# A Theoretical Study of the Electronic Structure of $\beta$-Substituted Alkyl Radicals

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**Abstract:** The conformational preferences of $\beta$-substituted alkyl radicals are examined theoretically by means of molecular orbital calculations. It is found that conformations of these species depend on a delicate balance of hyperconjugative effects and nonbonded interactions. Thus, hyperconjugation tends to favor the planar eclipsed or eclipsed anti (for nonplanar radical centers) conformations for radicals of the type $\cdot CR_2CH_2X^\beta$ (where $X^\beta$ is a substituent from the second or succeeding rows of the periodic table). An increased preference for the staggered conformation is obtained for nonplanar radicals with bulky $X^\beta$ substituents, such as Br or I, due to steric effects. The extent of p-p and d-p homoconjugation relative to hyperconjugation is also discussed. No p-p homoconjugation is found for very electronegative substituents such as $X^\beta$ = F or OR, but both p-p and d-p homoconjugation appears to be present for $X^\beta$ substituents such as Cl. A possible mechanism for the racemization of optically active $\cdot CR_1R_2CH_2X^\beta$ radicals is presented and the rate of racemization is traced to the bulkiness of the $X^\beta$ substituent.

$\beta$-Substituted alkyl radicals exhibit an interesting diversity of conformational preferences as deduced from EPR measurements. All $\beta$-substituted ethyl radicals which are known prefer the staggered conformation when the substituent is from the first row of the periodic table (e.g., $CH_3$,[1] $NH_2$,[2] OH,[3] $OCH_3$,[4] $OCF_3$,[4] F[5]), whereas substituents from the succeeding rows create a preference for the eclipsed conformation (e.g., $SiH_3$,[4] $GeH_3$,[4] $SnBu_3$,[4] $SCH_3$,[4] $SCF_3$,[4] Cl[5]). The preference for the eclipsed conformation has been ascribed to the stabilizing effect of p-d homoconjugation by Krusic and Kochi,[4] whereas Lyons and Symons[6] have proposed that hyperconjugation alone is responsible. Griller and Ingold[7] favor both hyperconjugation and p-d homoconjugation because of the similarity of the hfs of carbon- and silicon-substituted radicals. Meanwhile, Kawamura, Edge, and Kochi[8] have argued on the basis of g shifts that the largest stabilizing factor for the eclipsed conformation of the $\beta$-chloroethyl radical is a result of p-p homoconjugation.

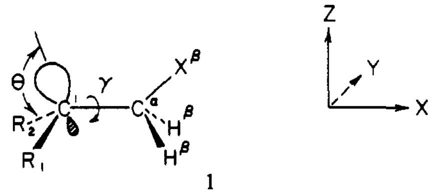
It has been noted that alkyl substitution at the trigonal carbon generally causes a preference for the eclipsed conformation, regardless of the nature of the $\beta$ substituent.[7,9] This phenomena has been thought to be a result of simple steric repulsion between the alkyl groups and the $\beta$ substituent. However, the $\beta$-bromo and $\beta$-iodo-*tert*-butyl radicals have recently been reported to exist in a staggered conformation[10] and this was taken as evidence for nonplanarity at the radical site. The relatively high barrier to rotation/inversion reported in this study[10] (>3 kcal/mol) is similar to the activation energy of racemization reported for "bridged" $\beta$-bromo alkyl radicals.[11]

A theoretical study of the relationship between geometric preference and $\beta$ substituent for alkyl radicals will allow conclusions to be drawn regarding the fundamental reasons for their observed conformational behavior and will shed additional light on the exact nature of "bridged" free radicals. The present work reports the results of calculations on the $\beta$-halo ethyl and $\beta$-halo-*tert*-butyl radicals in terms of (1) electronic effects involving hyperconjugation of the C-$X^\beta$ bond with the unpaired electron and (2) familiar steric repulsions between nonbonded atoms. The individual interactions will be discussed separately and their effects on the stable conformations of these species will be examined.

## Results and Discussion

**1. Hyperconjugative Effects.** Hyperconjugation as considered here is the interaction of orbitals on a methyl or substituted methyl group with a $\pi$ system and can be very important in determining the equilibrium conformations of molecules. The concepts of Hoffmann et al.[12] concerning the role of hyperconjugation in determining conformational preferences of substituted alkyl anions and cations will now be extended to $\beta$-substituted alkyl radicals.

The coordinate system along with the angles which were varied is shown in **1.** The angle $\theta$ measures the degree of nonplanarity about the central radical carbon (C′), maintaining local $C_{3v}$ symmetry. Angle $\gamma$ describes the rotation about the C′-$C^\alpha$ bond and measures the dihedral angle between the local $C_{3v}$ axis and the $C^\alpha$-$X^\beta$ bond. Several important conformations using the above convention are given in **2.**



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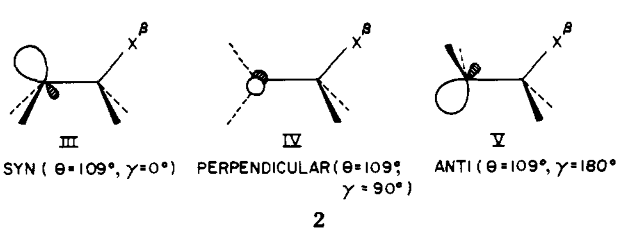


I ECLIPSED (θ = 90°, γ = 0°)

II STAGGERED (θ = 90°, γ = 90°)

III SYN (θ = 109°, γ = 0°)

IV PERPENDICULAR (θ = 109°, γ = 90°)

V ANTI (θ = 109°, γ = 180°)

2

An interaction diagram showing the interaction of a p orbital on the planar $CR_2$ fragment with a $CH_2X^\beta$ group in planar $\cdot CR_2$-$CH_2X^\beta$ is given in Figure 1. The notation of $\sigma\pi$ and $\sigma\pi^*$ describing the hyperconjugation is adapted from Libit and Hoffmann.[13] For substituents of comparable electronegativity with hydrogen (e.g., $X^\beta$ = Cl, Br, I, $SiR_3$, SR), the order of the $\sigma\pi$ orbitals is as shown in Figure 1. The order of $\sigma\pi_z$ and $\sigma\pi_y$ is reversed when $X^\beta$ is much more electronegative than H (e.g., $X^\beta$ = F, OR). Interactions 2 and 4 are stabilizing since these

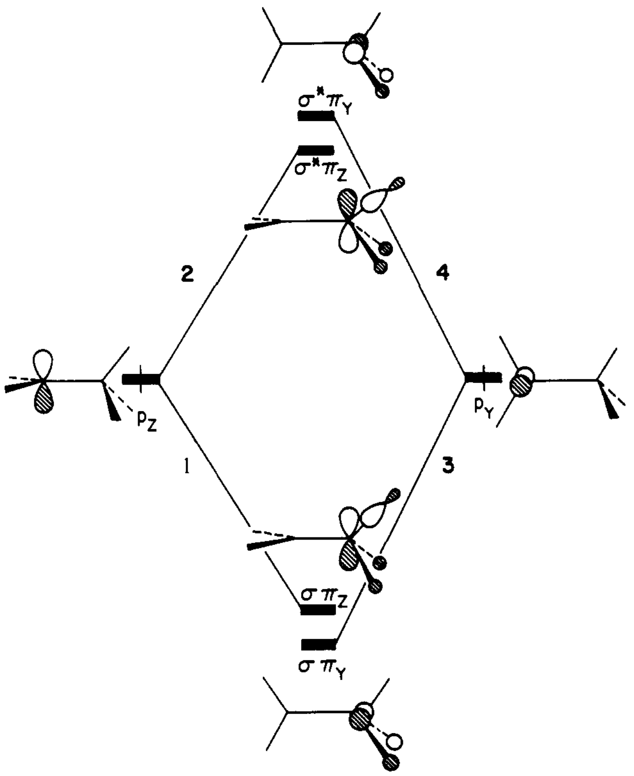


**Figure 1.** An interaction diagram of a p orbital on a planar $CR_2$ fragment with a $CH_2X^\beta$ group.

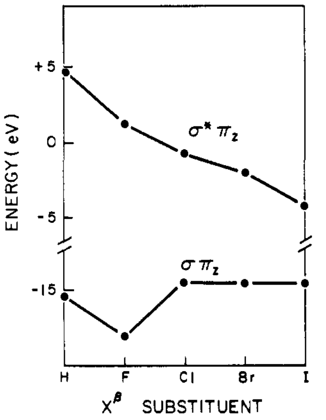


**Figure 2.** The change in the $\sigma\pi_z$ and $\sigma\pi_z{}^*$ orbital energies as a function of $X^\beta$ substituent.

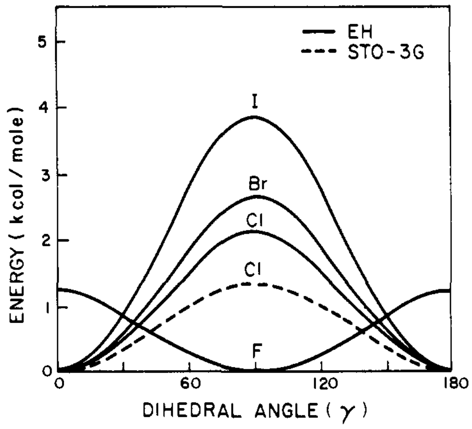


**Figure 3.** The energies of planar β-haloethyl radicals as a function of the rotation angle, γ. The most stable conformation is assigned zero energy.

**Table I.** Charges and Overlap Populations for Planar $\cdot CH_2CH_2X$ Radicals Calculated by the Extended Hückel Method (EH)

| | Charges[a] | | | Overlap populations[a] | | |
|---|---|---|---|---|---|---|
| | C′ | $X^\beta$ | $H^\beta$ | C′-$C^\alpha$ | $C^\alpha$-$X^\beta$ | $C^\alpha$-$H^\beta$ |
| H | −0.173 | +0.047 | +0.034 | 0.801 | 0.764 | 0.781 |
| | −0.173 | +0.028 | +0.043 | 0.801 | 0.786 | 0.769 |
| P | −0.133 | −0.681 | +0.014 | 0.808 | 0.344 | 0.788 |
| | −0.199 | −0.678 | +0.029 | 0.816 | 0.355 | 0.772 |
| Cl | −0.211 | −0.133 | +0.018 | 0.823 | 0.562 | 0.788 |
| | −0.194 | −0.197 | +0.034 | 0.816 | 0.590 | 0.772 |
| Br | −0.207 | −0.118 | +0.023 | 0.825 | 0.543 | 0.788 |
| | −0.187 | −0.176 | +0.038 | 0.815 | 0.573 | 0.773 |
| I | −0.197 | −0.118 | +0.031 | 0.839 | 0.489 | 0.789 |
| | −0.177 | −0.176 | +0.044 | 0.815 | 0.525 | 0.774 |

[a] For a particular column the first and second numbers correspond to values for the eclipsed and staggered conformations, respectively.

involve the interaction of a half-filled with an unfilled orbital.[14] In addition, the three-electron orbital interactions 1 and 3 can also be stabilizing.[14]

The $\sigma\pi_z$ and $\sigma\pi_z{}^*$ orbital energies as a function of the $X^\beta$ substituent calculated by the extended Hückel method[15] (EH) are shown in Figure 2. The geometries and parameters used in the EH calculations are given in the Appendix. The $\sigma\pi_z$ and $\sigma\pi_z{}^*$ orbital energies can be understood in terms of the electronegativity of the $X^\beta$ substituent and the $C^\alpha$-$X^\beta$ overlap. When the β substituent is very electronegative (e.g., $X^\beta = F$), both the $\sigma\pi_z$ and $\sigma\pi_z{}^*$ will be depressed.[12] For the less electronegative substituents $X^\beta$ = Cl, Br, I, the $C^\alpha$-$X^\beta$ overlap decreases steadily allowing the $\sigma\pi_z{}^*$ to fall in energy while the $\sigma\pi_z$ remains essentially constant.

The effect of the trend in the $\sigma\pi$ and $\sigma\pi^*$ levels on the charges and overlap populations in $CH_2CH_2X$ radicals is shown in Table I. When $X^\beta = F$ the charge on C′ is more negative for the staggered conformation (II) indicating that interaction 3 (cf. Figure 1) is dominant for this case. The increased C′-$C^\alpha$ overlap population also seems to indicate that the staggered conformation is preferred for $X^\beta = F$. For $X^\beta$ = Cl, Br, or I this trend is reversed as witnessed by a more negative charge on C′ and a larger overlap population for the C′-$C^\alpha$ bond in the eclipsed conformation (I). The smaller $C^\alpha$-$X^\beta$ overlap population in the eclipsed conformation also indicates significant interaction of the $\sigma\pi_z{}^*$ orbital (interaction 2). Thus for the less electronegative β substituents, both the $\sigma\pi_z$ and $\sigma\pi_z{}^*$ can contribute significantly toward stabilizing the radical center. The energies of planar substituted haloethyl radicals as a function of the rotation angle γ are given in Figure 3. The energy differences between staggered and eclipsed when calculated by the EH method indicate that the eclipsed conformation is always preferred except for that of the $\cdot CH_2CH_2F$ radical. The ab initio calculations on the $\cdot CH_2CH_2Cl$ radical employing an STO-3G basis[16] also show about a 1.5 kcal preference for the eclipsed conformation. The STO-3G calculations for $\cdot CH_2CH_2F$ are not shown in Figure 3 since the energy remains essentially constant for rotation about the C′-$C^\alpha$ bond as previously noted.[12]

**2. Steric Repulsion.** A great deal of experimental evidence points to the fact that $\cdot CR_2CH_2X$ radicals are nonplanar at the radical site[17] in those cases when R ≠ H, although the barrier to inversion is not large. A nonplanar radical center introduces steric interactions similar to those that exist in substituted ethanes.[23] These steric interactions impose conformational constraints on β-substituted alkyl radicals which

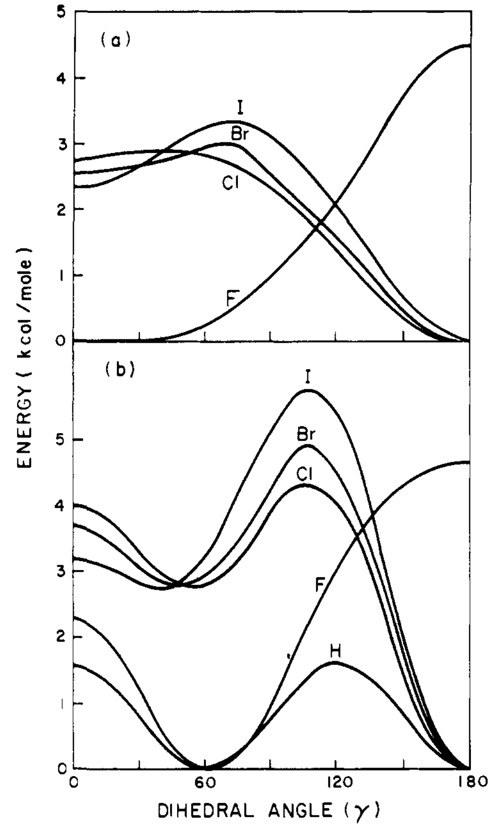


**Figure 4.** The energies of nonplanar $\beta$-haloethyl radicals as a function of the rotation angle, $\gamma$, for (a) matrix elements deleted and (b) full calculations. The most stable conformation is assigned zero energy.

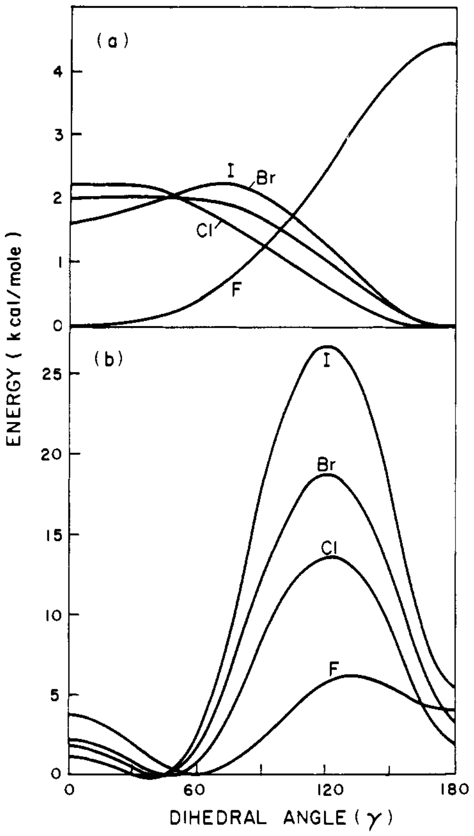


**Figure 5.** The energies of nonplanar $\beta$-halo-*tert*-butyl radicals as a function of the rotation angle, $\gamma$, for (a) matrix elements deleted and (b) full calculation. The most stable conformation is assigned zero energy.

can become an important and even dominant effect in determining the equilibrium conformations of these species.

Relative energies calculated by the EH method for several nonplanar $\beta$-halo alkyl radicals, $\cdot CR_2CH_2X$, as a function of the dihedral angle ($\gamma$) are given in Figure 4b (R = H) and Figure 5b (R = $CH_3$). In addition, the nonbonded interactions between the atoms on C′ with the atoms on $C^{\alpha}$ were deleted by setting the off-diagonal pseudo-Fock matrix elements, $H_{ij}$, along with the corresponding overlap matrix elements $S_{ij}$ for the particular atoms under consideration to zero. The corresponding curves for each of the same molecules with matrix elements deleted are also given in Figures 4a and 5a. Several important features arising from these curves are noted.

1. There are two minima (except for $\cdot CH_2CH_2F$) for each of the potential energy curves involving both $\beta$-substituted ethyl radicals (R = H) and the $\beta$-substituted tertiary butyl radicals (R = $CH_3$). One of the minima corresponds to a staggered conformation with $\gamma \approx 60°$ (or 300°) and the other minimum is equivalent to the anti conformation (V) with $\gamma = 180°$. It is interesting that both these conformations would correspond to a staggered one in a substituted ethane.

2. The potential energy curves with matrix elements between nonbonded atoms on C′ and $C^{\alpha}$ deleted are remarkably similar for both the $\beta$-substituted ethyl and tertiary butyl radicals. The minimum at $\gamma = 60°$ disappears and a very shallow, broad minimum develops at $\gamma = 0°$ with the minimum at $\gamma = 180°$ still surviving (except for F).

3. The potential energy curves for the full calculation show that the relative energies of the two minima at $\gamma = 60$ and 180° are inverted in going from $\beta$-substituted ethyl to $\beta$-substituted tertiary butyl radicals. This also results in an increased barrier to rotation about the $C'$-$C^{\alpha}$ single bond especially as the $X^{\beta}$ substituent is changed from F to a bulkier one such as I. In fact, for the case of $\cdot CH_2CH_2F$ there is no minimum at $\gamma = 180°$ but one appears in the $\cdot C(CH_3)_2CH_2F$ radical. The potential energy barrier between the two stable conformations ($\gamma = 60° \rightleftarrows \gamma = 180°$) is smallest in $\cdot C(CH_3)_2CH_2F$, but becomes increasingly larger as the $X^{\beta}$ substituent gets bulkier. Similar results were obtained for the $\cdot CH_2CH_2X$ and $\cdot C(CH_3)CH_2X$ (X = F, Cl) radicals by performing ab initio calculations employing an STO-3G basis[16] and are shown in Figure 6.

**3. Comparison with Experiment.** The above discussion indicates that equilibrium conformations of $\beta$-substituted alkyl radicals depend on both steric and hyperconjugative effects. It is interesting that Pople[24] previously rationalized the rotation about the single bond in ethanelike molecules in terms of a potential function including threefold, twofold, and onefold components, the former two of which may be analogous to the steric repulsions and hyperconjugative interactions. The onefold term, a dipole-dipole interaction, may not play as important a role in neutral radicals. It is difficult to predict a priori the most stable conformation of $\beta$-substituted alkyl radicals in terms of steric effects and hyperconjugation since they may tend to work in opposite directions. For example, hyperconjugation favors the eclipsed (syn or anti) conformations (except perhaps for fluoroethyl) as evidenced in Table II where $\pi_z(C'\text{-}C^{\alpha})$ overlap populations for both planar and pyramidal radicals are given. The $\pi_z(C'\text{-}C^{\alpha})$ overlap populations generally decrease from the planar to the pyramidal radical, but are still larger in the eclipsed (syn or anti) than in the staggered conformation. When steric repulsions become important, however, the syn conformation becomes energetically unfavorable. Thus, from Figures 4 and 5 the gauche ($\gamma$ = 60 and 300°) and anti conformations are of comparable stability for each of the halogens, yet the anti conformation is destabilized as bulky substituents such as Br and I are substituted for F or Cl. This trend may explain why the experimental evidence for $\beta$-substituted tertiary butyl radicals[10] points to

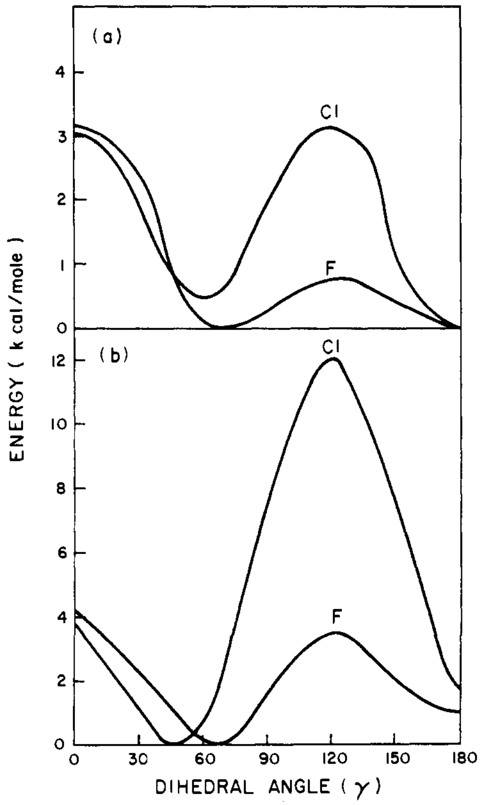


**Figure 6.** The STO-3G energies as a function of the rotation angle, $\gamma$, of (a) nonplanar $\beta$-haloethyl radicals and (b) nonplanar $\beta$-halo-*tert*-butyl radicals. The most stable conformation is assigned zero energy.

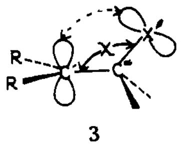
**Table II.** $\pi_z(C'-C^\alpha)$ Overlap Populations for $\cdot CR_2CH_2X$ (R = H) Radicals

| | Extended Hückel (EH) | | STO-3G | |
|---|---|---|---|---|
| $X^\beta$ | $\theta = 90°$ [a] | $\theta = 110°$ [b] | $\theta = 90°$ [a] | $\theta = 110°$ [b] |
| F | 0.0322 | 0.0362 | 0.0396 | 0.0246 |
| | 0.0326 | 0.0273 | 0.0202 | 0.0124 |
| | | 0.0137 | | 0.0282 |
| Cl | 0.0457 | 0.0408 | 0.0284 | 0.0182 |
| | 0.0334 | 0.0277 | 0.0096 | 0.0059 |
| | | 0.0332 | | 0.0201 |

[a] The first number in the column indicates eclipsed, the second number, staggered. [b] The first number in a column indicates syn, the second number perpendicular, and the third number anti.

an eclipsed anti conformation for $X^\beta$ = F, Cl, but a gauche conformation when $X^\beta$ = Br or I. The factors in determining the equilibrium conformation of $\beta$-substituted alkyl radicals involve a delicate balance between electronic effects such as hyperconjugation and steric effects as determined by the bulkiness of large $X^\beta$ substituents.

From the calculations on $\beta$-halo alkyl radicals, a weak electronic effect involving the direct, through-space interaction of the unpaired electron with a lone pair on the $X^\beta$ substituent also appears to be operative. This interaction is shown in **3** for



**3**

a planar radical center with the $C^\alpha-X^\beta$ bond eclipsing the unpaired electron orbital. Both the p-p and d-p homoconjugative interactions have been previously discussed in terms of substantially influencing the conformations of $\beta$-substituted alkyl radicals, but the calculations discussed here indicate that homoconjugation is much smaller in magnitude than the hyperconjugative interaction. This means that the homoconjugative interactions do not significantly contribute to the conformational preferences of the $X^\beta$ substituent relative to the unpaired electron orbital. In order to more clearly demonstrate the relative orders of magnitude of both the hyperconjugative and homoconjugative interactions, a plot of the $\pi_z(C'-C^\alpha)$, $p_z$-p(Cl), $p_z$-d(Cl) EH overlap populations as a function of the angle of pyramidality, $\chi$, defined in **3** is shown in Figure 7 for the planar $\cdot CH_2CH_2Cl$ radical.

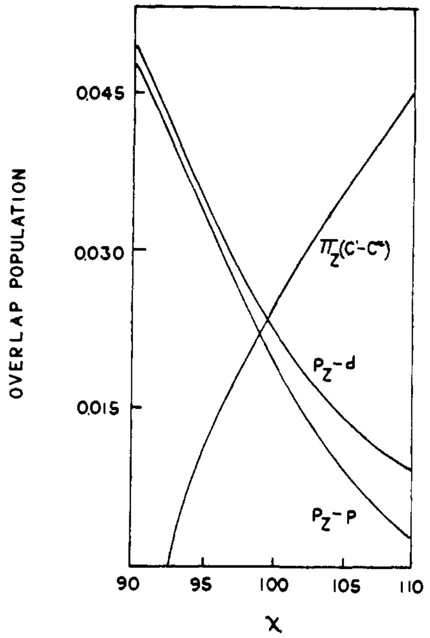


**Figure 7.** The $\pi_z(C'-C^\alpha)$, $p_z$-p, and $p_z$-d overlap populations as a function of the pyramidality angle, $\chi$, for the planar $\cdot CH_2CH_2Cl$ radical.

It can be readily seen from Figure 7 that the $\pi_z(C'-C^\alpha)$ overlap population is much larger than either the $p_z$-p(Cl) or $p_z$-d(Cl) overlap populations for reasonable values of angle $\chi$. This trend indicates that hyperconjugation is the dominant effect in determining the orientation of the $CH_2X^\beta$ group relative to the $\cdot CR_2$ group. Our calculations show no significant p-p overlap populations for the very electronegative first row $\beta$ substituents such as F or OR indicating the absence of p-p homoconjugation in these systems. The $p_z$-d(Cl) overlap populations should be viewed with caution since the parameters for d orbitals on Cl do not have well-defined values. When d orbitals are included in the basis set of the chlorine atom, the $p_z$-p(Cl) overlap population shown in Figure 7 disappears and only the $p_z$-d(Cl) overlap population remains. This effect seems to indicate that if d orbitals do play a role in the small homoconjugative interactions in these radical systems, they may wash out the effect of p-p homoconjugation.

The discussion thus far has centered around considering the relative stabilities of the syn, anti, and gauche conformations of $\beta$-substituted alkyl radicals and comparing calculated results with experimentally observed structures. For radicals of the type $\cdot CR_1R_2CH_2X$ ($R_1 \neq R_2$) the nonplanar radical center is optically active and racemization is known to occur.[11] It is interesting to consider the mechanism for racemization based on the calculated results from above and to present the possible pathways that would connect two optically active, stable epimers. In addition, it may be feasible to relate the differences in the rates of racemization for the various $\beta$ substituents ($X^\beta$

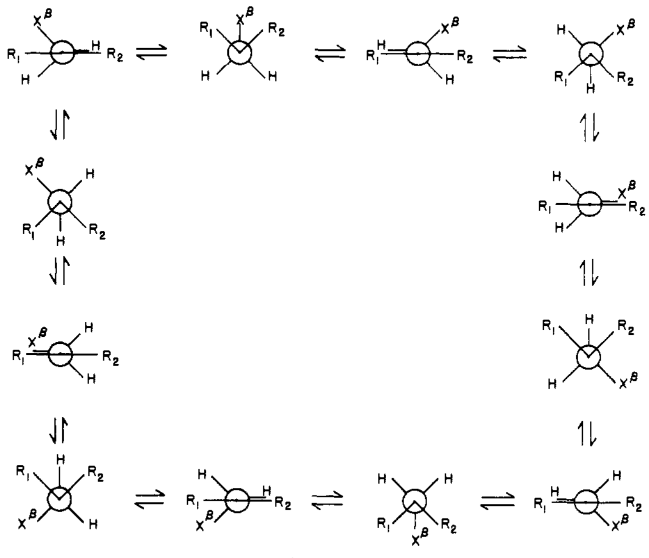


**Figure 8.** A possible mechanism for the interconversion of optically active radicals of the type $\cdot CR_1R_2CH_2X^\beta$.

**Table III.** Parameters Used in Extended Hückel Calculations

| Atom | Orbital | Exponent[a] | $H_{ii}$, eV |
|---|---|---|---|
| H | 1s | 1.300 | −13.60 |
| C | 2s | 1.625 | −21.40 |
| | 2p | 1.625 | −11.40 |
| F | 2s | 2.564 | −40.00 |
| | 2p | 2.550 | −18.10 |
| Cl[b] | 3s | 2.356 | −24.00 |
| | 3p | 2.039 | −13.00 |
| Br | 4s | 2.638 | −24.00 |
| | 4p | 2.256 | −13.00 |
| I | 5s | 2.681 | −24.00 |
| | 5p | 2.322 | −13.00 |

[a] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963). [b] The Cl 3d orbitals were assigned an exponent of 1.8 and an $H_{ii}$ = −6.0 eV. These values were chosen to allow for the maximum interaction of the d orbitals on Cl with the $p_z$ orbital on C′.

= F, Cl, Br, and I) to the electronic and steric factors previously discussed.

It is not unreasonable to assume a planar transition state for the neutral radicals in the racemization process involving inversion about the C′ radical center. Both experimental[10,11] and calculational evidence[25] points to low inversion barriers in these radicals. One possible scheme for racemization invoking a planar transition state at the radical center is shown in Figure 8 for a $\cdot CR_1R_2CH_2X$ radical. It is obvious that the highest energy points along the interconversion pathway will involve $X^\beta$ eclipsing either $R_1$ or $R_2$. A comparison of the STO-3G calculations for the planar (cf. Figure 3) and the pyramidal (cf. Figure 6) $\cdot CH_2CH_2X^\beta$ ($X^\beta$ = F, Cl) radicals reveals a significant reduction in the potential energy barrier of the former when the $X^\beta$ substituent eclipses one of the α hydrogens. It would also be expected that the larger the $X^\beta$ group, the more hindered the racemization process.

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## Appendix

The following geometries for the $\cdot CR_2CH_2X$ (R = H, $CH_3$) radicals were used in both the STO-3G and extended Hückel calculations: C–H = 1.09 Å, C–C = 1.514 Å, C–F = 1.375 Å, C–Cl = 1.779 Å, C–Br = 1.940 Å, and C–I = 2.207 Å. The C–H and C–C bond distances were taken from the optimized geometry for the ethyl radical[25] and the C–$X^\beta$ bond distances ($X^\beta$ = F, Cl, Br, I) were obtained from available experimental data on the ethyl halides.[26] The parameters for the extended Hückel calculations are given in Table III. All bond distances were kept fixed and idealized geometries involving tetrahedral $CH_2X^\beta$ and $CH_3$ groups were assumed.

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(17) The nonplanarity of the *tert*-butyl radical is indicated by the anomalous temperature dependences of its $^{13}C$ and $^1H$ hfs (ref 18–21) and more recently by its photoelectron spectrum (ref 22).
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