A Theoretical and Experimental Study of the Bonding in $PF_3{\cdot}BH_3$

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Summary The bonding in $PF_3{\cdot}BH_3$ is discussed using the results of *ab initio* SCF–MO calculations and the photoelectron spectrum.

THE bonding in trifluorophosphine borane $PF_3{\cdot}BH_3$, has been discussed in terms of the electron donor and acceptor properties of PF_3 and BH_3, respectively, but such descriptions have lacked any quantitative basis, either theoretical or experimental. We present here the results of *ab initio* SCF–MO calculations and the experimental photoelectron spectrum of this complex.

The basis orbitals for the calculation consisted of a minimal basis of Slater-type orbitals (STO) (except for the fluorine $2p$-orbital where an atomic orbital was used), with best atom exponents,[1] and a hydrogen $1s$ exponent of 1·2, augmented by phosphorus $3d$-orbitals of exponent 1·77, the optimum value for PF_3. Integral evaluation was carried out by expanding each STO in three Gaussian-type functions and the fluorine $2p$ atomic orbital in four functions, using the least-squares criterion. Polarization of the $3d$-orbitals was allowed for as previously described.[2] The results of the calculation are shown in Tables 1 and 2 together with the pertinent results for PF_3 and BH_3 for comparison.

TABLE 1

Bonding in $PF_3{\cdot}BH_3$

Atomic populations

		PF_3	BH_3 (C_{3v})	$PF_3{\cdot}BH_3$
Phosphorus	$3s$	1·51		1·19
	$3p$ (a_1)	1·05		0·96
	$3p$ (e)	0·83		0·92
	$3d$(a_1)	0·13		0·20
	$3d$ (e)	0·53		0·64
	atomic charge	+1·02		+1·16
Fluorine	$2s$	1·91		1·91
	$2p$	5·43		5·40
	atomic charge	−0·34		−0·31
Boron	$2s$		1·15	0·99
	$2p$		2·16	2·61
	atomic charge		−0·30	−0·59
Hydrogen	$1s$		0·90	0·88

The He(I) photoelectron spectrum of PF_3BH_3 is shown in the Figure; the experimental conditions have been described.[3,4] From comparison with the spectra of other BH_3 complexes, the first band probably includes ionization from the BH_3 pseudo-π(e) orbitals.[4] In all the complexes examined so far the band from this orbital pair shows a strong Jahn–Teller splitting, but the shape of the first band in the Figure cannot arise solely from such splitting, since the second maximum is higher than the first.[5] We have used an analogue computer (Dupont Curve Resolver) to fit the corresponding *e* bands of BH_3CO and $(CH_3)_3NBH_3$, and the resulting shape is shown as the first dotted curve in the Figure. The second dotted curve is the additional component necessary to fit the first band, which from the intensity corresponds to a singly degenerate orbital. This curve fitting shows that the first ionization potential (I.P.) corresponds to an *e* orbital pair if the Jahn–Teller splitting is assumed. However, if the splitting is not assumed, a fit with the second I.P. as *e* is possible (we thank the referee for pointing out this ambiguity in the curve fitting). The vertical I.P. and the assignments deduced from intensities and correlation with PF_3, are shown in Table 2, together with those for PF_3.

TABLE 2

Experimental[a] *and theoretical vertical IPs* (ev)

PF_3			$PF_3\cdot BH_3$		
Symmetry	Energy		Symmetry	Energy	
$8a_1$	12·6	(12·3)	$7e$	13·6	(12·0)[b]
$1a_2$	17·8	(15·8)	$10a_1$	13·9	(12·6)[b]
$6e$	18·2	(16·3)	$1a_2$	19·4	(16·8)
$5e$	19·6	(17·5)	$6e$	19·9	
$7a_1$	21·0	(18·6)	$9a_1$	20·5	(17·6)
$4e$	21·4	(19·4)	$5e$	21·3	(18·4)
			$4e$	23·1	(20·2)

[a] The experimental values are given in parentheses.

[b] These values are the measured positions of the two maxima on the first band, and not the resolved components shown in the Figure.

The major changes in the orbital populations on formation of the complex are the decrease in the phosphorus 3*s*-population by 0·32e and a smaller increase in that of the 3*d* orbitals by 0·18e. The change in the 3*s* population is due to the electron donor properties of PF_3. The "lone pair" orbital of PF_3 ($8a_1$) has 34% phosphorus 3*s* character whereas in the corresponding molecular orbital of the complex ($10a_1$) it is reduced to 14%. The delocalization of the "lone pair" orbital over the BH_3 group results in a calculated increase in the I.P. by 1·3 ev compared with the experimental increase of at least† 0·3 ev. The small degree of back-donation is reflected in the small increase (0·1e) in the 3*d*(*e*) population on complex formation. The highest filled orbital of $PF_3\cdot BH_3$ ($7e$) is calculated to be 95% localized on the BH_3 group; its calculated orbital energy of −13·6 ev is to be compared with the first I.P. of 12·0 ev. The predominantly non-bonding M.Os consisting mainly of fluorine 2*p*-orbitals ($1a_2$, $6e$, $5e$, and $4e$) are calculated to decrease in energy by *ca.* 1·7 ev compared with the corresponding orbitals of PF_3, the experimental decrease (Table 2) being about 0·8 ev. This decrease is caused partly by the electron migration from the phosphorus atom to the BH_3 group and partly by the smaller negative charge on the fluorine atoms in $PF_3\cdot BH_3$ compared with the free ligand (Table 1). The absolute values of the energies of these non-bonding orbitals are in error by 2—3 ev. However, the predicted stabilisation of *all* the orbitals of PF_3 upon complex formation is about 0·9 ev greater than that observed, although the relative stabilisations are quite accurately predicted. This overestimation of the stabilisation may possibly indicate that the π-back donation has been underestimated, similar observations having been made in the comparison[4] of experiment and calculations for CO and BH_3CO.

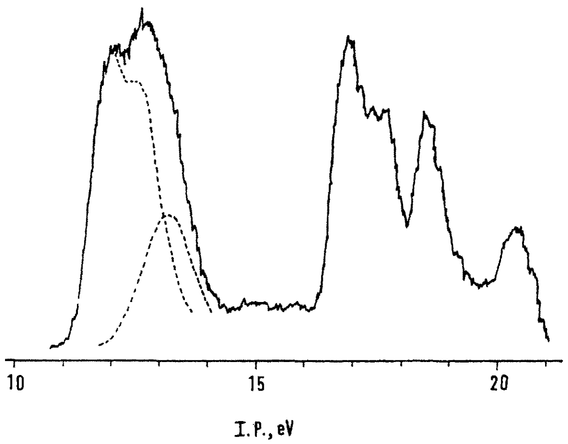

FIGURE. *The photoelectron spectrum of* $PF_3\cdot BH_3$, *and the resolved components (dotted lines) of the first band.*

The major components of the B–P bond overlap population involve the boron 2*p*σ-orbital with the phosphorus 3*s* and 3*p*σ orbitals, which contribute 0·33 and 0·24, respectively, to the overlap population. The degree of B–P π-bonding is much smaller, the overlap populations being 0·08 for both 2*p*π–3*d*π and 2*p*π–3*p*π interactions.

The near-minimal basis set calculation described here predicts a dipole moment of 1·74D (the direction being B^-–P^+); the agreement with the experimental value[6] of 1·64D gives confidence in the overall charge distribution yielded by the calculation. The energy of the B–P bond, assuming dissociation to PF_3 and planar BH_3 is calculated to be 13 kcal, compared with the experimental value[6] of 24 kcal.

As we have noted[7,8] for other complexes of PF_3, the decrease in the P–F bond length (0·03 Å) and increase in FPF angle (2·1°)[6] on co-ordination arise from the delocalization of the "lone pair" of PF_3, this orbital having a significant P–F antibonding component.

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† If the curve fitting is accurate, the increase is about 0·8 ev.

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