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## Photoelectron Spectra of the Symmetric Trimethylborazines

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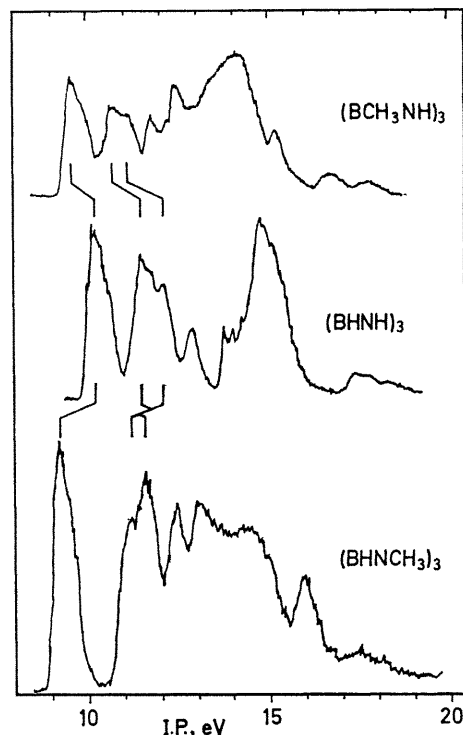
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**Summary** The He(I) photoelectron spectra and the measured vertical ionization potentials of *B*-trimethylborazine and *N*-trimethylborazine, are reported and compared with those of borazine, and with the results of CNDO/2 calculations, to show that the highest-lying occupied orbital in all three compounds is of  $\pi$  type, and not  $\sigma$  as is indicated for borazine by calculations.

THE photoelectron spectrum of borazine has been reported as showing six ionization bands before 21eV; from correlation with calculations the first ionization potential (I.P.) was assigned to  $e'$  ( $\sigma$ ) orbitals.<sup>1</sup> We have also reported this spectrum, and that of *B*-trifluoroborazine, but we believe that the borazine spectrum contains ionizations from seven orbital sets; from correlation of the two spectra with calculations,<sup>†</sup> and analysis of the fine structure, we have assigned the first I.P. to  $e''$  ( $\pi$ ) orbitals.<sup>3</sup> We report now the spectra of *B*-trimethylborazine ( $(\text{BCH}_3\text{NH})_3$ ) and *N*-trimethylborazine ( $(\text{BHNCH}_3)_3$ ), which support our assignment of the borazine spectrum.

The spectra of the two methyl derivatives, obtained using He(I) resonance radiation, are shown in the Figure together with that of borazine. The instrument (Perkin-Elmer PS15) uses the electron velocity analyser potentials to scan the spectrum, so the apparent intensity of bands decreases approximately linearly with electron energy (21.22 I.P.), giving the borazine spectrum a slightly different appearance from that shown in ref. 1. Correlation lines are drawn for the lowest I.P. bands on the basis of band contours and intensities. The photoelectron bands from doubly degenerate orbitals are expected to show some Jahn-Teller splitting, so the first band in all three compounds may be assigned as  $e'$  or  $e''$  from the shoulder or convex shape on the high I.P. side; this conclusion is supported by the relatively high intensity of the band. The second band

in  $(\text{BHNH})_3$  has been assigned as  $1e''$  from calculations,<sup>1</sup> but this band has a shoulder and a subsidiary maximum on the high I.P. side. Because of this shape we have assigned the band as arising from an  $e$ -orbital pair



FIGURE

<sup>†</sup> Calculations in ref. 1 used the INDO method,<sup>2</sup> those in ref. 3 used the CNDO/2 method.<sup>3</sup> We have carried out calculations by both methods for all the borazines discussed here. Orbital sequences are independent of the method used, for the orbitals discussed here.

(maximum + shoulder) and an  $a$  orbital (subsidiary maximum).<sup>3</sup> In support of this,  $(\text{BCH}_3\text{NH})_3$  shows a second band very similar to that of  $(\text{BHNH})_3$ , but  $(\text{BHNCH}_3)_3$  has a shoulder on the *low* I.P. side of the maximum. This shape cannot arise from a Jahn-Teller splitting alone,<sup>4</sup> so we consider that in the latter compound the  $a$  and  $e$  components of the second band are closer in energy than in the other two compounds. Without knowing whether or not the Jahn-Teller effect in the  $e$  component is large enough to affect the shape, it is not possible to decide which component is at higher energy.<sup>5</sup> With this interpretation of band contours, the measured vertical I.P. with standard deviations in parentheses are:  $(\text{BCH}_3\text{NH})_3$ : 9.64(3), 10.90(3), 11.87(1), 12.46(4), 14.07(5), 15.24(1), 16.68(1), 17.65(2);  $(\text{BHNH})_3$ : 10.14(1), 11.44(2), 12.06(3), 12.83(2), 13.82(3), 14.76(3), 17.47(3) eV;  $(\text{BHNCH}_3)_3$ : 9.28(2), 11.14(9), 11.48(10), 12.41(1), 12.96(10), 14.05(20), 15.93(2), 17.51(2) eV. The fine structure in  $(\text{BHNH})_3$  has already been discussed,<sup>3</sup> and the third band in  $(\text{BCH}_3\text{NH})_3$  has a subsidiary maximum 0.28 eV from the main peak, but no other fine structure could be detected in the methyl derivatives. *B*-Trimethylation of borazine leaves the energy separations of the first three orbital sets almost unchanged, but *N*-trimethylation increases the separation between the two  $e$  sets by at least 0.6 eV. Similar effects to those of *N*-trimethylation are produced by *B*-trifluorination.<sup>3</sup>

Our calculations for these compounds were carried out with an energy zero<sup>6</sup> of 4 eV, and with the methyl group aligned to give  $C_{3h}$  symmetry to preserve  $\sigma$ - $\pi$  orthogonality. Using the CNDO/2 method the eigenvalues of the three highest occupied orbitals are, in eV,  $(\text{BCH}_3\text{NH})_3$  9.14( $e'$ ) 9.97( $e''$ ), 12.13( $a'$ );  $(\text{BHNH})_3$  9.78( $e'$ ), 10.25( $e''$ ), 14.61( $a_1'$ );  $(\text{BHNCH}_3)_3$  9.31( $e''$ ), 9.88( $e'$ ), 11.92( $a'$ ); *i.e.* the calculations

predict an inversion of the two highest occupied levels on *N*-trimethylation, but not on *B*-trimethylation of borazine. Similar results have been reported using a modified CNDO/1 calculation.<sup>7</sup> From the band intensities in the Figure, it is unlikely that there is such an interchange. Also, because of the interchange the predicted separation of these two decreases on *N*-trimethylation whereas the actual separation *increases* by at least 0.6 eV. However, the *changes* in I.P. for individual orbitals are well predicted by the calculations if in all three compounds the highest occupied orbitals are the  $e''$  pair. Thus *B*-trimethylation is predicted to destabilise both the  $e''$  and  $e'$  orbitals, but *N*-trimethylation is predicted to destabilise  $e''$  considerably while leaving the energy of the  $e'$  orbitals almost unchanged, and this is observed if  $e''$  lies above  $e'$ .

If the reorganisations of the calculated borazine orbital sequence suggested by us<sup>3</sup> are made, the shifts of all the remaining bands on *B*- or *N*-trimethylation are quite well predicted by the calculations. In all three compounds the highest occupied orbital is therefore most probably  $e''$ , and although the relative shifts of orbital energies are well predicted by the CNDO/2 and INDO calculations the absolute energies are not predicted to better than about 2 eV. The conclusion that the first band in the borazine spectrum corresponds to the  $1e''$  orbital has also been reached by Bock and Fuss,<sup>8</sup> by a different argument from that used here.

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<sup>4</sup> The expected shape of a Jahn-Teller split band is discussed by A. W. Potts, H. J. Lemka, D. G. Streets, and W. C. Price, *Phil. Trans.*, 1970, A, 268, 59.

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