Notes

Chem. Pharm. Bull.
29(2) 554—558 (1981)

Energy Decomposition Analyses of Diborane

Hideaki Umeyama* and Takako Kudo

*School of Pharmaceutical Sciences, Kitasato University,*1) *9–1, Shirokane 5-Chome, Minato-ku, Tokyo, 108, Japan*

(Received February 28, 1980)

Diborane as a molecular complex was studied by using a double zeta *ab initio* MO method and energy decomposition analyses. For diborane, a qualitatively major contribution of HOMO-LUMO transfers was reported by Yamabe *et al.* on the basis of configuration analyses by using a single zeta basis set. However, no quantitative work on the origin on the complex formation has been reported. In this note, we show that the charge transfer energy is the dominant contributor to the complex formation ($2BH_3 \rightarrow B_2H_6$). The charge transfer energy and the exchange repulsion are analyzed at the molecular orbital (MO) levels.

Keywords——diborane; *ab initio*; molecular orbital; structure; complex; borane; charge transfer; molecular complex; MO

The origins of dimer formation by LiH, NH_3, OH_2 and FH have been studied from a quantum chemical point of view.2) The dimers of NH_3, OH_2 and FH form linear hydrogen bonds mainly as a result of electrostatic interaction energy. The principal reason why the linear geometry is preferred in the dimer complexes of OH_2 and FH is the contribution of the electrostatic interaction energy. However, the cyclic dimer of LiH is more stable than the linear dimer, and its stabilization energy is due largely to the electrostatic term (54%) and the charge transfer term (37%). BH_3 also forms a cyclic dimer. Thus, we sought to elucidate the origin of the cyclic dimer formation of BH_3 in comparison with NH_3, OH_2, FH and LiH dimers.

Diborane, which is composed of two BH_3 molecules, has a structure with D_{2h} symmetry, as shown in Fig. 1.3) Theoretical studies4) on the electronic structures of boron hydrides and molecular orbital (MO) studies5) on its molecular properties have been carried out. Gelus *et al.*5f) pointed out that the contribution of the correlation energy to the binding energy in the dimerization process of boranes was important. Yamabe *et al.* carried out calculations of the charge density and reported that configuration analyses in terms of the MO's of deformed BH_3 are in good accord with the configurations corresponding to the HOMO-LUMO transfers. They made qualitatively distinct the concept of donation and back-donation by using a single zeta basis set.6) However, they did not calculate the stabilization energy due to the charge transfer, and did not carry out energy decomposition analysis. Thus, the nature of the complex formation of the diborane has not been clarified quantitatively. In order to elucidate the energy source driving the complex formation, therefore, energy decomposition analyses were performed in this work. Since calculations using a single zeta basis set overestimate the charge transfer energy, their use for a system in which the charge

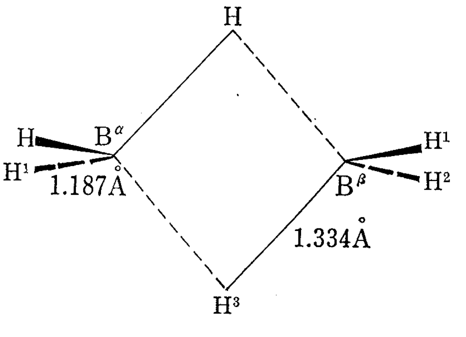

Fig. 1. Structure of Diborane
r(BB)=1.77 Å. H^1BH^2=121.5°.

transfer energy is large is not appropriate.[7] For the complex of H_3N-BH_3, calculations including polarization functions in addition to the double zeta basis set were performed by Umeyama and Matsuzaki, and it was found that the polarization functions had no effect on the charge transfer energy or the exchange repulsion.[7] The double zeta basis set was adopted, since we are interested in the contribution of the charge transfer energy to the stabilization energy of complex formation.

Molecular orbital calculations were carried out within the closed-shell LCAO-SCF approximation by the *ab initio* method on HITAC 8700 and 8800 computers at the Tokyo University Computer Center. *Ab initio* calculations were performed by using the GAUSSIAN 70 program.[8] The basis set used was 4-31G.[9] Energy decomposition analyses in our *ab initio* calculations were carried out by the method of Morokuma *et al.*[10] The intermolecular interaction energy ΔE was divided into five terms: electrostatic (ES), exchange repulsion (EX), polarization (PL), charge transfer (CT), and a mixing term (MIX).

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

EX is divided into two terms, X and EX′, where X is exchange attraction and EX′ is overlap repulsion.

MO levels of deformed BH_3 are shown in Table I, where "π MO" refers to the quasi-π MO having an antisymmetric AO on the boron within the plane consisting of two BH groups in Fig. 1. The total energy of the deformed BH_3 molecule is −26.31596 Hartrees, and it

TABLE I. Molecular Orbital Levels in Hartrees of Deformed BH_3 obtained by Using a 4-31G Basis Set and Molecular Orbital Electron Densities

No.	π or σ	MO level	*a*)	*b*)
15	π_{15}^*	1.254		0
14	σ_{14}^*	1.248		0.377
13	σ_{13}^*	1.147		0.006
12	σ_{12}^*	0.916		0.102
11	σ_{11}^*	0.745		2.269
10	σ_{10}^*	0.694		0.268
9	π_9^*	0.667		0
8	π_8^*	0.327		0
7	σ_7^*	0.311		0.474
6	σ_6^*	0.283		0.002
5	σ_5^*	0.068		0.557
4	σ_4	−0.451	0.203	
3	π_3	−0.504	0	
2	σ_2	−0.700	0.029	
1	σ_1	−7.168	0	

a) Molecular orbital electron density on H^3.
b) Molecular orbital electron density on the B^α atomic orbital directed to H^3 in Fig. 1.

TABLE II. The Interaction Energy in kcal/mol between two Deformed BH_3 Molecules and the Energy Decomposition Analyses calculated by Using a 4-31G Basis Set

Term	kcal/mol
ΔE	−54.3
ES	−106.0(31%)
EX	193.4
PL	−62.3(18%)
CT	−170.8(50%)
MIX	91.6

is less stable by 20.9 kcal/mol than the undeformed BH_3 molecule.[10e)] The interaction energy between two deformed BH_3 molecules is −54.3 kcal/mol, as shown in Table II. The heat of complex formation is estimated to be −12.5 kcal/mol; the value is obtained from the equation $-54.3-(-20.9\times2)$ within the closed shell SCF MO calculations. The heat, ΔH, of the complex-formation reaction $2BH_3(g)\rightarrow B_2H_6(g)$ was estimated experimentally to be −28.5 kcal/mol by McCoy and Bauer.[11,12)] The difference between the experimental and calculated values may be largely due to the correlation energy.[5)] The interaction energy of −54.3 kcal/mol was decomposed into five terms as shown in Table II. The CT term is the dominant contributor, and the ES term is next most significant. Accordingly, diborane is a "charge transfer complex". For $H_3N\text{-}BH_3$, the ES term was the main contributor,[10e)] and for $H_3B\text{-}CO$ the CT term was comparable with the ES term.[10e)]

Calculations of the contributions of σ and π MO's to the total CT term shown in Table II were carried out. Table III shows the results. The contribution of the CT term including MO interactions between σ MO's of one molecule and σ^* MO's of the other molecule is very large. The MO interactions between π MO of one molecule and π^* MO's of the other molecule contribute very little.

TABLE III. CT in kcal/mol obtained from σ or π Intermolecular MO Interactions

	One molecule	The other molecule	CT
(a)	σ's and π σ^*'s and π^*'s	σ^*'s and π^*'s σ's and π	−170.8
(b)	σ's σ^*'s	σ^*'s σ's	−169.3
(c)	π π^*'s	π^*'s π	−2.3
(d)	σ's	σ^*'s	−79.2
(e)	π	π^*'s	−1.1

σ's means σ MO's.
π's means π MO's.
"*" means an unoccupied MO.
(a) is the total CT term.
(b) is the CT term through σ MO's.
(c) is the CT term through π MO's.
(d) is the CT term from σ MO's of one molecule to σ MO's of the other molecule.
(e) is the CT term from π MO's of one molecule to π MO's of the other molecule.

In connection with the charge transfer energy, MO interactions at the MO levels were calculated as shown in Table IV. The contribution of HOMO-LUMO interaction, which was proposed on the basis of calculations of the charge density by Yamabe *et al.*,[6)] is large. Moreover, there are some MO interactions contributing to the CT term; for example the charge transfer energy of $\sigma_4\rightarrow\sigma_{11}^*$ is the largest. In the fourth and fifth columns of Table I, the occupied MO electron densities on H^3 and the unoccupied MO electron densities on the B^α atomic orbital directed to H^3 are shown. The values for σ_4 and σ_{11}^* are very large. Accordingly, the MO electron densities explain the large contribution of $\sigma_4\rightarrow\sigma_{11}^*$.

The EX′ term in the intermolecular interaction plays a repulsive role. The EX′ term was analyzed at the MO levels, as shown in Table V. The EX′ term obtained from the MO interactions between σ MO's of one molecule and σ MO's of the other molecule account for virtually all of the total EX′ term. The EX′ term between the core MO of one molecule and valence MO's of the other molecule, in addition to that between valence MO's sets of both molecules, is significant. At the MO levels, moreover, the MO interactions between σ_2 and σ_2 and between σ_2 and σ_4 are large. However, the MO interaction of HOMO (σ_4)-HOMO (σ_4) is very small.

Table IV. CT in kcal/mol obtained from Intermolecular MO Interactions

One molecule	The other molecule	CT
σ_2	$\sigma_5{}^*$	−3.9
	$\sigma_6{}^*$	−0.9
	$\sigma_7{}^*$	−1.0
	$\sigma_{10}{}^*$	−3.8
	$\sigma_{11}{}^*$	−2.7
	$\sigma_{12}{}^*$	−5.1
	$\sigma_{13}{}^*$	−1.3
	$\sigma_{14}{}^*$	−0.0
σ_4 (HOMO)	$\sigma_5{}^*$ (LUMO)	−11.2
	$\sigma_6{}^*$	−0.3
	$\sigma_7{}^*$	−0.3
	$\sigma_{10}{}^*$	−0.7
	$\sigma_{11}{}^*$	−14.4
	$\sigma_{12}{}^*$	−8.3
	$\sigma_{13}{}^*$	−2.1
	$\sigma_{14}{}^*$	−0.3

CT between σ's and π's is zero.
CT from σ_1 to σ^*'s was calculated to be zero.

Table V. EX′ in kcal/mol obtained from Intermolecular MO Interactions

	One molecule	The other molecule	EX′
(a)	σ's and π	σ's and π	396.0
(b)	σ's	σ's	385.2
(c)	π	π	11.3
(d)	Valence	Valence	279.1
(e)	Core	Valence	47.8
(f)	Valence	Core	47.8
(g)	Core	Core	0.0
(h)	σ_2	σ_2	94.0
(i)	σ_2	σ_4	98.6
(j)	σ_4	σ_2	98.6
(k)	σ_4	σ_4	3.2

Valence means valence MO's.
Core means 1s MO.
(a) is the total EX′ term.
(d) is the EX′ term between valence MO's sets.
The EX′ term between σ valence MO's sets is 268.3 kcal/mol.

In conclusion, our results may be summarized as follows.

(1) Diborane, consisting of two deformed BH_3 molecules, is a "charge transfer complex" according to closed shell SCF MO calculations.

(2) In connection with the charge transfer energy, the MO interactions between the MO lower than HOMO and the MO higher than LUMO are significant, as well as the HOMO-LUMO interaction. The CT term from π MO of one molecule to π^* MO's of the other molecule is very small.

(3) In connection with the exchange repulsion, the core-valence MO interactions are significant, in addition to the valence-valence MO interactions; the core region should be considered in intermolecular interactions such as those of the BH_3 dimer. The MO method including core MO's as an approximation is not appropriate for calculations of strong intermolecular interaction.

References and Notes

1) Location: *9-1, Shirokane 5-chome, Minato-ku, Tokyo, 108, Japan.*
2) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 1316 (1976).
3) L.E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chemical Society, London, 1958.
4) *a*) W.N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954); *b*) W.H. Eberhardt, B. Crawford, Jr., and W.N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954); *c*) R. Hoffmann, and W.N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962); *d*) F.P. Boer, M.D. Newton, and W.N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2361 (1966).
5) *a*) W.C. Hamilton, *Proc. Roy. Soc.* (Lond.), **A235**, 395 (1956); *b*) L. Burnelle and J.J. Kaufman, *J. Chem. Phys.*, **43**, 3540 (1965); *c*) R.J. Buenker, S.D. Peyerimhoff, L.C. Allen, and J.L. Whitten, *J. Chem. Phys.*, **45**, 2835 (1966); *d*) W.E. Palke and W.N. Lipscomb, *J. Chem. Phys.*, **45**, 3948 (1966); *e*) M. Yamazaki, *J. Chem. Phys.*, **27**, 1401 (1957); *f*) M. Gelus, R. Ahlrichs, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Letters*, **7**, 503 (1970); *g*) E.A. Laws, R.M. Stevens, and W.N. Lipscomb, *J. Am. Chem. Soc.*, **94**, 4461 (1972); *h*) B.M. Gimare, *J. Am. Chem. Soc.*, **95**, 1417 (1973).
6) S. Yamabe, T. Minato, H. Fujimoto, and K. Fukui, *Theor. Chim. Acta*, **32**, 187 (1973).
7) H. Umeyama and T. Matsuzaki, *Chem. Pharm. Bull.*, **27**, 1626 (1979).
8) W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton, and J.A. Pople, Gaussian 70, Quantum Chemistry Program Exchange, Indiana University (1974).
9) R. Ditchfield, W.J. Hehre, and J.A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
10) *a*) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); *b*) K. Kitaura and K. Morokuma, *Int. J. Quantum Chem.*, **10**, 325 (1976); *c*) H. Umeyama, K. Kitaura, and K. Morokuma, *Chem. Phys. Lett.*, **36**, 11 (1975); *d*) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 4400 (1976); *e*) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 7208 (1976).
11) R.E. McCoy and S.H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).
12) The reaction $2BH_3 \rightarrow B_2H_6$ was selected in the energy decomposition analyses, even though other reactions such as $BH_2^+ + BH_4^- \rightarrow B_2H_6$, *etc.*, should be considered, because borane was thought to be an intermediate in the process of the $B\langle{}^{H}_{H}\rangle B$ bridge breaking for diborane.[13]
13) H.I. Schlesinger and A.B. Burg, *Chem. Revs.*, **31**, 1 (1942).

Chem. Pharm. Bull.
29(2) 558—563 (1981)

Quinones and Related Compounds in Higher Plants. XIII.[1] Absolute Structure of 2-Carboxy-2-prenyl-4-oxo-1-tetralone, a Key Intermediate in the Biosynthesis of Naphthoquinone Congeners of *Catalpa ovata*

KENICHIRO INOUE, YOSHINORI SHIOBARA, SHIGENORI OOKAWA, HIROYUKI INOUYE,*
TOORU TAGA, KAZUYO YOSHIDA, and KENJI OSAKI

Faculty of Pharmaceutical Sciences, Kyoto University, Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto 606, Japan

(Received September 22, 1980)

The absolute configuration at C-2 of 2-carboxy-2-prenyl-4-oxo-1-tetralone (**2**), a key intermediate in the biosynthesis of prenylnaphthoquinone congeners of the wood and callus tissues of *Catalpa ovata*, was verified to be *S* by X-ray crystallographic analysis of the *p*-bromobenzoate (**8**) derived from **2**.

Keywords——(2*S*)-(−)-2-carboxy-2-prenyl-4-oxo-1-tetralone; biosynthetic intermediate; prenylnaphthoquinones; absolute structure; X-ray analysis

In the course of studies on the naphthoquinone congeners of the wood and tissue cultures of *Catalpa ovata* G. DON (Bignoniaceae), we clarified their biosynthetic pathway.[2–6] In particular, by radiochemical dilution experiments, we demonstrated that the stereochemical course in the biosynthesis of (2*R*)-(−)-catalponone ((2*R*)-**1**) from 2-carboxy-4-oxo-1-tetralone