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Molecular Orbital Study on the Structure and Barrier to Internal Rotation of Phosphine-Borane

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The heat of complex formation of H_3PBH_3 was calculated to be -15.3 kcal/mol by double zeta *ab initio* LCAO MO SCF calculations; this is very similar to the experimental values for $(CH_3)_3PB(CH_3)_3$ and $(CH_3)_3PBF_3$. The origin of complex formation of H_3PBH_3 was elucidated by energy decomposition methods. The order of contributions is $ES(41\%) > CT(37\%) > PL(22\%)$. The *d* atomic orbitals on phosphorus play a role in increasing the polarization energy upon complex formation.

The barrier to internal rotation of H_3PBH_3 was calculated to be 2.4 kcal/mol, which is in very good agreement with the experimental value of 2.47 kcal/mol. The exchange repulsion and the charge transfer energy related to the staggered form contribute to the barrier to internal rotation. The change of the charge transfer energy corresponds to the difference of the barrier heights between H_3PBH_3 and H_3SiCH_3. The energies of complex formation of F_3PBH_3 and $(CH_3)_3PBH_3$ were calculated, to investigate the origin of the barrier to internal rotation.

Keywords——phosphine-borane; phosphine; borane; *ab initio*; structure; rotational barrier; molecular orbital; MO; complex; energy decomposition

The nature of the complex formed between phosphorus and boron as electron-donating and electron-accepting trivalent groups has been a source of controversy. Graham and Stone proposed that the classical σ dative bond was supplemented by d_π—p_π bonding between the phosphorus *d* orbitals and the electrons of the BH_3 group.[2] However, Alton proposed a simple P–B bond.[3,4] In connection with the charge transfer energy, the *d* orbitals take part in the σ dative bond d_σ—p_σ bonding[4] or supplement the dative bond by d_π—p_π bonding.[2] On the other hand, the electrostatic energy, the exchange repulsion and the polarization energy are connected with the stabilization due to the *d* orbitals. In this paper, the contribution of *d* orbitals on phosphorus on the complex formation between H_3P and BH_3 is studied.

Umeyama and Morokuma elucidated the origin of complex formation of H_3NBH_3 by means of *ab initio* LCAO MO calculations.[5] The dominant contributor was the electrostatic energy (61%) rather than the charge transfer energy (22%) or the polarization energy (17%).[5] Similar analyses were applied to the elucidation of phosphorus-borane complexes in the present work.

In addition to the interest in the origin of complex formation, there is considerable interest in the origin of the barrier to internal rotation. The experimental barriers to internal rotation of H_3PBH_3,[6] HF_2PBH_3,[7] and F_3PBH_3[3,8] are higher than to those of H_3SiCH_3,[9] HF_2SiCH_3,[10] and F_3SiCH_3,[11] respectively, as shown in Table I, although the central bond lengths of the compared molecules are essentially identical.[12] Durig *et al.* indicated that the increase of

Table I. Barriers in kcal/mol to Internal Rotation of X_3PBH_3 and X_3SiCH_3 where X_3 is H_3, HF_2, or F_3

X_3	X_3PBH_3	X_3SiCH_3
H_3	2.47[6)]	1.67[9)]
HF_2	3.6—4.5[7)]	1.25[10)]
F_3	3.24[4)]	1.39[11)]

0.8 kcal/mol of H_3PBH_3 in comparison with H_3SiCH_3 could be rationalized in terms of the contribution from the hydrogen repulsive potential, since the H······H distances of closest approach decreased by 0.5 Å for H_3PBH_3.[6)]

If the difference of the rotation-barrier heights between H_3SiCH_3 and H_3PBH_3 is attributable to the nuclear repulsion of the terminal nuclei, the dominant contributor to the rotation-barrier heights would be the electrostatic terms. However, Umeyama and Matsuzaki carried out energy decomposition analyses of the rotational barrier of H_3SiCH_3 and found that the exchange repulsion term was substantial;[13)] the electrostatic term is negligible in relation to the rotation-barrier height. Hence, the nuclear repulsion of the terminal nuclei should not be implicated in the increase of 0.8 kcal/mol of H_3PBH_3 in comparison with H_3SiCH_3, since it is included in the electrostatic term. In this paper, it is shown that the contribution of the charge transfer energy to the rotational barrier of H_3PBH_3, in addition to the exchange repulsion, should be considered.

Method

All the *ab initio* calculations were carried out by a closed-shell LCAO MO SCF method. The Gaussian 70 program was used.[14)] STO-3G[15)] and 4-31G[16)] basis sets were used. The *d* atomic orbitals (*AO*'s) on phosphorus were included with the exponent 0.39[17)] in the calculations of H_3PBH_3 and F_3PBH_3.

Energy decomposition analyses were performed by the method of Morokuma *et al.*[18)] The mechanics of the calculations of energy components have been summarized in the paper of Umeyama and Morokuma.[19)] The interaction energies at the MO level between A_1 symmetry MO's sets and between E symmetry MO's sets were calculated by the generalized method of Umeyama and Morokuma.[20)] A_1 MO's are σ MO's, and E MO's are π MO's.[13)] ΔE is the interaction energy upon complex formation, and can be divided as follows.

$$\Delta E = ES + EX + PL + CT + MIX,$$

where *ES* is electrostatic energy, *EX* is exchange repulsion, *PL* is polarization energy, *CT* is charge transfer energy, and *MIX* is coupling energy. *EX* was separated into two parts, *X* and *EX'*.[19,21)]

$$EX = X + EX',$$

where *X* is the attractive contribution of exchange integrals, and *EX'* the repulsive contribution of overlap integrals.

The barrier to internal rotation is given by $d\Delta E$,

$$d\Delta E = \Delta E(A\cdots B_{\text{eclipsed}}) - \Delta E(A\cdots B_{\text{staggered}}),$$

where *A* and *B* are isolated molecules. Three dots denote a complex. Energy decomposition analysis for each conformer allows the barrier to be written as a sum of components,[13,19,21,22)]

$$d\Delta E = dES + dEX + dPL + dCT + dMIX.$$

In the calculations of the barrier to internal rotation, a rigid-rotor approximation was applied.[13)]

The enthalpy of association (ΔH_g) of isolated molecules has two contributing terms: ΔH_r, the enthalpy of structural change of the isolated molecules; ΔH_k, the enthalpy on complex formation between both deformed molecules.

$$\Delta H_g = \Delta H_r + \Delta H_k$$

The energy for the effect of *d AO*'s on phosphorus was calculated as follows.

$$\Delta\Delta E = \Delta E_2 - \Delta E_1,$$

where ΔE_1 is the interaction energy upon complex formation between the PH_3 and BH_3 groups without *d AO*'s on phosphorus, and ΔE_2 is that with *d AO*'s on phosphorus. $\Delta\Delta E$ can be separated into five terms;

$$\Delta\Delta E = \Delta ES + \Delta EX + \Delta PL + \Delta CT + \Delta MIX.$$

Geometries——The geometry of H_3PBH_3 as judged from microwave spectra[6] is r(PB) = 1.937 Å, r(PH) = 1.399 Å, r(BH) = 1.212 Å, ∠BPH = 116.9°, and ∠PBH = 103.6°, and, on the other hand, r(PB) as determined by X-ray analysis is 1.93 Å.[23] The data based on the microwave spectra were adopted. The structure is shown in Fig. 1. The geometry of F_3PBH_3 as judged from microwave spectra[8] is r(PB) = 1.836 Å, r(PF) = 1.538 Å, r(BH) = 1.207 Å, ∠PBH = 103.03°, and ∠BPF = 117.94°. The geometry of $(CH_3)_3PBH_3$ as judged from microwave spectra[24] is r(PB) = 1.901 Å, r(PC) = 1.819 Å, r(BH) = 1.212 Å, ∠PBH = 105.06°, and ∠BPC = 113.64°. In the complex of $(CH_3)_3PBH_3$, the geometry of the methyl groups is $r(CH_s)$ = 1.112 Å, $r(CH_a)$ = 1.090 Å, $\angle PCH_s$ = 111.4°, $\angle PCH_a$ = 109.8°, the dihedral angle of $BPCH_s$ = 180°, and the dihedral angle of $BPCH_a$ = 60° or −60° in the clockwise direction as judged from the microwave spectra of trimethylphosphine.[25]

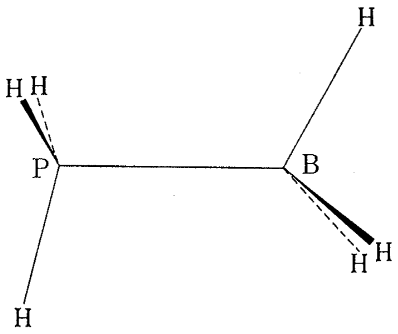

Fig. 1. Structure of H_3PBH_3

Calculations were carried out on HITAC 8700 and 8800 machines in the Tokyo University Computer Center.

Results and Discussion

Complex Formation of H_3PBH_3

The structure and conformation of trimethylphosphine reported by Bryan and Kuczkowski showed that the phosphorus possessed an unshared electron pair.[25] Since the form of isolated PH_3 is similar to that of the PH_3 group in the complex H_3PBH_3, the deformation energy (ΔH_r) of PH_3 is assumed to be about zero. ΔH_r of BH_3 was calculated to be 12.4 kcal/mol.[26] The heat on complex formation (ΔH_k) was calculated to be −27.7 kcal/mol, as shown in Table II.[27] From the equation $\Delta H_g = \Delta H_r + \Delta H_k$, the enthalpy of association of H_3PBH_3 is −15.3 kcal/mol. The heats of association of $(CH_3)_3PB(CH_3)_3$ and $(CH_3)_3PBF_3$ were experimentally determined as −16.5 and −18.9 kcal/mol, respectively.[28] Therefore the value of −15.3 kcal/mol for H_3PBH_3 is reasonable.

Table II. Interaction Energy in kcal/mol between the PH_3 and BH_3 Groups and Energy Decomposition Analyses (4-31G Basis Set)

	4-31G with *d AO*'s on P	4-31G without *d AO*'s on P		Effect of *d AO*'s on P
ΔE	−27.7	−20.2	$\Delta\Delta E$	−7.5
ES	−71.8(41%)	−79.1	ΔES	7.3
EX	113.4	113.8	ΔEX	−0.4
PL	−38.8(22%)	−23.0	ΔPL	−15.8
CT	−65.8(37%)	−64.1	ΔCT	−1.7
MIX	35.3	32.3	ΔMIX	3.0

In order to elucidate the origin of complex formation of H_3PBH_3, energy decomposition analyses were performed, and the results are also shown in Table II. The order of contribution to the complex formation is $ES(41\%) > CT(37\%) > PL(22\%)$. In comparison with the complex of H_3NBH_3,[13] the contribution of ES is lower, while that of CT is higher. Nevertheless, the origin of the H_3PBH_3 complex is predominantly due to ES. The 63% contribution of $ES+PL$ is much larger than that of CT, and, hence, this complex is not linked by a simple dative bond to which only CT contributes. The stabilization energy, $\Delta\Delta E$, due to the effects of *d AO*'s of phosphorus on the complex formation was calculated to be 7.5 kcal/mol. In other words, the association enthalpy (ΔH_g) of the complex is estimated to be stabilized by the *d* orbitals on phosphorus by 7.5 kcal/mol. The polarization energy is the major contributor to the stabilization. The charge transfer energy and the exchange repulsion are almost unchanged. Since the *PL* term is not involved in the intermolecular electron overlaps, the P–B bond of the complex between H_3P and BH_3 is not supplemented by d_π—p_π and d_σ—p_σ bonding between *d* electrons on phosphorus and electrons of the BH_3 group. Thus, the calculated results show that the contributions of the d_π—p_π bonding proposed by Graham and Stone[2)] and the d_σ—p_σ bonding taking part in the simple dative bond[4)] are negligible in the complex formation of H_3PBH_3.

Table III. Barrier to Internal Rotation in kcal/mol of H_3PBH_3 and Energy Decomposition Analyses Relative to Staggered Conformation (4-31G Basis Set)

	4-31G with *d AO*'s on P	4-31G without *d AO*'s on P	Effect of *d AO*'s on P
dΔE[a)]	2.4	2.1	0.3
dES	0.1	0.0	0.1
dEX	1.4	1.2	0.2
dPL	−0.0	−0.0	0.0
dCT	0.9	1.0	−0.1
dMIX	0.0	−0.2	0.2

a) *dΔE* is the rotational barrier between eclipsed and staggered forms. The experimental value of the rotational barrier is 2.47±0.05 kcal/mol.[6)]

Barrier to Internal Rotation of H_3PBH_3

The barrier to internal rotation of H_3PBH_3 was calculated to be 2.4 kcal/mol, as shown in Table III. This value is in fairly good agreement with the experimental value of 2.47 kcal/mol.[6)] *dEX* is the dominant contributor, and *dCT* is next most significant. The *dEX* value of 1.4 kcal/mol is comparable with that of 1.3 kcal/mol for H_3SiCH_3 reported by Umeyama and Matsuzaki.[13)] In the calculations for H_3SiCH_3 the dominant contributor is *dEX*. The *dEX* term is similar to that of the H_3PBH_3 complex. The difference of the barrier heights between H_3SiCH_3 and H_3PBH_3, 0.9 (=2.4−1.3), was found to be due to *dCT*. The proposal of Durig *et al.*, who viewed the difference in terms of nuclear repulsion of the terminal nuclei, can be ruled out, since the *dES* term does not affect the barriers to internal rotation of H_3SiCH_3 and H_3PBH_3.

The barrier height without *d AO*'s on phosphorus provides insight into the contribution of *d AO*'s to the barrier to internal rotation, and it was calculated to be 2.1 kcal/mol, as shown in Table III. The change of the barrier height is only 0.3 kcal/mol, and the effect of *d AO*'s

Table IV. Analyses of the Barrier to Internal Rotation of H_3PBH_3 Based on Overlap Repulsion Terms Obtained from Calculations by Using a 4-31G Basis Set without *d AO*'s on P

MO's of PH_3	MO's of BH_3	*EX'*[a)] of staggered	*EX'* of eclipsed	*dEX'*
All occupied MO's	All occupied MO's	321.4 (309.2)[b)]	323.5 (311.5)[b)]	2.1 (2.3)[b)]
Occupied p_π MO's	Occupied p_π MO's	19.2	21.6	2.4
Occupied valence p_π MO's	Occupied valence p_π MO's	18.7	21.0	2.3

a) *EX'*=*EX*−*X*.
b) The values obtained from calculations by using a 4-31G basis set with *d AO*'s on phosphorus.

on *dEX* is small (only 0.2 kcal/mol). Since the barrier height due to the *EX* term without *d AO*'s is similar to that with *d AO*'s, the exchange repulsion between d_π electrons of phosphorus and p_π electrons of the BH_3 group is not important in determining the barrier height.

Moreover, in order to elucidate the origin of *dEX*, *dEX*' was calculated and analyzed at MO level, as shown in Table IV. *dEX*' is entirely due to the overlap repulsion between valence p_π MO's of the PH_3 and BH_3 groups. On the other hand, since *dX* is -0.9 kcal/mol (including *d AO*'s), the contribution of the *X* term to the barrier height is not significant.

TABLE V. Barriers to Internal Rotation in kcal/mol of H_3PBH_3 and $(CH_3)_3PBH_3$, and Energy Decomposition Analyses (STO-3G Basis Set)

	H_3PBH_3	$(CH_3)_3PBH_3$
$d\Delta E^{a)}$	$1.6(2.47)^{b)}$	1.8
dES	$0.1(0.2)^{c)}$	0.0
dEX	$0.8(1.2)^{c)}$	1.1
dPL	$0.0(0.0)^{c)}$	0.0
dCT	$0.6(1.1)^{c)}$	0.5
$dMIX$	$0.1(0.2)^{c)}$	0.2

a) $d\Delta E$ is the barrier height between eclipsed and staggered forms.
b) Experimental values.
c) Parentheses show the scaled values in comparison with the experimental values.
These values were obtained from the equation,
the scaled value=the calculated decomposition term
$\times \dfrac{\text{the experimental barrier height}}{\text{the calculated barrier height}}$

Barrier to Internal Rotation of $(CH_3)_3PBH_3$

Since *dEX* and *dCT* contribute significantly to the barrier to internal rotation of H_3PBH_3, similar calculations on the barrier to internal rotation of $(CH_3)_3PBH_3$ were carried out, as shown in Table V, with an STO-3G basis set. The barrier height of $(CH_3)_3PBH_3$ is due to *dEX* and *dCT*. In the case of H_3PBH_3, the calculations with an STO-3G basis set do not affect the conclusion that *dCT* is a significant contributor to the barrier to internal rotation. Hence, the use of the STO-3G basis set to estimate the contribution of *dCT* to the barrier height appears to be valid. In the case of H_3PBH_3, the energy decomposition terms in Table V (scaled in relation to the experimental barrier height) are in fairly good agreement with the energy decomposition terms in Table III.

Barrier to Internal Rotation of F_3PBH_3

The energy decomposition terms for the rotation-barrier height of the F_3PBH_3 complex, which were calculated with a 4-31G basis set, are scaled as shown in Table VI. *dCT* is the

TABLE VI. Barrier to Internal Rotation in kcal/mol or F_3PBH_3, and Energy Decomposition Analyses (4-31G Basis Set)

	4-31G with *d AO*'s on phosphorus		4-31G with *d AO*'s on phosphorus
$d\Delta E^{a)}$	$2.4(3.24)^{b)}$	dPL	$-0.1(-0.1)^{c)}$
dES	$0.1(0.1)^{c)}$	dCT	$1.5(2.0)^{c)}$
dEX	$0.9(1.2)^{c)}$	$dMIX$	$-0.0(-0.0)^{c)}$
(dEX')	$(1.3)\,(1.8)^{c)}$		

a) $d\Delta E$ is the barrier height between eclipsed and staggered forms.
b) Experimental values.
c) Parentheses show the scaled values in comparison with the experimental values. These values were obtained from the equation,
the scaled value=the calculated decomposition term
$\times \dfrac{\text{the experimental barrier height}}{\text{the calculated barrier height}}$

most significant contributor to the barrier to internal rotation, and *dEX* is also siginificant. Moreover, the difference (1.85 kcal/mol) of barrier heights between F_3PBH_3 and F_3SiCH_3, as shown in Table I, is thought to be attributable to *dCT* by analogy with the discussions on the difference of the barrier heights between H_3PBH_3 and H_3SiCH_3.

Conclusion

(1) The origin of the complex formation of H_3PBH_3 was studied. The order of energy contribution is $ES(41\%) > CT(37\%) > PL(22\%)$. The *d AO*'s on phosphorus increase the polarization energy upon complex formation.

(2) The origin of the barrier to internal rotation of H_3PBH_3 is *dEX* and *dCT*. The difference of barrier heights between H_3PBH_3 and H_3SiCH_3 may be attributed to *dCT*. The overlap repulsion *dEX*' in *dEX* is due to the MO interactions between occupied valence p_π MO's sets of the PH_3 and BH_3 groups.

(3) The barriers to internal rotation of F_3PBH_3 and $(CH_3)_3PBH_3$ are due to *dEX* and *dCT*. The difference of the barrier heights between F_3PBH_3 and F_3SiCH_3 is thought to be attributable to *dCT*.

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