CHEMICAL & PHARMACEUTICAL BULLETIN

Vol. 28, No. 8 August 1980

Regular Articles

Chem. Pharm. Bull.
28(8)2279—2285(1980)

Molecular Orbital Studies on the CH_3CN-BH_3, HCN-BH_3, CH_3NC-BH_3 and HNC-BH_3 Complexes

Hideaki Umeyama and Tomoko Nomoto

School of Pharmaceutical Sciences, Kitasato University[1]

(Received September 19, 1979)

Molecular orbital studies on the binding forces of CH_3CN–BH_3, HCN–BH_3, CH_3NC–BH_3 and HNC–BH_3 complexes were carried out in comparison with other borane compounds. For the CH_3CN–BH_3 and HCN–BH_3 complexes, the electrostatic energy contributes dominantly, while the charge transfer energy and polarization energy are also significant. For the CH_3NC–BH_3 and HNC–BH_3 complexes, on the other hand, the polarization energy, the charge transfer energy and the electrostatic energy contribute comparably. The bonding of BH_3 with nitriles and isonitriles is end-on rather than side-on, since electrostatic interaction is most favored when the electron-deficient B of BH_3 approaches the N (or C) end of RCN (or RNC) along an extension of the CN (or NC) axis.

Keywords——structure; complex; nitrile; isonitrile; quantum chemistry; borane; compound; nitrogenase; MO; energy decomposition

Molecular orbital studies on borane compounds have been carried out. The formation of H_3N–BH_3 is predominantly due to the electrostatic term.[2] The large methyl substituent effect at the NH_3 part of the complex is attributable to the difference in polarization energy.[2] The formation of OC–BH_3 is due to the charge transfer energy, the polarization energy and the electrostatic interaction energy to almost equal extents.[2] The binding forces of HCN–BH_3, CH_3CN–BH_3, HNC–BH_3 and CH_3NC–BH_3 complexes are also compared with those of H_3N–BH_3 and OC–BH_3.

Method

All the calculations were performed within the framework of a closed-shell single determinant of the *ab initio* LCAO–SCF theory, using the Gaussian 70 program.[3] The split-valence 4-31G basis set was used with the suggested standard scale factors.[4]

Energy decomposition analyses of the intermolecular interaction energy were performed by the method of Morokuma *et al.*[5] The stabilization energy (ΔE) between one molecule and the other can be decomposed into five terms,

---

[1] Location: *9-1, Shirokane 5-chome, Minato-ku, Tokyo 108, Japan.*

[2] H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 7208 (1976).

[3] W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton, and J.A. Pople, Gaussian 70 Program 236, Quantum Chemistry Program Exchange, Indiana University, **1974.**

[4] R. Ditchfield, W.J. Hehre, and J.A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

[5] *a*) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); *b*) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976).

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

where ES is the electrostatic interaction energy, EX is the exchange repulsion, PL is the polarization energy, CT is the charge transfer energy, and MIX is the coupling energy. Calculations were carried out on a Hitachi M-180 computer at the Institute for Molecular Science.

Geometries——Experimental values are: for CH_3CN, $r(CH)=1.1025$ Å, $r(CC)=1.45836$ Å, $r(CN)=1.15710$ Å and $\angle HCC=109.5°$;⁽⁶⁾ for CH_3NC, $r(HC)=1.10146$ Å, $r(CN)=1.42393$ Å, $r(NC)=1.16616$ Å and $\angle HCN=109.1°$;⁽⁶⁾ for BH_3, $r(BH)=1.20$ Å and $\angle XBH=104.606°$;⁽⁷⁾ for HCN, $r(HC)=1.0632$ Å and $r(CN)=1.1571$ Å;⁽⁶⁾ for HNC, $r(HN)=0.98$ Å⁽⁸⁾ and $r(NC)=1.1571$ Å.⁽⁶⁾

Results and Discussion

HCN-BH_3 Complex

Calculations of stabilization energies were carried out at various distances (changing by 0.01 Å) and conformations between HCN and BH_3. The stabilization energy was found to be minimum at a distance of 1.65753 Å and the value was calculated to be −22.1 kcal/mol. The structure is shown in Fig. 1. The stabilization energies for $\alpha=30°$, 60° and 85° were also calculated, where α is the angle between the axis of the $C_{\infty v}$ symmetry of HCN and that of the C_{3v} symmetry of BH_3. The differences of the stabilization energies at $\alpha=0°$ and 30°, 60° or 85° are given in Fig. 1.⁽⁹⁾ The structure in which the axis of the $C_{\infty v}$ symmetry of HCN coincides with that of the C_{3v} symmetry of BH_3 was found to be most stable. On the other hand, when BH_3 approaches the CN center of mass,⁽¹⁰⁾ the stabilization energy was found to be minimum at a distance of 2.652 Å. The value was calculated to be −2.7 kcal/mol. The side-on bonding structure is shown in Fig. 1, but this is much less stable than the end-on bonding structure.

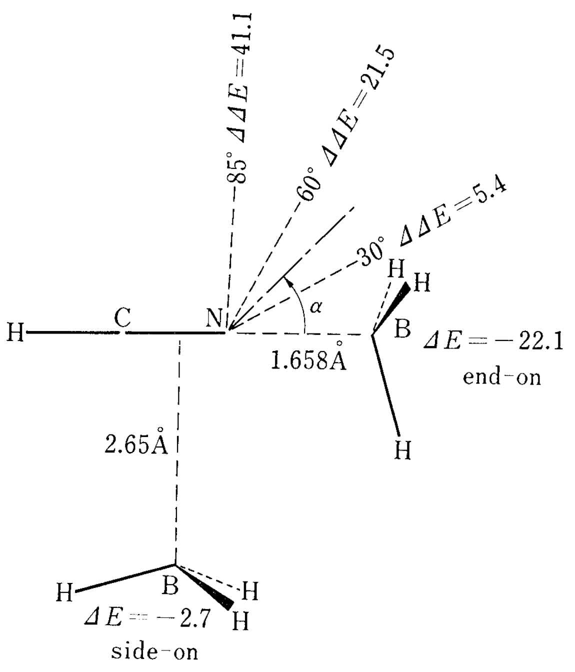

Fig. 1. The Structure of the HCN–BH_3 Complex

In the C_{3v} symmetry structure of the complex, the distance between N and B is 1.658 Å. ΔE is the stabilization energy in kcal/mol for the end-on or the side-on binding structure. $\Delta\Delta E$ is the destabilization in kcal/mol from the C_{3v} symmetry structure upon change of α.

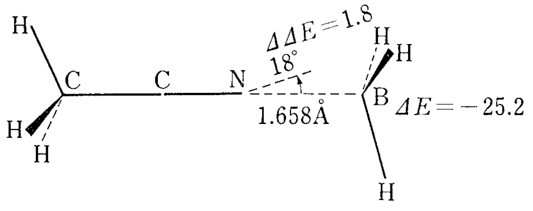

Fig. 2. The Structure of the CH_3CN–BH_3 Complex

ΔE is the stabilization energy in kcal/mol between CH_3CN and BH_3. $\Delta\Delta E$ is the destabilization in kcal/mol from the C_{3v} symmetry structure.

---

6) *a*) L.E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, **1958**; *b*) L.E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions (Supplement)," The Chemical Society, London, **1965**,

7) W. Gordy, H. Ring, and A. Burg, *Phys. Rev.*, **78**, 512 (1950).

8) The distance $r(HN)$ was optimized using a 4-31G basis set.

9) Although the distance $r(N–B)$ does not change with increase of α, the conclusions are qualitative.

10) D.H. Liscow, C.F. Bender, and H.F. Schaefer III, *J. Am. Chem. Soc.*, **94**, 5178 (1972); The CN center of mass was used in calculations of methyl isocyanide isomerization.

TABLE I. Stabilization Energies and Energy DecompositionAnalyses in kcal/mol of the CH_3CN-BH_3 and $HCN-BH_3$ Complexes using a 4-31G Basis Set

	CH_3CN-BH_3							$HCN-BH_3$
	C_{3v} symmetry structure ($\alpha=0°$)						$\alpha=18°$	C_{3v} symmetry structure
	(1) 1.63 (Å)	(2) 1.65 (Å)	(3) 1.65717[a)] (Å)	(4) 1.65753[b)] (Å)	(5) 1.68 (Å)		(6) 1.65753 (Å)	(7) 1.65753 (Å)
ΔE	−25.10	−25.17	−25.18	−25.18	−25.13	*ΔΔE*	1.8[e)]	3.1[f)]
ES	−65.86	−62.78	−61.71	−61.66	−58.42	*ΔES*	1.8	3.2
EX	90.37	84.56	82.56	82.46[c)]	76.48	*ΔEX*	0.0	−0.9
PL	−41.79	−38.08	−36.83	−36.76	−33.12	*ΔPL*	1.5	1.8
CT	−43.56	−40.39	−39.32	−39.26[d)]	−36.11	*ΔCT*	0.6	0.0
MIX	35.74	31.52	30.12	30.06	26.05	*ΔMIX*	−2.2	−1.0

a) The value obtained from a polynominal fit of the values at distances of 1.63, 1.65, 1.65753 and 1.68 Å.
b) The value obtained from a parabolic fit of the values at distances of 1.63, 1.65 and 1.68 Å.
c) The *EX* term can be divided into *EX'* and *X* terms.[2)] *EX'* is the repulsion energy due to intermolecular overlaps. *X* is the electron exchange attraction. *EX'* and *X* are 174.72 and −92.26 kcal/mol, respectively.
d) The *CT* term can be divided into two terms, *i.e.*, *CT* from one molecule to the other molecule ($CT_{\mathrm{A}\to\mathrm{B}}$) and CT from the latter to the former ($CT_{\mathrm{B}\to\mathrm{A}}$).
e) The energy of the CH_3CN-BH_3 complex relative to the C_{3v} symmetry structure in which the distance between N and B is 1.65753 Å.
f) The energy of the $HCN-BH_3$ complex relative to the C_{3v} symmetry structure of the CH_3CN-BH_3 complex in which the distance between N and B is 1.65753 Å.

CH_3CN-BH_3 Complex

Since three atoms, H, C, and N are on the axis of the C_{3v} symmetry in the most stable $HCN-BH_3$ structure, only the C_{3v} symmetry structure of the CH_3CN-BH_3 complex was optimized at various distances between N and B. The resulting structure is shown in Fig. 2. The stabilization energies and the energy decomposition analyses are listed in Table I. From a parabolic fit of the three distances of 1.63, 1.65 and 1.68 Å, the complex is considered to be most stable at a distance of 1.65717 Å. The ratios of *ES*, *CT* and *PL* were calculated to be 45, 27 and 29%, respectively, in the terms contributing to the stabilization of the complex. *ES* was most significant, followed by *CT* and *PL*. *CT* was calculated to be −39.3 kcal/mol. When the *CT* term was divided into $CT_{\mathrm{CH_3CN\to BH_3}}$ and $CT_{\mathrm{BH_3\to CH_3CN}}$, where the former is *CT* from CH_3CN to BH_3 and the latter is *CT* from BH_3 to CH_3CN, the ratio of $CT_{\mathrm{CH_3CN\to BH_3}}$ was estimated to be 61%. $\mathrm{CT}_{\mathrm{CH_3CN\to BH_3}}$ itself can be divided into two terms, $CT_{\sigma\to\sigma}$ and $CT_{\pi\to\pi}$, where the former is *CT* through σ MO interactions from CH_3CN to BH_3, and the latter is *CT* through π MO interactions from CH_3CN to BH_3. $CT_{\sigma\to\sigma}$ was estimated to account for 97%. Therefore the total *CT* is predominantly due to *CT* from CH_3CN to BH_3 through σ–σ MO interactions. Intermolecular interaction forces at various distances between N and B were calculated (Table I). Figure 3 shows the results. *PL* force was largest, followed by *ES* force and *CT* force. When the angle between the C_{3v} symmetry axis of CH_3CN and the C_{3v} symmetry axis of BH_3 is 18°, the energy change is 1.8 kcal/mol from the total energy of the CH_3CN-BH_3 complex corresponding to the C_{3v} symmetry structure. The destabilized value as shown in Table I is due mainly to *ΔES* and also to *ΔPL*. The charge distribution of CH_3CN may be schematically represented as: $H_3C-C^{+0.061(\pi)}$ $N^{-0.081(\pi)}$ [−0.255(σ)]. The net charges of π of –C⋞, π of N and σ of N were calculated to be 0.061, −0.081 and −0.255, respectively. The electrostatic interaction is most favored when the electron-deficient B of BH_3 approaches the N end of CH_3CN along the extension of the CN axis. As α increases, the B atom approaches more closely towards the π side of N, resulting in a decrease in the electrostatic stabilization.

When the stabilization energy and each of the energy decomposition terms of the CH_3CN-BH_3 complex are compared with those of the $HCN-BH_3$ complex, the methyl substituent effect on the complex formation between –CN and BH_3 can be seen. The results are shown

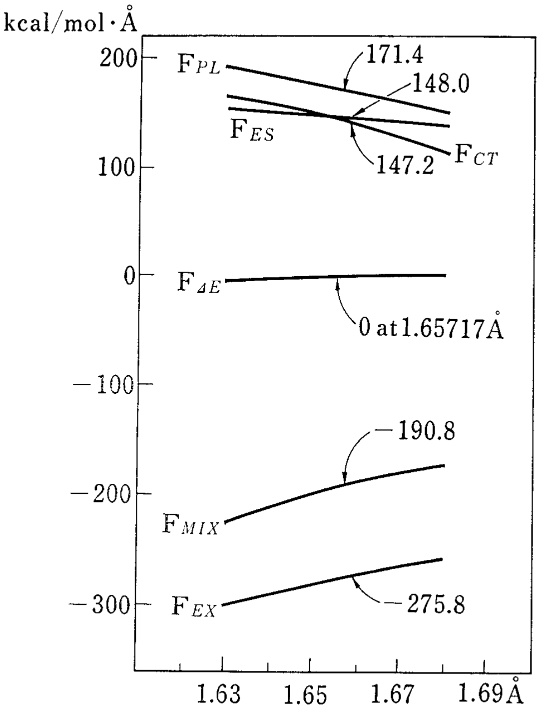

Fig. 3. Interaction Forces in kcal/mol·Å of CH_3CN–BH_3 Complex in the C_{3v} Symmetry Structure at Various Distances between N and B, and Force Decomposition Analyses

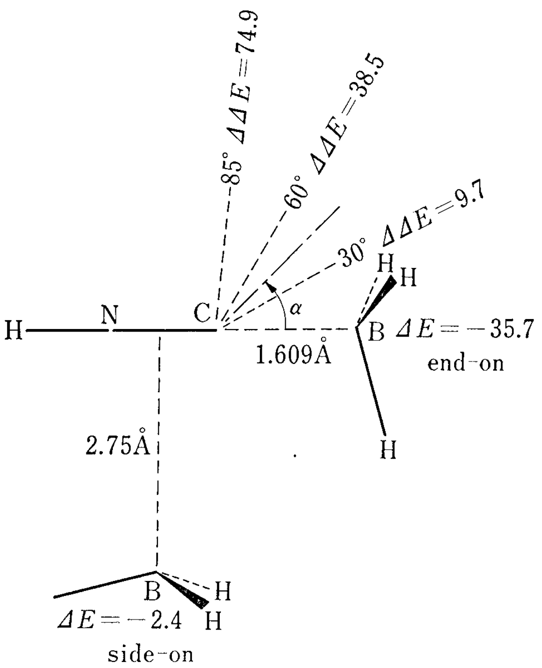

Fig. 4. The Structure of the HNC–BH_3 Complex

In the C_{3v} symmetry structure of the complex, the distance between N and B is 1.609 Å. ΔE is the stabilization energy in kcal/mol for the end-on or the side-on binding structure. $\Delta\Delta E$ is the destabilization in kcal/mol from the C_{3v} symmetry structure upon change of α.

in column (7) of Table I. The stabilization due to methyl substitution was estimated to be 3.1 kcal/mol. This value was largely due to ΔES and to a lesser extent, ΔPL. The charge distribution of HCN may be schematically represented as: $H\text{–}C^{+0.059(\pi)}\ N^{-0.059(\pi)}\ [-0.225(\sigma)]$. The net charge −0.225 due to σ of N is smaller by 0.03 than that of N in the CH_3CN–BH_3 complex. Therefore, the reduction of the net charge due to σ of N of the HCN–BH_3 complex in comparison with that of the CH_3CN–BH_3 complex accounts for the ΔES contribution to the stabilization which occurs on methyl substitution.

HNC-BH_3 Complex

The stabilization energies within the C_{3v} symmetry structure were calculated for the complex between HNC and BH_3. The HNC–BH_3 complex is most stable at a distance of 1.60891 Å. The stabilization energy was calculated to be −35.7 kcal/mol. When the angle α between the axis of the $C_{\infty v}$ symmetry of HNC and that of the C_{3v} symmetry of BH_3 is changed, the calculated destabilization is shown in Fig. 4. The charge distribution of HNC may be schematically represented as $H\text{–}N^{-0.482(\pi)}\ C^{+0.482(\pi)}\ [-0.667(\sigma)]$. The net charges due to π of N, π of ≡C and σ of ≡C were −0.482, 0.482 and −0.667, respectively. As α increases, the B atom approaches the positive π side of the isonitrile carbon more closely, resulting in a decrease in the electrostatic stabilization. Thus, the C_{3v} symmetry structure of the HCN–BH_3 is most stable.

On the other hand, when BH_3 approaches the NC center of mass,[10] the stabilization energy is minimum at a distance of 2.752 Å. The value was calculated to be −2.4 kcal/mol, as shown in Fig. 4. The side-on bonding structure in which BH_3 approaches the NC center of mass is much less stable than the end-on bonding structure of the C_{3v} symmetry complex.

CH_3NC-BH_3 Complex

In comparison with the CH_3CN–BH_3 complex, the stabilization energies for the CH_3NC–

BH_3 complex were calculated for various distances between C and B within the C_{3v} symmetry structure of the complex. The complex was found to be most stable at a distance of 1.61725 Å, as shown in Fig. 5. Moreover, the effects of changing the angle between the axis of the C_{3v} symmetry of CH_3NC and that of the C_{3v} symmetry of BH_3 are also shown in Fig. 5. The charge distribution of CH_3NC may be schematically represented as H_3C–$N^{-0.467(\pi)}$ $C^{+0.461(\pi)}$ [$-0.704(\sigma)$]. The net charges of π of N, π of ≡C, and σ of ≡C are -0.467, $+0.461$ and -0.704, respectively. The electrostatic interaction is most favored when the electron-deficient B end of BH_3 approaches the C end of the –NC group along the extension of the –NC axis. As α increases, the B atom approaches the positive π side of the isonitrile carbon more closely, resulting in a considerable decrease in the electrostatic stabilization. The difference in the net charges of σ and π of the isonitrile carbon accounts for the destabilization from the C_{3v} symmetry structure.

The stabilization energy and the energy decomposition analysis of the CH_3NC–BH_3 complex at a distance of 1.61725 Å are shown in Table II. *PL*, *CT* and *ES* contribute comparably to the stabilization of the complex. The results for the CH_3NC–BH_3 complex are compared with those for the HNC–BH_3 complex in Table II. The stabilization due to the methyl substitution was estimated to be 2.0 kcal/mol, mainly due to ΔEX.

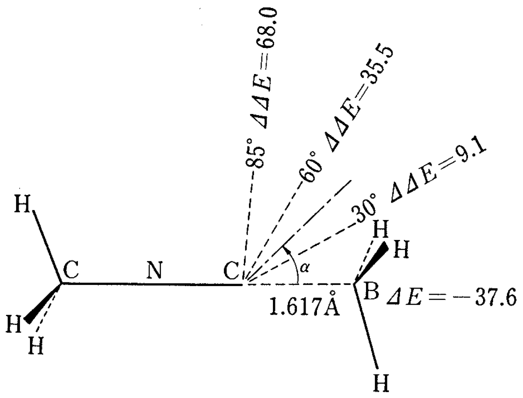

Fig. 5. The Structure of the CH_3NC–BH_3 Complex

ΔE is the stabilization energy in kcal/mol between CH_3NC and BH_3. $\Delta\Delta E$ is the destabilization in kcal/mol from the C_{3v} symmetry structure.

Table II. Stabilization Energies and Energy Decomposition Analyses in kcal/mol of the CH_3NC–BH_3 and HNC–BH_3 Complexes using a 4-31G Basis Set

	CH_3NC–BH_3 Intermolecular distance 1.61725 Å		HNC–BH_3 Intermolecular distance 1.60891 Å
ΔE	−37.6	$\Delta\Delta E$	2.0[a]
ES	−82.1	ΔES	0.5
EX	115.5	ΔEX	2.2
PL	−94.1	ΔPL	0.5
CT	−82.5	ΔCT	−2.5
MIX	105.5	ΔMIX	1.2

a) The stabilization energy of the HNC–BH_3 complex relative to that of the CH_3NC–BH_3 complex.

The intermolecular distance in the HNC–BH_3 complex is shorter than that in the CH_3NC–BH_3 complex by 0.01 Å, although the stabilization energy of the former complex is smaller. Since the σ total electron density of C of HNC is smaller than that of CH_3NC by 0.037, BH_3 will be able to approach nearer to HNC due to the smaller repulsive force.

Discussion

All the CH_3NC–BH_3, HNC–BH_3, CH_3CN–BH_3 and HCN–BH_3 complexes are C_{3v} symmetric structures with end-on binding. The stabilization energies of the CH_3NC–BH_3 and HNC–BH_3 complexes are larger than those of the CH_3CN–BH_3 and HCN–BH_3 complexes, as shown in Table III. The absolute values of all the energy decomposition terms of the

Table III. Difference in kcal/mol of the stabilization Energies and the Energy Decomposition Terms between the CH_3CN–BH_3 and CH_3NC–BH_3 Complexes, and between the HCN–BH_3 and HNC–BH_3 Complexes

	For CH_3XY–BH_3[a]	For HXY–BH_3[a]
$\Delta\Delta E$	−12.5	−13.6
ΔES	−20.4	−23.1
ΔEX	32.9	36.1
ΔPL	−57.2	−58.6
ΔCT	−43.2	−45.8
ΔMIX	75.4	77.8

a) $\Delta\Delta E=\Delta E_{CH_3NC-BH_3}-\Delta E_{CH_3CN-BH_3}$ for CH_3XY–BH_3.
$\Delta ES=ES_{CH_3NC-BH_3}-ES_{CH_3CN-BH_3}$ for CH_3XY–BH_3.
ΔEX, ΔPL, ΔCT and ΔMIX were obtained from equations similar to that for ΔES.

Table IV. MO Energy Levels of CH_3NC and CH_3CN, and the Electron Densities of C and N for CH_3NC and CH_3CN, respectively, within a Single MO

CH_3NC				CH_3CN		
(1)[a]	(2)[b]	(3)[c]	(4)[d]	(2)	(3)	(4)
7	1e	−0.637	0.013	1e	−0.626	0.016
8	1e			1e		
9	2e	−0.466	0.099	7a$_1$	−0.548	0.586
10	2e			2e	−0.460	0.260
11	7a$_1$	−0.459	0.841	2e		
12	3e	0.207	0.619	3e	0.202	0.427
13	3e			3e		
14	8a$_1$	0.234	0.087	8a$_1$	0.223	0.432
15	4e	0.317	0.227	4e	0.317	0.234
16	4e			4e		

a) (1): The number of the MO from the lowest MO energy level.
b) (2): MO symmetry.
c) (3): MO energy level (Hartrees).
d) (4): Electron density of C of CH_3NC or N of CH_3CN within a single MO.

CH_3NC–BH_3 and HNC–BH_3 complexes are larger than those of the CH_3CN–BH_3 and HCN–BH_3 complexes.

Table IV shows the MO levels of isolated CH_3NC and CH_3CN molecules and the electron densities of C and N for CH_3NC amd CH_3CN, respectively, within each single MO. In the H_3N–BH_3 complex, the highest occupied σ MO (σ HOMO) of NH_3 was most significant,[4] and the energy level of σ HOMO and the electron densities of the interacting atoms are compared in Table IV. The energy level of σ HOMO of CH_3NC is higher than that of CH_3CN, and the electron density of C within σ HOMO of CH_3NC is much larger than that of N within σ HOMO of CH_3CN. These results account for the larger CT term of the CH_3NC–BH_3 complex in comparison with that of the CH_3CN–BH_3 complex.

The total electron densities of C of CH_3NC and N of CH_3CN were calculated to be 5.783 and 7.416, respectively. The net charges of C and N of the two molecules were 0.217 and −0.416, respectively. The net charges of σ total electron densities of C and N of the two molecules were found to be −0.704 and −0.255. The larger net charge of C of CH_3NC accounts for the larger electrostatic interaction energy (ΔES), as shown in Table III.

When the angle α between the $C_{\infty v}$ symmetry axis of HNC or HCN and the C_{3v} symmetry axis of BH_3 increases, the HNC–BH_3 and HCN–BH_3 complexes are destabilized; the effect is greater with the HNC–BH_3 complex, as shown in Table V. The net charges of π total electron densities of C of CH_3NC and N of CH_3CN were obtained as 0.461 and −0.081, respectively. Similarly, for the HNC–BH_3 and HCN–BH_3 complexes, the corresponding values were 0.482 and −0.059, respectively. As α increases, the B atom in the HNC–BH_3 complex approaches the positive π side more than the B atom in the HCN–BH_3 complex. Therefore the destabilization with change of α will be larger for the HNC–BH_3 complex than for the HCN–BH_3 complex.

Table V. Stabilization Energies in kcal/mol of the HNC–BH_3 and HCN–BH_3 Complexes relative to the C_{3v} Symmetry Structures of These Complexes and the Difference of Relative Interaction Energies

α	$\Delta\Delta E$		$\Delta\Delta\Delta E$
	HNC–BH_3	HCN–BH_3	
0.0°	0.0	0.0	0.0
30.0°	9.7	5.4	4.3
60.0°	38.5	21.5	17.1
85.0°	74.9	41.1	33.8

In the study of the OC–BH_3 complex, the charge distribution of CO could be represented as $[+\delta]O^{-\delta}\ C^{+\delta}[-\delta]$,[4] while that of CH_3NC was $\text{-}N^{-\delta}\ C^{+\delta'}\ [-\delta'']$. Therefore the CH_3NC–BH_3 complex should be very similar to the OC–BH_3 complex.

Hoard *et al.* analyzed the structure of a CH_3CN–BF_3 complex by X-ray diffraction.[11] The CH_3CN–BF_3 complex had C_{3v} symmetry. The structure of the CH_3CN–BH_3 complex reported in this report is also C_{3v} symmetric. The distance between N and B in the CH_3CN–BF_3 complex was 1.635 Å, while that in the CH_3CN–BH_3 complex was 1.657 Å (Table I). Although the calculated distance between N and B in the CH_3CN–BH_3 complex is slightly longer than the experimental distance between N and B in the CH_3CN–BF_3 complex, the difference is only 0.02 Å.

Liskow *et al.* calculated the $CH_3NC \rightarrow CH_3CN$ potential surface by an *ab initio* method.[12] Taking the total energy of CH_3NC as a standard, the energies of CH_3CN and the saddle point relative to CH_3NC were −17.3 and 60.4 kcal/mol, respectively. CH_3CN was stable than CH_3NC. However, when BH_3 interacts with CH_3CN or CH_3NC, the stabilization energy between CH_3NC and BH_3 was found to be larger than that between CH_3CN and BH_3 by 12.5 kcal/mol due to ΔPL, ΔCT, and ΔES.

---

11) J.L. Hoard, S. Geller, and T.B. Owen, *Acta Cryst.*, **4**, 405 (1951).

12) D.H. Liskow, C.F. Bender, and H.F. Schaffer III, *J. Chem. Phys.*, **57**, 4509 (1972).