

# Vibrational Spectra of Some Heterocyclic Boron Compounds

## Part 2.—2-Chloro- and 2-Phenyl-1,3,2-Dithiaborolans

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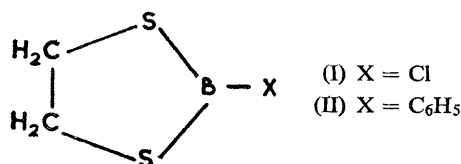
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The infra-red and Raman spectra of 2-chloro- and 2-phenyl-1,3,2-dithiaborolans have been measured. Evidence is presented for non-planarity ( $C_2$  symmetry) of the thiaborolan rings. A partial vibrational assignment, consistent with the computations of part 1 and with assignments of similar molecules, is proposed.

In part 1,<sup>1</sup> computations of vibrational frequencies and modes of 5- and 6-membered cyclic boron compounds were presented. In addition to the general frequency pattern it was demonstrated that severe mixing of B—Cl stretching modes with other vibrational modes occurred where this was permissible on symmetry grounds. The extent of mixing was such as to make the label B—Cl stretching vibration inappropriate for any real mode in these systems. Lack of experimental data other than liquid phase infra-red data made detailed comparisons between calculations and observations inappropriate.

In this paper experimental data are presented on the (I) 2-chloro- and (II) 2-phenyl-1,3,2-dithiaborolans. This system is characterized by considerable pyrolytic



stability.<sup>2a</sup> Molecular weight studies<sup>2b</sup> have shown that, unlike the oxygen analogues, there is no association in dilute benzene solution; assuming that this is also true in the pure phase, then the complications of the effects of dimerization and polymerization on the vibrational spectra are avoided. The 2-chloro-1,3,2-dioxaborolans and borinans proved too unstable for their Raman spectra to be obtained under normal conditions.

## EXPERIMENTAL

The infra-red spectra were run in the pure liquid phase on a Unicam SP 100 with grating accessories over the range 2000–400  $\text{cm}^{-1}$ , and at lower frequencies on a grating spectrometer designed and built in the department.<sup>3</sup> Raman spectra were recorded on a Cary 81 spectrograph utilizing slit widths of 8  $\text{cm}^{-1}$  and the mercury 4358 Å line for excitation. Polarization measurements were made using the method of Edsall and Wilson.<sup>4</sup> The observed values were corrected from calibration curves for the instrument determined using the true polarization ratios of carbon tetrachloride evaluated by Rank, Pfister and Grimm<sup>5</sup>. Observed spectra and frequencies are shown in tables 2 and 3 respectively.

Compounds were prepared by established procedures<sup>2a</sup> and manipulated in dry, oxygen-free enclosures. Satisfactory characterization was made by analysis and checking physical constants.

2-CHLORO-1,3,2-DITHIABOROLAN.—B.p. 25-26°C/0.05 mm,  $n_D^{25} = 1.5776$  (lit. values, b.p. 24-25/0.1 mm,  $n_D^{25} = 1.5778$ ); found % Cl, 25.5; % B, 7.78;  $C_2H_4S_2BCl$  requires Cl, 25.6; B, 7.82.

2-PHENYL-1,3,2-DITHIABOROLAN.—B.p. 90-92/0.05 mm,  $n_D^{25} = 1.6348$  (lit. values, b.p. 90-92/0.05 mm,  $n_D^{25} = 1.6346$ ); found B, 5.39;  $C_8H_9S_2B$  requires B, 5.56.

#### ASSIGNMENTS \*

It was assumed<sup>1</sup> that the 5-membered boron heterocyclic rings were planar. Following Mulliken<sup>6</sup> (recommendations 3 and 5a lead to z-axis as symmetry axis and x-axis as perpendicular to plane of molecular skeleton) the fundamental vibrational modes of I classify as

$$\begin{array}{ll} 5a_1 + 4b_2 + 2b_1 + a_2 & \text{(skeletal modes),} \\ + 3a_1 + 3b_2 + 3a_2 + 3b_1 & \text{(CH}_2 \text{ modes).} \end{array}$$

Two possible structures of lower symmetry exist. First, if the skeleton exists in the envelope form the molecular symmetry is  $C_S$  and the  $a_1$  and  $b_1$  and the  $a_2$  and  $b_2$  classes coalesce. In the puckered ring configuration the symmetry is  $C_2$  and the  $a_1$  and  $a_2$  and the  $b_1$  and  $b_2$  classes coalesce.

TABLE 1.—POTENTIAL ENERGY DISTRIBUTION IN  $C_2S_2BCl$

	sym	B—Cl	B—S	C—S	CC	SBS	BSC	SCC	CIBS
1381	$a_1$	26	22	5	21	16	9	1	0
1258	$b_2$	0	80	5	0	0	3	5	7
1218	$a_1$	15	14	12	49	5	0	4	0
1158	$b_2$	0	23	16	0	0	1	53	7
951	$a_1$	1	0	76	18	0	0	4	0
604	$b_2$	0	3	20	0	0	23	54	0
577	$a_1$	20	47	0	7	9	11	6	0
368	$a_1$	40	1	1	4	34	18	1	0
245	$b_2$	0	12	0	0	0	1	0	87

#### 2-CHLORO-1,3,2-DITHIABOROLAN (I)

There is a striking agreement between the frequencies and intensities of the bands above  $600\text{ cm}^{-1}$  of compound (I) and of the non-phenyl vibrations of the phenyl analogue (II). The only appreciable differences occur near  $950\text{ cm}^{-1}$ , the distribution of intensity amongst the components of the intense absorption complex being a little different in the two cases, and the frequencies of the chloro-compound being a little above those of the phenyl derivative. Corresponding Raman lines are strongly polarized. The band complex of the phenyl derivative is naturally assigned as due to the phenyl boron stretching mode by analogy with corresponding mass-sensitive bands of other phenyl derivatives.<sup>7</sup> Two arguments refute such a simple explanation. In the first case the computations presented in part I showed how considerably the B—Cl stretching mode mixed with other modes. Indeed, for the dioxa-analogue the band near  $1000\text{ cm}^{-1}$  was computed to have a relatively low B—Cl contribution. The mass changes inherent in substituting sulphur for oxygen could seriously affect the potential energy distribution, so this has been

\* The subsequent discussion relates only to frequencies below *ca.*  $2000\text{ cm}^{-1}$ .

computed for (I) (table 1). This indicates an even smaller B—Cl contribution. However, the cause of the mixing is the kinetic condition of momentum conservation more than the force field effects. The second argument is based on the spectra. It is difficult to estimate the effective mass of the phenyl ring but it ought to be less than that of the chlorine atom; first, the vibrational frequencies of the aromatic ring are close to the frequency of the band in question. Coupling of the modes will therefore occur rather than the phenyl unit vibrating as an entity. This indicates that the effective mass should probably be within twice that of an isolated carbon atom. Further, the B—Cl force constant is less than that of the B—C force constant in boron trimethyl.<sup>8</sup> This, in turn, should be less than that of the B-phenyl due to the  $\pi$  electron contributions to the bonding. This again will tend to reduce the "natural" B—Cl frequency as compared to the "natural" B-phenyl. The experimental evidence is that the frequency of the complex is higher for (I) than for (II). By the rule of mass effects<sup>9</sup> this indicates that the natural B-phenyl frequency lies above  $920\text{ cm}^{-1}$  and the natural B—Cl frequency lies below  $970\text{ cm}^{-1}$ . Mixing of modes then depresses the frequency of the intense complex in (II) but increases it in (I). It is believed that the principal contributing mode to both these complexes is the B—S stretching mode.

For a planar ring skeleton there are five  $a_1$  skeletal modes and two  $a_1$   $\text{CH}_2$  modes, a wag and a scissoring deformation. By analogy with the 1,2 disubstituted ethanes<sup>10</sup> the wag and scissoring modes are expected near  $1250$  and  $1430\text{ cm}^{-1}$ . The calculations of part 1 predict that the two highest skeletal modes are near  $1380$  and  $1220\text{ cm}^{-1}$ . These points show that the five strong polarized Raman bands at  $996$ ,  $948$ ,  $668$ ,  $477$  and  $338\text{ cm}^{-1}$  and the less strong  $841\text{ cm}^{-1}$  band are to be associated with the three remaining  $a_1$  fundamentals. The  $996$ ,  $948\text{ cm}^{-1}$  pair are readily explained as a fundamental in Fermi resonance with a combination band. The  $840\text{ cm}^{-1}$  band might be  $2 \times 420\text{ cm}^{-1}$ , though an alternative explanation is noted later. It seems unlikely that any of the other polarized bands arise from Fermi resonance and it is necessary to deduce that the skeleton is non-planar. The obvious mode possible for the additional band is the low-frequency rock. Other  $\text{CH}_2$  modes occur at too high frequencies to be responsible for the observed bands. The low-frequency rock belongs to the *A* class of gauche  $\text{XCH}_2\text{CH}_2\text{X}$  systems and is thus the out-of-phase mode. This would belong to the fully symmetric class of group  $C_2$  but not  $C_s$  showing that a thiaborolan ring is puckered and does not have the "envelope" configuration. The *B*-class rock is to be expected between  $900$  and  $800\text{ cm}^{-1}$ . Strong infra-red absorption occurs at  $840\text{ cm}^{-1}$  but a Raman band with this frequency shift is polarized. For the *B* rock to be polarized the ring must assume the envelope configuration but this is inconsistent with the previous analysis leading to a puckered ring unless the C—S—B angles are non-equivalent. This seems unlikely. The polarization of the Raman band is consistent with it being the overtone of a  $420\text{ cm}^{-1}$  fundamental. The strength of the infra-red absorption may be due either to some acquired intensity for the  $1010$ – $920\text{ cm}^{-1}$  complex or from overlapping with the *B*-type rock.

In the trans and in the gauche 1,2 disubstituted ethanes, the  $\text{CH}_2$  scissoring deformations all occur in the range  $1460$  to  $1410\text{ cm}^{-1}$ . In the gauche halogeno ethanes, the *A* and *B* deformations are not resolved and the Raman bands are depolarized. The  $1430\text{ cm}^{-1}$  bands are consequently identified with these modes. Four ring modes and four twisting and wagging modes remain to be located at frequencies above  $1000\text{ cm}^{-1}$ . On the present evidence they cannot be identified with certainty. The assignment presented in table 2 is based on the results of the computations as given in part 1 on the basis of a planar ring structure and on the expected ranges for the  $\text{CH}_2$  modes based on the analogous frequencies of the

ethylene dihalides.<sup>8</sup> These lead to the following approximate anticipated frequencies: *A* modes (skeletal) 1380, 1220 (CH<sub>2</sub>), 1325 and 1200 cm<sup>-1</sup>; *B* modes (skeletal) 1260, 1160 (CH<sub>2</sub>), 1350-1250, 1250-1100 cm<sup>-1</sup>. Clearly it is possible to identify all the major unassigned bands with the skeletal modes alone or with the CH<sub>2</sub> modes alone. A comparison of intensities with those of the ethylene dihalides would favour slightly the asterisked assignments.

## 2-PHENYL-1,3,2-DITHIABOROLAN (II)

A comparison of the observed spectra with those of phenyl boron dichloride leads to a classification of all absorption bands as phenyl vibrations or as alicyclic vibrations. The correspondence of frequencies and intensities is excellent throughout. We note the extreme weakness of the characteristic phenyl vibrations at 1500 cm<sup>-1</sup> which is due to an *a*<sub>1</sub> C—C stretching mode. This band is also very weak in the spectra of the corresponding borinan, but not in the -1,3,2-dioxaborolans and -borinans. It thus appears that this characteristic might

be diagnostic of the  $\begin{array}{c} -S \\ \diagup \\ B-\phi \\ \diagdown \\ -S \end{array}$  grouping when used in conjunction with the presence

of other characteristic phenyl vibrations. It is to be expected that the B— $\phi$  stretch will be near 1200 cm<sup>-1</sup> and it is certain that the very intense polarized Raman complex near this frequency is largely due to this mode probably interacting through Fermi resonance with the *a*<sub>1</sub> CH deformation. Of the remaining five mass-sensitive vibrations of the phenyl group<sup>7</sup> only three can be assigned with any degree of assurance. The *a*<sub>1</sub> vibration labelled *r* by Randle and Whiffen<sup>7</sup> and the low frequency vibration *x* have not been identified, but by comparison with other aromatics can be expected near 800 cm<sup>-1</sup> and near 200 cm<sup>-1</sup> respectively.

TABLE 2.—OBSERVED VIBRATIONAL FREQUENCIES OF 2-CHLORO-1,3,2-DITHIABOROLAN AND THEIR ASSIGNMENTS

Raman		infra-red	ring modes assignments	CH <sub>2</sub> modes
1433 vs	dp	1428 s		<i>A</i> , <i>B</i> ( $\delta$ )
1360 w	( $\sim 0.15$ )	1378 m	<i>a</i> <sub>1</sub> (calc. 1381)	
1291 m	(0.4 <sub>1</sub> )	1282 s		<i>A</i> (W)
1262 mw	dp	1258 m	<i>b</i> <sub>2</sub> (calc. 1258) *	<i>B</i> (W)
1215 w	( $\sim 0.8$ )	1197 w		<i>A</i> (T) *
1173 s	(0.6 <sub>1</sub> )	1162 w	<i>a</i> <sub>1</sub> (calc. 1218) *	
1128 ms	dp	1118 m	<i>b</i> <sub>2</sub> (calc. 1158) *	<i>B</i> (T)
996 s	(0.7 <sub>3</sub> )	1010 vs	} <i>a</i> <sub>1</sub> (calc. 951) + (2 $\times$ 477) + (338 + 668)	
977 sh		970 vvs		
948 m	(0.1 <sub>9</sub> )	942 vvs		
		920 vs		
841 m	(0.6 <sub>0</sub> )	840 s-vs	2 $\times$ 420	<i>B</i> (R)
760 vw		755 w		
		669 w-m		
668 vvs	(0.2 <sub>7</sub> )	664 s	} <i>a</i> <sub>1</sub> (calc. 577) +	<i>A</i> (R)
477 vvs	(0.01 <sub>1</sub> )			
460 sh		457 w		
420 m	dp	410 m	<i>b</i> <sub>2</sub> (calc. 604)	
338 vs	(0.4 <sub>1</sub> )	326 m	<i>a</i> <sub>1</sub> (calc. 368)	
		294 vw		
220 s	dp		<i>b</i> <sub>2</sub> (calc. 245)	

\* preferred assignments

dp measured ratios 0.8-0.9

The non-aromatic bands above  $600\text{ cm}^{-1}$  are explained in a similar manner to their counterparts in the chloro-compound. The low-frequency spectra of the two ring compounds do not agree, showing that the low-frequency modes are much more sensitive to the ring substituent. This is as expected but renders assignments more difficult. As a result of the increased restoring force on the inter-ring bridging carbon atom as compared with that on the chlorine, and as a result of the higher mass of the chlorine atom, it is to be expected that the phenyl substituent frequencies will be appreciably higher than those of the chloro compound. In particular, it seems reasonable that the  $477\text{ cm}^{-1}$  band of the chloro derivatives should be increased to above  $600\text{ cm}^{-1}$  and it is proposed that the two intense polarized Raman lines at  $675$  and  $642\text{ cm}^{-1}$  are due to two  $a_1$  fundamentals in resonance. However, it is disconcerting to have a strong polarized Raman band at  $260\text{ cm}^{-1}$  which must be compared with the  $338\text{ cm}^{-1}$  band of  $\text{C}_2\text{S}_2\text{BCl}$ . Other low-frequency assignments are difficult to justify and are listed as tentative proposals.

TABLE 3.—OBSERVED VIBRATIONAL FREQUENCIES OF 2-PHENYL-1,3,2-DITHIABOROLAN AND THEIR ASSIGNMENTS, TOGETHER WITH THE RELEVANT DATA FOR PHENYL BORON DICHLORIDE

$\text{S}-(\text{CH}_2)_2-\text{S}-\text{B}-\phi$ infra-red                      Raman		$\phi\text{BCl}_2$ infra-red	Raman	present in $\text{S}-(\text{CH}_2)_2-\text{S}-\text{B}-\text{Cl}$	assignment
1597 ms	1641 m 1600 vvs dp	1592 s			$\phi a_1 \nu_{\text{CC}}$ , $b_2 \nu_{\text{CC}}$
1495 vw	1548 w dp 1499 ms (0.57)	1488 w			$\phi a_1 \nu_{\text{CC}}$
1436 s 1427 m	1439 s dp	1433 ms		yes	$\phi b_2 \nu_{\text{CC}}$ Ac ring mixed
1336 w	1345 w				$a_1$ (1381) + $\text{CH}_2$ def
1313 vw 1284 m	1289 ms	1311 w 1271 m		yes	Ac ring? or $\text{CH}_2$ twist
1263 ms	1261 sh			yes	Ac ring? or $\text{CH}_2$ twist
1248 m 1236 vs	1238 vvs (0.36)	1244 s 1233/1221 vs			$\phi a_1 \nu_{\text{B}-\phi}$
1188 w 1164 m.w 1114 w	1193 s (0.41) 1163 vs (0.66) 1117 m dp	1188 m.s 1160 v.w		yes	$\phi a_1 \beta_{\text{CH}}$ $\phi b_2 \beta_{\text{CH}}$ Ac ring $b_2 \nu_{\text{CS}}$
1075 v.w 1034 vw 1002 m sharp 990 mw 955 ms	1074 m (0.41) 1036 vs (0.32) 1000 vs (0.4)	1001 m	1005		$\phi a_1 \beta_{\text{CH}}$ $\phi a_1 \nu$ ring
936 m 913 vs	957 w dp 908 w dp	968 m 953 s 920 vs		yes	Ac. ring $a_1$ $\nu_{\text{CS}}$

TABLE 3.—*contd.*

$\text{S}-(\text{CH}_2)_2-\text{S}-\text{B}-\phi$ infra-red Raman		$\phi\text{BCl}_2$ infra-red	Raman	present in $\text{S}-(\text{CH}_2)_2-\text{S}-\text{B}-\text{Cl}$	assignment
904 vs		899 vs			$\nu_{\text{CC}} + \text{CH}_2$ rocks
842 ms	854 w 803 w dp	757 s 691 s			
751 s	758 m dp				
694 s					$\phi b_1 \gamma_{\text{CH}}$
665 m	675 vs (0.6 <sub>7</sub> )				$\phi b_1 \gamma_{\text{CH}}$
632 s	642 vs (0.5 <sub>5</sub> )	633 m	640 m	yes	$\phi b_1 \gamma_{\phi\text{B}}$ ring
618 w	626 s dp	618 w	626		$\phi b_2 \alpha_{\text{CC}}$
579 vw		597 v.w			
547 m	543 dp	565, 551 m			$\phi$ vib.
535 s					
454 w	462 m dp				$\phi$ vib. $\gamma$
435	443 vs dp 407 w	445 vw 402 w		yes	Ac $\delta\hat{\text{C}}\text{CS}$ $\phi a_2 \phi_{\text{CC}}$
392 m					
347 vw					
304 s					Ac ring buckle
268 s	260 s (0.4 <sub>1</sub> )				Ac $a_1$ ring def.
			234		
	182 s		142		Ac torsion

## ABBREVIATIONS

Ac = acyclic,  $\phi$  = phenyl, vib. = vibration, s = strong, m = moderate, etc.

Numbers in parentheses refer to measured polarization ratios where these differ from 6/7. Due to experimental conditions, these values are not as reliable as for chloro analogue and little weight is to be attached to second significant figure.

<sup>1</sup> Finch and Steele, *Trans. Faraday Soc.*, 1964, **60**, 2125.

<sup>2</sup> (a) Finch and Pearn, *Tetrahedron*, 1964, **20**, 173. (b) Finch and Gardner, *J. Inorg. Nucl. Chem.*, 1963, **25**, 927.

<sup>3</sup> Hendra, Lane and Smethurst, *J. Sci. Instr.*, 1963, **40**, 457.

<sup>4</sup> Edsall and Wilson, *J. Chem. Physics*, 1938, **6**, 124.

<sup>5</sup> Rank, Pfister and Grimm, *J. Opt. Soc. Amer.*, 1943, **33**, 31.

<sup>6</sup> Mulliken, *J. Chem. Physics*, 1955, **23**, 1997.

<sup>7</sup> Randle and Whiffen in *Report of the Molecular Spectroscopy Conference* (London, 1954) (Institute of Petroleum, 1955), p 111.

<sup>9</sup> Ladd, Orville-Thomas and Cox, *Spectrochim. Acta*, 1963, **19**, 1911.

<sup>9</sup> (i) Rayleigh's rule—see Wilson, Decius and Cross, *Molecular Vibrations* (McGraw-Hill, London, 1955), p. 190. (ii) Steele and Whiffen, *Trans. Faraday Soc.*, 1959, **55**, 369.

<sup>10</sup> Brown and Sheppard, *Trans. Faraday Soc.*, 1952, **48**, 128.