# PMO Theory of Orbital Interactions (Part 7). $\sigma-\pi$ Interactions

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Orbital interactions of the types,  $\sigma-\pi$ ,  $\sigma^{+}-\pi$ ,  $\sigma-\pi^{*}$  and  $\sigma^{*}-\pi^{*}$  are investigated for the rotamers of  $\alpha$ -X-acetones (X = F and Cl) using STO-3G method of calculation. It was found that the interactions are possible only in gauche forms, and the  $\sigma^{*}-\pi^{*}$  interactions are in general greater than the  $\sigma-\pi$  interactions due to the greater overlap, in spite of the greater energy gap involved; the greater  $\sigma^{*}-\pi^{*}$  interaction causes greater lowering of  $\pi^{*}$  level relative to the lowering of  $\sigma$  in the  $\sigma-\pi$  interaction so that both  $\sigma-\pi^{*}$  and  $n-\pi^{*}$  interactions are enhanced in the gauche forms. The extra stability of the gauche form and the red shift in the  $n-\pi^{*}$  transition are thus found to be natural corollaries of the greater  $\sigma^{*}-\pi^{*}$  interaction in the gauche forms.

#### Introduction

Interactions between two degenerate orbitals, n-n,  $n-\pi$  or  $\pi^*-\pi^*$ , have been shown to take place through space (TSI), through bonds (TBI) and involving sigma aromaticity (SAI)<sup>1</sup>; TSI is a first-order perturbation giving a symmetry adapted pair  $(n_{\pm}, n_{\pm} \text{ or } n_{\pm}^*)$  for degenerate orbitals. It has been shown that energy splittings due to TSI between two  $\pi^*$  orbitals are greater than those between two  $\pi$  orbitals,  $\Delta E_s(\pi^*)$ , for a molecule with two  $\pi$  orbitals separated by n sigma CC bonds.<sup>2</sup>

Recently interactions between  $\sigma$  and  $\pi$  orbitals have attracted considerable interest in the interpretation of rotational barrier profiles of  $\pi$  bonded molecules.<sup>3</sup> The interactions involved between a  $\sigma$  and a  $\pi$  orbital within a molecule is a second-order perturbation due to the considerable energy gap between the two, in contrast to the first-order nature of the degenerate TSI. Olivato et al.36 attributed the increased stabilization of gauche rotamers of a-hetero substituted acetones, CH<sub>2</sub>XCOCH<sub>3</sub> (X = Cl, Br, I, OMe, Me<sub>1</sub>N, and MeS) to  $\sigma_{cr} - \pi_{co}$  and  $\sigma_{cr}^* - \pi_{co}^*$  orbital interactions; in the gauche forms of these compounds the hyperconjugative interaction between  $\sigma_{aa}^{*}$  and  $\pi_{aa}^{*}$  orbitals lower the  $\pi_{\omega}^*$  level causing the bathochromic shift and hyperchromic effect of  $n \rightarrow \pi^*$  transition, whereas the cis-and trans-rotamers do not exhibit any significant effect because of the absence of such  $\sigma^{*}-\pi^{*}$  orbital interactions. On the other hand, Yamabe et al.<sup>4</sup> reported the importance of  $\sigma^* - \pi^*$  orbital mixing for the nucleophilic displacement on the unsaturated carbon.

It has been shown however that  $\sigma - \pi^*$  type interactions may become overemphasized when neglect of differential overlap (NDO) types of calculations are used in the theoretical determination of preferred rotamer, leading to a grossly exaggerated estimate of the stability of gauche conformers in the  $\pi$ bonded molecules.<sup>5</sup>

The aim of the present work is to investigate the nature of such interactions between  $\sigma$  and  $\pi$  orbitals MO theoretically using ab initio(STO-3G) method.<sup>4</sup> We have shown that the interactions between  $\sigma^*$  and  $\pi^*$  orbitals are in general greater than that between  $\sigma$  and  $\pi$  orbitals so that the  $\sigma$ - $\pi^*$  type stabilizing interaction is enhanced in a rotamer in which such  $\sigma-\pi$  and  $\sigma^*-\pi^*$ interactions are present.

### Calculations

Ab initio LCAO-MO-SCF calculations were carried out on cis ( $\phi = 0^{\circ}$ ), gauche ( $\phi = 90^{\circ}$ ) and trans ( $\phi = 180^{\circ}$ ) rotamers of the a-X-acetones (I-II), X = F and Cl, using the STO-3G method.<sup>•</sup> The overlap integrals between two vicinal bonds were estimated by the INDO-LCBO method.<sup>7</sup>



## **Results and Discussion**

According to the perturbation molecular orbital (PMO) theory,<sup>‡</sup> two nondegenerate orbitals  $\psi_i^{\circ}$  and  $\psi_i^{\circ}$  can interact through space when (i) the two overlap substantially, the magnitude of the total interaction energy,  $d\epsilon$ (eq. 1), increasing with increasing overlap, (ii) the energy difference between the two interacting orbitals,  $\Delta E_{ij}^{\circ}$ , is not prohibitively large, the magnitude of the interaction energy being inversely proportional to  $\Delta E_{ij}^{\circ}$ , and (iii) the two orbitals interacting have the same symmetry. Orbital interaction scheme is illustrated in Figure 1.

$$\delta \epsilon - E_i^* - E_i \approx \frac{H_{ij}^*}{E_i^* - E_j^*} \approx \frac{k^2 S_{ij}^2}{\Delta E_{ij}^*} \tag{1}$$

$$\psi_i = \psi_i^* + \lambda \ \psi_j^*, \ \lambda \simeq \frac{kS}{\Delta E_{ij}^*} \tag{2}$$

The mixing coefficient  $\lambda$  is proportional to the overlap integral  $S_0$  and inversely proportional to the energy gap,  $\Delta E_0^{\circ}$ . At the present level of approximation the energy change  $\delta\varepsilon$  of the lower level and that of the upper level are equal.

Four types of intramolecular orbital interactions are conceivable between a sigma and a pi orbital ; $\sigma-\pi$ ,  $\sigma-\pi^*$ ,  $\sigma^*-\pi$  and

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Figure 1. Orbital interactions between two nondegenerate orbitals,  $\psi_i^o$  and  $\psi_i^o$ ,



**Figure 2.** Orbital patterns of the various  $\sigma - \pi$  orbital interactions for  $\sigma_{ex}$  and  $\pi_{ex}$ , where X=F or Cl.

 $\sigma^*-\pi^*$  types. Due to the requirement (i) above, intramolecular  $\sigma$ - $\pi$  orbital interactions are normally limited to the two orbitals in the vicinal position as in the  $\sigma$ -X-ketones. Orbital patterns for the four types of interaction in such a compound are illustrated schematically for  $\sigma_{cx}$  and  $\pi_{co}$ , where X = F or Cl, in Figure 2.<sup>9</sup>

Reference to Figure 2 reveals that (i) due to the electronegativity differences between the two atoms in the  $\sigma_{cx}$  and in the  $\pi_{co}$ bonds, vicinal overlap becomes the greatest in  $\sigma^* - \pi^*$ , while it is the smallest in  $\sigma$ - $\pi$  interaction,<sup>9</sup> and (ii) interaction of  $\sigma_{cx}$  is only with the nearest carbon 2p-AO of the  $n_{co}$  orbital since the overlap of  $\sigma_{cx}$  with the other end of  $\pi_{co}$  bond, *i.e.*, 2p-AO of O atom, is negligible due to the long distance involved. The symmetries of the 2p-AO and  $\sigma_{cx}$  can always be made to match, albeit the matching becomes partial when  $\sigma \mathcal{E}_{x}$  is involved. For the  $\alpha$ -haloacetones, CH<sub>2</sub>XCOCH<sub>3</sub>, the  $\sigma$ - $\pi$  interactions depicted in Figure 2 can operate only in the gauche forms, since  $\sigma$  and  $\pi$  orbitals in the cis and trans forms are orthogonal so that overlap between the two vanishes.3 The qualitative predictions as to the relative magnitude of the overlap in Figure 2 are substantiated by the overlap integral, S, calculated by the LCBO-INDO method summarized in Table 1 for the four types of  $\sigma-\pi$  orbital interactions in the gauche form of CH<sub>2</sub>FCOCH<sub>3</sub>. On account of the magnitude of overlap alone, we would expect from eq. (1) the  $\sigma^* - \pi^*$  interactions to be greater than the  $\sigma$ - $\pi$  interactions in  $\alpha$ -X-acetones. The STO-3G orbital energies of the  $\sigma_{cx}$ ,  $\pi_{co}$ ,  $\sigma_{cx}^*$  and  $\pi_{co}^*$  are presented in Table 2 for the three rotamers of  $CH_2XCOCH_3$  with X = F and Cl, together with the nonbonding orbitals on the oxygen atom,  $n_0$ . Inter-level spacings  $\Delta E(\sigma-\pi)$  and  $\Delta E(\sigma^*-\pi^*)$  are seen to decrease in  $\alpha$ -chloro (X = CI) compared to a-fluoro $(X \approx F)$  compound due to the relative raising of  $\sigma_{cx}$  and lowering of  $\sigma_{cx}^*$  orbitals as has been discussed by Bingham.<sup>11</sup> As a result, the energy splittings de due to  $\sigma - \pi$  and  $\sigma^* - \pi^*$  orbital interactions in the gauche forms

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TABLE 1: Overlap Integrals for the gauche form of CH<sub>3</sub>FCOCH, by LCBO-INDO Method

	0-ft	¢−π*	σ*-π	σ*-π*
s	0.0664	0.0739	0.0789	0.0850

TABLE 2: The STO-3G Orbital Energy Levels(eV) for Three Rotamers of CH<sub>2</sub>XCOCH<sub>3</sub>

x	χ, -	Forms		
		$cis(\Delta E)$	gauche ( $\Delta E$ )	trans ( $\Delta E$ )
F	σ	15.14 7.46	16.93	15.24
	π	7.68	7.41 9.52	7.67
	no	- 8.80	- 8.85	- 8.80
	T	- 10.76	-11.16	- 10.65
	o <sub>ce</sub>	- 15.68 4.92		-15,88 5.23
	$\Delta E(a-\pi^*)$	23.36	23.27	23.55
Cl	0 <b>*</b>	9.58	10.71	9.51
	स <b>*</b>	7.28 2.30	6.63 4.08	7.22 2.29
	no	- 9.40	-9.34	- 9.32
	π	-11.46	-11.29	-11.47
	0 cr	- 13.00	-13.54 2.25	- 12.96
	$\Delta E(\sigma - \pi^*)$	20.28	20.17	20.18
7분x	<u> </u>	****** <u></u>		
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acs.	,			σ <sub>cx</sub>
	cie gauch	e trans	cis caucha	trans
	I- 7		I = C1	

**Figure 3:** Energy level diagram for CH<sub>2</sub>XCOCH<sub>3</sub> showing level splittings in the gauche form due to the  $\sigma$ - $\pi$  and  $\sigma^*$ - $\pi^*$  orbital interactions.

are greater for X = Cl than for X = F. Furthermore the energy splittings are greater in the  $\sigma^*-\pi^*$  interactions than in the  $\sigma-\pi$ orbital interactions as has been anticipated from the magnitudes of overlap integrals in Table 1. The level diagrams are presented in Figure 3 for X = F and Cl, respectively; the inter-level splittings in the gauche forms due to the  $\sigma^*-\pi^*$  interactions are clearly demonstrated to be greater than those due to the  $\sigma-\pi$ interactions.

Effects of the greater orbital splitting in the  $\sigma^*-\pi^*$  interaction compared to the level splitting involved in the  $\sigma$ - $\pi$  interaction are two-fold: Lowering of the  $\pi^*$  level in the gauche form relative to the cis or trans form causes (i) a shift of the  $n \rightarrow \pi^*$ absorption to longer wavelength in the gauche form due to a decrease in the energy difference between  $\pi^*$  and *n* orbitals, the shift being greater, for  $\alpha$ -chloro compound<sup>3</sup>; (ii) and increased  $\sigma_{cx}-\pi^*_{co}$  interaction giving an extra stabilization to the gauche form,<sup>5</sup> again the magnitude of the stabilization being greater for  $\alpha$ -chloro compound (Figure 4). This two-orbital-twoelectron stabilizing interaction<sup>6</sup> is in fact great enough to dominate the conformational preference of the  $\alpha$ -chloro acetone



**Figure 4.** Decrease in the energy gaps in the  $n^{-n}\pi^*$  and  $\sigma_{-\pi}\pi^*$  interactions for the *gauche* form due to greater  $\sigma^* - \pi^*$  relative to  $\sigma_{-\pi}$  splitting

so that the gauche form is found to be the most stable form.<sup>3a</sup> The  $\sigma_{cx}-\pi_{co}^*$  interaction is also present in the gauche form of  $\alpha$ -fluoro acetone, but is small due to the relatively greater energy gap,  $\Delta E$ , involved;  $\Delta E$  values for X = F and Cl ar 23.27 and 20.17 eV, respectively. Although the  $\Delta E(\sigma-\pi^*)$  values are large, the overlaps between  $\sigma_{cx}$  and  $\pi_{co}^*$  (III) are also substantial so that the stabilization energy  $\delta \epsilon$  (eq. 1) becomes significant in CH<sub>2</sub>ClCOCH<sub>3</sub>. Similar type of  $\sigma-\pi^*$  interaction is involved in the stabilization of an axial form of the  $\alpha$ -halocyclohexanone relative to an equatorial form.<sup>12</sup>



Interactions between  $\sigma_{cx}^*$  and  $\pi_{co}$  are also conceivable since the overlap integral in Table 1 is seen to be comparable to that for the  $\sigma$ - $\pi^*$  interaction. However the energy gap involved here is even greater, 28 vs 23 eV for  $\Delta E(\sigma^*-\pi)$  vs  $\Delta E(\sigma-\pi^*)$  in the gauche form of  $\alpha$ -fluoro acetone, so that the energy effect due to the  $\sigma^*-\pi$  interaction may be insignificant.

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