196

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Interaction Frontier Orbitals

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Electron delocalization is known to be a major driving force of chemical reactions, yielding accumulation of the electron density in the intermolecular region between the reaction sites.[1,2] Frontier orbitals often play dominant roles,[3,4] but other molecular orbitals (MO's) also show subtle effects,[2,5,6] especially in large molecular systems. We report here that a pair of transformations of the canonical MO's of the fragments in a composite reacting system give rise to presumably the most succinct description of the delocalization interaction, including the contributions of all the relevant MO's.

Let the interaction between the occupied MO ϕ_i ($i = 1, 2, \ldots, s$) of the donor fragment and the unoccupied MO ψ_l ($l = 1, 2, \ldots, t$) of the acceptor fragment be denoted by D_{il}.[7] The "delocalization energy matrix" **D** comprising the elements D_{il} is rectangular, in general, of order $s \times t$, and, hence, one may construct the product $\mathbf{D}^\dagger \mathbf{D}$. This matrix is Hermitian and, therefore, can be diagonalized by a unitary transformation $\mathbf{V} = (V_{ij})$, giving the nonnegative eigenvalues $\Lambda = (\lambda_i)$:

$$\mathbf{D}^\dagger \mathbf{D} \mathbf{V} = \mathbf{V} \Lambda \qquad (1)$$

Assuming here that $s \leq t$ and that λ_i's are not zero for $i = 1, 2, \ldots, s$,[8,9] the following two sets of transformations convert the canonical MO's into a set of paired molecular hybrids of the fragments:

$$\phi_i' = \lambda_i^{-1/2} \sum_{j=1}^{s} \sum_{k=1}^{t} D_{jk} V_{ki} \phi_j \qquad (i = 1, 2, \ldots, s) \qquad (2)$$

and

$$\psi_l' = \sum_{k=1}^{t} V_{kl} \psi_k \qquad (l = 1, 2, \ldots, t) \qquad (3)$$

Unlike the corresponding orbitals by Amos and Hall,[10] one has to repeat the transformations by evaluating the matrix elements D_{il}' for the new set of orbitals to complete the true "pairing" of orbitals.[11] Upon convergence one gets $D_{ii}' = -\lambda_i^{1/2}$ and $\sum_{i=1}^{s} \sum_{l=1}^{t} D_{il} = \sum_{i=1}^{s} D_{ii}'$.[12] That is, the hybrid orbital ϕ_i' interacts only with the counterpart ψ_i' and vice versa and the interactions between the canonical MO's, $s \times t$ in number, are reduced to the interactions of, at the most, the s pairs of hybrids, s being the smaller of the number of the occupied MO's and the number of the unoccupied MO's participating in the interaction.

The square root of the eigenvalue λ_i' represents the strength of the interaction between ϕ_i' and ψ_i'. The largest one grows steadily during the iterations and the corresponding hybrid gains amplitude in the region of the interaction in each fragment.[13] Incidentally, one may carry out similar transformations with

a

b

Figure 1. The lone-pair orbitals of (a) ammonia and (b) methylamine participating in the electron donation to proton.

Figure 2. Lone-pair orbital of pyrazine taking part in the electron donation to proton.

regard to the combination of the unoccupied MO's of the donor and the occupied MO's of the acceptor. The new orbitals ϕ' and ψ' obtained each constitute an orthonormal set, retaining the electronic structures of the fragments unchanged.

The following ab initio STO-6G MO calculations provide examples to illustrate the foregoing argument.[14] By placing a proton, for simplicity, on the C_3 axis of ammonia 1.03 Å away from the nitrogen atom, we got a single hybrid taking part in the delocalization interaction, as shown in Figure 1.[15] Of the remaining four occupied orbitals, one constitutes the inner shell and the other three are localized in the N–H bond regions and have zero matrix elements in **D** with the proton 1s orbital. The hybrid is shown to be of stronger p character than the lone-pair hybrid calculated by the Edmiston–Ruedenberg procedure.[16] These results suggest that the lone-pair orbital having the large s component stabilizes the molecule in an isolated state, but it has to enhance the p nature in order to create the new N–H bond in ammonium ion. The lone-pair hybrid of methylamine calculated similarly is seen to have almost the same shape as that of ammonia.

Figure 2 shows the lone-pair orbital of pyrazine, participating exclusively in the delocalization interaction with a proton located 1.03 Å away from the N_1 atom on the C_2 axis. It is given approximately by a 1:1 mixture of the $6a_1$ (the highest occupied) MO and the $5b_{2u}$ (the next highest occupied) MO with concom-

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(8) If $s \geq t$, the transformations given by eq 2 and 3 are interchanged.

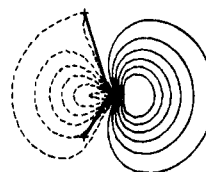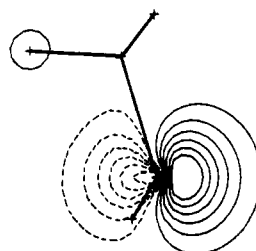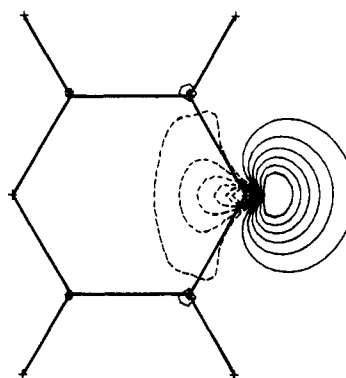(9) The treatment of zero eigenvalues is trivial.

(10) Amos, A. T.; Hall, G. G. *Proc. R. Soc. London, Ser. A* **1961**, *263*, 483.

(11) Lödwin, P.-O. *J. Appl. Phys. Suppl.* **1962**, *33*, 251.

(12) Prime is used to distinguish the molecular hybrids from the canonical MO's.

(13) In BH₃–NH₃, for example, two pairs of hybrids with the a_1 symmetry take part in the electron donation from NH₃ to BH₃. The ratio of $\lambda'^{1/2}$ was found to be about 1:10⁻⁴.

(14) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. GAUSSIAN 70, Program No. 236, QCPE, Indiana University, Bloomington, IN.

(15) The hybrid determined in this manner depends more or less on the kind of reagent and on the geometry of mutual approach.

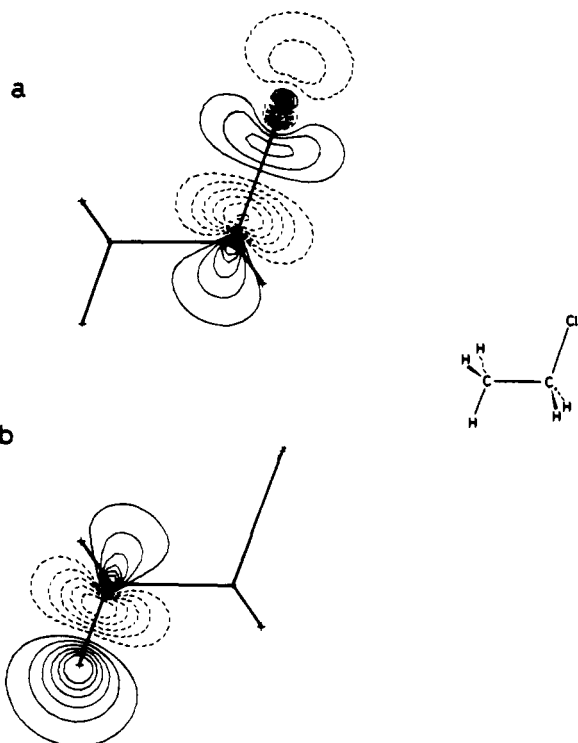(16) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457.

Figure 3. Unoccupied molecular hybrids of ethyl chloride participating in the delocalization interactions with hydride ion. (a) S_N2 and (b) E2.

itant mixing in of the lower-lying occupied MO's. The in-phase combination of these delocalized MO's at N_1 causes the resultant orbital to be localized almost perfectly on the site under attack. The orbital is of stronger s character relative to the lone-pair hybrid of ammonia.

Molecular hybrids of ethyl chloride are presented in Figure 3. They were calculated by placing a hydride ion on the C_α–Cl bond axis (in the S_N2 type model) and the C_β–H bond axis (in the E2 type model) at a distance which is 1.5 times the normal C–H and H–H bond lengths, away from C_α and H_β, respectively. The remaining six unoccupied orbitals have greatest amplitudes in other bond regions and do not contribute to the delocalization interaction in each case. The results of calculation suggest that the inversion at C_α in the S_N2 reaction and the breaking of the C_α–Cl bond in the E2 reaction should be ascribed to other sorts of interactions, probably to the exchange and polarization interactions.[5,6]

It was shown above that the one-electron orbitals participating virtually in the delocalization interaction are localized surprisingly well in the region of initial attacks. The stronger the localization is, the greater the delocalization stabilization would be. The present method will be of use to clarify the outcome of the delocalization interaction, particularly in the interactions of large systems with small reagents. A pair of hybrids, having the amplified lobes around the frontier of interaction, are determined with regard to each symmetry element of the composite reacting system.

On CNDO/2-Predicted Charge Alternation

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Much attention has been given the CNDO/2 prediction of alternation of induced charge in saturated molecules.[1] The

$$\begin{array}{cccc} \delta- & \delta+ & \delta\delta- & \delta\delta\delta+ \\ \text{F} & \text{C} & \text{C} & \text{C} \end{array}$$

$$\begin{array}{cccc} \delta- & \delta+ & \delta\delta+ & \delta\delta\delta+ \\ \text{F} & \text{C} & \text{C} & \text{C} \end{array}$$

Classical

Figure 1. Calculated induced charges.

Table I. Comparison of the $e \rightleftarrows a$ Conformational Free Energy Difference, ΔG°, for **1** and **2** in $FCCl_3$

compound[a]	method	T, °C	ΔG°, kcal/mol
1	¹H integration	−124	−0.37 ± 0.05
1-2,2,6,6-d_4	¹H integration	−125	−0.37 ± 0.04
1	¹⁹F integration	−124	−0.41 ± 0.08
1-2,2,6,6-d_4	¹H bandwidth[b]	−124	−0.42 ± 0.10[c]
2	¹H integration	−86	−0.50 ± 0.03
2-2,2,6,6-d_4	¹H bandwidth[b]	−86	−0.52 ± 0.07[c]

[a] Deuterium substitution (2,2,6,6-d_4) has no measurable influence upon ΔG° but makes bandwidth measurement more accurate by eliminating long-range proton–proton coupling. [b] Extrapolated to −124 °C from a range of −35 to +66 °C. [c] 1% confidence limits. [d] Extrapolated to −86 °C from a range of −36 to +69 °C.

CNDO/2 and the classical model[2] of the inductive effect are shown in Figure 1. Some experimental data have been interpreted as being consistent with alternation of induced charge[3] while other data have been interpreted as being inconsistent.[4] In order to provide a critical experimental test for the existence of induced-charge alternation, we studied the effect upon conformational enthalpies of net electrostatic interactions among induced charges. We report here the results of an experimental evaluation of the electrostatic component of the enthalpy difference between the two chair conformations of 4-chloro-1,1-bis(trifluoromethyl)-cyclohexane (**1**).[5] The results are compared with those for 4-chloro-1,1-difluorocyclohexane (**2**).[6,7] Our results are not consistent with charge alternation.
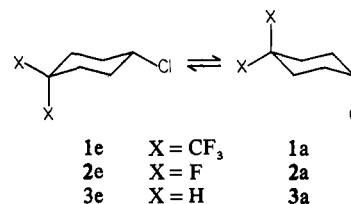
	X = CF₃	
1e	X = CF_3	**1a**
2e	X = F	**2a**
3e	X = H	**3a**

For the equilibrium **1e** $\rightleftarrows$ **1a**, the electrostatic component of the conformational enthalpy change, ΔH_e, is given by eq 1.[8] A

$$\Delta H_e^\circ(1) = \Delta H^\circ(1) - \Delta H^\circ(3) \qquad (1)$$

similar relationship for the equilibrium **2e** $\rightleftarrows$ **2a** is given by eq 2. The conformational enthalpy change for chlorocyclohexane

$$\Delta H_e^\circ(2) = \Delta H^\circ(2) - \Delta H^\circ(3) \qquad (2)$$

(**3**) is taken from the literature[9] [$\Delta H^\circ(3) = +0.45 \pm 0.005$

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