that we derived previously. It may be seen that the agreement is very poor in the case of hexabenzo-coronene; again we cannot offer an explanation for this discrepancy.

## Discussion

We already discussed the accuracy of the various results in the previous sections for each group of molecules separately. We consider the overall agreement between theory and experiment satisfactory. We should not speculate about the accuracy of the experimental values that we have quoted but we have seen in other experiments, where the susceptibility values were remeasured independently, that deviations of 2 to 3% in the experimental values are quite common and deviations of up to 10% occur every once in a while. Our theoretical values agree with the experimental results to within these limits.

As a final check it may be interesting to compare the theoretical and experimental ratios between the $\pi$-electron susceptibilities of pyrrole and benzene. The experimental ratio is given by $(R/D)$ where $R$ is given by eq 26 and $D$ by eq 24; it is equal to 0.263. The theoretical ratio may be derived from susceptibility expressions 22 and 19 for pyrrole and benzene and from expressions 21 and 16 of the two parameters $\gamma$ and $\gamma_0$. If we assume that the bond distances $R$ and $R_0$ are the same in benzene and pyrrole the theoretical ratio is 0.270. There is excellent agreement between the two values, and we conclude that there is no basic difference between the behavior of the $\pi$ electrons in five-membered or six-membered ring systems as far as the diamagnetic susceptibility is concerned.

# Molecular Orbital Calculation of the Electronic Structure of Borane Carbonyl[1]

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**Abstract:** An *ab initio* molecular orbital calculation has been carried out on the adduct of borane and carbon monoxide, *i.e.*, borane carbonyl. By performing configuration analysis, the electronic structure of this complex has been analyzed in terms of each electronic configuration, and the origin of charge transfer and bond formation has been studied. A chemically graspable representation for the mode of interaction between borane and carbonyl has been devised.

On the electronic structure of molecular complexes, there have been extensive studies from both experimental and theoretical directions.[2a] In the theoretical field, Mulliken originally proposed the intermolecular charge-transfer theory and elucidated the force of complex formation and the spectra.[2c] After his theory, some more detailed treatments were devised by the use of the perturbation method, and numerical calculations were carried out on the interaction energies and their components (Coulomb, charge transfer, and dispersion energy, etc.).[3] Thus, the dominant role of the charge-transfer effect has been emphasized to interpret the characteristic nature of molecular complexes, and these theories give the chemically acceptable concepts concerning the donor-acceptor interaction. Such treatments, however, have a defect that they cannot be applied with a sufficient accuracy to the case of "strong" complexes, for the interaction between two species is too strong to be dealt with as a perturbation.

On the other hand, the molecular orbital (MO) calculations were performed on several complexes, regarding the two molecules of the complex as an entity, and the discussions on their stability were made from the point of view of energy and charge distribution. Among these studies, *ab initio* MO calculations have particularly afforded reliable information about the properties of the complexes.[4] The pictures thus obtained, however, are often ambiguous for understanding the chemical features of complex formation, that is, the conceptual aspects of the donor-acceptor interaction.

Recently, we have analyzed the electronic structure of borazane,[5] by expanding the MO's of the complex in terms of those of its two fragments ($NH_3$ and $BH_3$) and performing the configuration analysis,[5,6] and pointed out that the method proposed there seems to be useful for the interpretation of chemically interacting systems which cannot be described by a perturbative procedure reported so far.

(1) The IUPAC name for this compound is carbon monoxide(*C-B*)-borane.

(2) (a) See, for instance, R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969; (b) R. Foster, "Organic Charge Transfer Complexes," Academic Press, London, 1969; (c) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952); *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956); see also ref 2a.

(3) (a) M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968); (b) M. W. Hanna and D. E. Williams, *ibid.*, **90**, 5358 (1968); (c) J. L. Lippert, M. W. Hanna, and P. J. Trotter, *ibid.*, **91**, 4035 (1969); (d) E. G. Cook, Jr., and J. C. Schug, *J. Chem. Phys.*, **53**, 723 (1967).

(4) See, for instance, E. Clementi, *J. Chem. Phys.*, **46**, 3851 (1967); **47**, 2323 (1967).

(5) H. Fujimoto, S. Kato, S. Yamabe, and K. Fukui, *J. Chem. Phys.*, in press.

(6) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).
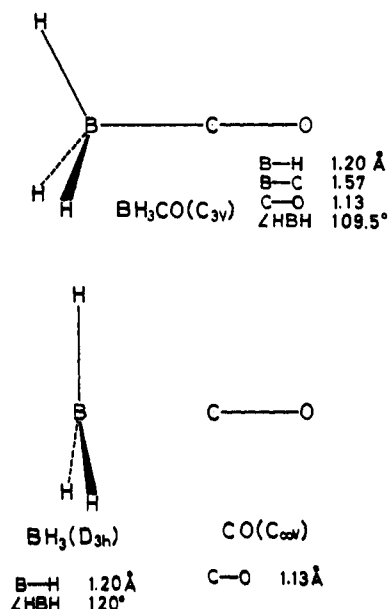
In the present paper, we intend to extend our previous method and apply this advanced way of calculation to another typical molecular complex of borane carbonyl ($BH_3 \cdot CO$). On this complex, there have been several spectroscopic studies,[7] and an MO calculation was performed by Armstrong and Perkins.[8] They discussed the stability of this complex by the electron distribution obtained by the calculation on the whole complex. Here we explain its electronic structure by the use of configuration interaction language, regarding it is composed of two interacting fragmental parts ($BH_3$ and CO).

## Procedure of Calculation

In this section, we make a brief description of the theoretical aspect in relation to the method previously reported.[5]

First, we consider two fragmental parts which have closed-shell structures, say A and B, and their composite system, A–B. The MO's of each system are given by a linear combination of atomic orbitals (LCAO). The notation of MO's is given in Chart I. We repre-

**Chart I**

| System | | MO |
|---|---|---|
| A | occupied | $\phi_i(i = 1, 2, \ldots, M)$ |
| | unoccupied | $\phi_j(j = M + 1, M + 2, \ldots, m)$ |
| B | occupied | $\chi_k(k = m + 1, m + 2, \ldots, m + N)$ |
| | unoccupied | $\chi_l(l = m + N + 1, m + N + 2, \ldots, m + n)$ |
| A–B | occupied | $\psi_g(g = 1, 2, \ldots, M + N)$ |
| | unoccupied | $\psi_h(h = M + N + 1, M + N + 2, \ldots, m + n)$ |

sent the MO's of the A–B by a linear combination of the MO's of A and B.

$$\psi_g(1) = \sum_{i=1}^{M} d_i^{(g)}\phi_i(1) + \sum_{j=M+1}^{m} d_j^{(g)}\phi_j(1) + \sum_{k=m+1}^{m+N} d_k^{(g)}\chi_k(1) + \sum_{l=m+N+1}^{m+n} d_l^{(g)}\chi_l(1) \quad (1)$$

The coefficients, $d_i^{(g)}$, etc., are easily obtained by solving the $m + n$ dimensional simultaneous equation with respect to the AO coefficients. To express the wave function of the complex, $\Psi$, in a chemically graspable form, we rewrite it by a combination of wave functions which contain various electronic configurations, i.e., a CI wave function[9]

$$\Psi = C_0\Psi_0 + \sum_i^{occ}\sum_l^{uno} C_{i\to l}\Psi_{i\to l} + \sum_k^{occ}\sum_j^{uno} C_{k\to j}\Psi_{k\to j} + \sum_i^{occ}\sum_j^{uno} C_{i\to j}\Psi_{i\to j} + \sum_k^{occ}\sum_l^{uno} C_{k\to l}\Psi_{k\to l} + \ldots \quad (2)$$

where the symbols $\Sigma^{occ}$ and $\Sigma^{uno}$ imply the summation over occupied and unoccupied MO's, respectively, and $i \to l$, for instance, stands for the one-electron shift from the $i$th occupied MO of A to the $l$th unoccupied MO of B. The procedure to get the coefficients, $C_0$ and $C_{i\to l}$, etc., is given in our previous paper, and we show here

(7) (a) R. T. Holzmann, R. L. Hughes, I. C. Smith, and E. W. Lawless, "Production of the Boranes and Related Research," Academic Press, London, 1967, p 56, and references therein; (b) R. M. Adams, "Boron, Metallo-Boron Compounds and Borane," Interscience, New York, N. Y., 1964, p 546, and references therein.
(8) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 1044, (1969).
(9) (a) J. N. Murrel, M. Randić, and D. R. Williams, *Proc. Roy. Soc., Ser. A*, **284**, 566 (1965); (b) see also K. Fukui, H. Fujimoto, and S. Yamabe, *J. Phys. Chem.*, **76**, 232 (1972).

the formal expression of each CI wave function following the conventional abbreviation.[10]

State of zero configuration

$$C_0\Psi_0 = D(0)^2 T(0/0)\frac{1}{N_0}|\phi_1\bar{\phi}_1\phi_2\ldots\phi_M\bar{\phi}_M\chi_{m+1}\bar{\chi}_{m+1}\ldots$$
$$\chi_{m+N}\bar{\chi}_{m+N}| \quad (3)$$

Monotransferred configuration (from the $i$th occupied MO of A to the $l$th unoccupied one of B)

$$C_{i\to l}\Psi_{i\to l} = D(0)D(i\to l)[2\{T(0/0)T(i\to l/i\to l) + T(0/i\to l)^2\}]^{1/2} \times \frac{1}{\sqrt{2}}\frac{1}{N_{i\to l}}\{|\phi_1\bar{\phi}_1\ldots\bar{\phi}_{i-1}\phi_i\phi_{i+1}\ldots$$
$$\bar{\phi}_M\chi_{m+1}\bar{\chi}_{m+1}\ldots\bar{\chi}_{m+N}\bar{\chi}_l| - |\phi_1\bar{\phi}_1\ldots\bar{\phi}_{i-1}\bar{\phi}_i\phi_{i+1}\ldots$$
$$\bar{\phi}_M\chi_{m+1}\bar{\chi}_{m+1}\ldots\bar{\chi}_{m+N}\chi_l|\} \quad (4)$$

Monoexcited configuration (from the $i$th occupied MO to the $j$th unoccupied one in A)

$$C_{i\to j}\Psi_{i\to j} = D(0)D(i\to j)[2\{T(0/0)T(i\to j/i\to j) + T(0/i\to j)^2\}]^{1/2} \times \frac{1}{\sqrt{2}}\frac{1}{N_{i\to j}}\{|\phi_1\bar{\phi}_1\ldots\bar{\phi}_{i-1}\phi_i\phi_{i+1}\ldots$$
$$\bar{\phi}_M\chi_{m+1}\bar{\chi}_{m+1}\ldots\bar{\chi}_{m+N}\bar{\phi}_j| - |\phi_1\bar{\phi}_1\ldots\bar{\phi}_{i-1}\bar{\phi}_i\phi_{i+1}\ldots$$
$$\bar{\phi}_M\chi_{m+1}\bar{\chi}_{m+1}\ldots\bar{\chi}_{m+N}\phi_j|] \quad (5)$$

where $N_0$, $N_{i\to l}$, and $N_{i\to j}$ are the normalization constants, $D(0)$ and $T(0/0)$ are given by the determinantal forms shown in eq 6 and 7, and $S_{ik}$ is the overlap inte-

$$D(0) = \begin{vmatrix} d_1^{(1)}d_1^{(2)}\ldots\ldots\ldots d_1^{(g)} \\ d_2^{(1)}d_2^{(2)}\ldots\ldots\ldots d_2^{(g)} \\ d_M^{(1)}d_M^{(2)}\ldots\ldots d_M^{(g)} \\ d_{m+1}^{(1)}d_{m+1}^{(2)}\ldots d_{m+1}^{(g)} \\ d_{m+N}^{(1)}d_{m+N}^{(2)}\ldots d_{m+N}^{(g)} \end{vmatrix} \quad (6)$$

$$T(0/0) = \begin{vmatrix} S_{11}S_{12}\ldots\ldots S_{1M}S_{1m+1}S_{1m+2}\ldots\ldots S_{1m+N} \\ S_{21}S_{22}\ldots\ldots S_{2M}S_{2m+1}S_{2m+2}\ldots\ldots S_{2m+N} \\ S_{M1}S_{M2}\ldots S_{MM}S_{Mm+1}S_{Mm+2}\ldots S_{Mm+N} \\ S_{m+11}S_{m+12}\ldots\ldots\ldots\ldots\ldots\ldots S_{m+1m+N} \\ S_{m+N1}S_{m+N2}\ldots\ldots\ldots\ldots\ldots\ldots S_{m+Nm+N} \end{vmatrix} \quad (7)$$

gral between $\phi_i$ and $\chi_k$

$$S_{ik} = \int \phi_i(1)\chi_k(1)dv_1$$

$D(i \to l)$ is the determinant obtained by replacing the $i$th column by $d_l^{(g)}$ ($g = 1, 2, \ldots, M + N$) in eq 6. $T(0/i \to l)$ is obtained by the replacement of suffix $i$ in the $i$th column by $l$, $T(i \to l/i \to l)$ is also given by replacing the suffix $i$ in the $i$th column and the $i$th row by $l$ in eq 7, respectively, and so on. Other CI wave functions are given in a straightforward way similarly.

Using the CI representation of the wave function of the complex, eq 2, we construct the first-order spinless density matrix,[11] and the electron density is partitioned into the several parts in terms of each electronic configuration.

(10) See, for instance, K. Fujui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **41**, 1989 (1968).
(11) R. McWeeny, *Proc. Roy. Soc., Ser. A*, **223**, 63 (1954); **232**, 114 (1955).

Figure 1. Geometries of $BH_3CO$, $BH_3$ ($D_{3h}$), and CO.

$$\rho(A-B) = \left[ C_0{}^2\rho_p(A\cdot B) + \left(\sum_i^{occ}\sum_l^{uno} C_{i\rightarrow l}{}^2\right)\rho_p(A^+\cdot B^-) + \right.$$

$$\left(\sum_k^{occ}\sum_j^{uno} C_{k\rightarrow j}{}^2\right)\rho_p(A^-\cdot B^+) + \left(\sum_i^{occ}\sum_j^{uno} C_{i\rightarrow j}{}^2\right) \times$$

$$\left. \rho_p(A^*\cdot B) + \left(\sum_k^{occ}\sum_l^{uno} C_{k\rightarrow l}{}^2\right)\rho_p(A\cdot B^*) + \ldots \right] +$$

$$\left[ \left(2\sum_i^{occ}\sum_l^{uno} C_0C_{i\rightarrow l}S_{0,i\rightarrow l}\right)\rho_c(A^+\cdot B^-) + \right.$$

$$\left(2\sum_k^{occ}\sum_j^{uno} C_0C_{k\rightarrow j}S_{0,k\rightarrow j}\right)\rho_c(A^-\cdot B^+) +$$

$$\left(2\sum_i^{occ}\sum_j^{uno} C_0C_{k\rightarrow j}S_{0,i\rightarrow j}\right)\rho_c(A^*\cdot B) +$$

$$\left(2\sum_k^{occ}\sum_l^{uno} C_0C_{k\rightarrow j}S_{0,k\rightarrow l}\right)\rho_c(A\cdot B^*) + \ldots \right] + \ldots \quad (8)$$

where

$$\rho(A-B) = n_e\int \Psi\Psi d\xi_1 d\tau_2 \ldots d\tau_{n_e}$$

$$\rho_p(A\cdot B) = \rho_{0,0}(1|1)$$

$$\rho_p(A^+\cdot B^-) = \sum_i^{occ}\sum_l^{uno} C_{i\rightarrow l}{}^2\rho_{i\rightarrow l,i\rightarrow l} \Big/ \sum_i^{occ}\sum_l^{uno} C_{i\rightarrow l}{}^2$$

$$\rho_c(A^+\cdot B^-) = \sum_i^{occ}\sum_l^{uno} C_0C_{i\rightarrow l}S_{0,i\rightarrow l}\rho_{0,i\rightarrow l}(1|1) \Big/$$

$$\sum_i^{occ}\sum_l^{uno} C_0C_{i\rightarrow l}S_{0,i\rightarrow l}$$

$$\rho_{0,0}(1|1) = n_e\int \Psi_0\Psi_0 d\xi_1 d\tau_2 \ldots d\tau_{n_e}$$

$$\rho_{i\rightarrow l,i\rightarrow l} = n_e\int \Psi_{i\rightarrow l}\Psi_{i\rightarrow l}d\xi_1 d\tau_2 \ldots d\tau_{n_e}$$

$$\rho_{0,i\rightarrow l} = n_e\int \Psi_0\Psi_{i\rightarrow l}d\xi_1 d\tau_2 \ldots d\tau_{n_e}$$

$$S_{0,i\rightarrow l} = \int \Psi_0\Psi_{i\rightarrow l}d\tau_1 d\tau_2 \ldots d\tau_{n_e}$$

in which $n_e$ is the electron number of the whole system $(2(M + N))$. These density matrices are still nor-

malized to the electron number. The terms of the first brackets of eq 8 are the diagonal elements of configurations, and we call them the "pure" terms hereafter. $\rho_p(A\cdot B)$ is the density which corresponds to the zero configuration, $\rho_p(A^+\cdot B^-)$ is that of configurations in which one electron is transferred from A to B, and $\rho_p(A^-\cdot B^+)$ is the reversely donated state. $\rho_p(A^*\cdot B)$ is the local monoexcited state in A and so on. These "pure" states are well in accordance with the classical concept of the covalent, ionic, and polarized structures.

Next, the terms within the second brackets are somewhat incomprehensible in the classical sense compared with "pure" states. They are "cross" terms originating from the overlapping of the zero configuration wave function with the other ones and hence designated as $\rho_c$. The explicit formulas of respective density matrices are not tabulated except for the zero configuration in the Appendix.

## Results and Discussion

The wave functions are determined through the self-consistent field (SCF) ab initio MO procedure[12] with the minimal basis set of Slater type AO's (STO's). The orbital exponents of STO's are taken from the standard values by Pople, et al.[13] The STO's are expanded by three Gaussian type functions for the ease of the computation of multicenter integrals.[13,14] The coefficients and exponents of this expansion are adopted from Stewart's result.[15]

First, we calculated the electronic structures of $BH_3CO$, $BH_3$ ($D_{3h}$ symmetry), and CO in their isolated states. The geometrical structures are shown in Figure 1.[16] The energies of respective molecules are given in Table I. The calculated heat of formation of

Table I. Total Energy $E_T$ and Absolute Value of the Ratio between Kinetic Energy $E_K$ and the Total Energy[a]

| System | $E_T$ | $-E_K/E_T$ |
|---|---|---|
| $BH_3CO$ | $-137.3143$ | $0.9923$ |
| $BH_3$ ($D_{3h}$) | $-26.0634$ | $1.0031$ |
| CO | $-111.2073$ | $0.9963$ |

[a] Energies are given in atomic units for the configuration given in Figure 1.

$BH_3CO$ is 24.2 kcal/mol, which is comparable with the experimental value (18.8 kcal/mol).[17]

Next, the MO's of the two fragmental parts of this complex, $BH_3$ ($C_{3v}$ symmetry) and CO parts, were also calculated with the same structures as in the adduct. The MO's are displayed in Figure 2.[18]

$BH_3$ has been suggested to act as a b acceptor because of its effective ability as a v acceptor and at the same time as a hyperconjugative $\pi$ donor.[19] As to

(12) C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).
(13) W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2651 (1969).
(14) (a) K. O-ohata, H. Taketa, and S. Huzinaga, J. Phys. Soc. Jap., 21, 2306 (1966); (b) H. Taketa, S. Huzinaga, and K. O-ohata, ibid., 21, 2313 (1966).
(15) R. F. Stewart, J. Chem. Phys., 52, 431 (1970).
(16) L. E. Sutton, Ed., Chem. Soc., Spec. Publ., No. 11 (1956).
(17) R. F. McCoy and S. H. Bauer, J. Amer. Chem. Soc., 78, 2061 (1956).
(18) S. Ahrland, J. Chatt, and N. Davies, Quart. Rev., Chem. Soc., 12, 265 (1958).
(19) W. A. G. Graham and F. G. A. Stone, J. Inorg. Nucl. Chem., 3, 164 (1956).

borane carbonyl, it has been pointed out qualitatively that its stability is caused by two different types of charge-transfer actions, namely the $\sigma$ type donation from CO to $BH_3$ and the hyperconjugative back donation,[20] but the quantitative discussion concerning these matters has not been performed up to the present. Therefore, it is of interest to analyze its electronic structure in relation to the interaction between $BH_3$ and CO.

By expanding the MO's of $BH_3CO$ in terms of the MO's of $BH_3$ ($C_{3v}$) and CO, eq 1, we can define the occupation number of MO's of fragmental parts due to the interaction. For the MO $\phi_i$

$$\nu_i = 2 \sum_{g=1}^{M+N} \left\{ (d_i^{(g)})^2 + \sum_{k=m+1}^{m+N} d_i^{(g)} d_k^{(g)} S_{ik} + \sum_{l=m+N+1}^{m+n} d_i^{(g)} d_l^{(g)} S_{il} \right\}$$

They are given in Table II. It may be seen that the

**Table II.** The Occupation Number of the MO's of $BH_3$ and CO Parts[a]

| ——BH₃—— | | ——CO—— | |
|---|---|---|---|
| MO | $\nu$ | MO | $\nu$ |
| 1a₁ | 2.0009 (2) | 1σ | 2.0000 (2) |
| 2a₁ | 1.9468 (2) | 2σ | 2.0009 (2) |
| 1e | 1.9342 (2) | 3σ | 1.9936 (2) |
| | 1.9342 (2) | 4σ | 1.9590 (2) |
| 3a₁* | 0.4831 (0) | 1π | 1.9985 (2) |
| 2e* | 0.0009 (0) | | 1.9985 (2) |
| | 0.0009 (0) | 5σ | 1.6059 (2) |
| 4a₁* | 0.0000 (0) | | |
| | | 2π* | 0.0663 (0) |
| | | | 0.0663 (0) |
| | | 6σ* | 0.0095 (0) |

[a] The number in the parentheses is the occupation number before the interaction. The excess of 2 in the occupation number of some MO's, e.g., 1a₁ of $BH_3$, may be due to the application of the ordinary population analysis of Mulliken to such heteropolar bonds. However, these excesses are negligibly small in the present case.

major change indicated in Table II is that the electrons are removed from the $5\sigma$ MO of CO and are added to the $3a_1^*$ MO of $BH_3$. Electrons are also removed from the $1e$ MO of $BH_3$ and are added to the $2\pi^*$ MO of CO to some extent. These seem to support the suggestion of the stability of this complex.

**Wave Function.** We have seen the electron rearrangement caused by the interaction between $BH_3$ and CO in terms of the orbital occupancies. By the use of the above mentioned CI wave function, we can develop a chemically more intuitive discussion about the electronic structure of this complex. The coefficient of the zero configuration, $C_0$, was calculated to be 0.5475. The coefficients of various monotransferred and monoexcited configurations are shown in Tables III and IV. Among these states, the contribution caused by the charge transfer from the $5\sigma$ MO of CO to the $3a_1^*$ MO of $BH_3$ is the largest one. This means that the charge-transfer action from the lone-pair orbital on the carbon atom to the $p\sigma$ orbital on the boron is important in the complex formation. As to

(20) Examination of the occupation number affords us information on the number of electrons donated and accepted with respect to each MO.
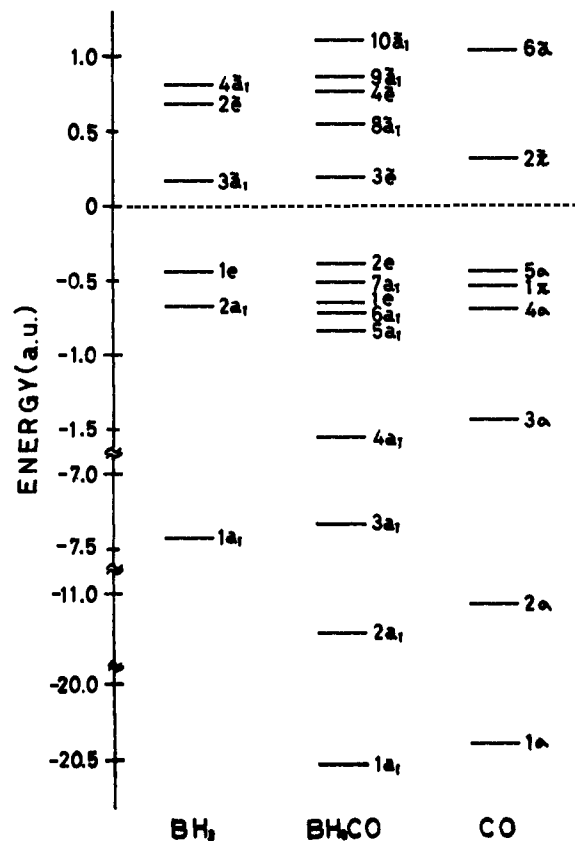


Figure 2. MO levels of $BH_3$ ($D_{3h}$ and $C_{3v}$), $BH_3CO$, and CO. The symbol * implies the unoccupied MO. The symmetry of MO's of $BH_3$ ($D_{3h}$) is termed in the $C_{3v}$ structure.

**Table III.** Coefficients of Monotransferred Electronic Configuration[a]

| | | $|C_{i \rightarrow l}|$ | | |
|---|---|---|---|---|
| | | | —————l————— | |
| | | 2π* | | 6σ* |
| $i$ | 1a₁ | 0 | 0 | 0.0001 |
| | 2a₁ | 0 | 0 | 0.0124 |
| | 1e | 0.1036 | 0 | 0 |
| | | 0 | 0.1036 | 0 |

| | | $|C_{k \rightarrow j}|$ | | |
|---|---|---|---|---|
| | | | ————j———— | |
| | | 3a₁* | 2e* | 4a₁* |
| $k$ | 1σ | 0.0006 | 0 | 0 | 0.0001 |
| | 2σ | 0.0045 | 0 | 0 | 0.0006 |
| | 3σ | 0.0206 | 0 | 0 | 0.0021 |
| | 4σ | 0.0585 | 0 | 0 | 0.0006 |
| | 1π | 0 | 0.0048 | 0 | 0 |
| | | 0 | 0 | 0.0048 | 0 |
| | 5σ | 0.2910 | 0 | 0 | 0.0055 |

[a] $i$ and $j$ denote the occupied MO and the unoccupied MO of the $BH_3$ part, respectively, and $k$ and $l$ indicate the occupied MO and the unoccupied MO of the CO part, respectively.

the back donation, the $\pi$ type charge transfer from the $1e$ MO of $BH_3$ to the $2\pi^*$ MO of CO is unexpectedly large. The contribution of the polarized state is far smaller than that of the charge-transferred state.

We also define the dative state functions. For instance, the function which corresponds to the monotransferred configuration from CO to $BH_3$ is given in the following form

$$\sum_{k}^{occ} \sum_{j}^{uno} C_{k \rightarrow j} \Psi_{k \rightarrow j} \simeq \left\{ \sum_{k}^{occ} \sum_{j}^{uno} (C_{k \rightarrow j})^2 \right\}^{1/2} \Psi(BH_3^- \cdot CO^+)$$

**Table IV.** Coefficients of Monoexcited Electronic Configurations[a]

| | | $|C_{i \to j}|$ | | |
|---|---|---|---|---|
| | | 3a$_1$* | 2e* | 4a$_1$* |
| $i$ | 1a$_1$ | 0.0063 | 0 | 0 | 0.0008 |
| | 2a$_1$ | 0.0693 | 0 | 0 | 0.0107 |
| | 1e | 0 | 0.0024 | 0 | 0 |
| | | 0 | 0 | 0.0024 | 0 |

| | | $|C_{k \to l}|$ | | |
|---|---|---|---|---|
| | | 2$\pi$* | 6$\sigma$* |
| $k$ | 1$\sigma$ | 0 | 0 | 0.0001 |
| | 2$\sigma$ | 0 | 0 | 0.0014 |
| | 3$\sigma$ | 0 | 0 | 0.0034 |
| | 4$\sigma$ | 0 | 0 | 0.0015 |
| | 1$\pi$ | 0.0209 | 0 | 0 |
| | | 0 | 0.0209 | 0 |
| | 5$\sigma$ | 0 | 0 | 0.0474 |

[a] The same as in Table III.

where $\Sigma_k^{occ}$ and $\Sigma_j^{uno}$ denote the summations over all the occupied MO's of CO and the unoccupied MO's of BH$_3$, respectively. The other contributions are summarized in the same way. As a result of the calculation, the wave function of borane carbonyl is represented by

$$\Psi(BH_3 \cdot CO) = 0.5475\Psi(BH_3 \cdot CO) +$$

$$0.2977\Psi(BH_3^- \cdot CO^+) + 0.1470\Psi(BH_3^+ \cdot CO^-) +$$

$$0.0560\Psi(BH_3 \cdot CO^*) + 0.0705\Psi(BH_3^* \cdot CO) +$$

$$0.0602\Psi(BH_3^{2-} \cdot CO^{2+}) + 0.0243\Psi(BH_3^{2+} \cdot CO^{2-}) +$$

$$0.0683\Psi(BH_3^{\mp} \cdot CO^{\pm}) + 0.0074\Psi(BH_3^* \cdot CO^*) + \ldots$$

where, in the two-electron transferred and two-electron excited states, all possible configurations were taken into account.

**Electron Population.** The electron population[21] of the adduct and the difference population of the adduct minus two fragments are shown in Table V. It may be

**Table V.** Electron Population of BH$_3$CO and the Difference of the Adduct Minus Two Fragments[a]

| | Adduct (BH$_3$CO) | Difference |
|---|---|---|
| | (i) Atom Population | |
| B | 5.1828 | +0.2490 |
| H | 1.0395 | +0.0174 |
| C | 5.5997 | −0.2037 |
| O | 8.0991 | −0.0975 |
| | (ii) Atom Bond Population | |
| | Adduct | Difference |
| B–C ($\sigma$) | 0.4978 | +0.4978 |
| ($\pi$) | 0.0744 | +0.0744 |
| C–O ($\sigma$) | 0.4632 | +0.1048 |
| ($\pi$) | 0.6852 | −0.0154 |
| B–H | 0.7773 | −0.0144 |

[a] The atom population and the atom bond population are calculated following Mulliken's definition, ref 21.

seen in Table V that electrons are mainly removed from the carbon atom of CO and are added to the boron atom of BH$_3$, which becomes considerably negative in consequence. As for the B–C bond population, the strong $\sigma$ type bonding and the slight $\pi$ type bonding are

(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

observed. The appreciable increase of the C–O bond population also occurs mainly on the $\sigma$ type component, which well supports the spectroscopic study that the C–O stretching frequency increases by the complex formation.[22]

To clarify the reason why the electron distribution is changed by the interaction between BH$_3$ and CO, we have analyzed the contribution of each electronic configuration defined in eq 8 to the electron population of the whole BH$_3 \cdot$CO system. To begin with, we are able to get the "weight" of each configuration. We show in Table VI the relative weights to the zero con-

**Table VI.** Relative Weight of Each Electronic Configuration

| | "Pure" | "Cross" |
|---|---|---|
| BH$_3 \cdot$CO | 1 | |
| BH$_3^- \cdot$CO$^+$ | 0.2957 | 0.8899 |
| BH$_3^+ \cdot$CO$^-$ | 0.0721 | 0.1429 |
| BH$_3^* \cdot$CO | 0.0166 | 0.0866 |
| BH$_3 \cdot$CO* | 0.0105 | 0.0096 |
| BH$_3^{2-} \cdot$CO$^{2+}$ | 0.0121 | 0.0998 |
| BH$_3^{2+} \cdot$CO$^{2-}$ | 0.0019 | 0.0039 |
| BH$_3^{\pm} \cdot$CO$^{\mp}$ | 0.0156 | 0.0634 |
| BH$_3^* \cdot$CO* | 0.0002 | 0.0011 |

figuration. Among a number of configurations, the pure monotransferred ones and their cross terms with the zero configuration have large weight. Therefore, we give our attention to the zero configuration, the monotransferred configuration, and the "cross" terms coming from the zero configuration and the mono-transferred ones. We have calculated the electron population of respective configurations and show it in Table VII. As to the zero configuration, the B–C

**Table VII.** Electron Population Corresponding to Electronic Configurations[a]

| | (i) Atom Population | | | |
|---|---|---|---|---|
| | B | H | C | O |
| $\rho_p(BH_3 \cdot CO)$ | 4.7834 | 1.0602 | 5.8313 | 8.2147 |
| $\rho_p(BH_3^- \cdot CO^+)$ | 5.8112 | 1.0573 | 4.9227 | 8.0942 |
| $\rho_p(BH_3^+ \cdot CO^-)$ | 4.5605 | 0.8601 | 6.5022 | 8.4978 |
| $\rho_c(BH_3^- \cdot CO^+)$ | 5.3455 | 1.0561 | 5.2824 | 8.2038 |
| $\rho_c(BH_3^+ \cdot CO^-)$ | 4.8383 | 0.8736 | 5.9972 | 8.5529 |

| | (ii) Atom Bond Population | | | |
|---|---|---|---|---|
| | | B–C | C–O | B–H |
| $\rho_p(BH_3 \cdot CO)$ | ($\sigma$) | −0.3183 | 0.3462 | 0.8225 |
| | ($\pi$) | −0.0252 | 0.7038 | |
| $\rho_p(BH_3^- \cdot CO^+)$ | ($\sigma$) | 0.3111 | 0.4700 | 0.7915 |
| | ($\pi$) | −0.0252 | 0.7037 | |
| $\rho_p(BH_3^+ \cdot CO^-)$ | ($\sigma$) | −0.3172 | 0.3169 | 0.6945 |
| | ($\pi$) | −0.0128 | 0.4000 | |
| $\rho_c(BH_3^- \cdot CO^+)$ | ($\sigma$) | 0.9345 | 0.4363 | 0.8162 |
| | ($\pi$) | −0.0196 | 0.7031 | |
| $\rho_c(BH_3^+ \cdot CO^-)$ | ($\sigma$) | −0.2904 | 0.2804 | 0.7021 |
| | ($\pi$) | 0.6986 | 0.6477 | |

[a] The same as in Table V.

bond population that originates from the overlap of both occupied orbitals of BH$_3$ and CO subsystems is strongly antibonding, arising from the exchange repulsive interaction as shown in an example of two

(22) (a) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1118 (1957); (b) R. C. Taylor, *ibid.*, **26**, 1131 (1957); **27**, 979 (1957); (c) S. Sundaram and F. F. Cleveland, *ibid.*, **32**, 166 (1960).

helium atoms.[23] Accordingly, we cannot interpret the bond formation shown in Table V by the contribution of the zero configuration term only. The pure mono-transferred configuration from CO to $BH_3$ gives a slight bonding component in the B–C region but does not make an essential contribution to the newly formed bond. This is because the orbital overlapping is necessary in order to cause an accumulation of the overlap density in the bonding region. Furthermore, the reversely donated configuration yields an anti-bonding density in both the $\sigma$ type and the $\pi$ type components. On the other hand, the cross terms produced by the overlapping of the monotransferred configurations with the zero configuration may render great services to the bond formation through the overlap between the occupied MO's of one fragmental part and the unoccupied MO's of the other. On the $\sigma$ type bond population, the cross term of the charge-transferred configuration from CO to $BH_3$ with the zero configuration plays the most important role, as shown in Table VII. The $\pi$ type bonding component is also created by the overlap of the back-donated configuration with the zero configuration. Consequently, the chemical bond between the boron atom and the carbon atom is formed by the charge-transfer actions in both directions, and the overlapped products of the charge-transferred configurations with the zero configuration play the most essential role.

Of interest next is the somewhat unexpected increase of the C–O bond population by reflecting that the electron transfer from CO to $BH_3$ takes place to a large extent. From Table VII, this tendency mainly originates from the contribution of charge transfer from CO to $BH_3$, removing electrons from the $5\sigma$ MO of CO which has an antibonding character in the region of the C–O bond. This relaxation of the antibonding nature helps to strengthen the $\sigma$ type component of the C–O chemical bond.

## Conclusion

In this report, we have analyzed the electronic structure of borane carbonyl in a chemically graspable form. Among various electronic configurations, an essential role of the charge-transfer configuration to the formation of this complex is confirmed. It is also pointed out that the B–C bond formation is mainly contributed

(23) J. C. Slater, *Phys. Rev.*, **32**, 349 (1928).

by the overlapped product of the charge-transfer configuration with zero configuration. Although it should be noted that the extent of the charge transfer depends on the B–C bond length, we believe that the conclusion in this paper is not changed for a slight variation of the geometry. Lastly, it is worthwhile to point out that, although the usual SCF procedure for the whole complex cannot divide the contributions into the part from the donation and that from the back donation, this method does provide information with respect to the sites of donor–acceptor interaction and their mechanism on a molecular level, as shown in the borane carbonyl system.

## Appendix

By integrating the density matrix $\rho_p(A \cdot B)$ in eq 8, we get the electron populations corresponding to the zero configuration

$$\int \rho_p(A \cdot B) dv_1 =$$

$$\left[ 2 \sum_{i=1}^{M} \sum_{i'=1}^{M} \sum_{t=1}^{m} \sum_{t'=1}^{m} T_i^{(i')}(0/0) c_t^{(i)} c_{t'}^{(i')} s_{tt'}/T(0/0) \right] +$$

$$\left[ 2 \sum_{k=m+1}^{m+N} \sum_{k'=m+1}^{m+N} \sum_{u=m+1}^{m+n} \sum_{u'=m+1}^{m+n} T_{k-m+M}^{(k'-m+M)} \times \right.$$

$$\left. (0/0) c_u^{(k)} c_n^{(k')} s_{uu'}/T(0/0) \right] +$$

$$\left[ 4 \sum_{i=1}^{M} \sum_{k=m+1}^{m+N} \sum_{t=1}^{m} \sum_{u=m+1}^{m+N} T_i^{(k-m+M)} \times \right.$$

$$\left. (0/0) c_t^{(i)} c_n^{(k)} s_{tu}/T(0/0) \right]$$

where $T_i^{(i')}(0/0)$ implies the $(i,i')$th minor of the determinant $T(0/0)$. $c_t^{(i)}$ is the $t$th AO coefficient of the $i$th MO, and $s_{tu}$ is the overlap integral between the $t$- and $u$th AO's.

The first and second brackets are the intrasystem populations in A and B, respectively. The terms of the third bracket correspond to the intersystem populations caused by the interaction between A and B.