Bonding in Phosphineborane and Phosphine Oxide: an *Ab initio* SCF–LCAO–MO Study

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Summary From *ab initio* SCF–MO calculations, *d*-orbital participation and π-back-donation appears important in PH_3O but rather small in $PH_3{\cdot}BH_3$.

THERE is much speculation concerning the nature of the co-ordinate bonding by the phosphine molecule PH_3. Two simple adducts of this molecule are the phosphineborane molecule $PH_3{\cdot}BH_3$[1] and the hypothetical phosphine oxide molecule PH_3O.[2] The importance of 3*d*-orbitals in phosphorus bonding has been a controversial question for a long time and, for instance, it has been assumed that the co-ordination in $PF_3{\cdot}BH_3$ is enhanced by back-donation to the phosphorus empty *d*-orbitals.[3] Much discussion has been devoted to the nature of the P–O bond in phosphoryl molecules, whether it is best considered as a P=O double bond or as a σ-dative bond with some π-back-bonding.[4]

We report here the results of *ab initio* SCF–LCAO–MO calculations for the PH_3O and PH_3BH_3 molecules, together with calculations for the parent compounds PH_3 and BH_3 (in a tetrahedral conformation). We used a basis set of twelve *s* and nine *p* Gaussian functions on phosphorus,[5] ten *s* and six *p* functions on boron and oxygen,[6] five *s* functions on hydrogen;[6] to these orbitals, a set of *d* functions on P (exponent 0·55) and on O (exponent 1·0), a d_{xz} and d_{yz} function on B (exponent 1·0), and a set of *p* functions on H (exponent 0·8) have also been added.†

Calculations have been performed with the following geometries: P–H bond length 1·420 Å (experimental value in PH_3[7]), P–B bond length 1·93 Å (experimental value[8]), P–O bond length 1·48 Å (experimental value in Me_3PO[9]), B–H bond length 1·19 Å (average B–H bond length [10]). All angles were assumed to be tetrahedral: this assumption appears reasonable on the basis of the experimental values for the C–P–C and C–P–O angles, respectively 106° and 112° in trimethylphosphine oxide.[9]

	$PH_3{\cdot}BH_3$	PH_3O	PH_3	BH_3
Total energy (a.u.)	−368·8480	−417·3168	−342·4382	−26·3521
Dipole moment (D)	5·51	4·74	1·11	1·04
Atomic populations				
P 3*s*	1·46	1·20	1·54	
$3p_\sigma$	1·26	0·74	1·67	
$3p_\pi$	1·70	1·62	1·56	
$3d_\sigma$	0·08	0·14	0·06	
$3d_\pi$	0·05	0·22	0·03	
Total	14·55	13·92	14·87	
X 2*s*	0·75	1·84		0·86
$2p_\sigma$	0·46	1·34		0·01
$2p_\pi$	1·64	3·50		1·72
Total	4·86	8·72		4·58
H_P 1*s*	1·00	1·10	1·02	
Total	1·02	1·12	1·04	
H_X 1*s*	1·16			1·12
Total	1·18			1·14
Overlap populations				
P–X (σ)	0·458	0·586		
P–X (π)	0·100	0·646		
P–X (Total)	0·558	1·232		
3*s* 2*s*	−0·022	−0·097		
$3p_\sigma$ 2*s*	0·018	0·007		
$3d_\sigma$ 2*s*	0·006	0·025		
$3p_\pi$ $2p_\pi$	0·084	0·438		
$3d_\pi$ $2p_\pi$	0·016	0·190		
3*s* $2p_\sigma$	0·200	0·239		
$3p_\sigma$ $2p_\sigma$	0·244	0·343		
$3d_\sigma$ $2p_\sigma$	0·012	0·057		

The results are summarised in the Table. As a test of the quality of our wave functions, we shall first compare our results for the phosphine molecule with those reported recently.[11] The basis set used in ref. 11 differs from our basis set only by the use of two sets of *d* functions. The corresponding energy value for a tetrahedral angle (pyramid height of 0·47 Å) is − 342·440 a.u., slightly lower than our value. The corresponding values for the dipole moment, the phosphorus 3*d* population, and total population are 0·90 D, 0·17, and 14·85, to be compared with our values of 1·11 D, 0·09, and 14·87. Apart from a slight reduction in the *d* orbital population due to the use of only one set of *d* functions, our results are very close to the one reported by Lehn and Munsch.

A much debated question is the *d*-orbital participation in phosphorus compounds. From the Table, it is apparent that this participation is much more important in PH_3O than in $PH_3{\cdot}BH_3$ or in PH_3. The *d*-orbital population is 0·09 in PH_3 and 0·13 in PH_3BH_3, but rises to 0·36 in PH_3O

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† The ternary axis of the molecules has been taken as the *z*-axis.

Most of the 3*d* population in PH_3O is of $3d_\pi$ type, while it is of $3d_\sigma$ type in PH_3 and $PH_3{\cdot}BH_3$. The *d*-orbital participation is also apparent from the overlap populations. The contribution of phosphorus 3*d*-orbitals to the overlap population for the P–X bond (X = B or O) is only 0·034 in $PH_3{\cdot}BH_3$ but rises to 0·272 in PH_3O.

Examination of the overlap population reveals some important differences in the nature of the P–B and P–O co-ordinate bonding. In both molecules, there is an appreciable σ-bonding between the 3*s* and $3p_\sigma$ orbitals of phosphorus and the $2p_\sigma$ orbital of boron or oxygen. In addition, there is in PH_3O a significant π-bonding between the $3p_\pi$ and $3d_\pi$ orbitals of phosphorus and the $2p_\pi$ orbital of oxygen. Such π-bonding is much weaker in $PH_3{\cdot}BH_3$. This π-bonding and the correlative participation of phosphorus 3*d*-orbitals may be correlated with the π-donor ability of the co-ordinated group, the borane group being a very poor donor and the oxygen atom a relatively good one. A similar conclusion has been reached by Hillier and Saunders in a discussion of the bonding for the ligands PF_3 and PMe_3.[12]

Some insight into the nature of the co-ordinate bonding is also given by an examination of the charge transfer. The formal charge of the phosphorus atom is +0·13 in PH_3, +0·45 in $PH_3{\cdot}BH_3$, and +1·08 in PH_3O, the charge of the boron atom is −0·42 in BH_3 and −0·14 in $PH_3{\cdot}BH_3$ and the charge of the oxygen atom −0·72 in PH_3O. This indicates that the charge transfer in $PH_3{\cdot}BH_3$ is relatively small, about 0·3 e, which is of the same order of magnitude as in $NH_3{\cdot}BH_3$.[13] The π-charge-transfer is negligible and most of the σ-charge-transfer goes from the $3p_z$ orbital of phosphorus to the $2p_z$ orbital of boron. The large charge-transfer in PH_3O is the result of a large σ-charge-transfer of about 1·2e towards oxygen and of a smaller π-back-donation from the oxygen atom towards the phosphine group of about 0·5e. In the three compounds $PH_3{\cdot}BH_3$, $NH_3{\cdot}BH_3$,[13] and NH_3O[14] which exhibit no back-donation, the computed dipole moments are very close, respectively 5·5, 5·8, and 5·7 D. In PH_3O, this value is decreased to 4·7 D by back-donation of π-electrons.

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