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Commentationes

Molecular Orbital Theory of Electron Donor-Acceptor Complexes

IV. A Self-Consistent Linear Combination of Molecular Orbitals Approximation

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The linear combination of molecular orbitals (LCMO) approximation of electron donor-acceptor (EDA) interactions [1] has been extended to a polyelectron treatment. This has been implemented by a self-consistent field formalism. Calculations have been performed within the π-electron approximation on a number of EDA complexes. For comparison, polyconfiguration calculations based on Mulliken's dative bond approximation have also been made using the same parameterization. It was found that for highly symmetrical systems such as benzene-TCNE the traditional approach of one orbital from the donor and one from the acceptor was sufficient to reproduce spectral transitions and to qualitatively predict orders of stability. For unsymmetrical systems, such as benzene-trinitrofluorenone, more than one orbital from the donor and acceptor are important. The SC LCMO treatment can handle these cases as well as cases involving multiple complexes in a straightforward manner.

Die Näherung der Linearkombination von Molekülorbitalen (LCMO) für die Elektronendonator-Acceptor-Wechselwirkung (EDA-Wechselwirkung) [1] wurde zu einem Mehrelektronenverfahren erweitert. Dies wurde durch einen SCF-Formalismus erreicht. Innerhalb der π-Elektronen-Näherung wurden Rechnungen an einer Reihe von EDA-Komplexen durchgeführt. Zum Vergleich wurde Mullikens Näherung der dativen Bindung mit derselben Parametrisierung angewendet. Es wurde gefunden, daß bei hochsymmetrischen Systemen wie Benzol-Tetracyanoäthylen die traditionelle Darstellung mit einem Orbital vom Donator und einem vom Acceptor genügt, um die spektralen Übergänge zu reproduzieren und die Reihenfolge der Stabilität qualitativ vorherzusagen. Für unsymmetrische Systeme wie Benzol-Trinitrofluorenon ist mehr als je ein Orbital von Donator und Acceptor von Bedeutung. Diese Fälle, sowie Fälle mit mehrfacher Komplexbildung können mit den SC-LCMO-Verfahren vorteilhaft behandelt werden.

Extension à un traitement polyélectronique de l'approximation LCMO (linear combination of molecular orbitals) pour les interactions de type donneur-accepteur d'électrons (EDA) [1]. Un formalisme de champ self-consistant est greffé sur ce traitement. Un certain nombre de complexes EDA ont été calculés dans l'approximation des électrons π. A titre de comparaison, des calculs polyconfigurationnels basés sur l'approximation de la liaison dative de Mulliken, ont été réalisés en utilisant la même paramétrisation. On a trouvé que pour les systèmes fortement symétriques comme benzène-TCNE l'approche traditionnelle utilisant une orbitale du donneur et une orbitale de l'accepteur est suffisante pour reproduire les transitions spectrales et pour prédire qualitativement les ordres de stabilité. Pour des systèmes non symétriques, comme benzène-trinitrofluorénone, il est important d'introduire plus d'une orbitale sur le donneur et l'accepteur. Le traitement SC LCMO peut prendre directement en charge ces cas tout comme ceux impliquant des complexes multiples.

Introduction

In the first three papers of this series (hereafter referred to in order as I, II and III) [1, 2, 3] the linear combination of molecular orbitals (LCMO) treatment of electron-donor-acceptor (EDA) interactions was developed with a one-electron approximation, in such a manner as to incorporate the maximum amount of empirical data into a theoretical description of such interactions. The ultimate result was to relate the stabilities of ground state complexes to the ionization potential of the donor, the electron affinity of the acceptor, the "charge-transfer" spectral transition and the "incipient charge" which would result if an electron were completely transferred from the donor to the acceptor. All of these quantities, except the stabilization due to the incipient charge, were either experimental values or estimates of experimental values. The incipient charge stabilization was estimated from a point charge approximation. The model successfully reproduced the experimental results for a variety of complexes with neutral [1] or charged [2] donors and acceptors. It does, however, rely heavily on experimental data, and, consequently, cannot be readily applied to systems for which the experimental data is not available.

In a recent paper, Ohata, Kuroda and Kunii presented a treatment of EDA complexes based on a semiempirical SCF–MO–CI method [4]. In their treatment the complex is treated as a single conjugated system of π-electrons. All of the π-type atomic orbitals are included in their basis set. The spectra, which were calculated by standard configuration interaction techniques, were in good agreement with experiment. No discussion of the stabilities of the complexes was given.

The equations of our one-electron treatment were justified in the appendix of II on the basis of both a polyelectron single-configuration molecular orbital treatment and a two-configuration valence bond treatment. The present work presents the results of direct calculations within a self-consistent-field poly-electron molecular orbital formalism, again using the molecular orbitals of the isolated donor and acceptor as the starting basis functions. This starting basis set is further restricted to include only a few of the molecular orbitals of the donor and acceptor. To establish a reference for comparison of the results, polyconfiguration calculations based on the Mulliken description of EDA complexes [5] were also performed.

These calculations employ no experimental data from the complexes other than the geometry. The π-electron calculations were performed within the context of the Pariser-Parr-Pople [6, 7] approximations. These have been shown by many workers to give reasonable spectral results for many diverse systems. Any other suitable computational scheme should be equally applicable, however. Results are presented for several electron-donor-acceptor complexes. The calculations presented here are to test the feasibility of the SC LCMO method, rather than to attempt to give accurate reproductions of experimental data.

For simple 1 : 1 complexes the SC LCMO method offers possible advantages for workers with limited computational facilities. The largest basis set involved at any stage of the calculations is that of the larger of the constituents. Thus, systems which could not be handled by single system methods such as those of Ref. [4] can be treated. Its greatest promise, however, lies in the ability to treat multicomponent systems, where the complete basis set would tax the limits of even the largest computers, and in the ability to treat many different relative orientations of the constituents with a minimum of computational time.

Method

a) SC LCMO *Formalism*

The most convenient method for performing calculations on a polyelectron system is the Hartree-Fock self-consistent-field (SCF) method. The method approximates the many-electron wave function by an antisymmetrized product of one-electron functions. These one-electron functions are obtained by solving for the motion of one individual electron in an averaged field of the other electrons. This field is made self-consistent by an iterative process. When the wave function is to be approximated by a linear combination of starting basis functions, the basic equation to be solved is the matrix equation

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{E} \tag{1}$$

where $\boldsymbol{E}$ is the diagonal eigenvalue matrix, $\boldsymbol{C}$ the matrix of linear coefficients relating the one-electron solutions to the starting basis set, $\boldsymbol{S}$ is the overlap matrix and $\boldsymbol{F}$ is the Fock matrix. In terms of the starting basis set of χ_μ's the individual $\boldsymbol{S}$ and $\boldsymbol{F}$ matrix elements are [8]

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \tag{2}$$

$$F_{\mu\nu} = \langle \chi_\mu | \hat{F} | \chi_\nu \rangle \tag{3}$$

where $\hat{F}$ is the Fock operator. If the starting basis functions are assumed to be orthonormal (the zero differential overlap, or ZDO approximation) the overlap matrix becomes the unit matrix and Eq. (1) becomes

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{C}\boldsymbol{E}\,. \tag{1a}$$

Within the context of the ZDO approximation (which we shall use for the molecular orbital basis set in the LCMO treatment of the complexes as well as for the atomic orbital basis set from which the molecular orbitals are constructed) the elements of the $\boldsymbol{F}$ matrix for a closed shell system [8] are

$$F_{\nu\nu} = \langle \chi_\nu | \hat{f} | \chi_\nu \rangle + 2 \sum_i^{\text{occ.}} \sum_\mu C_{i\mu}^2 \gamma_{\nu\mu} + \sum_i^{\text{occ.}} C_{i\nu}^2 \gamma_{\nu\nu} \tag{4}$$

$$F_{\nu\mu} = \langle \chi_\nu | \hat{f} | \chi_\mu \rangle - \sum_i^{\text{occ.}} C_{i\nu} C_{i\mu} \gamma_{\nu\mu} \tag{5}$$

where $\hat{f}$ is that portion of $\hat{F}$ which is a function of the coordinates of one electron only, $\gamma_{\nu\mu}$ is the two-electron repulsion integral representing the interaction of an electron in the ν^{th} basis function with one in the μ^{th} function. The indices ν and μ refer to members of the starting basis set while i refers to the orbitals which are solutions of Eq. (1) or (1a). The summation is over only the occupied orbitals. If not all of the electrons in a system are to be considered explicitly, the operator $\hat{f}$ becomes an "effective core" operator which includes the interactions of the electrons being considered with the nuclei and with the electrons which are not explicitly considered. (For example, within the π-electron approximation this includes all of the $\sigma-\pi$ interactions [9].) In the present case, the effective core for the complex will include some of the electrons which were considered explicitly in constructing the molecular orbitals of the individual components. The effective core integrals will have to be defined in such a manner as to account for this.

Let us adapt, as an indexing convention, the Greek indices $\mu, \nu, -$ for the atomic basis functions, the lower case indices $i, j, -$ for the molecular orbitals and the capital indices $A, B, -$ for the orbitals of the entire complex. Subscripts will be used to label matrix elements and superscripts to label the matrices or vectors. Vectors will be written in lower case and matrices in upper case.

One-electron integrals over atomic orbitals may be related to integrals over molecular orbitals by the relationship

$$M_{ij} = \sum_{\mu} \sum_{\nu} c_{i\mu}^{*} c_{j\nu} M_{\mu\nu} \tag{6}$$

where $\boldsymbol{M}^{\mu\nu}$ is the matrix of any general one-electron operator over the atomic basis set. For two-electron integrals, the relationship is

$$R_{ik}^{jl} = \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} c_{i\mu}^{*} c_{j\nu}^{*} c_{k\lambda} c_{1\sigma} R_{\mu\lambda}^{\nu\sigma} \tag{7}$$

where $R_{\mu\lambda}^{\nu\sigma}$ is a two-electron integral over as many as four basis functions. Within the ZDO approximation over atomic orbitals, this reduces to

$$R_{ik}^{jl} = \sum_{\mu} \sum_{\nu} c_{i\mu}^{*} c_{j\nu}^{*} c_{k\mu} c_{1\nu} R_{\mu\mu}^{\nu\nu}, \tag{7a}$$

while the ZDO approximation over molecular orbitals further reduces it to

$$R_{ii}^{jj} = \sum_{\mu} \sum_{\nu} c_{i\mu}^{2} c_{j\nu}^{2} R_{\mu\mu}^{\nu\nu}. \tag{7b}$$

The $\boldsymbol{f}^{\mu}$ and $\gamma^{\mu\nu}$ matrices over atomic orbitals for the complex can be constructed by placing the components in the assumed geometry and directly calculating the various elements from appropriate formulas for integrals over atomic basis functions. For constructing the $\boldsymbol{F}^{\mu}$ for the complex it is convenient to first construct an expanded $\boldsymbol{C}^{i\mu'}$ matrix for the non-interacting components having the block diagonal form

$$\boldsymbol{C}^{i\mu'} = \begin{bmatrix} \boldsymbol{C}^{j\mu} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{C}^{k\mu} \end{bmatrix}, \tag{8}$$

where $\boldsymbol{C}^{j\mu}$ and $\boldsymbol{C}^{k\mu}$ are the coefficients matrices of the individual components. (Since construction of the individual F_{ij} elements involves summations over occupied orbitals, it may be convenient to reorder the $\boldsymbol{C}^{i\mu'}$ matrix according to the values of the eigenvalues of the individual components.) The elements of the expanded $\boldsymbol{f}'$ matrix over the orbitals of the components are

$$f'_{ij} = \sum_{\mu} \sum_{\nu} c'_{i\mu} c'_{j\nu} f_{\mu\nu} \tag{9}$$

and those of the expanded $\gamma^{ij'}$ matrix are

$$\gamma_{ij'} = \sum_{\mu} \sum_{\nu} c'^{2}_{i\mu} c'^{2}_{j\nu} \gamma_{\mu\nu}. \tag{10}$$

If the elements of $\boldsymbol{F}^{i'}$, the expanded $\boldsymbol{F}$ matrix, are expanded analogously to Eqs. (4) and (5) we have

$$F'_{ii} = \langle i|\hat{f}|i\rangle + 2 \sum_{A}^{\text{occ.}} \sum_{j\neq i} C_{Aj}^2 \gamma_{ij} + \sum_{A}^{\text{occ.}} C_{Ai}^2 \gamma_{ii} \tag{11}$$

$$F'_{ij} = \langle i|\hat{f}|j\rangle - \sum_{A}^{\text{occ.}} C_{Ai} C_{Aj} \gamma_{ij} \,. \tag{12}$$

If some of the electrons which were used to construct the molecular orbitals are to be considered as part of the effective core in the complex (i.e. if only certain orbitals, such as the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor, are to be considered in the complex), the repulsion integrals involving the electrons and orbitals not considered must be included in the effective core for the complex, yielding

$$\langle i|\hat{f}|i\rangle^e = \langle i|\hat{f}|i\rangle + 2 {\sum_{A}}' \sum_{j\neq i} C_{Aj} \gamma_{ij}^2 + {\sum_{A}}' C_{Ai}^2 \gamma_{ii} \tag{13}$$

or from Eq. (11)

$$= F'_{ii} - 2 {\sum_{A}}'' \sum_{j\neq i} C_{Aj}^2 \gamma_{ij} - {\sum_{A}}'' C_{Ai}^2 \gamma_{ii} \tag{13a}$$

$$\langle i|\hat{f}|j\rangle^e = \langle i|\hat{f}|j\rangle - \sum_{A} C_{Ai} C_{Aj} \gamma_{ij} \tag{14}$$

$$= F'_{ij} + {\sum_{A}}'' C_{Ai} C_{Aj} \gamma_{ij} \tag{14a}$$

where the single primed summation indicates summation over the occupied orbitals not to be considered, the double primed summation indicates summation over those to be considered and the superscript e indicates effective core integrals. These effective core integrals are constructed for the initial situation before the components are allowed to interact, consequently the C_{Ai} will equal unity for an occupied orbital on a given component and zero for an unoccupied orbital on that component or any orbital on any other component. Thus, Eqs. (13a) and (14a) become

$$\langle i|\hat{f}|i\rangle^e = F'_{ii} - 2 \sum_{j\neq i}^{\substack{\text{occ.}\\ \text{on}\, A}} \gamma_{ij} - \gamma_{ii} \tag{15a}$$

$$\langle i|\hat{f}|j'\rangle^e = F'_{ij} \tag{15b}$$

where the summation in (15a) is over only to the other occupied orbitals on the same component as orbital i. The F'_{ii} elements are simply the eigenvalues of the Hartree-Fock equations for the individual components. It should be pointed out here that separation of the π-electrons into two sets is a rather gross approximation in that the effective core should be expected to change as the molecular orbitals on the components are allowed to interact. There is no general symmetry induced orthogonality between the core and the "peel" as there is when applying the π-electron approximation to unsaturated systems [9]. On the other hand, we know from perturbation theory that the interaction of two orbitals is inversely proportional to their energy difference, consequently useful information should be obtained from such a treatment in spite of the crudeness of the approximation. The problem is essentially the same as that encountered in all valence-electron molecular calculations. The valence orbitals on one center are not orthogonal to the inner-shell orbitals on other centers. In that case, however, the approximation of neglecting such interactions is less severe than it is in the present case since the energy differences are larger and interactions are probably smaller.

For performing the LCMO calculations, calculations were first performed on the isolated components. The atomic positions for the complex and the eigenvectors for the isolated components were then fed back into the program and the intermolecular $\gamma_{\mu\nu}$ and $f_{\mu\nu}$ elements were calculated using the same equations as for the intramolecular case. These were converted to integrals over molecular orbitals by use of Eqs. (9) and (10) (no iteration was performed at this stage). The appropriate elements of the γ^{ij} matrix were used directly while the elements of the $f^{i'}$ matrix were constructed from Eqs. (15a) and (15b). These were fed back into the program and iteration to self-consistency was performed to obtain the complex orbitals (as linear combinations of the molecular orbitals of the donor and acceptor) and eigenvalues. The spectral transitions were estimated with configuration interaction, employing all of the one-electron excitations over the complex orbitals. The stabilization energy was taken to be difference of the sum over occupied orbitals of the expectation values of the core matrix and the F matrix for the initial and self-consistent states.

b) Dative Bond Formalism

Polyconfiguration dative bond calculations were performed to use as a reference for comparison with the SC LCMO results. The method of doing this requires only the use of standard configuration interaction equations [10] based on the molecular orbitals of the isolated donor and acceptor (see the appendix of II). Calculations were first performed on the isolated components, then the interaction elements of the $\gamma^{\mu\nu}$ and f^{μ} matrices were calculated over the atomic basis functions and the CI calculations were performed. Twenty six configurations were employed; the "no bond" configuration and the 25 lowest energy configurations involving the promotion of one electron in any of the manners $(D \rightarrow A)$, $(A \rightarrow D)$, $(D \rightarrow D)$, or $(A \rightarrow A)$. The stabilization energy was taken to be the difference between the lowest eigenvalue of the CI matrix and the sum of the energies of the isolated components.

c) Parameterization

For all calculation the $\gamma_{\mu\nu}$ integrals were estimated from the approximation of Nishimoto and Matage [11] while the $f_{\mu\nu}$ integrals were from the approximation of Flurry and Bell [12]. The valence state data were from Hinze and Jaffé [13] and the Slater effective nuclear charges were used.

Since these approximations are for coplanar π-atomic orbitals, where the π-overlap is smaller than for the $p\sigma$ type overlap encountered for the interplanar systems, the effective interplanar spacing was varied to yield the experimental charge transfer transition for the benzene- tetracyanoethylene (TCNE) complex. The effective spacing so obtained (2.65 A) was used for the other complexes and

Table 1. *Interaction elements for the* HOMO *of benzene and the* LUMO *of* TCNE

	This work[a]	Refs. [1, 2][b]	CNDO/2[c]
f_{ij}	−0.16 eV	−0.63 eV	−0.28 eV
γ_{ij}	3.23 eV	3.95 eV	3.72 eV

[a] Eqs. (10) and (15b).
[b] The f_{ij} is the β_{DA} and γ_{ij} is the V_{es}.
[c] R. L. Flurry, Jr. and D. Breen, unpublished results.

was the only parameter adjusted specifically for the complexes. It should be emphasized that this is a *parameterization* only. Different parameterizations at the molecular level would give different optinum spacings; consequently no physical significance should be attached to the value obtained. The f_{ij} and γ_{ij} elements for the interaction of the HOMO of benzene and the LUMO of TCNE are listed in Table 1. Also included in Table 1 are the empirical values used in Ref. [1] and [2] for TCNE and methyl-substituted benzene complexes and a value obtained from an all valence electron CNDO/2 calculation for benzene-TCNE, using an interplanar spacing of 3.36 A. The similarity of these values implies that the values used in the present work are of the right order of magnitude.

The calculations reported here were carried out on the Oxford University English Electric *KDF*-9 and the L.S.U. Baton Rouge I.B.M. 360/65 digital computers using a modification of the π-electron SCF program of Bloor and Gilson [14].

Results and Discussion

Calculations were performed on two highly symmetrical systems, the complexes of benzene and hexamethylbenzene (HMB) with tetracyanoethylene (TCNE) and two unsymmetrical systems, the complexes of benzene and HMB with 2, 4, 7-trinitrofluorenone (TNF). The formalism, as developed here, allows the inclusion of as many molecular orbitals as is desired from the donor and acceptor into the LCMO description of the complex, consequently the effect of the size of the molecular orbital basis set was also studied. Calculations within the dative bond formalism which considered 26 dative bond configurations were used as the standard of comparison in each case. Table 2 presents the results of some calculated properties of the isolated components.

Table 3 presents the results for the TCNE complexes. The structure chosen used the experimental bond lengths and angles for the two components, with the six-fold benzene axis coincident with the out-of-plane two-fold axis of TCNE. The 26 configuration dative bond treatment reveals that, because of the high symmetry of the systems, of these 26 configurations, only configurations arising from the two highest occupied donor orbitals and the two lowest acceptor orbitals can interact with the "no-bond" configuration. Furthermore, it does not matter whether the ethylene axis of the TCNE intersects bonds or angles of the benzene ring. Both the two-orbital and four-orbital SC LCMO treatments are essentially equivalent to the reference calculation, provided that in the two-orbital treatment

Table 2. *Some calculated properties of the component molecules*

	Benzene	HMB[a]	TCNE[b]	TNF[c]
Ionization Potential	9.91 eV	9.00 eV	10.64 eV	10.03 eV
Electron Affinity	0.56 eV	0.37 eV	3.39 eV	4.32 eV
${}^1\Delta E_1^d$	4.73 eV	4.23 eV	4.89 eV	2.97 eV[e]
${}^1\Delta E_2$	6.03 eV	5.30 eV	5.89 eV	3.41 eV
${}^1\Delta E_3$	6.86 eV	6.11 eV	5.90 eV	3.49 eV
μ_π	0	0	0	2.03 *D*

[a] Hexamethylbenzene.

[b] Tetracyanoethylene.

[c] 2, 4, 7-Trinitrofluorenone.

[d] Nine single excited configurations were used for all compounds except TNF where 15 were used.

[e] This transition is primarily an intramolecular charge-transfer excitation from the ring system to the 2-nitro group. Experimentally, no transition is seen near this energy; possibly due to a non-planarity of the nitrogroup.

Table 3. *Spectral transitions and stabilization energies for* TCNE *complexes*

		SC LCMO			Reference[a]	Exp.
		2 orb.		4 orb.		
Donor		*A*[b]	*B*[b]			
Benzene	ΔE_{ct}	3.28 eV	3.33	3.29	3.29	3.24[c]
	ΔE_{st}	0.36 kcal/mole	0.0	0.36	0.37	3.35[d]
HMB	ΔE_{ct}	2.64 eV	2.68	2.70	2.69	2.27[c]
	ΔE_{st}	0.40 kcal/mole	0.0	0.42	0.41	7.75[d]

[a] Twenty-six dative bond configurations.

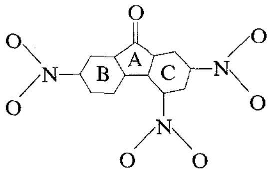
[b] *A*, maximum overlap of highest occupied donor orbital and lowest vacant acceptor orbital; *B*, zero overlap.

[c] Lepley, A. R.: J. Amer. chem. Soc. **86**, 2545 (1964) (solution phase values).

[d] Briegleb, G.: Elektronen – Donator – Acceptor – Komplexe, p. 129. Berlin: Springer-Verlag 1961.

the proper real form is chosen from the degenerate pair for the highest occupied orbital of the donor. The calculated stabilization energies are only approximately one tenth the observed value. This is to be expected, however, since various authors have pointed out that charge transfer interactions account for only a small fraction of the total stabilization of such complexes [15]. The direction of the trend from benzene to HMB is, nevertheless, in the right order.

The structure of TNF (I) for these calculations was



I

approximated from that of fluorene [16] with standard values for the bond lengths and angles of the nitro and carbonyl groups. Here there is no obvious

Table 4. *Spectral transitions and stabilization energies for* TNF *complexes*

Donor	Position[a] on Acceptor	SC LCMO 2 orb.	4 orb.	6 orb.	Reference[b]	Exp.[c]
Benzene	$A\ \Delta E_{ct}$	3.33 eV	3.27	2.73	3.01	2.98 eV
	ΔE_{st}	0.037 kcal/mole	0.037	0.051	0.196	2.9 kcal/mole
	$B\ \Delta E_{ct}$	3.01 eV	2.97	2.97	2.84	
	ΔE_{st}	0.0 kcal/mole	0.0	0.018	0.0	
	$C\ \Delta E_{ct}$	3.53 eV	2.99	2.75	2.84	
	ΔE_{st}	0.0 kcal/mole	0.007	0.007	0.0	
HMB	$A\ \Delta E_{ct}$	2.44 eV	2.38	2.33	2.30	2.61 eV
	ΔE_{st}	0.046 kcal/mole	0.058	0.024	0.231	4.8 kcal/mole
	$B\ \Delta E_{ct}$	2.08 eV	2.07	2.06	1.95	
	ΔE_{st}	0.014 kcal/mole	0.018	0.037	0.0	
	$C\ \Delta E_{ct}$	2.65 eV	2.30	2.28	1.94	
	ΔE_{st}	0.0 kcal/mole	0.010	0.010	0.0	

[a] Ring over which donor is situated.

[b] Twenty-six dative bond configurations.

[c] R. F. Shokes and R. L. Flurry, Jr. To be published. The experimental orientation is uncertain.

choice of where to place the donor. Separate calculations were made with the benzene ring centered on each of the three rings of TNF. These are labeled A, B and C to correspond to the ring labeling in I. The results are shown in Table 4. The absence of symmetry in this case allows interaction among all 26 of the configurations in the reference calculations. It also shows up dramatically in the SC LCMO calculations. First of all, the two-orbital SC LCMO results are in much poorer agreement with the reference calculations in all cases than was the case for the TCNE complexes. The charge-transfer transition energy is too high while for the *A* structure (the only one predicted to be stable by the reference calculations) the stabilization energy is too low. In all cases, increasing the size of the molecular orbital basis set to four offers improvement in the charge transfer transition. This, in effect, allows the two degenerate levels on the donor to interact freely with the acceptor orbitals without the arbitrary symmetry restriction imposed by choosing one of the degenerate pair. Increasing the basis set to six molecular orbitals introduces an occupied acceptor orbital. For the HMB complexes this is again an improvement. For two of the three orientations in the benzene complex, however, the strong interaction of the TNF local excitation with the charge transfer excitation brings the charge transfer transition below the reference calculation. Further expansion of the basis set should bring this back in line; however, the more the molecular orbital basis set is expanded, the less advantage there is to using the LCMO formalism. From these results on TNF it appears that, if an LCMO formalism is to be used, a molecular orbital basis set sufficiently large to include symmetry induced degeneracies in the highest occupied donor orbitals and lowest occupied acceptor orbitals will give qualitatively correct spectral results. It would be expected that if there are no such symmetry induced degeneracies, the angular orientation of the components could be very important.

Table 5. *Spectral transitions and stabilization energies for some multiple complexes of benzene and* TNF

		Orientation[a]				
		AA	*AB*	*AC*	*BB*	*BC*
D_2A[b]	ΔE_{ct}	3.33 eV	3.01	3.53	3.01	3.53
	ΔE_{st}	0.07 kcal/mole	0.04	0.04	0.00	0.00
DA_2[c]	ΔE_{ct}	3.33 eV	3.01	3.53	3.01	3.53
	ΔE_{st}	0.07 kcal/mole	0.04	0.04	0.00	0.00

[a] Acceptor rings over which donor is situated.
[b] Two donors to one acceptor.
[c] One donor to two acceptors. These calculations are based on a three orbital model.

One advantage that the LCMO formalism has over the dative bond formalism is the ability to include more than two molecular units in a straightforward manner. Such calculations were applied to the D_2A and DA_2 (where D stands for donor and A for acceptor) complexes of benzene and TNF. The results are shown in Table 5 for a three-orbital model. Quite unexpectedly, the spectral predictions were precisely the same as for a 1 : 1 complex and the stabilization energies were the same as the sum of two 1 : 1 complexes, in this approximation. The explanation for this is easy to see (after the fact). In these cases the transition is still primarily charge-transfer in character and is consequently controlled by a large electrostatic term. In going from the π-system of ethylene to that of the allyl anion, a situation which, on the surface, seems analogous, there is very little charge-transfer character to the transition. The change is primarily controlled by a large β term.

One other observation is yielded by the calculations reported here. The Eq. (17)

$$\Delta E_{ct} - I_D - A_A - C_{DA}$$

(where I_D is the ionization potential of the donor, A_A the electron affinity of the acceptor and C_{DA} the electrostatic term arising from the charge-transfer) seems, from the calculations, to be much more nearly correct than was previously believed (see Table 6). The usual assumption [1] has been that for a series of

Table 6. *Comparison of* SC LCMO *spectral results to "pure charge transfer" results*

System		ΔE_{ct}	
		SC LCMO[a]	I_D–A_A–C_{DA}[b]
Benzene–TCNE		3.28 eV	3.28 eV
HMB–TCNE		2.64 eV	2.64 eV
Benzene–TNF	(*A*)	3.32	3.33
	(*B*)	3.01	3.01
	(*C*)	3.53	3.53
HMB–TNF	(*A*)	2.44	2.43
	(*B*)	2.08	2.08
	(*C*)	2.65	2.65

[a] Two orbital model.
[b] Calculated quantities for I_D, A_A and C_{DA}.

closely related donors with a given acceptor the electrostatic term was essentially constant. Thus, a plot of ΔE_{ct} *vs.* I_D which gave a slope significantly different from unity was taken to imply that other types of interaction were important. The present results imply that the electrostatic term can vary sufficiently to account for this. Thus, more reasonable estimates of this electrostatic interaction, along with experimental ionization potentials and electron affinities might give quite good estimates of charge-transfer transition energies.

Conclusion

The calculations reported here indicate that the SC LCMO method is a reasonable method for treating molecular interactions. Even the two-orbital model seems to give qualitatively correct results for complexes of closely related donors with a given acceptor; however, if the systems are of low symmetry more orbitals should be included for more reliable results.

Perhaps the greatest advantage of the LCMO method over the dative bond treatment for such systems is the ability to treat more than two components in a straightforward way. Work is actively underway along these lines [18, 19].

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