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A SPECTROSCOPIC STUDY OF PHENYLBORON HALIDES

FREDERICK C. NAHM, EUGENE F. ROTHERGY AND KURT NIEDENZU
Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506 (U.S.A.)

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SUMMARY

Phenylfluoroboranes have been prepared by the fluorination of the corresponding bromides with titanium tetrafluoride. The infrared spectra of the phenylhaloboranes, $R_{3-n}BX_n$ ($R=C_6H_5$, $X=F$, Cl, Br, I), have been recorded in the 4000–250 cm^{-1} region; an assignment of the fundamentals is suggested and characteristic frequency trends are discussed. An evaluation of the spectral data suggests that the structure of phenylfluoroboranes is distinctly different from that of the other halides in the series.

INTRODUCTION

With the advent of the organotin method[1,2] phenylboron chlorides and bromides have become convenient starting materials for the synthesis of organoboron compounds. Recently, a satisfactory method for the preparation of phenyliodoboranes has been advanced[3,4] and a convenient synthesis of phenylfluoroboranes is described in the present work. Since all of the possible phenylhaloboranes of the type $R_{3-n}BX_n$ ($R=C_6H_5$, $X=F$, Cl, Br, I) are now readily available a systematic study of their physical properties has become feasible.

In the present work an investigation of the infrared spectra of phenylhaloboranes is presented and particular emphasis is placed on an elucidation of frequency trends of boron–halogen vibrations and of specific vibrations of phenyl groups bonded to boron. Also, some magnetic resonance data are discussed briefly.

The infrared spectra of a few selected arylhaloboranes in the potassium bromide region have been reported previously[5] and Becher has discussed the inner vibrations of phenyl groups bonded to boron in aminoborane systems[6,7]. Utilizing these data in conjunction with the present results it is possible to assign the major vibrations of the phenylhaloboranes and to discuss characteristic frequency trends.

EXPERIMENTAL

Tetraphenyltin and the boron trihalides are commercial products. Dichlorophenylborane was prepared by the reaction of tetraphenyltin with boron trichloride[8]. Modifications of this basic procedure[2,4] yielded the phenylhaloboranes of the type $R_{3-n}BX_n$ ($R=C_6H_5$, $X=Cl$, Br, I). The phenylfluoroboranes were prepared by the

TABLE 1

INFRARED SPECTRA OF PHENYLDIHALOBORANES, $C_6H_5BX_2$[a]

X=F	X=Cl	X=Br	X=I
3067 mw	3075 m	3072 mw	3071 mw
3042 m	3053 m	3052 mw	3052 mw
3031 m	3043 (sh)	3042 (sh)	
3019 m	3017 mw	3016 w	3018 w
1970 w	1965 w	1965 w	1963 w
1908 w	1907 w	1908 w	1911 w
1830 w	1820 w	1820 w	1818 w
1670 vw	1683 w	1685 w	1685 w
1608 s	1594 s	1603 m	1595 s
		1592 s	1585 (sh)
1499 mw	1489 mw	1493 w	1483 w
1442 s	1437 s	1438 s	1434 s
1388 (sh)	1386 mw	1385 w	1382 w
1378 s			
1340 vs	1341 mw	1340 w	1335 w
1310 m	1318 ms	1318 mw	1314 m
	1295 (sh)		
1288 w	1285 (sh)	1285 w	
	1277 s	1279 mw	1281 mw
		1247 s	1251 (sh)
			1238 ms
	1240 vs		
		1230 (sh)	
		1225 vs	1220 (sh)
			1208 vs
1188 vw	1190 s	1190 s	1193 s
1161 vw	1162 mw	1162 w	1161 w
	1101 m		
1077 ms			
	1075 mw	1072 w	1065 w (b)
1035 ms	1033 w	1033 w	1032 mw
1030 sh			
	1001 s	1001 m	1001.m
	963 s (sh)		
	949 s		
	910 vs		
		887 m	
		864 s	
			862 ms
850 vw (b)	850 mw	843 s	845 s
		808 vs	
			807 mw
760 w, b	756 s	755 s	753 s
			717 s
	705 (sh)	700 (sh)	691 (sh)
698 (sh)	690 s	689 s	685 s
670 vs			
646 (sh)			
	640 s		
620 mw	622 mw	622 mw	621 m
		607 ms	

TABLE 1 (*continued*)

X=F	X=Cl	X=Br	X=I
			591 m
			585 s
581 w			
569 m	568 m		
	551 s		
		538 mw	530 mw
		525 ms	
			510 (sh)
			500 m

[a] Frequencies in cm^{-1}; w weak, m medium, s strong, v very, sh shoulder, b broad.

interaction of the corresponding phenylbromoboranes with titanium tetrafluoride as outlined below[9]. All experiments were performed in an atmosphere of dry nitrogen. Infrared spectra were recorded on the neat liquids on a Perkin–Elmer Model 621 double-beam spectrophotometer using potassium bromide windows. (Cesium iodide reacts readily with the phenylhaloboranes.) Also, dilute solutions of the materials in carbon tetrachloride were recorded in the 4000–250 cm^{-1} region utilizing cesium iodide windows. All listed spectral data are the averages of several recordings.

Proton magnetic resonance spectra were recorded with a Varian spectrometer Model HA-60IL on the neat liquids with external TMS standard. ^{11}B NMR spectra were recorded at 19.3 MHz using boron trifluoride etherate as external standard.

Elemental analyses were provided by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

Phenyldifluoroborane (Typical fluorination experiment)

Phenyldibromoborane, 24.8 g (0.1 mole) and titanium tetrafluoride (11.4 g, 0.1 mole) were mixed in a dry nitrogen atmosphere to give a pasty material. The mixture began to liquify after stirring for about 15 min and within one half hour all of the material was liquid. The mixture was heated to gentle reflux for two hours and phenyldifluoroborane, b.p. 66–68° (lit.[10] 98°; lit.[2] 78°), was stripped from the reaction mixture to yield 4.9 g (49%) of pure material. (Found: C, 56.7; H, 3.9; B, 8.5; F, 29.6. Mol. wt. (by cryoscopy in benzene), 123. $C_6H_5BF_2$ calcd.: C, 57.23; H, 4.00; B, 8.59; F, 30.18%. Mol. wt., 125.91.)

In an analogous procedure diphenylfluoroborane, b.p. 42°/100 mm, was prepared from diphenylbromoborane (24.5 g, 9.1 mole) and titanium tetrafluoride (11.4 g, 0.1 mole) in 54% yield (10 g). (Found: C, 77.9; H, 5.5; B, 5.6; F, 10.1. Mol. wt. (by cryoscopy in benzene), 179. $C_{12}H_{10}BF$ calcd.: C, 78.32; H, 5.48; B, 5.88; F, 10.32%. Mol. wt., 184.02.)

INFRARED SPECTRA OF PHENYLHALOBORANES

Analysis of the infrared spectra was accomplished in several steps. By comparing the spectra of all the phenylhaloboranes and utilizing previous data[7] on (dimethylamino)diphenylborane it was possible to select the inner vibrations of

TABLE 2

INFRARED SPECTRA OF DIPHENYLHALOBORANES, $(C_6H_5)_2BX^a$

X=F	X=Cl	X=Br	X=I
3091 m	3092 w (sh)	3089 w	3086 w (sh)
3077 m	3079 m	3077 m	3072 m
3061 m	3052 m	3054 m	3052 m
3040 s	3045 w (sh)	3030 w (sh)	3031 w (sh)
1960 w	1964 w	1962 w	1960 w
1907 w	1907 w	1907 w	1905 w
1815 w	1819 w	1812 w	1818 w
1606 ms	1600 s	1596 s	1592 s
1575 w	1593 s	1569 w	1568 w
1500 m	1489 mw	1490 mw	1488 mw
1481 m			1477 mw
1442 ms	1432 s	1438 s	1431 s
1394 (sh)	1377 m (sh)		
1375 m	1359 s		
1348 ms	1344 s		1350 m
1338 (sh)	1335 m (sh)		
1307 mw	1302 m	1306 ms	1303 ms
1289 mw	1271 ms	1275 s	1275 s
		1261 s	1260 s
		1251 m (sh)	1248 m (sh)
	1245 s		
	1222 s		
1181 mw	1187 ms	1187 ms	1187 ms
		1178 s	1175 (sh)
		1167 s	1166 s
			1144 (sh)
1078 m			
1055 w, b	1065 w	1066 mw	1067 mw
1027 mw	1022 m	1028 m	1028 mw
	998 m	997 m	996 m
	942 ms	925 w	924 w
935 w		925 w	924 w
	910 s		
906 w		907 w	903 w
	896 m	892 ms	887 m
		879 ms	872 ms
		867 ms	
		837 s	829 m
			811 s
750 w	753 s	760 s	755 s
	730 mw	743 s	740 s
710 (sh)			725 mw
700 (sh)			
696 mw			
688 (sh)	687 vs	689 s	688 s
671 w			
	631 ms	647 s	633 ms
	619 w	618 m	615 m
582 w	580 m	590 ms	601 mw
		580 s	585 mw
			571 ms

TABLE 2 (*continued*)

X=F	X=Cl	X=Br	X=I
	565 m		
	547 m	550 vw	550 w
			438 mw
	400 mw	393 mw	387 mw
	372 mw		

[a] See footnote, Table 1.

boron-bonded phenyl groups since their frequencies are quite constant. Subsequently, the boron–carbon(phenyl) modes were identified for each of the two series of compounds, $C_6H_5BX_2$ and $(C_6H_5)_2BX$. The frequencies of these latter modes are somewhat dependent upon the nature of the halogen bonded to the same boron atom. However, in each of the compounds they can be recognized by the similarity of their

TABLE 3

ASSIGNMENT AND COMPARISON OF THE MAJOR FUNDAMENTALS OF THE PHENYLDIHALOBORANES[a]

Modes	$C_6H_5BF_2$	$C_6H_5BCl_2$	$C_6H_5BBr_2$	$C_6H_5BI_2$
Inner vibrations of the phenyl groups				
ν(CH)	3067	3075	3072	3071
ν(CH)	3042	3053	3052	3052
ν(CH)	3019	3017	3016	3018
ν(CC)	1670	1683	1685	1685
ν(CC)	1608	1594	1592	1585
ν(CC)	1499	1489	1493	1483
ν(CC)	1442	1437	1438	1434
ν(CC)	(1388)	1386	1385	1382
ν(CC)	(1340)	1341	1340	1335
ν(CC)	1310	1318	1318	1314
δ(CH)	1188	1190	1190	1193
δ(CH)	1161	1162	1162	1161
δ(CH)	1077	1075	1072	1065
δ(CH)	1035	1033	1033	1032
δ(CH)		1001	1001	1001
γ(CH)		850	843	845
γ(CH)	760	756	755	753
δ(ring)	698	690	689	685
δ(ring)		622	621	620
B–C(phenyl) vibrations				
ν(B–phenyl)	1340	1240	1225	1208
δ(B–phenyl)	646	640	607	585
B–X vibrations				
ν(B–X)	1378	949	864	717
ν(B–X)		910	808	691
δ(B–X)	570	551	525	500

[a] In cm^{-1}.

band shape since they are strong and relatively broad absorptions. The observation of ^{10}B isotope bands facilitated identification of the modes. Finally, the boron–halogen modes were selected amongst the remaining absorptions of major intensity. A detailed discussion of the assignments can be found elsewhere[11].

The recorded spectra of the four diphenylhaloboranes are listed in Table 1, those of the phenyldihaloborane series are compiled in Table 2.

The assigned infrared vibrations for the two series of phenylhaloboranes are compiled in Tables 3 and 4. As expected, frequencies of the inner vibrations of the boron-bonded phenyl groups are virtually unaffected by the nature of the halogen bonded to the same boron atom. However, the latter exhibit a recognizable effect on the frequencies of the boron–phenyl modes. In the case of the phenylfluoroboranes observed frequency shifts are most pronounced and appear to be considerably larger than expected on the basis of mass or electronegativity differences.

Also, a larger than expected difference is noted for the B–F stretching mode as compared with the other boron–halogen stretches in the diphenylhaloborane series. In the phenyldihaloborane series two B–X stretching modes can be observed with the exception of the spectrum of the fluorine compound. In the latter case, either accident-

TABLE 4

ASSIGNMENT AND COMPARISON OF THE MAJOR FUNDAMENTALS OF THE DIPHENYLHALOBORANES[a]

Modes	$(C_6H_5)_2BF$	$(C_6H_5)_2BCl$	$(C_6H_5)_2BBr$	$(C_6H_5)_2BI$
Inner vibrations of the phenyl groups				
ν(CH)	3091	3092	3089	3086
ν(CH)	3077	3079	3077	3072
ν(CH)	3061	3052	3054	3052
ν(CC)	1606	1600	1596	1592
ν(CC)	1500	1489	1490	1488
ν(CC)	1442	1432	1438	1431
ν(CC)	1307	1302	1306	1303
δ(CH)			1275	1275
δ(CH)	1181	1187	1187	1187
δ(CH)	1078	1065	1066	1067
δ(CH)	1027	1022	1028	1028
δ(ring)		998	997	996
γ(CH)		896	892	887
γ(CH)	750	753	760	755
γ(CH)		730	743	740
γ(CH)	688	687	689	688
B–C(phenyl) vibrations				
ν(B–Ph)	1375	1335	1261	1260
ν(B–Ph)	1338	1222	1167	1166
δ(B–Ph)	671	631	647	633
δ(B–Ph)	582	580	580	571
B–X vibrations				
ν(B–X)	1348	910	837	811
δ(B–X)	696	565	550	438

[a] In cm^{-1}.

al degeneracy of the B–F stretching vibration with the B–C(phenyl) modes or a change in symmetry may explain the missing second B–F frequency.

All in-plane B–X deformational modes were assigned in a relatively small frequency region. The ranges of the various B–X vibrations can be summarized: B–F stretching modes, 1380–1330; B–Cl stretching modes, 950–900; B–Br stretching modes, 870–800; B–I stretching modes, 730–680; B–X deformational modes, 600–490 cm^{-1}.

The shifts of the B–X stretching modes for the chlorine, bromine, and iodine compounds appear to be completely due to mass and electronegativity differences among the halides. It should be noted that several frequencies observed in the spectra of the other phenylhaloboranes were not observed in the spectrum of the fluorine compound.

The present spectroscopic data make it possible to discuss the structure of the diphenylhaloboranes. It is reasonable to assume that the phenyl rings are distorted out of the skeletal plane of the molecule and, since the spectral data support C_2 symmetry and equivalent phenyl groups, this indeed appears to be the case for the chlorine, bromine, and iodine compounds. In the fluorine compound it seems reasonable to assume that the phenyl groups are virtually in the plane of the molecule. This coplanarity could explain the relatively high B–C(phenyl) stretching frequency and also the reduced number of observable fundamentals in the spectrum of the fluorine compound. If the phenyl groups are coplanar with the rest of the molecule, then the electron density of the ring will be more available for donation into the B–C(phenyl) bond, thus strengthening the bond. Also, the planarity of the phenyl groups will change the symmetry of the molecule, for which a possible conformation is C_{2v}. For C_{2v} symmetry, A_2 modes would be inactive in the infrared. However, this reasoning cannot be confirmed without adequate Raman data, which were not obtained since the compounds decomposed when introduced into a laser beam.

Summarizing the spectroscopic data on the phenylhaloboranes, the following statements can be made.

(1). The inner vibrations of boron-bonded phenyl groups do not vary appreciably throughout the series.

(2). The boron–carbon(phenyl) vibrations are readily identified and the assignments support the proposed structure with respect to ring distortion.

(3). The boron–halogen bond data show a shift for the chlorine, bromine, and iodine compounds relating to mass and electronegativity differences only. However, for the fluorine compounds there seem to be other factors present.

MAGNETIC RESONANCE SPECTRA

^{11}B NMR spectra were recorded on the phenyldihaloboranes and the following chemical shift data were obtained (Table 5).

A coupling constant J(BF) 59±5 Hz was observed for phenyldifluoroborane.

The proton magnetic resonance spectra of all phenylhaloboranes are typical spectra of a monosubstituted benzene ring in which substituents constitute an electron withdrawing group. Two groups of peaks are observed the area of which integrates to a low field/high field ratio of 2/3. The two less shielded protons are those in *ortho* position to the boron group attached to the benzene ring and the data are summarized in Table 6.

TABLE 5

^{11}B NMR DATA OF $C_6H_5BX_2$

X	Chemical shift δ (ppm)[a]	
	Found	Lit.[b]
F	−23.8	−24.8
Cl	−54.5	−54.8
Br	−56.1	−57.9
I	−44.6	−48.2

[a] Relative to external BF_3-etherate. [b] See ref. 2.

TABLE 6

PROTON MAGNETIC RESONANCE SPECTRA OF PHENYLHALOBORANES[a]

Compound	Chemical shift δ(ppm)	
	Ortho hydrogen	*Meta/para* hydrogen
$(C_6H_5)_2BF$	7.33 (7.68)	7.83 (8.22)
$(C_6H_5)_2BCl$	7.72	8.37
$(C_6H_5)_2BBr$	7.40 (7.97)	8.07 (8.35)
$(C_6H_5)_2BI$	7.72 (8.00)	8.43 (8.42)
$C_6H_5BF_2$	7.13	7.55
$C_6H_5BCl_2$	8.10 (7.87)	8.75 (8.53)
$C_6H_5BBr_2$	8.53 (8.08)	9.25 (8.87)
$C_6H_5BI_2$	8.42 (8.02)	9.20 (8.82)

[a] Center of peaks, neat liquids, external TMS references; chemical shift data in parenthesis are those observed on solutions in deuterobenzene.

MASS SPECTRAL DATA

Mass spectra were obtained on the phenyldihaloboranes, $C_6H_5BX_2$ with X = F, Cl, Br, and on diphenylbromoborane.

The mass spectrum of phenyldifluoroborane is fairly simple. The base peak at *m/e* 125 corresponds to the $(P-1)^+$ ion but the parent peak has a relative intensity of 94%. Additional peaks of high intensity are those due to a phenyl group and its fragments as well as for a BF_2 group. These data indicate that in phenyldifluoroborane the boron–carbon bond apparently is readily cleaved and the BF_2 group is left intact.

On the other hand, phenyldichloroborane has a base peak at *m/e* 122 indicating ready loss of HCl from the parent molecule. An analogous situation is noted in the spectrum of phenyldibromoborane where the base peak *m/e* 164 corresponds to a loss of HBr from the parent molecule. The spectrum of phenyldibromoborane is considerably more complex than the spectra cited above and has not been studied in detail.

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