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Self-Consistent Molecular Orbital Calculations on Organoboron Compounds

Part III. Dihalogenophenylboranes

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The π electronic structures of three dihalogenophenylboranes have been investigated by the Pariser-Parr-Pople method. The agreement between the observed and calculated electronic spectra is quite good.

Die π-Elektronen-Strukturen von drei Dihalogenphenylboranen wurden mit der PPP-Methode untersucht. Beobachtete und berechnete Elektronenspektren stimmen recht gut überein.

On a étudié par la méthode de Pariser-Parr-Pople les structures électroniques π de trois dihalogénophénylboranes. L'accord entre les spectres électroniques observés et calculés est assez satisfaisant.

In two previous papers [1, 2] the π electronic structures of the methylvinyl- and halogenovinylboranes were investigated by the Pariser-Parr-Pople L.C.A.O.–M.O.–S.C.F. technique [10, 11]. In this paper similar methods were used to study the π electronic structures of the dihalogenophenylboranes.

The positions of the electronic transition bands and corresponding extinction coefficients have been measured [5] for these compounds and are given below.

$PhBF_2$	α-band: 4.686, 4.642, 4.574, 4.537, 4.456, 4.425 eV	(ε_{max} 970)
	p-band: 5.442, 5.343, 5.237 eV	(ε_{max} 10500)
$PhBCl_2$	α-band: 4.711, 4.611, 4.525, 4.438, 4.413 eV	(ε_{max} 1110)
	p-band: 5.442, 5.343, 5.237 eV	(ε_{max} 23600)

1. Calculational Details

All the C–C distances were taken as 1.397 Å, the B–C distance as 1.55 Å [1] and the boron-halogen distances from ref. [12]. The one-centre repulsion integrals and the core Hamiltonian diagonal matrix elements were given the same values as those previously used [1]. For all the calculations the Mataga approximation [7] for the two-centre electron repulsion integrals was employed as it achieved better overall agreement between the observed and calculated energies of the first three excited states of benzene ($^1B_{2u}$, $^1B_{1u}$, $^1E_{1u}$) than the previous preferred 'refined' Mataga approximation [8] (see Tab. 1).

Four calculations, (a) to (d), were performed on each of the compounds. Calculations (a) and (b) used a value of -2.39 eV for β_{CC} and in the latter account was also taken of the polarisation of the σ-electrons in the boron-halogen bonds [13]. Calculations (c) and (d) were similar to those of (a) and (b) respectively, except that β_{CC} was given the value -2.33 eV. This yields better agreement with experiment [6] for the $^1B_{2u}$ state of benzene within the rest of our

Table 1. *Electronic states of benzene*

State	$^1B_{2u}$	$^1B_{1u}$	$^1E_{1u}$	$^3B_{1u}$
Observed energy (eV)	4.767	5.96[a]	6.76[a]	3.59[a]
'Refined' MATAGA approx. ($\beta_{CC} = -2.39$ eV)	4.821	4.940	6.985	—
MATAGA approx. ($\beta_{CC} = -2.39$ eV)	4.891	5.920	6.722	2.951
MATAGA approx. ($\beta_{CC} = -2.33$ eV)	4.771	5.800	6.602	2.823

[a] Ref. [*9*].

calculational framework than the 'universally' used value of -2.39 eV. The electronic states were constructed from linear combinations of the configurations generated from all possible one-electron excitations from the three highest occupied to the three lowest vacant molecular orbitals. The energies of all nine states and that of the lowest $n \rightarrow \pi^*$ transitions ($^{1,3}U$) were calculated.

2. Results

The energies and oscillator strengths of the electronic states from calculations (*a*) – (*d*) are presented in Tab. 2. The three highest are not recorded as their energies exceed 7.5 eV.

The first two calculated low energy transitions are in quite good agreement with the observed bands and their intensities, although only extinction coefficients are available for the latter. The best agreement is obtained when the C–C resonance integral is assigned the value -2.33 eV and allowance is made for the polarity of the boron-halogen bond. All the calculations yield oscillator strengths for the first two transitions which are in similar ratios to those of their measured extinction coefficients.

Table 2. *Electronic state energies and oscillator strengths*

Caln. No. Sym.	$E(^1\Psi_{0\rightarrow 1})f_1$ B_1	$E(^1\Psi_{0\rightarrow 2})f_2$ A_1	$E(^1\Psi_{0\rightarrow 3})f_3$ A_1	$E(^1\Psi_{0\rightarrow 4})f_4$ B_1	$E(^1\Psi_{0\rightarrow 5})f_5$ A_1	$E(^1\Psi_{0\rightarrow 6})f_6$ B_1
1. Difluorophenylborane						
a	4.827 .004	5.782 .049	6.561 1.127	6.611 1.055	8.044 .023	8.124 .068
b	4.764 .008	5.581 .171	6.400 .865	6.441 .803	7.440 .184	7.442 .317
c	4.711 .003	5.670 .044	6.446 1.100	6.496 1.040	7.903 .022	7.983 .063
d	4.650 .007	5.473 .162	6.281 .849	6.328 .790	7.299 .186	7.303 .310
2. Dichlorophenylborane						
a	4.838 .002	5.803 .040	6.583 1.159	6.621 1.046	8.177 .009	8.283 .048
b	4.812 .003	5.725 .092	6.508 1.090	6.553 .923	7.794 .045	7.815 .147
c	4.721 .002	5.689 .036	6.468 1.140	6.506 1.032	8.030 .009	8.137 .044
d	4.696 .003	5.614 .084	6.393 1.074	6.439 .914	7.653 .045	7.723 .014
3. Dibromophenylborane						
					(B_1)	(A_1)
a	4.840 .002	5.797 .047	6.575 1.165	6.615 1.008	7.691 .165	8.141 .002
b	4.824 .003	5.739 .090	6.518 1.123	6.560 .847	7.077 .316	7.630 .000
c	4.723 .002	5.684 .042	6.460 1.146	6.500 .997	7.630 .155	8.013 .007
d	4.708 .003	5.628 .082	6.403 1.107	6.448 .854	7.015 .290	7.561 .000

Table 2 (Continued)

Caln. No. Sym.	$E(^3\Psi_{0\to1})$ A_1	$E(^3\Psi_{0\to2})$ B_1	$E(^3\Psi_{0\to3})$ A_1	$E(^3\Psi_{0\to4})$ B_1	$E(^3\Psi_{0\to5})$ A_1	$E(^3\Psi_{0\to6})$ B_1	$E(^1U_{0\to1})$ A_2	$E(^3U_{0\to1})$ A_2
				1. Difluorophenylborane				
a	3.262	4.091	4.123	4.855	6.517	6.610	12.782	12.763
b	3.300	4.030	4.093	4.822	6.343	6.578	—	—
c	3.138	3.975	4.006	4.736	6.341	6.427	12.737	12.728
d	3.183	3.917	3.976	4.704	6.192	6.421	—	—
				2. Dichlorophenylborane				
a	3.407	4.108	4.133	4.853	7.599	7.683	8.671	8.639
b	3.397	4.085	4.121	4.835	7.271	7.326	—	—
c	3.289	3.991	4.015	4.735	7.440	7.519	8.605	8.595
d	3.279	3.969	4.003	4.718	7.134	7.279	—	—
				3. Dibromophenylborane				
					(B_1)	(A_1)		
a	3.415	4.113	4.138	4.853	7.436	7.592	7.496	7.487
b	3.414	4.099	4.133	4.844	6.658	7.369	—	—
c	3.296	3.996	4.020	4.735	7.388	7.436	7.451	7.442
d	3.296	3.983	4.015	4.726	6.612	7.233	—	—

3. Discussion

The electronic states which give rise to the three low-energy bands of benzene can be written as

$$\Psi\,(E'_{1u}) = \sqrt{\tfrac{1}{2}}\,(\psi_{1'}^{-1'} - \psi_1^{-1})\,,$$
$$\Psi\,(E_{1u}) = \sqrt{\tfrac{1}{2}}\,(\psi_{1'}^{-1} + \psi_1^{-1'})\,,$$
$$\Psi\,(B_{1u}) = \sqrt{\tfrac{1}{2}}\,(\psi_{1'}^{-1'} + \psi_1^{-1})\,,$$
$$\Psi\,(B_{2u}) = \sqrt{\tfrac{1}{2}}\,(\psi_{1'}^{-1} - \psi_1^{-1'})\,,$$

where 1, 1′ and −1, −1′ refer to the degenerate pairs of occupied and unoccupied molecular orbitals respectively. Their corresponding atomic orbital coefficients are given in Fig. 1.

In the dihalogenophenylboranes the degeneracies of these pairs are lifted as the molecular symmetry is lowered to C_{2v}. The 1′ and −1′ orbitals then correlate with b_2 orbitals and the 1, −1 pair with a_2 orbitals*. This can be seen from a comparison of the eigenvectors of difluorophenylborane with those of benzene [see Fig. 2, 3].

The energies of the a_2 orbitals do not differ appreciably from those of the corresponding 1 and −1 orbitals of benzene as they contain only a very small contribution from the fluorine atomic orbitals. This is also true for the highest occupied orbital of b_2 symmetry which contains only a small proportion of boron and fluorine. The lowest vacant b_2 orbital, however, contains an appreciable contribution from boron and is lower in energy than the corresponding −1′ orbital of benzene. A correlation diagram for the molecules is shown in Fig. 3.

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* The filled orbitals are numbered in order of increasing energy while the vacant orbitals (indicated by a negative sign) are in order of decreasing energy.

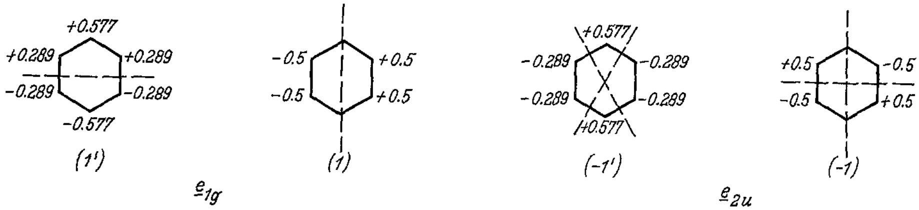

Fig. 1. AO coefficients of benzene MO's

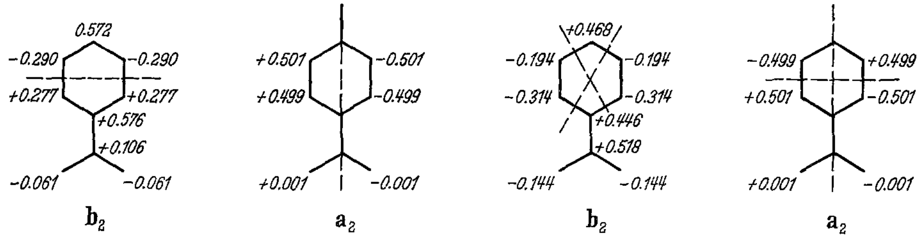

Fig. 2. AO coefficients of PhBF$_2$ MO's

The depression of the energy of the lowest vacant b_2 orbital is proportional to the square of the boron coefficient in this orbital as expected from perturbation theory. Moreover, the lowering is largest when boron is bonded to the most electronegative halogen atoms. The energies of the configurations and the electronic states arising from configuration interaction are shown in Fig. 4.

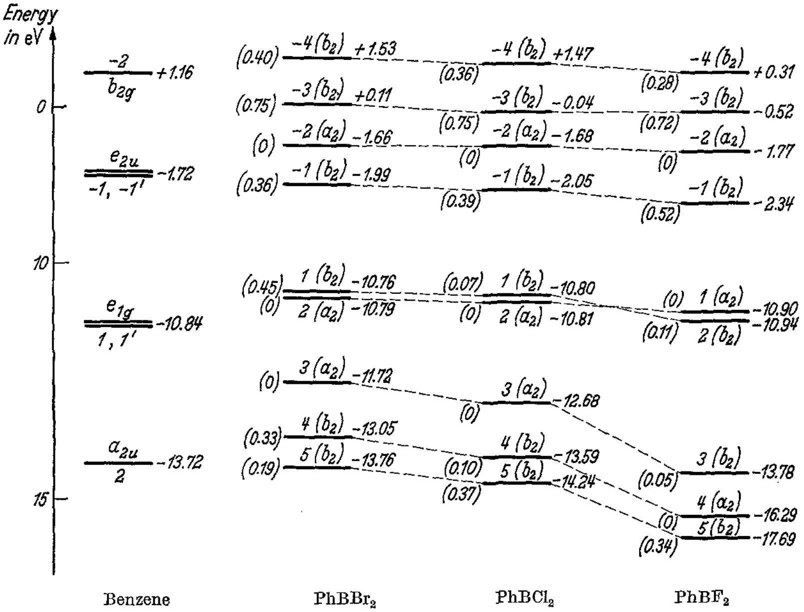

Fig. 3. Energies of molecular orbitals [from calc. (*d*)]. Symmetries of orbitals and boron mixing coefficients therein are in brackets. (No linear energy scale. MO's 3,4 of PhBCl$_2$ and PhBF$_2$ are wrongly joined.)

As expected, the configuration which has the lowest energy is that which involves a transition to the lowest vacant b_2 orbital from the highest filled a_2 orbital. This is red-shifted with respect to the corresponding transition in benzene. Strong interaction occurs between the first four low energy configurations and produces four excited electronic states corresponding closely to the $^1B_{2u}$, $^1B_{1u}$ and the (split) $^1E_{1u}$ states of benzene. The contributions from the principal spin configurations to the resultant electronic states are given in Tab. 3.

The weights of the configurations in these states approach those of benzene more closely on passing from difluoro- to dibromophenylborane. This is because the energy gap between the two highest filled a_2 and b_2 orbitals and the vacant b_2 orbital lessens in this order and this factor influences directly the contribution of the configurations $(a_2)^2\,(b_2)^1\,(b_2)^1$ and $(a_2)^1\,(b_2)^2\,(b_2)^1$ to the lowest states $^1\Psi_{0\rightarrow1}\,(B_1)$, $^1\Psi_{0\rightarrow2}\,(A_1)$. By contrast the magnitude of the contribution of these configurations to the third and fourth states $^1\Psi_{0\rightarrow3}\,(A_1)$, $^1\Psi_{0\rightarrow4}\,(B_1)$ are in the opposite order.

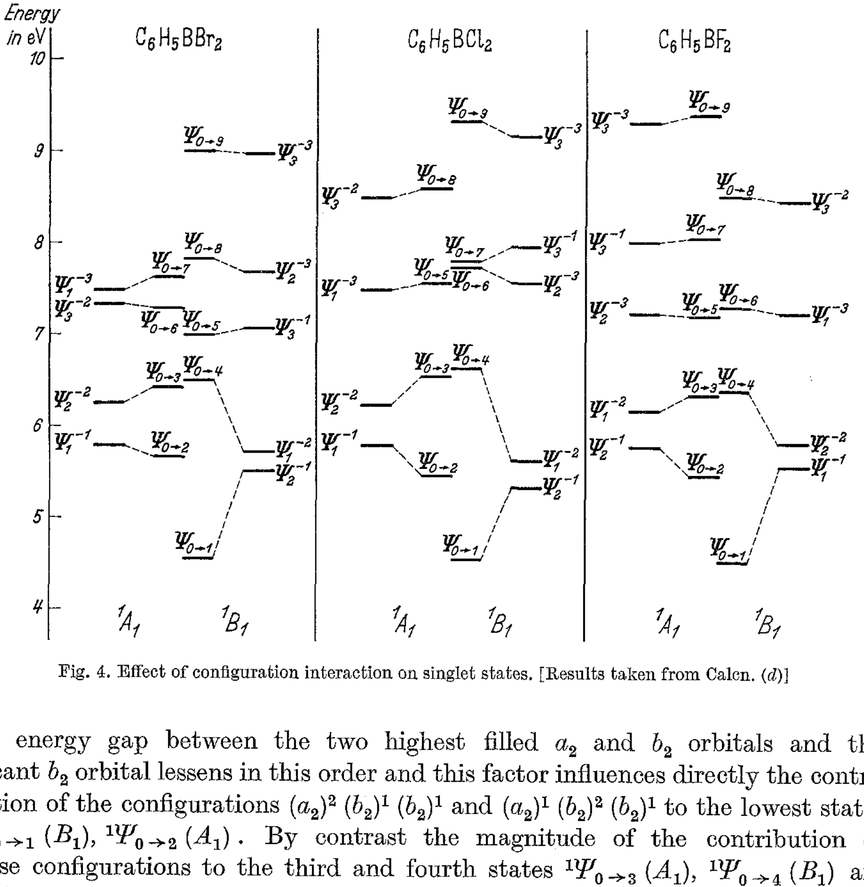

Fig. 4. Effect of configuration interaction on singlet states. [Results taken from Calcn. (*d*)]

The bathochromic shift of the first four electronic states of these compounds relative to those of benzene depends on the energies of the transitions to the first vacant b_2 level and therefore these shifts will be in the order $PhBF_2 > PhBCl_2 > PhBBr_2$. The five remaining electronic states are virtually unaltered by configuration interaction and are effectively transitions between single molecular orbitals.

The small transition moments for the first $^1B_1$ and $^1A_1$ states result from the virtual cancellation of the contributions from each configuration. The transition moments for the first $^1B_1$ and $^1A_1$ excited states are in the order $PhBF_2 > PhBCl_2$

Table 3. *Coefficients of the Principal Spin Configurations of the Electronic State*

Transition		Coefficients		Transition		Coefficients	
			Difluorophenylborane				
$^1\Psi_{0\to1}$	(B_1)	$.755\,\psi_1^{-1}$	$.629\,\psi_2^{-2}$	$^3\Psi_{0\to1}$	(A_1)	$.657\,\psi_1^{-2}$	$.703\,\psi_2^{-1}$
$^1\Psi_{0\to2}$	(A_1)	$.406\,\psi_1^{-2}$	$.911\,\psi_2^{-1}$	$^3\Psi_{0\to2}$	(B_1)	$.812\,\psi_1^{-1}$	$.528\,\psi_2^{-3}$
$^1\Psi_{0\to3}$	(A_1)	$.883\,\psi_1^{-2}$	$.382\,\psi_2^{-1}$	$^3\Psi_{0\to3}$	(A_1)	$.750\,\psi_1^{-2}$	$.627\,\psi_2^{-1}$
$^1\Psi_{0\to4}$	(B_1)	$.656\,\psi_1^{-1}$	$.733\,\psi_2^{-2}$	$^3\Psi_{0\to4}$	(B_1)	$.518\,\psi_1^{-1}$	$.848\,\psi_2^{-2}$
$^1\Psi_{0\to5}$	(A_1)	$.237\,\psi_1^{-2}$	$.948\,\psi_2^{-3}$	$^3\Psi_{0\to5}$	(A_1)	$.692\,\psi_2^{-3}$	$.665\,\psi_3^{-1}$
$^1\Psi_{0\to6}$	(B_1)	$.964\,\psi_1^{-3}$	$.259\,\psi_2^{-2}$	$^3\Psi_{0\to6}$	(B_1)	$.699\,\psi_1^{-3}$	$.691\,\psi_3^{-2}$
			Dichlorophenylborane				
$^1\Psi_{0\to1}$	(B_1)	$.663\,\psi_1^{-2}$	$.737\,\psi_2^{-1}$	$^3\Psi_{0\to1}$	(A_1)	$.710\,\psi_1^{-1}$	$.680\,\psi_2^{-2}$
$^1\Psi_{0\to2}$	(A_1)	$.854\,\psi_1^{-1}$	$.520\,\psi_2^{-2}$	$^3\Psi_{0\to2}$	(B_1)	$.598\,\psi_1^{-2}$	$.782\,\psi_2^{-1}$
$^1\Psi_{0\to3}$	(A_1)	$.517\,\psi_1^{-1}$	$.844\,\psi_2^{-2}$	$^3\Psi_{0\to3}$	(A_1)	$.662\,\psi_1^{-1}$	$.733\,\psi_2^{-2}$
$^1\Psi_{0\to4}$	(B_1)	$.736\,\psi_1^{-2}$	$.671\,\psi_2^{-1}$	$^3\Psi_{0\to4}$	(B_1)	$.801\,\psi_1^{-2}$	$.589\,\psi_2^{-1}$
$^1\Psi_{0\to5}$	(A_1)	$.989\,\psi_1^{-3}$	—	$^3\Psi_{0\to5}$	(A_1)	$.970\,\psi_1^{-3}$	$.243\,\psi_1^{-1}$
$^1\Psi_{0\to6}$	(B_1)	$.909\,\psi_2^{-3}$	$.386\,\psi_3^{-1}$	$^3\Psi_{0\to6}$	(B_1)	$.913\,\psi_3^{-1}$	$.390\,\psi_3^{-3}$
			Dibromophenylborane				
$^1\Psi_{0\to1}$	(B_1)	$.668\,\psi_1^{-2}$	$.734\,\psi_2^{-1}$	$^3\Psi_{0\to1}$	(A_1)	$.702\,\psi_1^{-1}$	$.694\,\psi_2^{-2}$
$^1\Psi_{0\to2}$	(A_1)	$.848\,\psi_1^{-1}$	$.529\,\psi_2^{-2}$	$^3\Psi_{0\to2}$	(B_1)	$.605\,\psi_1^{-2}$	$.780\,\psi_2^{-1}$
$^1\Psi_{0\to3}$	(A_1)	$.527\,\psi_1^{-1}$	$.840\,\psi_2^{-2}$	$^3\Psi_{0\to3}$	(A_1)	$.679\,\psi_1^{-1}$	$.720\,\psi_2^{-2}$
$^1\Psi_{0\to4}$	(B_1)	$.729\,\psi_1^{-2}$	$.668\,\psi_2^{-2}$	$^3\Psi_{0\to4}$	(B_1)	$.796\,\psi_1^{-2}$	$.597\,\psi_2^{-1}$
$^1\Psi_{0\to5}$	(B_1)	$.977\,\psi_3^{-1}$	—	$^3\Psi_{0\to5}$	(B_1)	$.940\,\psi_3^{-1}$	$.342\,\psi_3^{-3}$
$^1\Psi_{0\to6}$	(A_1)	$.999\,\psi_3^{-2}$	—	$^3\Psi_{0\to6}$	(A_1)	$.975\,\psi_1^{-3}$	—

$>$ $PhBBr_2$, those for the A_1 states being greater than those of the B_1 states. This is due to unequal weighting of the configurations which is greater for the A_1 states; this inhomogenity increases in the order $PhBBr_2 < PhBCl_2 < PhBF_2$ for both states.

Electron densities and bond orders

The bond orders and electron densities are shown in Tab. 4. In general, electron density on boron mainly originates from the halogen π orbitals and that contributed by the phenyl ring to the boron amounts to between 0.02 and 0.04.

Table 4. *Electron densities and bond orders*

	C_1	C_2	C_3	C_4	B	X	C_1–C_2	C_2–C_3	C_3–C_4	B–C_1	B–X
					[From Caln. (*c*)]						
$PhBF_2$	1.009	0.985	1.001	0.991	0.164	1.932	0.657	0.668	0.666	0.169	0.352
$PhBCl_2$	1.001	0.988	1.002	0.994	0.236	1.894	0.657	0.668	0.666	0.164	0.431
$PhBBr_2$	0.998	0.989	1.003	0.996	0.253	1.885	0.657	0.668	0.666	0.166	0.446
					[From Caln. (*d*)]						
$PhBF_2$	1.004	0.981	1.002	0.988	0.258	1.891	0.652	0.669	0.665	0.205	0.434
$PhBCl_2$	0.997	0.987	1.003	0.994	0.295	1.867	0.655	0.669	0.665	0.184	0.473
$PhBBr_2$	0.995	0.988	1.003	0.995	0.296	1.865	0.655	0.669	0.665	0.182	0.475

This is of the same magnitude as the contributions to boron from the vinyl and methyl groups found previously [*1*, *2*]. Alternatively one may regard the $-BX_2$ radical as a weak π-electron withdrawing group which has the greatest power for $-BF_2 > -BCl_2 > -BBr_2$. The π electron withdrawal from the *ortho* and *para* carbon atoms is more marked in the difluoro- than in the dichloro- and dibromo-phenylboranes and hence it should be more prone to nucleophilic attack.

The boron-carbon bond order is greatest in the difluoro-compound and is approximately equal in the dibromo- and dichlorophenylboranes. These bond orders may be correlated with the boron-phenyl stretching frequencies (see Tab. 5). Because the $-BX_2$ group acts only as a weakly perturbing influence on the benzene ring, as might be expected, the carbon-carbon bond orders differ only very slightly from those of benzene.

Table 5. Ph–B *stretching frequencies for the Dihalogenophenylboranes*

Compound	Ph–B stretching frequency (cm^{-1})
$PhBF_2$ [*4*]	1300 (^{11}B:1292)
$PhBCl_2$ [*3*]	1233 (^{11}B:1221)
$PhBBr_2$ [*3*]	1230 (^{11}B:1221)

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