

# A PMO Approach to Orbital Interactions Through Space and Through Bonds

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Through-space and through-bonds interactions between two nonbonding orbitals are shown to be first-order and second-order perturbations of nonbonding orbitals by the framework sigma orbitals. Through-space interactions for diamines and triplet diradicals are always destabilizing, but through-bonds interactions are stabilizing owing to their coupling with through-space effect. Anomalies in level ordering and magnitudes of energy splitting can be rationalized with the present approach. Orbital interactions predicted with the PMO method were found to be consistent with those obtained by STO-3G calculations and photoelectron spectroscopy.

Through-space and through-bonds interactions of nonbonding ( $n$ ) orbitals in diradical and diamines have attracted much interest.<sup>1</sup> While it is well known that the former is a destabilizing interaction,<sup>1a</sup> a net stabilizing effect of the latter is not well understood. Moreover it is important to recognize that two types of interactions do not occur independently but the two are coupled and form composite parts of the total interaction, even though one of them may be dominant; an interaction of two nonbonding orbitals,  $n_1$  and  $n_2$ , will be destabilizing, *i.e.*, the total energy of the  $n_1$  and  $n_2$  orbitals is raised as a result of interaction, when through-space interaction is dominant, while it will be stabilizing, *i.e.*, the total energy is lowered, when through-bonds interaction is dominant.

In this paper we wish to clarify these and other aspects of through-bonds interaction following a perturbational molecular orbital (PMO)<sup>2</sup> approach with simplifications involving use of frontier orbitals (FMO)<sup>3</sup> and "C-approximation".<sup>4</sup> In the latter approximation,  $CC\sigma$  MOs are formed as linear combinations of  $sp^3$  hybrids and numerical values are obtained by using the Hückel procedure, and hence the highest occupied (HO) and lowest unoccupied (LU) sigma MOs of an  $N$  sigma bond system resemble those of the pi MOs of a system with  $N$  double bonds. General features of the FMOs in this approximation are that: (i) nodes in the HO- $\sigma$  pass through every intervening carbon atoms, whereas those in the LU- $\sigma^*$  pass through centers of all the  $N$  intervening CC sigma bonds, and (ii) magnitudes of hybrid AO coefficients in the HO- $\sigma$ -MO are the same as those of the corresponding hybrid AO coefficients in the LU- $\sigma^*$ -MO.

The FMO patterns for the systems with  $N=3$  and 4 are illustrated in Figure 1.

## The Perturbational Formalism

Perturbation theory has been used successfully for the investigation of substituent effects on MO properties of molecular framework.<sup>5</sup> According to the theory the MOs of complex molecules are built up from those of subsystems, the substituent (A) and framework (B). The interaction of the MOs of the two subsystems A and B leads to a perturbed or new wave function  $\Psi_i$  in terms of the unperturbed wave function,  $\Psi_j^0$  of A and  $\Psi_k^0$  of B.

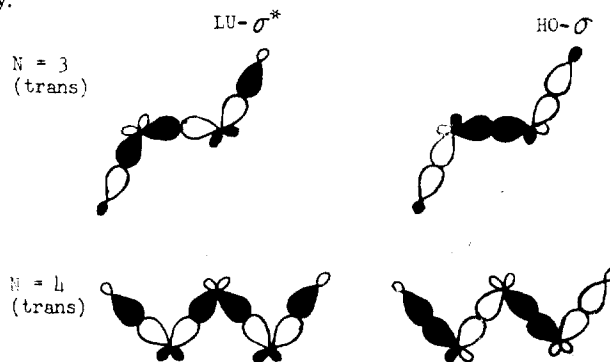


Figure 1. FMO patterns for  $N=3$  and 4 systems.

$$\Psi_i = \Psi_i^0 + \sum_{j=1}^A a_{ji} \Psi_j^0 + \sum_k^B b_{ki} \phi_k^0 \quad (1)$$

where  $a_{ji}$  and  $b_{ki}$  are mixing coefficients which measure how much orbitals  $j$  and  $k$  mix into orbital  $i$ , respectively.

Likewise the perturbed energy  $E_i$  to second order is given as,

$$E_i = E_i^0 + E_i' + E_i'' = E_i^0 + H_{ii} + \sum_{k \neq i} \frac{H_{ik}^2}{\epsilon_i^0 - \epsilon_k^0} \quad (2)$$

The integral  $H_{mn}$  is defined as  $H_{mn} = \langle \Psi_m^0 | H' | \Psi_n^0 \rangle$  in which  $H'$  is the perturbation.

## The Basis Level, $\epsilon_0$

In an alkyl monoradical or a monoamine, the nonbonding orbital  $n$  of energy  $e_0=0$  will interact with the framework sigma MOs, and the perturbed wave function  $n'$  and energy  $\epsilon_0$  are approximately given as equations (3) and (4) considering only the FMOs.

$$n' = n + b_{HO} \Psi_{HO}^0 + b_{LU} \Psi_{LU}^0 \quad (3)$$

$$\epsilon_0 = e_0 + \epsilon' - \frac{H_{n\sigma^*}^2}{e_{LU} - \epsilon'} + \frac{H_{n\sigma}^2}{\epsilon' - e_{HO}} \quad (4)$$

where the first order perturbation energy  $\epsilon' = \langle n | H' | n \rangle$  is an electrostatic interaction energy<sup>6</sup> between nonbonding electrons ( $n$ ) and the framework which is devoid of an electron (radical) or a pair of electrons (amine) in the nonbonding orbital. The  $\epsilon'$  will thus be a negative quantity,  $\epsilon' < 0$ . In the second order perturbation energy expressions in eq. (4), we have used the  $\epsilon'$  as the energy of the orbital  $n$ .<sup>7</sup> The second order terms can be simplified using the approximation  $H_{mn} \cong -ks_{mn}$ ,<sup>5a</sup> where  $k$  is a positive constant,  $s_{mn} = \langle \Psi_m^0 | \Psi_n^0 \rangle$ ,

and  $\Delta\epsilon = e_{LU} - e_0 = e_0 - e_{HO}$ .

$$\frac{H_{n\sigma}^2}{e_{LU} - \epsilon'} = \frac{\langle n | H' | \Psi_{LU}^0 \rangle^2}{\Delta\epsilon - \epsilon'} \cong \frac{k^2 s_{n\sigma}^2}{\Delta\epsilon - \epsilon'} \cong \frac{k^2 s_{n\sigma}^2}{\Delta\epsilon} \left(1 + \frac{\epsilon'}{\Delta\epsilon}\right) \cong x \left(1 + \frac{\epsilon'}{\Delta\epsilon}\right) \quad (5)$$

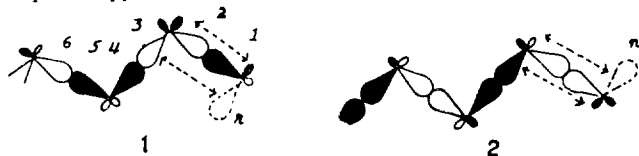
$$\frac{H_{n\sigma}^2}{\epsilon' - e_{HO}} = \frac{\langle n | H' | \Psi_{HO}^0 \rangle^2}{\Delta\epsilon + \epsilon'} \cong \frac{k^2 s_{n\sigma}^2}{\Delta\epsilon + \epsilon'} \cong \frac{k^2 s_{n\sigma}^2}{\Delta\epsilon} \left(1 - \frac{\epsilon'}{\Delta\epsilon}\right) \cong y \left(1 - \frac{\epsilon'}{\Delta\epsilon}\right) \quad (6)$$

where  $x = \frac{k^2 s_{n\sigma}^2}{\Delta\epsilon}$  and  $y = \frac{k^2 s_{n\sigma}^2}{\Delta\epsilon}$ .

Thus since  $e_0 = 0$ ,

$$\begin{aligned} \epsilon_0 &\cong e_0 + \epsilon' + (y-x) - \frac{\epsilon'}{\Delta\epsilon} (y+x) \\ &= \epsilon' + (y-x) - \frac{\epsilon'}{\Delta\epsilon} (y+x) \end{aligned} \quad (7)$$

The overlap integrals  $s_{n\sigma} = \langle n | \psi_{HO}^0 \rangle$  and  $s_{n\sigma}^* = \langle n | \psi_{LU}^0 \rangle$  can be taken as those between the nonbonding orbital lobe and a vicinal hybrid AO, *i.e.*,<sup>4c,d</sup> AO 3 of the framework HO- $\sigma$  and LU- $\sigma^*$  orbitals constructed using the "C-approximation", as illustrated in 1 and 2 for the vicinal *cis* and *trans* overlaps of *n* with the framework LU- $\sigma^*$  and HO- $\sigma$  orbitals, respectively.



Since in the "C-approximation" magnitudes of AO coefficients for the AO 3 in the LU- $\sigma^*$  and HO- $\sigma$  MOs are the same,  $x \cong y$ . However more accurate calculations have shown that the magnitudes of  $s_{n\sigma}$  is somewhat greater than that of  $s_{n\sigma}^*$  due to partial cancellation effect of overlap between *n* and hybrid AO 4 of LU- $\sigma^*$  in the latter<sup>1a</sup>; this means that actually the *n* level is slightly more destabilized (raised) by the interaction with the HO- $\sigma$  than it is stabilized (lowered) by the interaction with the LU- $\sigma^*$  of the framework. This raising effect will be larger as the overlap increases. Table 1 shows that  $\epsilon_0$  is higher with *n-trans* as in 2 than with *n-cis* as in 1, for the same N.<sup>8</sup>

This is consistent with the fact that a vicinal *trans* overlap is greater than a vicinal *cis*,  $s(\text{trans}) > s(\text{cis})$ <sup>9</sup> In no cases however the raising of *n* level caused by the second order perturbation will be greater than  $\epsilon'$  since the later is the first order term and is greater in magnitude than the former; the basis level,  $e_0$ , will be lower than the unperturbed level  $e_0$ , which is zero,  $\epsilon_0 < 0$ .

### Through-Space and Through-Bonds Interactions

Let us now consider interactions between the two nonbonding orbitals,  $n_1$  and  $n_2$ , in a diradical (triplet state) or diamines. Since the two should have the same energy of  $e_0 = 0$ , linear combination of the two forms two symmetry adapted pairs,  $n_+$  and  $n_-$ , with the same energy of  $e_0 = 0$ .<sup>1</sup>

$$\begin{aligned} n_+ &= \frac{1}{\sqrt{2+2S}} (n_1 + n_2) \\ n_- &= \frac{1}{\sqrt{2-2S}} (n_1 - n_2) \end{aligned} \quad (8)$$

TABLE 1: Averages,  $\epsilon_{av}$ , Basis Levels,  $\epsilon_0$  and Energy Splitting,  $\Delta E$  (kcal) for Diradicals and Diamines Calculated by STO-3G method

| Diradicals*                 |                                  | $\epsilon_{av}$ | $\epsilon_0$ | $\Delta E$ |
|-----------------------------|----------------------------------|-----------------|--------------|------------|
| N=2                         | all- <i>trans</i>                | -225            | -215         | 50         |
|                             | all- <i>cis</i>                  | -222            | -219         | -15        |
| 3                           | all- <i>trans</i>                | -220            | -210         | 46         |
|                             | all- <i>cis</i>                  | -219            | -217         | 16         |
| 4                           | all- <i>trans</i>                | -215            | -208         | 35         |
|                             | all- <i>cis</i>                  | -217            | -215         | 10         |
| <b>Diamines<sup>+</sup></b> |                                  |                 |              |            |
| N=3                         | all- <i>trans</i>                | -204            | -193         | 43         |
|                             | ( <i>trans</i> ) all- <i>cis</i> | -198            | -196         | 20         |
| 3                           | all- <i>trans</i>                | -204            | -193         | 5          |
|                             | ( <i>cis</i> ) all- <i>cis</i>   | -186            | -196         | -9         |
| 4                           | all- <i>trans</i>                | -199            | -192         | 29         |
|                             | ( <i>trans</i> ) all- <i>cis</i> | -195            | -195         | 12         |
| 5                           | all- <i>trans</i>                | -196            | -191         | 20         |
|                             | ( <i>trans</i> )                 |                 |              |            |

\*I. Lee, To be submitted for publication. +Calculated using standard geometries.

where  $S = \langle n_1 | n_2 \rangle$ .

Since we will be primarily concerned with interaction energies to second order in overlap, we need to include overlap integral *S* in the expression (eq. 8) of symmetry adapted pair of orbitals. There are obvious and crucial consequences of including overlap: it is a well known result that, when two levels interact *directly*, the energy of perturbation is not the same for the two levels, *i.e.*, one level is destabilized ( $\delta\epsilon_h$ ) more than the other is stabilized ( $\delta\epsilon_l$ ),  $\delta\epsilon_h > \delta\epsilon_l$ .<sup>1a</sup> This net destabilizing effect of direct interaction is a consequence of the first order perturbation of the two levels,  $n_+$  and  $n_-$ .

$$\begin{aligned} e_+ &= \langle n_+ | H' | n_+ \rangle = \frac{\epsilon' + H_{12}}{1+S} = \frac{\epsilon' - kS}{1+S} = \epsilon' - \delta\epsilon_l \\ e_- &= \langle n_- | H' | n_- \rangle = \frac{\epsilon' - H_{12}}{1-S} = \frac{\epsilon' + kS}{1-S} = \epsilon' + \delta\epsilon_h \end{aligned} \quad (9)$$

where  $H_{12} = \langle n_1 | H' | n_2 \rangle \cong -kS$ ,  $\delta\epsilon_l \cong S(k+\epsilon')(1-S)$  and  $\delta\epsilon_h \cong S(k+\epsilon') \cdot (1+S)$ . Equation (9) shows that through-space interaction places  $e_+$  below  $e_-$  by an amount of  $\Delta E_{sp}$ ,

$$\Delta E_{sp} = e_- - e_+ = \delta\epsilon_h + \delta\epsilon_l \cong 2S(k+\epsilon') \quad (10)$$

and the net destabilization of the direct interaction is given by eq. (11).

$$\delta\epsilon_h - \delta\epsilon_l = (e_- - \epsilon') - (\epsilon' - e_+) \cong 2S^2(k+\epsilon') \quad (11)$$

This is only true for diamines and triplet state of diradicals; for singlet diradicals direct interaction can also be stabilizing as shown by Borden *et al.*<sup>10</sup>

For the second order perturbation energies of  $n_+$  and  $n_-$ , the same procedure will be adopted as that used in the second order terms for the basis level: the nonbonding levels are allowed first to interact directly as represented by first order perturbation terms, eq. (9), and then the second order perturbation is applied.<sup>7</sup> The perturbed energies of  $n_+$  and  $n_-$

levels to second order can therefore be given as,

$$\begin{aligned}\epsilon_+ &\cong e_0 + (\epsilon' - \delta\epsilon_l) - \frac{H_{n\sigma}^2}{e_{LU} - e_+} + \frac{H_{n\sigma}^2}{e_+ - e_{HO}} \\ \epsilon_- &\cong e_0 + (\epsilon' + \delta\epsilon_h) - \frac{H_{n\sigma}^2}{\epsilon'_{LU} - e_-} + \frac{H_{n\sigma}^2}{e_- - e_{HO}}\end{aligned}\quad (12)$$

where  $e_+ = \epsilon' - \delta\epsilon_l$  and  $e_- = \epsilon' + \delta\epsilon_h$ . The denominators of second order terms may be transformed using relations shown in Figure 2;  $e_{LU} - e_+ = \Delta\epsilon + \delta\epsilon_l - \epsilon'$ ,  $e_+ - e_{HO} = \Delta\epsilon - \delta\epsilon_l + \epsilon'$ ,  $e_{LU} - e_- = \Delta\epsilon - \delta\epsilon_h - \epsilon'$  and  $e_- - e_{HO} = \Delta\epsilon + \delta\epsilon_h + \epsilon'$ .

Second order perturbation energy terms in eq. (12) are orbital interaction energies between  $n_+$  and  $n_-$  and the framework  $\sigma$  MOs; this is none other than the interactions of  $n_1$  and  $n_2$  through the N framework  $\sigma$  bonds. One of the two second order perturbation (through-bonds interaction) energy terms each in the expressions of eq. (12), however, vanishes depending on whether the N is odd or even numbers.

Let us now illustrate this using interaction schemes of  $n_+$  and  $n_-$  with the HO- $\sigma$  and LU- $\sigma^*$  MOs of the framework sigma system for the N=odd case. Whenever  $n_1$  and  $n_2$  overlap with a framework  $\sigma$  MO with different signs, *i. e.*,

$$s_1 = -s_2, \text{ matrix element vanishes since } H_{n\sigma} = \frac{1}{\sqrt{2 \pm 2S}} \langle n_1 \pm n_2 | H' | \sigma \rangle = \frac{-k}{\sqrt{2 \pm 2S}} (s_1 \pm s_2) \text{ where } s_i = \langle n_i | H' | \sigma \rangle \text{ and } S = \langle n_1 | n_2 \rangle.^{11}$$

For the  $N=3$  ( $N=odd$ ), the interaction energy of  $n_+$  ( $n_-$ ) level with the LU- $\sigma^*$  (HO- $\sigma$ ) of the framework is zero as shown by orbital overlap patterns in Figure 3. On the other hand the interaction energies of  $n_+$  and  $n_-$  levels with the HO- $\sigma$  and LU- $\sigma^*$  are  $2y\left(1 + \frac{\delta\epsilon_l}{\Delta\epsilon} - \frac{\epsilon'}{\Delta\epsilon}\right)$  and  $-2x\left(1 + \frac{\delta\epsilon_h}{\Delta\epsilon} + \frac{\epsilon'}{\Delta\epsilon}\right)$ , respectively. Likewise the second order perturbation, *i. e.*, through-bonds interaction, energies are obtained for the  $N=even$  system as they are summarized in Table 2.

Inclusion of the second order perturbation energies leads to new energy levels,  $\epsilon_+$  and  $\epsilon_-$ , for the symmetry adapted pair of nonbonding orbitals  $n_+$  and  $n_-$  as a result of through-space and through-bonds interactions. That the total interaction is partitioned into direct (through-space) and indirect (through-bonds) contributions is thus a natural consequence of the PMO approach.

$$\epsilon_+ \cong (\epsilon' - \delta\epsilon_l) + 2y\left(1 + \frac{\delta\epsilon_l}{\Delta\epsilon} - \frac{\epsilon'}{\Delta\epsilon}\right)$$

$$\epsilon_- \cong (\epsilon' + \delta\epsilon_h) - 2x\left(1 + \frac{\delta\epsilon_h}{\Delta\epsilon} + \frac{\epsilon'}{\Delta\epsilon}\right)\quad (13)$$

for  $N=odd$  systems.

$$\begin{aligned}\epsilon_+ &\cong (\epsilon' - \delta\epsilon_l) - 2x\left(1 - \frac{\delta\epsilon_l}{\Delta\epsilon} + \frac{\epsilon'}{\Delta\epsilon}\right) \\ \epsilon_- &\cong (\epsilon' + \delta\epsilon_h) + 2y\left(1 - \frac{\delta\epsilon_h}{\Delta\epsilon} - \frac{\epsilon'}{\Delta\epsilon}\right)\end{aligned}\quad (14)$$

for  $N=even$  systems.

These set of equations show that through-space interaction always stabilizes the  $\epsilon_+$  level by an amount of  $\delta\epsilon_l = S(k + \epsilon')$  ( $1 - S$ ), which is somewhat smaller than the destabilization of the  $\epsilon_-$  level,  $\delta\epsilon_h = S(k + \epsilon')(1 + S)$ .

Through-bonds interaction however stabilizes the  $n_-$  level by an amount of  $2x\left(1 + \frac{\delta\epsilon_h}{\Delta\epsilon} + \frac{\epsilon'}{\Delta\epsilon}\right)$  whereas it destabilizes

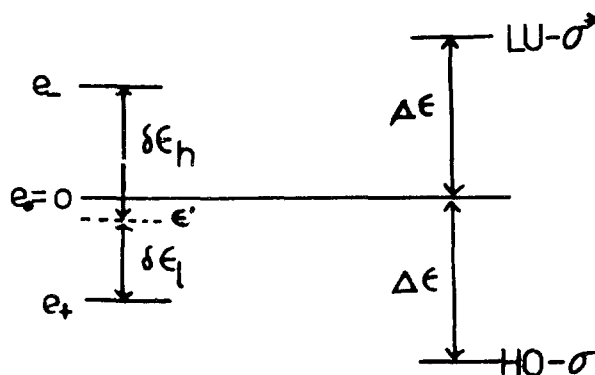


Figure 2. Level ordering and inter-level energy differences.

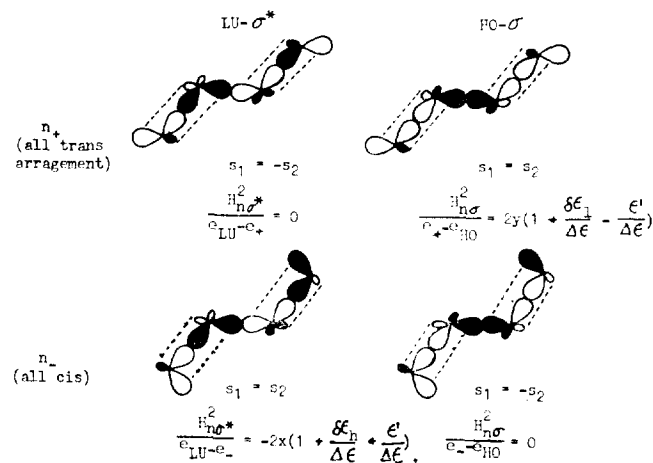


Figure 3. Through-bonds interaction of  $n_+$  and  $n_-$  with Framework LU- $\sigma^*$  and HO- $\sigma$  for  $N=3$  (*trans*).

TABLE 2: Interaction Energies between Symmetry Adapted Pairs and Framework FMOs

| Symm. Adapt. Pairs | Framework FMOs |   |  |   |
|--------------------|----------------|---|--|---|
|                    |                | N=odd   |  | N=even  |
| Through Bonds      | $n_+$          | $2y\left(1 + \frac{\delta\epsilon_l}{\Delta\epsilon} - \frac{\epsilon'}{\Delta\epsilon}\right)$ | 0  | 0   |
|                    | $n_-$          | 0   | $-2x\left(1 + \frac{\delta\epsilon_h}{\Delta\epsilon} + \frac{\epsilon'}{\Delta\epsilon}\right)$ | $2y\left(1 - \frac{\delta\epsilon_l}{\Delta\epsilon} - \frac{\epsilon'}{\Delta\epsilon}\right)$ |
| Through Space      | $n_+$          |   | $-S(k + \epsilon')(1 - S)$   |   |
|                    | $n_-$          |   | $S(k + \epsilon')(1 + S)$  |   |

For energy notations, refer to Figure 2.

the  $n_+$  level by an amount of  $2y\left(1 + \frac{\delta\epsilon_l}{\Delta\epsilon} - \frac{\epsilon'}{\Delta\epsilon}\right)$  for  $N=$  odd system. Thus for  $N=$  odd system,  $n_-$  is below  $n_+$  when interactions between  $n_1$  and  $n_2$  are through-bonds dominated.

On the other hand, the two types of interactions tend to operate cooperatively in  $N=$  even system although contribution from through-bonds interaction is reduced due to cancelling effect of cross interaction terms,  $2x\frac{\delta\epsilon_l}{\Delta\epsilon}$  and  $2y\frac{\delta\epsilon_h}{\Delta\epsilon}$  which contain contributions from both through-space ( $\delta\epsilon_h$  and  $\delta\epsilon_l$ ) and through-bonds ( $x$  and  $y$ ) interactions.

Overall energy splitting for  $N=$  odd,  $\Delta E_{\text{odd}}$ , and for  $N=$  even,  $\Delta E_{\text{even}}$ , can be obtained from eqs. (13) and (14), respectively.

$$\begin{aligned} \Delta E_{\text{odd}} &= \epsilon_- - \epsilon_+ \cong \Delta E_{\text{sp}} - 2(x+y) \\ &\quad + \frac{2\epsilon'}{\Delta\epsilon}(y-x) - \frac{2}{\Delta\epsilon}(y\delta\epsilon_l + x\delta\epsilon_h) \\ \Delta E_{\text{even}} &= \epsilon_- - \epsilon_+ \cong \Delta E_{\text{sp}} + 2(x+y) \\ &\quad - \frac{2\epsilon'}{\Delta\epsilon}(y-x) - \frac{2}{\Delta\epsilon}(y\delta\epsilon_h + x\delta\epsilon_l) \end{aligned} \quad (15)$$

Here  $\Delta E_{\text{sp}}$  is the through-space energy splitting which is defined by eq. (10). Eq. (15) shows that total energy splitting consists of contributions from through-space, through-bonds and cross interactions. For  $N=$  odd system, the latter two contributions oppose through-space contribution while for  $n=$  even system the cross term opposes the other two contributions. In the through-bonds dominated interactions,  $\Delta E_{\text{even}}$  will be decreased due to the opposing cross interaction contribution; reference to Table 1 indicates that drops in  $\Delta E$  values are larger from  $N=$  odd to  $N=$  even, in support of this prediction.

Level ordering can be predicted from the sign of overall energy splitting,  $\Delta E$ ;  $n_+$  is below  $n_-$  when  $\Delta E > 0$  and vice versa. Thus in the through-space dominated interactions,  $n_+$  will be below  $n_-$  level, as for the all *cis* form of *cis*-diaminoethane ( $n=3$ ) in Table 1. However if the cross interaction term becomes exceptionally large,  $\Delta E_{\text{even}}$  may become negative so that level order can reverse to  $n_-$  below  $n_+$  level. This may be the situation for the all *cis* arrangement of  $N=2$  (Table 1).

The  $\Delta E$  values in through-bonds dominated interaction is seen to depend on the magnitude of  $x$  and  $y$ , which in turn is dependent on the vicinal overlap  $s$  between  $n$  and framework sigma orbitals.<sup>9</sup> Thus for the all *trans* forms  $\Delta E$  will be larger than the all *cis* forms, since vicinal *trans* overlap is larger than vicinal *cis* overlap. This prediction is also shown to be consistent with our STO-3G results in Table 1.

Comparison of the average of two levels,  $\epsilon_{\text{av}} = \frac{\epsilon_+ + \epsilon_-}{2}$ , with the basis level  $\epsilon_0$  will indicate whether interaction of two nonbonding orbitals,  $n_1$  and  $n_2$ , is stabilizing ( $\epsilon_{\text{av}} < \epsilon_0$ ) or destabilizing ( $\epsilon_{\text{av}} > \epsilon_0$ )<sup>4c</sup>; we already know that the interaction is destabilizing when it is through-space dominated as for the all *cis* form of *cis* diaminoethane (Table 1), and hence stabilizing interaction will only result from through-bonds dominated interactions.

The average of the two levels for  $N=$  odd system is given as

$$\begin{aligned} \epsilon_{\text{av}}(\text{odd}) &= \frac{\epsilon_+ + \epsilon_-}{2} \cong \epsilon' + \frac{\delta\epsilon_h - \delta\epsilon_l}{2} + (y-x) \\ &\quad - \frac{\epsilon'}{\Delta\epsilon}(x+y) - \frac{1}{\Delta\epsilon}(x\delta\epsilon_h - y\delta\epsilon_l) \end{aligned} \quad (16)$$

In this expression  $\delta\epsilon_h$  and  $\delta\epsilon_l$  are originated from through-space interaction, while  $x$  and  $y$  are from through-bonds interaction; the last term represents therefore a cross interaction or through-space-through-bonds coupling effect. Eq. (16) can be simplified using eqs. (7) and (11).

$$\epsilon_{\text{av}}(\text{odd}) - \epsilon_0 \cong S^2(k + \epsilon') - \frac{1}{\Delta\epsilon}(x\delta\epsilon_h - y\delta\epsilon_l) \quad (17a)$$

Likewise for  $N=$  even system

$$\epsilon_{\text{av}}(\text{even}) - \epsilon_0 \cong S^2(k + \epsilon') - \frac{1}{\Delta\epsilon}(y\delta\epsilon_h - x\delta\epsilon_l) \quad (17b)$$

Eq. (17) shows that through-space interaction has a destabilizing effect,  $S^2(k + \epsilon') > 0$ , while the cross interaction term has a stabilizing effect since  $\delta\epsilon_h$  is greater than  $\delta\epsilon_l$ . However eq. (17a) also indicates that  $N=$  odd system can be easily through-space dominated since in the coupling term  $y$  is greater than  $x$  and hence the effect of the stabilizing term is reduced. Magnitude of the coupling term *i.e.*, magnitude of stabilization, depends on values of  $x$  and  $y$ , which in turn are dependent on the overlap,  $s$ , between  $n$  and the framework  $\sigma$  orbitals. This means  $\epsilon_{\text{av}} - \epsilon_0$  will be more negative and hence the interaction of  $n_1$  and  $n_2$  is more stabilizing for the vicinal *trans* arrangement of  $n$  with the framework  $\sigma$  system. This is borne out in our STO-3G results of Table 1, where the value of  $\epsilon_{\text{av}} - \epsilon_0$  is seen to be larger for the all *trans* than that for the all *cis* forms. The effect of overlap,  $s$ , on the magnitude of  $\epsilon_{\text{av}} - \epsilon_0$  can be seen more clearly using simplified form of  $\epsilon_{\text{av}}$  with the assumption that  $x \cong y$ .

$$\begin{aligned} \epsilon_{\text{av}} &\cong \epsilon' + S^2(k + \epsilon') - \frac{2x}{\Delta\epsilon}\epsilon' - \frac{2x}{\Delta\epsilon}S^2(k + \epsilon') \\ &= \left(\epsilon' - \frac{2x}{\Delta\epsilon}\epsilon'\right) + S^2(k - \epsilon') \left(1 - \frac{2x}{\Delta\epsilon}\right) \\ &= \epsilon_0 + S^2(k + \epsilon') \left(1 - \frac{2x}{\Delta\epsilon}\right) \\ \epsilon_{\text{av}} - \epsilon_0 &\cong S^2(k + \epsilon') \left(1 - \frac{2x}{\Delta\epsilon}\right) \end{aligned} \quad (18)$$

TABLE 3: Photoelectron Spectroscopic Data for Some Diazine Compounds

|   | $\epsilon_{\text{av}}$ | $\epsilon_0$ | $\Delta E$ |
|---|------------------------|--------------|------------|
| 1 | -198                   | -186         | 49         |
| 2 | -170                   | -164         | 24         |
| 3 | -169                   | -181         | -26        |

(1), 1,4-diazabicyclo [2.2.2] octane (DABCO); (2), 1,5-diazabicyclo [3.3.3] undecane; (3), 1,6-diazabicyclo [4.4.4] tetradecane.

Substitution of approximate values,  $k \cong 0.8$  hartrees,<sup>12</sup>  $\Delta\epsilon \cong 0.06$  hartrees,<sup>13</sup>  $s \cong 0.089$  (for *trans* overlap)<sup>12</sup> and  $s \cong 0.072$

(for *cis* overlap),<sup>12</sup> into  $\frac{2x}{\Delta\epsilon} = 2\left(\frac{ks}{\Delta\epsilon}\right)^2$  indicates that

$1 < \frac{2x}{\Delta\epsilon}$  and  $\epsilon_{av} - \epsilon_0$  is always negative. However  $\frac{2x}{\Delta\epsilon}$  is

approximately 2.82 for *trans* while it is 1.84 for *cis* reducing the magnitude of  $\epsilon_{av} - \epsilon_0$  for the *cis* to approximately 2/3 of that for the *trans*.

The average,  $\epsilon_{av}$ , is always lower than the basis level  $\epsilon_0$  in eq. (18), irrespective of whether the  $N$  is odd or even. Moreover according to eq. (18), through-space dominated (destabilizing) interaction is not possible. This absurdity is of course a result of the approximation that  $x \cong y$ .

Photoelectron spectroscopic data<sup>1e</sup> included in Table 3 are in full accord with our predictions: (i) the nitrogen atoms in 1,6-diazabicyclo [4.4.4] tetradecane must be inwardly pyramidalized increasing the direct overlap so that the interaction is through-space dominated and is destabilizing,  $\epsilon_{av} > \epsilon_0$ , (ii) interactions in the other two diazabicyclo compounds are through-bonds dominated and are stabilizing,  $\epsilon_{av} < \epsilon_0$ , (iii) energy splitting,  $\Delta E$ , for  $N = \text{odd}$  (DA BCO) is larger than that for  $N = \text{even}$  [1,5-diazabicyclo (3.3.3) undecane] even allowing for the increase in  $N$  by 1.

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## References

- (1) (a) R. Hoffmann, A. Imamura and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) A. Imamura and K. Hirao, *Bull. Chem. Soc. Japan*, **51**, 3443 (1978); (c) E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3818 (1970); (d) E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, **58**, 936 (1975); (e) R. W. Alder, R. J. Arrow-smith, A. Casson, R. B. Sessions, E. Heilbronner, B. Kovac, H. Huber and M. Taagepera, *J. Amer. Chem. Soc.*, **103**,

- 6137 (1981).
- (2) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Org. Chem.," Plenum Press, New York, 1975.
- (3) (a) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); (b) I. Fleming, "Frontier Orbitals and Org. Chem. Reactions", John Wiley, London, 1976.
- (4) (a) C. Sandorfy and R. Daudel, *Comp. Rend.*, **238**, 93 (1954); (b) W. C. Herndon, "Prog. Phys. Org. Chem.", **9**, 99 (1972); (c) M. N. Paddon-Row, H. K. Patney, R. S. Brown and K. N. Houk, *J. Amer. Chem. Soc.*, **103**, 5575 (1981); (d) J. W. Verhoeven and P. Pasman, *Tetrahedron*, **37**, 943 (1981).
- (5) (a) L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, **96**, 1370 (1974); (b) S. Inagaki, H. Fujimoto and K. Fukui, *ibid.*, **98**, 4693 (1976).
- (6) A. D. Buckingham, "Intermolecular Interactions", ed. Chapt. 1. B. Pullman, John Wiley, New York, 1978.
- (7) This corresponds to adopting the PT 1 procedure of Hoffmann *et al.*<sup>1a</sup>
- (8) The  $\epsilon_0$  is also raised slightly as the  $N$  increases (Table 1). This may be due to the decrease in the magnitude of electrostatic (attraction) energy,  $|\epsilon'|$ , since the net charge density of the framework should decrease with the size, *i. e.*, with the increase in the  $N$ .
- (9) (a) N. D. Epiotis, R. L. Yates, J. R. Larson, C. R. Kirmaier and F. Bernardi, *J. Amer. Chem. Soc.*, **99**, 8379 (1977); (b) T. K. Brunck and F. Weinhold, *ibid.*, **101**, 1700 (1979).
- (10) W. T. Borden and E. R. Davidson, *ibid.*, **102**, 5409 (1980).
- (11) Note that  $S$  is for the direct overlap between  $n_1$  and  $n_2$  while  $s$  is for the overlap between  $n$  and framework  $\sigma$  orbitals.
- (12) These are overlap integrals for Hamiltonian matrix elements  $H_{n\sigma}$  and  $\langle n_N | \sigma_{CH} \rangle$ ; T. K. Brunck and F. Weinhold, *J. Amer. Chem. Soc.*, **98**, 3745 (1976).
- (13) The "C-Approximation" gives HOMO energies ranging 0.052~0.062 a.u. for  $N = 2 \sim 5^{3d}$  assuming  $\beta \cong 2\text{eV}$ .<sup>14</sup>
- (14) Ref. (2), p.363.

## Kinetic Study on Bromine-Exchange Reaction of Antimony Tribromide with *t*-Butyl Bromide in Nitrobenzene and in 1,2,4-Trichlorobenzene\*

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The kinetic study on the bromine-exchange reaction of antimony tribromide with *t*-butyl bromide in nitrobenzene or 1,2,4-trichlorobenzene has been carried out, using Br-82 labelled antimony tribromide. The results show that the exchange reaction is first order with respect to *t*-butyl bromide and 1.5th order with respect to antimony tribromide. It is assumed that the 1.5th order indicates the coexistence of first- and second-order kinetics. Reaction mechanisms for the exchange reaction are proposed.

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