

Semiempirical Magnetic Susceptibilities of Nitrogen-Containing Heterocycles¹

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Abstract: We applied a previously derived semiempirical theory of diamagnetic susceptibilities to a series of nitrogen-containing heterocycles. We considered six-membered conjugated ring systems with one or more nitrogen atoms in the ring and their derivatives, pyrrole, indole, etc. The agreement between theory and experiment is satisfactory except for the benzoacridine derivatives where the deviations between theory and experiment range from 1 to 5%.

In some recent papers^{2,3} we presented a semiempirical theory of the diamagnetic susceptibilities of a series of aromatic hydrocarbons and of a series of benzene derivatives.³ This work constitutes an extension of previous work^{4,5} on saturated organic molecules to systems that contain delocalized π -electron orbitals. We found that the diamagnetic susceptibility of a conjugated molecule may be represented as

$$\chi = \chi_{\sigma} + \chi_{\pi} - \chi_{\sigma\pi} \quad (1)$$

Here χ_{σ} is the susceptibility of the σ electrons, χ_{π} is the susceptibility of the π electrons, and $\chi_{\sigma\pi}$ is the susceptibility contribution due to the interaction between π and σ electrons.

The σ susceptibility may be written as a sum of bond susceptibilities and bond-bond interactions and it may be treated in the same way as in saturated molecules. We showed² that the term $\chi_{\sigma\pi}$ may also be written as a sum of bond-bond interactions if the π -electron density on each carbon atom is equal to unity. It may then be treated in the same way as the σ -electron susceptibility χ_{σ} , and the two terms may be combined.

The π -electron susceptibility χ_{π} may be evaluated by means of London's method,⁶ using gauge invariant atomic orbitals. In this calculation χ_{π} is expressed in terms of an atomic parameter and by estimating the magnitude of this parameter we obtain the absolute value of χ_{π} . We have argued before² that the relative values of the results of the London calculations for a series of different molecules are much more reliable than the result for one particular molecule because of the uncertainties in estimating the atomic parameter. Accordingly, we represent the π -electron susceptibility $\chi_{\pi,M}$ of an arbitrary conjugated molecule M as

$$\chi_{\pi,M} = K_M \chi_{\pi,\text{benz}} \quad (2)$$

Here K_M is the ratio of the theoretical London values for the molecule M and for benzene. In this approach the π -electron susceptibility of the benzene molecule is treated as an adjustable parameter.

In the present paper we wish to extend the semiempirical theory of diamagnetic susceptibilities to

(1) Work supported by the National Science Foundation.

(2) P. S. O'Sullivan and H. F. Hameka, *J. Amer. Chem. Soc.*, **92**, 1821 (1970).

(3) M. E. Stockham and H. F. Hameka, *J. Amer. Chem. Soc.*, **94**, 4076 (1972).

(4) H. F. Hameka, *J. Chem. Phys.*, **34**, 1996 (1961).

(5) P. S. O'Sullivan and H. F. Hameka, *J. Amer. Chem. Soc.*, **92**, 25 (1970).

(6) F. London, *J. Phys. Radium*, **8**, 397 (1937).

nitrogen-containing heterocyclic aromatic molecules. It will prove to be convenient to separate these molecules into two groups. Group I contains all molecules that contain six-membered ring systems only. Typical representatives of this group are pyridine, triazine, quinoline, acridine, etc. Group II contains molecules that have a five-membered ring system, such as pyrrole, indole, carbazole, and their derivatives. Finally, we also consider a few aromatic hydrocarbons because some additional information has become available which makes it necessary to revise and complement previous work.²

In our previous treatment of the aromatic hydrocarbons we made use of the values K_M for the various π -electron susceptibilities that are available in the literature.⁷ In our present study on nitrogen-containing heterocycles these values are not available and they must all be calculated. In order to do this we must first choose suitable values for the various Coulomb and exchange parameters α and β for the conventional Hückel treatments of the molecules that we consider. We should recognize that we deal with two different types of nitrogen atoms, namely the N atom occurring in a pyridine ring and the N atom occurring in a pyrrole ring; this latter N atom has a hydrogen atom attached to it. If we define the Coulomb and exchange parameters of the benzene molecule as α and β , then we choose the Coulomb parameters for the two type of N atoms as

$$\alpha_{\text{N(pyridine)}} = \alpha + 0.4\beta \quad (3)$$

$$\alpha_{\text{N(pyrrole)}} = \alpha + 2.7\beta$$

These values are consistent with the values we have used before in dipole-moment calculations of N-containing heterocycles.^{8,9} We take all exchange parameters β_{CN} and β_{NN} equal to each other and to the benzene exchange parameter $\beta_{\text{CC}} = \beta$. Finally, we take the Coulomb parameter for a carbon atom with a methyl group attached to it equal to

$$\alpha(\text{toluene}) = \alpha + 0.1\beta \quad (4)$$

Again, this value is consistent with the customary use.³

Since we have to determine the π -electron susceptibility parameters K_M for some fairly large and nonsymmetric molecules, we found the customary procedure, where the determinants are calculated explicitly, some-

(7) B. Pullman and A. Pullman, "Les Théories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952.

(8) H. F. Hameka and A. M. Liquori, *Mol. Phys.*, **1**, 9 (1958).

(9) H. Hamano and H. F. Hameka, *Tetrahedron*, **18**, 985 (1962).

what inconvenient. Instead, we used a different approach, which is somewhat more elaborate but which enables us to use a computer for the whole calculation. We discuss this method in the next section.

Calculation of the π -Electron Susceptibility

London's theoretical description of the π -electron diamagnetic susceptibility of an aromatic molecule is the analog of the conventional Hückel MO theory in the presence of a magnetic field. We denote the Hückel molecular orbitals by ϕ_k and the corresponding energies by ϵ_k ; the molecular orbitals ϕ_k are obtained as linear combinations of atomic π orbitals π_j by solving the secular equation. In the London method, the molecular orbitals ψ_k in the presence of a magnetic field \mathbf{H} are written as linear combinations of gauge invariant atomic π orbitals.

$$\psi_k = \sum_j a_{k,j} f_j \pi_j \quad (5)$$

The phase factors f_j are given by

$$f_j = \exp[(2\pi ie/hc)(\mathbf{A}_j \cdot \mathbf{r})] \quad (6)$$

where A_j is the value of the vector potential at the position of nucleus j .

The London molecular orbitals ψ_k and the corresponding energies ϵ_k' are obtained by solving the secular equation

$$|\langle f_m \pi_m | \mathcal{H} | f_n \pi_n \rangle - \epsilon \langle f_m \pi_m | f_n \pi_n \rangle| = 0 \quad (7)$$

We may simplify these equations by a procedure that is similar to the Hückel equations. In the diagonal elements the phase factors cancel and we may substitute

$$\langle f_m \pi_m | \mathcal{H} | f_m \pi_m \rangle = \alpha \quad (8)$$

The matrix elements between adjacent atoms take the form

$$\langle f_m \pi_m | \mathcal{H} | f_n \pi_n \rangle = \beta \epsilon_{m,n} \quad (9)$$

$$\epsilon_{m,n} = \exp[(\pi ie/hc)(X_m Y_n - X_n Y_m) H^2]$$

where X_m , etc., denote the Cartesian coordinates of the two nuclei. The overlap integrals are all neglected and we substitute

$$\langle f_m \pi_m | f_n \pi_n \rangle = \delta_{m,n} \quad (10)$$

In London's method the secular equations are all solved by means of analytical methods. It is not possible to solve the equations exactly but we only need to know the eigenvalues up to quadratic terms in the magnetic field, and it is possible to derive this result analytically. However, for larger, nonsymmetric molecules this method becomes very laborious and we decided to use a different approach.

If the Hückel orbitals ϕ_k are given by

$$\phi_k = \sum_j C_{k,j} \pi_j \quad (11)$$

we define a set of functions ϕ_k' by adding in the phase factors f_j .

$$\phi_k' = \sum_j C_{k,j} f_j \pi_j \quad (12)$$

We then determine a matrix b_k , which elements are given by

$$b_{k,l} = \langle \phi_k' | \mathcal{H} | \phi_l' \rangle = \sum_i \sum_j C_{k,i} C_{l,j} \langle f_i \pi_i | \mathcal{H} | f_j \pi_j \rangle \quad (13)$$

Obviously, this matrix reduces to diagonal form

$$b_{k,l} = \epsilon_k \delta_{k,l} \quad (14)$$

when the magnetic field H_z becomes zero. In the presence of a magnetic field the various matrix elements are functions of H_z but the off-diagonal elements are at least linear in H_z . This means that we may approximate the eigenvalues ϵ_k' of the matrix $b_{k,l}$ as

$$\epsilon_k' = b_{k,k} - \sum_{l \neq k} \frac{b_{k,l} b_{l,k}}{\epsilon_l - \epsilon_k} \quad (15)$$

This expression is accurate up to quadratic terms in H_z which is just what we need for our purpose.

We found the above method more convenient than the previous analytical methods because in our method we can use the computer for most of the procedure and the method can be conveniently applied to large nonsymmetric molecules. The method must be slightly modified if any of the unperturbed eigenvalues ϵ_k are degenerate, but this did not present any great problems.

In six-membered ring systems, for example the pyridine molecule, we assume that the C-C, C-N, and N-N bond lengths are all equal to a constant value R . The molecular orbital energies ϵ_k' may then be expressed in terms of a parameter γ which is given by

$$\gamma = \frac{1}{2} \sqrt{3} R^2 H_z (e\pi/hc) \quad (16)$$

We find that the lowest molecular orbital energies of the pyridine molecule are given by

$$\begin{aligned} \epsilon_1' &= -2.0815 + 0.9590\gamma^2 \\ \epsilon_2' &= -1.1342 - 21.4819\gamma^2 \\ \epsilon_3' &= -1.0000 + 22.5000\gamma^2 \end{aligned} \quad (17)$$

Here we have used the Coulomb parameter values of eq 3. In the molecular ground state there are two electrons in the lowest three molecular orbitals each and the molecular ground state energy is given by

$$E_0(\text{pyr}) = -8.314 + 3.9543\gamma^2 \quad (18)$$

By means of the same method we find that the ground state energy of benzene is given by

$$E_0(\text{benz}) = -8 + 4\gamma^2 \quad (19)$$

It follows that the ratio $K(\text{pyr})$ between the π -electron susceptibilities of pyridine and benzene, as defined in eq 2, is

$$K(\text{pyr}) = 0.9886 \quad (20)$$

The values of the parameters K_M that are listed in Table I for the molecules of group I (pyridine type molecules) were all obtained by means of the above procedure.

In discussing the group II molecules, which all contain a five-membered pyrrole type ring, we use the same method for calculating the π -electron susceptibilities but we utilize the results differently. In the case of pyrrole we again take the C-C and C-N bond lengths all equal to a constant R_0 and we find then that the molecular orbital energies may be expressed in terms of a parameter

$$\gamma_0 = R_0^2 H_z (e\pi/hc) \quad (21)$$

We find then that the ground state energy of the pyrrole molecule is obtained as

$$E_0(\text{pyrr}) = -10.69432 + 0.810094\gamma_0^2 \quad (22)$$

Here we have again used the parameter values of eq 3.

Table I. Diamagnetic Susceptibilities of the Group I Molecules (Cgs Units $\times 10^{-6}$)

Molecule		χ_{theor}	χ_{exptl}
Pyridine	$A + P + 0.9886D$	48.034	48.40 ^{a,f}
α -Picoline	$A + P + M + N + 0.9921D$	60.351	61.22 ^{b,f}
β -Picoline	$A + P + M + 0.9848D$	60.381	62.15 ^{b,f}
γ -Picoline	$A + P + M + 0.9911D$	60.452	61.83 ^{b,f}
2,4-Lutidine	$A + P + 2M + 2N + 0.9939D$	72.760	73.11 ^{b,f}
2,6-Lutidine	$A + P + 2M + 2N + 0.9949D$	72.661	73.10 ^{b,f}
2,4,6-Collidine	$A + P + 3M + 2N + 0.9959D$	85.062	83.30 ^{b,f}
Pyridazine	$A + 2P + Y + 0.9937D$	40.500	40.50 ^{c,f}
Pyrimidine	$A + 2P + U + 0.9654D$	42.177	43.10 ^{c,f}
s-Triazine	$A + 3P + 3U + 0.9878D$	38.207	37.90 ^{c,f}
Pyrazine	$A + 2P + 0.9902D$	41.085	38.0 ^{c,f}
Quinoline	$A + P + B + N + 2.1638D$	84.613	86.62 ^{b,f}
Isoquinoline	$A + P + B + 2.1677D$	84.769	83.88 ^{d,f}
2-Methylquinoline	$A + P + B + 2N + 2.1723D$	96.986	99.86 ^{d,f}
4-Methylquinoline	$A + P + B + M + B + 2.1691D$	97.062	94.71 ^{d,f}
6-Methylquinoline	$A + P + B + M + N + 2.1597D$	96.956	97.43 ^{d,f}
7-Methylquinoline	$A + P + B + M + N + 2.1657D$	97.024	97.86 ^{d,f}
8-Methylquinoline	$A + P + B + M + N + 2.1585D$	96.942	96.57 ^{d,f}
2,4-Dimethylquinoline	$A + P + B + 2M + 2N + 2.1762D$	109.421	108.54 ^{d,f}
9-Methyl-3,4-benzoacridine	$A + P + 3B + M + 2N + 4.3672D$	168.610	161.1 ^e
5,9-Dimethyl-1,2-benzoacridine	$A + P + 3B + 2M + 2N + 4.3534D$	180.845	184.3 ^e
5,7,9-Trimethyl-3,4-benzoacridine	$A + P + 3B + 3M + 2N + 4.3529D$	193.230	183.7 ^e
5,7,9-Trimethyl-1,2-benzoacridine	$A + P + 3B + 3M + 2N + 4.3425D$	193.112	184.5 ^e
5,7,8,9-Tetramethyl-3,4-benzoacridine	$A + P + 3B + 4M + 2N + 4.3572D$	205.667	196.3 ^e
5,7,8,9-Tetramethyl-1,2-benzoacridine	$A + P + 3B + 4M + 2N + 4.3498D$	205.584	209.2 ^e
1,2,5,6-Dibenzoacridine	$A + P + 4B + 2N + 5.4152D$	191.474	186.4 ^e

^a C. M. French, *Trans. Faraday Soc.*, **47**, 1056 (1951). ^b S. A. Zaveri and M. G. Datar, *Indian J. Chem.*, **3**, 11 (1965). ^c J. D. Wilson, *J. Chem. Phys.*, **53**, 467 (1970). ^d R. Manzoni-Ansidei and G. M. Ghe, *Boll. Sci. Fac. Chim. Ind. Bologna*, **5**, 5 (1944-1947). ^e A. Pacault, *Ann. Chim. (Paris)*, **1**, 527 (1946). ^f These values were used to fit the parameters.

Table II. Diamagnetic Susceptibilities of the Group II Molecules (Cgs Units)

Molecule		χ_{theor}	χ_{exptl}
Pyrrole	$L + R$	47.4382	48.70 ^a
2-Methylpyrrole	$L + M + N + 0.7929R$	59.1010	60.10 ^a
2,4-Dimethylpyrrole	$L + 2M + N + 1.1245R$	72.4759	69.64 ^a
2,5-Dimethylpyrrole	$L + 2M + 2N + 1.0227R$	72.0616	71.92 ^a
2,3,5-Trimethylpyrrole	$L + 3M + 2N + 0.6824R$	83.4406	82.31 ^a
Indole	$L + B + N + 5.2056R$	83.2310	85.0 ^b
Carbazole	$L + 2B + 2N + 8.8382R$	117.3212	117.4 ^b

^a G. B. Bonino and R. Manzoni-Ansideri, *Chem. Ber.*, **76**, 553 (1943). ^b Footnote e Table I.

Table III. The Diamagnetic Susceptibilities of Some Polyacenes (Cgs Units)

Molecule		χ_{theor}	χ_{exptl}
Triphenylene	$A + 3B + 4.076^cD$	160.1207	156.6 ^{a,c}
Chrysene	$A + 3B + 4.440D$	164.2372	168.5 ^c
Ovalene	$A + 9B - 10C + 15.018^cD$	337.8118	353.8 ^{b,c}
Hexabenzocoronene	$A + 12B - 12C + 14.948^cD$	389.9687	346.0 ^{a,c}

^a H. Abamater and M. Kinoshita, *Bull. Chem. Soc. Jap.*, **32**, 773 (1958). ^b H. Abamater and Y. Matsurage, *ibid.*, **26**, 364 (1953). ^c These values were obtained through private communication with Yoshio Matsunaga, 1973.

We decided to express the π -electron susceptibilities of the group II molecules all in terms of the π -electron susceptibility of pyrrole, rather than express them in terms of the benzene π -electron susceptibility. Consequently, we define a set of parameters K_M' by means of

$$\chi_{\pi, M} = K_M' \chi_{\pi, \text{pyrr}} \quad (23)$$

These are the values of the parameters that we have listed in Table II for the group II molecules. Naturally there should be a connection between the π -electron susceptibilities of benzene and pyrrole, which may be derived from eq 22 and from the definitions of γ and

γ_0 , and we discuss this relation at the end of the paper. But we felt that we would get a more precise description of the diamagnetic susceptibilities if we allow for the possibility that the π -electron susceptibilities of five- and six-membered ring systems may be slightly different.

The π -electron susceptibilities in Tables I, II, and III were all easily obtained by means of the method that we described above. For those ring systems that contain a methyl group attached to the ring we took the Coulomb parameter for the carbon atom to which the methyl group is attached equal to $\alpha + 0.1\beta$, just as we did in a previous paper.³

Group I Molecules

In describing the susceptibilities of the group I molecules we make use of the parameters A , B , and D that we introduced previously² for describing the aromatic hydrocarbons. Here we represent the susceptibility of benzene as $A + D$, where D is the π -electron susceptibility and A is the sum of the σ -electron susceptibility and the susceptibility due to σ - π interactions. We mentioned already that in the aromatic hydrocarbons the two contributions may be combined because the π -electron density on every ring atom is equal to unity. This is not true for the heterocyclic aromatics, but the differences in π -electron density are quite small and they did not seem to have any effect on the susceptibility in the cases that we considered. Consequently, we decided to combine $\chi_{\Sigma\pi}$ with χ_{Σ} in the heterocyclic molecules in the same way as we did for the aromatics. We use the parameter values that we derived previously² for aromatics

$$A = 43.8286, B = 23.4107, D = 11.3003 \quad (24)$$

Even though we previously derived a value for the parameter that represents methyl substitution in a benzene ring,³ we varied this parameter anew in our present treatment because we feel that methyl substitution may have a different effect on a pyridine ring as opposed to a benzene ring. We use the symbol M to denote the change in susceptibility due to methyl substitution.

The other parameters that we have introduced in Table I are all new parameters and they must be determined by means of a least-squares fit with the experimental values. The parameter P is the difference between the σ -electron susceptibilities of pyridine and benzene; it represents the change in diamagnetic susceptibility upon replacing a C-H group in a benzene ring by a nitrogen atom. Hence, the σ -electron susceptibility of pyridine is equal to $A + P$. If we introduce a second nitrogen in the ring in the para position, as in pyrazine, the σ -electron susceptibility becomes $A + 2P$. If the second nitrogen is in the meta position, as in pyrimidine, we must consider also the extra interactions between the adjacent C-N bonds; this is represented by a parameter U and the σ -electron susceptibility of pyrimidine is given by $A + 2P + U$. Similarly, if the two nitrogen atoms are ortho the extra interactions are represented by a parameter Y and the σ -electron susceptibility of pyridazine is given by $A + 2P + Y$.

Similar considerations apply to α -, β - and γ -picoline. In γ -picoline, where the N and the CH_3 group are para, the σ -electron susceptibility is $A + P + M$. In α -picoline, where the two groups are ortho, there is an additional interaction between them which we represent by a parameter N , so that the susceptibility is given by $A + P + M + N$. In β -picoline, where the two groups are meta, the σ -electron susceptibility is the same as in the para compound.

It should be noted that in fitting the parameters P , M , N , U , and Y we did not include the set of susceptibility values of footnote *e* in Table I. We have no reason to suspect the accuracy of these measurements, but these values do not seem to agree too well with our theoretical values and we decided that they should not be used for determining the parameters. Even so, the largest deviation between the experimental and theo-

retical values for the molecules in this group is only 5% (for 5,7,9-trimethyl-3,4-benzoacridine). On the whole, the agreement between the experimental values and our theoretical results may be considered satisfactory. The parameter values which we found and which we used to derive the values of Table I are

$$\begin{aligned} P &= -6.9664 \\ M &= 12.3899 \\ N &= -0.1120 \\ Y &= -0.6252 \\ U &= 1.3719 \end{aligned} \quad (25)$$

It is interesting to note that we predict a small negative value for the parameter N . It may be verified from Table I that this agrees with the experimental values because the susceptibility of α -picoline is slightly smaller than the values for the corresponding β and γ compounds. In the lutidine compounds this trend is less noticeable, but our predictions are still consistent with experiments. The largest discrepancy occurs for pyrazine; we cannot offer an explanation for this.

Group II Molecules

The group II molecules that we have listed in Table II are all derivatives of pyrrole. Since pyrrole is a five-membered ring system, which is quite different from the six-membered pyridine ring, we decided to represent its susceptibility by means of two new parameters. We denote the σ -electron susceptibility of the pyrrole ring by L and its π -electron susceptibility by R ; the susceptibility of pyrrole is then given by $L + R$. We evaluated the π -electron susceptibilities of both pyrrole and the other molecules and we expressed the π -electron susceptibilities of all of them in terms of R , according to eq 23. Methyl substitution is again represented by the same parameters M and N as we defined in the previous section, and the addition of another benzene ring, as in indole, is represented by a parameter B .

We must then determine the values of the two new parameters L and R and we find that

$$L = 44.4675 \text{ and } R = 2.97077 \quad (26)$$

The corresponding theoretical susceptibility values are listed in Table II. The overall agreement with the experiments is satisfactory, but it is disappointing that our theory does not make an accurate prediction about the difference in susceptibility between 2,4- and 2,5-dimethylpyrrole.

Polyacenes

In a previous calculation on polyacenes² we obtained very poor agreement for the chrysene molecule. It was pointed out to us later¹⁰ that this discrepancy was due to an error in the value of the parameter K for the π -electron susceptibility that was reported in the literature.⁷ We recalculated the π -electron susceptibility for chrysene and we found that the K value for this molecule is indeed different from the reported value. In Table III we list our calculations for chrysene and for some additional aromatic hydrocarbons that we have calculated, using the values of the parameters A , B , C , and D

(10) Y. Matsunaga, private communication.

that we derived previously. It may be seen that the agreement is very poor in the case of hexabenzocoronene; 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 π -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 γ and γ_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 π electrons in five-membered or six-membered ring systems as far as the diamagnetic susceptibility is concerned.

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Molecular Orbital Calculation of the Electronic Structure of Borane Carbonyl¹

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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).