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Preparation and HeI Photoelectron Spectra of the Dihaloboranes, HBX_2 (X = Cl and Br)

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Abstract: The unstable dihaloboranes, $HBCl_2$ and $HBBr_2$, have been generated in the gas phase from the virtually quantitative reaction of gaseous BX_3 with solid $NaBH_4$ at ca. 250 °C. HeI photoelectron spectra have been obtained and interpreted with the aid of ab initio calculations.

Previous studies of trigonal boron compounds with the use of ultraviolet photoelectron spectroscopy (UPS) have focused on the trihaloboranes,[1-4] mixed halogenomethylboranes,[5-7] and mixed species containing NR_2,[3,5,7,8] OR,[7] or SR[7] groups, with a view to investigating the bonding in such molecules. Essentially no studies of compounds containing a B–H bond in this simple planar environnment have been reported (apart from $(R_2N)_2BH$[8]), due mainly to the unstable nature of such molecules. In the gas phase, it is difficult to obtain pure samples of the HBX_2 (X = halogen) molecules because of their propensity to disproportionate to B_2H_6 and BX_3.[9-11] The free H_2BX molecules are essentially unknown, apart from the suggestion of the presence of H_2BCl in the gaseous reaction of B_2Cl_4 and B_2H_6.[12] In solution, species of the type HBX_2 and H_2BX (usually as etherates) function as mild selective reducing[13] and hydroborating agents.[14-16]

Gas-phase infrared spectra have been reported for the $HBCl_2$[17-20] and $HBBr_2$[21-24] molecules, usually in the presence of BX_3 and B_2H_6, although there is some controversy in the vibrational assignments.[25] The vibrationl frequencies and a force field for $HBCl_2$ have been calculated by the Green's function method.[26] Infrared and gas-chromatographic methods have been used to assess the composition of such mixtures.[9,27,28]

One of our primary goals is to establish techniques whereby unstable molecules can be generated in the gas phase for spectroscopic investigation. To this end we find the technique of photoelectron spectroscopy to be particularly efficaceous since it monitors all products of a reaction, thereby permitting reaction conditions to be optimized. We have applied this technique to a study of the HBX_2 molecules (X = Br, Cl, and F[29]), and have established the conditions for production of pure HBX_2 molecules. In the following sections we present the methods of production of the $HBCl_2$ and $HBBr_2$ molecules, their photoelectron spectra, assignments thereof, and the ab initio calculations used to assess their electronic structures. The photoelectron spectrum of HBF_2 is the subject of another paper[29] since it is more amenable to study by other theoretical methods including perturbation corrections to Koopmans' theorem.

Experimental Section

Preliminary experiments were conducted with the use of mixtures of BX_3 and H_2 subjected to either (a) thermolysis over Mg[30] or (b) a weak microwave discharge. In both cases the effluent was trapped and subsequently fractionated directly into the ionization chamber of a photoelectron spectrometer.[31]

Procedure a. An approximately 1:1 mixture of BCl_3 and H_2 was passed at low pressure (ca. 1–3 torr) over granular Mg in a 12 mm o.d. quartz tube maintained at ca. 500 °C over a 15 cm length. The reaction mixture was trapped at liquid-nitrogen temperature for about 60 min and slowly fractionated, with HCl, $HBCl_2$, and BCl_3 coming off in succession. With this method it proved feasible to obtain relatively clean spectra of $HBCl_2$. The technique was less successful however for the production of $HBBr_2$; yields were low, and it proved difficult to separate the desired product from HBr and excess BBr_3.

Procedure b. A mixture of BX_3 and excess H_2 flowing through a quartz tube at low pressure was subject to a weak microwave discharge. Again the products were collected, typically for 60 min, in a liquid-nitrogen-cooled trap and fractionated. For the BBr_3/H_2 system the products vaporized in the following order, B_2H_6, HBr, $HBBr_2$, and unreacted BBr_3. Spectra of pure $HBBr_2$ could be obtained by this method but the long-term stability of such a system was poor. Application of the discharge method to the synthesis of $HBCl_2$, although successful, resulted in much lower yields than the thermolysis method.

We should add that in neither case was there any evidence for the formation of B_2H_5X, an oft-postulated intermediate,[10-12,32,33] or, particularly in the case of the discharge method, B_2X_4.[34]

In the search for an efficient, stable, flow-system procedure capable of generating HBX_2 we were led to consider the classic diborane synthesis involving reduction of BX_3 with an active metal hydride[35] and studies involving reaction of BX_3 and B_2H_6.[10-12,35-38] In all such reactions the

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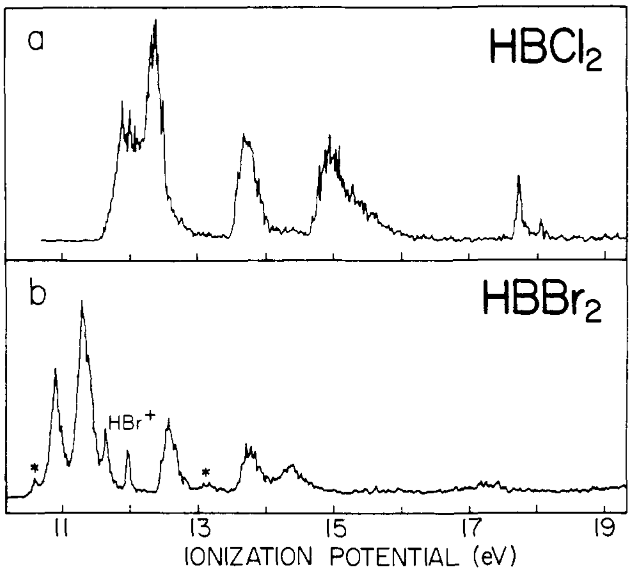

Figure 1. The HeI photoelectron spectra of (a) $HBCl_2$ and (b) $HBBr_2$. Asterisks are residual BBr_3.

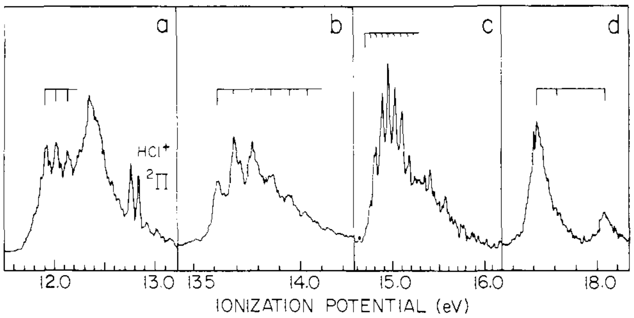

Figure 2. Expansions of the photoelectron spectrum of $HBCl_2$: (a) first three IP's (NeI); (b) fourth IP (NeI); (c) fifth and sixth IP's (NeI); and (d) seventh IP (HeI).

intermediacy of mono- and dihaloboranes is suggested, and so in a variant of these methods we have adopted a procedure (c) involving passage of gaseous BX_3 over *solid* sodium borohydride. This method proves to be extremely efficient for the formation of HBX_2 (X = Br, Cl, and F) in the gas phase at low pressure.

Procedure c. BX_3 at low pressure (1-3 torr) was slowly passed through a 12 mm o.d. Pyrex tube loosely packed over 15 cm with commerical crystalline $NaBH_4$. No reaction occurs at room temperature, but at ca. 250 °C, HBX_2 is formed, *virtually quantitatively*, and the photoelectron spectra can be obtained without the necessity of trapping and fractionating the products. Under these conditions there was no evidence for the intermediacy of B_2H_5X or H_2BX. The former have been isolated,[33] but the latter are extremely unstable, although we are making efforts to detect them. If the flow rate is too slow some B_2H_6 is formed (complete reaction), and if it is too fast, unreacted BX_3 passes through. At temperatures much in excess of 250 °C the solid $NaBH_4$ tends to decompose giving H_2.

The photoelectron spectrometer used in these experiments has been described previously.[31] Calibration was effected by using the known ionization potentials (IP's) of HX and Ar. Resolution was variable, but generally in the 25-40 meV range. HeI excitation was used, with the occasional use of NeI to investigate the possibility of autoionization, and to provide an assessment of band intensity changes.

Results and Assignments

The HeI photoelectron spectra of $HBCl_2$ and $HBBr_2$ are shown in Figures 1a,b, respectively. The spectrum of $HBCl_2$ is quite clean, and that of $HBBr_2$ shows some HBr (from hydrolysis of BBr_3) and traces of residual BBr_3 (asterisks). The spectra show no additional bands up to 21.2 eV. Expansions of those bands in $HBCl_2$ exhibiting vibrational structure are shown in Figure 2. The experimental IP's and associated vibrational structure are listed in Tables I and II for $HBCl_2$ and $HBBr_2$, respectively. Also included in Table I are the results of the ab initio calculations that we have performed on $HBCl_2$, using the extended basis set (ST04-31G) internal to the GAUSSIAN 70 program.[39] The quoted values are 0.92 of the Koopmans' values.[40] Since the gas-phase structure of $HBCl_2$ has not been definitively established (apart from a preliminary rotational analysis of the ν_1 fundamental[17]), we have assumed a planar structure, in keeping with all trigonal boron compounds, and bond lengths and angles estimated from those of similar molecules, viz., B-Cl = 1.728 Å; B-H = 1.189 Å and ClBCl, 120°. We have also performed some CNDO/BW calculations[41] for $HBCl_2$ and $HBBr_2$ (not reproduced here) where, for both molecules, the $3b_2$ and $2b_2$ orbitals are predicted to be excessively destabilized and the overall distribution is poor. However, these calculations do indicate that the assignments for $HBBr_2$ should closely follow those for $HBCl_2$.

By comparison with the BX_3 molecules[1-4] we expect replacement of one halogen by an H atom to lower the symmetry from D_{3h} to C_{2v} and raise the degeneracies of the three e orbitals. Two halogen p type orbitals are lost, bringing to seven the total number of expected orbitals in the HeI region when the three a type orbitals are included. This is supported by the ab initio calcu-

Table I. Cation States, Ionization Energies, Vibrational Structure and ab Initio Orbital Energies, ϵ_J, for $HBCl_2$

	experimental		calculated	
cation state	IP,[a] eV	ν^+,[b] cm^{-1}	molecular orbital[c]	ϵ_J, eV[d]
$\tilde{X}\,^2B_2$	(11.91) 11.91	860 ± 40	$4a_1$	−11.60
$\tilde{A}\,^2A_1$	12.35	(320 ± 40)?	$3b_2$	−11.63
$\tilde{B}\,^2A_2$	12.35		$1a_2$	−11.85
$\tilde{C}\,^2B_1$	(13.60) 13.68	650 ± 40	$1b_1$	−13.27
$\tilde{D}\,^2B_2$	(14.65) 14.95	610 ± 40	$2b_2$	−14.39
$\tilde{E}\,^2A_1$	15.29		$3a_1$	−15.27
$\tilde{F}\,^2A_1$	17.71	670 ± 60 2510 ± 40	$2a_1$	−17.79
			$1b_2$	−28.01

[a] Vertical IP's (adiabatic IP's in parentheses); all bands ±0.02 eV, except that at 15.29 eV (±0.05). [b] Corresponding molecular ground state values in cm^{-1} are, ν_1, ^{11}BH stretch, 2617; ν_2, ^{11}BCl stretch, 740; ν_3, ^{11}BCl symmetrical deformation, ~290 (calculated).[19] [c] Valence orbital numbering. [d] STO4-31G basis set. Koopmans' IP's scaled by 0.92. Total energy = −943.27106 au.

Table II. Ionization Energies, Vibrational Structure, and Assignment for $HBBr_2$

experimental		
IP,[a] eV	ν^+,[b] cm^{-1}	assignment[c]
10.92		$3b_2$
11.32		$4a_1$
11.42		$1a_2$
12.59	430 ± 60	$1b_1$
13.79	500 ± 60	$2b_2$
14.36		$3a_1$
17.2		$2a_1$

[a] Vertical IP's. All bands ±0.02 eV except the last. [b] Molecular ground state values in cm^{-1} are ν_1, ^{11}BH stretch, 2622; ν_2, ^{11}BBr stretch, 595; ν_3, ^{11}BBr symmetric deformation, ~185 (calculated).[22] [c] Valence orbital numbering.

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lations, Table I, where the eighth orbital is predicted at 28.01 eV. In the following discussion where a comparison with the BX_3 molecules is made, the orbital sequence and ionization energies from ref 3 are adopted.

The first two distinct bands in the photoelectron spectrum of $HBCl_2$ are within 0.45 eV of each other (Figure 2a), and must be assigned to three IP's belonging to the $3b_2$, $4a_1$, and $1a_2$ orbitals. Since the calculated values are within 0.25 eV, Koopmans' approximation clearly cannot be relied upon to give the correct ordering, particularly since a larger basis set, or change in geometry, could change the relative ordering. As the second band in both $HBCl_2$ and $HBBr_2$ is relatively more intense it probably contains two IP's. We place the $1a_2$ orbital of $HBCl_2$ in this band (12.35 eV) since, being unique, it is expected to be a sharp band in keeping with the observed Franck–Condon envelope. Also, since the $1a_2$ π type orbital is derived from the $1e''$ orbital of the corresponding BX_3 molecule its position will be essentially unchanged (cf. $1e''$, BCl_3, 12.54 eV, Figure 3).

The assignment of the remaining two orbitals within this group to $3b_2$ and $4a_1$ is not straightforward, since the ab initio calculation gives a separation of only 0.03 eV. The first IP of $HBCl_2$ (Figure 2a) with coincident adiabatic and vertical IP's (11.91 eV) exhibits a vibrational progression (860 ± 40 cm^{-1}) of at least four members, corresponding to an increased B–Cl stretching frequency (740 cm^{-1} for ν_2, ^{11}B–Cl stretch in the ground state molecule.[19] Assigning this band to the $3b_2$ (σCl) orbital concurs with the B–Cl antibonding character, and places it between the $1a_2'$ and $3e'$ orbitals of BCl_3 from which it is derived. This also follows the assignments for the highest occupied orbitals of CH_3BCl_2[7] and $FBCl_2$,[4] although the assignment of the former is reached contrary to the minimal and extended basis set calculations.[7] We do note, however, that for CH_3BCl_2, as the basis set becomes bigger, the b_2 and a_1 orbitals converge. The alternative assignment for the first band of $HBCl_2$ is to the $4a_1$ orbital (σCl with some B–H bonding), again with an increased vibrational frequency, and thereby following the assignment for the HBF_2 molecule,[29] where the $4a_1$ orbital is unequivocally the first occupied. We prefer the first possibility, however, even though it means a different ordering for $HBCl_2$ and HBF_2, since the $3e'$ orbital of BCl_3 from which the $3b_2$ and $4a_1$ orbitals partially derive should give the $4a_1$ orbital to higher energy as it is B–H bonding and therefore stabilized. Our ordering for the first three IP's is therefore $3b_2$, $4a_1$, and $1a_2$, the latter two being essentially degenerate. This is similar to the assignment reached for CH_3BCl_2 although we reiterate that it is feasible that the $3b_2$ and $4a_1$ orbitals could be interchanged.

The remaining four bands in the photoelectron spectrum of $HBCl_2$ are assigned to the $1b_1(\pi)$, $2b_2$, $3a_1$, and $2a_1$ orbitals, since they derive from the $1a_2''$, plus $1e''$, $2e'$, and $2a_1'$ orbitals of BCl_3[6] (Figure 3). This ordering also follows that obtained from the ab initio calculation (Table I). Thus, the fourth IP with adiabatic and vertical IP's of 13.60 and 13.68 eV is assigned to the $1b_1$ orbital which is B–Cl π bonding. An expansion of this band is shown in Figure 2b, where a vibrational progression of 650 ± 40 cm^{-1} is observed, extending over at least six members. This corresponds to the ν_2 frequence (B–Cl stretch) in the ion, reduced from a neutral value of 740 cm^{-1} (^{11}BCl)[19], in accord with the overall bonding character of this orbital (cf. the corresponding $1a_2''$ orbital of BCl_3; $\nu_1' = 406$ cm^{-1}, $\nu_1'' = 471$ cm^{-1})[3].

The next two IP's which are overlapping have maxima at 14.95 and 15.29 eV, and are assigned to the $2b_2$ and $3a_1$ orbitals, respectively, on the basis of the observed vibrational structure, relative intensities, and correspondence with the ab initio calculations. These orbitals derive from the $2e'$ orbital of BCl_3, and as with the first two occupied orbitals, the a_1 is stabilized relative to the b_2. The $2b_2$ orbital with adiabatic and vertical IP's of 14.65 and 14.95 eV (at $v' = 4$), respectively, gives a Franck–Condon envelope of at least nine components, which extend over the weaker $3a_1$ orbital (Figure 2c). The observed ionic frequency of 610 ± 40 cm^{-1} corresponds to a reduced B–Cl stretching frequency since this orbital is B–Cl bonding. This is rather nicely demonstrated by putting the ionic frequency and the difference between the vertical and adiabatic IP's into the empirical expression,[42] $I_v - I_a = 1.2(\omega''/\omega' - 1)$, whereby ω'' is calculated to be 760 cm^{-1}, in good agreement with the value for the neutral molecule. The $3a_1$ orbital is weakly B–Cl bonding, strongly Cl- - -Cl bonding, and B–H bonding. With the incorporation of H 1s character it is thus weaker in intensity, and apparently featureless.

The seventh and final IP at 17.71 eV is quite distinctive, being sharp with two resolvable vibrational frequencies of 670 ± 60 and 2510 ± 60 cm^{-1} (Figure 2d). These ionic frequencies correspond to reduced B–Cl and B–H stretching frequencies (ν_2'', ^{11}BCl, 740 cm^{-1} and ν_1'', ^{11}BH, 2617 cm^{-1})[19] in accord with the weak B–Cl and strong B–H bonding character of this, the $2a_1$, orbital. This orbital, mainly of B 2s character, is Cl 3s–B 2s antibonding and, Cl 3p–B 2s and H 1s–B 2s bonding giving a net nonbonding result. This is therefore analogous to the sharp band at 17.70 eV exhibited in the photoelectron spectrum of BCl_3. This band incurs no shift from BCl_3 to $HBCl_2$, and its position is reasonably well predicted by the ab initio results.

The assignment of the $HBBr_2$ photoelectron spectrum (Figure 1b) is taken to follow that for $HBCl_2$. There is an approximate 1 eV shift to lower IP for all bands except the seventh (Table II), due to a large halogen P orbital contribution to almost all of the valence orbitals. Again, three orbitals, $3b_2$, $4a_1$, and $1a_2$, must be placed in the first two bands at 10.92 and 11.32 eV, although there is an additional shoulder at 11.42 eV which we have assigned to the $1a_2$ orbital rather than a vibrational component. We therefore adopt the assignment for the first three orbitals as given in Table II. The fourth IP at 12.59 eV, which is assigned to the $1b_1$, πBBr orbital, shows 4–5 resolvable vibrational components with an ionic frequency of 430 ± 60 cm^{-1}, which, following the analogous band in $HBCl_2$, must belong to a reduced B–Br stretching frequency ($\nu_2'' = 595$ cm^{-1} for ^{11}BBr in the ground state molecule).[22] The $2b_2$ and $3a_1$ orbitals with vertical IP's of 13.79 and 14.36 eV are not as overlapped as in $HBCl_2$. The first exhibits a progression of at least seven members with an average vibrational frequency of 500 ± 60 cm^{-1}, again a slightly reduced B–Br stretching frequency. The final band at 17.2 eV is rather intriguing, since unlike the corresponding band of $HBCl_2$ it is broad and unstructured. The corresponding band in BBr_3 is also relatively broad and is split into two component 16.74 and 17.14 eV[2] (16.70 and 17.10 eV)[1]. This has puzzled earlier workers[2] but is a real effect and probably arises from a breakdown of the quasiparticle picture.[43] It is thus difficult to estimate whether the $2a_1$ orbital of $HBBr_2$ remains approximately the same as the corresponding orbital of BBr_3 (as in the $HBCl_2/BCl_3$ case) or is slightly stabilized. It is certainly no longer nonbonding since the Br 4s–B 2s antibonding character has now increased.

Discussion

With the assignment of the photoelectron spectra in hand, several interesting features may now be considered. We have alluded previously to a correspondence, particularly for the first four IP's, with the photoelectron spectra of the $MeBX_2$[6,7] and the $FBCl_2$[4] molecules, and so we shall not consider this in any detail here. The ordering for the first four orbitals of the $MeBX_2$ molecules (essentially the halogen lone pairs) is the same, viz., b_2, (a_1, a_2), b_1. For $FBCl_2$, four distinct bands are observed[4,44] and here the ordering is b_2, a_2, a_1, b_1; in this case the in-plane b_2 and a_1 orbitals are stabilized with the incorporation of the F atom, whereas the out-of-plane a_2 and b_1 orbitals remain essentially unchanged. This is a manifestation of the well-known perfluoro effect.

We should also point out a correspondence between the photoelectron spectra of $HBCl_2$ and B_2Cl_4. The local symmetry of the BCl_2 fragment (whose orbitals dominate the spectrum of HBX_2) is perturbed in the first instance by a single hydrogen atom;

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Table III. Gross Orbital Populations[a]

	B			Cl					
molecule	total	σ	π	total	σ	π	H total	LUMO, eV	$\Delta\pi$,[b] eV
BCl_3	4.632	4.199	0.433	17.123	15.244	1.879		+2.07	2.10
$HBCl_2$	4.666	4.367	0.299	17.181	15.307	1.874	0.971	+2.17	1.42
H_2BCl	4.695	4.538	0.157	17.237	15.371	1.866	1.034	+2.38	

[a] STO4-31G basis set. [b] Calculated π stabilization energy. $\Delta\pi$ BCl_3 = $1a_2'' - 1e''$, $\Delta\pi$ $HBCl_2$ = $1b_1 - 1a_2$.

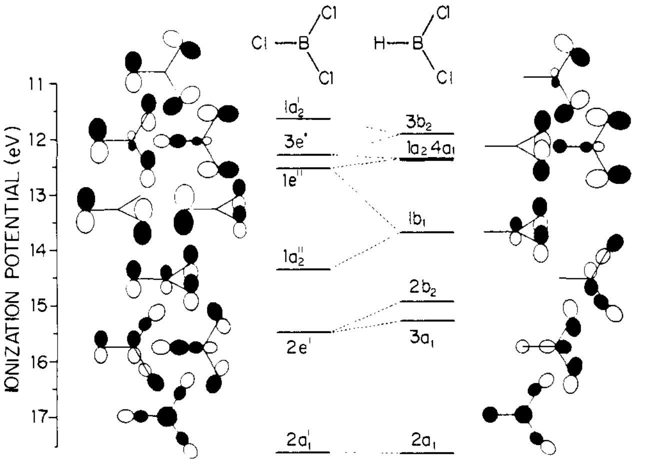

Figure 3. Schematic orbital diagrams and a comparison of the photoelectron spectra of $HBCl_2$ and BCl_3.

in the latter case the resulting spectrum derives from a combination of two BCl_2 units via. a direct B–B bond.

Figure 3 is instructive, since as well as illustrating the orbital character of the $HBCl_2$ molecule, it also shows how the orbitals derive from those of the corresponding BCl_3 molecule. All of the following comments are also germane to the $HBBr_2$ molecule. Starting from the lowest lying level it is apparent from the correlation that the B 2s ($2a_1$) orbitals are essentially unchanged, and those orbitals ($4a_1$ and $3a_1$) arising from the 3e′ and 2e′ orbitals of BCl_3 remain almost unchanged, whereas the $3b_2$ and $2b_2$ orbitals also arising from 3e′ and 2e′ are destabilized to the extent of 0.4–0.5 eV (0.5–0.6 eV for $HBBr_2$) since they have no H 1s character. The $1b_1$ out-of-plane π orbital in $HBCl_2$, derived from the $1a_2''$ and 1e″ orbitals of BCl_3, is destabilized to the extent of 0.67 eV (0.59 eV for $HBBr_2$), since it is now π bonding over only two chlorine atoms with some central B atom character. The other out-of-plane orbital, $1a_2$, in the $HBCl_2$ molecule is a reasonable facsimile of the 1e″ orbital of BCl_3 and so remains essentially unchanged. The two highest occupied molecular orbitals in BCl_3, $1a_2'$ and 3e′, are combinations of in-plane Cl 3p orbitals, and reduce to the $3b_2$ and $4a_1$ orbitals of $HBCl_2$. The net result is that the highest occupied molecular orbital of $HBCl_2$ ($3b_2$) has a higher IP than that of BCl_3 since removal of one of the antibonding Cl atoms reduces the halogen–halogen interaction. The stabilization is 0.29 and 0.27 eV for $HBCl_2$ and $HBBr_2$, respectively, relative to the corresponding trihalides. Since the halogen–halogen interactions are reduced, the separation of the in-plane and out-of-plane nonbonding orbitals ($3b_2$ and $1a_2$) also decreases relative to the separation between the corresponding orbitals ($1a_2$,′ and 1e″) of the BX_3 molecules.

The one orbital of great relevance to the chemistry of these molecules in terms of their Lewis acidity is the $2b_1$ orbital, the first unoccupied orbital, which has considerable boron pπ character and participates in the formation of donor–acceptor complexes. This orbital is not accessible via photoelectron spectroscopy, and so information on the relative Lewis acidity of these molecules is difficult to establish directly. Such an assessment is complicated by several competing effects, including the relative energy of the lowest unoccupied molecular orbital (LUMO), the reorganization energy, the differing σ and π effects, and for the small B atom steric effects. However, it has been suggested[2] that the difference between the occupied π levels ($\Delta\pi$ $1b_1/1a_2$, in this case), which gives a measure of the π stabilization, may indicate the relative acidity. As the nonbonding zero can be taken, to a first approximation, as the energy of the $1a_2$ level, which is virtually unshifted from the 1e″ of the corresponding BX_3 molecule, then the relatively large reduction in $\Delta\pi$ for the HBX_2 molecules is significant. The $\Delta\pi$ $1b_1/1a_2$ values for $HBCl_2$ and $HBBr_2$ are 1.33 and 1.17 eV, respectively, and so the π stabilization is less than that for the BX_3 analogues ($\Delta\pi$ = 1.82 and 1.47–1.82 eV for BCl_3 and BBr_3, respectively) implying, contrary to observations,[46] that the HBX_2 molecules are better Lewis acids. This decrease in $\Delta\pi$ is followed by the ab initio calculation for BCl_3, $HBCl_2$, and H_2BCl (Table III). However, this over-simplified view does not take into account the competition between the increasing positive charge at boron with increasing chlorination and the corresponding increase in B–Cl π bonding. In addition, the reorganization energy required to convert planar $HBX_2(C_{2v})$ to pyrimidal $HBX_2(C_s)$ will be different from that required for BX_3 $D_{3h} \rightarrow C_{3v}$. However, we might infer from the measured π stabilization energies ($\Delta\pi$) that $HBBr_2$ is a better Lewis acid than $HBCl_2$.

Some of the points raised can be clarified by looking at the calculated trends in the total charges for the series BCl_3, $HBCl_2$, and H_2BCl (Table III). These values are obtained from extended basis set (ST04-31G) calculations, using experimental (BCl_3) and reasonable estimated geometries ($HBCl_2$ and H_2BCl). Thus, there is an increasing positive charge (decreasing electronic population) on boron with increasing chlorination. This is in accord with the expected sequence of Lewis acidity, i.e., $BCl_3 > HBCl_2 > H_2BCl$.[46] However, if we now look at the π electron density on B this is seen to increase with increasing chlorination which would serve to decrease the Lewis acidity. The chlorine and hydrogen electron populations remain essentially constant. The LUMO energy (Table III) is seen to remain essentially constant with increased chlorination, although the fluoro analogues show a more pronounced trend with increasing fluorination.[47] The overall conclusion is that it is difficult to establish an ordering of Lewis acidities on the basis of measured π energies and valence double-ζ ab initio calculations. The only true tests would be direct measurements of the energies of the vacant orbitals and the reorganization energies.

Finally, we would like to make some comment about our ability to generate pure HBX_2 molecules in the gas phase, since in all previous work these molecules have been prepared in the presence of other species, particularly decomposition products. Unlike most previous methods which utilize mixtures of gases, e.g., B_2H_6/BX_3[10,11,38] or BX_3/H_2,[9,30] we have generated the HBX_2 species *directly* from the reaction of gaseous BX_3 and solid $NaBH_3$ at slightly elevated temperatures. Thus no other gaseous species are present during the initial synthesis which occurs at a low temperature and which may be represented by

$$4BX_3(g) + NaBH_4(s) \rightarrow 4HBX_2(g) + NaBX_4(s)$$

Once formed the disproportionation of these molecules is actually quite slow,[9,48] thus enabling us to observe them in the absence of B_2H_6 and BX_3, the major products.

Conclusion

The unstable HBX_2 molecules (X = Cl and Br) have been produced by three methods. The first two, pyrolysis of BX_3/H_2 mixtures and microwave discharge of the same, have limited

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application. A new flow route was devised, involving passage of BX_3 over solid $NaBH_4$; this results in the almost quantitative formation of the HBX_2 species (X = Cl, Br, and F[29]), enabling them to be studied by UPS. This route should also prove useful for the study of these molecules by other spectroscopic methods. The observed ionization energies have been assigned by comparison with those of the known BX_3 molecules, and with the aid of extended basis set ab initio calculations. The calculations also serve to assist with an assessment of the relative total and π electronic charge distribution for the series BCl_3, $HBCl_2$, and H_2BCl, which is relevant to the question of the Lewis acidity of these molecules.

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Phosphorus-Containing Cyclohexanes. Nuclear Magnetic Resonance Studies and Conformational Analysis of 1,3,2-Dithiaphosphorinanes[1]

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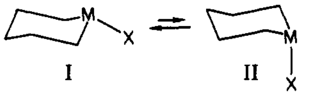
Abstract: Proton, carbon-13, and phosphorus-31 NMR spectroscopic data were obtained for a variety of tricoordinate 1,3,2-dithiaphosphorinanes as well as tetracoordinate 2-oxo and 2-thiono derivatives. The tricoordinate compounds adopt a chair conformation in which an axial orientation is strongly preferred for many polar and nonpolar P substituents (CH_3, C_2H_5, C_6H_5, OCH_3, Cl), but an equatorial orientation is strongly preferrd for the *P-tert*-butyl group. The 2-oxo compounds show a tendency to populate a twist conformation in solution, but the 2-thiono compounds do not. Single-crystal X-ray analyses of 11 derivatives (**5**, **6**, **7a**, **11b**, **19**, **20a**, **22**, **23**, **24**, **28**, **31**) are employed to verify structural assignments and to provide solid-state conformational viewpoints. Three 2-oxo compounds (**5**, **6**, and **28**) adopt a twist conformation in the solid state. A chloride-catalyzed chlorine-exchange process in 2-chloro-1,3,2-dithiaphosphorinanes and the stereospecificity of certain ^1H and ^{13}C NMR parameters are discussed. A general discussion of twist preferences in 1,3,2-dithiaphosphorinanes, and congeneric systems, is presented.

The equilibrium between chair conformations of monosubstituted cyclohexanes (eq 1, M = CH)[3,4] and N-monosubstituted piperidines (eq 1, M = N:)[5] favors the equatorial conformer, I, for almost every substitutent (X) studied (*A* value = $-\Delta G° = RT \ln K > 0$). However, conformational preferences can be substantially reversed in saturated, six-membered heterocycles which contain, in place of CH–X or N–X, atoms from the second or third row of the periodic table,[6] such as sulfur (S–X),[7] phosphorus (P–X),[8] selenium (Se–X),[7i,9] and arsenic (As–X).[10]



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In this connection, phosphorus-containing cyclohexanes have received considerable attention over the past decade.[11] Tricoordinate 1,3,2-dioxaphosphorinanes and 1,3,2-dithiaphosphorinanes exhibit axial preferences for both nonpolar (e.g., CH_3, C_6H_5) and polar (e.g., Cl, OCH_3) phosphorus substituents; phosphorinanes exhibit axial preferences for nonpolar groups at normal temperatures.[11] The reversal of energetics by introduction of tricoordinate phosphorus into a six-membered ring is dramatically illustrated by comparison[11] of free-energy values ($-\Delta G°$) for **1** (3.1 kcal/mol)[12] and **2** (~−1.2),[13] and for **3** (1.7)[4] and **4** (~−0.4).[8a,8b]

Our NMR studies,[14] and those of Robert and co-workers,[15] on tricoordinate 1,3,2-dithiaphosphorinanes have established that the ring adopts a chair conformation and that an axial orientation for phosphorus substituents strongly predominates for C_6H_5, OCH_3, Cl, CH_3, C_2H_5, and 1-aziridinyl groups; an equatorial orientation is highly favored for $t\text{-}C_4H_9$ and bulky dialkylamino

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