$$

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* For Part IV see ref. 1.

By this method, the compounds Ph_2N_4BPh, Ph_2N_4BMe, Et_2N_4BEt, Me_2N_4BMe were prepared. The compound Me_2N_4BVi was also prepared by this route, although some reduction of the vinyl group took place to give a product contaminated with Me_2N_4BEt, and the latter compound was obtained by catalytic hydrogenation of the vinyl-substituted compound. During the preparations, the magnesium-containing intermediates separated as yellow crystalline solids from fluorescent solutions in the phenyl-substituted compounds, or as colourless oily liquids or white crystalline solids in the fully alkylated compounds, and were readily decomposed with saturated aqueous ammonium chloride to give *B*-organo-substituted tetrazaborol-2-ines with hydrogen evolution.

The reaction of the hydrogen attached to boron with Grignard reagents therefore suggests that the B–H bond is essentially polarised $B^{\delta+}$–$H^{\delta-}$.

It was earlier suggested[2,3] that the reaction of organic azides with amine-boranes to give tetrazaborol-2-ines probably occurred through the intermediate formation of [R–N=B–H] which was subsequently involved in a 1,3-dipolar cyclo-addition with the organic azide. Recent work in these laboratories[7] has indicated that in fact this reaction is probably more complex than has been suggested, since attempts to prepare unsymmetrically *N*-substituted tetrazaborol-2-ines has resulted in mixed products. However, Paetzold[8,9] has shown that the thermal decomposition of diphenylboron azide proceeds through the loss of nitrogen, followed by a Curtius-type rearrangement to the boron imide intermediate [Ph–B=N–Ph], and that although this can be isolated as the dimer $(PhBNPh)_2$, cyclo-addition with 1,3-dipolar compounds will occur. Similarly, we find that thermal decomposition of diphenylboron azide in the presence of phenyl azide yields triphenyltetrazaborol-2-ine.

$$Ph_2BN_3 \xrightarrow[-N_2]{\text{heat}} [Ph_2BN] \xrightarrow{\Delta} [PhBNPh] \xrightarrow{PhN_3} Ph_2N_4BPh$$

Physical properties

The physical properties of the compounds prepared are presented in Table 1.

The effect of substitution at boron on the first electronic transition is slight for methyl, ethyl or phenyl groups, and the value of λ_{max} of 239 mμ for Ph_2N_4BMe compares reasonably well with the earlier prediction of 244 mμ for that compound[10]. However a bathochromic shift is observed when the substituent group is vinyl. This suggests that some π-interaction takes place between the vinyl group and the boron atom since an isolated olefinic group would be expected to absorb near 180–190 mμ. It is probable that the absorption near 215 mμ corresponds to a $\pi \rightarrow \pi^*$ transition of the system, and the extrapolated intensity is comparable with the fully alkylated tetrazaborol-2-ines. It is interesting to note that we have not been able to detect $n \rightarrow \pi^*$ transitions in these compounds. Such transitions are often observed in compounds containing the azo grouping but the intensities are usually weak[11].

The substitution of the hydrogen at boron by methyl, ethyl or phenyl groups results in a downfield displacement of the ^{11}B NMR chemical shift of about 6 ppm. This effect is of the same order of magnitude as that observed in borazines, although there are some ambiguities in the literature[12]. *B*-Vinyl substitution results in a downfield displacement of only about 2 ppm, and the difference is again probably due to π-interaction of the vinyl group with the boron atom. A similar effect is observed with the borazines[12]. The ^{11}B NMR of Me_2N_4BD is one of the few examples in which

TABLE 1

PHYSICAL DATA FOR *B*-SUBSTITUTED TETRAZABOROL-2-INES R_2N_4BR''

Compound	M.p. (°C)	UV		^{11}B NMR δ (ppm)^a	^{1}H NMR, τ (ppm)^b	
		λ_{max} (mμ)	ε_{max} (l·cm^{-1}·mole^{-1})		Group R	Group R''
Me_2N_4BD	10.5	198		-20.3 [J(BD) 31 Hz]	$\delta(CH_3)$ 6.65	
Me_2N_4BMe	12.2	200	9.2×10^3	-26.8	$\delta(CH_3)$ 6.55	$\delta(CH_3)$ 9.51
Me_2N_4BEt		199	7.4×10^3	-26.7	$\delta(CH_3)$ 6.55	$\delta(C_2H_5)$ 8.92^c
Me_2N_4BVi		215	7.8×10^3	-22.5	$\delta(CH_3)$ 6.46	δ(Vi) 3.59^c
Et_2N_4BH	<-50	199	7.3×10^3	-19.8 [J(BH) 159 Hz]	$\delta(CH_3)$ 8.65 $\delta(CH_2)$ 6.02 J(HH) 7.2 Hz	δ(BH) 5.42 J(BH) 163 Hz
Et_2N_4BEt	-34	204	5.5×10^3	-25.2	$\delta(CH_3)$ 8.70 $\delta(CH_2)$ 6.13 J(HH) 7.2 Hz	$\delta(C_2H_5)$ 8.88^c
Ph_2N_4BMe	116	239	2.4×10^4	-26.9	δ(Ph) 2.66^c	$\delta(CH_3)$ 9.20
Ph_2N_4BPh	186	239	2.6×10^4	-26	δ(Ph) 2.60^c	δ(Ph) 2.60^c

^{a} Reference BF_3Et_2O. ^{b} Reference Me_4Si. ^{c} Broad absorption or complex multiplet.

the B–D coupling is observed. The poorly resolved essentially symmetric triplet was analysed graphically to yield J(BD) of 31 Hz, which compares well with the calculated value of 26 Hz on the basis of:

$$\frac{J(^{11}B{-}^{1}H)}{J(^{11}B{-}^{2}D)} = \frac{k_1\cdot\gamma(^1H)}{k_2\cdot\gamma(^2D)},$$

assuming $k_1 = k_2$, and the observed $J(^{11}B{-}H)$ of 166 Hz[3].

In the proton NMR spectra of the compounds, protons on a carbon atom adjacent to the boron are shifted to high field in a similar manner to that observed in borazines[12]. However, in *B*-trimethyl-*N*-triphenylborazine the methyl resonances are shifted so far to high field that they occur upfield of Me_4Si[13], and this has been interpreted as strong evidence for the phenyl rings lying perpendicular to the plane of the B_3N_3 ring. In *B*-methyl-*N*-diphenyltetrazaborol-2-ine the methyl resonance occurs significantly downfield from that in *B*-methyl-*N*-dimethyltetrazaborol-2-ine and we therefore suggest that the phenyl rings are coplanar with the BN_4 ring, since the ring current effect in the phenyl rings would then favour a downfield displacement. When the substituent at the boron atom is ethyl, the CH_2 protons accidentally coincide with those of the CH_3 group, and a broad absorption showing some structure is observed near τ 8.9 ppm.

The effect of substitution on the electronegativities of the nitrogen atoms adjacent to the boron can be estimated using the revised Dailey–Schoolery formula[14]:

$$E = 0.684[\tau(CH_3) - \tau(CH_2)] + 1.78$$

for Et_2N_4BH, $E = 3.58$ and Et_2N_4BEt, $E = 3.54$, with the implication[13] that π-bonding is greater with the ethyl-substituted compound. This is in qualitative agreement with the earlier[10] calculations on Ph_2N_4BH and Ph_2N_4BMe, in which the π-densities at boron were respectively calculated as 0.114 e and 0.148 e, although the B–N π-bond orders were calculated as 0.314 and 0.299 respectively.

In Me_2N_4BVi, the vinyl group occurs as a broad poorly resolved multiplet near τ 3.59 ppm, and the methyl groups are unresolved at 40°. An examination of the proton NMR spectrum over a range of temperatures might give information on the barrier to rotation of the vinyl group and hence the extent of π-interaction.

Infrared spectra

The infrared spectra of the substituted tetrazaborol-2-ines has been examined, and a number of the bands of the spectra have been assigned by analogy with previously examined compounds[2,4].

Ring modes. It has been shown[4] that tetrazaborol-2-ines with C_{2v} symmetry have nine skeletal fundamental modes of vibration distributed amongst the symmetry classes as follows: $4A_1$, $1A_2$, $3B_1$, $1B_2$, of which $3A_1$ and $2B_1$ modes are essentially stretching modes. The frequencies at which these modes occur is sensitive to the nature of the substituents on the ring, and in particular to the substituents at nitrogen. It should also be mentioned that when the boron or nitrogen substituent is ethyl or vinyl, the molecule no longer belongs to C_{2v} point group, and it might be anticipated that inactive modes (A_2 for C_{2v} molecules) become allowed, although their intensities may be too low to be observed.

A number of bands in Me_2N_4BH were previously assigned to the ring stretching modes. In the present series of *N*-methyl- and *N*-ethyl-substituted compounds, corresponding frequencies are observed which vary only slightly on changing the substituent at boron. We therefore assign these bands to the analogous modes, and list these in Table 2.

TABLE 2

RING STRETCHING MODES OF *N*-DIMETHYL- AND *N*-DIETHYLTETRAZABOROL-2-INES

Mode of vibration	X in Me_2N_4BX					X in Et_2N_4BX	
	H	D	Me	Et	Vi	H	Et
ω_4	1408	1409	1397	1395	1395	1410	1413
ω_5	1363	1355	1376	1377	1366	1344	1355
ω_3	1342	1342	1337	1339	1337	1300	1300
ω_2 ^{10}B		987	1007	1026	1021		
^{11}B	991	979	992	1005	1014	1018	1023
ω_1 ^{10}B			908		974 sh	943	951
^{11}B	953	951	898	959	960	927	936

It is less easy to identify corresponding ring deformation modes, but the band at 736 cm^{-1} in Me_2N_4BH, which was assigned to the b_1 ring deformation ω_6, has counterparts in the other compounds as indicated: Me_2N_4BD, 732 cm^{-1}; Me_2N_4BMe, 754 cm^{-1}; Me_2N_4BEt, 797 cm^{-1}; Me_2N_4BVi, 794 cm^{-1}; Et_2N_4BH, 794 cm^{-1}; Et_2N_4BEt, 792 cm^{-1}.

The assignment of ring modes in Ph_2N_4BH was necessarily more tentative in the absence of infrared band contours and Raman data[2], and a number of bands

TABLE 3

RING MODES OF PHENYL-SUBSTITUTED TETRAZABOROL-2-INES

Ring mode	Ph_2N_4BH	Ph_2N_4BMe	Ph_2N_4BPh
V	1418, 1405	1412, 1389	1416, 1393
VI	1200, 1190	1274, 1261	–, 1264
II	1109, 1091	1109, 1086	1109, 1086
I	1062	1060	1057
VII	968	988	953
III	915, 905	894, 886	912, 907
IV	668	665	667
VIII	420	422	422

differed considerably from those in Me_2N_4BH. However, the bands assigned to ring vibrations in the spectrum of Ph_2N_4BH have counterparts in the spectra of Ph_2N_4BMe and Ph_2N_4BPh, and these are listed in Table 3.

C–N modes. The C–N stretching modes of *N*-dimethyltetrazaborol-2-ine were previously assigned to bands at 1046 (a_1) and 1213 (b_1) cm^{-1}, and the band at 1231 cm^{-1} was assigned to a combination band. In the series of *N*-methyl-substituted compounds examined, a consistently strong band was observed near 1240 cm^{-1}, and we now favour this as the antisymmetric C–N stretching mode. The band at 1213 cm^{-1} would then be the symmetric C–N stretching frequency.

The C–N deformations of Me_2N_4BH were originally assigned to bands near 411 and 283 cm^{-1}. Weak bands are observed near 640 cm^{-1} in many of the substituted compounds, and it is possible that this may be one of the C–N deformation modes.

Substituent vibrations. (*a*) *N-Substituents.* The internal vibrations associated with *N*-methyl groups in the substituted compounds occur at similar frequencies to those in Me_2N_4BH. Bands in the C–H stretching, CH_3 deformation, and CH_3 rocking regions can be identified.

Bands associated with *N*-ethyl groups are necessarily more complicated, and complete assignments were not attempted due to severe overlapping of bands.

Phenyl modes in *N*-phenyl-substituted compounds are observed at frequencies close to those previously reported for Ph_2N_4BH[2].

(*b*). *B-Substituents.* The C–H stretching modes of *B*-methyl groups are little affected by the proximity of the boron, and are not distinguished from other C–H vibrations in the vicinity in Me_2N_4BMe, but are readily recognised at 2973, 2919, 2852 cm^{-1} in Ph_2N_4BMe. In the deformation region, the antisymmetric modes are obscured by other vibrations, but the symmetric modes are probably best assigned to the band at 1318 cm^{-1} in Me_2N_4BMe, and the band at 1323 cm^{-1} in Ph_2N_4BMe.

In Me_2N_4BVi, the vinyl C–H stretching frequency occurs at 3065 cm^{-1} and the C=C stretching mode is observed at 1620 cm^{-1}. The in-plane and out-of-plane hydrogen deformations, which are normally observed near 990 and 910 cm^{-1} probably occur in this compound as components of the complex bands observed near 1021 and 960 cm^{-1}.

B–X vibrations. The B–H stretching frequencies of Me_2N_4BH have already been assigned, and that of Et_2N_4BH is similar. Deuteration further confirms this assignment, and the ^{10}B–D and ^{11}B–D stretching modes are observed at 2004 and 1988 cm^{-1}. The ^{10}B–D and ^{11}B–D in-plane and out-of-plane deformation modes occur at 825, 816 cm^{-1}, and 708, 690 cm^{-1}. The bands were identified by their contours from the vapour spectrum.

The B–C stretching frequency is found near 1070 and 1080 cm^{-1} for methyl, ethyl, and vinyl substituents, but probably occurs at higher frequencies for phenyl substitution. The B–C deformation modes are less certain but the in-plane B–Me modes may occur near 565 cm^{-1} for Me_2N_4BMe and 506 cm^{-1} for Ph_2N_4BMe. The out-of-plane B–C modes are probably below 400 cm^{-1}.

EXPERIMENTAL

Solvents and intermediates

Solvents were dried and purified by standard procedures. LiD and $LiBD_4$ were used as supplied (Fluka). Diborane (Callery Chemical Co.) was used from a cylinder first cooled to −78°. Methyl and ethyl azides were prepared by treating aqueous sodium azide with dimethyl or diethyl sulphate. Diphenylboron azide was prepared by the action of lithium azide on diphenylboron chloride in boiling benzene under dry nitrogen[8]. *N*-Dimethyl-* and *N*-diphenyltetrazaborol-2-ine were prepared as previously reported[2,3], and also by heaving equimolar quantities of dimethyl sulphate, methylammonium azide and lithium borohydride in ether solvent in a sealed tube at 120° for 48 h. The products were fractionated under vacuum, and a good yield of Me_2N_4BH was collected in a trap at −30°.

N-Dimethyltetrazaborol-2-ine-d, Me_2N_4BD

Attempts to exchange the hydrogen in Me_2N_4BH by heating with either lithium deuteride or lithium borodeuteride gave only trace amounts of the deuterated compound. It was therefore prepared by heating methylammonium chloride (1.1 g, 16 mmoles), lithium borodeuteride (0.4 g, 16 mmoles) with methyl azide* (1.38 g, 24 mmoles) and diethyl ether solvent in a sealed ampoule at 130° for 60 h to yield 0.35 g (23%) Me_2N_4BD. The compound was confirmed by its IR, NMR, and mass spectra. The intensities of the molecular ion peaks at *m/e* 98, 99 due to ^{10}B and ^{11}B were in the expected ratios.

N-Diethyltetrazaborol-2-ine, Et_2N_4BH

This was prepared by the general route of heating ethylamine-borane (prepared from ethylamine and diborane) with ethyl azide* in a sealed ampoule at 130° for 24 h. Almost quantitative evolution of hydrogen was observed, and the colorless oily product was redistilled under high vacuum, and collected in a trap at −10°. A small amount of a non-volatile liquid remained in the ampoule. (Found: C, 38.32; H, 8.91; B, 8.36; N, 44.50. $C_4H_{11}BN_4$ calcd.: C, 38.14; H, 8.80; B, 8.58; N, 44.48%.) Molecular ion peaks were observed at *m/e* 125, 126 in the expected ratios for the isotopes ^{10}B and ^{11}B.

Reaction of Grignard reagents with tetrazaborol-2-ines

A three-necked flask fitted with a 100 ml tap funnel, mercury sealed stirrer

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* *Caution.* With reference to the published method of preparation of tetrazaborol-2-ines, we have found that occasionally severe explosions occurred when methyl azide was condensed under vacuum into an ampoule using liquid nitrogen.

and reflux condenser was flushed with nitrogen, and a slight excess of the Grignard reagent was prepared in the flask in the usual way. The solvent used was normally diethyl ether, except for the vinyl Grignard reagent when tetrahydrofuran was used[15]. A solution or slurry of R_2N_4BH in solvent was slowly added from the tap funnel and the mixture stirred at room temperature for about 24 h. When Ph_2N_4BH was added to PhMgBr, the first drop produced a deep green fluorescent solution. On further addition, the green fluorescent colour was replaced by a bright yellow precipitate and a bright yellow fluorescent solution. Similar colour changes were observed on adding Ph_2N_4BH to MeMgI, but the complex was much more soluble. When Et_2N_4BH was added to EtMgI, no fluorescence was observed but a colourless viscous oil separated on standing. Me_2N_4BH and MeMgI produced a similar oil, but the addition of an ether solution of Me_2N_4BH to ViMgBr produced a white crystalline complex. In general, the products were treated with an excess of saturated ammonium chloride solution and effervescence occurred. The ethereal solutions were separated, and the aqueous layer extracted with several portions of diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulphate and molecular sieve, filtered and concentrated. Ph_2N_4BPh and Ph_2N_4BMe were obtained as white crystals from the concentrate, and were recrystallised from ether/light petroleum (b.p. 60–80°). Me_2N_4BMe, Me_2N_4BVi and Et_2N_4BEt were isolated as colourless liquids by distillation on the vacuum line and were collected in traps at $-40°$. They were further purified by distillation from traps at 0°. Gas–liquid chromatography of the vinyl substituted compound showed it to be a mixture of two products in the approximate ratio 5 : 1. An examination of the mass spectrum showed parent ion peaks at *m/e* 123, 124, 125 and 126 in the ratios for a 5.25 : 1 mixture of Me_2N_4BVi and Me_2N_4BEt. The subsequent fragmentation pattern further confirmed both compounds in the light of the generalised fragmentation which has been observed for these com-

TABLE 4

EXPERIMENTAL DATA

Compound	Starting material (mmoles)	Yield (%)	Analyses found (calcd.) (%) C	H	B	N	Parent ions *m/e*
Me_2N_4BMe	15.1	79	32.4 (32.2)	8.2 (8.1)	9.7 (9.7)	50.2 (50.0)	111 112
Et_2N_4BEt	11.5	80	46.6 (46.8)	9.6 (9.8)	7.3 (7.0)	36.5 (36.4)	153 154
Ph_2N_4BMe	9.0	88	66.2 (66.1)	5.6 (5.6)	4.4 (4.6)	23.8 (23.7)	235 236
Ph_2N_4BPh	13.5	72	72.2 (72.5)	5.2 (5.1)	3.6 (3.6)	18.5 (18.8)	297 298
Me_2N_4BVi	14.4	64[a]					123 124
Me_2N_4BEt							125 126

[a] In 5 : 1 mixture with Me_2N_4BEt.

pounds[1,16]. The details of experimental quantities, yields, and analysis data are given in Table 4.

During the preparation of Ph_2N_4BPh and Ph_2N_4BMe, the magnesium-containing complexes were isolated by concentrating the ethereal solution after the parent compound had been added to the Grignard reagent, and the product filtered in a dry nitrogen-filled glove box. The complexes were extremely sensitive to air and moisture, and were not characterised further.

Preparation of Ph_2N_4BPh using diphenylboron azide

Diphenylboron azide (4.00 g, 19.3 mmoles) and phenyl azide (2.30 g, 19.3 mmoles) were dissolved in dry ether in a 200 ml ampoule which was previously flushed with dry nitrogen in a glove box. The ampoule was sealed under vacuum and heated at 90–100° for 60 h in a protective metal tube. A dark brown liquid was produced which on cooling deposited colourless crystals, and the nitrogen evolved during the reaction measured 364 ml at N.T.P. (84% of the theoretical quantity) using a Töpler pump. The gas was identified by mass spectrometry. The crystalline compound was filtered in the glove box and recrystallised from ether/light petroleum. The product was shown to be identical with that obtained from the Grignard reaction by its infrared and mass spectra. The molecular ion peak at m/e 298 was measured as m/e 298.1386 (theoretical m/e 298.1411). Yield 23%.

Catalytic hydrogenation of the Me_2N_4BVi mixture

The mixture of Me_2N_4BVi and Me_2N_4BEt (0.4996 g) was dissolved in light petroleum (b.p. 60–80°), and placed with PtO catalyst in a standard hydrogenation apparatus. A typical zero-order reaction was observed, and a total of 85.0 ml of hydrogen was absorbed (theoretical for a 5.25/1 mixture, 84.9 ml). The product was isolated by vacuum distillation, and showed parent ion peaks at m/e 125, 126.

Attempted hydroboration of ethylene and 1-butene

Equimolar quantities of 1-butene and dimethyltetrazaborol-2-ine, and also ethylene and dimethyltetrazaborol-2-ine were condensed into ampoules with ether solvent, and heated respectively for periods of time up to 48 h at 110° and 135°. Distillation of the products under vacuum gave unchanged starting materials in each case.

Nuclear magnetic resonance spectra

These were obtained on a Perkin–Elmer R10 Spectrometer, at 60 MHz for ^1H and 19.3 MHz for ^{11}B spectra. Proton chemical shifts were obtained with reference to internal tetramethylsilane as standard, and solutions in $CDCl_3$ or pure liquids were used. ^{11}B chemical shifts were obtained with reference to external BF_3Et_2O.

Ultraviolet spectra

These were obtained on a Unicam SP.800 Spectrophotometer. The λ_{max} values for the volatile compounds were obtained from vapour spectra, and those for the non-volatile compounds were obtained as solutions in cyclohexane. The extinction coefficients of the latter compounds were measured directly, but those of the vapours were estimated from the sides of the bands observable in cyclohexane solution.

Mass spectra

Spectra were obtained on A.E.I. MS. 2, MS. 9 and MS. 12 mass spectrometers. Solid compounds were introduced by direct insertion probes, and volatile liquids by cold inlet and hot box systems.

Raman spectrum

The Raman spectrum of pure liquid Et_2N_4BH was obtained on a Hilger and Watts E.612 Spectrograph fitted with flint glass prisms and FL12 Mercury arc source with potassium nitrite filter. The exciting line was the Hg 4358 Å line. The spectrum was recorded photographically, and the frequency shifts calculated using an Elliott 4120 computer. The observed Raman shifts were: 2986 s, 2940 s, 2913 s (P?), 2824 mw, 2493 ms, 2460 mw, 2234 w, 1458 mw, 1414 vw, 1376 ms, 1352 mw, 1094 vw, 1026 mw, 989 w (P), 934 s, 594 vw, 181 w, 151 mw cm^{-1}.

Infrared spectra

These were recorded on a Grubb–Parsons Spectromaster Grating spectrometer between 4000 and 400 cm^{-1} using thin films of pure liquids, or KBr discs of the crystalline solids. In addition, the vapour spectrum of Me_2N_4BD was obtained in a 10 cm cell.

ACKNOWLEDGEMENTS

We wish to thank Dr. A. FINCH for helpful discussions, Dr. R. L. WILLIAMS and Professor ELVIDGE for providing us with NMR facilities, and Dr. B. REUBEN, The National Physical Laboratory and B.P. Chemicals (U.K.) Ltd., for obtaining mass spectra.

REFERENCES

1 E. F. H. BRITTAIN, J. B. LEACH AND J. H. MORRIS, *J. Chem. Soc., A*, (1968) 340.
2 N. N. GREENWOOD AND J. H. MORRIS, *J. Chem. Soc.*, (1965) 6205.
3 J. H. MORRIS AND P. G. PERKINS, *J. Chem. Soc., A*, (1966) 580.
4 A. J. DOWNS AND J. H. MORRIS, *Spectrochim. Acta*, (1966) 957.
5 J. B. LEACH AND J. H. MORRIS, *J. Chem. Soc., A*, (1967) 1590.
6 (a) A. GRACE AND P. POWELL, *J. Chem. Soc., A*, (1966) 673.
  (b) J. H. SMALLEY AND S. F. STAFIEJ, *J. Amer. Chem. Soc.*, 81 (1959) 582.
7 J. B. LEACH AND J. H. MORRIS, to be published.
8 P. I. PAETZOLD, *Z. Anorg. Allg. Chem.*, 326 (1963) 53.
9 P. I. PAETZOLD, *Z. Anorg. Allg. Chem.*, 326 (1963) 58.
10 J. H. MORRIS AND P. G. PERKINS, *J. Chem. Soc., A*, (1966) 576.
11 C. N. R. RAO, *U.V. and Visible Spectroscopy*, Butterworths, London, 1961.
12 H. STEINBERG AND R. J. BROTHERTON, *Organoboron Chemistry*, Vol. 2, *Boron–Nitrogen and Boron–Phosphorus Compounds*, Interscience, New York, 1966, p. 365.
13 E. F. MOONEY, *Spectrochim. Acta*, 18 (1962) 1355.
14 (a) B. P. DAILEY AND J. N. SHOOLERY, *J. Amer. Chem. Soc.*, 77 (1955) 3977.
  (b) J. R. CAVANAUGH AND B. P. DAILEY, *J. Chem. Phys.*, 34 (1961) 1099.
15 D. SEYFERTH, *Org. Synt., Collective Vol.* 4 (1963) 258.
16 E. F. H. BRITTAIN, J. B. LEACH AND J. H. MORRIS, *Enfield Symposium on Mass Spectrometry*, July 1967, Butterworths, London, to be published.