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LCAO–MO–CNDO/2 Analysis of the Trisdimethylaminophosphine and of the Related Oxide Sulphide and Borane

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The main geometrical parameters and the electronic structures of trisdimethylaminophosphine and trisdimethylaminophosphine oxide, sulphide and borane are calculated.

The nature of the phosphorus–X bonds (X = O, S, B, N) is discussed and the comparison to the cognate triaminophosphine series shows the inductive effect of the dimethylamino groups and the existence, in the phosphine, of an important conjugation between the phosphorus and the nitrogen atoms.

Either the forecasting or the rationalization of the donor site and of the chemical behaviour are inferred from the composition of the highest occupied molecular orbital.

The dissociation of the borane complex is analyzed in terms of geometry, energy and atomic populations, and a mechanism of the formation of the phosphorus–boron link is described.

Introduction

Considerable interest has been recently focused on the chemistry of phosphorus–nitrogen compounds, and a special attention has been directed on the aminophosphines and their derivates.

In this laboratory, an earlier investigation has dealt with the electronic structure and chemical properties of the triaminophosphine series $XP(NH_2)_3$ (X = :, O, S, BH_3)[1]. In this paper, we present the theoretical analysis of the geometries, electronic structures and reactivity of the trisdimethylaminophosphine $P[N(CH_3)_2]_3$ and of the related oxide, sulphide and borane.

The main geometrical parameters of these molecules are calculated and compared to the experimental values of cognate compounds. The nature of the phosphorus–X bonds (X = O, S, B and N) is investigated and the comparison with earlier data[1,2] shows the inductive properties of the dimethylamino groups. The forecasting of the coordination sites and of the chemical behaviour of these compounds is analyzed on the basis of the composition of the highest occupied molecular orbital (h.o.m.o.) and the results compared to experimental reports.

The pathway of dissociation of the borane complex $H_3B–P[N(CH_3)_2]_3$ is theoretically discussed in terms of energy, atomic population and geometry variation, and the detailed sigma–pi composition of the phosphorus–boron bond is evaluated as a function of the P–B distance.

Theoretical Part

As it was developed in earlier publications,[1,2] the main parameters are computed using the SCF–MO–CNDO/2 method of Pople and Segal[3,4] with the additionnal transformations previously presented[1]. The mathematical data needed for this purpose are reported in the literature[5]. The calculations have been carried out on the UNIVAC 1110 computer of the Nuclear Research Center of Strasbourg–Cronenbourg.

Results and Discussion

Geometries

Experimental structural results are available only for trisdimethylaminophosphine $P[N(CH_3)_2]_3$[6]. Since the geometrical parameters of the molecules are necessary to calculate the internuclear distances, the molecular geometries of all the compounds must be preliminarily determined. The theoretical geometry is obtained by the calculation of the minimal total energy configuration. In contrast with the $P(NH_2)_3$ series, the size of these molecules does not allow to take account of all the variables, and constant local geometries are used to prevent exaggerated amounts of computation.

The geometry of the dimethylamino group is evaluated by the comparison with the experimental molecular structures of difluorodimethylaminophosphine $F_2PN(CH_3)_2$[7], tris-dimethylaminophosphine $P[N(CH_3)_2]_3$[6], and of the complex MoO_5, $OP[N(CH_3)_2]_3$, H_2O[8]; the following configuration is used in all the compounds: (i) both carbon atoms and the nitrogen are planar with the phosphorus atom. The C–N distance is equal to 1.48 Å and the $\widehat{CNC}$ angle to 116°; (ii) methyle groups are tetrahedral, with CH = 1.11 Å, and arranged in order to obtain the C_{3v} symmetry for all the $XP[N(CH_3)_2]_3$ molecules.

With these particular conditions, the optimization is performed by the simultaneous variation (Δ = 0.5 degree for the angles and 0.01 Å for the distances) of the following parameters:

PN and $\widehat{NPN}$ in $P[N(CH_3)_2]_3$
XP, PN and $\widehat{XPN}$ in $XP[N(CH_3)_2]_3$ X = O, S
PB, BH, BN, $\widehat{PBH}$ and $\widehat{BPN}$ in $H_3B–P[N(CH_3)_2]_3$

The results of the computation are reported in Table I. The most important difference between the theoretical model and experimental data concerns the $\widehat{NPN}$ angle of the tris-dimethylaminophosphine. The calculation shows that the lowest total energy of this molecule corresponds to a nearly planar configuration ($\widehat{NPN}$ = 118°), in contrast with the experimental angle (96.5°) determined by Vilkov and coll.[6] in the vapor state. This latter value is equal to the FPF angle observed in PF_3[9] and appears thus to be very small, since the dimethylamino groups generally present a greater steric hindrance than the fluorine atoms. Moreover, when the calculation is carried out using the geometrical model of Vilkov, the molecule of tris-dimethylaminophosphine is found to be less stable ($\Delta > 3$ a.u.), and the lone pair of phosphorus is not localized in the highest occupied molecular orbital (homo), as it has been observed in all previous studies about phosphines by MO calculations or photoelectron spectroscopy. In order to prevent further contradiction, the electronic structure of tris-dimethylaminophosphine has been determined using the geometrical configuration calculated above (Table I).

The oxide and sulphide are respectively compared to the cognate complex MoO_5, $OP[N(CH_3)_2]_3$, H_2O and triethylenethiophosphoramide $SP[N(CH_2)_2]_3$.[10]

The boron complex is compared to BH_3, $P(NH_2)_3$[11] and is shown to be the most stable in the staggered configuration, with a free rotation barrier of 15 Kcal/mol. The phosphine moiety is weakly perturbed by the borane molecule and keeps the nearly planar configuration observed for the free tris-dimethylaminophosphine.

Except the case of the tris-dimethylaminophosphine discussed above, the calculated values are generally in good agreement with the experimental data; however, the accuracy is less important than in the $XP(NH_2)_3$ series[1], principally as a consequence of the geometrical approximations previously described.

The contribution of the 3d orbitals of the phosphorus atom to the P–X link (X = O, S) is substantial, since the neglect of these orbitals in the calculation of the bond lenghth leads to very bad results: 1.71 Å and 1.96 Å respectively for the P–O and P–S distances. This contribution is less important in the formation of the phosphorus–boron bond, and an accurate distance (PB = 1.89 Å) is obtained when a simple (2s, 2p) basis set is used for phosphorus. As we demonstrated it previously[1], the sulphur atom can be reasonably described with a (2s, 2p) basis set.

Electronic Structures

The atomic populations are respectively calculated from the CNDO 2 Orthogonal Basis Set (O.B.S.) and from a corresponding Non Orthogonal Basis Set (N.O.B.S.) in order to evaluate the bond overlap population[12]. The results are reported in Table II and the contribution of the atomic orbitals to the formation of the main bonds can be clearly analyzed. The comparison of the electronic charges of the nitrogen, carbon and hydrogen atoms before and after the coordination of the X

TABLE I. Experimental and Calculated Geometrical Parameters of the $XP[N(CH_3)_2]_3$ Molecules (X = :, O, S, BH_3).

Geometrical Parameters	$P(NMe_2)_3$		$OP(NMe_2)_3$		$SP(NMe_2)_3$		$H_3BP(NMe_2)_3$	
	exp.	calc.	exp.[a]	calc.	exp.	calc.	exp.	calc.
PX (Å)			1.52	1.51		1.86		1.80
PN	1.70	1.63	1.62	1.69		1.68		1.63
BH								1.24
$\widehat{XPN}$(degr.)	$\widehat{NPN}$ 96°5	$\widehat{NPN}$ 118°	109°8	99°		98°		91°
$\widehat{PBH}$								112°

[a] In MoO_5,$OP[N(CH_3)_2]_3$, H_2O.

TABLE II. Electronic Structures of the Compounds $XP[N(CH_3)_2]_3(X = :, O, S, BH_3)$.

Atom	Atomic Orbital	$P(NMe_2)_3$		$OP(NMe_2)_3$		$SP(NMe_2)_3$		$H_3B–P(NMe_2)_3$	
		O.B.S.	N.O.B.S.	O.B.S.	N.O.B.S.	O.B.S.	N.O.B.S.	O.B.S.	N.O.B.S.
P	s	1.65	1.71	0.98	1.00	1.06	1.13	1.25	1.39
	$p(A_1)$	0.65	0.62	0.70	0.59	0.82	0.77	0.72	0.71
	p(E)	1.17	0.82	1.30	1.05	1.29	1.03	1.18	0.86
	$d(A_1)$	0.75	0.59	0.47	0.35	0.49	0.41	0.82	0.73
	d(E)	0.92	0.61	1.29	0.99	1.09	0.80	0.99	0.68
	Total	5.14	4.35	4.74	3.98	4.75	4.14	4.96	4.37
N	s	1.17	1.41	1.13	1.34	1.15	1.36	1.17	1.41
	$p(A_1)$	1.54	1.57	1.69	1.72	1.65	1.68	1.49	1.52
	p(E)	2.36	2.39	2.30	2.30	2.31	2.31	2.38	2.42
	Total	5.07	5.37	5.12	5.36	5.11	5.35	5.04	5.35
C	s	1.04	1.22	1.04	1.22	1.04	1.22	1.04	1.22
	$p(A_1)$	0.95	0.91	0.96	0.91	0.96	0.92	0.97	0.93
	p(E)	1.84	1.75	1.84	1.75	1.84	1.74	1.83	1.74
	Total	3.83	3.88	3.84	3.88	3.84	3.88	3.84	3.89
H	H	1.03	1.01	1.03	1.00	1.02	0.99	1.00	0.97
	H'	1.01	1.00	1.02	1.01	1.01	1.00	1.01	1.00
	H''	1.04	1.02	1.04	1.01	1.03	1.01	1.03	1.01
	H_{BH_3}							1.17	1.20
X	s			1.74	1.94	1.82	1.93	0.85	0.91
	$p(A_1)$			1.39	1.33	1.03	0.90	0.60	0.41
	p(E)			3.20	3.25	3.51	3.55	1.56	1.40
	Total			6.33	6.52	6.36	6.38	3.01	2.72
P–X	σ				0.32		0.39		0.42
	$p\pi$				0.29		0.30		0.08
	$d\pi$				0.47		0.20		0.03
	Total				1.08		0.89		0.53
P–N	Total		0.37		0.84		0.80		0.58

moiety on a molecule of tris-dimethylaminophosphine ($X = O, S, BH_3$) shows that the atomic populations of these centers are essentially unaltered; as a consequence the variation of the electronic population in the phosphorus orbitals can be directly associated with the formation of the P–X link. In the hexamethylphosphoramide molecule, the formation of the P–O bond is accompanied by a sigma transfer of nearly one electron from phosphorus to oxygen, with simultaneous backbonding from the latter to the 3p(E) (0.25e) and 3d(E) (0.40e) orbitals of phosphorus. The P–O overlap population (1e) has mainly pi character (70%), whereas the sigma contribution (30%) is principally supported by the overlap: $(p_zO*p_zP)>(p_zO*sP)>(p_zO*d_{z^2}P)$.

In the sulphide $SP[N(CH_3)_2]_3$, there is a P→S sigma transfer from the 3s (0.6e) and 3p (A_1) (0.2e) orbitals of phosphorus. The back donation from the sulphur atom (0.40e) is weaker than in the case of oxygen coordination, and in particular the transfer to the 3d(E) orbitals of phosphorus (0.20e). The phosphorus–sulphur overlap population presents a substantial sigma character (45%), principally submitted by (p_zS*sP) and (p_zS*p_zP) overlap.

The coordination of a BH_3 unit on a molecule $P[N(CH_3)_2]_3$ in the staggered configuration is accompanied by a transfer of 0.33 e from the phosphine to the borane; this variation is more important than the one observed in the formation of the triaminoborane complex $H_3B–P(NH_2)_3$ (0.26e)[1] and can be rationalized by the inductive properties of the dimethylamino groups–$N(CH_3)_2$ compared to the simple amino functions. The detailed atomic population (Table II) shows a loss of 0.3e in the phosphorus 3s orbital, but a small gain in the p(E) (0.04e) and d(E) (0.07e) orbitals. On the boron, the electronic gain is essentially localized in the $2p_z$ orbital (0.4e), but the other orbitals lose a total charge of 0.04e.

The main difference between the borane complex and the oxide and sulphide is the very small perturbation of the 3d orbitals of phosphorus during the coordination, indicating that no significant back bonding of the boron atom is manifest. A similar situation exists in other borane complexes, and particularly in BH_3–PF_3[13–14] and BH_3–NH_3[15]. The overlap population between phosphorus and boron is less important than in the triaminophosphine borane (0.5e) but presents comparable sigma character (80%). The main overlap can be ordered as: $(p_zB^*sP) >> (p_zB^*p_zP) > (sB^*p_zP) >> (p_zB^*d_{z^2}P)$.

Donor and Acceptor Properties

The electron donor properties of the $XP[N(CH_3)_2]_3$ compounds can be directly associated with the composition of their highest occupied molecular orbitals (HOMO), which generally corresponds to the lone pair of the donor center. Simultaneously, the analysis of the lowest unoccupied molecular orbitals (LUMO) gives interesting information about the acceptor ability of the atoms.

To this purpose, we have studied the energies, components (electronic densities) and overlap population of the main valence molecular orbitals, in order to forecast the reactivity and chemical behaviour of the molecules $XP[N(CH_3)_2]_3$ (X = :, O, S, BH_3). The data are reported in Table III. In a general way, the atomic contributions to the HOMO are more important than in the aminocomplexes $XP(NH_2)_3$, and highly localized in only a few orbitals; as a consequence, the reactivity of the tris-dimethylamino compounds *versus* donor–acceptor reactions will be greater than in the amino series and this behaviour is demonstrated in the literature.

In the tris-dimethylaminophosphine $P[N(CH_3)_2]_3$ the main electronic contribution to the HOMO is localized on the 3s and $3d_{z2}$ orbitals of the phosphorus atom; thus, the latter possesses increased basicity with regard to the nitrogen atoms and will function as the donor center of the molecule. This behaviour is in agreement with the experimental data, since numerous $XP[N(CH_3)_2]_3$ compounds are described in the literature (X = O, S, halides, BH_3, $B(CH_3)_3$). The ab-

TABLE III. Analysis of the Composition of the Highest Occupied Molecular Orbitals (h.o.m.o).

Molecule	Sym.	Energy a.u.	Overlap Population	Atom	Main Atomic Contributions to the h.o.m.o
$P(NMe_2)_3$	A_1	−0.2832	PN =	P	$0.87\ s + 0.18\ d_{z2}$
			−0.63	N_1	$0.14\ s + 0.12\ p_x$
			N–N	N_2	$0.14\ s + 0.09\ p_y + 0.03\ p_x$
			+ 0.05	N_3	$0.14\ s + 0.09\ p_y + 0.03\ p_x$
$OP(NMe_2)_3$	E	−0.3810	P–N =	P	$0.01\ p_y + 0.01\ p_x$
			−0.05	N_1	$0.01\ s + 0.40\ p_z$
				N_2	$0.01\ s + 0.40\ p_z$
			N–N	N_3	$0.01\ s + 0.40\ p_z$
			+ 0.004	H	0.05 s
				H′	0.03 s
			P–O = 0.13	H″	0.01 s
				O	$0.22\ p_y + 0.22\ p_x$
$SP(NMe_2)_3$	E	−0.3305	P–N =	P	$0.01\ p_y + 0.01\ p_x$
			−0.03	N_1	$0.03\ s + 0.21\ p_z$
				N_2	$0.03\ s + 0.21\ p_z$
			N–N	N_3	$0.03\ s + 0.21\ p_z$
			+ 0.001	H	0.02
				H′	0.01
			P–S	H″	0.007
			+ 0.20	S	$0.63\ p_y + 0.63\ p_x$
BH_3–$P(NMe_2)_3$	A_1	−0.3353	PN =	P	$0.52\ s + 0.02\ p_z + 0.24\ d_{z2}$
			−0.39	N_1	$0.10\ s + 0.02\ p_z + 0.09\ p_x$
				N_2	$0.10\ s + 0.07\ p_y + 0.02\ p_z + 0.02\ p_x$
			N–N	N_3	$0.10\ s + 0.07\ p_y + 0.02\ p_z + 0.02\ p_x$
			+ 0.04	B	$0.01\ p_z$
			P–B = + 0.15		

normaly weak basicity of the nitrogen atoms in the phosphine can be rationalized by the existence of a "$p_N\pi \rightarrow d_P\pi$" electronic transfer, since the molecular orbitals having sustantial P–N bonding contribution possess an important electronic density in both $p_N(E)$ and $d_P(E)$ orbitals. This behaviour has been observed experimentaly in the tris-diethylaminophosphine where the donor center is always the phosphorus atom; however, when the "$p_N\pi \rightarrow d_P\pi$" transfer is hindered by the introduction of a methylene group between the phosphorus and the nitrogen atoms, the basicity of the latter is strongly increased and coordination occurs with priority through these atoms[16].

On the contrary in the oxide and the sulphide, the 3d orbitals of the phosphorus atom are strongly engaged in the P–X bond (X = O, S) and the $p_N \rightarrow d_P$ transfer becomes neglectible. The basicity of the nitrogens increases substantially but remains smaller than the basicity of the oxygen and sulphur atoms. On the other hand, the latter are sterically favored and further addition will occur through these centers. A great number of hexamethylphosphoramide compounds of this type are reported in the literature, and in particular with transition metals halides[17]. Complexes of the sulphide are less numerous, but in all the cases, the donor center is the sulphur atom[18–19]. In the tris-dimethylamino-phosphine–borane complex $H_3B–P[N(CH_3)_2]_3$ the phosphorus atom is mainly engaged in the coordination of the BH_3 moiety; however the electronic density on the nitrogens is small and delocalized and a strong Lewis acid will be necessary to allow further coordination. The reaction of a second molecule of borane on a nitrogen atom is therefore impossible, whereas the formation of the hydrogen chloride complex ($HCl–H_3B–P[N(CH_3)_2]_3$) occurs easily[20, 21].

In general, the forecasting of the reactions and the corresponding experimental reports on the $XP[N(CH_3)_2]_3$ molecules are in good agreement. The order of the valence orbitals of these compounds has neither experimental nor calculated model to be compared with; however it is generally very close to the order previously observed for cognate XPY_3 molecules[22–23].

Dissociation of the tris-dimethylaminophosphine-borane complex

In order to analyze the nature of the phosphorus–boron bond of the borane complex, we have studied the theoretical dissociation of the latter into the two components BH_3 and $P[N(CH_3)_2]_3$, by separating them along the C_3-axis of the molecule. For each P–B distance, the geometrical parameters P–N, B–H, $B\hat{P}N$ and $P\hat{B}H$ are optimized and the corresponding atomic populations and phosphorus–boron overlap population are calculated (*e.g.* PBH angle *vs.* P–B distance, Figure 1).

The distances are weakly perturbed during the elongation, but both BPN and PBH angles decrease when the phosphorus–boron distance increases. In particular, when $P–B > 4.5$ Å, the borane has the plane configuration (D_{3h} symmetry) of the free molecule whereas the phosphine has again the theoretical geometry previously optimized. This distance of the phosphorus–boron link can thus be considered as the limit of the bonding interaction between the two models and a further elongation has no more influence on them.

During the separation, the total energy of the system regularly increases and no activation path is observed between the free and coordinated states. On the phosphorus, the atomic population increases in the 3s orbital and the p(E) orbital again loses the small gain acquired during the coordination. On the boron atom, the population of the 2s orbital substantially increases, but the 2p (A_1) orbital becomes empty again. When the phosphorus–boron distance is greater than 4.5 Å, the two moieties possess the electronic structure of the free species.

The analysis of the P–B overlap population as a function of the P–B distance shows clearly the sigma and pi contributions to the phosphorus–boron bond and the mechanism of the formation of this link.

The total overlap population regularly decreases and has a strong sigma character up to the P–B distance of 4.5 Å. The pi contribution appears for $PB < 3$ Å and essentially reinforces the phosphorus–boron bond near the equilibrium distance (Figure 1).

Conclusion

The use of the CNDO/2 method to determine the conformational parameters of the molecules and their chemical behaviour, can be considered as a good tool in inorganic chemistry. The geometries and electronic structures of medium-sized molecules can thus be treated with a good precision and without exaggerated amounts of computation, as shown in the study of the $XP(NH_2)_3$ series[1]. When we pass from the latter to the trisdimethylamino series, the number of atoms increases substantially and it is not possible to calculate the full number of geometrical parameters without increasing unreasonably the time of computation.

A satisfactory procedure is obtained by optimizing only the parameters concerning the central atom, the others being fixed, according to the mean values found in the literature. In a general way, the accuracy appears to be smaller than in the case of a full treatment; however the results are of great interest, and in particular when no X-Ray structural determination has been made before (*e.g.* the liquid $OP[N(CH_3)_2]_3$).

The electronic structures are not appreciably modified by the approximations introduced on the geometry

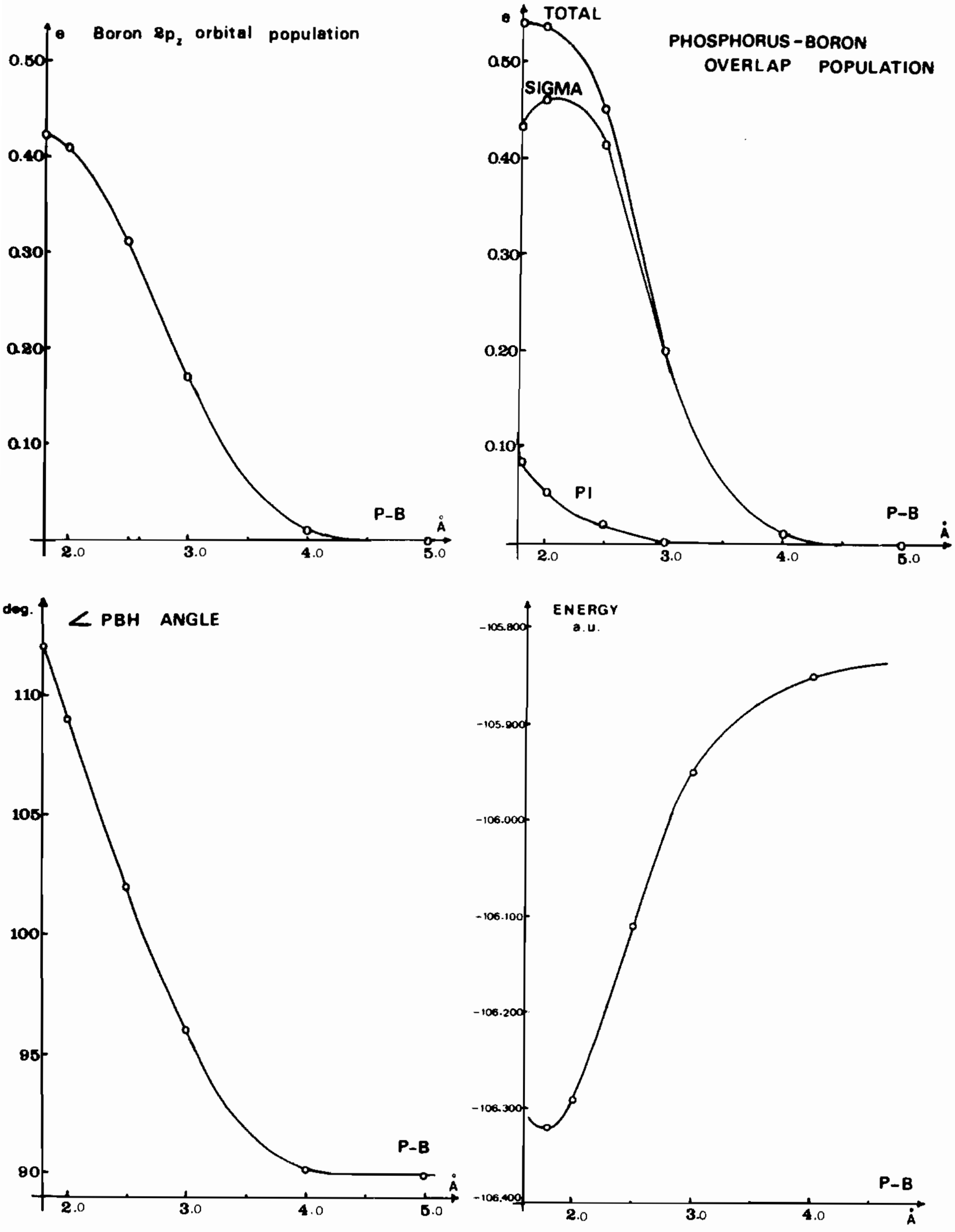

Figure 1 Variations of the geometry, energy and atomic populations during the axial dissociation of the complex BH_3–$P[N(CH_3)_2]_3$.

and give interesting information about the electronic transfers and the nature of the P–X bonds formed during the coordination (X = O, S, B, N). The phosphorus–oxygen and phosphorus–sulphur bonds can be described as essentially pi bonds, with an important contribution of the phosphorus 3d orbitals. On the contrary, no significant back-bonding is observed in the phosphorus–boron link, and the theoretical dissociation shows that the latter is mainly of the sigma type, with only a small pi contribution near the optimized P–B distance.

At last the study of the homo–lumo system of the $XP[N(CH_3)_2]_3$ compounds (X = :, O, S, BH_3) shows that it is possible to determine the relative basicity of the different centers of the molecules. This analysis consequently allows either to forccast thc chemical behaviour of these complexes, or to explain it clearly in the examples reported in the literature; in particular, the abnormally weak basicity of the nitrogens of the free phosphine can be rationalized by an important $p_N\pi \rightarrow d_P\pi$ transfer, which appreciably decreases the reactivity of these atoms, in help of phosphorus.

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