The Origin of the Internal Rotation Barrier of Borane Compounds

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The origin of the rotational barriers in borane molecular complexes, $\text{H}_3\text{N}-\text{BH}_3$, $\text{H}_3\text{N}-\text{BF}_3$, $(\text{CH}_3)_3\text{N}-\text{BH}_3$, $(\text{CH}_3)_3\text{N}-\text{BF}_3$ and $(\text{CH}_3)_3\text{N}-\text{B}(\text{CH}_3)_3$, 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 $\text{H}_3\text{N}-\text{BH}_3$, $\text{H}_3\text{N}-\text{BF}_3$, $(\text{CH}_3)_3\text{N}-\text{BH}_3$, $(\text{CH}_3)_3\text{N}-\text{BF}_3$ and $(\text{CH}_3)_3\text{N}-\text{B}(\text{CH}_3)_3$. 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 $\Delta\Delta E$,⁶⁾

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

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)}

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

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 $\text{H}_3\text{N}-\text{BH}_3$ is $r(\text{N} \cdots \text{B}) = 1.60 \text{ \AA}$,⁷⁾ $r(\text{NH}) = 1.0124 \text{ \AA}$, $r(\text{BH}) = 1.19 \text{ \AA}$, $\angle \text{HNB} = 106.67^\circ$, and $\angle \text{NBN} = 106.3^\circ$.²⁾ The geometry of $\text{H}_3\text{N}-\text{BF}_3$ is $r(\text{N} \cdots \text{B}) = 1.60 \text{ \AA}$,⁸⁾ $r(\text{NH}) = 0.9983 \text{ \AA}$,⁹⁾ $r(\text{BF}) = 1.38 \text{ \AA}$,⁸⁾ $\angle \text{HNB} = 111.467^\circ$,⁹⁾ and $\angle \text{NBF} = 107.895^\circ$.⁸⁾ The geometry of $(\text{CH}_3)_3\text{N}-\text{BH}_3$ is $r(\text{N} \cdots \text{B}) = 1.60 \text{ \AA}$,^{7,9,10)} $r(\text{BH}) = 1.248 \text{ \AA}$,⁹⁾ $\angle \text{NBH} = 106.581^\circ$,⁹⁾ and that of $(\text{CH}_3)_3\text{N}$ is assumed to be the

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same as in $(\text{CH}_3)_3\text{N}-\text{BF}_3$.¹¹ The geometry of $(\text{CH}_3)_3\text{N}-\text{BF}_3$ is $r(\text{N}\cdots\text{B})=1.673 \text{ \AA}$, $r(\text{BF})=1.374 \text{ \AA}$, $r(\text{NC})=1.485 \text{ \AA}$, $r(\text{CH})=1.100 \text{ \AA}$, $\angle\text{CNB}=109.3^\circ$, $\angle\text{NBF}=105.776^\circ$, $\angle\text{H}_s\text{CN}=111.7^\circ$, and $\angle\text{H}_a\text{CN}=110.1^\circ$.¹¹

The geometry of $(\text{CH}_3)_3\text{N}-\text{B}(\text{CH}_3)_3$ is $r(\text{N}\cdots\text{B})=1.80 \text{ \AA}$,¹² that of $\text{N}(\text{CH}_3)_3$ is assumed to be the same as in $(\text{CH}_3)_3\text{N}-\text{BH}_3$, as mentioned above, and that of $\text{B}(\text{CH}_3)_3$ is assumed to be the same as for the monomer ($r(\text{BC})=1.56 \text{ \AA}$).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 $\text{H}_3\text{N}-\text{BF}_3$, the rotational barrier was smaller than in $\text{H}_3\text{N}-\text{BH}_3$ due to ΔEX . Since the rotational barrier of $\text{H}_3\text{N}-\text{BH}_3$ 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 $\text{H}_3\text{B}-\text{NH}_3$, II is $\text{F}_3\text{B}-\text{NH}_3$, III is $\text{H}_3\text{B}-\text{N}(\text{CH}_3)_3$,
IV is $\text{F}_3\text{B}-\text{N}(\text{CH}_3)_3$, and V is $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_3$.

TABLE I. Internal Rotation Barriers in kcal/mol and Energy Decomposition Analyses of Borane Compounds, $\text{H}_3\text{N}-\text{BH}_3$, $\text{H}_3\text{N}-\text{BF}_3$, $(\text{CH}_3)_3\text{N}-\text{BH}_3$, $(\text{CH}_3)_3\text{N}-\text{BF}_3$ and $(\text{CH}_3)_3\text{N}-\text{B}(\text{CH}_3)_3$

	Rotational barrier and energy decomposition				
	$\text{H}_3\text{N}-\text{BH}_3$	$\text{H}_3\text{N}-\text{BF}_3$	$(\text{CH}_3)_3\text{N}-\text{BH}_3$	$(\text{CH}_3)_3\text{N}-\text{BF}_3$	$(\text{CH}_3)_3\text{N}-\text{B}(\text{CH}_3)_3$
ΔAE	3.0	0.2	6.1	4.7	7.0
ΔES	-0.3	-0.4	-1.4	-0.9	
ΔEX	2.7	1.2	6.9	6.8	7.1 ^{a)}
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) $\Delta(\text{ES}+\text{EX})$ 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 $\text{N}(\text{CH}_3)_3$, the rotational barrier increased due to ΔEX . The gross orbital charges of $2p_{\pi}$ of the nitrogens in NH_3 and $\text{N}(\text{CH}_3)_3$ 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 $\text{N}(\text{CH}_3)_3$. Hydrogen H_s 's of the $\text{N}(\text{CH}_3)_3$ 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 $\text{B}(\text{CH}_3)_3$, the rotational barrier increased due to $\Delta(EX+ES)$. The gross orbital charge of $2p_{\pi}$ of the boron in $\text{B}(\text{CH}_3)_3$ was 0.801. This value is smaller than that of the boron in BH_3 . Therefore the effect of replacement of NH_3 with $\text{N}(\text{CH}_3)_3$ can be considered in similar terms.

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