

Figure 1. Orbital interactions between two nondegenerate orbitals, ψ_i^0 and ψ_j^0 .

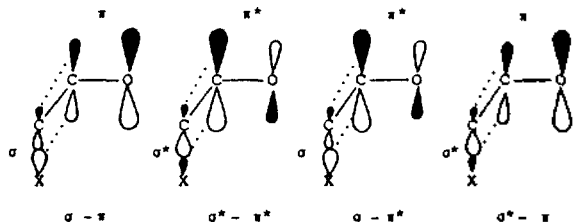


Figure 2. Orbital patterns of the various σ - π orbital interactions for σ_{CX} and π_{CO} , where $X = F$ or Cl .

$\sigma^*-\pi^*$ types. Due to the requirement (i) above, intramolecular σ - π orbital interactions are normally limited to the two orbitals in the vicinal position as in the α -X-ketones. Orbital patterns for the four types of interaction in such a compound are illustrated schematically for σ_{CX} and π_{CO} , where $X = F$ or Cl , in Figure 2.⁹

Reference to Figure 2 reveals that (i) due to the electronegativity differences between the two atoms in the σ_{CX} and in the π_{CO} bonds, vicinal overlap becomes the greatest in $\sigma^*-\pi^*$, while it is the smallest in σ - π interaction,⁹ and (ii) interaction of σ_{CX} is only with the nearest carbon $2p$ -AO of the π_{CO} orbital since the overlap of σ_{CX} with the other end of π_{CO} bond, i.e., $2p$ -AO of O atom, is negligible due to the long distance involved. The symmetries of the $2p$ -AO and σ_{CX} can always be made to match, albeit the matching becomes partial when σ_{CX}^* is involved. For the α -haloacetones, CH_2XCOCH_3 , the σ - π interactions depicted in Figure 2 can operate only in the gauche forms, since σ and π 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 σ - π orbital interactions in the gauche form of CH_2FCOCH_3 . On account of the magnitude of overlap alone, we would expect from eq. (1) the $\sigma^*-\pi^*$ interactions to be greater than the σ - π interactions in α -X-acetones. The STO-3G orbital energies of the σ_{CX} , π_{CO} , σ_{CX}^* and π_{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_o . Inter-level spacings $\Delta E(\sigma-\pi)$ and $\Delta E(\sigma^*-\pi^*)$ are seen to decrease in α -chloro ($X = Cl$) compared to α -fluoro ($X = F$) compound due to the relative raising of σ_{CX} and lowering of σ_{CX}^* orbitals as has been discussed by Bingham.¹¹ As a result, the energy splittings $\delta\epsilon$ due to σ - π and $\sigma^*-\pi^*$ orbital interactions in the gauche forms

TABLE 1: Overlap Integrals for the gauche form of CH_2FCOCH_3 by LCBO-INDO Method

	σ - π	σ - 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_2XCOCH_3

X	χ_i	Forms					
		cis (ΔE)	gauche (ΔE)	trans (ΔE)			
F	σ_{CX}^*	15.14	7.46	16.93	9.52	15.24	7.57
	π_{CO}^*	7.68		7.41		7.67	
	n_o	-8.80		-8.85		-8.80	
	π_{CO}	-10.76		-11.16		-10.65	
	σ_{CX}	-15.68	4.92	-15.86	4.70	-15.88	
	$\Delta E(\sigma-\pi^*)$	23.36		23.27		23.55	
Cl	σ_{CX}^*	9.58	2.30	10.71	4.08	9.51	2.29
	π_{CO}^*	7.28		6.63		7.22	
	n_o	-9.40		-9.34		-9.32	
	π_{CO}	-11.46		-11.29		-11.47	
	σ_{CX}	-13.00	1.54	-13.54	2.25	-12.96	
	$\Delta E(\sigma-\pi^*)$	20.28		20.17		20.18	

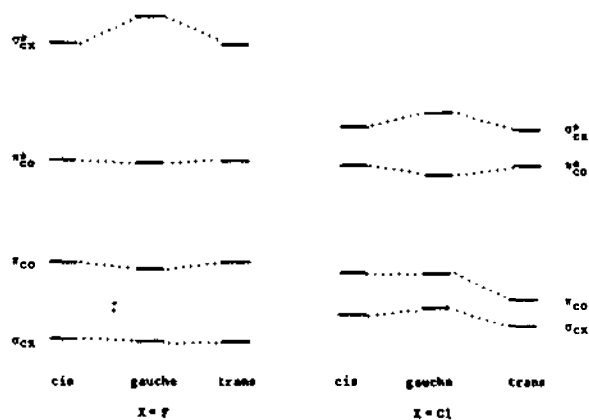


Figure 3: Energy level diagram for CH_2XCOCH_3 showing level splittings in the gauche form due to the σ - π and $\sigma^*-\pi^*$ orbital interactions.

are greater for $X = Cl$ than for $X = F$. Furthermore the energy splittings are greater in the $\sigma^*-\pi^*$ interactions than in the σ - π 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 σ - π interactions.

Effects of the greater orbital splitting in the $\sigma^*-\pi^*$ interaction compared to the level splitting involved in the σ - π interaction are two-fold: Lowering of the π^* 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 π^* and n orbitals, the shift being greater, for α -chloro compound²; (ii) and increased $\sigma_{CX}-\pi_{CO}^*$ interaction giving an extra stabilization to the gauche form,⁵ again the magnitude of the stabilization being greater for α -chloro compound (Figure 4). This two-orbital-two-electron stabilizing interaction⁸ is in fact great enough to dominate the conformational preference of the α -chloro acetone

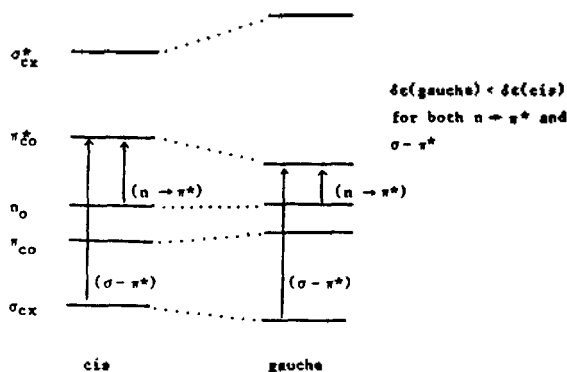
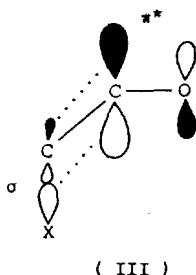


Figure 4. Decrease in the energy gaps in the $n \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ interactions for the *gauche* form due to greater $\sigma^* - \pi^*$ relative to $\sigma - \pi$ splitting

so that the *gauche* form is found to be the most stable form.^{3a}

The $\sigma_{CX} - \pi_{CO}^*$ interaction is also present in the *gauche* form of α -fluoro acetone, but is small due to the relatively greater energy gap, ΔE , involved; ΔE values for X = F and Cl are 23.27 and 20.17 eV, respectively. Although the $\Delta E(\sigma \rightarrow \pi^*)$ values are large, the overlaps between σ_{CX} and π_{CO}^* (III) are also substantial so that the stabilization energy $\delta\epsilon$ (eq. 1) becomes significant in $\text{CH}_2\text{ClCOCH}_3$. Similar type of $\sigma - \pi^*$ interaction is involved in the stabilization of an axial form of the α -halocyclohexanone relative to an equatorial form.¹²



Interactions between σ_{CX}^* and π_{CO} are also conceivable since the overlap integral in Table I 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 α -fluoro acetone, so that the energy effect due to the $\sigma^* - \pi$ interaction may be insignificant.

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References

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