0.08, Rf^2 0.13, single ninhydrin-positive spot. amino acid composition in the acid hydrolysate: Gly 1.00, Glu 0.91, Asp 0.99 (average recovery 84%); amino acid composition in the AP–M digest: Gly 1.00, Glu 0.89, Asp 0.98 (average recovery 87%).

Paper Electrophoresis——The tripeptide obtained by ion-exchange chromatography on DEAE–Sephadex A-25 was subjected to paper electrophoresis. Electrophoresis was carried out on Toyo Roshi No. 51 paper (10 × 40 cm) using pyridinium-acetate buffer, pH 6.7, at 600 V for 120 min, and the paper was stained with ninhydrin reagent. The isolated native tripeptide and the synthetic peptide showed identical mobilities.

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A Molecular Orbital Study on the $(CH_3)_2O$-BH_3 Donor-Acceptor Complex

HIDEAKI UMEYAMA

School of Pharmaceutical Sciences, Kitasato University[1]

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A molecular orbital study on the donor-acceptor complex of $(CH_3)_2O$–BH_3 was performed, in comparison with the $(CH_3)_3N$–BH_3 complex. The driving force for $(CH_3)_2O$–BH_3 complex formation was electrostatic interaction energy. The interaction energy between $(CH_3)_2O$ and BH_3 was smaller than that between NH_3 and BH_3 by 10.5 kcal/mol due to a difference between the electrostatic terms.

In the optimized structure of $(CH_3)_2O$–BH_3, the distance r (OB) was 1.65412 Å. The angle∠BOY, where Y is a point on the C_{2v} axis of $(CH_3)_2O$, was 152.8°. The results are in agreement with the electron diffraction analyses of $(CH_3)_2O$–BF_3 reported by Shibata and Iijima.

Keywords——*ab initio* calculation; molecular orbital; MO; complex; donor-acceptor complex; borane compound; dimethyl ether; boron trihydride; quantum chemistry; structure

Bauer *et al.* studied the structure of dimethyl ether-boron trifluoride ($(CH_3)_2O$-BF_3) by electron diffraction analysis.[2] The distance of r (BO) was 1.50 Å, and the boron and oxygen valence angles were tetrahedral. Although the electron diffraction photographs were consistent with the assumption that the oxygen valence angles are tetrahedral, the possibility that the ∠BOC's and even ∠COC are 120° could not be definitely eliminated.[2] The dimethyl ether part of the molecule remained essentially unaffected. Moreover, it was suggested that the bond formed in the association process could be regarded as being due to an electron pair rather than to dipole-dipole interaction.[2] Recently Shibata and Iijima performed electron diffraction experiments, and r (BO) was found to be 1.719 Å.[3] The bond distances and bond angles obtained by them were quite different from those of Bauer *et al.* The possibility that the ∠BOC's and even ∠COC are 120° was excluded, and a staggered form was concluded to exist.[3] The planar structure of the free BF_3 molecule[4] changed to a pyramidal structure due to the donor-acceptor σ-bond formation.[3] Since the heats of formation of the complexes were

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

[2] S.H. Bauer, G.R. Finlay and A.W. Laubengayer, *J. Amer. Chem. Soc.*, **65**, 889 (1943); *idem, ibid.*, **67**, 339 (1945).

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estimated to be 13.7⁵⁾ and 26.6⁶⁾ kcal/mol for the complexes of $(CH_3)_2O\text{-}BF_3$ and $(CH_3)_3N\text{-}BF_3$, respectively, the value of 1.719 Å for r (BO) at 16° and that of 1.673 Å for *r* (BN) at 130° are compatible with the heats of formation.³⁾ The molecular structure of the donor remained almost unchanged, and nitrogen in the complex was more active as a donor than oxygen.³⁾ On the other hand, we have studied the interaction energies of complexes of borane compounds from a quantum chemical point of view.⁷⁾ It is thus of interest to compare the complex of $(CH_3)_2O\text{-}BX_3$ (X=H in this note) with those of other borane compounds.

In this work, the following points were studied.

(1) Whether the data of Bauer *et al.* or of Shibata and Iijima are consistent with the calculated value of *r* (BO) in the complex of $(CH_3)_2O\text{-}BH_3$.

(2) The energy difference in stability between the staggered form of the complex of $(CH_3)_2O\text{-}BH_3$ and the structure where the ∠BOC's and even ∠COC are 120°.

(3) What is the driving force for $(CH_3)_2O\text{-}BH_3$ complex formation?

(4) Which complex, $(CH_3)_2O\text{-}BH_3$ or $(CH_3)_3N\text{-}BH_3$, is more stable, and why?

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.⁸⁾ The split-valence 4-31G basis set was used with the suggested standard scale factors.⁹⁾ Energy decomposition analysis was carried out as described in other papers.¹⁰⁾ When $\varDelta E$ is the interaction energy in the complex formation, it can be divided as follows.

$$\varDelta E = \mathrm{ES} + \mathrm{EX} + \mathrm{PL} + \mathrm{CT} + \mathrm{MIX},$$

where ES is the eletrostatic energy, EX is the exchange repulsion, PL is the polarization energy, CT is the charge transfer and MIX is the coupling energy.

The calculations were carried out by using a HITAC M-180 computer at the Institute for Molecular Science.

Geometries——For BH_3, *r* (BH) is 1.248 Å, and ∠XBH is 106.581°, where X is a point on the C_{3v} axis of BH_3.¹¹⁾ For $(CH_3)_2O$, *r* (CO) is 1.41 Å, *r* (CH) is 1.096 Å, and ∠COC is 111.7°.¹²⁾ When the complex is formed, the molecules are assumed to be rigid.

Results and Discussion

Figure 1 shows the complex of $(CH_3)_3O\text{-}BH_3$, where X is on the C_{3v} axis of BH_3 and Y is on the C_{2v} axis of $(CH_3)_2O$. Figure 2 shows the energy relative to the total energy at a distance of 1.65412 Å for r (BO), which is −180.20572 Hartrees, plotted against the distance $\varDelta r$ (BO) relative to a value of 1.65412 Å for *r* (BO). The *r* (BO) distance obtained as an optimized value from the calculations was in agreement with the value reported by Shibata and Iijima rather than that of Bauer *et al.* The curve is not symmetric with respect to *r* (BO)=1.65412 Å, and it shows unharmonicity of the bond stretching of *r* (BO). In Fig. 2, the COC plane was placed on the C_{3v} axis of BH_3, and ∠XOY was changed. The total energy was minimum at an angle of 27.2°, being −180.20672 Hartrees. Figure 3 shows the derivative of the interaction energy

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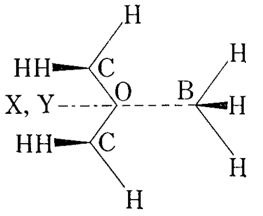

Fig. 1. The $(CH_3)_2O$-BH_3 Complex

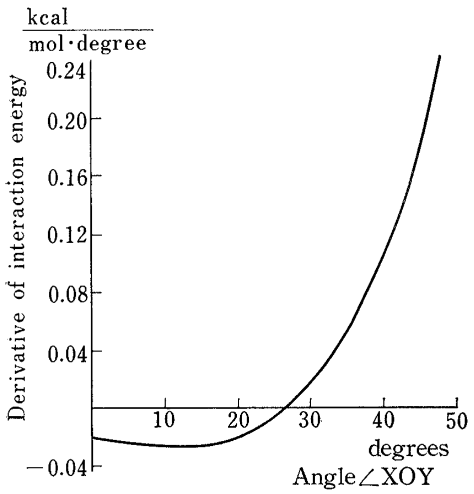

Fig. 3. Derivative Value (kcal/mol·degree) of the Interaction Energy Plotted Against the Angle XOY

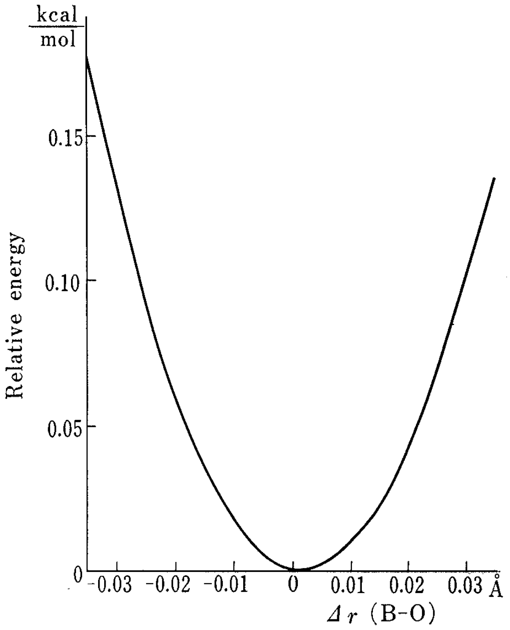

Fig. 2. The Energy (kcal/mol) Relative to the Total Energy at a Distance of 1.65412 Å for r (BO) Poltted Against Δr (BO) with r (BO) = 1.65412 Å

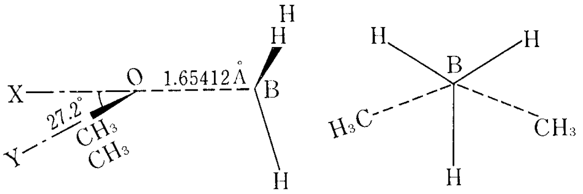

Fig. 4. Optimized Structure of $(CH_3)_2O$-BH_3

plotted against ∠XOY. The larger ∠XOY is over 27.2°, the larger is the derivative value. However, the change of the derivative value is small under 27.2°. The difference of the interaction energies between ∠XOY=0° and 27.2° was 0.63 kcal/mol. Athough the difference is small, it is suggested that the staggered form of the complex of $(CH_3)_2O$-BH_3 is more stable than the structure where the COC plane is placed on the C_{3v} axis of BH_3. Figure 4 shows the optimized structure.

Table I shows the results of interaction energy and energy decomposition analyses of the complex of $(CH_3)_2O$-BH_3. The interaction energy was −34.2 kcal/mol.[13] This was predominantly due to ES, although the terms PL and (CT+MIX) also contributed.[14] Therefore the $(CH_3)_2O$-BH_3 complex is an ES complex.[15] Since the interaction energy of $(CH_3)_3N$-BH_3 was comparable with that of H_3N-BH_3 at a distance of 1.705° Å between N and B,[7a] H_3N-BH_3 was used in place of $(CH_3)_3N$-BH_3 for comparison with $(CH_3)_2O$-BH_3. The interaction energy

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[13] The energy due to the conformation change of BH_3 from the planar to the pyramidal structure is as follows: $E_{BH_3(\text{pyramidal})} - E_{BH_3(\text{planar})} = 11.5$ kcal/mol.[7a] Therefore the heat of formation of the complex between $(CH_3)_2O$ and BH_3 can be calculated to be about −23 kcal/mol.

[14] The ES term in our calculations inculdes dipole-dipole interaction, and hence the suggestion by Bauer *et al.* that the bond formation can be regarded as being due to an electron pair rather than to dipole-dipole interaction is unlikely to be valid.

[15] From Table I it can be considered that ES cancels out EX, and, as a result, CT contributes to the stability of the complex. However, in order to determine the driving force for complex formation, all the terms contributing to the attraction between both molecules should be compared.

Table I. Interaction Energy in kcal/mol and Energy Decomposition Analyses of the Complexes $(CH_3)_2O\text{-}BH_3$ and $H_3N\text{-}BH_3$ Using a 4-31G Basis Set

	$(CH_3)_2O\text{-}BH_3$ $r(OB)=1.654$ Å $\angle XOY=27.0°$	$H_3N\text{-}BH_3$ $r(NB)=1.654$ Å[a]	 $r(NB)=1.68351$ Å[a,b]
ΔE	−34.2	−44.6(−9.1)[c]	−44.7(0)[c]
ES	−69.8	−104.4(238.9)	−97.6(223.9)
EX	72.3	103.0(−341.7)	93.4(−312.1)
PL	−19.8	−21.6(97.2)	−18.9(83.8)
CT		−32.3(114.2)	−29.1(99.3)
CT+MIX	−16.9	−21.8	−21.7
MIX		10.5	7.4

a) Values obtained from reference 7a) by using polynominal fits.
b) The optimized distance using a polynominal fit.
c) Numbers in parentheses show the interaction force in kcal/mol • Å and the results of force decomposition analysis.

and the energy decomposition analyses are also shown in Table I. The interaction energy of the $(CH_3)_2O\text{-}BH_3$ complex was smaller than that of the $H_3N\text{-}BH_3$ complex due to a difference between the ES terms. Accordingly, nitrogen in the complex is more active as a donor atom than oxygen.

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Syntheses of 9-Deazatheophyllines and 6-Deoxy-9-deazatheophyllines

Sadao Nishigaki, Yukako Kanamori,[1] and Keitaro Senga[1a]

Pharmaceutical Institute, School of Medicine, Keio University[1]

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The reaction of 1,3-dimethyl-5-nitro-6-styryluracils (IIa—e) with sodium dithionite in formic acid afforded the corresponding 8-aryl-9-deazatheophyllines (IVa—e). The reaction of IVa with phosphorus oxychloride gave 6-chloro-6-deoxy-8-phenyl-9-deazatheophylline (XIII), while the reaction of IVa with phosphorus oxychloride in the presence of arylamines provided the corresponding 6-arylamino-6-deoxy-8-phenyl-9-deazatheophyllines (XIV—XVI) in a single step.

Keywords——1,3-dimethyl-5-nitro-6-styryluracils; sodium dithionite-formic acid; reductive cyclization; 8-aryl-9-deazatheophyllines; phosphorus oxychloride; 6-chloro-6-deoxy-8-phenyl-9-deazatheophylline; 6-arylamino-6-deoxy-8-phenyl-9-deazatheophyllines.

The pyrrolo[3,2-*d*]pyrimidine (9-deazapurine) ring system has aroused considerable interest recently because of its close structural resemblance to purine as well as to other biologically important heterocycles, *e.g.*, pyrrolo[2,3-*d*]pyrimidine, pyrazolo[4,5-*d*]pyrimidine, and indole.[2] We report here the syntheses of two types of pyrrolo[3,2-*d*]pyrimidine related to theophylline,

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