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The Origin of the Internal Rotation Barrier of Borane Compounds

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The origin of the rotational barriers in borane molecular complexes, H_3N-BH_3, H_3N-BF_3, $(CH_3)_3N-BH_3$, $(CH_3)_3N-BF_3$ and $(CH_3)_3N-B(CH_3)_3$, was shown to be the exchange repulsion by *ab initio* closed shell LCAO MO SCF calculations.

The substituent effects of methyl groups and fluorines on the rotational barrier were attributed to the changes of the exchange repulsion.

Keywords——rotation barrier; borane compounds; *ab initio* calculations; structure; molecular orbital; energy decomposition

The rotational barrier between the eclipsed and staggered structures of borazane has been explained in terms of the difference of the exchange repulsion.[2] Moreover, the rotational barrier of NH_3BH_3 was studied at the MO level, and was attributed to the exchange repulsion among occupied pseudo π molecular orbitals.[3] In this paper, in order to clarify the origins of the rotational barriers of various borane compounds, calculations are performed for H_3N-BH_3, H_3N-BF_3, $(CH_3)_3N-BH_3$, $(CH_3)_3N-BF_3$ and $(CH_3)_3N-B(CH_3)_3$. The origins of substituent effects of methyl groups and fluorines are also elucidated.

Method

All the *ab initio* calculations were carried out using a closed shell LCAO MO SCF method. The Gaussian 70 program was used.[4] An STO-3G basis set was used,[5] since it is useful for the energy decomposition of the rotational barrier.[2,6] The barrier to internal rotation is given by $\varDelta\varDelta E$,[6]

$$\varDelta\varDelta E=\varDelta E(\mathrm{A\cdots B_{eclipsed}})-\varDelta E(\mathrm{A\cdots B_{staggered}}),$$

where A and B are isolated molecules. The energy decomposition analysis for each conformer allows the barrier to be written as a sum of components,[2,6]

$$\varDelta\varDelta E=\varDelta ES+\varDelta EX+\varDelta PL+\varDelta CT+\varDelta MIX$$

where ES is the electrostatic interaction energy, EX is the exchange repulsion energy, PL is the polarization energy, CT is the charge transfer energy, and MIX is the coupling energy. In calculations of the rotational barrier, a rigid-rotor approximation was applied.[3]

Geometries——The geometry of H_3N-BH_3 is $r(\mathrm{N\cdots B})=1.60$ Å,[7] $r(\mathrm{NH})=1.0124$ Å, $r(\mathrm{BH})=1.19$ Å, $\angle\mathrm{HNH}=106.67°$, and $\angle\mathrm{NBN}=106.3°$.[2] The geometry of H_3N-BF_3 is $r(\mathrm{N\cdots B})=1.60$ A,[8] $r(\mathrm{NH})=0.9983$ Å,[9] $r(\mathrm{BF})=1.38$ Å,[8] $\angle\mathrm{HNB}=111.467°$,[9] and $\angle\mathrm{NBF}=107.895°$.[8] The geometry of $(CH_3)_3N-BH_3$ is $r(\mathrm{N\cdots B})=1.60$ Å,[7,9,10] $r(\mathrm{BH})=1.248$ Å,[9] $\angle\mathrm{NBH}=106.581°$,[9] and that of $(CH_3)_3N$ is assumed to be the

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same as in $(CH_3)_3N-BF_3$.[11] The geometry of $(CH_3)_3N-BF_3$ is $r(N\cdots B)=1.673$ Å, $r(BF)=1.374$ Å, $r(NC)=1.485$ Å, $r(CH)=1.100$ Å, $\angle CNB=109.3°$, $\angle NBF=105.776°$, $\angle H_sCN=111.7°$, and $\angle H_aCN=110.1°$.[11]

The geometry of $(CH_3)_3N-B(CH_3)_3$ is $r(N\cdots B)=1.80$ Å;[12] that of $N(CH_3)_3$ is assumed to be the same as in $(CH_3)_3N-BH_3$, as mentioned above, and that of $B(CH_3)_3$ is assumed to be the same as for the monomer ($r(BC)=1.56$ Å).[13]

Calculations were carried out using a HITAC M-1602 at the National Cancer Center.

Results and Discussion

Figure 1 shows the calculated structures of the molecular complexes. Table I lists the results. The origin of the rotational barriers for all the borane compounds was the exchange repulsion. In the molecular complex of H_3N-BF_3, the rotational barrier was smaller than in H_3N-BH_3 due to ΔEX. Since the rotational barrier of H_3N-BH_3 can be explained in terms of the degenerate pseudo $2p_\pi$ MO's as described in the preceding paper and shown in Fig. 2,[3] the $2p_\pi$ gross orbital charges of boron and nitrogen are thought to be significant.

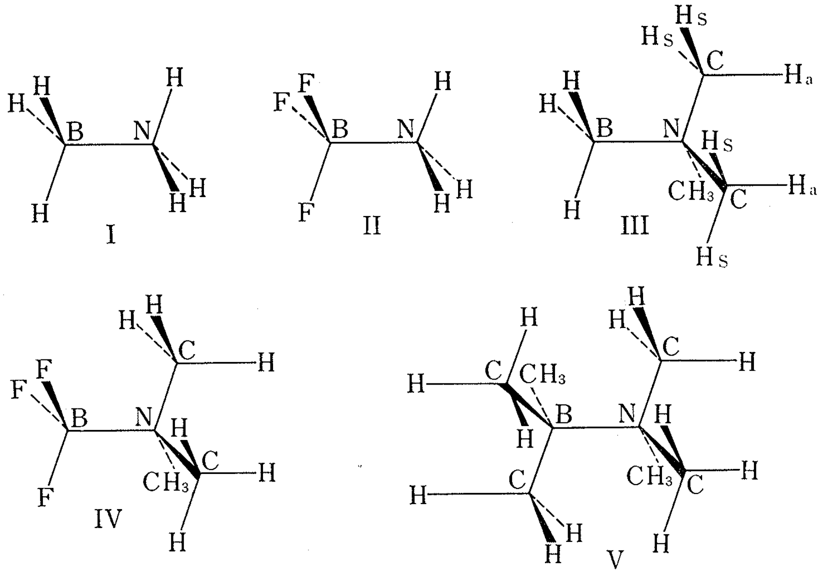

Fig. 1. Staggered Structures of Various Borane Compounds

I is H_3B-NH_3, II is F_3B-NH_3, III is $H_3B-N(CH_3)_3$, IV is $F_3B-N(CH_3)_3$, and V is $(CH_3)_3B-N(CH_3)_3$.

Table I. Internal Rotation Barriers in kcal/mol and Energy Decomposition Analyses of Borane Compounds, H_3N-BH_3, H_3N-BF_3, $(CH_3)_3N-BH_3$, $(CH_3)_3N-BF_3$ and $(CH_3)_3N-B(CH_3)_3$

	Rotational barrier and energy decomposition				
	H_3N-BH_3	H_3N-BF_3	$(CH_3)_3N-BH_3$	$(CH_3)_3N-BF_3$	$(CH_3)_3N-B(CH_3)_3$
$\Delta\Delta E$	3.0	0.2	6.1	4.7	7.0
ΔES	−0.3	−0.4	−1.4	−0.9	7.1[a]
ΔEX	2.7	1.2	6.9	6.8	
ΔPL	−0.1	−0.1	−0.0	0.0	
ΔCT	1.2	0.5	0.4	−0.7	
ΔMIX	−0.5	−1.0	0.1	−0.5	

a) $\Delta(ES+EX)$ is the term obtained without changing the MO's of the isolated molecules, *i.e.*, it is not perturbed.

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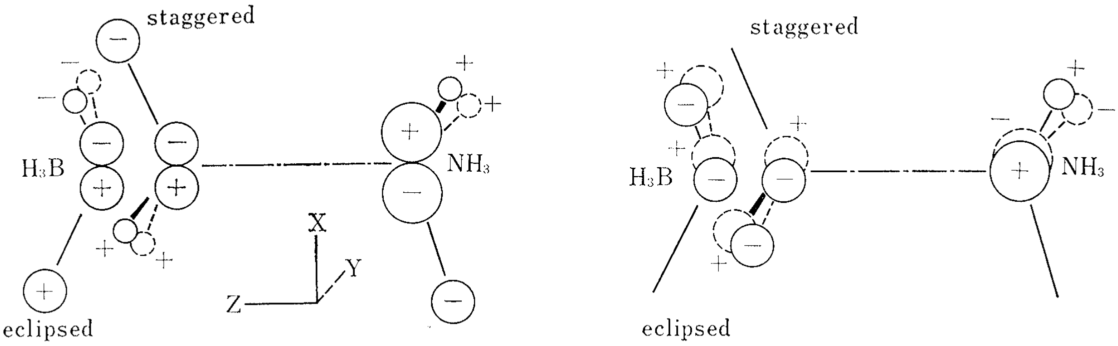

Fig. 2. Degenerate $2p_\pi$ MO's of BH_3 and NH_3 in the Staggered and Eclipsed Forms

The gross orbital charges of $2p_\pi$ of the borons in BH_3 and BF_3 were 0.888 and 0.586, respectively. The difference in the gross orbital charges of $2p_\pi$ of the borons between BH_3 and BF_3 may explain the decrease of the exchange repulsion on replacement of BH_3 with BF_3. On replacement of NH_3 with $N(CH_3)_3$, the rotational barrier increased due to ΔEX. The gross orbital charges of $2p_\pi$ of the nitrogens in NH_3 and $N(CH_3)_3$ were 1.068 and 0.995 respectively. The difference in the gross orbital charges between two nitrogens can not account for the increase of the rotational barrier on replacement of NH_3 with $N(CH_3)_3$. Hydrogen H_s's of the $N(CH_3)_3$ group in Fig. 1 are close to the $2p_\pi$ orbital of boron and the H orbitals of NH_3. The exchange repulsions between H_s orbitals and the $2p_\pi$ orbital of the boron and between H's orbitals of BH_3 and H_s's orbitals may contribute to the rotational barrier. On replacement of BH_3 with $B(CH_3)_3$, the rotational barrier increased due to $\Delta(EX+ES)$. The gross orbital charge of $2p_\pi$ of the boron in $B(CH_3)_3$ was 0.801. This value is smaller than that of the boron in BH_3. Therefore the effect of replacement of NH_3 with $N(CH_3)_3$ can be considered in similar terms.

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