

## A Molecular Orbital Interpretation of the Structure of Some Halogenoalkyl Radicals

By Lluís M. Molino, Josep M. Poblet, and Enric Canadell,\* Facultat de Química, Universitat de Barcelona, Pl. Imperial Tàrraco, Tarragona, Spain

The conformational preferences and structural trends for a series of fluorine- and chlorine-substituted methyl and ethyl radicals are rationalized. The methodology used to analyse the pyramidal structure of substituted methyl radicals is based upon a quantitative decomposition of the molecular orbitals for the pyramidal structure in terms of the molecular orbitals for the planar form. A second-order perturbation treatment is also applied in order to have a simple approximation to the aforementioned decomposition. Using these methods it is possible to evaluate quantitatively the relative contributions of electronegativity and conjugation effects in determining the extent of pyramidalization of the radicals. It is shown that the electronegativity of the substituents plays the major role. The conformational preferences for  $\beta$ -halogenoethyl radicals are also discussed. The calculations are of the MNDO type with UHF and half-electron formalisms

THE structure of halogen-substituted methyl and ethyl radicals has attracted much interest.<sup>1-38</sup> As a result of extensive experimental work some systematic regularities are now well established. For instance, the geometry of the methyl radicals becomes increasingly non-planar with the successive replacement of the hydrogens by fluorines.<sup>2</sup> The effect seems to be less important for chlorine substitution.<sup>8-10</sup> Consideration of inductive effects<sup>14</sup> leads to the conclusion that the tendency to pyramidalization does increase with the number of electronegative substituents, but conjugation effects are also at work here and should be included in a qualitative explanation, as they were in the reports by Dewar<sup>16</sup> and Bernardi.<sup>17</sup> In fact, many theoretical studies on these systems have been published<sup>16-25</sup> but they have been mainly concerned with the computation of geometrical parameters, spin populations, *etc.* Only a few<sup>16,17,19</sup> have tried to present a rationalization of the observed trends. The different effects of fluorine and chlorine, in particular, have been generally neglected in these discussions.

The halogen-substituted ethyl radicals have been extensively studied as well.<sup>25-38</sup> Strikingly, the  $\beta$ -fluoroethyl radical adopts a staggered conformation whereas in the  $\beta$ -chloroethyl radical the preferred conformation is eclipsed.<sup>26</sup> For the last radical, Kochi *et al.*<sup>27</sup> have pointed out the possibility of an asymmetrical bridging of the chlorine to the radical centre. The origin of these preferences has been a matter of considerable discussion.<sup>27,31-33</sup> Theoretical studies are less abundant here.<sup>34-37</sup> In the work by Rossi and Wood<sup>36</sup> the relative importance of hyperconjugation and non-bonded interactions was examined. The different effect on the pyramidalization of the radical centre produced by the substitution at  $\alpha$ - and  $\beta$ -carbons can be observed from the data of Krusic<sup>38</sup> and Bowles.<sup>26</sup>

Clearly, a full understanding of the structure of halogenated radicals requires a qualitative scheme easily amenable to evaluation of the energetic consequences of structural changes (a crucial condition for the comparison of first- and second-row substituents), and a method of calculation reliable but not so expensive as to forbid

the application to the more complex molecules. As a first step to a more general theoretical rationalization of the structure and reactivity of radicals, we present here our results for some simple halogenoalkyl radicals.

### RESULTS AND DISCUSSION

*Geometry Optimizations.*—With regard to the second requirement outlined above, we decided to test the usefulness of the MNDO method. There were two reasons: first, we chose to use a semiempirical method in order to be able to do the geometry optimizations for these and more complex molecules without any geometrical restriction; secondly, although MINDO/3 has proved to be very useful when applied to free radical chemistry problems<sup>39,40</sup> there are well known deficiencies when applied to fluorine-containing molecules.<sup>41</sup> This problem seems to be surmounted in MNDO.<sup>24</sup> Several alternative procedures have been used in the treatment of open shell systems: the spin-unrestricted Hartree-Fock (UHF) method,<sup>42</sup> the spin-restricted (RHF) method,<sup>43</sup> and the 'half-electron' (HE) method.<sup>44</sup> The usefulness of each one of them when applied to geometry optimizations has been discussed elsewhere.<sup>45</sup> In that work<sup>45</sup> a detailed comparison of the half-electron method and the generalized coupling operator (GCO)<sup>46,47</sup> version of RHF was presented and it was concluded that the predicted equilibrium geometries do not differ appreciably. The GCO optimizations generally required more computing time. So, we first carried out a comparison of the half-electron and UHF methods for a number of halogenomethyl radicals. Some of the results are presented in Table 1. As can be seen, the agreement between the UHF and HE geometries is excellent. This is a gratifying result because the UHF optimizations are appreciably faster than the HE ones.

Let us briefly comment on these results. If we take the series  $\dot{C}H_3$ ,  $\dot{C}H_2F$ ,  $\dot{C}HF_2$ ,  $\dot{C}F_3$ , it can be seen that the pyramidalization increases from  $\dot{C}H_2F$  to  $\dot{C}HF_2$  and  $\dot{C}F_3$  but  $\dot{C}H_2F$  remains planar. This is in full agreement with Krusic and Bingham<sup>38</sup> who concluded that significant nonplanarity is present only when two or more fluorines are present. Recent *ab initio* calculations<sup>17,18</sup>

indicate nonplanarity for  $\dot{\text{C}}\text{H}_2\text{F}$ . The calculated structure for  $\dot{\text{C}}\text{F}_3$  compares well with the experimental values.<sup>2</sup> There is a shortening of the C-H distance along the series and, at the same time, a lengthening of the C-F bond. When a fluorine is replaced by a chlorine in  $\dot{\text{C}}\text{F}_3$ , the pyramidalization decreases ( $\beta$  for  $\dot{\text{C}}\text{F}_3$  is 37.2 versus

TABLE I

Calculated geometries by the UHF and HE methods for some halogenomethyl radicals \*

Radical	Parameter <sup>a</sup>	Method	
		UHF	RHF
$\dot{\text{C}}\text{F}_3$	C-F	1.312	1.312 (1.33) <sup>d</sup>
	F-C-F	115.3	115.3 (111.1)
	$\alpha$ <sup>b</sup>	102.7	102.7 (107.8)
$\dot{\text{C}}\text{HF}_2$	C-F	1.311	1.309
	C-H	1.090	1.086
	F-C-F	112.8	113.1
	F-C-H	122.0	122.7
	$\beta$ <sup>c</sup>	17.0	11.8
$\dot{\text{C}}\text{H}_2\text{F}$	C-F	1.305	1.304
	C-H	1.086	1.086
	H-C-H	122.7	122.7
	F-C-H	118.6	118.6
	$\beta$	0.0	0.0
$\dot{\text{C}}\text{Cl}_3$	C-Cl	1.711	1.710
	Cl-C-Cl	120.0	120.0 (116, 113) <sup>e,f</sup>
	$\alpha$	90.0	90.0
$\dot{\text{C}}\text{F}_2\text{Cl}$	C-F	1.307	1.307
	C-Cl	1.756	1.755
	F-C-F	122.7	122.7
	F-C-Cl	119.2	119.3
	$\beta$	28.4	28.1
$\dot{\text{C}}\text{H}_2\text{Cl}$	C-Cl	1.724	1.724
	C-H	1.076	1.076
	H-C-H	124.2	124.3
	Cl-C-H	117.9	117.8
	$\beta$	0.0	0.0
$\dot{\text{C}}\text{HCl}_2$	C-Cl	1.715	1.714
	C-H	1.077	1.076
	Cl-C-Cl	120.4	119.9
	Cl-C-H	120.0	120.0
	$\beta$	0.3	0.4
$\dot{\text{C}}\text{H}_3$	C-H	1.078	1.078
	H-C-H	120.0	120.0
	$\alpha$	90.0	90.0

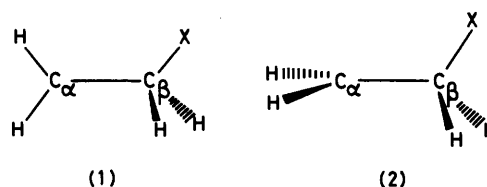
\* Experimental values in parentheses. <sup>a</sup> Bond lengths in Å, bond angles in degrees. <sup>b</sup> Angle determined by the  $C_{3v}$  symmetry axis and the bond CX. <sup>c</sup> Angle determined by the bisector of the XCX angle and the prolongation of the CY bond. <sup>d</sup> Ref. 2. <sup>e</sup> Ref. 9. <sup>f</sup> Ref. 10.

28.4° in  $\dot{\text{C}}\text{F}_2\text{Cl}$ ). This is consistent with our calculated results for the series  $\dot{\text{C}}\text{H}_2\text{Cl}$ ,  $\dot{\text{C}}\text{HCl}_2$ ,  $\dot{\text{C}}\text{Cl}_3$  and with the ideas of Pauling.<sup>14</sup> For  $\text{X}\dot{\text{C}}\text{F}_2$ , the angle XCF decreases along the series X = H, Cl, F. The radicals  $\dot{\text{C}}\text{HCl}_2$ ,  $\dot{\text{C}}\text{H}_2\text{Cl}$ , and  $\dot{\text{C}}\text{Cl}_3$  are all predicted to be planar. The result is not surprising for  $\dot{\text{C}}\text{H}_2\text{Cl}$ <sup>38</sup> and a nearly planar structure for  $\dot{\text{C}}\text{HCl}_2$  was also reported by Biddles *et al.*<sup>23</sup> from INDO calculations. There has been some controversy on the structure of  $\dot{\text{C}}\text{Cl}_3$ <sup>8-11</sup> but it seems now

well established that  $\dot{\text{C}}\text{Cl}_3$  is nonplanar although the degree of nonplanarity is inferior to that of  $\dot{\text{C}}\text{F}_3$ . Geometry optimizations at the STO-3G level<sup>48</sup> also show for  $\dot{\text{C}}\text{Cl}_3$  a value for  $\alpha$  (101.2°) intermediate between that of  $\dot{\text{C}}\text{F}_3$  (107.1°) and  $\dot{\text{C}}\text{H}_3$  (90.0°). The agreement is not as good as in the fluorine series but the qualitative trend on comparing fluorine and chlorine substitution is well accounted for.

A most stringent test for MNDO is provided by  $\beta$ -halogenoalkyl radicals. As mentioned, while the  $\beta$ -fluoroethyl radical prefers a staggered conformation (1), the  $\beta$ -chloroethyl radical adopts the eclipsed conformation (2).

Our UHF calculations for when X = H, F, Cl show free rotation about the C-C bond in  $\dot{\text{C}}\text{H}_2\text{CH}_3$  but a preference



for the staggered conformation in  $\text{FCH}_2\dot{\text{C}}\text{H}_2$  and for the eclipsed conformation in  $\text{ClCH}_2\dot{\text{C}}\text{H}_2$ . In all cases the  $\dot{\text{C}}\text{H}_2$  group was found to be locally planar. Csizmadia *et al.*<sup>37</sup> found a pyramidal form for  $\dot{\text{C}}\text{H}_2\text{CH}_2\text{Cl}$  0.3 kcal mol<sup>-1</sup> lower than the planar one but the degree of pyramidalization decreases with the more extended basis used. For  $\dot{\text{C}}\text{H}_2\text{CH}_3$ , Pacansky *et al.*<sup>49a</sup> also found a pyramidal structure 0.2 kcal mol<sup>-1</sup> more stable but an experimental study<sup>49b</sup> shows that this result cannot be taken as conclusive. The value for X = Cl is completely normal and does not support the idea of an asymmetrical bridging of chlorine.<sup>26</sup> The energy barrier for the 1,2 migration of Cl in this radical is found to be 26.3 kcal mol<sup>-1</sup>. For  $\dot{\text{C}}\text{H}_2\text{CF}_3$  and  $\dot{\text{C}}\text{F}_2\text{CH}_3$  there is essentially free rotation about the C-C bond. A significant lengthening of this bond is observed in  $\dot{\text{C}}\text{H}_2\text{CF}_3$  (1.540 Å) with respect to  $\dot{\text{C}}\text{H}_2\text{CH}_3$  (1.476 Å). The radical centre is locally planar in  $\dot{\text{C}}\text{H}_2\text{CF}_3$  but the potential for pyramidalization is very soft in  $\dot{\text{C}}\text{F}_2\text{CH}_3$ . The effect of the two fluorines is clear but apparently  $\text{CH}_3$  has an opposite and stronger influence. Thus, for the series  $\text{X}\dot{\text{C}}\text{F}_2$ , the pyramidalization decreases in the order F > Cl >  $\text{CH}_3$  as found by Bingham and Krusic.<sup>38</sup> From the comparison of  $\dot{\text{C}}\text{H}_2\text{CH}_3$  and  $\dot{\text{C}}\text{H}_2\text{CF}_3$  spin populations, we found that the  $\text{CF}_3$  group withdraws less spin density than the  $\text{CH}_3$  group, in agreement with the same authors<sup>38</sup> as well.

*Analysis of the Results.*—We turn now to the first objective raised in the introduction. It is well known that the extent of pyramidalization in  $\text{AH}_3$  molecules depends fundamentally on  $2a_1-3a_1$  mixing along the distortion.<sup>50-52</sup> Nevertheless, quantitative analysis of this mixing has not been carried out, with the exception of work by Levin<sup>50</sup> on  $\text{NH}_3$  and  $\text{PH}_3$ . In the subsequent discussion we will use the orbitals obtained by the half-electron method because the analysis is far more simple without changing any conclusion.

The decomposition of the molecular orbitals of the pyramidal form in terms of the molecular orbitals for the planar form can be done exactly or approached by perturbation theory. In all cases, we have found that the results of the exact decomposition are almost exactly reproduced by a one-electron perturbation treatment where the perturbation elements are evaluated as in equation (1). This expression follows from the usual

$$\langle \phi_i | \hat{p} | \phi_j \rangle = \sum_A \sum_{B < A} \sum_k \sum_l^B C_{ik} C_{jl} \cdot \frac{1}{2} (\beta_A + \beta_B) (\partial S_{kl} / \partial \alpha)_{\alpha=90} \cdot \delta \alpha \quad (1)$$

formula (2) for resonance integrals in semiempirical methods<sup>53,\*</sup> which when subjected to a pyramidalization  $\delta \alpha$  changes to (3) and assuming that the the pyramidaliz-

$$\beta_{kl} = \frac{1}{2} (\beta_A + \beta_B) S_{kl} \quad (2)$$

$$\delta \beta_{kl} = \frac{1}{2} (\beta_A + \beta_B) \delta S_{kl} \quad (3)$$

ation is not very strong  $\delta S_{kl}$  can be approximated by (4). We took the  $\beta$  values recommended by Pople

$$\delta S_{kl} = (\partial S_{kl} / \partial \alpha)_{\alpha=90} \cdot \delta \alpha \quad (4)$$

*et al.*<sup>53</sup> and the values for  $\delta S_{kl}$  were evaluated from Slater orbitals with standard exponents.

$\dot{\text{C}}\text{H}_3$ .—After renormalization, the perturbation expression for the SOMO at  $\alpha 110^\circ$  is  $2a_1 = -0.095(1a'_1) + 0.936(a''_2) + 0.337(2a'_1)$ . The other orbitals remain virtually unchanged at this  $\alpha$ . Analysis of the energy changes substantiates the well known result that SOMO–LUMO mixing cannot compensate for the destabilization of the  $1e'$  orbitals under pyramidalization.

$\dot{\text{C}}\text{F}_3$ .—Analysis of the different energy components along the pyramidalization co-ordinate shows that the core–core energy contribution grows with  $\alpha$ , but at the same time the electronic energy contribution decreases (and to a greater extent). This electronic stabilization results from two opposite effects: a raising in energy of the  $1e'$  orbitals and a greater energy lowering of the SOMO. The direct decomposition of the orbitals at  $\alpha 110^\circ$  shows that only the SOMO and LUMO mix strongly. In the language of perturbation theory we can say that the raising of the  $1e'$  orbitals is mostly a first-order effect and the lowering of the SOMO is fundamentally a second-order effect. Qualitatively, we have an exact parallelism with the  $\dot{\text{C}}\text{H}_3$  story. The participation of the LUMO in the new HOMO amounts to 0.559. This enhanced mixing with respect to that in  $\dot{\text{C}}\text{H}_3$  is ultimately responsible for the  $\dot{\text{C}}\text{F}_3$  pyramidality. Why does this increased mixing occur? The  $p_z$  orbital on the carbon in the planar form is destabilized by an out-of-phase combination with the  $p_z$  orbitals of the fluorines as shown in Figure 1. At the same time, there is an electronegativity effect that principally causes a

lowering of the LUMO energy. So, the conjugative and the inductive effects co-operate to produce a decrease in the energy gap between the orbitals that will mix upon pyramidalization (7.026 eV in planar  $\dot{\text{C}}\text{F}_3$  and 9.390 eV in  $\dot{\text{C}}\text{H}_3$ ). At the same time, there is an important participation by the  $p$  orbitals of fluorine in the LUMO as can be seen in Figure 1 and this factor can also contribute appreciably to the greater mixing.

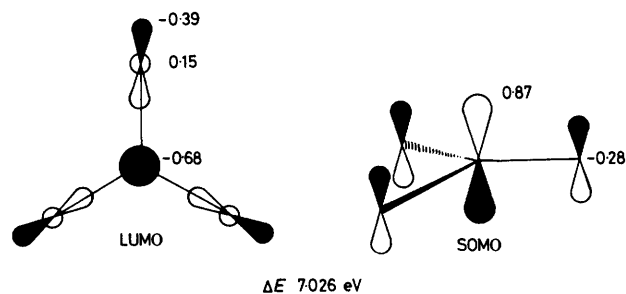


FIGURE 1 SOMO and LUMO for the planar  $\dot{\text{C}}\text{F}_3$  radical

The relative importance of the two effects can be evaluated by the perturbation treatment. The analysis for  $\alpha 110^\circ$  shows that the coefficient by which the LUMO contributes to the new SOMO is 0.541, in excellent agreement with the direct decomposition. The contributions of all the other orbitals are almost negligible. The comparison with the values for  $\dot{\text{C}}\text{H}_3$  shows that the increase in mixing is equally due to the decrease of the energy gap and to the increase in the perturbation element. The last effect may be due to the change in the electronegativity or to the introduction of the  $p$  orbitals. Analysis of the different contributions to the perturbation element shows that the increase in the electronegativity (through larger values of  $\beta$ ) is the dominant factor. Thus, the electronegativity effect contributes to both the numerator and the denominator of the first-order coefficient of mixing. To separate the conjugative and the inductive effects we can repeat the perturbation evaluation using the orbitals and energy gaps obtained in a calculation for the planar  $\dot{\text{C}}\text{F}_3$  radical, where the Fock matrix elements between the  $p_z$  orbitals of fluorines and the  $p_z$  orbital of carbon have been taken to be zero. In this way the conjugative effects are removed.

Comparison of the coefficients obtained by the two calculations shows that only 9.8% of the SOMO–LUMO mixing can be attributed to the conjugative effect.

In conclusion, the greater electronegativity of F over H seems to be the crucial factor in determining pyramidal *versus* planar geometry for the  $\dot{\text{C}}\text{F}_3$  and  $\dot{\text{C}}\text{H}_3$  radicals. The stabilization produced by the SOMO–LUMO mixing compensates for the increase in the core–core repulsions and the first-order energy effects that create a bias for the planar form. From a different point of view, Bernardi *et al.*<sup>17</sup> have reached the same conclusions.

$\dot{\text{C}}\text{Cl}_3$ .—The gap between the SOMO and the LUMO of the planar form has further decreased to 4.99 eV but the mixing is of the same order as it was for  $\dot{\text{C}}\text{F}_3$ . Always at

\* Several different choices are possible. We retained the CNDO expression because in this way we have only one value per atom. In the MNDO expression there are two different values per atom. As the qualitative trends are not strongly dependent on the particular formula used, we retained the simplest one.

$\alpha$  110°, the values are 0.555 from the direct decomposition treatment and 0.572 from the perturbation calculation. The decrease in the electronegativity of the substituents affects to a similar extent the perturbation element and the energy gap. The perturbation elements per unit angle  $\langle \text{SOMO} | \rho | \text{LUMO} \rangle / \delta\alpha$  for  $\dot{\text{C}}\text{H}_3$ ,  $\dot{\text{C}}\text{F}_3$ , and  $\dot{\text{C}}\text{Cl}_3$  are shown in Table 2.

TABLE 2  
Values for  $\langle \text{SOMO} | \rho | \text{LUMO} \rangle / \delta\alpha$  and  $\Delta E^{(2)}_{\text{SOMO-LUMO}} / \delta\alpha^2$  in  $\dot{\text{C}}\text{H}_3$ ,  $\dot{\text{C}}\text{F}_3$ , and  $\dot{\text{C}}\text{Cl}_3$

	$\dot{\text{C}}\text{H}_3$	$\dot{\text{C}}\text{F}_3$	$\dot{\text{C}}\text{Cl}_3$
$\langle \text{SOMO}   \rho   \text{LUMO} \rangle / \delta\alpha$	9.70	12.96	9.99
$\Delta E^{(2)}_{\text{SOMO-LUMO}} / \delta\alpha^2$	10.02	23.90	20.00

At this point, it may appear that the result of equal mixing, coupling with smaller core-core\* and first-order energy terms, would be an increase in the pyramidalization ability. This is not what happens due to the fact that the perturbation element is squared in the expression for the SOMO-LUMO second-order energy correction [equation (5)], and finally, the influence of mixing

$$\Delta E^{(2)}_{\text{SOMO-LUMO}} = \frac{[\langle \text{SOMO} | \rho | \text{LUMO} \rangle]^2}{\Delta \epsilon_{\text{SOMO-LUMO}}} = C^{(1)}_{\text{SOMO-LUMO}} \times \langle \text{SOMO} | \rho | \text{LUMO} \rangle \quad (5)$$

on the energy is smaller for  $\dot{\text{C}}\text{Cl}_3$  than  $\dot{\text{C}}\text{F}_3$ , even if the energy gap is more favourable. The values for these energy corrections per square unit angle are also shown in Table 2. The importance of the conjugative effect is even smaller than in  $\dot{\text{C}}\text{F}_3$  since it contributes 5.6% to the mixing.

In summary, the second-order energy stabilization is not strong enough to compensate for the destabilizing first-order energy correction in  $\dot{\text{C}}\text{H}_3$ , nor to compensate for the combined effect of the core-core and first-order energies in  $\dot{\text{C}}\text{Cl}_3$ , but finally imposes pyramidalization on  $\dot{\text{C}}\text{F}_3$ .

$\text{FCH}_2\dot{\text{C}}\text{H}_2$  and  $\text{ClCH}_2\dot{\text{C}}\text{H}_2$ .—As mentioned, the  $\beta$ -fluoroethyl radical adopts a staggered conformation (1) whereas the  $\beta$ -chloroethyl radical adopts an eclipsed conformation (2).

It is useful to consider the ethyl radical first. In this case we find free rotation and planarity at the radical centre. With the results for the methyl radicals in mind, it is not surprising that a single non-electronegative substituent would not induce pyramidalization.

The  $\rho$  orbital at the radical centre can interact with the  $\sigma\pi_z$  and  $\sigma^*\pi_z$  orbitals of  $\text{CH}_3$  in the eclipsed conformation and with the  $\sigma\pi_y$  and  $\sigma^*\pi_y$  orbitals in the staggered conformation, as shown in Figure 2. The net stabilization is the same in the two conformations. Along the rotation co-ordinate, one type of interaction disappears while the other increases. The result is free rotation.

The relative importance of the one electron-two orbitals interaction (1) and the three electrons-two orbitals (2) can be elucidated without recourse to the calculations because the first one results from charge withdrawal from the  $\rho$  orbital and the second from

\* The core charges are similar to those in  $\dot{\text{C}}\text{F}_3$  but the distances are now greater.

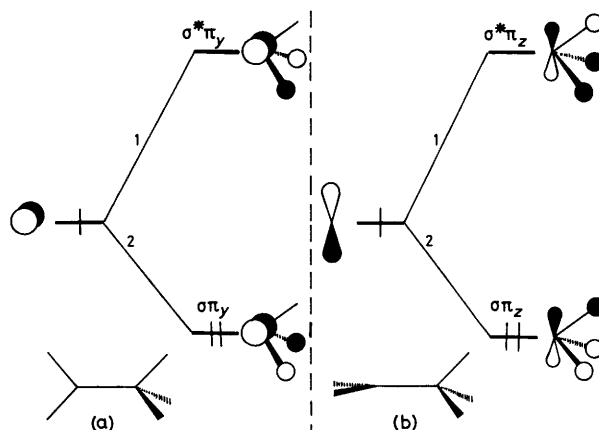


FIGURE 2 Interaction diagram for the  $\rho$  orbital in  $\text{CH}_2$  and the  $\pi$  methyl orbitals of  $\text{CH}_3$  in the eclipsed (b) and staggered (a) conformations

charge donation to the same orbital. Our calculations indicate a weak predominance of interaction (2). A preference for the eclipsed or staggered conformation will be created by removing the degeneracy of  $\sigma\pi_y - \sigma\pi_z$  and  $\sigma^*\pi_y - \sigma^*\pi_z$ . In Figure 3 we show how these

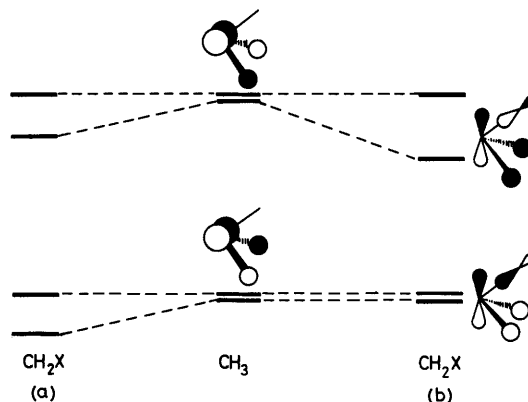


FIGURE 3 Change in the energies of the  $\pi$ -type orbitals of a  $\text{CH}_3$  group when one H is changed by: (a) a first-row more electronegative atom, (b) a second-row more electronegative atom

orbitals change by substitution of H by a first-row (a) and a second-row (b) more electronegative atom. In all cases, the increase in electronegativity ( $\Delta\alpha$ ) causes a decrease in energy of  $\sigma^*\pi_z$  and  $\sigma\pi_z$  while  $\sigma^*\pi_y$  and  $\sigma\pi_y$  are not affected. But we must take into account the fact that there is a  $\Delta\beta$  positive on going from fluorine to chlorine. This is due to the smaller electronegativity of the second-row atom and also to the decrease in the overlap. Thus, when the fluorine is substituted by the chlorine, the antibonding orbital will further decrease its energy † whereas the bonding orbital will increase its energy with the final result shown in Figure 3.

It is immediately seen from Figure 3 that the eclipsed conformation is clearly favoured for the  $\beta$ -chloroethyl radical. For the  $\beta$ -fluoroethyl radical the situation is

† This effect is largely responsible for the decrease in the SOMO-LUMO energy gap in  $\dot{\text{C}}\text{Cl}_3$  with respect to  $\dot{\text{C}}\text{F}_3$ .

less clear cut. With respect to  $\dot{\text{C}}\text{H}_2\text{CH}_3$  the two interactions favouring the staggered conformation are maintained, one of those leading to a preference for the eclipsed conformation has increased and the other has decreased. Then, the electronic effects cannot discriminate clearly between the two conformations and the fact that this radical adopts a staggered conformation is the result of a delicate balance between electronic and steric effects.

In conclusion, we feel that the PMO arguments used in conjunction with MNDO calculations provide a very clear understanding of the conformational preferences for halogenosubstituted alkyl radicals and in our opinion, the majority of the effects mentioned here are also operative when the substituents contain other less electronegative first- and second-row atoms.

We are greatly indebted with Dr. S. Olivella for his interest and for making available computer programs.

[1/1731 Received, 9th November, 1981]

## REFERENCES

- <sup>1</sup> For a review see L. Kaplan in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. II.
- <sup>2</sup> R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147; 1965, **43**, 2704; R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74.
- <sup>3</sup> D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1968, **48**, 2265.
- <sup>4</sup> L. Andrews, *J. Chem. Phys.*, 1968, **48**, 972.
- <sup>5</sup> J. H. Current and J. K. Burdett, *J. Phys. Chem.*, 1969, **73**, 3505.
- <sup>6</sup> T. G. Carver and L. Andrews, *J. Chem. Phys.*, 1969, **50**, 5100.
- <sup>7</sup> J. I. Raymond and L. Andrews, *J. Phys. Chem.*, 1971, **75**, 3235.
- <sup>8</sup> E. E. Rogers, S. Abramowitz, M. E. Jacox, and D. E. Milligan, *J. Chem. Phys.*, 1970, **52**, 2198.
- <sup>9</sup> C. Hesse, N. Leroy, and J. Roncin, *Mol. Phys.*, 1971, **22**, 137; J. P. Michaut and J. Roncin, *Chem. Phys. Lett.*, 1971, **12**, 95.
- <sup>10</sup> G. Maas, A. K. Maltsev, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1945.
- <sup>11</sup> T. L. Legget and D. A. Kohl, *J. Chem. Phys.*, 1973, **59**, 611.
- <sup>12</sup> J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1972, **23**, 209.
- <sup>13</sup> A. Hudson and H. A. Hussain, *Mol. Phys.*, 1969, **16**, 199.
- <sup>14</sup> L. Pauling, *J. Chem. Phys.*, 1969, **51**, 2767.
- <sup>15</sup> A. D. Walsh, *J. Chem. Soc.*, 1953, 2301.
- <sup>16</sup> R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, 1973, **95**, 7180.
- <sup>17</sup> F. Bernardi, W. Cherry, S. Shaik, and N. Epiotis, *J. Am. Chem. Soc.*, 1978, **100**, 1352.
- <sup>18</sup> G. Leroy, D. Peeters, C. Wilante, and M. Khalil, *Nouv. J. Chim.*, 1980, **4**, 403.
- <sup>19</sup> F. Bernardi, N. Epiotis, W. Cherry, H. B. Schlegel, M.-H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, 1976, **98**, 469.
- <sup>20</sup> K. Morokuma, L. Pedersen, and M. Karplus, *J. Chem. Phys.*, 1968, **48**, 4801.
- <sup>21</sup> D. L. Beveridge, P. A. Dobosch, and J. A. Pople, *J. Chem. Phys.*, 1968, **48**, 4802.
- <sup>22</sup> H. Konishi and K. Morokuma, *J. Am. Chem. Soc.*, 1972, **94**, 5603.
- <sup>23</sup> I. Biddles and A. Hudson, *Mol. Phys.*, 1973, **25**, 707.
- <sup>24</sup> M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 58.
- <sup>25</sup> A. Faucitano, A. Buttafava, F. Martinotti, G. Caporiccio, and C. Corti, *J. Chem. Soc., Perkin Trans. 2*, 1981, 425.
- <sup>26</sup> A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, 1970, **5**, 552.
- <sup>27</sup> T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Am. Chem. Soc.*, 1972, **94**, 1752.
- <sup>28</sup> K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 1383.
- <sup>29</sup> D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, 1972, **94**, 6485.
- <sup>30</sup> K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 794.
- <sup>31</sup> D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 6459; 1974, **96**, 6715.
- <sup>32</sup> A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 622.
- <sup>33</sup> P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 8461.
- <sup>34</sup> L. Radom, J. Paviot, J. A. Pople, and P. V. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 1974, 58.
- <sup>35</sup> A. Pross and L. Radom, *Tetrahedron*, 1980, **36**, 1999.
- <sup>36</sup> A. R. Rossi and D. E. Wood, *J. Am. Chem. Soc.*, 1976, **98**, 3452.
- <sup>37</sup> A. C. Hopkinson, M. H. Lien, and I. G. Csizmadia, *Chem. Phys. Lett.*, 1981, **71**, 557.
- <sup>38</sup> P. J. Krusic and R. C. Bingham, *J. Am. Chem. Soc.*, 1976, **98**, 230.
- <sup>39</sup> M. J. S. Dewar and S. Olivella, *J. Am. Chem. Soc.*, 1978, **100**, 5290; 1979, **101**, 4958.
- <sup>40</sup> P. Bischof, *Helv. Chim. Acta*, 1980, **63**, 1434.
- <sup>41</sup> See the optimized geometries for  $\dot{\text{C}}\text{F}_3$  and  $\dot{\text{C}}\text{F}_2\text{H}$ , in P. Bischof, *J. Am. Chem. Soc.*, 1976, **98**, 6844.
- <sup>42</sup> J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 1954, **22**, 571.
- <sup>43</sup> C. C. J. Roothaan, *Rev. Mod. Phys.*, 1960, **32**, 179.
- <sup>44</sup> M. J. S. Dewar, J. A. Hashmall, and G. Vernier, *J. Am. Chem. Soc.*, 1968, **90**, 1953; M. J. S. Dewar and N. Trinajstić, *Chem. Commun.*, 1970, 646.
- <sup>45</sup> M. J. S. Dewar and S. Olivella, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 829.
- <sup>46</sup> K. Hirao and H. Nakatsuji, *J. Chem. Phys.*, 1973, **59**, 1457; K. Hirao, *J. Chem. Phys.*, 1974, **60**, 3215.
- <sup>47</sup> R. Caballol, R. Gallifa, J. M. Riera, and R. Carbó, *Int. J. Quantum Chem.*, 1974, **8**, 373; R. Carbó, R. Gallifa, and J. M. Riera, *Chem. Phys. Lett.*, 1975, **30**, 43.
- <sup>48</sup> W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington.
- <sup>49</sup> (a) J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1978, **68**, 4276; (b) J. Pacansky and H. Coufal, *ibid.*, 1980, **72**, 5285.
- <sup>50</sup> C. C. Levin, *J. Am. Chem. Soc.*, 1975, **97**, 5649.
- <sup>51</sup> B. M. Gimarc, *Acc. Chem. Res.*, 1974, **7**, 384.
- <sup>52</sup> W. Cherry, N. Epiotis, and W. T. Borden, *Acc. Chem. Res.*, 1977, **10**, 167; W. Cherry and N. Epiotis, *J. Am. Chem. Soc.*, 1976, **98**, 1135.
- <sup>53</sup> J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.