PMO Theory of Orbital Interactions (Part 7). σ-π Interactions

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Orbital interactions of the types, σ-π, σ^*-π, σ-π^* and σ^*-π^* are investigated for the rotamers of α-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 σ^*-π^* interactions are in general greater than the σ-π interactions due to the greater overlap, in spite of the greater energy gap involved; the greater σ^*-π^* interaction causes greater lowering of π^* level relative to the lowering of σ in the σ-π interaction so that both σ-π^* and n-π^* interactions are enhanced in the gauche forms. The extra stability of the gauche form and the red shift in the n-π^* transition are thus found to be natural corollaries of the greater σ^*-π^* interaction in the gauche forms.

Introduction

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

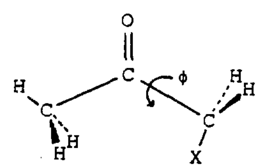
Recently interactions between σ and π orbitals have attracted considerable interest in the interpretation of rotational barrier profiles of π bonded molecules.[3] The interactions involved between a σ and a π orbital within a molecule is a second-order perturbation due to the considerable energy gap between the two, in contrast to the first-order nature of the degenerate TSI. Olivato *et al.*[3b] attributed the increased stabilization of gauche rotamers of α-hetero substituted acetones, CH_2XCOCH_3 (X = Cl, Br, I, OMe, Me_2N, and MeS) to σ_{cx}-π_{co} and σ^*_{cx}-π^*_{co} orbital interactions; in the gauche forms of these compounds the hyperconjugative interaction between σ^*_{cx} and π^*_{co} orbitals lower the π^*_{co} 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 σ^*-π^* orbital interactions. On the other hand, Yamabe *et al.*[4] reported the importance of σ^*-π^* orbital mixing for the nucleophilic displacement on the unsaturated carbon.

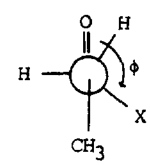
It has been shown however that σ-π^* type interactions may become overemphasized when neglect of differential overlap (NDO) types of calculations are used in the theoretical determination of preferred rotamer, leading to a grossly exaggerated estimate of the stability of gauche conformers in the π-bonded molecules.[5]

The aim of the present work is to investigate the nature of such interactions between σ and π orbitals MO theoretically using ab initio(STO-3G) method.[6] We have shown that the interactions between σ^* and π^* orbitals are in general greater than that between σ and π orbitals so that the σ-π^* type stabilizing interaction is enhanced in a rotamer in which such σ-π and σ^*-π^* interactions are present.

Calculations

Ab initio LCAO-MO-SCF calculations were carried out on *cis* ($\phi = 0°$), *gauche* ($\phi = 90°$) and *trans* ($\phi = 180°$) rotamers of the α-X-acetones (I-II), X = F and Cl, using the STO-3G method.[6] The overlap integrals between two vicinal bonds were estimated by the INDO-LCBO method.[7]





X = F and Cl

(I) (II)

Results and Discussion

According to the perturbation molecular orbital (PMO) theory,[8] two nondegenerate orbitals ψ_i^o and ψ_j^o can interact through space when (i) the two overlap substantially, the magnitude of the total interaction energy, $\delta\varepsilon$(eq. 1), increasing with increasing overlap, (ii) the energy difference between the two interacting orbitals, ΔE^o_{ij}, is not prohibitively large, the magnitude of the interaction energy being inversely proportional to ΔE^o_{ij}, and (iii) the two orbitals interacting have the same symmetry. Orbital interaction scheme is illustrated in Figure 1.

$$\delta\varepsilon = E_i^\circ - E_i \simeq \frac{H_{ij}^2}{E_i^\circ - E_j^\circ} \simeq \frac{k^2 S_{ij}^2}{\Delta E_{ij}^\circ} \quad (1)$$

$$\psi_i = \psi_i^\circ + \lambda \psi_j^\circ,\ \lambda \simeq \frac{kS}{\Delta E_{ij}^\circ} \quad (2)$$

The mixing coefficient λ is proportional to the overlap integral S_{ij} and inversely proportional to the energy gap, ΔE^o_{ij}. 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 ;σ-π, σ-π^*, σ^*-π and

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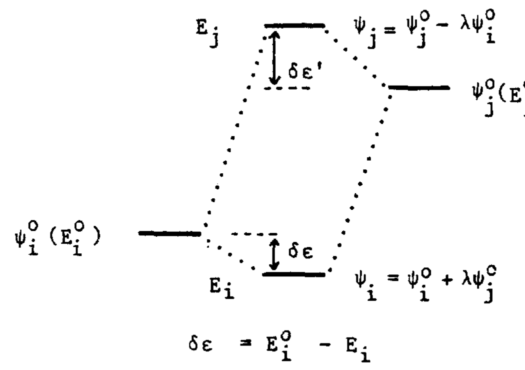


Figure 1. Orbital interactions between two nondegenerate orbitals, ψ_i^o and ψ^o_j.

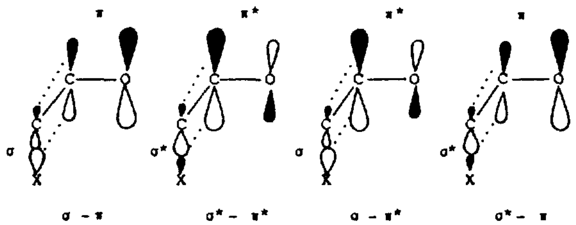


Figure 2. Orbital patterns of the various σ–π orbital interactions for σ_{cx} and π_{co}, where X = F or Cl.

σ^*–π^* 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 σ^*–π^*, 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 σ^*–π^* 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 $\delta\varepsilon$ due to σ–π and σ^*–π^* 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	4.92	−11.16	4.70	−10.65	5.23
	σ_{cx}	−15.68		−15.86		−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	1.54	−11.29	2.25	−11.47	1.49
	σ_{cx}	−13.00		−13.54		−12.96	
	$\Delta E(\sigma$–$\pi^*)$	20.28		20.17		20.18	

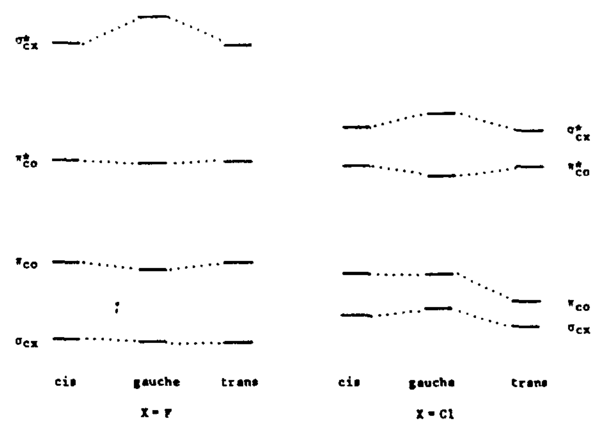


Figure 3: Energy level diagram for CH_2XCOCH_3 showing level splittings in the gauche form due to the σ–π and σ^*–π^* orbital interactions.

are greater for X = Cl than for X = F. Furthermore the energy splittings are greater in the σ^*–π^* 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 σ^*–π^* interactions are clearly demonstrated to be greater than those due to the σ–π interactions.

Effects of the greater orbital splitting in the σ^*–π^* 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 compound[3]; (ii) and increased σ_{CX}–π^*_{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 interaction[8] is in fact great enough to dominate the conformational preference of the α–chloro acetone

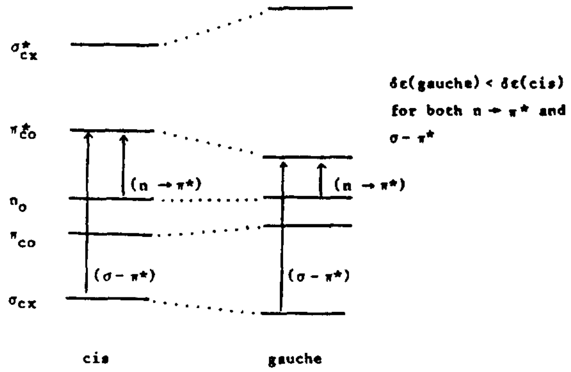
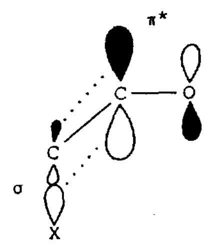


Figure 4. Decrease in the energy gaps in the $n \rightarrow \pi^*$ and $\sigma-\pi^*$ interactions for the *gauche* form due to greater $\sigma^*-\pi^*$ relative to $\sigma-\pi$ splitting.

so that the gauche form is found to be the most stable form.[3a] The σ_{CX}-π^*_{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 ar 23.27 and 20.17 eV, respectively. Although the $\Delta E(\sigma-\pi^*)$ values are large, the overlaps between σ_{CX} and π^*_{CO} (III) are also substantial so that the stabilization energy $\delta\varepsilon$ (eq. 1) becomes significant in $CH_2ClCOCH_3$. 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]



(III)

Interactions between σ^*_{CX} and π_{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 α-fluoro acetone, so that the energy effect due to the $\sigma^*-\pi$ interaction may be insignificant.

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References

(1) (a) I. Lee, *Tetrahedron*, **39**, 2049 (1983); (b) I. Lee, *Bull. Korean Chem. Soc.*, **3**, 140 (1982); (c) I. Lee, C.K. Sohn and W.K. Kim, *J. Korean Chem. Soc.*, **27**, 330 (1983); (d) I. Lee, K. Yang and H.S. Kim, *Tetrahedron*, in press.'

(2) (a) I. Lee and K. Yang, *Bull. Korean Chem. Soc.*, **5**, 131 (1984); (b) I. Lee, K. Yang, N. Lee and W.K. Kim, *J. Korean Chem. Soc.*, **29**, 23 (1985).

(3) (a) S.A. Guerrero, J.R.T. Barros, B. Wladislaw, R. Rittner and P.R. Olivato, *J. Chem. Soc. Perkin II*, 1053 (1983); (b) P.R. Olivato, S.A. Guerrero, A. Modelli, G. Granozzi, D. Jones and G. Distefarro, *ibid.*, 1505 (1984); (c) C.C. Levin, R. Hoffmann, W.J. Hehre and J. Hudec, *ibid.*, 210 (1973).

(4) S. Yamabe, T. Minato and Y. Kawabate, *Can. J. Chem.*, **62**, 235 (1984).

(5) J. Tyrrell, R.B. Weinstock and F. Weinhold, *Int. J. Quant. Chem.*, **19**, 781 (1981).

(6) (a) W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); (b) R. Ditchfield, W.J. Hehre and J.A. Pople, *ibid.*, **54**, 724 (1971).

(7) (a) F. Weinhold and T.K. Brunck, *J. Am. Chem. Soc.*, **98**, 3745 (1976); (b) T.K. Brunck and F. Weinhold, *ibid.*, **101**, 1700 (1979).

(8) T.A. Albright, J.K. Burdett and M.H. Whangbo, "Orbital Interactions in Chemistry," Wiley, New York, 1985.

(9) In general in bonding orbitals the AO coefficient of the more electronegative atom is greater while in antibonding orbitals the AO coefficient of the less electronegative atom becomes greater in a hetero-bond.[7, 10]

(10) (a) T.K. Brunck and F. Weinhold, *J. Am. Chem. Soc.*, **98**, 4392 (1976); (b) N.D. Epiotis, R.L. Yates, J.R. Larson, C.R. Kirmaier and F. Bernard, *ibid.*, **99**, 8379 (1977).

(11) R.C. Bingham, *J. Am. Chem. Soc.*, **97**, 6743 (1975).

(12) N.L. Allinger, J.C. Tai and M.A. Miller, *J. Am. Chem. Soc.*, **88**, 4495 (1966).