Journal of Organometallic Chemistry, 67 (1974) 1—6

THE INFRARED AND RAMAN SPECTRA OF TRIVINYLBORANE : EVIDENCE FOR B—C π-BONDING

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(Received July 17th, 1973)

Summary

The infrared and Raman spectra of trivinylborane are reported, and assigned upon the basis of the planar structure (C_{3h}) determined by electron diffraction. The assignments have been made using the group vibration approximation. Evidence for the presence of B—C π-bonding is presented.

Introduction

Trivinylborane has been the subject of much discussion, with particular reference to the nature of the B—C bond. Evidence for and against the existence of a B—C π-bond has been presented [1,2] for alkenylboron compounds. Trivinylborane has been studied by infrared [3], electronic [3,4] and photoelectron [5] spectroscopy, and has also been the subject of LCAO—MO—SCF [4] and CNDO [6] calculations.

The Raman spectrum of trivinylborane has not previously been published, and although the infrared spectrum has been reported [3,7], no detailed assignments have been made. We report here the Raman and infrared spectra of trivinylborane, and discuss their assignments in detail. Evidence for the existence of a π-interaction between the boron and the vinyl groups is presented.

Results and discussion

Structure of trivinylborane

A recent electron diffraction study [8] has shown that trivinylborane has a planar C_{3h} structure:

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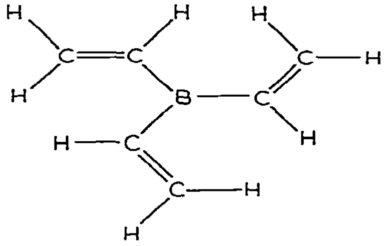

The C—C bond length is 1.373 ± 0.003 Å, the B—C bond length is 1.562 ± 0.006 Å and the mean C—H bond length is 1.093 ± 0.005 Å. The structure is planar, with a small amount of steric interaction between the three short H•••H contacts. The vibrational spectra, presented in this work, have been assigned assuming that trivinylborane retains this configuration in the liquid state. The similarities between the gas phase and liquid phase infrared spectra justify this assumption.

Assignment of the vibrational spectra

The vibrations arising from the vinyl group have been considered separately from those arising from the BC_3 skeleton. The planar BC_3 skeleton has D_{3h} symmetry, and mono-substituted ethylene (CH_2=CHX) has C_s symmetry. The descriptions and activities of the fundamental modes of vibration of these two groups are given in Table 1. The Raman and infrared spectra of trivinylborane are listed in Table 2, along with the proposed assignments.

TABLE 1

FUNDAMENTAL VIBRATIONS OF THE BC_3 SKELETON AND OF A GENERAL VINYL COMPOUND (CH_2=CHX)

Description	Symmetry	Activity[a]	
BC_3 skeleton; (D_{3h})			
BC symmetrical stretching mode	A'_1		R(p)
BC asymmetrical stretching mode	E'	IR	R(dp)
BC_3 in-plane deformation	E'	IR	R(dp)
BC_3 out-of-plane deformation	A''_2	IR	
CH_2=CHX; (C_s)			
C=C torsional oscillation	A''	IR	
CCH out-of-plane deformation	A''	IR	
CX stretching mode	A'	IR	R(p)
CCX in-plane deformation	A'	IR	R(p)
CH_2 out-of-plane deformation	A''	IR	
CH_2 in-plane, in-phase deformation	A'	IR	R(p)
CCH in-plane deformation	A'	IR	R(p)
CH_2 in-plane, out-of-phase deformation	A'	IR	R(p)
C=C stretching mode	A'	IR	R(p)
CH stretching mode	A'	IR	R(p)
CH_2 symmetrical stretching mode	A'	IR	R(p)
CH_2 asymmetrical stretching mode	A'	IR	R(p)

[a] IR = infrared; R = Raman; p = polarised; dp = depolarised.

TABLE 2

VIBRATIONAL SPECTRA OF TRIVINYLBORANE (cm^{-1})^a

Infrared		Raman		Assignment	
Liquid	Gas	Ar^+ laser	He/Ne laser		
		3192 vw	*	2 × 1600 = 3200	(A')
		3176 vw	*	2 × 1591 = 3182	(A')
	3130 vw			2 × 1604 = 3208?	(A')
3080 ms (sh) 3069 ms	3080 ms	3067 ms	3065 ms dp?	CH_2 asym. stretch	
3030 m	3038 m (sh)			1604 + 1423 = 3027	(A')
		3009 m (sh)	3009 m p	1596 + 1413 = 3009	(A')
2986 ms (sh)	2990 ms (sh)	2987 vs 2983 vs	2986 vs p 2982 vs p	CH stretch	
2962 ms	2967 ms	2959 m	2959 m p	CH_2 sym. stretch	
		2913 w	2919 w *	1605 + 1296 = 2901?	(A')
		2880 w	2894 w *	1596 + 1296 = 2892	(A')
1934 w	1935 w			2 × 970 = 1940	(A')
1606 s (sh) 1598 s	1604 s	1600 vvs 1591 vvs	1605 vvs p 1596 vvs p	C=C stretch	
1421 vs	1423 vs	1416 vs	1413 vs p	CH_2 in-plane, out-of-phase def.	
		1301 s			
1300 w	1301 w		1296 s p	CCH in-plane def.	
		1295 s			
1187 ms 1180 ms (sh)	1186 m	1199 vw	1192 vw *	^{10}BC asym. stretch	
1152 s	1156 ms	1162 vw	1156 vw *	^{11}BC asym. stretch	
1090 ms	1088 ms			CH_2 in-plane, in-phase def.	
1017 s	1017 s	1015 w	1015 w dp?	C=C torsional	
970 vs	970 vs	974 mw	971 mw dp?	CH_2 out-of-plane def.	
		803 vw		Impurity?	
749 vs	748 ms			CCH out-of-plane def.	
		665 w	664 vw p	2 × 327 = 654	(A')
		651 w	651 w p	BC sym. stretch	
*	*	596 vw	592 vvw *	Impurity?	
*	*	560 vvw		Impurity?	
*	*		435 vvw *	Borosilicate glass	
*	*	374 vw (br)			
* *	* *	327 m (br) 317 m (br)	321 m (br) p 316 m (br) p	CCB in-plane def.	

^{a} s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder; p = polarised; dp = depolarised; * = not examined; def. = deformation; sym. = symmetrical; asym. = asymmetrical.

Consider, initially, the bands occurring above 1200 cm^{-1}. These are due to the vinyl groups, and the vibrational spectra of other vinyl compounds are well documented in this region [9 - 12]. The bands in the infrared at 1604, 1423 and 1301 cm^{-1} can be assigned unambiguously to the C=C stretching mode, CH_2 in-plane out-of-phase deformation, and the C—C—H in-plane deformation, respectively. The band assigned to the C=C stretching vibration is a doublet in the Raman spectrum and possesses a shoulder in the infrared. This can be accounted for if the BC_6 skeleton is considered, since both a symmetrical and an antisymmetrical mode can be described.

The bands due to the CH and CH_2 stretching modes are expected around 3000 cm^{-1}. There has been some discrepancy in the literature as to the assignment of these bands in other vinyl compounds. Frankiss [11] and Davidson [13] assigned these bands in the order $\nu(CH_2)_{sym} > \nu(CH) > \nu(CH_2)_{as}$, whereas Kaesz and Stone [14] and Masetti and Zerbi [12] assigned the bands in the order $\nu(CH_2)_{as} > \nu(CH) > \nu(CH_2)_{sym}$. As both qualitative [15] and quantitative [16] treatments favour the latter assignments, the bands of trivinylborane have been assigned assuming that the asymmetric CH_2 stretching mode is of higher frequency than the symmetric mode. The assignments of these bands are given in Table 2. The band assigned to $\nu(CH_2)_{as}$ is depolarised in the Raman spectrum, and split in the infrared spectrum: this has been observed in the spectra of other vinyl compounds [12,13]. The band assigned to ν(CH) is also split in the Raman spectrum. These effects can be explained by a breakdown of the group vibration approximation.

The assignments of the vibrations of the vinyl group below 1100 cm^{-1} are reasonably straightforward, and are included in Table 2. They are in good agreement with those in the literature [11 - 13] for other vinyl compounds. As previously found [9,11 - 13] for other compounds, the CH_2 in-plane, in-phase deformation which should be Raman active was not observed in the Raman spectrum of trivinylborane.

The assignments of the B—C skeleton will now be considered. Boron has two isotopes (natural abundance : $^{11}B \approx 80\%$, $^{10}B \approx 20\%$), and so two bands are expected for the asymmetric B—C stretching mode, $\nu(^{10}BC)$ occurring higher than $\nu(^{11}BC)$. Thus, in the infrared, the bands at 1186 and 1156 cm^{-1} are assigned to these modes, respectively; the relative intensities of these bands are as expected for the relative isotopic abundances. The intensities of the corresponding Raman bands are very much weaker, probably due to the low polarisability of the B—C bond. This effect was also found in the spectra of trimethylborane [17,18] and triethylborane [19]. The three remaining fundamentals of the BC_3 skeleton are the BC symmetrical stretching mode, the BC_3 in-plane and the BC_3 out-of-plane deformation. $\nu(BC)_{sym}$ is only Raman active, as the BC_3 skeleton is planar, and is assigned to the band at 651 cm^{-1}. The Raman bands at 327 and 317 cm^{-1} are in the expected region for bands due to both the BC_3 in-plane deformation and C=C—B in-plane deformation. Both the observed bands are polarised, whereas the BC_3 in-plane deformation should give rise to a depolarised band. Thus both bands are assigned to the C=C—B deformation. Further evidence for this is that the corresponding bands in the Raman spectra of the vinyl compounds of Group IVB [12] are of high intensity, whereas in the spectrum of trimethylborane the band assigned to the BC_3 in-plane deformation is considerably weaker than the band due to $\nu(BC)_{sym}$. This would indicate that the band due to the BC_3 in-plane deformation is obscured by the C=C—B in-plane deformation, and by the "halo" of the exciting line. The BC_3 out-of-plane deformation is only infrared active, and was not observed as the infrared spectrum was not recorded below 625 cm^{-1}.

Finally, the infrared spectrum of trivinylborane contains many overtone and combination bands, especially in the high frequency region. These have been tentatively assigned by analogy with previous assignments in the literature for vinyl compounds.

Evidence for π-bonding

The electron diffraction data upon $B(C_2H_3)_3$ [8] is by far the strongest

TABLE 3

BOND LENGTHS FOR TRIVINYLBORANE AND RELATED COMPOUNDS

	r(C=C) (Å)	r(B—C) (Å)	Ref.
$B(C_2H_3)_3$	1.373	1.562	8
C_6H_6	1.397		20
C_2H_4	1.336		21
BMe_3		1.578	22
B_2Me_4		1.590	23

evidence for a π-interaction between the boron and the vinyl group. The data presented in Table 3 show that the B—C bond is shorter than that in trimethylborane, and that the C=C bond is longer than that in ethylene. The molecule is planar, which is the ideal situation for π-bonding.

The vibrational analysis also provides strong evidence for a B—C π-bond. The asymmetric boron—carbon stretching modes in trivinylborane occur at 1186 and 1156 cm^{-1} in the infrared, as compared with 1134 and 1120 cm^{-1} in the spectrum of triethylborane [19]. Similarly, the symmetric ν(BC) in $B(C_2H_3)_3$ occurs at 651 cm^{-1} in the Raman spectrum, as compared with 620 cm^{-1} for $B(C_2H_5)_3$ [19]. Thus, this would suggest a strengthened B—C bond in trivinylborane.

The absolute position of ν(C=C) in trivinylborane at 1604 cm^{-1} (in the infrared) cannot be used as an argument for π-bonding, despite the fact that ν(C=C) in allylboron difluoride occurs at 1650 cm^{-1} [1], since the lowering may be explained in terms of the electropositivity of boron [2]. However, Table 4 compares ν(C=C) and $\nu(^{11}BC)$ in trivinylborane (planar) with a few of its adducts [24] (in which there is no possibility of a π-interaction). As can be seen, upon removal of planarity, ν(C=C) increases and $\nu(^{11}BC)$ decreases. This is consistent with trivinylborane containing a B—C π-bond, which is lost upon complex formation.

Experimental

Trivinylborane was prepared by the reaction at low temperature between boron trichloride and tetravinyllead [25], and purified using a low temperature vacuum fractionation column. Gas and liquid phase infrared spectra were recorded in the range 4000 - 625 cm^{-1} using a Perkin—Elmer model 257 spectrometer, using cells suitably sealed from the atmosphere. The positions of the absorption bands were calibrated using the known vibrational frequencies of polystyrene. The Raman spectra were recorded on a Spex model 1401 laser Raman spectrometer using the 514.5 nm line of an Ar^+ laser of 800 mW, and

TABLE 4

SELECTED INFRARED DATA FOR TRIVINYLBORANE AND ITS COMPLEXES (cm^{-1})

	$B(C_2H_3)_3$	$B(C_2H_5)_3$ [a]	$Me_2NH.BVi_3$	$Me_3N.BVi_3$	$NH_3.BVi_3$
ν (C=C)	1601 [b], 1599 [c]		1615 [b]	1613 [c]	
ν (^{11}B—C)	1155 [b], 1152 [c]	1120 [d]		1120 [c], 1117 [e]	1106 [e]

[a] See ref. 19. [b] Solution in CCl_4. [c] Solution in CH_2Cl_2. [d] Gas. [e] KBr disc.

also the 632.8 nm line of a He/Ne laser of 70 mW. The samples were sealed in narrow cylindrical borosilicate glass tubes.

Acknowledgements

We would like to thank Professor D.A. Long for the use of Raman facilities at the University of Bradford, and the S.R.C. for a maintenance grant (to W.R.).

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