

# $\pi$ -Molecular Complexes: A Modified CNDO Study of the Benzene-Borazine System\*

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The standard CNDO/2 method is shown to be unable to produce meaningful potential curves for  $\pi$ - $\pi$ -type molecular complexes. A modification of this method in which pairs of atoms associated with the same molecule and with different molecules are differentiated leads to reduced intermolecular bonding and provides reasonable stabilization energies and intermolecular separations. Calculations based on this modified method indicate that benzene-borazine and borazine-borazine complexes in which the molecules are symmetrically disposed in parallel planes can exist in the ground state. The stabilization energies are calculated to be in the range 2–5 kcal/mole for benzene-borazine and 5–18 kcal/mole for borazine-borazine, with interplanar separations near 3 Å in both cases.

*Key words:* Molecular complexes – Benzene – Borazine

## 1. Introduction

Molecular complexes [1] have been examined by a variety of theoretical techniques in recent years. The approaches used to calculate properties of complexes such as geometry, interaction energy, spectra, and the extent of charge transfer have been semiempirical and include modified extended Hückel theory [2], SCF–MO–CI treatment [3], SC–LCMO treatment [4] and the CNDO and INDO methods [5–8]. These efforts have met with varying degrees of success. For  $\pi$ -type molecular complexes, the  $\pi$ -only approximation of extended Hückel theory provides reasonable relative geometries at constant interplanar intermolecular separations, but it fails to indicate absolute binding [2]. The SCF–MO–CI and SC–LCMO methods [3, 4] reproduce spectral transitions satisfactorily, and the latter method qualitatively predicts the correct order of stabilities for  $\pi$ -complexes.

The CNDO and INDO treatments have been applied to both  $n$ - $\sigma$ - and  $\pi$ - $\pi$ -type complexes. For the complexes of ammonia with fluorine and chlorine, entirely reasonable interaction energies (10.4 and 21.8 kcal/mole, respectively) have been calculated at rather short equilibrium intermolecular separations [7]. Unfortunately, these calculations also predict substantial interactions between

\* Dedicated to Professor Dr. H. Hartmann on the Occasion of his 60th Birthday.

ammonia and hydrogen ( $H_2$ ) and ammonia and nitrogen ( $N_2$ ) for which there is no experimental evidence. More recently, the complexes of the cage-structured amines 1-azabicyclo(2,2,2)octane (ABCO) and 1,4-diazabicyclo(2,2,2)octane (DABCO) [9] with chlorine have been studied by the CNDO method [8]. The interaction energies and equilibrium separations for these systems compare favorably with the experimental results for amine-iodine complexes. Used in conjunction with second order perturbation theory, the CNDO procedure provides good agreement between the experimental heats of formation and the interaction energies calculated at an arbitrarily chosen interplanar separation for the  $\pi$ - $\pi$ -complexes between tetracyanoethylene (TCNE) and aromatic hydrocarbons [5]. The situation is not as satisfactory when the CNDO treatment is applied to the TCNE-benzene complex in the form of a single molecule [6]. In this case, a stabilization energy of ca.  $-125$  kcal/mole is calculated at an intermolecular separation of  $1.75$  Å. The experimental heat of formation for this complex is ca.  $-3.5$  kcal/mole [10, 11] and, on the basis of crystal data, an interplanar separation of ca.  $3.3$  Å is expected.

The point of departure for the present study was the observation, made in the course of an investigation of the photochemistry of benzene-borazine mixtures at  $2580$  Å by Young *et al.* [12], that borazine quenches the triplet state of benzene. The implication of this result, which is that borazine has a low-lying triplet state of  $4.8$  eV, is in contradiction with the results of theoretical investigations. Thus, *ab initio* calculations place the lowest triplet state of borazine at  $6.46$  eV [13], and CNDO-CI calculations with parameter variation place it no lower than  $5.9$  eV [12, 14]. The discrepancy between the apparent experimental and calculated triplet energies indicate that a mechanism different from a simple transfer of triplet energy from benzene to borazine may be operative. Unger's suggestion [15] that a benzene-borazine molecular complex may intervene in the quenching of triplet state benzene led us to undertake a theoretical investigation of this system in the ground state.

Despite its apparent limitations in intermolecular calculations, the CNDO method was chosen for this study on the basis of our belief that at least an all-valence-electron self-consistent field treatment is necessary to produce meaningful results for molecular complexes. Clearly, without configuration interaction, this SCF method will not take dispersion force interactions into account. A detailed analysis of the benzene-benzene system led us to a modification of the standard CNDO method which provides reasonable interaction energies and geometries for  $\pi$ -type molecular complexes.

## 2. Results and Discussion

The systems investigated were benzene-benzene (BE-BE), borazine-borazine (BO-BO), benzene-TCNE (BE-TC), and benzene-borazine (BE-BO), for which the energies were calculated as a function of the interplanar intermolecular distance  $R$  (Fig. 1). The pertinent bond distances for these molecules are given in Table 1 and all bond angles were taken to be  $120^\circ$ ; these distances and angles were kept constant in all calculations. For the initial calculations, the CNDO/2

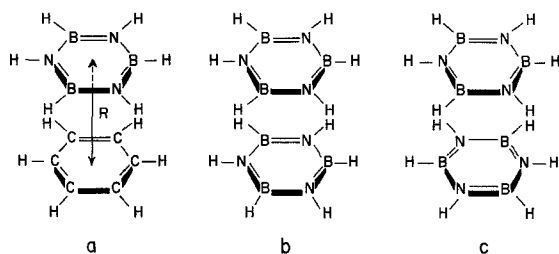


Fig. 1a-c. Structures of the systems studied. In each case the molecules are symmetrically disposed in parallel planes, with interplanar separation  $R$ . a Benzene-Borazine, BE-BO; b borazine-borazine, BO-BO (B/B); c borazine-borazine, BO-BO (B/N)

Table 1. Bond distances for benzene, borazine, and TCNE

Benzene	$R$ (Å)	Borazine	$R$ (Å)	TCNE <sup>a</sup>	$R$ (Å)
C-C	1.397	B-N	1.44	C=C	1.32
C-H	1.084	B-H	1.19	C-C	1.45
		N-H	0.995	C≡N	1.15

<sup>a</sup> Ref. [16].

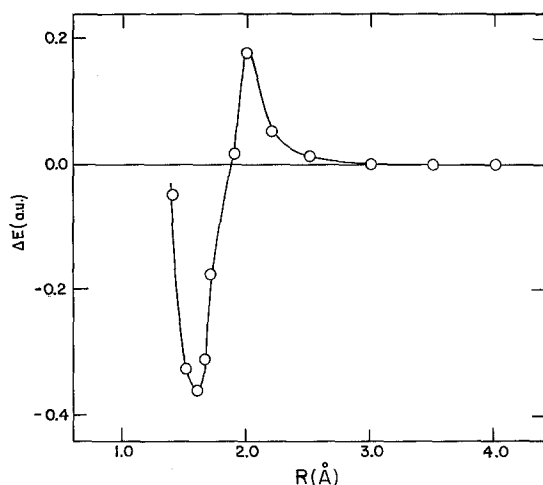


Fig. 2.  $\Delta E$  (a.u.) as a function of the interplanar separation  $R$  (Å) for benzene-borazine by standard CNDO/2 method

method was used without modification of the parameters developed by Pople and Segal [17, 18].

The standard CNDO/2 results for the BE-BE system are shown in Fig. 2. In this and in subsequent figures,  $\Delta E = E(R) - E(R = \infty)$ , the energy of the system relative to that of the two separated molecules. As  $R$  decreases from infinity, the interaction at first becomes repulsive as expected. However, the energy has a sharp maximum at 2 Å and then decreases rapidly to a minimum at 1.6 Å

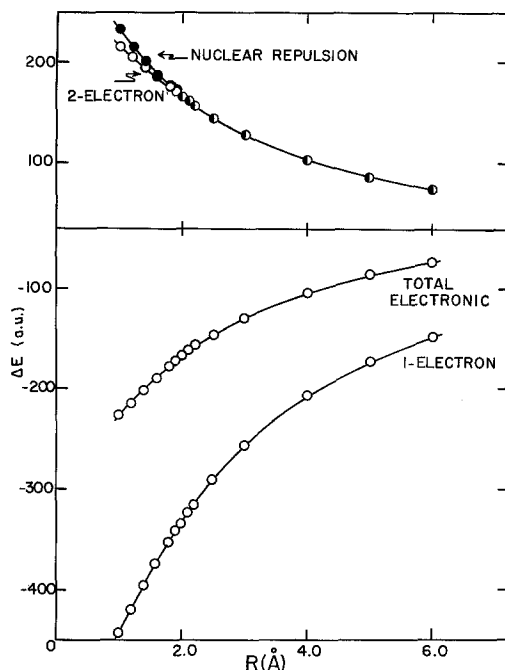


Fig. 3. Components of  $\Delta E$  (total energy) in a.u. as a function of the interplanar separation  $R(\text{\AA})$  for benzene-benzene by standard CNDO/2 method

which corresponds to a stabilization of the system by 226 kcal/mole. That this behavior is due to the crossing, in the vicinity of 2  $\text{\AA}$ , of curves belonging to different electron configurations was borne out by closer examination of the results. A breakdown of  $\Delta E$  (total energy) into its nuclear, 1-electron, 2-electron, and total electronic energy components reveals no substantial irregularities in the 1–3  $\text{\AA}$  region (Fig. 3); the magnitude of these energy increments will, of course, obscure non-regular behavior amounting to fractions of an a.u. On the other hand, analysis of the eigenvectors and corresponding eigenvalues as a function of intermolecular separation clearly shows crossing between occupied and virtual orbitals below 2  $\text{\AA}$ . As shown in Fig. 4 for the highest occupied and lower unoccupied orbitals, the behavior of the system is quite complex. The occupied  $e_{1g}$  and virtual  $e_{2g}$  orbitals cross over near 2  $\text{\AA}$  while, at the same time, apparent discontinuities become evident for the  $a_{2u}$  (occupied) and  $b_{1u}$  (virtual) orbitals. These latter orbitals then cross over near the energy minimum at 1.6  $\text{\AA}$ . In addition, there are numerous level crossings within the unoccupied and occupied manifolds between 1  $\text{\AA}$  and 3  $\text{\AA}$ .

If the results of Fig. 2 are taken at face value, they indicate that a covalently-bonded benzene dimer of substantial stability exists. Its formation would be symmetry-forbidden from the point of view of the Woodward-Hoffmann rules [19]. However, we believe that the deep minimum of Fig. 2 is without physical significance for the following reasons. 1. There is no experimental evidence for the existence of a strongly-bonded benzene dimer; 2. even if a dimer of benzene exists, the stabilization energy of >200 kcal/mole calculated by the CNDO/2

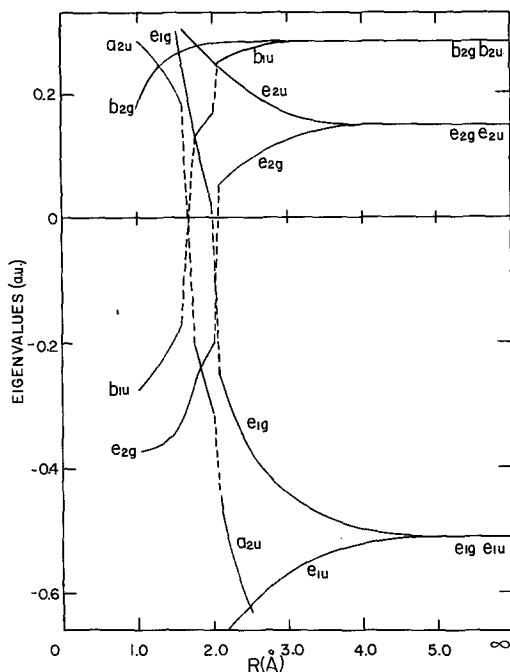
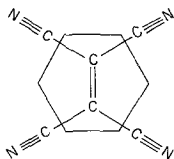


Fig. 4. Orbital energies (a.u.) as a function of the interplanar separation  $R(\text{\AA})$  for benzene-benzene by standard CNDO/2 method

method is surely much too large, particularly in view of the lack of accommodation of the intramolecular bond distances and angles (i.e., the calculated minimum energy structure is highly strained); 3. extended Hückel theory calculations reveal no stable dimer formation at any separation [20]. The excessive, unphysical binding encountered in this calculation is considered to be due to shortcomings of the CNDO method, which are possibly related to a deficiency in the basis set, such as that observed in minimal basis SCF calculations, and/or to the neglect of overlap.

The results of standard CNDO/2 calculations for the benzene-borazine, borazine-borazine, and benzene-TCNE systems are displayed in Fig. 5; the benzene-benzene case is included for comparison purposes. Note that for borazine-borazine, two extreme structures are considered, one (B/B) in which the boron and nitrogen atoms of one molecule are aligned with those of the second molecule, and the other (B/N) in which these atoms are staggered (Fig. 1). For benzene-TCNE, the TCNE molecule is symmetrically located above the benzene molecule as shown below.



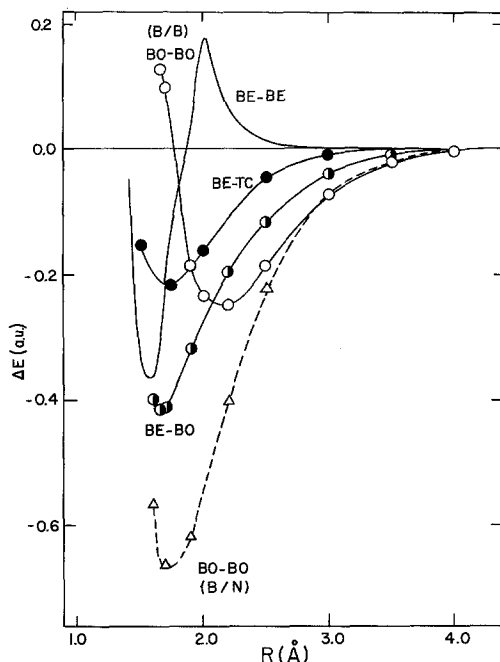


Fig. 5.  $\Delta E$  (a.u.) as a function of the interplanar separation  $R$  (Å) for benzene-benzene (BE-BE), benzene-TCNE (BE-TC), benzene-borazine (BE-BO), and borazine-borazine [BO-BO(B/B) and BO-BO(B/N)] by standard CNDO/2 method

Substantial binding is calculated for all these cases, which ranges from  $-143$  kcal/mole for benzene-TCNE (in agreement with Chesnut and Wormer's results [6]) to  $-415$  kcal/mole for borazine-borazine (B/N). The equilibrium separations ( $< 2.2$  Å) are shorter than the pertinent sums of van der Waals' radii. Significantly, repulsive interaction is encountered only for the benzene-benzene system, which also appears to be the only system exhibiting level crossings between the occupied and virtual orbitals. The absence of repulsive interactions and the similarity to the benzene-TCNE system for which complex formation has been experimentally demonstrated is taken to be a qualitative indication for the existence of benzene-borazine and borazine-borazine complexes. Attempts to obtain reasonable binding energies for these systems by using an averaging procedure within the unmodified CNDO framework to correct for excessive, non-physical binding were not successful.

A simple empirical approach to the reduction of intermolecular binding is to modify the off-diagonal matrix elements of the core Hamiltonian for all pairs of atoms belonging to different molecules, using experimental results to scale the calculations. In particular, for the CNDO scheme, the matrix elements in question are given as

$$H_{\mu\nu} = 0.5 C(\beta_A^\circ + \beta_B^\circ) S_{\mu\nu} \quad (1)$$

where  $S_{\mu\nu}$  is the overlap integral for orbitals  $\mu$  and  $\nu$  centered on atoms A and B, respectively,  $\beta_A^\circ$  and  $\beta_B^\circ$  are empirical bonding parameters, and  $C = 1$ . In the reduced

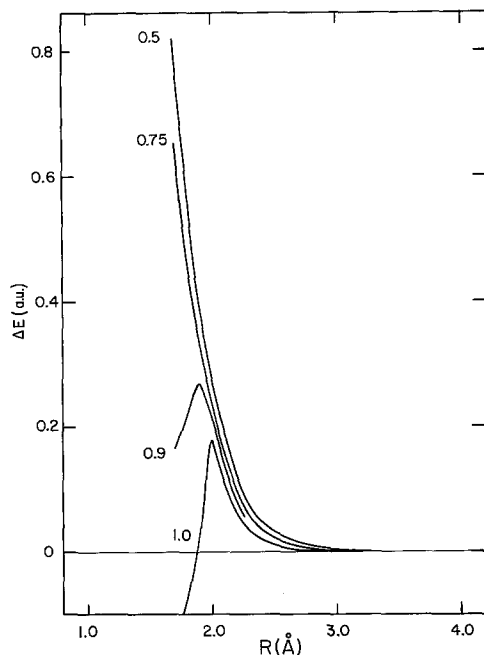


Fig. 6. Variation of  $\Delta E$  (a.u.) with the interplanar separation  $R(\text{\AA})$  for benzene-benzene. The numbers are the values of  $C$  in Eq. 1

bonding CNDO method, we distinguish between atoms A and B associated with molecules M and N such that  $C = 1$  if A and B both belong to M or to N, and  $C < 1$  if A belongs to M and B to N, or *vice versa*. The application of this modification to the benzene-benzene system is illustrated in Fig. 6. We find that the distance at which the energy is a maximum is shifted to smaller values as  $C$  is decreased; in fact, at any given distance  $R$ , decreasing  $C$  causes an increase in energy. The effect of varying  $C$  is greatest at short distances, and the modification is clearly capable of correcting the benzene-benzene potential in the desired manner.

For benzene-TCNE, we find that reasonable binding energies ( $\sim 1$  kcal/mole) are calculated with  $C$  values near 0.6 (Fig. 7). Similar results are obtained with the benzene-borazine and borazine-borazine (B/B) systems (Figs. 8 and 9), for which the minima disappear and the potentials become repulsive with  $C < 0.3$ . For these systems, the effect of decreasing  $C$  is to decrease the depth of the minimum, which is concomitantly shifted to larger  $R$  values.

The calculations with  $C = 0.5$  and  $C = 0.6$  are summarized in Figs. 10 and 11 and in Table 2. We note that with  $C = 0.5$  there is no binding predicted for the benzene-TCNE system while stabilization energies of ca. 5 kcal/mole are found for the benzene-borazine and borazine-borazine systems. Since different orbitals are involved in these combinations, it is not surprising that no single value of the reduction parameter  $C$  will accommodate them all. In any case, we infer from the calculations that stable benzene-borazine and borazine-borazine ground state

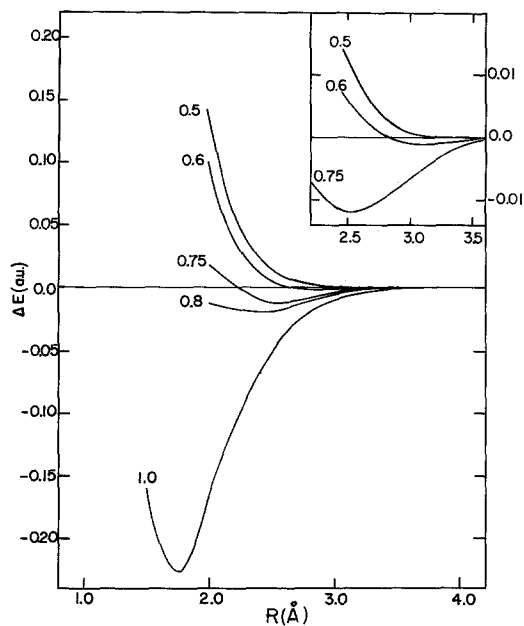


Fig. 7. Variation of  $\Delta E$  (a.u.) with the interplanar separation  $R$  (Å) for benzene-TCNE. Each curve is labelled with the value of  $C$  [Eq. (1)]

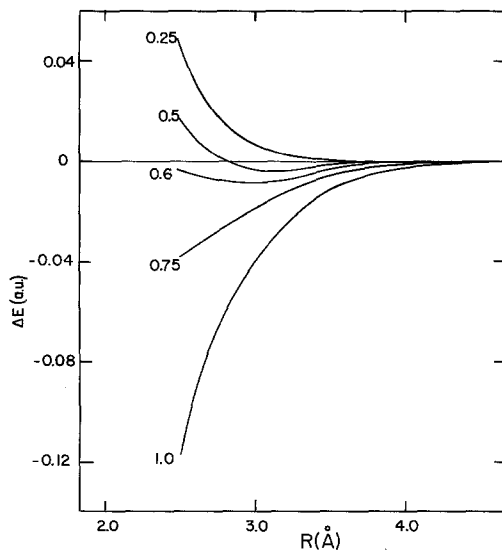


Fig. 8. Variation of  $\Delta E$  (a.u.) with the interplanar separation  $R$  (Å) for benzene-borazine. Each curve is labelled with the value of  $C$  [Eq. (1)]

complexes exist with intermolecular separations of about  $3 \text{ \AA}$ . No attempt was made to optimize the reduction parameter  $C$ , so that a greater stabilization energy obtained for the borazine-borazine system than for the benzene-borazine system may not be significant.



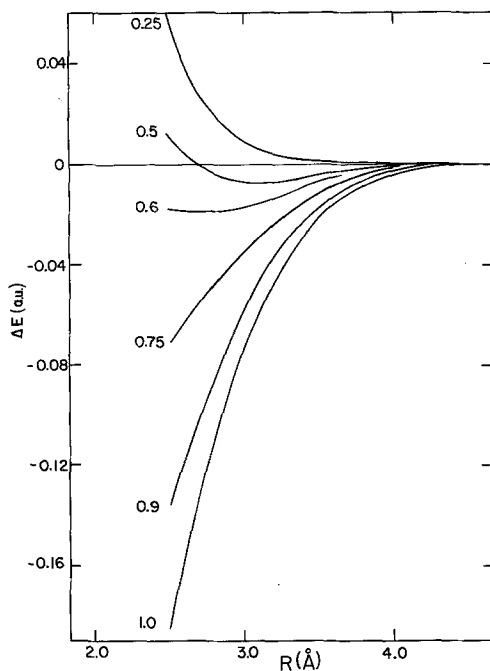


Fig. 9. Variation of  $\Delta E$  (a.u.) with the interplanar separation  $R$  (Å) for borazine-borazine (B/B). Each curve is labelled with the value of  $C$  [Eq. (1)]

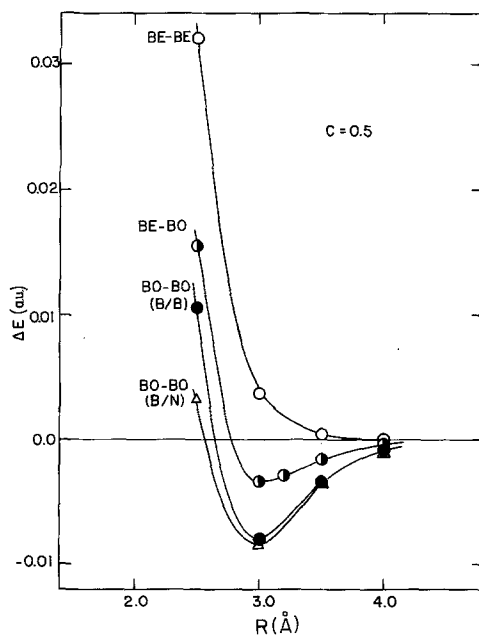


Fig. 10. Potential curves for benzene-benzene (BE-BE), benzene-borazine (BE-BO), and borazine-borazine [BO-BO (B/B) and BO-BO (B/N)] with  $C = 0.5$

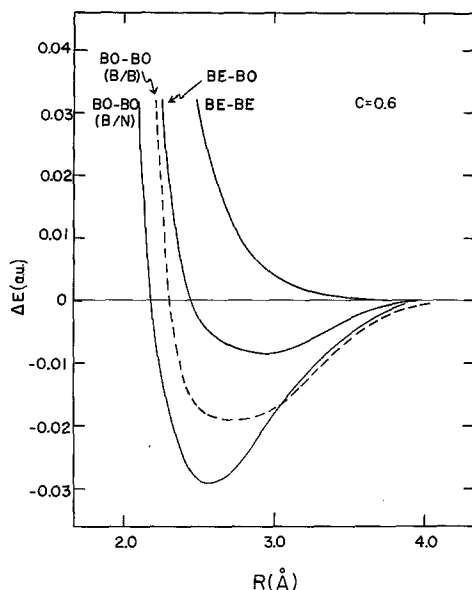


Fig. 11. Potential curves for benzene-benzene (BE-BE), benzene-borazine (BE-BO), and borazine-borazine [BO-BO (B/B) and BO-BO (B/N)] with  $C = 0.6$

Table 2. Stabilization energies and equilibrium separations for benzene-borazine, borazine-borazine, and benzene-TCNE complexes

System	$C = 1$		$C = 0.6$		$C = 0.5$	
	$-\Delta E^a$	$R_{\min}(\text{\AA})$	$-\Delta E^a$	$R_{\min}(\text{\AA})$	$-\Delta E^a$	$R_{\min}(\text{\AA})$
Benzene-TCNE <sup>c</sup>	143	1.75	0.52 <sup>e</sup>	3.1	<sup>b</sup>	
Benzene-Borazine	261	1.65	5.3	3.0	2.0	3.0
Borazine-Borazine (B/B)	157	2.2	11.2 <sup>f</sup>	2.75	4.9	3.0
Borazine-Borazine (B/N)	415 <sup>d</sup>	1.75	18.2 <sup>f</sup>	2.6	5.2	3.0

<sup>a</sup> In kcal/mole.

<sup>b</sup> Repulsive, no minimum.

<sup>c</sup> Experimental enthalpy ca.  $-3.5$  kcal/mole.

<sup>d</sup> Calculated at  $1.7 \text{\AA}$ .

<sup>e</sup> Calculated at  $3.0 \text{\AA}$ .

<sup>f</sup> Calculated at  $2.5 \text{\AA}$ .

The reduced bonding CNDO method provides more realistic estimates of the extent of charge transfer for  $\pi$ - $\pi$  complexes than does the standard CNDO/2 treatment. Thus, for benzene-borazine the charge transfer in units of electronic charge is 0.207 at  $R = 1.65 \text{\AA}$  for  $C = 1.0$  (standard CNDO/2) and 0.013 at  $R = 3.0 \text{\AA}$  for  $C = 0.5$ , with the borazine molecule negatively charged. For benzene-TCNE, with TCNE negative, the charge transfer values are 0.39 at  $R = 1.75 \text{\AA}$  for  $C = 1.0$  and 0.005 at  $3.0 \text{\AA}$  for  $C = 0.6$ , and the standard CNDO/2 method leads to substantially larger than expected dipole moments. While no net intermolecular

charge transfer occurs in the borazine-borazine system, the calculations indicate significant charge redistribution in the complex relative to the isolated borazine molecule.

### 3. Conclusions

It has been shown that the standard CNDO/2 method is unable to produce meaningful potential energy curves for  $\pi$ - $\pi$ -type molecular complexes. A reduced bonding modification of this method in which a distinction is made between pairs of atoms associated with the same molecule and with different molecules does yield reasonable intermolecular separations and stabilization energies. Calculations based on this modified method lead us to conclude that stable benzene-borazine and borazine-borazine complexes exist.

The inadequacy of the standard CNDO/2 treatment for  $\pi$ - $\pi$ -type complexes is apparently related to an overestimation of attractive  $p\sigma$ -interactions between the  $\pi$ -systems. This is perhaps not surprising since the basic zero-differential-overlap approximation of the CNDO method leads to invariance requirements which are satisfied by effectively suppressing the influence of the shape of the basis orbitals [18]. Thus, Coulomb integrals are uniformly computed with  $s$ -orbitals and overlap enters only as a scaling factor for the off-diagonal core Hamiltonian matrix elements [Eq. (1)]. The parametrization which is designed to partially compensate for these approximations in single-molecule calculations is evidently inadequate for particular (e.g.,  $p\sigma$ ) interactions involving several molecules. From this point of view, the reduced bonding modification described in the previous section nearly provides a more realistic balance between repulsive and attractive interactions for these cases. The usefulness of this approach lies mainly in its simplicity. Clearly, a systematic analysis of how the various approximations of the CNDO approach affect intermolecular terms must be carried out to point the way to a less empirical modification of the method.

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### References

1. For a general review, cf. Mulliken, R.S., Person, W.B.: Molecular complexes. New York: Wiley 1969; Foster, R.: Organic charge transfer complexes. London: Academic Press 1969
2. Chesnut, D.B., Moseley, R.W.: Theoret. Chim. Acta (Berl.) **13**, 230 (1969)
3. Ohata, T., Kuroda, H., Kuni, T.L.: Theoret. Chim. Acta (Berl.) **19**, 167 (1970)
4. Flurry, R.L., Jr.: Theoret. Chim. Acta **23**, 1 (1971), and earlier papers cited therein
5. Herndon, W.C., Feuer, J.: J. Am. Chem. Soc. **90**, 5914 (1968)
6. Chesnut, D.B., Wormer, P.E.S.: Theoret. Chim. Acta (Berl.) **20**, 250 (1971)
7. Carreira, L.A., Person, W.B.: J. Am. Chem. Soc. **94**, 1485 (1972)
8. Karlsson, G., Weiss, K.: to be published
9. Halpern, A.M., Roebber, J.L., Weiss, K.: J. Chem. Phys. **49**, 1348 (1968)
10. Briegleb, G., Czekalla, J., Reuss, G.: Z. Physik. Chem. (Frankfurt) **30**, 334 (1961)
11. Emslie, P.H., Foster, R.: Tetrahedron **21**, 2851 (1965)
12. Young, W.F., Grein, F., Passmore, J., Unger, I.: Can. J. Chem. **49**, 233 (1971)
13. Peyerimhoff, S.D., Buenker, R.J.: Theoret. Chim. Acta (Berl.) **19**, 1 (1970)

14. Dejadins, C. D., Grein, F., MacBeath, M. E., Passmore, J., Unger, I.: *J. Photochem.* **1**, 153 (1972/73)
15. Private communication, Professor I. Unger
16. Bekoe, D. A., Trueblood, K. N.: *Z. Kristallogr.* **113**, 1 (1960)
17. Pople, J. A., Segal, G. A.: *J. Chem. Phys.* **44**, 3289 (1966)
18. Pople, J. A., Beveridge, D. L.: *Approximate molecular orbital theory*. New York: McGraw-Hill 1970
19. Woodward, R. B., Hoffmann, R.: *The conservation of orbital symmetry*. Weinheim: Verlag Chemie 1970
20. Chesnut, D. B., Fritchie, C. J., Simmons, H. E.: *J. Chem. Phys.* **42**, 1127 (1965)

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