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Vibrational Spectra and Structure of Trivinylborane

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The infrared spectra (40–4000 cm^{-1}) of gaseous and solid (−196°) trivinylborane and the Raman spectra (50–3200 cm^{-1}) of gaseous, liquid, and solid (−196°) trivinylborane, $(C_2H_3)_3B$, have been recorded. The Raman spectra were, in general, rather weak and the spectrum of the liquid was characterized by extremely broad lines some of which had half-widths of 30–50 cm^{-1}. Several infrared and Raman bands in the fluid states disappeared with solidification. Several possible molecular symmetry species were considered. The spectra have been interpreted on the basis of the existence of two conformers in the fluid states, a planar C_{3h} and a nonplanar form probably of C_3 symmetry (vinyl groups twisted up out of the plane) with only the planar form present in the solid state. A temperature study was carried out in order to determine the relative stability of the rotamers. The planar form was found to be approximately 0.73 kcal/mol more stable than the other conformation. A complete vibrational assignment is given for the molecule in the solid state. The low-frequency Raman spectrum of the solid had at least ten sharp lines resulting from intermolecular modes which indicates that there are more than two molecules per primitive cell.

Introduction

The structure of trivinylborane has been the subject of some controversy. Infrared data of the gas and chemical reactivity have been used to postulate a planar structure for the molecule,[2] in which the π orbitals of the vinyl groups conjugate with the empty pπ orbital on the sp^2-hybridized boron. The ultraviolet and nmr data on methylvinylboranes[3] have been interpreted to show that there is limited conjugation between boron and vinyl groups and that boron exists in a hybridized form that is intermediate between sp^2 and sp^3. The photoelectron spectrum[4] of trivinylborane has been used to suggest that boron is either sp^2 hybridized with the vinyl groups twisted out of the plane or that the hybridization is intermediate with the molecule having a pyramidal structure. Changes in molecular symmetry resulting from trivinylborane being planar, nonplanar, or pyramidal should be detectable by vibrational spectroscopy and consequently a complete vibrational analysis was undertaken for this purpose. The results of this study are reported herein.

Experimental Section

All preparative work involved in the preparation of trivinylborane was carried out in a conventional high-vacuum system employing greaseless stopcocks. All ground-glass apparatus which came into contact with halogenated boranes was lubricated with Halocarbon vacuum grease; otherwise, Apiezon M grease was used.

The preparative route followed was that of Brinckman and Stone.[5] The initial step involved the preparation of chlorodivinylborane from boron trichloride and tetravinyltin. Boron trichloride was obtained commercially (Matheson) and was purified by trap-to-trap fractionation until the vapor pressure was 476 mm at 0°.[6] Tetravinyltin was also obtained commercially (Columbia Organic Chemicals, Inc.) and its purity was checked by ^{1}H nmr. An equimolar mixture of BCl_3 and $Sn(C_2H_3)_4$ was sealed in a 1000-ml bulb and allowed to stand at room temperature for 6 hr. The bulb was then opened to the vacuum system and the mixture was separated by distillation on a variable-temperature vacuum fractionation column.[7] Chlorodivinylborane was identified by its infrared spectrum.[5]

The $ClB(C_2H_3)_2$ obtained was condensed into a normal vacuum sublimation apparatus which contained a large excess of antimony trifluoride (Alfa). The SbF_3 had been "activated" by heating the apparatus with a cold flame while pumping. This served to sublime SbF_3 onto the cold finger and the walls of the apparatus. This mixture was then allowed to stand for approximately 15 hr at −50°. At several intervals during this period, the apparatus was cooled to −95° (toluene slush) and fluorodivinylborane was removed. This material was also purified on a low-temperature column.

Pure $FB(C_2H_3)_2$ was then condensed into a vacuum tube and sealed from the vacuum system. The tube was allowed to stand at ambient temperature for 12 hr. The tube was reopened and the reaction mixture $B(C_2H_3)_3$, $FB(C_2H_3)_2$, and $F_2BC_2H_3$ fractioned on the low-temperature column. The trivinylborane obtained exhibited a vapor pressure of 34 mm at 0° (lit. values: 35–40 mm,[5] 34 mm,[8] 24.4 mm[3]). Its infrared spectrum was in excellent agreement with that of Brinckman and Stone.[5]

The 32.1-MHz ^{11}B nmr spectrum (Varian Associates XL-100-15 spectrometer) exhibited a chemical shift of 56.4 ppm deshielded from external $BF_3 \cdot O(C_2H_5)_2$ (lit.[3] −55.2 ppm). The mass spectrum (Perkin-Elmer RMU-6 spectrometer 70 ev) exhibited a parent peak at *m/e* 92 with an intense P − 1 peak at *m/e* 91 as found by Good and Ritter.[3]

A Perkin-Elmer Model 621 infrared spectrophotometer purged with dry air was used for recording mid-infrared spectra from 4000 to 200 cm^{-1}. The instruments were calibrated with standard gases[9] in the high-frequency region and atmospheric water vapor[10] in the lowest region. A low-temperature cell equipped with a CsI window was employed to record the spectra of the solid samples. Conventional vacuum deposition techniques were used to obtain the solid film on the CsI substrate. The CsI substrate was held at −190° during deposition and then the solid films were annealed until there was no change in the spectrum. Typical spectra are shown in Figure 1 and the observed frequencies are listed in Table I.

Far-infrared spectra from 40 to 350 cm^{-1} were recorded with a Beckman Model IR-11 spectrophotometer. The atmospheric water vapor was removed from the instrument housing by flushing with dry air. The instrument was calibrated by using atmospheric water vapor.[10] Single-beam energy checks were made periodically to ensure the energy transmission was at least 10–15% at all times. A low-temperature cell similar to one described earlier[11] was employed to record the spectra of solid samples. Modifications have been made to allow the circulation of cold nitrogen liquid through a hollow brass cold finger. A wedged silicon window was used for the solid-film support plate. Deposition and annealing of the samples were similar to methods used for mid-infrared studies. Typical spectra are shown in Figure 2.

The Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer,[12] equipped with an Argon ion laser source with a frequency of 5145 Å for excitation. Raman spectra of the solids

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[1] Taken from the thesis of S. Riethmiller which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

[2] T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1962).

[3] C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, **84**, 1162 (1962); *J. Chem. Eng. Data*, **7**, 416 (1962).

[4] A. K. Holliday and W. Reade, *Chem. Commun.*, 51 (1971).

[5] F. E. Brinckman and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 6218 (1960).

[6] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[7] J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).

[8] A. K. Holliday and R. E. Pendlebury, *J. Organometal. Chem.*, **10**, 295 (1967).

[9] IUPAC, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, Washington, D. C., 1961.

[10] R. T. Hall and J. M. Dowling, *J. Chem. Phys.*, **47**, 2454 (1967); **52**, 1161 (1970).

[11] F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, **47**, 2104 (1967).

[12] This instrument was purchased with funds from the National Science Foundation through Grant GP-28068.

Table I. Observed Infrared and Raman Frequencies (cm^{-1}) of Trivinylborane[a]

Infrared		Raman			
Solid	Gas	Solid	Liquid	Gas	Assignment
	3664 w				$2\nu_{21} + \nu_{20} = 2 \times 1185 + 1300 = 3670$
	3190 w				$2\nu_{22} + \nu_{21} = 2 \times 1016 + 1154 = 3186$
			3187 vw, p		$\nu_1 + \nu_9 = 2987 + 200 = 3187$
		3164	3168 vw, p		$2\nu_4 = 2 \times 1587 = 3174$
3062 s	3072 b, s	3064 m	3064 m, dp	3073 m, dp	ν_{15}, C–H asym str (E′)
3056 sh, w		3054 m			
3030 w	3036 m				$2\nu_{22} + \nu_{25} = 2 \times 1025 + 978 = 3028$
2982 m	2990 s				ν_{16}, C–H asym str (E′)
2976 s					
		2983 s	2987 s, p	2998 sh, vs, p	ν_1, ν_2, ν_3, C–H sym str (A′)
		2976 sh,w	2982 s, p	2994 vs, p	
2954 s	2965 s	2952 w	2956 w, sh, dp	2967 sh, w, dp	ν_{17}, C–H asym str (E′)
		2873 v w	2872 w, p		$\nu_4 + \nu_6 = 1587 + 1287 = 2874$
1932 w	1936 m				$\nu_{21} + \nu_{11} = 1185 + 754 = 1939$
				1645 vw, p	$\nu_{10} + \nu_8 = 975 + 663 = 1638$
1597 s	1602 b, s	1598 m			ν_{18}, C=C asym str (E′)
			1596 vs, p	1601 vs, p	C=C sym str (isomer II)
		1584 s	1587 vs, p	1593 s, p	ν_4, C=C sym str (A′)
		1569 w	1572 w, sh, p	1576 sh, w, p	975 + 595 = 1570
		1430 w			$\nu_{11} + \nu_8 = 772 + 651 = 1423$
1420 s	1425 b, s	1424 m			ν_{19}, CH_2 scissors (E′)
1410 sh, m		1412 m	1416 s, p	1416 s, p	ν_5, CH_2 scissors (A′)
	1366 sh, w				CH in-plane bend (isomer II)
1310 w	1300 b, m	1307 w	1293 m, p	1297 m, p	ν_{20}, CH in-plane bend (E′)
		1287 w	1287 m, p		ν_6, CH in-plane bend (A′)
			1194 vw, p	1198 b, vw, p	CH in-plane bend (isomer II)
1182 sh, m					ν_{21}, $^{10}BC_3$ asym str (E′)
	1185 s				
1176 m		1178 vvw			
1158 m		1160 vw			ν_{21}, $^{11}BC_3$ asym str (E′)
	1154 s	1153 vw	1153 vw		
1150					
1098 w					$\nu_{11} + \nu_{23} = 771 + 325 = 1096$
	1120 m				746 + 380 = 1126
	1092 s		1089 vvw, dp		BC_3 asym str (isomer II)
1036 m		1032 vw			ν_{22}, CH_2 rock (E′)
	1016 s				
1025 s		1026 vw	1023 vw, dp?	1022 b, vw, dp	
		1018 vw			ν_7, CH_2 rock (A′)
		1014 vw			
		1011 vw	1012 vw, p		
		1008 vw			
		1006 vw			
987 s		982 vw			ν_{25}, CH_2 twist (A″)
	970 b, s				
978 s		977 vw			
		974 vw			ν_{10}, CH_2 twist (E″)
		968 vw			
		965 w	969 v, dp	975 vw, dp	
771 m	754 s	772 w			ν_{11}, ν_{26}, CH_2 wag (A″, E″)
751 s	746 s	752 w			
	667 vw				CO_2
			662	663 b, w, p	BC_3 sym str (isomer II)
		651 b, vw	647 w, p	649 b, w, p	ν_8, BC_3 sym str (A′)
	600 b, vw				CH out-of-plane (isomer II)
			593 vw, p	595 b, w, p	CH out-of-plane (isomer II)
		529 w			ν_{27}, CH out-of-plane (E″)
		514 vw			
		508 vw	500 vb, vw, dp?		
488 w		488 vvw			ν_{12}, CH out-of-plane (A″)
470 w		470 vw			ν_{13}, BC_3 out-of-plane (A″)
	430 b, w			439 b, w, p	BC_3 out-of-plane (isomer II)
	380 b, w		375 b, w, dp	372 b, w, dp	CBC bend (isomer II)
338 vw	320 b, w	338 w	320 b, w, p?	321 sh, vw, p?	ν_{23}, CBC bend (E′)
310 vw		314 vw		308 b, w, dp?	ν_{24}, BCC bend (E′)
		228 b, w	200 vb, w, p?	200 b, w, p?	ν_9, BCC bend (A′)
154 vvw					ν_{14}, torsion (A″)
		132 m	140 b, w, dp	139 b, w, dp	ν_{28}, torsion (E″)
		111 sh, m			Lattice modes
		98 sh, m			
89 vw		91 m			
		83 m			
		72 m			
		66 m			
56 vw		56 w			
41 vw		43 m			
		32 m			

[a] Abbreviations used: v, very; b, broad; sh, shoulder; s, strong; m, medium; w, weak; p, polarized; dp, depolarized.

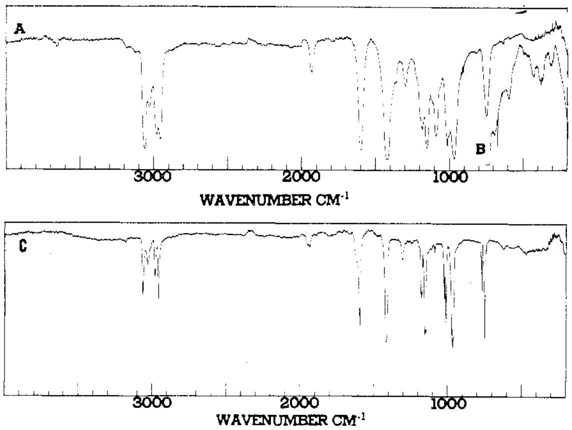

Figure 1. Infrared spectrum of gaseous trivinylborane at 10 Torr (A) and 50 Torr (B). Infrared spectrum of solid (−196°C) trivinylborane (C). Ordinate is in arbitrary units of intensity.

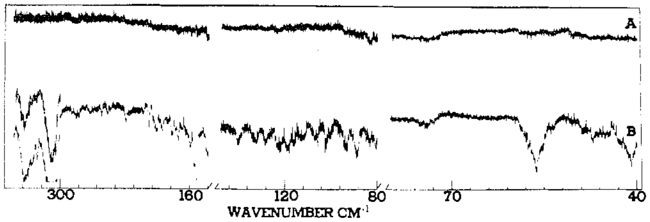

Figure 2. Far-infrared spectrum of solid (−196°) trivinylborane.

were obtained using a cold cell similar to that employed for the far-infrared instruments, except the sample holder consists of a solid brass plate at an angle of 75° from the normal. Deposition and annealing procedures are similar to those used for the mid-infrared studies. Typical spectra are shown in Figures 3-5.

Results

One of the most striking features of the Raman spectrum of trivinylborane is the extremely weak scattering found below 1300 cm^{-1}. Additionally, the Raman spectrum of the liquid is characterized by very broad lines in the low-frequency region with some having half-widths in excess of 30 cm^{-1}. There seems to be a fair correlation between the Raman spectrum of the gas with that of the liquid. For example, there is a one-to-one correspondence of all lines below 700 cm^{-1} in these two phases. However, on investigating the Raman spectrum of the solid, it is immediately evident that several of the more pronounced lines in the fluid states disappear with solidification (see Figures 3-5). Raman lines of the liquid state at 375, 593, 1089, and 1194 cm^{-1} are definitely missing in the spectrum of the solid. A similar observation was found between the infrared spectrum of the gas and solid where the bands at 380, 430, 600, and 1092 cm^{-1} for the vapor had no counterparts in the spectrum of the solid. Such changes are usually interpretable in terms of either the presence of more than one conformer in the fluid states or a change in molecular symmetry with changes in phase.[13]

One can consider any of the following conformations as possible for the trivinylborane molecule: planar (C_{3h}), nonplanar (C_3), three pyramidal forms (C_{3v}), a form with two vinyl groups up and one down with a plane of symmetry (C_s), and a form without any symmetry (C_1). The normal vibrations for a planar conformer span the representation 9 A′ (R) + 5 A″ (ir) + 10 E′ (R, ir) + 4 E″ (R), whereas those for a molecule of C_3 symmetry fall in the representations 14 A (R, ir) + 14 E (R, ir) or for the C_{3v} symmetry 9 A_1 (R, ir) + 5 A_2(−) + 14 E (R, ir). It is interesting to note that only the C_{3h} conformer has normal modes which should show mutual exclusion between several of the infrared and Raman bands. Such exclusion should be most pronounced for the skeletal motions.

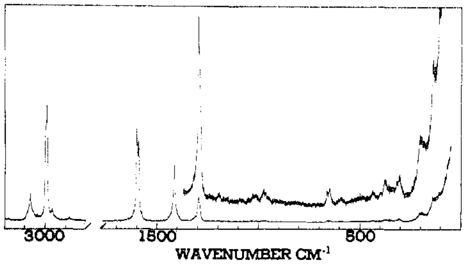

Figure 3. Raman spectrum of gaseous trivinylborane.

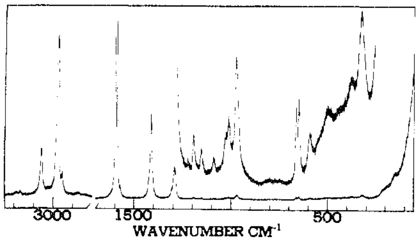

Figure 4. Raman spectrum of liquid trivinylborane.

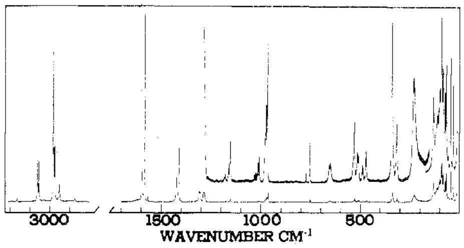

Figure 5. Raman spectrum of solid trivinylborane.

The first region which appears to show noncoincidence is the C=C stretching region (1600 cm^{-1}). If the molecule has C_{3h} symmetry, there should be a symmetric mode (A′, polarized) and a C=C antisymmetric stretch (E′, depolarized). Therefore the Raman spectrum should have two lines, one of which is polarized, whereas the infrared spectrum should have only one band in this region. At first glance, this appears to be just what is observed; however, both strong Raman lines at 1601 and 1593 cm^{-1} in the gas phase and at 1596 and 1587 cm^{-1} in the liquid phase are unquestionably strongly polarized. This means that these are not the A′ and E′ modes of the C_{3h} conformer and that one of these strong lines must be explained in another manner. A comparison of the Raman spectrum of the solid in this region shows that the higher frequency band at 1596 cm^{-1} is drastically reduced in intensity and in fact has a *higher* frequency of 1598 cm^{-1}. The interpretation of these lines is that the two polarized lines in the fluid phases arise from the symmetric stretch of two conformers, one of C_{3h} symmetry and the other of some other symmetry perhaps C_3 or C_{3v}. The Raman line at 1598 cm^{-1} in the solid phase (1597 cm^{-1} in the infrared) is the E′ mode for the isomer of C_{3h} symmetry and it is obscured by the strong polarized line of the second isomer in the fluid states. Failure to observe a second band in the infrared spectrum of gas in this region is probably because of the breadth of the 1602-cm^{-1} band. There is also a possibility that the conformer present in the fluid states could give rise to two polarized C=C stretching modes if the molecule has C_s symmetry

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(13) J. R. Durig, B. M. Gimarc, and J. D. Odom, "Vibrational Spectra and Structure," Vol. II, Marcel Dekker, New York, N. Y., 1973.

(two vinyl groups up and the other down). However, the low-frequency portion of the spectrum does not appear to be consistent with this interpretation.

The next strong band which disappears with solidification is the infrared band at 1092 cm^{-1} which can be assigned to the antisymmetric B–C stretch. There is a corresponding Raman line at 1089 cm^{-1} in the liquid phase which also disappears with solidification. The symmetric B–C stretch was observed in the Raman effect as a doublet at 662 and 647 cm^{-1} but only one band appears at 651 cm^{-1} in the spectrum of the solid. This assignment is consistent with the assignment of 681 cm^{-1} for the corresponding mode[14] for $B(CH_3)_3$ and neither of these bands has an infrared counterpart. Also, from the relatively equal intensity of these two bands, it is not possible to ascribe them to ^{10}B–^{11}B isotopic splitting of some nonplanar form. Conceivably these two polarized bands could arise from two A′ B–C stretching modes that would result from a molecule having C_s symmetry but this possibility seems to be excluded on the basis that no corresponding infrared bands are observed.

The Raman bands arising from the skeletal bending modes are all broad, and the band at 375 cm^{-1} disappears with solidification. Similarly the Raman band at 593 cm^{-1} in the fluid also is not present in the spectrum of the solid but it may well be due to a C-H out-of-plane mode rather than to a skeletal motion. Nevertheless, it appears quite clear from the Raman spectrum alone that there is at least one additional conformer in the fluid states and the isomer that is present in the solid is also present in the fluid states.

In order to verify that the disappearance of several of the Raman bands was not due to solid-state effects, a study of the Raman spectrum as a function of temperature was undertaken. The results of this study are shown in Figures 6 and 7. The sample solidified between the temperatures of −110 and −135°; therefore, spectra of the liquid sample are shown at six different temperatures. Both components of the doublet at 1596 and 1587 cm^{-1} have about equal intensity at 25°, but as the temperature is lowered, the higher frequency line decreases in a regular manner. A plot of the log of the relative intensity of these two lines *vs.* the reciprocal of the absolute temperature gives a straight line for these six temperatures. The slope of this line yielded a ΔH of 0.73 kcal/mol. Due to the changes in the density of the sample, it was not possible to determine ΔS experimentally but a rough estimate of a value of 1.6 eu was obtained from the intercept. Both of these values are in the range expected for conformational changes.[15] A similar plot of the doublet at 662 and 647 cm^{-1} gave nearly the same results. Thus, this temperature study shows conclusively that the variation in the intensity of several of the bands cannot be ascribed to solid-state effects but must result from the presence of more than one conformer in the fluid states.

Vibrational Assignment. It appears that the trivinylborane molecule has C_{3h} symmetry in the solid phase on the basis of the behavior of the skeletal vibrations. The C=C stretching modes have been discussed. The antisymmetric B–C stretch (E′) appears to be split in the solid state at 1158 and 1150 cm^{-1} for the ^{11}B isotope and at 1176 and 1182 cm^{-1} for the ^{10}B isotope. The B–C symmetric stretch has been assigned to the Raman band at 651 cm^{-1} as discussed previously. The A″ torsional mode is assigned to the infrared band at 154 cm^{-1} whereas the E″ torsional mode is assigned to the Raman line at 132 cm^{-1}. The two BCC bends, A′ and E′, respectively, are assigned to the lines at 228 and 314 cm^{-1}, respectively. The Raman line at 314 cm^{-1} has a corresponding infrared band at 310 cm^{-1} which is consistent with the assignment of this band as an E′ mode. The CBC bend (E′ symmetry) is assigned to the Raman line at 338 cm^{-1} which has a corresponding band in the infrared spectrum. The BC_3 out-of-plane bend (A″) is assigned to the infrared band at 470 cm^{-1}. A corresponding line is found in the Raman spectrum of the solid and the activity is attributed to the site symmetry of the molecule in the crystal phase. These assignments for the bending modes are consistent with those recently given for vinyldifluoroborane[16] and trimethylborane.[14,17]

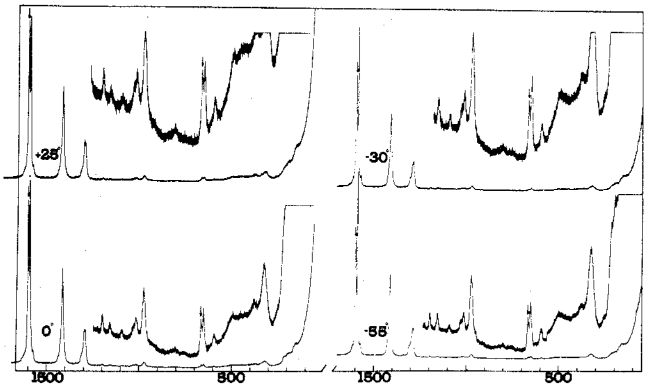

Figure 6. Raman temperature study of liquid trivinylborane. Arrows denote C=C stretching and B–C symmetric stretching regions.

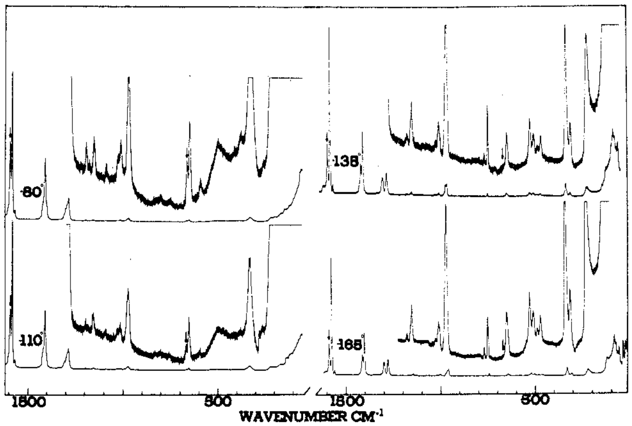

Figure 7. Raman temperature study of liquid trivinylborane. Arrows denote C=C stretching and B–C symmetric stretching regions.

The assignment of the CH motions follows directly from group frequencies for the monosubstituted vinyl moiety[18] along with the assignments for these motions in vinyldifluoroborane. The low-frequency CH out-of-plane motion is found between 488 and 529 cm^{-1} with the 488-cm^{-1} band being the A″ motion. The CH_2 wag, twist, and rock are found at 751-771, 965-982, and 1006-1032 cm^{-1}, respectively. Many of these CH motions are multiplets which are believed to arise from the presence of more than two molecules per unit cell along with low site symmetry. The CH in-plane bend is found at 1287 (A′) and 1307 cm^{-1} (E′) and the CH_2 scissors is found at 1412 (A′) and 1424 cm^{-1} (E′). The carbon-hydrogen stretching modes are found between 2952 and 3064 cm^{-1}.

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(14) R. J. O'Brien and G. A. Ozin, *J. Chem. Soc. A*, 1136 (1971).

(15) J. R. Durig, S. E. Hannum, and F. G. Baglin, *J. Chem. Phys.*, 54, 2367 (1971).

(16) J. R. Durig, R. O. Carter, and J. D. Odom, *Inorg. Chem.*, in press.

(17) L. A. Woodward, J. R. Hall, R. N. Dixon, and N. Sheppard, *Spectrochim. Acta*, 15, 249 (1959).

(18) W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, 15, 679 (1959).

There are at least nine sharp low-frequency (32-111 cm^{-1}) Raman lines which can only be assigned to intermolecular fundamentals. Several of these lines have corresponding infrared bands and there appear to be several additional infrared bands between 80 and 140 cm^{-1}. The low-frequency Raman lines are probably librational modes, whereas the infrared bands probably arise from mainly translational motions. Further characterization of these bands is not possible without knowing the crystal structure. However, it should be pointed out that such a large number of intermolecular fundamentals implies more than two molecules per unit cell.

Discussion

It appears quite clear from our data that there are at least two isomers present in the gas and liquid phases. One of the forms is the planar conformation which is the conformer that remains in the solid state. The planar conformation is the one expected on the basis of earlier studies on BX_3 molecules. However, it should be pointed out that there may be nonbonded H- - -H repulsions of the terminal CH_2 groups from our model calculations on the planar form. By assuming B–C, C=C, and C–H bond lengths of 1.60, 1.347, and 1.081 Å, respectively, the nonbonded distances between the hydrogens of the CH_2 group and those of the adjacent CH group were found to be 2.00 Å which is somewhat less than twice the van der Waals radius of hydrogen (2.4 Å). Therefore, one might expect the presence of a second conformer in the fluid states which would have the vinyl groups tilted out of the plane to some degree. The symmetry of this second conformer cannot be confidently determined from the vibrational study.

The C_{3v} pyramidal forms (three) cannot unequivocably be ruled out and there is some evidence for their existence. The 9 A′ and 5 A″ modes for the planar C_{3h} form become 10 A_1 and 4 A_2 modes in the pyramidal C_{3v} conformations. The BC_3 out-of-plane A″ mode for the C_{3h} form becomes the tenth A_1 mode in the C_{3v} conformer. The other 4 A″ modes for the C_{3h} form become A_2 modes under C_{3v} symmetry. According to selection rules for this symmetry A_2 modes are both Raman and infrared inactive. This could account for the lack of the observation of the CH_2 twist and wag and CH out-of-plane motions for the other conformer which is present in the gas and liquid states. Although a pyramidal C_{3v} structure cannot be ruled out, it would seem likely that, if a planar form is present which has H- - -H nonbonded repulsions, the vinyl groups would repel each other out of the plane into a form (C_3) which is closer to planar but has minimized the H- - -H repulsion rather than into a pyramidal form which requires a change of boron hybridization (sp^2–sp^3) and which may have H- - -H nonbonded distances closer than those for the C_3 form.

The C_s conformer seems improbable on the basis of the BC stretching motions as well as the low-frequency vibrational data. This is particularly true for the Raman spectrum of the gas phase where no Q branches were observed for the skeletal bending modes but would be expected for a conformer of C_s or C_1 symmetry.

The possibility exists that some association between trivinylborane molecules may occur since both acidic and basic sites are located in the trivinylborane moiety. Such association could give rise to the broadening of the lines, but it should be more prevalent in the liquid state than in the gaseous state. Since such behavior was not observed between the two fluid states, this explanation does not appear to be very probable.

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Registry No. $(C_2H_3)_3B$, 7217-01-8.

Contribution from the Department of Chemistry,
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Reaction of Methyldichlorophosphine with Some Simple Boron Compounds

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Boron trichloride, boron tribromide, and boron triiodide form 1:1 adducts with methyldichlorophosphine. Boron trifluoride does not react with methyldichlorophosphine, and diborane reacts with methyldichlorophosphine to give a mixture of products. Halogen exchange between methyldichlorophosphine and boron tribromide or boron triiodide is observed when phosphine–borane adducts derived from those compounds are formed.

Introduction

The formation of adducts between boron compounds and phosphines has been the subject of much recent work.[1-5] We have investigated the systems composed of boron trihalides or diborane and methyldichlorophosphine, in order to ascertain the basicity of this phosphine compared to that of trimethylphosphine or phosphorus trichloride. We also were interested in any similarity these systems might have to boronium compounds formed by the reactions of amines or phosphine oxides with boron trihalides.

Experimental Section

Materials. Boron trichloride and boron trifluoride were obtained from Matheson Coleman and Bell and were used without further purification. Boron tribromide and boron triiodide were obtained from RIC Chemicals and used as received. Diborane was prepared by standard procedures[6] on a vacuum line and was stored in an all-glass

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(1) See, for example, the excellent reviews by G. Urry and G. W. Parshall in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, pp 325 ff, 617 ff.

(2) R. Foester and K. Cohn, *Inorg. Chem.*, 11, 2590 (1972).

(3) R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, 93, 6821 (1971).

(4) J. D. Adorn, S. Riethmiller, J. D. Witt, and J. R. Durig, *Inorg. Chem.*, 12, 1123 (1973).

(5) L. F. Centofanti, *Inorg. Chem.*, 12, 1131 (1973).

(6) A. D. Norman and W. L. Jolly, *Inorg. Syn.*, 11, 15 (1968).