0.08, $R_f^2$ 0.13, single ninhydin-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 x 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.

**Acknowledgement** The authors thank Miss H. Asano for amino acid analysis, and the staff of the Central Analysis Laboratory, Pharmaceutical Institute, Tohoku University, for elemental analysis.

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**A Molecular Orbital Study on the (CH₃)$_2$O-BH₃ Donor-Acceptor Complex**

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(Received November 24, 1979)

A molecular orbital study on the donor-acceptor complex of (CH₃)$_2$O–BH₃ was performed, in comparison with the (CH₃)$_2$N–BH₃ complex. The driving force for (CH₃)$_2$O–BH₃ complex formation was electrostatic interaction energy. The interaction energy between (CH₃)$_2$O and BH₃ was smaller than that between NH₃ and BH₃ by 10.5 kcal/mol due to a difference between the electrostatic terms.

In the optimized structure of (CH₃)$_2$O–BH₃, the distance r (OB) was 1.65412 Å. The angle $\angle$BOY, where Y is a point on the C₂v axis of (CH₃)$_2$O, was 152.8°. The results are in agreement with the electron diffraction analyses of (CH₃)$_2$O–BF₃ 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 ([(CH₃)$_2$O–BF₃]) 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 $\angle$BOC's and even $\angle$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 $\angle$BOC’s and even $\angle$COC are 120° was excluded, and a staggered form was concluded to exist.³ The planar structure of the free BF₃ molecule⁴ changed to a pyramidal structure due to the donor-acceptor $\sigma$-bond formation.⁴ Since the heats of formation of the complexes were

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estimated to be 13.7\(^5\) and 26.6\(^6\) kcal/mol for the complexes of \((\text{CH}_3)_2\text{O-BF}_3\) and \((\text{CH}_3)_2\text{N-BF}_3\), 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 \((\text{CH}_3)_2\text{O-BX}_3\) (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 \textit{et al.} or of Shibata and Iijima are consistent with the calculated value of \(r\) (BO) in the complex of \((\text{CH}_3)_2\text{O-BH}_3\).

2. The energy difference in stability between the staggered form of the complex of \((\text{CH}_3)_2\text{O-BH}_3\) and the structure where the \(\angle\text{BOC}\)'s and even \(\angle\text{COC}\) are 120°.

3. What is the driving force for \((\text{CH}_3)_2\text{O-BH}_3\) complex formation?

4. Which complex, \((\text{CH}_3)_2\text{O-BH}_3\) or \((\text{CH}_3)_2\text{N-BH}_3\), is more stable, and why?

\textbf{Method}

All the calculations were performed within the framework of a closed-shell single determinant of the \textit{ab initio} LCAO–SCF theory using the Gaussian 70 program.\(^9\) 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 \(\Delta E\) is the interaction energy in the complex formation, it can be divided as follows.

\[ \Delta E = E_S + E_X + P_L + C_T + M_I \]

where \(E_S\) is the electrostatic energy, \(E_X\) is the exchange repulsion, \(P_L\) is the polarization energy, \(C_T\) is the charge transfer and \(M_I\) is the coupling energy.

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

\textbf{Geometries}——For \(\text{BH}_3\), \(r\) (BH) is 1.248 Å, and \(\angle\text{BHX}\) is 106.581°, where X is a point on the C\(_3\)v axis of \(\text{BH}_3\).\(^11\) For \((\text{CH}_3)_2\text{O}\), \(r\) (CO) is 1.41 Å, \(r\) (CH) is 1.096 Å, and \(\angle\text{COC}\) is 111.7°.\(^12\) When the complex is formed, the molecules are assumed to be rigid.

\textbf{Results and Discussion}

Figure 1 shows the complex of \((\text{CH}_3)_2\text{O-BH}_3\), where X is on the C\(_3\)v axis of \(\text{BH}_3\) and Y is on the C\(_3\)v axis of \((\text{CH}_3)_2\text{O}\). 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 \(r\) (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 \textit{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\(_3\)v axis of \(\text{BH}_3\), and \(\angle\text{XOY}\) was changed. The total energy was minimum at an angle of 27.3°, being \(-180.20672\) Hartrees. Figure 3 shows the derivative of the interaction energy


\(^{7}\) a) H. Umeyama and K. Morokuma, \textit{J. Amer. Chem. Soc.}, \textbf{98}, 7208 (1976); b) H. Umeyama and T. Matsu-


\(^{11}\) a) K. Kitaura and K. Morokuma, \textit{Int. J. Quantum Chem.}, \textbf{10}, 325 (1976); b) H. Umeyama and K. Moro-


plotted against $\angle XOY$. The larger $\angle XOY$ 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 $\angle XOY = 0°$ and 27.2° was 0.63 kcal/mol. Although the difference is small, it is suggested that the staggered form of the complex of (CH₃)₂O–BH₃ is more stable than the structure where the COC plane is placed on the C₃, axis of BH₃. Figure 4 shows the optimized structure.

Table 1 shows the results of interaction energy and energy decomposition analyses of the complex of (CH₃)₂O–BH₃. 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 (CH₃)₂O–BH₃ complex is an ES complex.¹⁵ Since the interaction energy of (CH₃)₃N–BH₃ was comparable with that of H₂N–BH₃ at a distance of 1.705° Å between N and B,⁷ the H₂N–BH₃ was used in place of (CH₃)₃N–BH₃ for comparison with (CH₃)₂O–BH₃. The interaction energy

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¹³ The energy due to the conformation change of BH₃ from the planar to the pyramidal structure is as follows: $E_{BH3(pyramidal)} - E_{BH3(planar)} = 11.5$ kcal/mol.⁷ Therefore the heat of formation of the complex between (CH₃)₂O and BH₃ can be calculated to be about −23 kcal/mol.

¹⁴ The ES term in our calculations includes 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.
and the energy decomposition analyses are also shown in Table I. The interaction energy of the (CH₃)₂O-BH₃ complex was smaller than that of the H₃N-BH₃ complex due to a difference between the ES terms. Accordingly, nitrogen in the complex is more active as a donor atom than oxygen.


**Syntheses of 9-Deazatheatheophyllines and 6-Deoxy-9-deazatheatheophyllines**

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(Received November 29, 1979)

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

**Keywords**—1,3-dimethyl-5-nitro-6-styrylaracil; sodium dithionite-formic acid; reductive cyclization; 8-aryl-9-deazatheatheophyllines; phosphorus oxychloride; 6-chloro-6-deoxy-8-phenyl-9-deazatheatheophylline; 6-arylamino-6-deoxy-8-phenyl-9-deazatheatheophylline.

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[3,2-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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