Photoelectron Studies of Boron Compounds I. Diborane, Borazine and B-trifluoroborazine

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Photoelectron studies of boron compounds
I. Diborane, borazine and *B*-trifluoroborazine

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The photoelectron spectra of diborane, hexadeuterodiborane, borazine and *B*-trifluoroborazine are presented, and adiabatic and vertical ionization potentials have been measured. The vibrational fine structure observed on some of the diborane bands is shown to be consistent with the forms of the molecular orbitals calculated by rigorous s.c.f. methods. The vertical i.p. of diborane are in better accord with a calculation which predicts a boron–boron bond in addition to the hydrogen bridge than with the calculations which indicate no direct boron–boron interaction. In borazine it is shown that the uppermost orbital is of π type rather than the σ type predicted by calculations, and that the extent of the π bonding, as measured by the energy separation of the π-type orbitals, is about 85% of that in benzene. The effect of fluorination of borazine, as in benzene, is to stabilize the σ orbitals more than the π orbitals.

INTRODUCTION

Compounds of boron frequently show unusual types of chemical bonding. The boron hydrides and their derivatives are all formally 'electron deficient' and their stability has only been satisfactorily explained in terms of delocalized molecular orbitals. The boron–nitrogen link is isoelectronic with the carbon–carbon link, and the physico-chemical relations between boron–nitrogen compounds and corresponding organic compounds have been studied for some time; in particular several molecular orbital studies of some boron–nitrogen compounds have been published in recent years. This paper reports a beginning study of the photoelectron spectra of representative boron compounds of both these types. Diborane is the simplest boron hydride and the simplest electron deficient molecule; borazine is isoelectronic with the simplest aromatic compound benzene. Comparisons with the available molecular orbital studies of these compounds are made, and the results on borazine are compared with photoelectron spectral studies of benzene.

EXPERIMENTAL

Diborane was prepared from lithium aluminium hydride and boron trifluoride etherate (Geanangel & Shore 1966) and stored under pressure in a cylinder. Samples for examination were vacuum distilled into glass bulbs, and the bulbs were stored at −25 °C until ready for use. Before running photoelectron spectra the diborane was frozen down and the bulb pumped out to remove any traces of hydrogen, and the spectrometer inlet system was filled by allowing the diborane to evaporate into it; this ensured that traces of any higher boron hydrides were not introduced. Infrared spectra showed no measurable amount of ethane, which is the only likely impurity of comparable volatility to diborane. Diborane-d$_6$, B_2D_6, was prepared from lithium borohydride-d$_4$ and boron trifluoride etherate. Infrared spectra showed the presence of traces of diethyl ether but no other impurity, and the photoelectron spectrum showed no diethyl ether.

Borazine was prepared by pyrolysis of a mixture of lithium aluminium hydride and ammonium chloride (Schaeffer, Schaeffer & Schlesinger 1951; Kennedy 1960), and *B*-trifluoroborazine was prepared by the method of Beyer, Jenne, Hynes & Niedenzu (1964). Both compounds were purified by vacuum distillation, and gas-phase infrared spectra showed no detectable impurities. Borazine was introduced into the photoelectron spectrometer in the same way as diborane, but the trifluoro derivative, which has a much lower vapour pressure, was allowed to evaporate into the instrument continually at room temperature.

The photoelectron spectra were obtained on a Perkin Elmer PS 15 spectrometer, which is similar to the instrument described by Turner (1968). Most of the spectra were obtained with a gas pressure of 6 to 7 N m^{-2} in the ionization chamber (Pirani gauge) and with the electron analyser slit set to give a peak width at half weight of 0.025 to 0.030 eV for the argon lines. Operation at higher resolution (0.020 eV) did not show any further detail but greatly reduced the signal strength. All the ionization potentials (i.p.) reported for diborane and borazine have been determined from runs in which argon, krypton or xenon have been added to the gas as an internal calibrant, but for *B*-trifluoroborazine the internal calibrants were added only occasionally; no significant variation of the calibration positions was observed between runs.

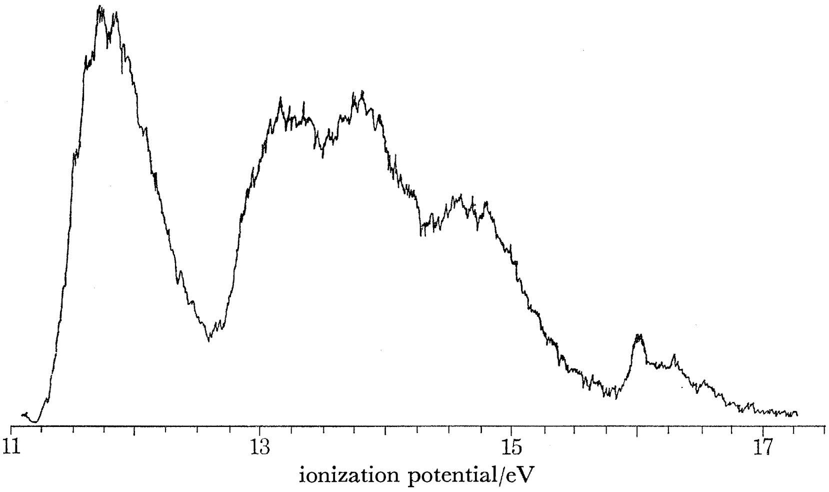

FIGURE 1. Photoelectron spectrum of diborane.

RESULTS

The spectrum of diborane is shown in figure 1. Five bands are observed and, beginning at the band of lowest i.p., the first, second and fifth of these show fine structure. Many of our spectra appear to show some very broadened structure in the third band but consistent readings of position could not be obtained except for the peak maximum; no structure of any kind could be detected in the fourth band. Figure 2 shows expanded scale runs over those bands which show reproducible structure. The first band shows a progression of at least eight components. Analysis of the spacings measured from twelve runs showed no significant departure from a constant value through the progression, and an average value of the spacing was calculated from readings of the positions of alternate components from the second to the seventh.

The second band shows a less clear progression of about five components, and between the second and third components a broad shoulder which may be part of another progression for which the other components are not resolved. The fifth band shows one clear progression with a fairly wide spacing and evidence of a weaker progression with a closer spacing.

The spectrum of diborane-d_6 is essentially similar to that of the ^1H compound, but structure is much less well resolved; the third band also seems to have somewhat greater intensity in the deutero compound. Appropriate portions of the spectra are shown in figure 3, and the structure which is resolved seems to be similar for the two isotopic compounds. Vibrational spacings were averaged over the components shown on figure 3.

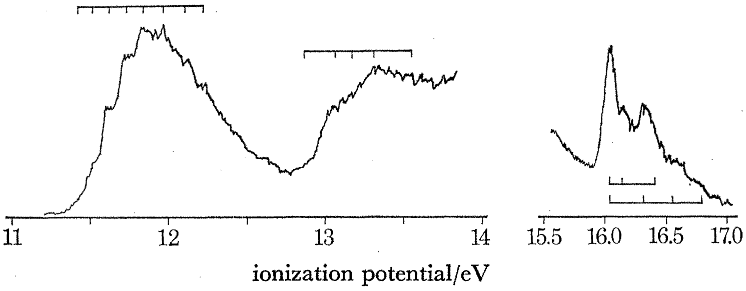

FIGURE 2. The fine structure of the diborane bands. Expanded scale runs over the first, second and fifth of the bands shown in figure 1.

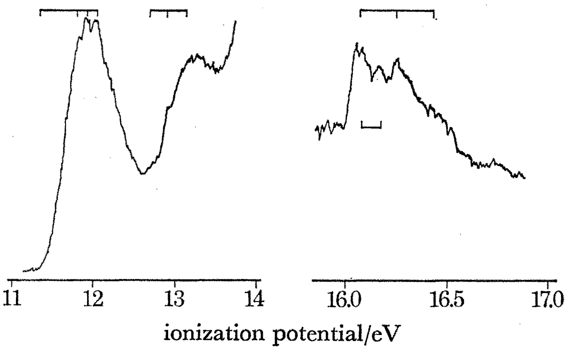

FIGURE 3. The fine structure in diborane-d_6.

Adiabatic i.p. have been estimated, where no vibrational structure is evident, as the apparent onset of the band plus the instrumental energy resolution, and vertical i.p. have been taken as peak maxima. Where vibrational spacing has been observed the maximum on the first component has been taken as the adiabatic i.p., since in all cases the onset of the band plus the energy half width is identical with the first component maximum, usually within one standard deviation but always within two standard deviations. The vertical i.p., where a vibrational progression continues through the band maximum, has been estimated as the mean of the two most intense components, weighted according to their intensities. The i.p. and vibrational spacings measured are recorded in table 1; the assignments are discussed in the following section.

The spectrum of borazine is shown in figure 4. Two of the bands show clear vibrational fine structure, and in addition the first band has a pronounced shoulder on the high i.p. side, and the band at 14.8 eV has a shape which suggests a similar splitting of smaller magnitude. The band in the region 11 to 12.5 eV has a more complex shape; there is a shoulder similar to that on the first band, but at higher i.p. there is also a distinct peak of fairly small intensity, the most reasonable interpretation of this is that the band has two main components, one intense band with a shoulder and a single weak band. A very similar structure in ethane has been assigned in this way (Price 1968). On this interpretation the borazine spectrum shows seven bands, three of which are weak and show no shoulders, three of which are strong and show shoulders or possible shoulders, and one band, that of highest i.p., which appears to be weak and shows a very pronounced shoulder. However, some of the apparent weakness of this last band is a result of the instrumental energy half width decreasing with decreasing electron energy (Turner & May 1966; Turner 1968) and a spectrum obtained with a slotted grid retarding field instrument (cf. Price 1968) shows that the intensity of this last band is higher than the intensities of the other weak bands, and may be comparable to that of the first band.

The band beginning at 13.8 eV shows pronounced vibrational structure, and is shown at a greater scale expansion in figure 5. Two vibrational progressions appear to be present, though the exact positions of the higher members are difficult to fix because of the onset of the much more intense 14.9 eV band. Three members of the more intense sequence can be observed,

TABLE 1. IONIZATION DATA FOR DIBORANE

band number	i.p./eV		vibrational spacings/cm^{-1}		assignments	
	adiabatic	vertical	B_2H_6	B_2D_6	vibrational	orbital
1	11.41 (2)	11.89 (2)	900 (60)	800 (120)	ν_3	$1b_{3g}$
2	12.83 (4)	13.30 (1)	1700 (300)	1500 (300)	ν_2	$3a_g$
3	13.81 (6)	13.91 (2)	—	—	—	$1b_{2u}$
4	14.42 (4)	14.75 (3)	—	—	—	$1b_{3u}$
5	16.08 (1)	16.11 (2)	2200 (150)	1500 (80)	ν_1	—
			1000 (140)	650 (160)	ν_3	$2b_{1u}$

Standard deviations are given in parentheses after each quantity; the number is in the same units as the least significant figure quoted for the quantity. Assignments are discussed in the text.

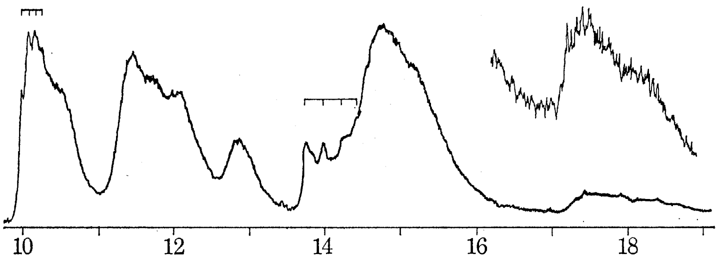

FIGURE 4. The photoelectron spectrum of borazine. The inset shows a portion at greater recorder expansion.

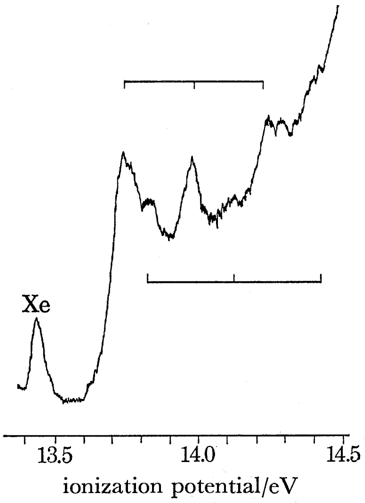

FIGURE 5. The fine structure in the 13.8 eV band of borazine. A trace of xenon was added for calibration.

and three weaker bands are observed as pronounced shoulders. These weaker bands have a distinctly wider separation than the strong bands. Vertical and adiabatic i.p., together with average vibrational spacings, are reported in table 2.

The spectrum of *B*-trifluoroborazine is shown in figure 6. Vibrational structure is observed on the first and fourth bands, with a single progression in each case, but the second band shows one main progression with weaker peaks in between. The separation of the first and third strong peaks (0.362 ± 0.008 eV) is probably significantly different from the separation of the first and third weak peaks (0.381 ± 0.004 eV) so we assume that there are two separate progressions, of which the more intense progression has almost double the spacing of the weak one.

TABLE 2. IONIZATION DATA FOR BORAZINE

band number	adiabatic i.p./eV	vertical i.p./eV	vibrational spacing/cm^{-1}	vibrational assignment	orbital assignment
1	9.88 (2)	10.14 (1)	700 (100)	ν_4	$1e''$
		10.50 (3) (sh)			
2	11.11 (6)	11.42 (2)	—	—	$4e'$
		11.73 (6) (sh)			
3	11.99 (3)	12.06 (3)	—	—	$1a_2''$
4	12.60 (9)	12.83 (2)	—	—	$1a_2'$
5	13.73 (1)†	13.84 (3)	1900 (150)	ν_2	$3a_1'$
			2400 (250)	ν_1	
6	—	14.76 (3)	—	—	$3e'$
7	17.10 (5)	17.47 (3)	—	—	$2e'$
		18.18 (7) (sh)			

Standard deviations are given in parentheses after each quantity. sh: inflexion point of shoulders observed. Assignments are discussed in the text: orbital numbering ignores 1s shells of B and N.

† The first observed component; this is not necessarily the adiabatic i.p., see text.

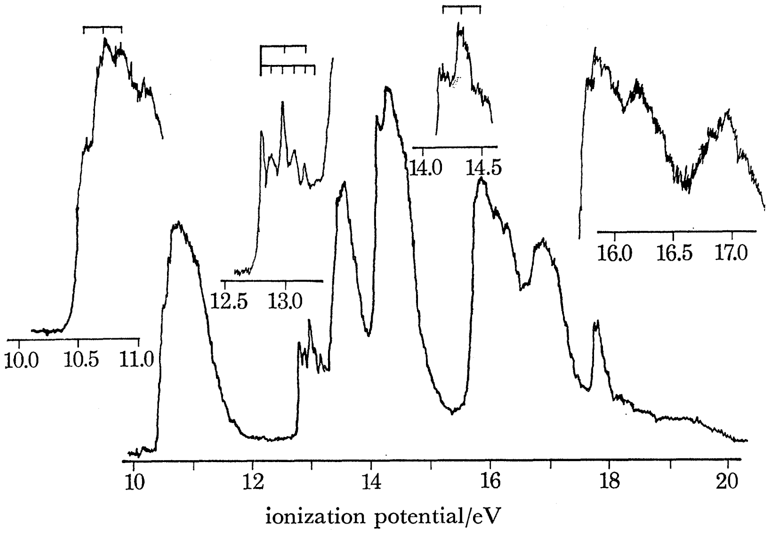

FIGURE 6. The photoelectron spectrum of *B*-trifluoroborazine. The insets show portions of the spectrum with a greater scale expansion, and a longer time constant.

As the inset on figure 6 shows, the region 15.5 to 17.4 eV contains three distinct peaks. The intensities of the peaks vary, but an approximate classification as strong or weak is possible, so that there are three weak peaks (12.98, 16.20 and 17.73 eV) and five stronger ones. The only band to show a distinct shoulder is the one of lowest i.p., though those at 14.29 and 16.87 show convex shapes on the high i.p. side. Vertical and adiabatic i.p. are recorded in table 3.

TABLE 3. IONIZATION DATA FOR *B*-TRIFLUOROBORAZINE

band number	adiabatic i.p./eV	vertical i.p./eV	vibrational spacing/cm^{-1}	vibrational assignment
1	10.46 (1)	10.79 (2)	1050 (160)	ν_2
2	12.85 (1)	12.98 (1)	1500 (120), 750 (100)	ν_2, ν_3
3	13.35 (1)	13.53 (3)	—	—
4	14.05 (1)	14.29 (2)	1200 (200)	ν_2
5	15.42 (2)	15.85 (3)	—	—
6	16.11 (3)	16.20 (5)	—	—
7	16.69 (2)	16.87 (4)	—	—
8	17.67 (3)	17.73 (2)	—	—

Standard deviations are given in parentheses after each quantity.

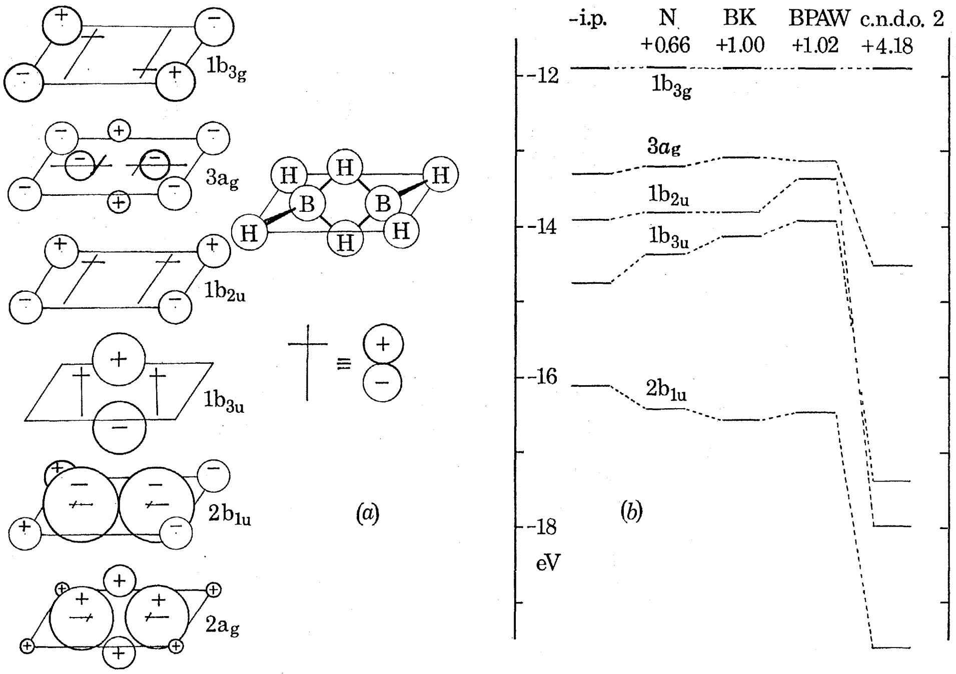

FIGURE 7. (*a*), valence orbitals in diborane. (*b*), the vertical i.p. of diborane compared with eigenvalues from calculations. The eigenvalues have been adjusted by adding the amounts of energy indicated to each set of calculations. N, results of Newton *et al.* (1965); BK, results of Burnelle & Kaufman (1966); BPAW, results of Buenker *et al.* (1966); c.n.d.o. 2, present calculations.

DISCUSSION

Diborane

Five bands are clearly observed in the photoelectron spectrum of diborane, in agreement with the prediction of a number of s.c.f. molecular orbital calculations, of varying degrees of rigour, that there are only five molecular orbitals of energy greater than −21.22 eV in this molecule. In figure 7*b* the measured vertical i.p. are compared with the eigenvalues from the three rigorous calculations available, those by Newton, Boer, Palke & Lipscomb (1965) who used a minimal basis set of Slater orbitals with optimized exponents,† by Burnelle & Kaufman

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† Similar results have been reported by Palke & Lipscomb (1966) for a non-optimized set of exponents; the eigenvalue differences are almost identical but the absolute eigenvalues differ by about 0.7 eV.

(1966) and by Buenker, Peyerimhoff, Allen & Whitten (1966); the latter groups used large Gaussian basis sets of orbitals. For this comparison the eigenvalues have been adjusted to obtain agreement with the experimental i.p. for the first band by adding to them the energies indicated in figure 7*b* so that relative energies rather than absolute energies are being compared. The agreement is seen to be very good; in particular the results of Newton *et al.* (1966) are in excellent agreement for the relative energies and also predict the first i.p. rather better than the other two calculations. For comparison with these accurate s.c.f. results a calculation by the c.n.d.o. 2 method of Pople & Segal (1966) has been carried out and the resulting eigenvalues are also shown in figure 7*b*. The orbital energy sequence predicted by this calculation is almost correct, as judged by the accurate calculations, but the overall energy spread is too large. Further c.n.d.o. 2 calculations are discussed in the following sections.

The agreement of the relative eigenvalues from the calculations with the measured vertical i.p. strongly suggests that the bands in the photoelectron spectrum may be assigned in the sequence of orbital types given by the calculations, and considerable evidence to support this is provided by the vibrational structure of the bands. The symmetry types of the principal valence orbitals are shown in figure 7*a* with approximate indications of their principal atomic orbital components. The orbitals have nodal surfaces such that they may be classified as bonding mainly the terminal hydrogen atoms ($1b_{3g}$, $2b_{1u}$ and $1b_{2u}$), the bridge ($1b_{3u}$) or the entire molecule ($2a_g$, $3a_g$). More detailed analysis of the bonding predicted by calculations may be carried out by evaluating overlap populations for the individual molecular orbitals. This has been performed using the results of Palke & Lipscomb (1966), and in the following we assume that the probability that a particular vibration will be excited upon ionization from an orbital is related to the partial overlap population of that orbital in the regions of the molecule which are most affected by the vibration.

The first photoelectron band shows only a single vibration of frequency 900 cm^{-1} (B_2H_6) or 800 cm^{-1} (B_2D_6). The length of the progression, or the large difference between adiabatic and vertical i.p., shows that the equilibrium conformation of the ground ionic state must be rather different from that of the molecule and that most probably the frequency of vibration will be appreciably different from that in the molecule (cf. Turner this volume, p. 7). The only comparable totally symmetric vibration frequencies in the molecule are (Nakamoto 1963) ν_3 (B_2H_6 1180 cm^{-1}, B_2D_6 915 cm^{-1}) and ν_4 (B_2H_6 794 cm^{-1}, B_2D_6 700 cm^{-1}); of these ν_4 is unlikely since an *increase* in frequency upon ionization implies occupancy of an antibonding orbital in the molecule. We take ν_3 as the most likely assignment, so the frequency in the ion is about 80 % of that in the molecule. ν_3 is essentially a bending mode of the terminal B–H bonds, so we deduce that the molecular orbital of highest energy is mainly localized in the region of the boron atoms and terminal hydrogen atoms, and since a bending rather than a stretching mode is excited it is likely that the orbital is directional, i.e. has a large boron p orbital component. This is fully consistent with the character of the orbital $1b_{3g}$ (see figure 7*a*); the B–H (terminal) overlap population is 0.23 with all other contributions to the total population very small.

The second photoelectron band shows a progression with a vibration frequency of 1700 cm^{-1} (B_2H_6) or 1500 cm^{-1} (B_2D_6). A shoulder additional to this progression appears in both B_2H_6 and B_2D_6 spectra but the corresponding vibrational spacing is uncertain. The progression corresponds to about 80 % of ν_2, the B–H stretching mode of the bridge. The orbital $3a_g$ is mainly B–H bridge bonding; the B–H (bridge) overlap population is 0.15 compared to a B–H (terminal) population of only 0.01, so excitation of ν_2 is very likely upon ionization from $3a_g$. The spacing of the extra shoulder from the previous member of the progression is 800 ± 250 cm^{-1} (B_2H_6) or 400 ± 80 cm^{-1} (B_2D_6) which corresponds to ν_4, the B–H–B bending mode, which is also consistent with the orbital $3a_g$.

The fifth band contains a well-marked progression and some additional structure which is most simply interpreted as a second progression, as indicated on figure 2. The spacings correspond to 90 % of ν_1, (B–H (terminal) stretch, main progression) and 85 % of ν_3 (weak progression), i.e. the bonding character of the orbital is mainly B–H (terminal), similar to the first band except that the orbital should be much less directional. The orbital $2b_{1u}$ has a B–H (terminal) overlap population of 0.24, compared with a B–B overlap population of only -0.06, and though the orbital has some 2p character this provides only about one-quarter of the total B–H overlap population; this may account for the weak excitation of ν_3 compared to ν_1. No direct evidence is available on the third and fourth photoelectron bands, but the assignments of the other three bands are in such good agreement with the predictions of the calculations that we are confident in assigning these two as $1b_{2u}$ and $1b_{3u}$ respectively from the agreement of eigenvalues and vertical i.p.

Although the agreement of all three rigorous calculations with experiment is good, the eigenvalues of Newton *et al.* (1966) are clearly in better agreement with the i.p. than those of the other workers. This is a little surprising since the calculations with extended Gaussian basis sets of orbitals are expected to give better results than those using minimal basis sets, and certainly the extended set calculations give lower total energies than the minimal basis set. However, although the two Gaussian calculations agree on the total energy to 0.06 eV (in 1.4×10^3 eV) the individual eigenvalues vary by as much as 0.66 eV (for $2a_g$) between the two sets. The most consistent deviations between calculation and experiment occur with the fourth and fifth photoelectron bands (see figure 7*b*): all the calculations underestimate the stabilization of $1b_{3u}$ and slightly overestimate the stabilization of $2b_{1u}$. This may be related to the fact that the principal point of difference between the calculations of Palke & Lipscomb (1966) and those of the other workers is that the former report a significant (0.291) total B–B overlap population, whereas the latter report this quantity to be essentially zero. Now $1b_{3u}$ has a positive contribution to the B–B overlap while $2b_{1u}$ has a negative contribution. An increase in B2p character in the orbital $1b_{3u}$ would probably bring the eigenvalue closer to the i.p. and would certainly increase the B–B overlap population; the opposite argument applies to $2b_{1u}$. The deviations between i.p. and eigenvalues may of course be due to the approximations in Koopmans's theorem,† but there is also evidence from attempts to fit the vibrational spectra of diborane with sets of force constants that a direct B–B interaction exists (Ogawa & Miyazawa 1964; Adams, personal communication) so we conclude that the Slater basis wavefunctions of Newton *et al.* (1966) give the best available description of the experimental properties of diborane.

Borazine

No rigorous calculations have yet been published for borazine, so the interpretation of the spectrum depends mainly on the experimental data. The molecule has D_{3h} symmetry (Bauer 1938) so singly and doubly degenerate orbitals are expected. We assume that most probably the weaker bands are due to ionization from orbitals of a symmetry and the stronger ones to ionization from e orbitals. An additional guide may be provided by the operation of the

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† The effects of electron reorganization upon ionization have been partially taken care of in constructing figure 7*b* by adjusting the calculations to fit the first i.p.

Jahn–Teller effect, which gives two possible states for the ions produced by removal of an electron from a doubly degenerate pair of orbitals. If the energy separation of the states is large enough (Price 1968), shoulders may be observed on the photoelectron bands. Four of the bands in borazine may be assigned as e on the basis of intensity (at 10.14, 11.42, 14.76 and 17.47 eV) and of these, the bands at 10.14, 11.42 and 17.47 eV show distinct shoulders, and the band at 14.76 shows an unusual convex shape on the high i.p. side, which may be an incipient shoulder. None of the three remaining (weak) bands show indications of shoulders, so the assignments on the basis of intensity and band envelope are consistent.

Further information is provided by the fine structure. The first band shows a vibrational progression with an average separation of 700 cm^{-1}. In the molecule there are four vibrations which maintain the total symmetry of the molecule, $\nu_1 = 3452$, $\nu_2 = 2535$, $\nu_3 = 940$ and $\nu_4 = 852\ cm^{-1}$ (Watanabe, Narisada, Nakagawa & Kubo 1960) and of these ν_4, a combination of B–N stretch and ring deformation, is the closest in energy to the observed spacing. The excitation of the ring vibration suggests that the band may be due to ionization from the π type orbital e″, analogous to the e_g orbital in benzene, whose photoelectron band shows similar but better resolved structure (Turner 1967).

The vibrational spacings on the fifth band, 1900 and 2400 cm^{-1}, are about 75 % of ν_2 and ν_1 respectively. ν_1 is almost entirely N–H stretching and ν_2 is almost entirely B–H stretching in character, so we deduce that this band arises from a singly degenerate orbital with considerable B–H and N–H bonding character. However, the two vibrational progressions do not begin at the first band, the first N–H peak is observed separately from the first B–H peak. Since there can only be one ground vibrational state for the ion, this suggests either that the first peak observed is not the adiabatic transition but an excited B–H vibrational state, or that the N–H progression is excited at the same time as a single quantum of a third vibration whose energy corresponds to the difference in energy between the first strong peak and the first weak peak in the band. Extrapolating both the B–H and N–H series back one quantum brings both series into coincidence, within experimental error, at 13.51 eV, just on the wing of the Xe peak shown in figure 5, but examination of expanded scale traces with no Xe present shows no detectable peak, so if the first interpretation is correct the adiabatic transition has less than 2 % of the intensity of the 13.74 eV peak. The alternative explanation, invoking a third vibration, seems more probable in the light of some preliminary experiments on *B*-trideuteroborazine. In our spectra of this compound the progression assigned to N–H is not resolved but the progression assigned to B–H appears with a reduced spacing of about 1300 cm^{-1}. From the data so far available the first peak seems to have the same i.p. as that in the undeuterated compound, so it is most probable that this first peak is the adiabatic transition. The third vibration in the ion has an energy of 700 cm^{-1}, which corresponds to 83 % of the ring vibration ν_4 in the molecule. This must indicate that the orbital corresponding to this fifth band has a small amount of B–N bonding character in addition to the B–H and N–H character.

Any more detailed assignment can only be attempted with the aid of calculations. The two published sets of calculations in which all the valence electrons have been included (Kuznesov & Shriver 1968; Davies 1968*a*) do not agree in all details (figure 8) but both sets predict that three a and three pairs of e orbitals have energies lying within 6 eV (Kuznesov & Shriver 1968) or 8.1 eV (Davies 1968*a*) of the first i.p. This compares well with our results, in which three weak and three strong bands are observed before 15 eV. A seventh orbital of e type is predicted at −21.88 eV (Davies 1968*a*) or −20 eV (Kuznesov & Shriver 1968), whereas our seventh band appears at 17.47 eV. The first i.p. is also quite well predicted by the c.n.d.o. 2 calculations (Davies 1968*a*) if a zero of 4 eV is assumed (Davies 1968*b*). The number of orbitals within the experimental energy range is correctly predicted by the calculations but, as was observed for diborane, the energy spread is exaggerated. However, the sequence of orbital degeneracies in these calculations do not agree with the sequence of degeneracies deduced above from the photoelectron bands shapes and intensities which we observe (see figure 4). The adjustments of orbital energies needed to fit the calculations to our observed sequence are all less than 3 eV so it seems likely that the wave functions from the calculations may be a reasonable guide to the bonding nature of the orbitals. We have calculated bonding characters as the sum of products of atomic orbital coefficients, for nearest neighbours only, for some of the molecular orbitals obtained from a c.n.d.o. 2 calculation.

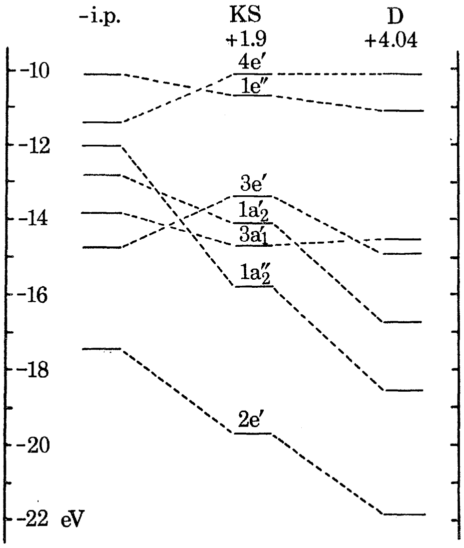

FIGURE 8. The vertical i.p. of borazine compared with eigenvalues from calculations. The eigenvalues have been adjusted by adding the amounts of energy shown to each set of calculations. KS, results of Kuznesov & Shriver (1968); D, results of Davies (1968*a*). The assignments of the experimental bands are explained in the text.

Of the three singly degenerate orbitals which are predicted to lie in the region of interest, only one, $3a'_1$, can have any B–H or N–H bonding character: the other two are $1a''_2$ and $1a'_2$ which have no H components. The B–H and N–H characters of $3a'_1$ are 0.49 and 0.20. The B–N bonding system, which includes p orbitals, has both σ and π character: summing these separately gives a σ character of $+0.06$ and a π character of -0.13 so the overall B–N bonding character is probably close to zero. This is in very good accord with the vibrational analysis of the band at 13.84 eV and this band is therefore definitely assigned as $3a'_1$.

Both the calculations are in agreement that the highest occupied orbital is 4e′, with the π type orbital 1e″ as the next orbital. By symmetry, 1e″ can have no B–H or N–H character, and the bonding characters for 4e′ are B–H $= 0.21$, N–H $= 0.08$, $\text{B–N}_\sigma = +0.20$, $\text{B–N}_\pi = -0.26$. As with $3a'_1$, the B–N bonding character of 4e′ is probably very close to zero, so it is very unlikely that ionization from this orbital would excite the ring vibrations; even if the c.n.d.o. 2 wavefunction is not correct in all details it is most improbable that the true 4e′ function is mainly B–N bonding, yet the only vibration we observe on the first photoelectron band seems to be ν_4 (ring only). We suggest therefore that the uppermost orbital is the π type orbital 1e″, and this is in accord with interpretations of the ultraviolet spectra (Rector, Schaeffer & Platt 1949) with some observations upon trends in the first i.p. determined by electron impact (Kuznesov & Shriver 1968), and with our observations upon *B*-trifluoroborazine (see below).

Since there is only one orbital of e″ type, the three other intense bands are all e′. The remaining problem is the assignment of the weaker bands at 12.1 and 12.8 eV. One of these must be $1a_2'$ (σ) and the other $1a_2''$ (π). No direct evidence is available from the photoelectron data, but a comparison with benzene allows a decision. In benzene the separation of the π orbitals a_{2u} and e_{1g} has been found to be 2.24 eV (Baker *et al.* 1968; Baker, this volume, p. 131). It is most unlikely that the π bonding in borazine will be greater than in benzene, but if the 12.8 eV band were assigned as a_2'' then the separation $1e''$–$1a_2''$ would be 2.69 eV, greater than the corresponding benzene separation. However, if the band at 12.1 eV is assigned as a_2'', the separation of the π orbitals is only 1.92 eV, which is consistent with the separation in benzene. The observed photoelectron spectrum is thus fully assigned. A correlation of our observed i.p. and these assignments with the orbital eigenvalues from the two sets of c.n.d.o. calculations is shown in figure 8. Both sets of calculations greatly overestimate the π separation, and this has been observed also in comparisons of photoelectron spectra with c.n.d.o. 2 calculations for boron trifluoride (D. R. Lloyd & P. J. Bassett, unpublished work). As in benzene (Baker, this volume) the separation of the π orbitals in borazine is predicted more accurately by π-only calculations than by the full valence electron calculations; typical values of the calculated energy separation of $1e''$ and $1a_2''$ are 1.98 eV (Perkins & Wall 1966) and 2.54 eV (Chalvet, Daudel & Kaufman 1965). Some evidence in support of our orbital assignments comes from the following study.

B-trifluoroborazine

In the discussion of borazine it is evident that the c.n.d.o. 2 calculations do not predict the individual orbital energies well enough to give the correct sequence of energies, but that they are good enough to predict how many orbitals of each type may be expected within a given range of energies. A c.n.d.o. 2 calculation has been carried out for *B*-trifluoroborazine, and orbital energies have been referred to a zero of 4 eV (Davies 1968*b*). This predicts thirteen orbitals above 21.22 eV, three singly degenerate and five degenerate pairs, which is in good agreement with the five strong bands and three weak ones observed in the photoelectron spectrum of the compound. In attempting to assign these bands it has been assumed that the numbers of each type of orbital are correctly predicted by the calculations. Although the sequence of orbital energies is not expected to be accurate in the calculations it seems likely that the directions of orbital energy changes upon fluorination will be more accurately predicted. The orbital energies calculated for borazine and for *B*-trifluoroborazine are shown on the left-hand half of figure 9.

According to the c.n.d.o. 2 calculations the σ type $4e'$ orbital is the highest occupied orbital in borazine but in *B*-trifluoroborazine the highest e′ orbital has been stabilized by 1.75 eV relative to the highest e″ orbital so that in the fluoro compound the highest occupied orbital is of π type (e″), but the energy separation of the two highest occupied orbitals in both compounds is about the same (0.9 eV). Experimentally we observe that the separation of the first two intense bands in the fluoro compound is 1.46 eV greater than in borazine, and if the energy trends are even approximately predicted by the calculations this must mean that both in borazine and in *B*-trifluoroborazine the uppermost orbital is of e″ symmetry. Assignments to vibrational frequencies in *B*-trifluoroborazine are complicated by the absence of Raman data for this compound, but from examination of the normal coordinate analysis of *B*-trichloroborazine (Watanabe *et al.* 1960) and the infrared spectrum of *B*-trifluoroborazine (Beyer *et al.* 1964) the symmetric ring frequencies are to be expected in the regions 850 to 950 cm^{-1} (ν_3) and about 400 cm^{-1} (ν_4), the N–H stretch (ν_1) at about 3500 cm^{-1} and the B–F stretch (ν_2) in the region 1150–1450 cm^{-1}. The vibrational structure on the first and fourth bands with intervals of about 1100 cm^{-1} probably corresponds to B–F stretching. Analysis of bonding characters from the c.n.d.o. 2 calculations is inconclusive since both e′ and e″ orbitals may have

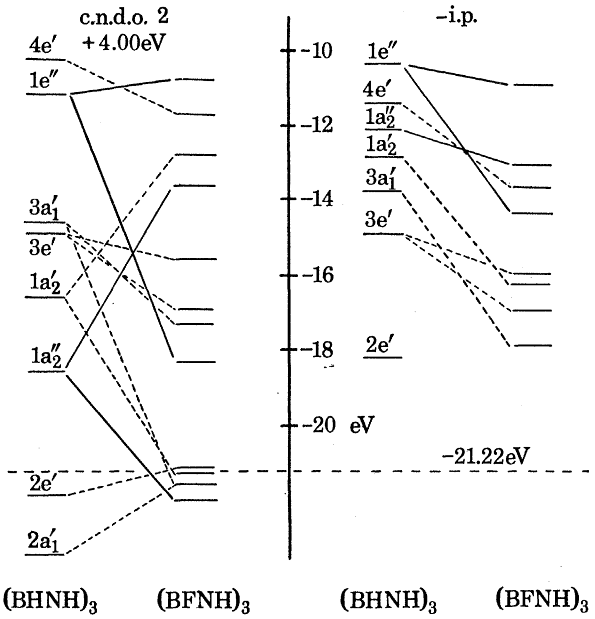

FIGURE 9. Eigenvalues calculated for borazine and *B*-trifluoroborazine by c.n.d.o. 2 method, and vertical i.p. for the compounds.

B–F bonding character, but the first band was assigned above as 2e″ on the basis of i.p. comparisons. The similar shape, structure and intensity of the fourth and first bands suggest that the fourth band may be 1e″. The only other band to show fine structure is that at 13 eV, which probably corresponds to a singly degenerate orbital because of its low intensity. The structure on the band indicates excitation of vibrations at 1500 cm^{-1} and 750 cm^{-1} which most probably correspond to B–F (ν_2) and ring (ν_3) vibrations. The structure is well resolved with no trace of N–H vibrations, so the $2a_2'$ or $2a_2''$ orbitals are the most likely ones. The calculated bonding characters of these two orbitals are quite similar to each other, but analogy with the spectra of benzene derivatives (Turner 1967; Baker *et al.* 1968) where π orbitals show structured bands far more commonly than σ orbitals, suggests that this band is most likely to be due to $2a_2''$.

The remaining assignments shown in figure 9 are tentative only and are arrived at from comparison of the trends in i.p. predicted by the calculations. The pattern of strong stabilization of σ orbitals and weaker π stabilization upon fluorination is similar to that observed in comparing benzene and hexafluorobenzene (Turner 1967). However, since only three fluorine atoms are introduced in our comparison the orbital 7e′, which according to the calculations is mainly localized on the N and H atoms, is still in the energy region of the π orbitals whereas in hexafluorobenzene all the σ orbitals are thought to be deeper lying than the π orbitals.

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