The Photoelectron Spectra of NH_3BH_3 and BH_3CO

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Summary The correlation of the spectra of the title compounds with those of the free donors is consistent with simple σ donor–acceptor bonding in NH_3BH_3, but with σ-donation and π-back-donation in BH_3CO; recent calculations agree well with experiment for NH_3BH_3 but less well for BH_3CO.

IN a study of the nature of the bonding in donor–acceptor complexes we have recently presented results from photoelectron spectroscopy for some compounds of this type.[1-3] Ammonia and carbon monoxide are two of the simplest donor molecules, and though their complexes are generally very different chemically, both form compounds with BH_3. These complexes have been the subject of recent theoretical investigations,[4,5] and since the photoelectron spectra of the free donors are well known[6,7] we have examined the spectra of the complexes, using helium resonance radiation (21·22 ev).

The spectra of the two complexes are shown in Figure 1. Both compounds are unstable, and the BH_3CO spectrum was obtained by direct evaporation from a sample at about $-150°$ into the instrument. Because of the low volatility of NH_3BH_3, the freshly-prepared sample had to be kept at 50°. This results in some decomposition, giving traces of hydrogen in the spectrum, and the electron count rate is low, so the spectrum is of poor quality. However, the correlation with the spectra of the mono-, di-, and trimethylamine complexes[8] is such that we are confident the spectrum shown is that of NH_3BH_3.

Three bands are observed in NH_3BH_3, with vertical I.P. of 10·33(4), 13·92(9), and 17·75(7) ev, where the bracketed quantities are standard deviations. The first band shows a shoulder at 10·90(10) ev. In the methyl derivatives, this first band has a very well-defined shoulder and a vibrational progression which from deuteriation experiments corresponds to the B–H stretching frequency. The spectrum of BH_3CO shows four bands, with vertical I.P. 11·92(2), 14·13(2), 16·98(3), 18·68(2) ev.† The shoulder on the first band appears at 12·51(2) ev, and the average spacing between the components of the fourth band is 0·206(4) ev or 1660(30) cm^{-1}. Indications of fine structure on the leading edge of the first band have been observed but are not well enough defined for analysis.

In both complexes the first band is clearly the highest-lying e-orbital, mainly localised upon the BH_3 group and made up of boron $2p$-orbitals perpendicular to the B–X bond, and appropriate group combinations of the hydrogen $1s$-orbitals. The shoulder is almost certainly associated with the strong Jahn–Teller effect expected for removal of an electron from a degenerate orbital which binds hydrogen atoms; such shoulders have been observed particularly in photoelectron spectra of CH_3 compounds.[9] Since in the free donor molecules the first I.P. is that of the donor orbital, or lone pair,[6,7] the second I.P. in the complexes can probably be correlated with the "donor–acceptor" orbital arising from combination of the lone pair of the donor with the empty acceptor orbital of BH_3. The rest of the spectrum can be correlated with the remaining orbitals of the donor molecule; thus the third band in NH_3BH_3 may be correlated with the $1e$-orbitals of NH_3, and the third and fourth bands in BH_3CO with the 1π- and $4\ \sigma$-orbitals of CO (see ref. 10 for detailed contours of these orbitals). The correlation of our fourth I.P. in BH_3CO with 4σ of CO is made very probable by the vibrational progression, whose interval is indistinguishable from that[11] of 1680 cm^{-1} in the corresponding state of CO^+. The relative intensities of the vibrational components of this progression are also almost unchanged.[6]

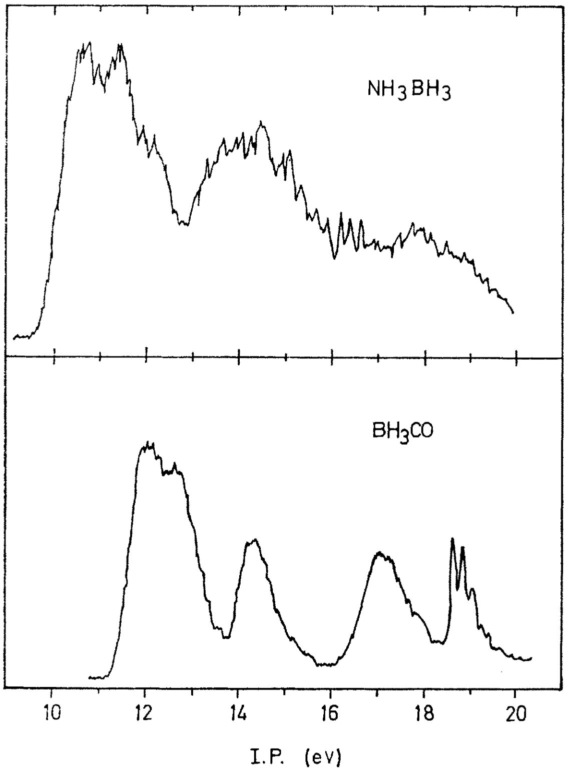

FIGURE 1. *Photoelectron spectra of* NH_3BH_3 *and* BH_3CO. *The spectrum of* NH_3BH_3 *shows traces of hydrogen between* 15·5 *and* 17·0 ev.

These experimental correlations are shown in Figure 2, together with correlations of the calculated I.P. for the four compounds.[4] For this comparison the calculated eigenvalues have been multiplied[12] by 0·92. The agreement of theory and experiment is very good for the NH_3 and NH_3-BH_3 comparison. Other calculations[5] differ only slightly. The donor a_1-orbital of NH_3 is stabilised by the B–N bond formation, and the e-orbitals are also stabilised, though to a lesser extent, presumably from the donation of charge. We have observed an exactly similar correlation[2] between PF_3 and OPF_3. However, a feature of the calculation

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† First vibrational component.

which could not be deduced from the spectrum is the presence of an a_1-orbital almost degenerate with the 1e-orbital in NH_3BH_3. Since the spectrum is not well defined in this region it is quite possible that there is an additional ionization hidden under the third band, and in the methyl derivatives we have resolved a corresponding band. Eigenvectors for the orbitals have not been published, but from our unpublished CNDO/2 calculations this a_1-orbital correlates with the a_1-orbital of pyramidal BH_3.

The experimental correlation of CO with BH_3CO shows that the orbital energies of 1π and 5σ are almost unchanged on complex formation, and that that of 4σ actually rises. However, although the energy of 5σ is so similar, the second band in Figure 1 is broad, *i.e.* the orbital is strongly bonding, whereas in the photoelectron spectrum of CO the first band is very sharp, consistent with the "carbon lone-pair" character of this orbital. Since the orbital becomes bonding in the complex with so little change in I.P., we deduce that the bonding in the complex is different from that in NH_3BH_3, and the most obvious rationalisation of the constancy in energy is that, as has long been suspected,[13] there is considerable π-back-donation of charge to CO from the BH_3 e-orbitals, which tends to raise the energy of CO-localised orbitals. The constancy of the 1π-orbital energy probably arises from a similar cancellation of effects, but since the back-donation should be mainly to carbon it is not clear why 4σ, mainly oxygen localised, should rise in energy on complex formation, especially since its CO bonding character seems unchanged. Although an additional orbital is suspected in BH_3NH_3 this is clearly absent in BH_3CO before 21 ev; an accidental degeneracy is not possible in the fourth band since both orbitals would have the same symmetry. Accordingly, in comparing BH_3CO with BH_3NH_3 we deduce that the BH_3 e-orbitals are stabilised by 1·5 ev and that the BH_3 a_1-orbital is stabilised by at least 3 ev; this may be partly due to back-donation, but since the σ-effect is greater than the π, the charges on the donor atoms are probably also responsible.

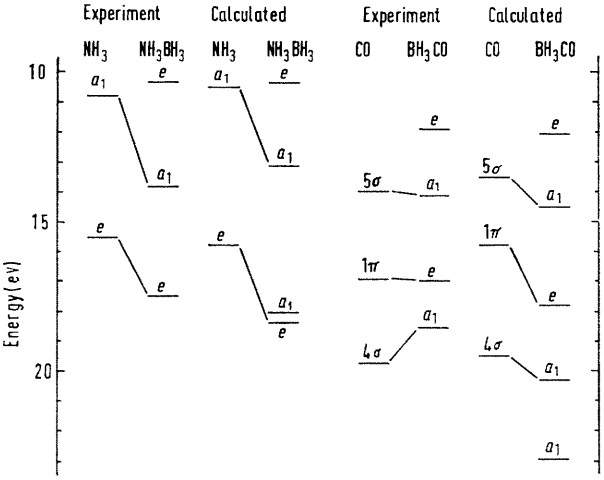

FIGURE 2. *Correlations of experimental and calculated vertical I.P. for* NH_3 *and* CO *with their borane complexes. The calculated I.P. from ref.* 4 *have been multiplied by* 0·92, cf. *ref.* 12; *experimental I.P for* CO *from ref.* 6, *for* NH_3 *from ref.* 7.

The I.P. for CO and BH_3CO are less well predicted by the calculation than for the other pair of compounds, and in particular the CO type orbital eigenvalues are about 1 ev too negative; a possible explanation is that the calculation underestimates the extent of back-donation in the complex.

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