

in two steps (61%); (1) vinylmagnesium bromide addition
(2) pyridinium chlorochromate oxidation; J. H. Babler,
B. J. Invergo and S. J. Sarussi, *J. Org. Chem.*, **45**, 4241

(1980).

(8) (Z)-7-Eicosen-11-one prepared by this method was
proved biologically active by its field tests in South Korea.

PMO Theory of $\pi^*-\pi^*$ Interaction

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Recently chemical as well as physical consequences of $\pi^*-\pi^*$ orbital interaction have been demonstrated¹. Direct experimental examination of such orbital interaction has been practicable using electron transmission spectroscopy (ETS)^{1b,2}. Two important, yet unaccounted-for, features of the experimental results on $\pi^*-\pi^*$ orbital interactions through 2 and 4 C-C σ bonds ($N=2$ and 4) of the connecting σ framework² were: (i) level splitting (ΔE) of the symmetry adapted orbitals (SAO), π_+^* and π_-^* , is considerably greater than that for the corresponding $\pi-\pi$ interactions, and (ii) the average level (ε_{av}) of the two SAO is above the basis level (ε_0), the π^* level for monoene.

In this work we will show that these features are the results of enhanced effect of through-space interaction (TSI) in the $\pi^*-\pi^*$ interaction compared with that in the $\pi-\pi$ interaction.

To second-order in overlap S , the levels ε_+ and ε_- of the SAO, π_+ and π_- , (or n_+ and n_-) had the expressions (1a) and (1b) for N =odd and even systems respectively³.

$$\left. \begin{aligned} \varepsilon_+ &\cong e' - \delta e_l + 2y(1 + \alpha + \beta) \\ \varepsilon_- &\cong e' + \delta e_h - 2x(1 + \alpha - \beta) \end{aligned} \right\} \quad (1a)$$

$$\left. \begin{aligned} \varepsilon_+ &\cong e' - \delta e_l - 2x(1 + \alpha - \beta) \\ \varepsilon_- &\cong e' + \delta e_h + 2y(1 + \alpha + \beta) \end{aligned} \right\} \quad (1b)$$

where e' , which is negative, is the environment adjusted level of the basis level, δe_l and δe_h are depression and elevation of e' due to TSI, and x , y , α and β are positive quantities defined as:

$$x = \frac{\langle \pi | H' | \Psi_{LU}^0 \rangle^2}{\Delta e}, \quad y = \frac{\langle \pi | H' | \Psi_{HO}^0 \rangle^2}{\Delta e},$$

$$\alpha = \left| \frac{e''}{\Delta e} \right|^2 + \left| \frac{e'''}{\Delta e} \right|^4 + \dots, \text{ and}$$

$$\beta = \left| \frac{e''}{\Delta e} \right| + \left| \frac{e'''}{\Delta e} \right|^3 + \dots^{3,4}.$$

Equations (1a) and (1b) clearly indicate that the effects of second-order perturbation (through-bond interaction (TBI)) is to elevate one of the SAO (π_+ and π_- for N =odd and even cases respectively) substantially but to depress the other by a small amount. These are natural consequences of narrow (wide) energy gaps involved in the interactions of π_{\pm} with the framework HO- σ (LU- σ^*) orbitals. The depression effect on a SAO has been shown to be small

but by no means negligible⁵, as expected from eq(1), since $(\beta - \alpha) < 1.0^3$.

In $\pi^*-\pi^*$ orbital interactions, the environment adjusted level of the basis orbital, e^* , should be approximately equal to the π^* level of ethylene since there will be no first-order (electrostatic) interaction between an empty π^* orbital and a neutral molecule. The basis level is therefore given as

$$\varepsilon_0 \cong e^* - x(1 + \alpha + \beta) + y(1 + \alpha - \beta) \quad (2)$$

where $e^* \cong e_{\pi}$, (ethylene) > 0 and x , y , α and β are positive quantities similarly defined as above. It is evident from eq (2) that the basis level is somewhat depressed relative to the ethylenic π^* level since the second-order effect is to depress (by an amount $x(1 + \alpha + \beta)$) more than to elevate (by an amount $y(1 + \alpha - \beta)$) the level e^* . This is in accord with the experimental results² (see Table).

The environment adjusted levels e_+ and e_- for the SAO, π_+^* and π_-^* , are obtained using the usual approximation, $H_{mn} \cong -kS_{mn}^3$, where k is a positive constant.

$$\left. \begin{aligned} e_+ &\cong e^* + \langle \pi_+^* | H' | \pi_+^* \rangle \cong e^* - \delta e_l \\ e_- &\cong e^* + \langle \pi_-^* | H' | \pi_-^* \rangle \cong e^* + \delta e_h \end{aligned} \right\} \quad (3)$$

where $\delta e_l \cong kS(1 - S)$ and $\delta e_h \cong kS(1 + S)$. The level splitting, ΔE_S , and energy destabilization, $\delta \varepsilon_S$, as a result of TSI are thus given as,

$$\Delta E_S = e_- - e_+ = \delta e_l + \delta e_h \cong 2kS \quad (4)$$

$$\delta \varepsilon_S = \delta e_h - \delta e_l \cong 2kS^2 \quad (5)$$

The corresponding ones for $\pi-\pi$ TSI are³: $\Delta E_S(\pi) \cong 2S(k + e_1)$ and $\delta \varepsilon_S \cong 2(k + e_1)S^2$ where e_1 is the first-order level depression of π orbital, $e_1 < 0$. Hence $\Delta E_S(\pi^*)$ and $\delta \varepsilon_S(\pi^*)$ should be larger (positive quantities) than $\Delta E_S(\pi)$ and $\delta \varepsilon_S(\pi)$ respectively.





Inclusion of second-order (TBI) terms gives the final expressions (6a) and (6b) for N =odd and even cases respectively.

$$\left. \begin{aligned} \varepsilon_+ &\cong e^* - \delta e_l + 2y(1 + \alpha - \beta) \\ \varepsilon_- &\cong e^* + \delta e_h - 2x(1 + \alpha + \beta) \end{aligned} \right\} \quad (6a)$$

$$\left. \begin{aligned} \varepsilon_+ &\cong e^* - \delta e_l - 2x(1 + \alpha + \beta) \\ \varepsilon_- &\cong e^* + \delta e_h + 2y(1 + \alpha - \beta) \end{aligned} \right\} \quad (6b)$$

Thus in $\pi^*-\pi^*$ TBI, one of the SAO (π_+^* and π_-^* for N

TABLE 1: Experimental Results from Photoelectron and Electron Transmission² Spectroscopies (energies in eV)

Compound	$\bar{\nu}$	ΔE (π_{\pm})	$\delta\epsilon$ (π_{\pm})	$\bar{\nu}^*$	ΔE (π_{\pm}^*)	$\delta\epsilon$ (π_{\pm}^*)
Ethylene	-10.51			1.78		
	-8.97			1.70		
		0.86	-0.15		1.52	0.10
	-8.60			1.68		
		1.26	-0.47		1.45	0.10

=odd and even cases respectively) is substantially depressed (by an amount $2x(1+\alpha+\beta)$) while the other is elevated (by a small amount $2y(1+\alpha-\beta)$). These are of course natural consequences of the narrow (wide) energy gaps involved in the interactions of π_{\pm}^* with the framework LU- σ^* (HO- σ) orbitals. The overall splitting ΔE and energy change $\delta\epsilon$ are given as,

$$\begin{aligned} \Delta E_{\text{odd}} &= \epsilon_- - \epsilon_+ \cong \Delta E_S - 2\{(1+\alpha)(x-y) + \beta(x+y)\} \\ &= \Delta E_S - \Delta E_b \end{aligned} \quad (7a)$$

$$\Delta E_{\text{even}} = \Delta E_S + \Delta E_b \quad (7b)$$

$$\delta\epsilon = \epsilon_{av} - \epsilon_0 = \delta\epsilon_S > 0 \quad (8)$$

These expressions are exactly the same as the corresponding ones for π - π interactions³. However since ΔE_S is shown to be considerably greater for π^* - π^* TSI compared with π - π TSI, ΔE_{even} (π^*) will be greater, while ΔE_{odd} (π^*) will be smaller than the corresponding values of $\Delta E(\pi)$ for systems in which TSI is not negligible. This is confirmed

by the ETS results² (Table 1) on systems with $N=2$ and 4. ETS data on $N=3$ system with the possibility of TSI will provide a further test for the validity of our PMO approach to orbital interactions. Overall destabilization, $\delta\epsilon > 0$, of π^* - π^* intersessions with non-negligible TSI is also borne out by the ETS results² (Table 1). Finally we should add that level orderings expected from considerations of eq (7) were all found to be consistent with experimental² as well as theoretical results⁶.

We are grateful to the Ministry of Education and the Korea Research Center for Theoretical Physics and Chemistry for support of this work.

References

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- (4) Other notations are: Δe = half-width of framework frontier σ MO gap and $e'' = e' - \delta e$ where δe is the elevation of framework σ FMO's due to environment adjustment. It has been shown that $(\beta - \alpha) < 1.0^3$.
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