k_{23} are in good agreement with k_{H_2O} of the corresponding metal ions. This fact suggests that in the present systems, like the Co(II)- and alkaline-earth-EDTA systems, the complex exists in two forms, pentacoordinate and hexacoordinate structures, and that the water-substitution process is the rate-determining process of the hexacoordinate complex formation. Furthermore, the consistent results obtained by use of the estimated values of K_0 and ΔV suggest the correctness of the estimation of these values.

Registry No. Cd-EDTA, 36077-58-4; Zn-EDTA, 12519-36-7.

On the Stability and Properties of Organic Metals and Their Isomeric Charge-Transfer Complexes

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Abstract: A methodology for conceptualizing the aggregation isomers of D–A adducts is presented. It is concluded that the mixed-stacks isomer . . .D–A–D–A. . . leads to *stabilization* of the *ground no-bond configuration.* On the other hand, the segregated-stacks isomer . . .DD||AA. . . leads to *stabilization of excited charge-transfer configurations* which form the delocalized state . . .$D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho}$. . . with a partial degree of electron transfer (ρ). It is argued from first principles that this state is not always truly delocalized. In such cases, *there will be a barrier for electron hopping* (e.g., $A^-A \rightarrow AA^-$). A mechanism of curve-band crossing is responsible for stabilizing . . .$D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho}$. . . below the no-bond state. The value of ρ in this isomer is determined by a combination of two factors: $I_D - A_A$ and the reorganization energy obtained by relaxing D^+ and A^- from the geometry of their neutrals. The recognition that the mixed-stacks isomer originates from a ground no-bond configuration, while the (often conducting) segregated-stacks isomer arises from crossing of the excited charge-transfer pack of configurations, indicates that the latter isomer could in principle be the less stable one. Experimental data are examined in light of the model.

Introduction

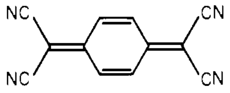
There are two classes of aggregation isomers within the ensemble of the D–A (donor–acceptor) adducts. The first type is the class of charge-transfer complexes,[1] in which the addends aggregate in mixed stacks of alternating donor (D) and acceptor (A) molecules:

$$. . .D\text{–}A\text{–}D\text{–}A. . . \qquad (1)$$

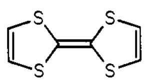
The second class of D–A adducts involves complexes in which the donor and the acceptor molecules aggregate in segregated stacks as shown schematically in eq 2, where the double vertical line represents the segregation.

$$. . .D\text{–}D||A\text{–}A. . . \qquad (2)$$

The most attractive subset within the latter class is probably the group of organic metals,[2] among which the first and the best known member is the TTF·TCNQ (**1** and **2**) complex.[3] All the members of this subgroup aggregate in segregated stacks of donors and acceptors (eq 2), and many of them conduct electricity along the stacks in a metallic like fashion.[2] It is this feature which made them of special interest to chemists and physicists alike.



1 (TCNQ)



2 (TTF)

Our interest in this subgroup has been aroused since, from our experience in applying the charge-transfer model[1a] to organic reactions,[4] we reasoned that for D's and A's with moderate donor and acceptor abilities, the segregated stacks which characterize the organic metals should be a form which stabilizes an excited state of the D–A aggregate,[5] whereas the mixed stacks should be the form which stabilizes the ground state of the D–A aggregate. Therefore, we suspected that in principle organic metals may not necessarily be the most stable isomers, a point which has been raised before in one form or another by Perlstein,[2a] Torrance,[6a] and Sandman.[6b]

Further support of this point was provided by computational results[7] which show that the electrostatic energy for the TTF·TCNQ complex does not seem to be sufficient to stabilize any significant degree of electron transfer (ρ) from D to A. Since the experimentally determined ρ for TTF·TCNQ and other organic metals is ≥ 0.5,[8] then the mere existence of these stable organic metals is puzzling.

Thus we are facing here a complex problem. First of all, one would like to know what factors may influence the selection of the aggregation mode for a given D–A pair. An answer to this

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[1] For comprehensive reviews on the subject, see: (a) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969. (b) Herbstein, F. H. In "Perspectives in Structural Chemistry"; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1971; Vol. 4, pp 166–395. (c) Foster, R. *J. Phys. Chem.* **1980**, *84*, 2138–2141.

[2] Some of the reviews are: (a) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519–534. (b) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79–86. (c) Shibaeva, R. P.; Atovmyan, L. O. *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 514–531. (d) "Molecular Metals"; Hatfield, W. E., Ed.; Plenum Press: New York, 1979. (e) "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977.

[3] (a) Ferraris, J.; Cowan, D. O.; Walatka, V. V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

[4] See, for example: (a) Epiotis, N. D.; Zander, W.; Shaik, S. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980. (b) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692–3701.

[5] Note the striking resemblence between the segregated mode of stacking and the mode of D–A exciplex quenching by other D and A quenchers. See: Beens, H.; Weller, A. *Chem. Phys. Lett.* **1968**, *2*, 82.

[6] (a) Torrance, J. B., in ref 2d, p 7. (b) Sandman, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5230–2.

[7] (a) Metzger, R. M.; Bloch, A. N. *J. Chem. Phys.* **1975**, *63*, 5098–5107. (b) Metzger, R. M. *Top. Curr. Phys.*, in press. (c) Torrance, J. B.; Silverman, B. D. *Phys. Rev. B* **1977**, *15*, 788–801.

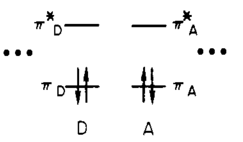
[8] For recent determination, see: Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442–3.

0002-7863/82/1504-5328$01.25/0

question is crucial for anyone who attempts synthesis of organic metals. Our second question concerns the electronic nature of the segregated-stacks isomer and the mechanism of its formation. How does it achieve $\rho \neq 0$? What could be the factors which determine the value of ρ? Thus, our general goal is to present a methodology for conceptualizing and understanding these molecules, with an intention to provide guidelines which may be utilized in chemical synthesis. The strategy underlying our approach[9] involves the use of the charge-transfer theory which was developed by Mulliken.[1a] In this manner, the two isomers are treated along the same lines, and the qualitative chemical insight can be projected in an easy and coherent manner.

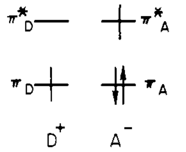
I. Theory

Imagine a collection of n donor molecules (D) and n acceptor molecules (A), each represented by a pair of frontier orbitals, HOMO and LUMO of the π and π^* variety. This collection of molecules has one no-bond configuration, denoted as $(DA)_n$:



(3)

Above this configuration there is a "sea" of charge-transfer configurations which are generated by transferring single electrons from the various π_D's to π^*_A's. This ensemble of configurations can be subdivided into blocks which differ in their degree of electron transfer ρ. If we number the blocks as $i = 1, 2, 3, \ldots, n$, then a general block i will be denoted by $(DA)_{n-i}(D^+A^-)_i$ which means that this block contains i D^+A^- pairs (eq 4) which together



(4)

yield $\rho = i/n$ ($i = 1, 2, \ldots, n$). Assuming an equal number (n) of D's and A's, the number of modes of transferring i single electrons from i D's to i A's is $\binom{n}{i}^2$, per block. For example, the block of $\rho = 1/3$ for a collection of 3D's and 3A's contains nine charge-transfer forms which differ in their sites of electron transfer, and we show three of them in eq 5.

$$D^+DDA^-AA;\ D^+DDAA^-A;\ D^+DDAAA^- \qquad (5)$$

Each such charge-transfer form represents several wave functions which arise from assigning spins to the electrons, and each spin state in block i has several wave functions which arise from different modes of pairing up the individual spins. The total number of configurations in block i for each spin state, S, becomes then:[10a]

$$N(n,i,S) = \frac{(2S+1)\binom{n}{i}^2(2i)!}{(i+S+1)!(i-S)!};\quad S = 0, 1, 2, \ldots, i \qquad (6)$$

The states of the aggregate can be generated from linear combinations within this ensemble of configurations using an effective one-electronic Hamiltonian. Under this simplification *two configurations interact if they are mutually related by a single electron shift. The interaction matrix element (β) is proportional to the resonance integral of the two orbitals which are involved in the electron shift.*

Successive blocks of configurations are related to one another by an electron shift from the HOMO of a donor (π_D) to a LUMO of an acceptor (π^*_A). For example, in the case of one D–A pair ($n = 1$), the two blocks DA and D^+A^- ($\rho = 0$, and $\rho = 1$) are mutually related by an electron shift from π_D to π^*_A (eq 3 and 4), and hence,

$$\langle DA|H|D^+A^-\rangle = 2^{1/2}\langle\pi_D|H|\pi^*_A\rangle = 2^{1/2}\beta_{DA} \qquad (7)$$

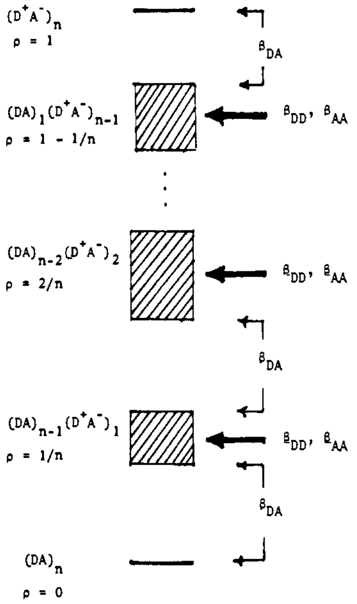


Figure 1. Schematic description of the interaction pattern of the no-bond, $(DA)_n$, and the various charge-transfer blocks, $(DA)_{n-i}(D^+A^-)_i$. Two successive blocks interact via β_{DA}. Configurations belonging to the same block interact via β_{DD} and β_{AA}.

This result, which is familiar from the Mulliken charge-transfer theory,[1a] will persist for larger systems, and, in general, the members of two successive blocks (i, $i + 1$) will interact via the HOMO(D)–LUMO(A) resonance integral, labeled as β_{DA} (eq 7).

Within each block, the configurations are generated from one another by shifting an electron among the LUMOs (π^*_A) of the acceptors or among the HOMOs (π_D) of the donors, while keeping ρ constant. Therefore they interact among themselves either via the HOMO(D)–HOMO(D) or the LUMO(A)–LUMO(A) resonance integrals (β_{DD} and β_{AA}, respectively).[10a,b] For example, $D_1^+D_2^+D_3D_4A_1^-A_2^-A_3A_4$ ($\rho = 0.5$) is generated from $D_1^+D_2D_3^+D_4A_1^-A_2^-A_3A_4$ by an electron shift from the HOMO of D_2 to the HOMO of D_3, and hence,

$$\langle D_1^+D_2^+D_3D_4A_1^-A_2^-A_3A_4|H|D_1^+D_2D_3^+D_4A_1^-A_2^-A_3A_4\rangle = \beta_{D_2D_3} \qquad (8)$$

These conclusions are summarized in Figure 1, which illustrates that there is a dichotomy between inter- and intra-block interactions. The interactions between successive blocks are of the HOMO(D)–LUMO(A) variety (β_{DA}), whereas, the interactions within each block are of the HOMO(D)–HOMO(D) and LUMO(A)–LUMO(A) varieties (β_{DD} and β_{AA}).

These two types of interactions are *in principle mutually exclusive*, and therefore the dichotomy must be involved in creating the division of the complexes into the two isomeric forms discussed in the Introduction (eq 1 and 2). Each mode of aggregation will, in its turn, "turn off" one interaction and "turn on" the other. Thus, in the segregated-stacks isomer . . .D–D||A–A. . . (eq 2), one "turns off" the β_{DA} interactions and "turns on" β_{DD} and β_{AA} interactions, while exactly the opposite situation obtains for the mixed-stacks isomer . . .D–A–D–A. . . (eq 1). This pattern makes the interaction matrices for the two isomers complementary and

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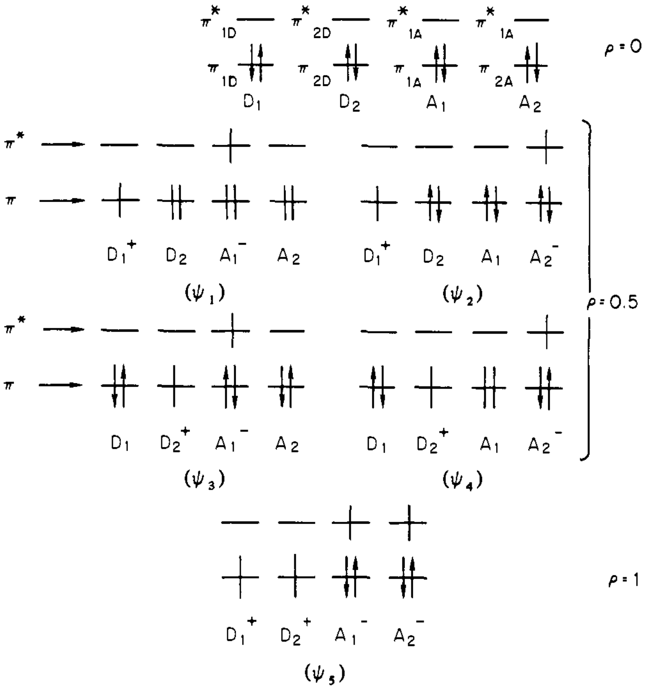
(9) Soos has treated the magnetic and spectroscopic behavior of alternating . . .DA. . . rings, and of stacks with variable ρ, using an elegant diagramatic VB method in a second quantized formalism. Our treatment in this paper is quite similar to his in many respects. (a) Soos, Z. G.; Mazumdar, S. *Phys. Rev. B.*, **1978**, *18*, 1991–2003. (b) Mazumdar, S.; Soos, Z. G. *Synth. Met.* **1978/80**, *1*, 77–94. (c) Bondeson, S. R.; Soos, Z. G. *Chem. Phys.* **1979**, *44*, 403–14.

(10) (a) Ditransfer configurations (e.g., $D^{2+}DDA^{2-}AA$) are neglected owing to their higher energy (see ref 2b and 9). (b) Their omission does not alter the qualitative conclusions and may be compensated by parametrization of the resonance integral β for more quantitative purposes.

Scheme I. No-Bond (ψ_0) and Charge-Transfer (ψ_1-ψ_5) Configurations for (D-A)$_2$



quite easy to solve. These are *Hückel-type matrices* having $E - \alpha_i$ on the diagonal and β's as off diagonal elements. α_i is the energy of a charge-transfer configuration in block i, and it is related to the difference in the ionization potential of the donor (I_D) and the electron affinity of the acceptor (A_A), and to the average (per D–A pair) of all the coulomb-type interactions, Q, in the ensemble. Relative to the no bond, α_i reads:

$$\alpha_i(\rho_i) = \rho_i(I_D - A_A) + Q(\rho_i) \qquad (9)$$

If we can solve these complementary interaction matrices for the two isomers, we will be able *in principle*, to predict their relative stabilities for a given D–A pair, and to understand and establish the relationship between them.[9]

II. Electronic States of (D-A)$_2$

The (D–A)$_2$ unit is the smallest segment which can display aggregation–isomerism (eq 1 and 2). This is also the smallest crystalline segment which can model the behavior of a segregated-stacks isomer with $\rho < 1$. Thus, there is much that we can learn about the problem already from this simple unit.

The relevant configurations are shown in Scheme I, where the ordering of the molecules does not, as yet, imply any particular mode of stacking. This basis set consists of the no-bond form (D$_1$D$_2$A$_1$A$_2$) the four $\rho = 0.5$ charge-transfer configurations ($D_1^+D_2A_1^-A_2$, $D_1^+D_2A_1A_2^-$, $D_1D_2^+A_1^-A_2$, $D_1D_2^+A_1A_2^-$), and the single $\rho = 1$ charge-transfer configuration ($D_1^+D_2^+A_1^-A_2^-$). As we introduce spins, this group of configurations forms different sets which have the same orbital description as in Scheme I, but differ in their spin description. Thus, for the $\rho = 0.5$ block (ψ_1–ψ_4) we have one singlet and one triplet set. For the $\rho = 1$ configuration we have two singlets, three triplets, and one quintet configurations, all having the orbital description of ψ_5 (Scheme I). The two singlets arise from the two possible modes of pairing up the four spins into two couples.[11] Assuming moderate donor–acceptor pairs, then $\alpha_1(\rho = 1) > \alpha_1(\rho = 0.5) > 0$ (eq 9), and this relation sets the energy ordering of the blocks with the no bond (ψ_0) being the lowest and the $\rho = 1$ configurations (ψ_5, ψ_5') being the highest.[12]

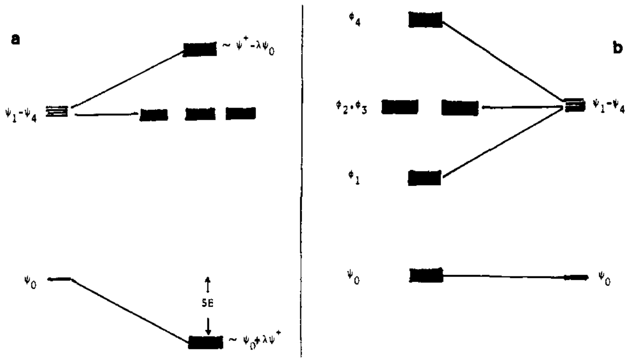


Figure 2. Interaction diagram for (D–A)$_2$. Only the no-bond (ψ_0) and the $\rho = 0.5$ configurations (ψ_1–ψ_4) are shown. (a) The mixed-stacks isomer. ψ^+ is an all-positive linear combination of the $\rho = 0.5$ configurations (ψ_1–ψ_4). SE is the resulting stabilization energy of ψ_0. (b) The segregated-stacks isomer. The no-bond configuration ψ_0 remains nonbonding. The $\rho = 0.5$ configurations (ψ_1–ψ_4) mix and spread into the charge-transfer states (ϕ_1–ϕ_4).

The interaction pattern of these singlet configurations (ψ_0–ψ_5') follows directly from the interaction rule which was stated in section I. Thus, D$_1$D$_2$A$_1$A$_2$ interacts with each of the $\rho = 0.5$ charge-transfer configurations via a HOMO(D)–LUMO(A)-type (β_{DA}) matrix element, e.g.,

$$\langle D_1D_2A_1A_2|H|D_1^+D_2A_1^-A_2\rangle = 2^{1/2}\langle \pi_{1D}|H|\pi^*_{1A}\rangle = 2^{1/2}\beta_{D_1A_1} \qquad (10)$$

The $\rho = 0.5$ charge-transfer configurations interact among themselves too, but via HOMO(D)–HOMO(D) and LUMO(A)–LUMO(A)-type matrix elements. For example:

$$\langle D_1^+D_2A_1^-A_2|H|D_1^+D_2A_1A_2^-\rangle = \langle \pi^*_{1A}|H|\pi^*_{2A}\rangle \equiv \beta_{A_1A_2} \qquad (11)$$

and

$$\langle D_1^+D_2A_1^-A_2|H|D_1D_2^+A_1^-A_2\rangle = -\langle \pi_{1D}|H|\pi_{2D}\rangle \equiv -\beta_{D_1D_2} \qquad (12)$$

In a similar manner, the $\rho = 1$ charge-transfer configuration is generated from the $\rho = 0.5$ block by a HOMO(D) → LUMO(A) electron shift (Scheme I), and, hence, it interacts with the set members via the HOMO(D)–LUMO(A)-type (β_{DA}) interaction. Thus, we get the familiar hierarchy of interactions described in Figure 1. *This interaction pattern holds stereochemical information about the preferred mode of aggregation, the relative orientation of two neighboring molecules,*[12] *and the stacking sequence.* This *information is hidden in the matrix elements* β_{DA} *vs.* β_{DD} *and* β_{AA} *which behave like the corresponding MO overlaps.*

The ground configuration of the repeat unit is the no-bound ψ_0 (D$_1$D$_2$A$_1$A$_2$). Since this configuration can interact with the members of the $\rho = 0.5$ block only via β_{DA} (HOMO–LUMO), then *in order to stabilize the ground state of the complex, we must arrange the donors and the acceptors in a manner which maximizes the* β_{DA} *interactions.* This kind of arrangement begins the formation of a mixed-stacks isomer with alternating D and A. Moreover, in order to enjoy all possible interactions, the stack would tend to curl up and form a ring[9a] of alternating D and A.

The interaction diagram is shown in Figure 2a. Under the constraint $\beta_{DD} = \beta_{AA} = 0$ and $\beta_{DA} \neq 0$, the no-bond configuration, ψ_0, is stabilized mainly by mixing with the in-phase combination, ψ^+ of the $\rho = 0.5$ configurations (ψ_1–ψ_4), and it also mixes indirectly some of ψ_5 and ψ_5'. The matrix element with ψ^+ is:

$$\langle \psi_0|H|\psi^+\rangle = 2\cdot 2^{1/2}\beta_{DA} \qquad (13)$$

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[11] The two wave functions are:

$$\psi_5 = (1/2)[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta]$$

$$\psi_5' = (1/\sqrt{12})[2\alpha\beta\alpha\beta + 2\beta\alpha\beta\alpha - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta]$$

where α and β are spins of electrons in the MOs π_{1D}, π_{2D}, π^*_{1A}, and π^*_{2A}, respectively (Scheme I).

[12] Other energy terms such as overlap repulsion in ψ_0 and in ψ_1–ψ_5' must enter into $\alpha_i(\rho)$ if one is interested in effects such as the mutual slip of the D's and A's along the stacks. For our purposes, these terms can be neglected or else enter α implicitly through Q.

If the stack is forced to maintain loose ends, then one interaction ($\beta_{D_1A_2}$) is lost, and the matrix element is now between ψ_0 and a linear combination of ψ_1, ψ_3, and ψ_4 and, hence, is slightly smaller ($\sqrt{6}\beta_{DA}$) than before. The stabilization energy (SE in Figure 2) will, of course, depend also on the energy gap α_1 and α_2 which in turn depends on the donor-acceptor abilities of the addends.[1a]

The excited state of the $(D-A)_2$ segment originates from the $\rho = 0.5$ charge-transfer block in Scheme I. The $\rho = 0.5$ configurations are flanked by β_{DA} (HOMO-LUMO) interactions, and they interact among themselves via β_{DD} (HOMO-HOMO) and β_{AA} (LUMO-LUMO) interactions. Clearly then, *in order to stabilize the excited state of the unit, one must arrange the addends in the manner which maximizes the* HOMO-HOMO (β_{DD}) *and the* LUMO-LUMO (β_{AA}) *interactions and simultaneously minimizes the* HOMO-LUMO (β_{DA}) *interaction.* The arrangement which meets these requireements perfectly is the segregated-stacks isomer, D-D||A-A, where the double line excludes π-π interactions between D and A. Assuming $\beta_{DD} \approx \beta_{AA} = \beta$, the secular determinant becomes block diagonal, and for the block of the $\rho = 0.5$ charge-transfer configuration eq 14 applies.

$$\begin{vmatrix} \alpha_1 - E & \beta & -\beta & 0 \\ & \alpha_1 - E & 0 & -\beta \\ & & \alpha_1 - E & \beta \\ & & & \alpha_1 - E \end{vmatrix} = 0 \qquad (14)$$

This is reminiscent of a Hückel matrix of the π orbitals of cyclobutadiene (with two sign inversions). Indeed, if each configuration is taken to represent a vertex whose connectivity is the number of β interactions it has with other configurations, then we have four vertices, each with connectivity, 2. Therefore, the four charge-transfer configurations will spread like the π levels of cyclobutadiene, and the energies of the four states will become $\alpha_1 + 2\beta$, α_1 (two states), and $\alpha_1 - 2\beta$ in increasing order.

The interaction diagram is shown in Figure 2b, and there will be a corresponding diagram for the triplet configurations (with $\rho = 0.5$). The comparison of Figures 2a and 2b is almost self-explanatory. One aggregation isomer, this with the mixed stacks, D-A-D-A, leads to stabilization of the ground no-bond configuration, whereas the second aggregation isomer, the one with the segregated stacks, D-D||A-A, leads to the stabilization of a block of charge-transfer configurations with $\rho = 0.5$.

III. How Delocalized Is the $\rho = 0.5$ State of the D-D||A-A Isomer?

The representation of the $\rho = 0.5$ states in Figure 2b means a complete delocalization of the charges, such that the lowest state (ϕ_1 in Figure 2b) is the resonance hybrid:

$$D^{+0.5}D^{+0.5}||A^{-0.5}A^{-0.5} \qquad (15)$$

in which each addend is in its intermediate valence state ($\rho = 0.5$). One hidden assumption made there is that the block configurations are degenerate in any point in space and therefore the configurations interact via β and develop into the delocalized states. This is, of course, always true if D and A are just point molecules without any specific geometry. This is, however, not true in reality. Let us take, for example, the two acceptors in their $\rho = 0.5$ configurations: $A_1^-A_2^0$ and $A_1^0A_2^-$ (0 and - stand for charges). These two configurations are indeed degenerate but not in the same coordinate space! In fact, in the very geometries which correspond to relaxed A_1^- and A_2^0, the $A_1^0A_2^-$ configuration is higher in energy than the $A_1^-A_2^0$ configuration, and vice versa, because the equilibrium relaxed geometries of A^- and A^0 are always different. For example, the geometry of $TCNQ^0$ is quinoid whereas that of $TCNQ^-$ is benzenoid.[1b,2a]

The energies of $A_1^-A_2^0$ and $A_1^0A_2^-$ as a function of a relaxation coordinate are shown in Figure 3. C is a coordinate which describes the distortion of A_1 from the relaxed geometry of A^0 to that of A^-, and simultaneously the distortion of A_2 from the relaxed geometry of A^- to that of A^0. Therefore, when $C = 0$, $A_1^0A_2^-$ is the lowest energy configuration, and $A_1^-A_2^0$ lies higher (by ΔE) and is denoted by $(A_1^-A_2^0)^*$. As distortions begin $A_1^0A_2^-$ rises up in energy, while $(A_1^-A_2^0)^*$ descends. Eventually, the two curves cross one another and interchange in energy when C reaches its maximum value, d. *The crossing point of the two curves is the locus where the two configurations are degenerate in the same coordinate space.* Since the two configurations differ by one electron shift, they can interact via β, and the crossing of the two curves is avoided. This mixing leads to the formation of the truly delocalized intermediate valence state:

$$A_1^-A_2^0 \leftrightarrow A_1^0A_2^- \equiv A_1^{-0.5}A_2^{-0.5} \qquad (16)$$

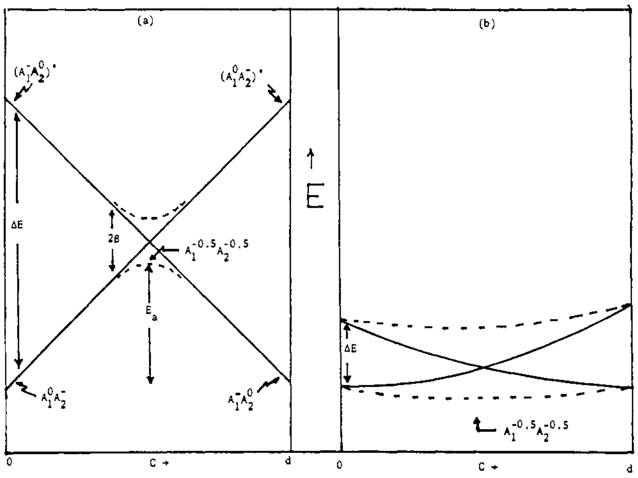

Figure 3. Avoided crossing (dashed lines) mechanism for the segregated-stacks isomer of $\rho = 0.5$, modeled by the acceptors. C is the coordinate which describes the distortion (from 0 to d) of a relaxed $A_1^0A_2^-$ to a relaxed $A_1^-A_2^0$. $(A_1^-A_2^0)^*$ and $(A_1^0A_2^-)^*$ are nonrelaxed configurations. $A_1^{-0.5}A_2^{-0.5}$ is the delocalized state. (a) $\Delta E >> \beta$. $A_1^{-0.5}A_2^{-0.5}$ is less stable than the localized configurations. E_a is the barrier for electron hopping. (b) ΔE is small. The delocalized state is as stable (or more so) as the localized configurations.

The exact same considerations apply to two donors, and their delocalized intermediate valence state will be obtained from an avoided crossing of $D_1^+D_2^0$ and $D_1^0D_2^+$.

Whether the delocalized state becomes available or not, depends on the relative size of the energy gap of the two configurations at $C = 0$ (ΔE), and the avoided crossing resonance integral $|\beta|$. Figures 3a and 3b describe two extreme cases. In the first case $\Delta E >> \beta$ and the resulting delocalized state, $A_1^{-0.5}A_2^{-0.5}$ is higher in energy than the two *localized* states $A_1^0A_2^-$ and $A_1^-A_2^0$. In this case, the configurations will remain localized and very weakly split (with energy $\sim\alpha_1$, eq 9), and *there will be a barrier for electron hopping as the system passes the point of curve crossing* (*Figure 3a*). When ΔE is quite small, the avoided crossing can stabilize the delocalized intermediate valence state which becomes accessible (Figure 3b). *Now an electron can migrate from one site to another* ($A_1 \rightarrow A_2$ and $D_1 \rightarrow D_2$) *without activation.*

As can be seen from Figure 3a, the activation barrier follows the general expression,

$$E_a = f(\Delta E) - |\beta| \qquad f < 1 \qquad (17)$$

where f is a parameter whose value depends on the relative slopes of the two intersecting curves. For small geometric differences (e.g., between A^0 and A^-), the curves can be approximated by parabolas[13] and one obtains the familiar expression from the Marcus theory of electron transfer with $f = 0.25$.[14] Thus, we

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(13) (a) The two potential curves E_1 and E_2 become:

$$E_1 = \frac{\omega}{2}C^2 \text{ and } E_2 = \frac{\omega}{2}C^2 - kC + \Delta E$$

ω is the frequency of the mode defining the reaction coordinate. kC is the linear term which is responsible for the relaxation of $(A_1^-A_2^0)^*$ to its equilibrium geometry at $C = d$. The barrier E_a is determined by the constraints $E_1(C = 0) = E_2(C = d) = 0$ and $\partial E_2/\partial C = 0$. (b) $\Delta E = d^2\omega/2$.

(14) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

have means for anticipating the absence or presence of a barrier for electron migration, as well as the variation in this barrier. Minimizing this barrier requires small ΔE and large $|\beta|$ and one can provide quite simple guidelines for achieving this purpose.

ΔE is proportional to the extent of geometric differences between the relaxed ionic state and the neutral state (e.g., A^- vs. A^0).[13b] The more extensive these differences, the larger ΔE.[15a]

The extent of geometric relaxation of A^- and D^+ away from the neutrals' geometry can be predicted, in many cases, from the properties of the frontier orbitals, LUMO(A) and HOMO(D) of the neutral molecules.[15b] As a rule of thumb, *whenever the products of the orbital coefficients on neighboring atoms (in the frontier orbitals) are small, the bonds' overlap population will change only slightly upon ionization, and hence minor geometric differences between the ion and the neutral are expected.* In such cases ΔE will be small, the barrier for electron migration will vanish (eq 17), and the state will be delocalized (eq 16).

An interesting application of this rule, for instance, is to try and select which of two acceptors (having the same electron affinity) will yield a better conducting $\rho = 0.5$ state with TTF. If the two acceptors are, for example, TCNQ and TCNE (tetracyanoethylene), then based on the above rule, one expects that TCNQ will achieve the intermediate valence state more easily than TCNE, and hence will couple with TTF to form a better conductor. This could be one reason why the TTF·TCNE complex is an insulator.[16]

Decreasing the barrier for electron migration can also be achieved by using addends which have large $|\beta|$. $|\beta|$ is proportional to the overlap of the orbitals which partake in the electron shift, e.g., the LUMO's of the acceptors (i.e., $\beta = \beta_{A_1A_2}$; see eq 11), and, hence, increasing these MO overlaps between successive addends along the stack will also increase $|\beta|$.

The structural data indicate that 3.2–3.5 Å is a typical distance between successive addends in a stack (in the segregated-stacks isomer). At these distances MO overlaps are very small ($|\beta| \approx$ 0.1 eV), and, therefore, the best way of increasing these overlaps is by using D's and A's substituted with heavy atoms which have high atomic overlaps even at these distances. This will increase $|\beta|$, will lower or erase the barrier for electron migration, and stabilize the delocalized intermediate valence state (eq 16). There is ample experimental evidence[2] showing the heavy-atom effect on conductivity in the organic metals family.

Another factor which is expected to affect the relative stabilities of the localized states (e.g., $D_1^+D_2^0A_1^-A_2^0$) and the intermediate valence state ($D^{+0.5}D^{+0.5}A^{-0.5}A^{-0.5}$) is the preferential stabilization of the localized state. For example, when the cation is small, or possesses a high charge density, the coulomb energy would prefer the localization of the negative charge on one anion. Such a situation was inferred for the complex salt $(Et_3NH)^+(TCNQ)_2^-$ where the $(TCNQ)_2^-$ unit was suspected to have a localized nature, $TCNQ^-TCNQ^0$, rather than be delocalized, $TCNQ^{-0.5}TCNQ^{-0.5}$.[1b] Despite earlier evidence to support this,[17a] later and more careful work showed that the $(TCNQ)_2^-$ supermolecular ion is delocalized.[17b,c] In the related complex salt $Cs_2(TCNQ)_3$, the localization has been proven unequivocally, and the $(TCNQ)_3^{2-}$ unit appears as a triad $TCNQ^-TCNQ^0TCNQ^-$, rather than $(TCNQ^{-2/3})_3$.[17d] Interestingly, all the complex salts of TCNQ exhibit barriers for conduction, ranging from 0.08 eV for ditoluenechromium$^+$-$(TCNQ)_2^-$, to 0.3 eV for $(CH_3PPh_3)^+(TCNQ)_2^-$.[2c]

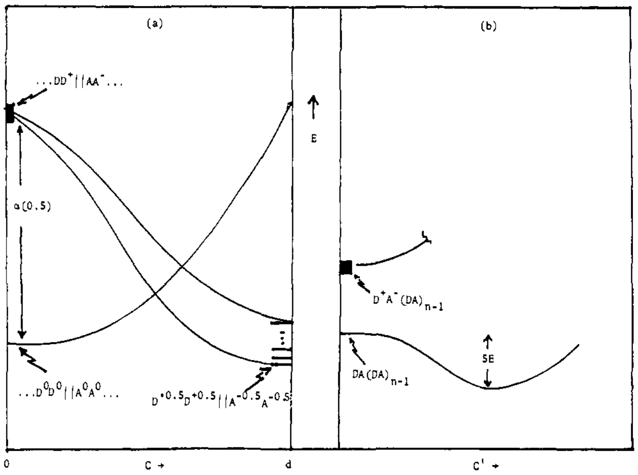

Figure 4. (a) Curve-band crossing model describing the formation of a $\rho = 0.5$ segregated-stacks isomer. C is the collective coordinate which describes the distortions of D^0's and A^0's to the geometries of $D^{+0.5}$'s and $A^{-0.5}$'s from 0 to the maximum value d. The block spreads into a band of charge-transfer states. The horizontal lines inside the band indicate discrete energy levels. (b) Stablization of the mixed-stacks isomer by interaction of the no-bond configuration $DA(DA)_{n-1}$ with the adjacent charge-transfer block, $D^+A^-(DA)_{n-1}$. SE is the stabilization energy. C' is a coordinate describing the D–A approach. The charge-transfer states are not shown explicitly.

In summary, the validity of the description of the $\rho = 0.5$ states of the segregated-stacks isomer (DD||AA) in Figure 2b depends very much on the identity of D and A. It will apply to molecules whose ionic states do not differ much in geometry from their neutral states, and molecules which can maintain large $|\beta|$ between them. But it may break down for cases where the ionic and the neutral states differ greatly in geometry, or in cases where either the cation or the anion have concentrated charges and hence prefer the localized states (e.g., $D^+D^0A^-A^0$) over the intermediate valence state ($D^{+0.5}D^{+0.5}A^{-0.5}A^{-0.5}$). In any event, the barrier (E_a, eq 17) is never expected to be large, and, therefore, *the $\rho = 0.5$ (and in general $\rho < 1$) state should be fluxional, having a dynamic nature with localized and delocalized appearances, depending on conditions such as temperature and pressure.*

States of $(D-A)_n$. As we increase the segment, the number of charge-transfer configurations in each block becomes overwhelming. For example, already for $(D-A)_6$ there are 2000 singlets, 3600 triplets, 2000 quintets, and 400 septets (eq 6) in the $\rho = 0.5$ block. Still the qualitative trends which were displayed by the small segment $(D-A)_2$ will carry over to larger aggregates.[18]

As in the small segment, the two aggregation isomers (eq 1 and 2) of $(D-A)_n$ will lead to stabilization of different states via the dichotomy of β_{DA} vs. β_{DD} and β_{AA} interactions (see Figures 2a vs. 2b). In the segregated-stacks isomer the configurations belonging to each block will interact among themselves in a pattern which is still based on the elementary topology of the Hückel cyclobutadiene unit.[18] In this manner, the various ρ blocks will spread into bands of delocalized charge-transfer states $\ldots D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho}\ldots$ (e.g., Figure 2b) with the largest spread occurring for the $\rho = 0.5$ block which possesses the largest number of configurations. As before, the stability of these delocalized states will depend on the size of $|\beta|$, and on the extent of geometric reorganization of D^+ and A^- relative to D and A (eq 17).

IV. Formation of the Segregated-Stacks Isomer

For moderate D–A pairs with $I_D - A_A \geq 4$ eV, the electrostatic energy seems to be insufficient to stabilize any charge-transfer block below the no-bond configuration,[7] and, hence, $\alpha(\rho) \geq 0$ (eq 9). How can one conceptualize then the formation of the ground state of the segregated-stacks isomer with $\rho \neq 0$?

Without yet attempting to account for the prospective value of ρ, we shall select the $\rho = 0.5$ block and follow up its energy,

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(15) ΔE can be estimated empirically as twice the difference between the adiabatic and vertical values of A_A (for the A's stack) or of I_D (for the D's stack). (b) There are cases where D^+ and A^- may lose the symmetry of their neutrals. In such cases the geometric relaxation is not determined from just the HOMO(D) and LUMO(A) properties. See, for example: Köppel, H.; Domcke, W.; Cederbaum, L. S.; von Niessen, W. *J. Chem. Phys.* **1978**, *69*, 4252.

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relative to the no-bond state, . . .$D^0D^0\|A^0A^0$. . .. At the coordinate space which corresponds to relaxed D^0 and A^0, the $\rho = 0.5$ block is an excited block, with $\alpha \geq 0$. At the coordinate space which corresponds to the relaxed geometries the $D^{+0.5}$ and $A^{-0.5}$, the $\rho = 0.5$ configurations are stabilized relative to the no-bond state, . . .$D^0D^0\|A^0A^0$. . ., which is destabilized by the *reorganization energy* needed to distort D^0 and A^0 to the relaxed geometries of $D^{+0.5}$ and $A^{-0.5}$, respectively. This effect can already place the $\rho = 0.5$ configurations near or below . . .$D^0D^0\|A^0A^0$. . ., depending on α (eq 9). Additional stabilization of the $\rho = 0.5$ block can be effected as the configurations are allowed to interact (see, however, Figure 3a) and spread as a band of charge-transfer states. Eventually, the lower states of the $\rho = 0.5$ block cross the no-bond state, . . .$D^0D^0\|A^0A^0$. . ., and thus, the excited state becomes a ground state for the organic metal, by means of a curve-band crossing, which is described in Figure 4a. In solution, the solvent is expected to play a significant role in facilitating this curve-band crossing[19] by fortifying the ionic state (e.g., $\rho = 0.5$) and thereby lowering the barrier to its formation. Therefore, one expects to encounter significant solvent effect on the formation of segregated-stacks materials and on their ρ value.

The so-formed charge-transfer state could correspond to an endothermic macrospecies relative to the van der Waals no-bond state (prior to crossing). Or, it may be an exothermic macrospecies, if $\alpha(\rho)$ is small enough or zero. For TTF·TCNQ, Metzger[20] found experimentally that the organic metal ($\rho \approx 0.5$) is $\sim$8.9 ± 1 kcal/mol more stable than the separate crystalline neutral TTF and TCNQ. We can take the $I_D - A_A$ value for this complex ($\sim$4 eV) as a limit beyond which the $\rho \neq 0$ state . . .$D^{+\rho}D^{+\rho}\|A^{-\rho}A^{-\rho}$. . . would correspond to a thermoneutral or to an endothermic macrospecies. Thus, complexes of TTF or TSF with worse acceptors than TCNQ may be athermic or endothermic species.

For the same D–A pair of Figure 4a there exists another option: the formation of the mixed-stacks isomer. Now β_{DA} is "turned on" and the no-bond configuration . . .$D^0A^0D^0A^0$. . . is stabilized by interacting with the charge-transfer blocks, as shown in Figure 4b. Stabilization energies of mixed-stacks charge-transfer complexes with $I_D - A_A \approx 4$ eV are in the range of a few kcal/mol[1], close to the value obtained by Metzger[20] for the segregated-stacks complex TTF·TCNQ. Therefore, we conclude (Figures 4a and 4b) that for the class of D and A with moderate donor and acceptor abilities ($I_D - A_A \approx 4$ eV), the mixed-stacks isomer . . .D-A-D-A. . . should be of comparable thermodynamic stability to the segregated-stacks organic metal isomer, *and that there is a range of* $(I_D - A_A) \geq 4$ eV, *where the electricity transporting material is not the thermodynamically most stable isomer.*[21]

There is some evidence which points to the instability of the segregated-stacks isomers. Most of the evidence is as yet suggestive rather than compelling. For example, as was noted by Perlstein,[2a] some of the conducting materials such as TMTSF·TCNQ[22] and 3,3-diethylthiacyanine(TCNQ)$_2$[23] were obtained by nonequilibrium recrystallization. Strzelecka et al.[24] are quite explicit and state that in order to obtain conducting phases one must apply conditions of kinetic control, rather than those of thermodynamic control. Torrance et al.[6a] suggest that the formation of the segregated-stacks isomer might occur by default.

Another type of suggestive evidence is the prevalent polymorphism[2] which is reported for D–A adducts and the fact that there is no clear divider which determines the distribution of the D–A pairs between the two aggregation isomers. The two isomers can be found for D–A pairs with very similar $I_D - A_A$ values.[2,25]

Firmer evidence exists for the complexes of TCNQ, with TMPD (tetramethylphenylenediamine) and NMP (*N*-methylphenazine). Thus, TCNQ and TMPD form the two aggregation isomers,[26] but with different stoichiometries (1:1 and 2:1). NMP·TCNQ crystallizes also in the two forms. One, the segregated-stacks isomer, is a metallic conductor, and the other, the mixed-stacks isomer, is an insulator.[27] However, it seems that the nonconducting material contains protonated NMP units.[27c]

The best evidence, probably, exists for the complexes of tetrahalo-*p*-benzoquinone with TTF and TMTTF, some of which are reported[28] to form the conducting partially ionic segregated-stacks isomer as well as the neutral mixed-stacks isomer in 1:1 D–A ratio. These last cases show that even when the orbital symmetries of HOMO(D) and LUMO(A) mismatch, D and A (e.g., TTF and fluoranil) can stack up in such an orientation which preserves β_{DA} and stabilizes the mixed-stacks isomer. Thus, the two isomers may coexist in any event, and if one wishes to ensure efficient synthesis of organic metals, *one must design molecules where the segregation of the stacks is built in.*

An interesting structural modification in the segregated-stacks isomer is its tendency toward two-dimensionality. This featue is related to the competition between the two modes of aggregation. Since the various ρ blocks are expected to be close in energy in the region of crossing (Figure 4a), the interblock interactions via β_{DA} (review Figures 1 and 2) can compete with the intrablock interactions (via β_{DD} and β_{AA}), and the crystalline state can be stabilized in an arrangement which maximizes the β_{DD} and β_{AA} interactions and simultaneously affords β_{DA} interactions. This will lead to a formation of a two-dimensional structure where the stack of the D's and that of the A's now interact. Such behavior has been reported for TTF·TCNQ and TSF·TCNQ as temperature is lowered[29a] to $\sim$38 and 28.5 K, respectively. On the other hand, HMTSF·TCNQ[29b] exhibits two-dimensional structure at room temperature. Thus, the HMTSF·TCNQ organic metal can be thought of as being caught in the process of attempting the macroscopic transformation . . .D-D||A-A. . . → . . .D-A-D-A. . ..

ρ Value of the Ground State of an Organic Metal. What determines which ρ block first crosses the no-bond state and becomes the ground state of the organic metal?

Based on the model of the curve-band crossing in Figure 4a we propose that (in a given solvent) ρ is determined by the combined influences of the energy gap $\alpha(\rho)$ and the reorganization energy needed to distort D^0 and A^0 to the relaxed geometries of $D^{+\rho}$ and $A^{-\rho}$. The energy gap (eq 9) which is dominated by $(I_D - A_A)$ tends to favor crossing of blocks with small ρ, while the distortion effect favors the crossing of the largest ρ block. This competition results in a compromise, which is the crossing of a block having some intermediate ρ value. Thus, the ρ value of the ground state of an organic metal should not necessarily correlate with the $I_D - A_A$ value of the D–A pair, as is indeed shown by the experimental data.[8] As a rule of thumb, the combination of low $I_D - A_A$ and extensive geometric reorganization (of D^+ and

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(21) For D–A pairs with $\alpha(\rho) < 0$ (i.e., ionic cases), the electrostatic energy is usually expected to favor the mixed-stacks isomer (see ref 7a,b). When the electrostatic energy is comparable for the two isomers, the configuration interaction will determine their relative stability. This will be comparable unless orbital symmetry mismatch (between HOMO(D) and LUMO(A)) tips the balance in favor of the segregated-stacks isomers, as may be in the case of TTF·TCNQF$_n$ (n = 1, 2). See: Saito, G.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1979**, 1027–9.

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A^-) are expected to lead to a high ρ value.

Conclusions

We have described here a theoretical framework which provides some guidelines for designing conducting D–A complexes, and which forms a basis for future studies of specific case. Our conclusions follow.

(a) We propose that for many of the segregated-stacks organic metals there should in principle exist a thermodynamically more or as stable mixed-stacks form. In this, we are in sympathy with the spirit of section 9 in Perlstein's excellent article.[2a] Thus, to ensure the formation of segregated-stacks materials, for any D–A pair, one must design molecules where the segregation is built in.

(b) The two-dimensionality is one way of stabilizing the conducting isomer which now "feels" some of the interactions of a mixed-stacks isomer.

(c) The value of ρ of the segregated-stacks isomer depends on the combined effects of $I_D - A_A$, and the extent of geometric reorganization of the ions D^+ and A^-. This interplay merits further studies.

(d) This $\rho \neq 0$ state of the segregated-stacks isomer can lie anywhere from an endothermic to an exothermic species with respect to the neutral . . .$D^0D^0||A^0A^0$. . . relaxed state. D–A pairs with $I_D - A_A \geq 4$ eV are expected to be at the limit of thermoneutrality and may exhibit reversible . . .$D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho} \rightarrow$ . . .$D^0D^0||A^0A^0$. . . transitions, with a barrier of $\sim{}^1/_4\alpha(\rho)$ (eq 9).

(e) The $\rho \neq 0$ configurations of the segregated-stacks isomer can develop into a band of delocalized charge-transfer states *in a manner which resembles the interactions and the level spread in Hückel systems.* This treatment can be used to study other similar systems[9] such as complex salts (e.g., Cs_2TCNQ_3).

(f) The delocalized intermediate valence states of the segregated-stacks isomer, . . .$D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho}$, may be less stable than a collection of localized states. This leads to a small barrier for electron hopping (Figure 3a). In the macroscopic stacks, the variants of the elementary instability (Figure 3a) increase. For example, in the $\rho = 0.5$ state, there will be a tendency for localization of dimers (e.g., . . .$A^{-0.5}A^{-0.5}A^-A^0$. . .) or of tetramers (e.g., . . .$A^-A^0A^-A^0$. . .) etc. Minimization of this barrier can be achieved by selecting D's and A's which can maintain large intra-stack overlap (large β_{DD} and β_{AA}), and whose ionic states D^+ and A^- involve only small geometric reorganization.

Application to specific systems will be treated in future papers.

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Photoelectron Spectroscopic Studies of the Intermolecular Complexes $(CH_3)_2O\cdot HF$ and $(CH_3)_2S\cdot HF$

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Abstract: The He I photoelectron spectra of the gas-phase complexes formed by dimethyl ether and dimethyl sulfide with hydrogen fluoride have been measured by using a pinhole inlet system with high-pressure equilibrium mixtures of the respective gases. Spectra representing each complex in a "pure" form are obtained by a spectrum-stripping procedure which removes the appropriate monomer spectra from each mixed spectrum. The results of molecular orbital calculations show good agreement with the measured ionization potential shifts occurring on complexation. The data show that the intermolecular hydrogen bond stabilizes the nonbonding electrons of n_O in $(CH_3)_2O$ by 1.0 eV and the nonbonding electrons of n_S in $(CH_3)_2S$ by 0.8 eV. This is found to be mainly due to the electrostatic effect of the polar HF moiety which has a greater influence in the stronger complex. By comparison the apparent destabilization of the nonbonding π_F electrons by 1.6 eV in $(CH_3)_2O\cdot HF$ and 1.2 eV in $(CH_3)_2S\cdot HF$ is also influenced by charge transfer and the relaxation effect of electron rearrangement accompanying ionization.

Ultraviolet photoelectron (PE) spectroscopy has recently been applied to the study of gas-phase intermolecular complexes. While relatively strong complexes had been studied earlier by Lloyd and Lynaugh[1] and by Lake[2] using the normal low vapor pressure regime of the typical PE spectrometer, the study of weaker complexes has required the use of effusive nozzle inlet systems,[3,4] as well as supersonic molecular beam techniques.[5]

In recent studies in this laboratory the He I spectra of some carboxylic acid dimers[6,7] and the dimethyl ether–hydrogen chloride complex[8] have been measured. The technique used in this latter study has been utilized in obtaining the He I spectra of the related complexes $(CH_3)_2O\cdot HF$ and $(CH_3)_2S\cdot HF$ that are reported in this paper.

The gas-phase heterodimer of $(CH_3)_2O$ and HF has been detected in infrared spectroscopic studies.[9–11] The complex has been found to have a hydrogen bond energy (ΔH) of 43 kJ mol^{-1}, and the intermolecular hydrogen bond vibration has been identified at 170 cm^{-1}. These studies show that higher cluster species other than the 1:1 complex exist in negligible concentrations in mixtures containing an excess of $(CH_3)_2O$.

The same studies have shown indications of hydrogen bonding in mixtures of $(CH_3)_2S$ and HF, though investigation of the complex is less complete.[9] This is not surprising in view of the

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