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FRAGMENT INTERACTION ANALYSIS IN THE FRAMEWORK OF ab-initio UHF-MO COMPUTATIONS

Part IV[1]. The Second Row Effect in β-substituted ethyl radicals.

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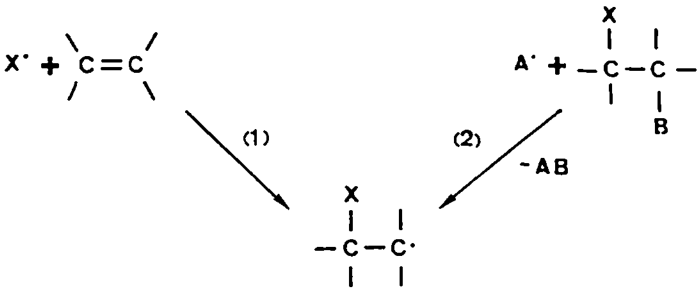
Abstract - The conformational preference in β-substituted ethyl free-radicals has been analysed using a quantitative perturbational MO (PMO) analysis performed in the framework of an ab-initio UHF-MO treatment. The second-row effect, i.e. the increase of the rotaional barrier around the C_α-C_β bond when the β substituent belongs to the second-row has been analysed in details. It has been found that the hyperconjugation is mainly responsible for this effect. In the 2-chloro-ethyl radical the delocalization of the single electron of the SOMO into the antibonding σC-Cl orbital represents the principal contribution to the second-row effect. On the other hand, in the 2-mercapto, 2-phosphino and 2-silyl-ethyl radicals this effect is mainly due to the electron delocalization from the bonding σC-X (X=SH, PH_2, SiH_3) into the SOMO. It has also been found that in all cases the contribution associated with the steric effects and the homoconjugation p-d are small and the one associated with the homoconjugation p-p is practically negligible.

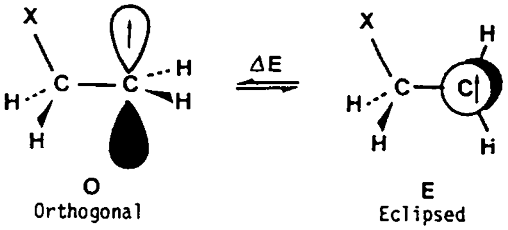
β-substituted alkyl free-radicals are transient species often implied in free-radical chemistry. They can be chiefly generated by addition upon a double bond (1) [2a,b] or by abstraction (2) [2c] (cf. Scheme 1).



Scheme 1

They generally disappear in a transfer step, or in an inter (polymerization) or in an intra (cyclisation) molecular addition step [2d], or by β-fragmentation [2e].

β-substituted alkyl radicals exhibit an interesting diversity of conformational preferences as deduced from ESR measurements or from ab-initio UHF-MO studies. From ESR spectra, all β-substituted ethyl radicals which are known prefer the eclipsed conformation E with a first-row β-substituent (e.g. CH_3 [3a,b], NH_2 [4], OH [5], F [6a-c,f]) whereas substituents from the second-row (e.g. SiH_3 [2e], SCH_3 [2e], Cl [6a-e]) favor the orthogonal conformation O.



Scheme 2

In recent ab-initio UHF-MO studies [7-12] with full geometry optimisation, it was found that substitution of a β-hydrogen atom in the ethyl radical with a substituent belonging to the first-row (e.g. CH_3 [7,8], NH_2 [7,9], OH [7], F [10]) has a small effect upon the rotational barrier around the Cα-Cβ bond. On the other hand when the substituent belongs to the second-row (e.g. SiH_3 [7], PH_2 [7,11] SH [7,11] SH [7,11], Cl [12]) the rotational barrier is found to be larger (at least 1.6 kcal/mol more) [7], the orthogonal rotamer being favoured.

This second row preference for the orthogonal rotamer has been ascribed to three different types of stabilizing effects :

(i) the hyperconjugation, i.e. a delocalisation mechanism involving the Single Occupied MO (SOMO) of the radical center and the C-X bond orbital [2e,6d,e, 13].

(ii) the p-p homoconjugation, i.e. a delocalisation mechanism involving the SOMO of the radical center and the heteroatom lone pair [6b-e, 13b, 13e-f].

(iii) the p-d homoconjugation, i.e. a delocalisation mechanism between the SOMO of the radical center and the d-orbitals of the X substituents [2e, 13c, 14].

However the relative importance of these mechanisms has not been clearly established yet. In fact, there has been only one quantitative investigation at the ab-initio level [11], based on a Fourier expansion analysis and various qualitative MO studies [15]. In a previous study on first-row β-substituted ethyl radicals [16], we have shown that not only the interactions involving the SOMO are important ; but also the interactions associated with the π and π^* MO's of the $-\dot{C}H_2$ fragment since a complete quantitative MO picture of the conformation equilibrium must be include them. In this paper we present a complete detailed analysis for ethyl radicals substituted in β by a first or second-row element. The procedure used is a quantitative PMO analysis performed in the framework of ab-initio UHF-MO computations where the energy effects associated with the various types of orbital interactions are explicitly calculated [17].

COMPUTATIONAL PROCEDURE

The quantitative PMO analysis has been performed at the STO-3G [18], and STO-3G* [19] levels, along the lines described in ref. 17 and 20. All the SCF computations have been carried out with the MONSTERGAUSS series of programs [21]. To simplify the problem we have kept the radical center planar and we have considered only rigid rotation. Therefore, in our analysis we have compared the two structures shown in Scheme 2. For the orthogonal conformation we have used the geometry obtained in a full optimization [7] with subsequent planarization of the radical center, and the eclipsed geometry was obtained through a rigid rotation of the previously defined orthogonal geometry. The orthogonal conformations have been fully optimized with a gradient procedure using the 3-21G basis set [22] when X=CH_3, NH_2, OH, F and the 3-21G* basis set [23] (i.e. with the addition of a set of d orbitals on the second row atom) when X : SiH_3, PH_2, SH, Cl.

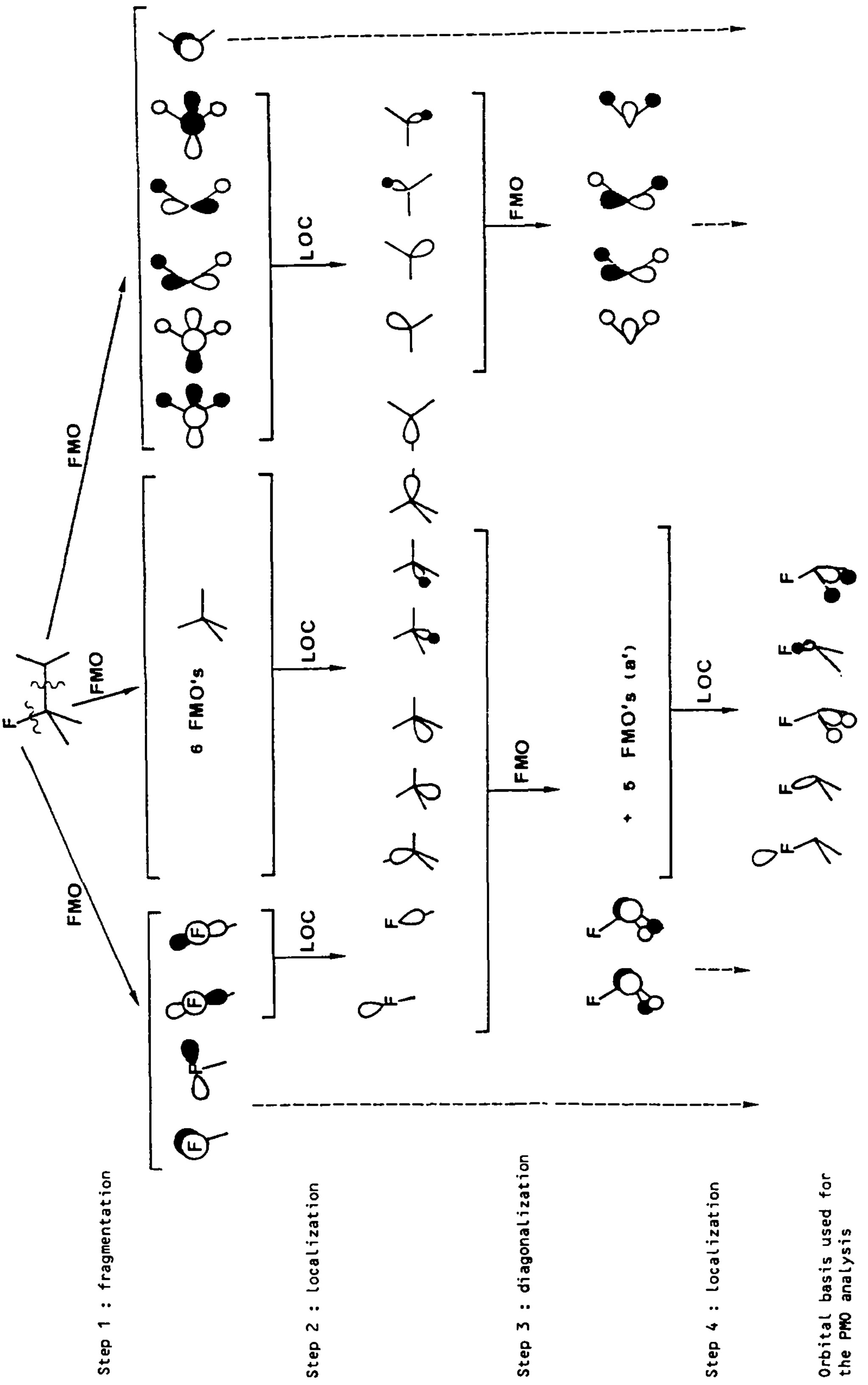


Figure 1. Schematic representation of the procedure used to obtain the fragment orbitals.

The orbital representation used in the PMO analysis has been obtained in the following way (the full procedure is schematically summarized on Figure 1). In a first step, when X belongs to the first-row, the molecule $XCH_2\dot{C}H_2$ in both conformations has been dissected into three fragments (1)-$\dot{C}H_2$; (2)-CH_2- ; (3)-X. When X belongs to the second-row, the X fragment includes the orbitals of X except the d orbitals which are in a fourth fragment dX. For each fragment we have computed the corresponding set of canonical MO's [17,20].

subsequent step we have localized the various canonical MO's previously obtained. More precisely we have localized all the MO's of the -$\dot{C}H_2$ fragment except the singly occupied p orbital (SOMO), the full set of MO's of the -CH_2- fragment without any exception, and finally all the MO's of the -X fragment except those having a local π symmetry with respect to the C-X axis (for example the two p lone-pairs when X = F or Cl).

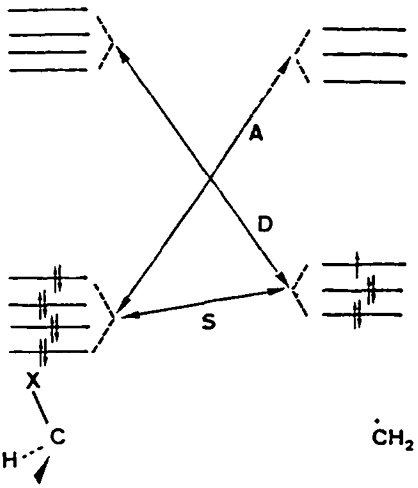
In the next step we have gathered these localized orbitals (LMO's) into two subfragments and we have diagonalized them separately. These two subfragments are a $\dot{C}H_2$ fragment which includes all LMO's of the -$\dot{C}H_2$ fragment except that one pointing towards the β-carbon, and a XCH_2 fragment formed by the LMO's of the -CH_2- fragment (except that one pointing towards the α-carbon) plus the LMO's of the X fragment.

The orbitals obtained with this procedure represent fragment canonical MO's with correct orbital occupancy. As a final step, in order to obtain a better description of the C-X bond, we have localized only the canonical MO's of the fragment XCH_2 having an a' symmetry with respect to the plane of symmetry of the molecule.

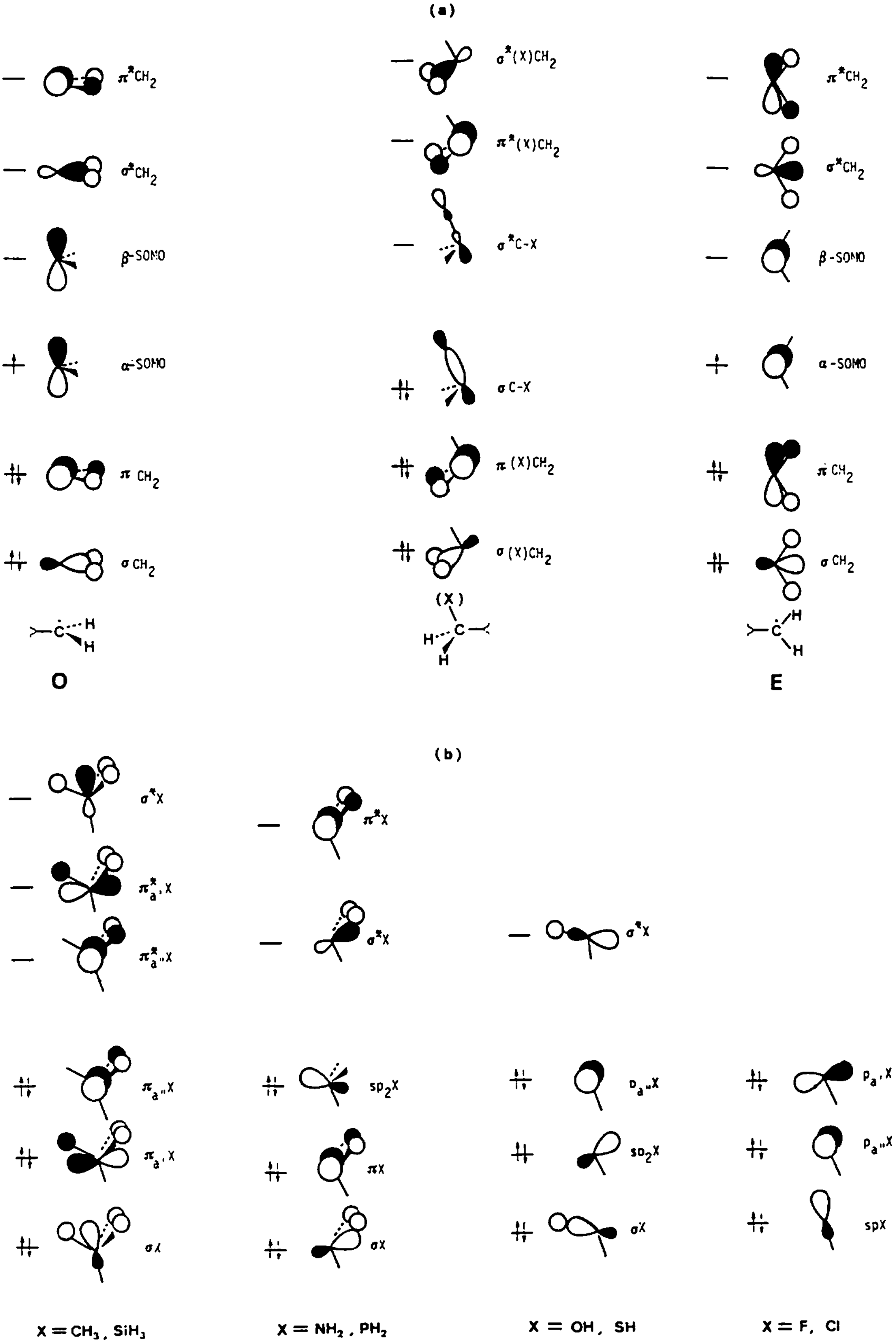
The various MO's obtained with this procedure are represented in part (a) and (b) of Figure 2. The energy effect associated with the interaction between two orbitals are calculated using the method described in ref. 17.

RESULTS AND DISCUSSION

This type of fragmentation allows us to express the second-row effect in β-substituted ethyl radicals in terms of hyperconjugation and homoconjugation p-p and d-p. Furthermore, an estimation of the steric effects can be obtained from the repulsive interactions between occupied MO's. The conjugative effects can be split further into two parts [15c] ; the positive conjugation A which implies delocalisation of electrons belonging to XCH_2 fragment into the empty MO's of the $\dot{C}H_2$ fragment and the negative conjugation D which implies delocalisation of electrons belonging to $\dot{C}H_2$ into the empty MO's of XCH_2 (cf Scheme 3).



Scheme 3



<u>Figure 2</u> : Valence orbitals obtained (a) for the $-\dot{C}H_2$ fragment in the two O and E conformations and for the $(X)CH_2$ fragment, and (b) for the X fragment. The d orbitals of X are not shown.

In Table 1, the conformational preferences are expressed as $\Delta E=E(E)-E(0)$ i.e. the differences of energy between the two rotamers E and 0.

	ΔE^{SCF} (a)	ΔE^{SCF} (b)	ΔE^{PMO}_{σ}	ΔE^{PMO}_{SOMO}	ΔE^{PMO}_{π}	$\Delta E^{PMO}_{SOMO+\pi}$	ΔE^{PMO}_{TOTAL}
$CH_3CH_2\dot{C}H_2$	0.14	0.09	0.27	0.64	-0.85	-0.21	0.06
$NH_2CH_2\dot{C}H_2$	-0.21	0.30	0.07	2.69	-3.33	-0.64	-0.57
$HOCH_2\dot{C}H_2$	-0.87	-0.13	-0.09	4.02	-4.58	-0.56	-0.66
$FCH_2\dot{C}H_2$	-0.64	0.58	0.13	6.60	-6.26	0.34	0.21
$SiH_3CH_2CH_2$	1.96(1.82)	1.36	0.22	-0.83	1.67	0.84	1.06
$PH_2CH_2\dot{C}H_2$	2.09(1.47)	1.66	0.24	0.95	0.36	1.31	1.55
$HSCH_2\dot{C}H_2$	2.33(1.17)	1.46	0.12	1.94	-0.79	1.15	1.26
$ClCH_2CH_2$	3.98(2.02)	2.81	0.12	7.67	-3.45	4.22	4.34

Table 1 : $\Delta E=E(E)-E(0)$ is the energy difference between energy values associated with the orthogonal 0 and eclipsed E conformations for β-substituted ethyl radicals. ΔE^{SCF} refers in (a) to 3-21G//3-21G computations (in parenthesis to 3-21G*//3-21G* ones) and in (b) to STO-3G//3-21G computations (when X belongs to the first-row) and to STO-3G*//3-21G* ones (when X belongs to the secon-row). ΔE^{PMO}_{σ}, ΔE^{PMO}_{SOMO}, ΔE^{PMO}_{π} denote the partial PMO energy differences associated with the σ, SOMO and π orbitals of the $\dot{C}H_2$ fragment. $\Delta E^{PMO}_{SOMO+\pi}$ is the sum of the two last terms and ΔE^{PMO}_{TOTAL} the sum of these three terms.

ΔE^{SCF} denotes the difference between the SCF energy values of the two rotamers. In particular the 3-21G//3-21G results have been obtained at the 3-21G level using the fully optimised 3-21G geometries while, the STO-3G//3-21G results have been obtained at the STO-3G level using the 3-21G geometry with the constraint of the planar radical center, as specified above. The remaining terms represent different contributions to the conformational preferences calculated with the PMO procedure previously described [17].

The ΔE^{SCF} values shows that the more interesting aspect of this problem i.e. the reversal of conformational preference between first and second-row substituents, is well described at the 3-21G//3-21G level. It can also be seen that with the first-row substituents the conformational preference is very small (being in all cases less than 1 Kcal/mol), while the conformational preference becomes significantly more pronounced with the second-row substituents. This trend, i.e. very small conformational preference with the first-row substituent, and larger conformational preference with second-row substituents, is reproduced also at the STO-3G level, and it is this trend that we try to rationalize in the present paper. The analysis of the rsults of Table 1 shows that the STO-3G ΔE^{SCF} values compares satisfactory with the corresponding ΔE^{PMO}_{TOTAL} values, which represent the overall conformational preferences computed with the PMO treatment [17]. In particular the second-row effect appears clearly and therefore we can proceed to analyse with confidence the PMO results.

The analysis of Table 1 shows that the differences of energy effects associated with the interactions involving the σ-type orbitals of the $\dot{C}H_2$ fragment (ΔE^{PMO}_{σ}) are very small in all cases. Consequently they have a slight influence on the conformational equilibrium and on the second-row effect.

It can also be seen that the usual approximation of considering explicitly only the energy effects associated with the SOMO of the radical center (ΔE^{PMO}_{SOMO}) leads to a conformational preference in favour of the 0 rotamer for all radicals except $SiH_3CH_2\dot{C}H_2$. This conformational preference increases with the electronegativity of the β-substituent. Furthermore the energy differences are much too large and they are reduced to the correct order of magnitude only when the energy effects associated with the π MO's of the CH_2 fragment (ΔE^{PMO}_{π}) are taken into account (compare in Table 1 the two last columns). This trend can be understood considering the decomposition of the

SOMO in its α and β spin components (see Figure 2a). The α-SOMO and the β-SOMO are, in fact, very similar to the πCH_2 and $\pi^* CH_2$MO respectively the only difference being the occupancy of the CH_2 orbital which is twice that of the SOMO, but this effect is counterbalanced by a larger overlap associated with the SOMO. Because the two types of orbitals lie on orthogonal planes, when we change conformation the interactions associated with the SOMO's are replaced by the interactions associated with the πCH_2 orbitals and vice versa. For this reason the ΔE values become small when both types of interactions are taken into account (cf $\Delta E^{PMO}_{SOMO+\pi}$ in table 1).

Therefore, to obtain a satisfactory rationalization of this problem, we have to consider explicitly the various types of orbital interactions involving either the SOMO's or the πCH_2 orbitals. We have also found convenient to separate further the various interactions according to the symmetry of the MO's involved. Because, in fact, all the conformations examined here have a plane of symmetry, the MO's of the various fragments in the canonical representation are either symmetric (a' type) or antisymmetric (a" type) with respect to this plane. Furthermore all fragment MO's have been classified as σ or π with respect to local symmetry of the various fragments.

	$\Delta E^{PMO}_{a'}$	$\Delta E^{PMO}_{a''}$
$CH_3CH_2\dot{C}H_2$	4.28	-4.49
$NH_2CH_2\dot{C}H_2$	3.94	-4.58
$HOCH_2\dot{C}H_2$	4.11	-4.67
$FCH_2\dot{C}H_2$	4.90	-4.56
$SiH_3CH_2\dot{C}H_2$	5.42	-4.58
$PH_2CH_2\dot{C}H_2$	6.13	-4.82
$HSCH_2\dot{C}H_2$	5.99	-4.85
$ClCH_2\dot{C}H_2$	9.30	-5.08

Table II : Contributions of the interaction between a'-orbitals ($\Delta E^{PMO}_{a'}$) and a" orbitals ($\Delta E^{PMO}_{a''}$) to the conformational preference (ΔE = E(E) - E(O) in Kcal/mol) in β-substituted ethyl radical.

The analysis of the energy differences associated with a' and a" MO's listed in table II, shows that the interactions between a' MO's favour the O rotamer, while the interactions between a" MO's favour the E rotamer. Furthermore the interactions involving the fragment orbitals of a" symmetry are not significantly affected by the β-substituent, and their energy difference in the two conformations remains of the order of magnitude found in the ethyl radical[16]. This trend is caused by the fact that the a"-MO's contain the β-substituent in their nodal plane of symmetry which is also the nodal plane of the molecule, and therefore their effect do not change significantly with the change of the β-substituent. *It is clear from Table II that the second-row effect must be found in the frame of the energy effects associated with the fragment MO's of a' symmetry.*

In Table III the contributions to the conformational equilibrium due to the orbitals of a' symmetry, i.e. the energy differences between interactions due to πCH_2 and $\pi^* CH_2$ in rotamer E and those due to the α-SOMO and β-SOMO in rotamer O has been decomposed in four subgroups ; i) a' type d orbitals ii) other a' MO's belonging to the X group, iii) the C-X bond and iv) the a'-type MO's of $(X)CH_2$, i.e. $\sigma(X)CH_2$ and $\sigma^*(X)CH_2$.

For the subgroups ii), iii) and iv) the conformational preference has been dissected into three contributions a) the steric effect (S) due to repulsion between occupied MO's, b) the negative conjugation, or donor effect (D) of the $\dot{C}H_2$ fragment, due to interactions between occupied MO's of $\dot{C}H_2$ with unoccupied MO's of XCH_2 subfragments, c) the positive conjugation, or acceptor effect (A) of the CH_2 fragment, due to interactions between unoccupied MO's of $\dot{C}H_2$ with occupied MO's of XCH_2 subfragments.

In table IV, the second-row effect is tentatively measured in terms of the difference $\Delta\Delta E = \Delta E$(2nd-row) - ΔE(1st-row) for radicals having β-substituents belonging to the same column of the periodic table. In the a'-MO's subspace, we have considered the contribution of each group (dX, X, C-X, (X)CH_2) to $\Delta\Delta E$ and in each group the steric and conjugative (donor and attractor) contributions.

In table IV a positive number means that the second row β-substituent favors more the O rotamer than the corresponding first row β-substituent. We proceed now to discuss the second-row effect in detail ;

dX ORBITAL INTERACTIONS

The values of Table IV show very clearly that in all cases the d-orbital interactions reinforce the second-row effect, even if the contribution is quite small. A more close analysis of this effect shows that the d-orbital of a' symmetry interacts in the O rotamer only with the singly occupied α-SOMO and in the E rotamer with the doubly occupied πCH_2MO (cf. Figure 3).

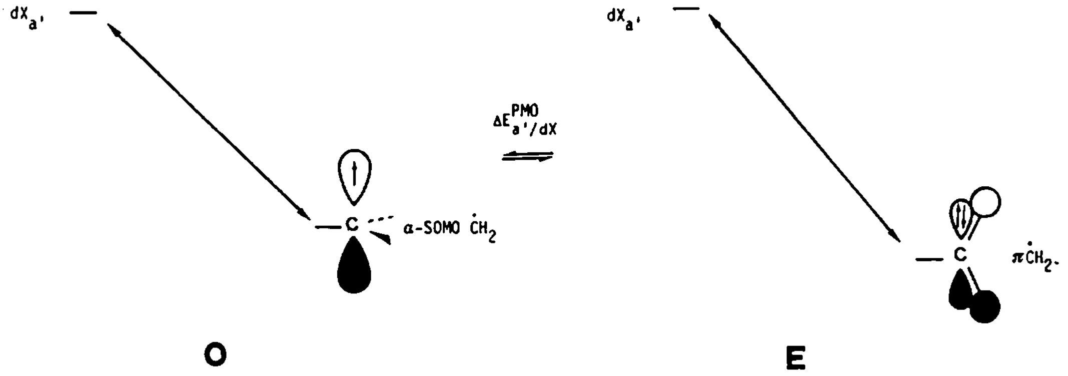


Figure 3. Representation of the $dX_{a'} \leftrightarrow \alpha$-SOMO and $dX_{a'} \leftrightarrow \pi\dot{C}H_2$ interactions respectively in the O and E rotamers of XCH_2CH_2.

But the effect of orbital occupancy is counterbalanced by a better overlap which is roughly twice larger in the interaction da'↔α-SOMO than in interaction da'↔πCH_2 and by an energy gap which is also more favorable for the da'↔α-SOMO interaction.

X GROUP INTERACTIONS

The analysis of the results of Table III shows that these types of energy effects are rather small. It is also found that in all cases only the repulsive contribution (S) is significant, so that these effects are mainly steric in nature. In all cases they favour the O conformation. This means that there is more repulsion in the E rotamer with the πMO's of CH_2 than in the O rotamer with the SOMO.

From Table IV it appears that there is not a clear trend about the second-row effect. There is no effect for the pair $HSCH_2\dot{C}H_2/HOCH_2\dot{C}H_2$. For the pair $ClCH_2\dot{C}H_2/FCH_2\dot{C}H_2$, the second-row effect is due to a difference of repulsive effect with the in-plane lone pair pa' that is larger when X = Cl than when X = F (cf. Figure 2a).

There is also a surprising difference of behavior between the pairs $PH_2CH_2\dot{C}H_2/NH_2CH_2\dot{C}H_2$ and $SiH_3CH_2\dot{C}H_2/CH_3CH_2\dot{C}H_2$. This arises mainly from the difference of steric interaction between the σPH_2, σNH_2, $\pi_{a'}SiH_3$ and $\pi_{a'}CH_3$ orbitals with the SOMO in the O rotamer or with the πCH_2 orbital in the E rotamer.

X		CH_3	NH_2	HO	F	SiH_3	PH_2	HS	Cl
$\Delta E^{PMO}_{a'/dX}$	A	-	-	-	-	0.35	0.31	0.47	0.59
$\Delta E^{PMO}_{a'/X}$	S	0.77	0.46	0.30	0.12	0.41	0.90	0.37	0.58
	D	0.06	0.02	0.09	-	0.19	0.00	0.10	-
	A	0.16	0.17	0.25	0.55	0.04	0.25	0.09	0.66
	Σ	0.99	0.65	0.64	0.67	0.64	1.15	0.56	1.24
$\Delta E^{PMO}_{a'/C-X}$	S	0.61	0.48	0.13	0.31	0.99	0.68	0.85	0.65
	D	1.23	1.78	2.11	2.78	0.71	1.47	1.82	4.75
	A	0.50	0.36	0.21	0.13	1.58	1.38	1.09	0.63
	Σ	2.34	2.62	2.45	3.22	3.28	3.53	3.76	6.03
$\Delta E^{PMO}_{a'/(X)CH_2}$	S	0.10	-0.09	0.27	0.18	0.22	0.21	0.31	0.52
	D	0.64	0.61	0.64	0.71	0.59	0.66	0.63	0.80
	A	0.21	0.15	0.11	0.12	0.34	0.27	0.26	0.12
	Σ	0.95	0.67	1.02	1.01	1.15	1.14	1.20	1.44

Table III : Contributions to the conformational preference in $XCH_2\dot{C}H_2$ ($\Delta E = E(E)-E(O)$ in kcal/mol) due to orbitals of a' symmetry belonging to subgroups dX, X, C-X and $(X)CH_2$. For the three last subgroups the total contribution (Σ) has been dissected into Steric (S), Donor (D) and Acceptor (A) effects.

X_{2nd}/X_{1st}		SiH_3/CH_3	PH_2/NH_2	HS/HO	Cl/F
$\Delta\Delta E^{PMO}_{a'/dx}$	A	0.35	0.30	0.46	0.59
$\Delta\Delta E^{PMO}_{a'/X}$	S	0.36	0.44	0.07	0.46
	D	0.13	-0.02	0.01	-
	A	-0.12	0.08	-0.16	0.11
	Σ	0.35	0.50	-0.08	0.57
$\Delta\Delta E^{PMO}_{a'/C-X}$	S	0.38	0.20	0.72	0.34
	D	-0.52	-0.31	-0.29	1.97
	A	1.08	1.02	0.88	0.50
	Σ	0.94	0.91	1.31	2.81
$\Delta\Delta E^{PMO}_{a'/(X)CH_2}$	S	0.12	0.30	0.04	0.34
	D	-0.05	0.05	-0.01	0.09
	A	0.13	0.12	0.15	0.00
	Σ	0.10	0.47	0.18	0.43

Table IV : Second-row effect, $(X_{2nd}CH_2\dot{C}H_2/X_{1st}CH_2\dot{C}H_2)$ measured in kcal/mol as $\Delta\Delta E = \Delta E(2nd\text{-}row)-\Delta E(1st\text{-}row)$. ΔE(2nd-row) and ΔE(1st-row) are those given in Table III. The total contribution (Σ) has been dissected into Steric (S), Donor (D) and Acceptor (A) effects.

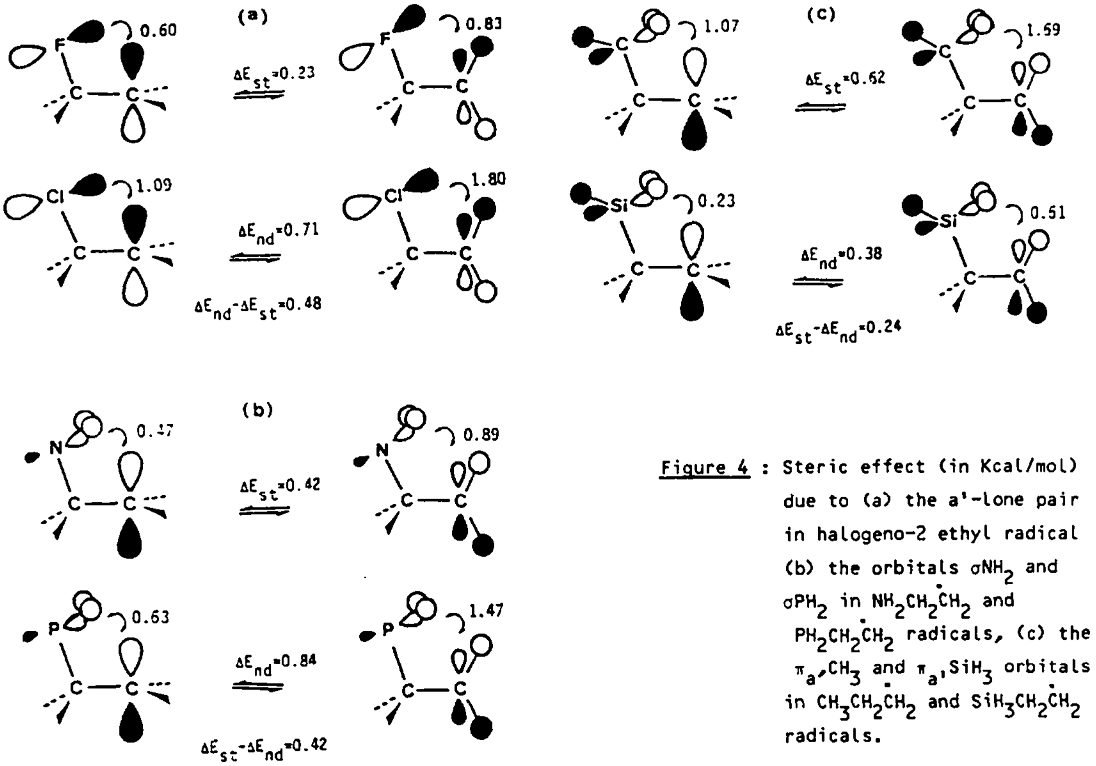


Figure 4 : Steric effect (in Kcal/mol) due to (a) the a'-lone pair in halogeno-2 ethyl radical (b) the orbitals σNH_2 and σPH_2 in $NH_2CH_2\dot{C}H_2$ and $PH_2CH_2\dot{C}H_2$ radicals, (c) the $\pi_{a'}CH_3$ and $\pi_{a'}SiH_3$ orbitals in $CH_3CH_2\dot{C}H_2$ and $SiH_3CH_2\dot{C}H_2$ radicals.

From the values given in Figure 4b and 4c it appears that a SiH_3 group shows less steric hindrance to the $C_\alpha-C_\beta$ rotation than a CH_3 group. But on the other hand a PH_2 group shows more repulsion with the CH_2 group than the NH_2 one. Actually these trends can be easily explained looking at the geometry of these molecules. The groups SiH_3 and CH_3 have roughly the same hybridization if one measure the angle between the YH_2 plane and the Y-C bond (Y = Si or C), respectively 126.0° and 126.6°. But the Si-C bond is longer than a C-C and consequently the SiH_3 group shows less hindrance to the rotation of the $\dot{C}H_2$ group then the CH_3 group. In $PH_2CH_2\dot{C}H_2$ the C-P bond is longer than the C-N bond in $NH_2CH_2\dot{C}H_2$, but the angle of the PH_2 plane with P-C is much smaller (101.5) than the angle of NH_2 with N-C (132.1). It follows that, in the E rotamer, the H's bound to P come closer to the H bound to the radical center than the H's bond to N (2.73 Å against 2.79 Å). Consequently there is more steric hindrance to the rotation of the $\dot{C}H_2$ group in the $PH_2CH_2\dot{C}H_2$ radical than in the $NH_2CH_2\dot{C}H_2$ one, which is part of the second-row effect.

C-X BOND INTERACTION

Interactions of the $\sigma C-X$ and $\sigma^* C-X$ orbitals with the α- and β-SOMO's in the O rotamer and the πCH_2 and $\pi^* CH_2$ in the E rotamer provide the main contribution to the second-row effect. From Table IV one can notice that the steric contribution always favours the second-row effect, but the main contribution comes from the donor effect of the $\dot{C}H_2$ fragment if one compares $FCH_2\dot{C}H_2$ to $ClCH_2\dot{C}H_2$, and comes from the acceptor effect of the $\dot{C}H_2$ fragment if one compares the three other pairs.

1) The steric interaction between C-X and CH_2

This effect is due to the $\sigma C-X \leftrightarrow \alpha$-SOMO interaction in the O rotamer and to the $\sigma C-X \leftrightarrow \pi CH_2$ interaction in the E rotamer. Between the three kinds of interactions S, D and A (cf Scheme 4), the steric one is, in magnitude, the largest one. These steric interactions are more repulsive when X is a second-row substituent than when it is a first-row one (cf Figure 5). A detailed analysis shows this is due to a larger overlap between the orbitals when X belongs to the second-row. Furthermore the $\sigma C-X \leftrightarrow \pi CH_2$ interactions is always more destabilizing than the $\sigma C-X \leftrightarrow \alpha$-SOMO one, and that difference is more pronounced if X belongs to the second-row. Consequently the related

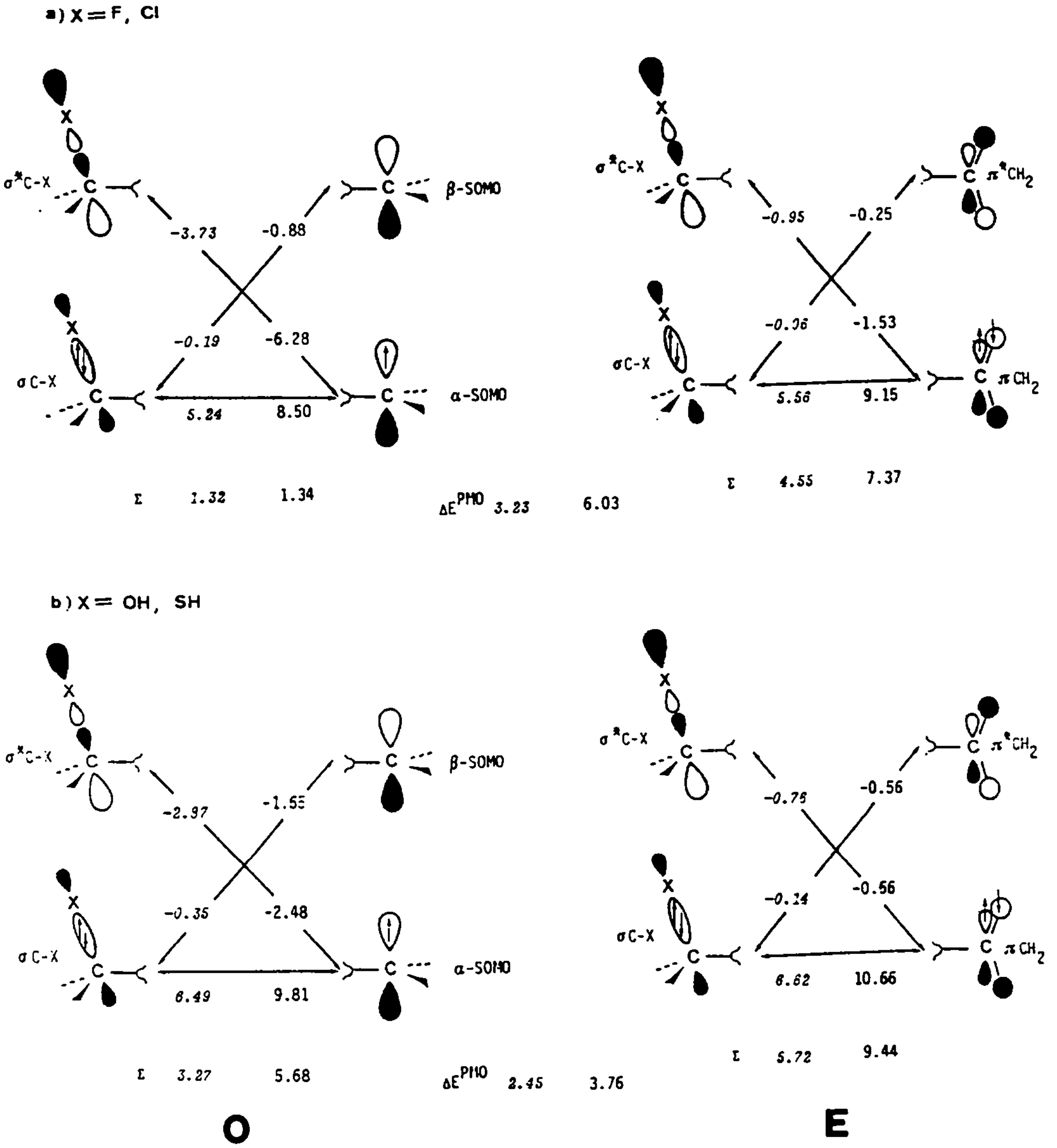


Figure 5 : Hyperconjugative and steric effects (in Kcal/mol) with the σC-X and σ^*C-X orbitals into the O and E rotamers of the X-CH_2CH_2 radicals. Σ represents the sum of the effects and $\Delta E^{PMO} = \Sigma E(E) - \Sigma E(O)$. Italic numbers refer to X first-row and straight numbers to X second-row.

ΔE's are larger for the second-row β-substituted radical (cf Table III). Then the $\Delta\Delta E$'s indicate a slight steric tendency in favor of the second-row effect (cf. Table IV).

2) The Acceptor effect of CH_2

This effect comes from the $\sigma C\text{-}X \leftrightarrow \beta$-SOMO interaction in the O rotamer and from the $\sigma C\text{-}X \leftrightarrow \pi^* CH_2$ interaction in the E rotamer. Due to a higher energy of the σC-X orbitals and also to a better overlap, these interactions are always more stabilizing when X is a second-row substituent. Furthermore the $\sigma C\text{-}X \leftrightarrow \beta$-SOMO interaction is always more stabilizing than the $\sigma C\text{-}X \leftrightarrow \pi^* CH_2$ one, and that difference is more pronounced if X belongs to the second-row. Consequently values of ΔE are smaller when X is a first-row substituent than when it is a second-row one (cf Table III). It follows that the Acceptor interactions contribue to the second-row effect. For the radicals $SiH_3CH_2\dot{C}H_2$, $Ph_2CH_2\dot{C}H_2$ and $HSCH_2\dot{C}H_2$ it is actually the largest contribution to the second-row effect (cf Table IV).

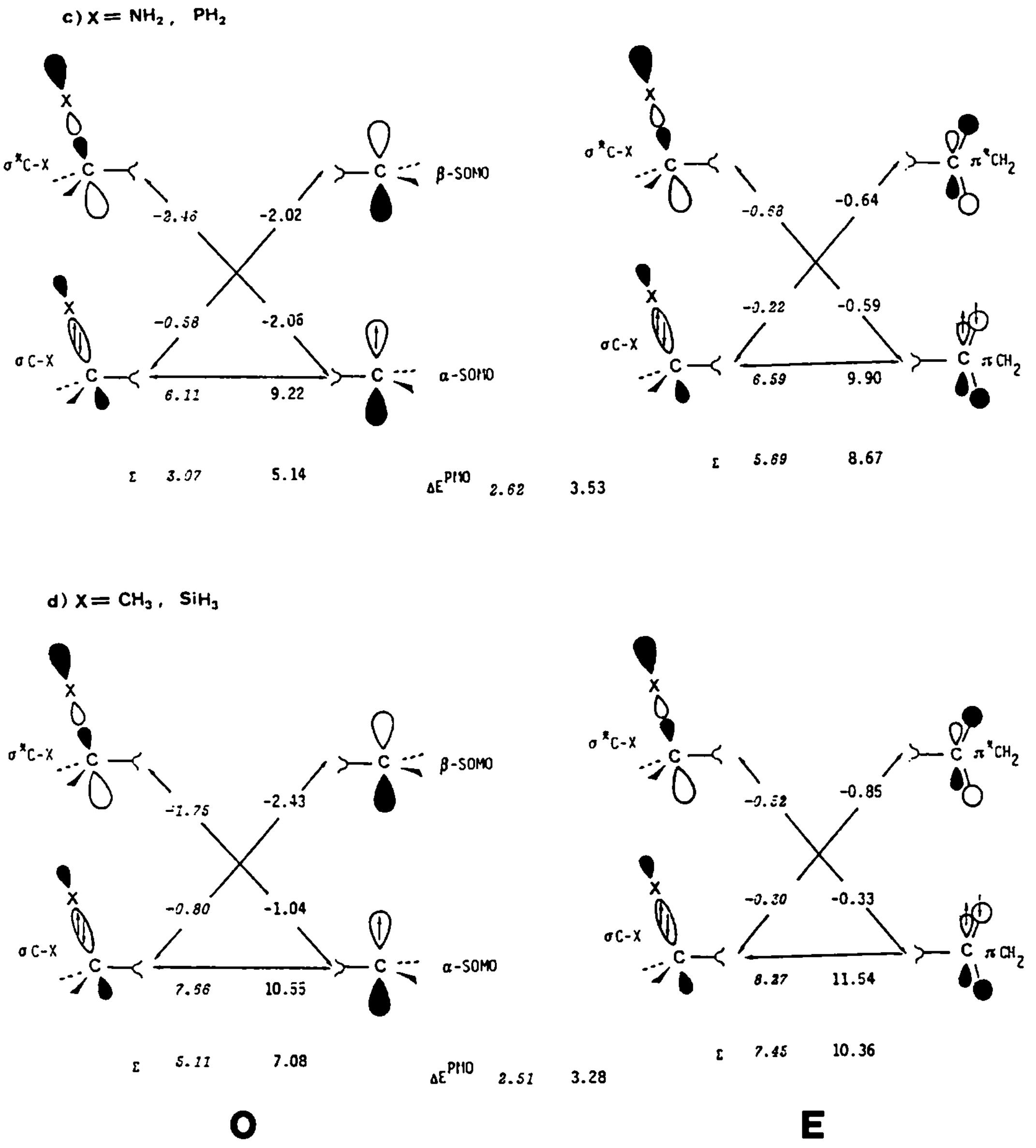


Figure 5 : See comments on preceeding page

3) The Donor effect of CH_2

This effect comes from the σ^*C-X↔α-SOMO interaction in the O rotamer and from the σ^*C-X↔πCH_2 in the E rotamer. Due to a lower overlap between the orbitals, these interactions are less stabilizing for $SiH_3CH_2\dot{C}H_2$, $PH_2CH_2\dot{C}H_2$ and $HSCH_2\dot{C}H_2$ than in the corresponding radicals of the first-row. But in $ClCH_2\dot{C}H_2$, these interactions are more stabilizing than in $FCH_2\dot{C}H_2$. That particular behavior is mainly due to a much more favorable value of the Hij integral in $ClCH_2\dot{C}H_2$ than in $FCH_2\dot{C}H_2$. Futhermore, for all radicals, the σ^*C-X↔πCH_2 interaction in the E rotamer is always less stabilizing than the σ^*C-X↔α-SOMO are in the O rotamer. Consequently the Acceptor effect of $\dot{C}H_2$ works again the second-row effect in $SiH_3CH_2\dot{C}H_2$, $PH_2CH_2\dot{C}H_2$ and $HSCH_2\dot{C}H_2$, but reinforces it in $ClCH_2\dot{C}H_2$ since the interaction σ^*C-X↔α-SOMO is much more stabilizing than the σ^*C-X↔πCH_2 (cf. Figure 5). For $ClCH_2\dot{C}H_2$ it is actually the main contribution to the second-row effect.

(X)CH_2 GROUP INTERACTIONS

For all radicals the (X)CH_2 group interactions contribute very slightly to the second-row effect an all individual contributions (S, D, A) are small.

CONCLUSION

Experimental and theoretical results indicate that in β-substituted ethylradicals operates the so-called second-row effect, i.e. the conformational equilibrium between the O and E rotamers is more in favor of the O rotamer when the β-substituents belongs to the second-row. To understand the origin of this effect, we have performed a quantitative PMO analysis in the framework of an ab-initio UHF-MO treatment on a series of β-substituted ethyl radicals and we have compared the energy effects associated with the various types of orbital interactions.

For all radicals studied here, the main contribution to the second-row effect comes from the hyperconjugation with the σC-X bond. But the nature of the hyperconjugation is quite different in the various radicals. In $ClCH_2\dot{C}H_2$ it is the interaction pα-SOMO↔σ^*C-X (negative hyperconjugation) which is mainly responsible of the second-row effect, whereas in the radicals $SiH_3CH_2\dot{C}H_2$, $PH_2CH_2\dot{C}H_2$, $HSCH_2\dot{C}H_2$ it is the interaction β-SOMO↔σC-X (positive hyperconjugation) which provides the largest contributions. Other less significant contributions come from the d-orbitals (d-p homoconjugation and from the steric effect, while the p-p homoconjugation plays no role.

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