

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 demonstrated<sup>1</sup>. Direct experimental examination of such orbital interaction has been practicable using electron transmission spectroscopy (ETS)<sup>1b,2</sup>. Two important, yet unaccounted-for, features of the experimental results on  $\pi^*-\pi^*$  orbital interactions through 2 and 4 C-C  $\sigma$  bonds ( $N=2$  and 4) of the connecting  $\sigma$  framework<sup>2</sup> were: (i) level splitting ( $\Delta E$ ) of the symmetry adapted orbitals (SAO),  $\pi_+^*$  and  $\pi_-^*$ , is considerably greater than that for the corresponding  $\pi-\pi$  interactions, and (ii) the average level ( $\epsilon_{av}$ ) of the two SAO is above the basis level ( $\epsilon_0$ ), the  $\pi^*$  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  $\epsilon_+$  and  $\epsilon_-$  of the SAO,  $\pi_+$  and  $\pi_-$ , (or  $n_+$  and  $n_-$ ) had the expressions (1a) and (1b) for  $N$ =odd and even systems respectively<sup>3</sup>.

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

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

where  $e'$ , which is negative, is the environment adjusted level of the basis level,  $\delta e_l$  and  $\delta e_h$  are depression and elevation of  $e'$  due to TSI, and  $x$ ,  $y$ ,  $\alpha$  and  $\beta$  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 ( $\pi_+$  and  $\pi_-$  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  $\pi_\pm$  with the framework HO- $\sigma$  (LU- $\sigma^*$ ) orbitals. The depression effect on a SAO has been shown to be small

but by no means negligible<sup>5</sup>, 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  $\pi^*$  level of ethylene since there will be no first-order (electrostatic) interaction between an empty  $\pi^*$  orbital and a neutral molecule. The basis level is therefore given as

$$\epsilon_0 \cong e^* - x(1 + \alpha + \beta) + y(1 + \alpha - \beta) \quad (2)$$

where  $e^* \cong e_c$  (ethylene)  $> 0$  and  $x$ ,  $y$ ,  $\alpha$  and  $\beta$  are positive quantities similarly defined as above. It is evident from eq (2) that the basis level is somewhat depressed relative to the ethylenic  $\pi^*$  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 results<sup>2</sup> (see Table).

The environment adjusted levels  $e_+$  and  $e_-$  for the SAO,  $\pi_+^*$  and  $\pi_-^*$ , 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,  $\Delta E_S$ , and energy destabilization,  $\delta \epsilon_S$ , as a result of TSI are thus given as,

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

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

The corresponding ones for  $\pi-\pi$  TSI are<sup>3</sup>:  $\Delta E_S(\pi) \cong 2S(k + e_1)$  and  $\delta \epsilon_S \cong 2(k + e_1)S^2$  where  $e_1$  is the first-order level depression of  $\pi$  orbital,  $e_1 < 0$ . Hence  $\Delta E_S(\pi^*)$  and  $\delta \epsilon_S(\pi^*)$  should be larger (positive quantities) than  $\Delta E_S(\pi)$  and  $\delta \epsilon_S(\pi)$  respectively.





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

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

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

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

TABLE 1: Experimental Results from Photoelectron and Electron Transmission<sup>2</sup> Spectroscopies (energies in eV)

| Compound  | $\bar{\pi}$ | $\Delta E$<br>( $\pi_{\pm}$ ) | $\delta\epsilon$<br>( $\pi_{\pm}$ ) | $\bar{\pi}^*$ | $\Delta E$<br>( $\pi_{\pm}^*$ ) | $\delta\epsilon$<br>( $\pi_{\pm}^*$ ) |
|---|-------------|-------------------------------|-------------------------------------|---------------|---------------------------------|---------------------------------------|
| 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  $\pi_{\pm}^*$  with the framework LU- $\sigma^*$  (HO- $\sigma$ ) orbitals. The overall splitting  $\Delta E$  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  $\pi$ - $\pi$  interactions<sup>3</sup>. However since  $\Delta E_S$  is shown to be considerably greater for  $\pi^*$ - $\pi^*$  TSI compared with  $\pi$ - $\pi$  TSI,  $\Delta E_{\text{even}}$  ( $\pi^*$ ) will be greater, while  $\Delta E_{\text{odd}}$  ( $\pi^*$ ) 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 results<sup>2</sup> (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  $\pi^*$ - $\pi^*$  intersessions with non-negligible TSI is also borne out by the ETS results<sup>2</sup> (Table 1). Finally we should add that level orderings expected from considerations of eq (7) were all found to be consistent with experimental<sup>2</sup> as well as theoretical results<sup>6</sup>.

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## References

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