

On the Origin of π -Facial Diastereoselectivity in Nucleophilic Additions to Chiral Carbonyl Compounds. 1. Rotational Profiles of Propionaldehyde 1, Chloroacetaldehyde 2, and 2-Chloropropionaldehyde 3.

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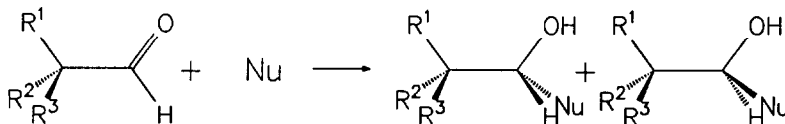
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Summary : The conformational profiles for rotation around the C-C(=O) bond α and the energy minimum conformations are calculated for propionaldehyde 1, chloroacetaldehyde 2, and 2-chloropropionaldehyde 3 at MP2/6-31G(d)//HF/6-31G(d). The energy level of the LUMO is calculated as a function of α for 1, 2, and 3 and discussed in relationship to the Felkin-Anh model.

Introduction

The addition of nucleophiles such as Grignard reagents or metal hydrides to chiral carbonyl compounds yields a mixture of diastereomers. If the stereogenic center is at the α -position, 1,2-asymmetric induction may lead to unequal amounts of the product diastereomers (Figure 1). The search for reagents, catalysts, solvents, and reaction conditions which optimize the diastereofacial selectivity of addition reactions to carbonyl compounds has been a very active field of organic chemistry for many years.¹

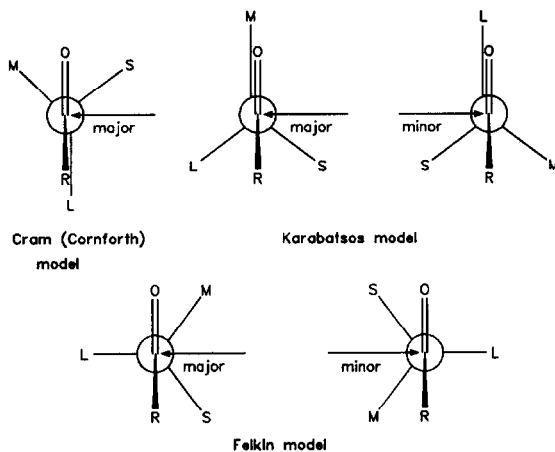
Figure 1.



In order to understand the observed 1,2-asymmetric induction, several models have been suggested. In Cram's open-chain model², the relevant conformer is the one in which the CO group bisects the adjacent CM and CS bonds, as shown in Figure 2 (s = small, m = medium, l = large). The major (minor) diastereomer results from a nucleophilic attack on the side of

the small (medium) substituent. Cornforth's model³ is a variant of Cram's model which is relevant when one of the substituents is a highly polar group such as a halogen atom. In that case, the halogen atom takes the place of the large substituent, because the dipolar interactions are believed to be most favorable when the carbon-halogen bond is trans to the carbonyl group (Figure 2).

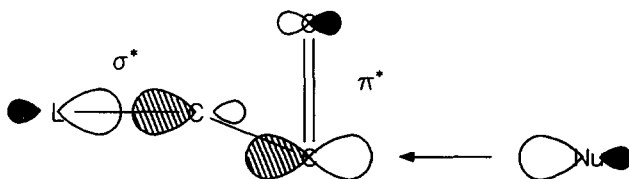
Figure 2. Schematic representation of the Cram (Cornforth), Karabatsos, and Felkin models.



Karabatsos' model⁴ uses two conformers in which the carbonyl group eclipses either the CM bond or the CL bond (Figure 2). It is assumed that the nucleophile always attacks from the less hindered side, and that the ratio of major to minor isomer is largely determined by the ground state equilibrium of the two conformations.

In Felkin's model⁵ the transition state for the addition of the nucleophilic reagent is also supposed to be reactant-like. However, Felkin argues that "torsional strain (Pitzer strain) involving partial bonds (in transition states) represents a substantial fraction of the strain between fully-formed bonds, even when the degree of bonding is quite low".⁵ The importance of torsional interactions for stereochemistry had previously been recognized by Schleyer.⁶ It follows that the energetically favored transition states have the large substituent trans to the attacking nucleophile (Figure 2). Again, if one of the three substituents (S,M,L) is a polar group, it takes the role of the large substituent. It is then postulated that the different steric interactions of the small and medium substituents with the group R cause the different yields of the major and minor product.⁵

Figure 3. Postulated $\sigma^*-\pi^*$ interaction in the Felkin transition state (Anh model).



In 1970, Anh and Eisenstein^{7a} published the first ab initio study of 1,2 asymmetric induction in carbonyl addition reactions. Using 2-chloropropionaldehyde as the carbonyl component and hydride ion as the model nucleophilic reagent, they calculated the energy of the reacting system as a function of the torsion angle α with standard geometries at a fixed distance between the carbonyl carbon atom and H^- of 1.5 Å. They found that the low energy conformations of the calculated model transition states correspond closely to what is suggested by Felkin et al.⁵ Further calculations mimicking the influence of counter ions and solvent molecules did not alter this conclusion.⁷ An important modification of Felkin's model was proposed concerning different modes of interactions in the two transition states which lead to the major and minor isomers (Figure 2). Rather than steric interactions between R and substituents M and S, which should be negligible when R = H, the crucial role of a non perpendicular attack of Nu was implemented⁷ as originally proposed by Bürgi and Dunitz in the nucleophilic addition to simple carbonyl compounds.⁸ Using results from experimental and theoretical studies of the stereochemistry of reaction paths at carbonyl centers, the latter⁸ had concluded that the transition state of a nucleophilic addition reaction will show an angle of $110 \pm 5^\circ$ between the carbonyl group and the attacking nucleophile. Relating this to the problem of 1,2-asymmetric induction, Anh⁷ proposed that such a phenomenon should enhance the difference in steric interactions in the transition states leading to major and minor isomer (Figure 2).

The second and equally essential part of the Anh model concerns electronic effects used to explain the preference for the antiplanar attack of the nucleophilic group with respect to the large or polar substituent. Accordingly, the primary orbital interactions in the

nucleophilic addition takes place between the HOMO of the nucleophile and the LUMO of the aldehyde. The latter corresponds in most cases to the π^* orbital of the C=O group (Figure 3). With a perpendicular C-L group, the corresponding CL antibonding σ^* orbital can mix with the C=O π^* MO which lowers the orbital energy of the latter. Since the HOMO-LUMO interactions increase with decreasing orbital energy gaps⁹, the π^* - σ^* mixing (secondary orbital interactions) leads to more favored interactions. The σ^* orbital of C-R bonds with electronegative groups are rather low-lying and, therefore, polar groups such as OR, NR₂, or halogen atoms can take the role of the group L in the Felkin model (Figure 2). The combined results of the studies by Felkin *et al.*⁵ and by Anh's group⁷ have led to what is now called the "Felkin-Anh model".

More recent ab initio calculations carried out on a higher theoretical level with complete optimization of the transition state geometry¹⁰ corroborated Felkin's hypothesis that in the transition states leading to the major and minor isomers the attack of the nucleophilic agent is antiperiplanar to the CL bond bisecting the CS and CM bonds (Figure 2). However, there is an ongoing controversy as to (i) which substituents preferably take the position of the L group and (ii) what kind of interactions are in fact responsible for the conformation in the transition state. Anh⁷ argues that the best acceptor ligand takes the role of L because of the π^* - σ^* interactions described above. The opposite position is taken by Cieplak.¹¹ In his model, the dominating interactions in the transition state are between the occupied CL σ -bond and the σ^* -orbital of the forming bond between Nu and the carbonyl carbon atom.¹¹ Consequently, the L position in the Felkin transition state should be taken by the best donor ligand. Cieplak's model is based on the rather paradoxical assumption that in the transition state electrons are shifted into the antibonding orbital of an incipient bond. Arguments in favor of Cieplak's proposal came from several authors and were based on experimentally observed substituent effects in nucleophilic addition reactions of carbonyl compounds.¹² The various arguments for and against the models suggested by Anh⁵ and Cieplak¹¹ have recently been discussed by Cieplak *et al.*^{12b}. A recent ab initio study by Wong and Paddon-Row^{10b} showed that an acceptor group (fluorine) is more favored in the anti-position than a donor group (methyl). It should be pointed out that both models consider electronic effects as dominating the stereoselectivity of nucleophilic attack. More recently, Wong and Paddon-Row^{10c,d} emphasized that electrostatic rather than hyperconjugative electronic effects could be more important in determining conformational preferences in

nucleophilic addition reactions.

In this and the following¹³ study we report the results of our theoretical study in which we address the following questions: (a) What are the geometries and relative energies of the conformational minima of propionaldehyde **1**, chloroacetaldehyde **2**, and 2-chloropropionaldehyde **3**? (b) What are the geometries and relative energies of the transition states for the addition of a model nucleophile (LiH) to **1**, **2**, and **3**? (c) How do the conformational minima of **1**, **2**, and **3** compare with the conformations calculated for the transition state structures? (d) What type of interactions determine the differences in the activation barriers for addition of LiH to **1**, **2**, and **3**? (e) How well does the theoretically predicted diastereoselectivity of the addition of the model nucleophile (LiH) to **3** agree with the experimentally observed product ratio of the two diastereomers for different nucleophilic agents?

We have chosen 2-chloropropionaldehyde **3** as a model for a chiral carbonyl compound because it contains substituents with different electronic properties and because it allows a direct comparison with the theoretical study by Anh and Eisenstein^{7a}. We also calculated the conformational profiles of propionaldehyde **1** and chloroacetaldehyde **2** and the corresponding transition state structures for addition of LiH in order to investigate the effect of a methyl and chloro substituent separately.

Theoretical Details

The calculations were carried out using the CONVEX version of the GAUSSIAN 88¹⁴ program series. Optimized geometries and theoretical vibrational frequencies were obtained using the 6-31G(d) basis set which has a set of d-type orbitals for third-row elements.¹⁵ Potential energy minima and transition state structures are characterized by the number of negative eigenvalues i of the corresponding Hessian matrix with $i = 0$ for minima and $i = 1$ for transition states. The frequencies and corresponding zero-point vibrational energies (ZPE) were scaled by a factor of 0.89 to account for deficiencies in the basis set, neglect of correlation energy, and errors due to the harmonic approximation.¹⁶ Correlation energy was estimated using Møller-Plesset perturbation theory¹⁷ terminated at second order. Thus, the highest level of theory is denoted MP2/6-31G(d)//6-31G(d). Unless otherwise noted, energy values are given at that level of theory. The optimized geometries are plotted using the program Schakal.¹⁸

Results and Discussion

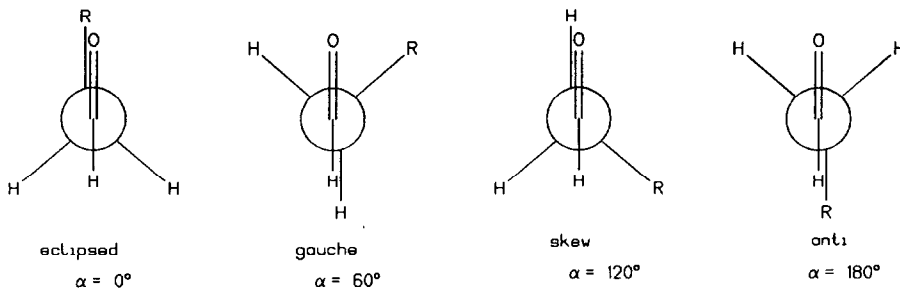
The following definitions and notations will be used throughout this paper. The torsion angle α is defined as the value for the clockwise

rotation of the CR bond around the CC bond relative to the C=O double bond viewed from C=O toward CR (Figure 4). Then, the principal conformations are eclipsed ($\alpha = 0^\circ$), gauche ($\alpha = 60^\circ$), skew ($\alpha = 120^\circ$), anti ($\alpha = 180^\circ$), with the actual torsion angles deviating more or less for the different conformations. The calculated energies of the conformational minima are shown in Table 1.

Table 1. Calculated total energies E_{tot} (hartrees), relative energies E_{rel} (kcal/mol) and zero-point vibrational energies ZPE (kcal/mol) scaled by 0.89.

	6-31G(d)//6-31G(d)			MP2/6-31G(d)//6-31G(d)	
	E_{tot}	E_{rel}	ZPE	E_{tot}	E_{rel}
1a	-191.9523	0.0	50.8	-192.5115	0.0
1b	-191.9505	1.1	50.7	-192.5093	1.4
2a	-611.8094	1.5	28.7	-612.3660	0.8
2b	-611.8117	0.0	28.7	-612.3673	0.0
3a	-650.8512	0.0	45.7	-651.5401	0.0
3b	-650.8505	0.5	45.7	-651.5392	0.6
3c	-650.8471	2.6	45.7	-651.5368	2.1

Figure 4. Principal conformations of substituted aldehydes.



Propionaldehyde

Figure 5 shows the calculated rotational profile for propionaldehyde (1). There are two rotational minima, the eclipsed conformation **1a** ($\alpha =$

0°) and the higher lying skew ($\alpha = 126^\circ$) rotamer **1b**. The optimized structures are shown in Figure 6. Table 2 shows our calculated energy values and the activation barriers for rotation around the central C-C σ -bond in comparison with previous calculations¹⁹ and experimentally obtained²⁰ data. There is agreement that **1a** is the global minimum energy conformation for propionaldehyde. The energy difference **1a** - **1b** is calculated to be 1.37 kcal/mol, the experimental values are between 0.9 and 1.17 kcal/mol.²⁰ The theoretically predicted activation barriers agree very well with the reported microwave data^{20a,b} while the results obtained from vibrational spectroscopy^{20c} indicate higher rotational barriers.

Rotational barriers of this type may be analyzed by decomposing them into onefold, twofold, and threefold terms²⁵:

$$V_\alpha = \sum 0.5 V_n (1 - \cos n\alpha) \quad (1)$$

The calculated values for the V_n terms of **1** at MP2/6-31G(d)//6-31G(D) are $V_1 = 0.900$ kcal/mol, $V_2 = 0.940$ kcal/mol, $V_3 = 1.150$ kcal/mol. Earlier calculations show similar results.^{19a} The V_1 term, which can be interpreted in as the result of dipole/dipole interactions²⁵, indicates a stabilization at 0° . The twofold terms represents a stabilization at 0° and 180° which is usually discussed in terms of orbital interactions²⁵. The threefold term indicates a stabilization at 0° , 120° , and 240° . The three terms have about the same magnitude, which means that neither type of interaction is dominant.

Figure 5 shows also the energy levels of the HOMO and the LUMO of **1** as a function of α (OCCC). The HOMO is roughly parallel to the total energy of **1**. The LUMO exhibits a greater variance of the eigenvalue and a contrasting behaviour compared with the HOMO, i.e. a minimum of the LUMO corresponds roughly to a maximum of the HOMO. Rather sharp minima for the LUMO are calculated for $\alpha = 60^\circ$ and $\alpha = 180^\circ$ (Figure 5). It is interesting to note that a minimum for the LUMO²⁴ occurs for $\alpha = 60^\circ$ and not $\alpha = 90^\circ$, which could have been expected from the Felkin-Anh^{5,7} model (Figure 3). Figure 5 clearly shows that the low-energy conformation corresponds to a maximum of the LUMO, and that the largest "Felkin-Anh" type $\pi^*-\sigma^*$ mixing occurs at a rotational maximum ($\alpha = 60^\circ$).

Figure 5. Calculated (MP2/6-31G(d)//HF/6-31G(d)) rotational profile for rotation around the C-C bond and energy level of the HOMO and LUMO of propionaldehyde **1**.

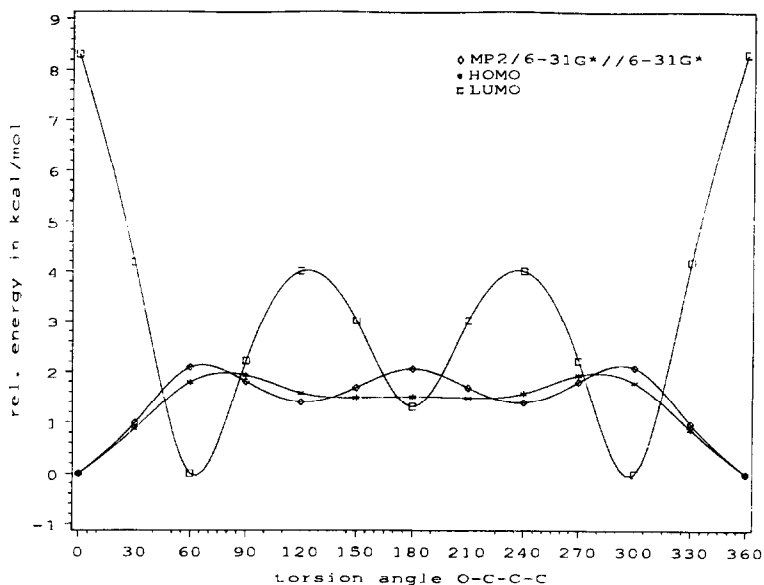


Figure 6. Calculated (MP2/6-31G(d)//HF/6-31G(d)) rotational minima **1a** and **1b**.

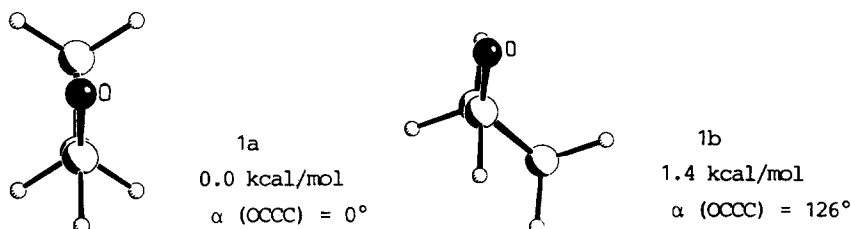


Table 2. Calculated and experimentally observed energy differences ΔE and activation barriers ΔE^* (kcal/mol) for propionaldehyde **1**.

$\Delta E_{\text{ecl-skew}}$	$\Delta E^*_{\text{ecl-skew}}$	$\Delta E^*_{\text{skew-skew}}$	$\Delta E^*_{\text{skew-ecl}}$	Method
1.37	2.15	0.68	0.77	Ab initio ^a
0.95	2.10	0.60	1.15	MW ^b
0.9	2.28			MW ^c
1.0				NMR ^d
0.69	2.96	1.21	2.29	IR, Raman ^e
1.17				IR, Raman ^f
1.03				IR, Raman ^g

^aMP2/6-31G(d)//HF/6-31G(d), this work. ^bRef. 20a. ^cRef. 20b. ^dRef. 20f.

^eRef. 20c. ^fRef. 20d. ^gRef. 20e.

Chloroacetaldehyde

Figure 7 shows our calculated rotational profile for chloroacetaldehyde **2**. As in propionaldehyde **1**, there are two conformational minima, one with an eclipsed conformation **2a** ($\alpha = 0^\circ$), and the other with an anti form **2b** ($\alpha = 156^\circ$). Unlike in **1**, where the global minimum has an eclipsed conformation, the eclipsed form **2a** is 0.85 kcal/mol higher in energy than the anti form **2b**. This can be explained by the dipole/dipole interactions between the C=O bond dipole and the C-CH₃ bond dipole in **1**, which are antiparallel in the eclipsed conformation **1a**¹⁹, while they are parallel between C=O and C-Cl in **2a**. There is a small "hump" calculated for $\alpha = 180^\circ$ which is in agreement with experimental results obtained by electron diffraction.²² Table 3 shows the calculated energy differences for the interconversion of **2a** and **2b** in comparison with previous theoretical results²¹ and experimental data^{22,23}. Our calculated energy difference **2a** - **2b** is within the rather large range obtained for **2** by NMR studies in various solvents.²³

The analysis of the rotational barrier via equation (1) supports the assumption that dipole/dipole interactions are responsible for the different rotational profile of **2** compared with **1**. The calculated values for the different terms are: $V_1 = -2.193$ kcal/mol, $V_2 = 1.833$ kcal/mol, $V_3 = 1.343$ kcal/mol. The V_1 term for **2** has a negative sign, indicating destabilizing dipole/dipole interactions at $\alpha = 0^\circ$, while V_1 is positive for **1**.

Figure 7 shows that the LUMO of **2** has a deep minimum²⁴ at $\alpha = -75^\circ$. The minimum is much deeper (~20 kcal/mol relative to $\alpha = 0^\circ$, ~13 kcal/mol relative to $\alpha = 180^\circ$) than in the case of **1** (~8 kcal/mol relative to $\alpha = 0^\circ$, ~4 kcal/mol relative to $\alpha = 120^\circ$). Thus, the C-Cl bond in **2** lowers the energy level of the adjacent C=O π^* orbital to a much higher degree than the C-C and C-H bonds do in **1**. However, the lowest lying energy level for the LUMO of **1** and **2** is close to a rotational maximum and not an energy minimum (Figure 5 and 7). The HOMO of **2** shows as a function of α a contrasting behaviour similar to **1**, i.e. it is parallel to the total energy.

Figure 7. Calculated (MP2/6-31G(d)//HF/6-31G(d)) rotational profile for rotation around the C-C bond and energy level of the HOMO and LUMO of chloroacetaldehyde 2.

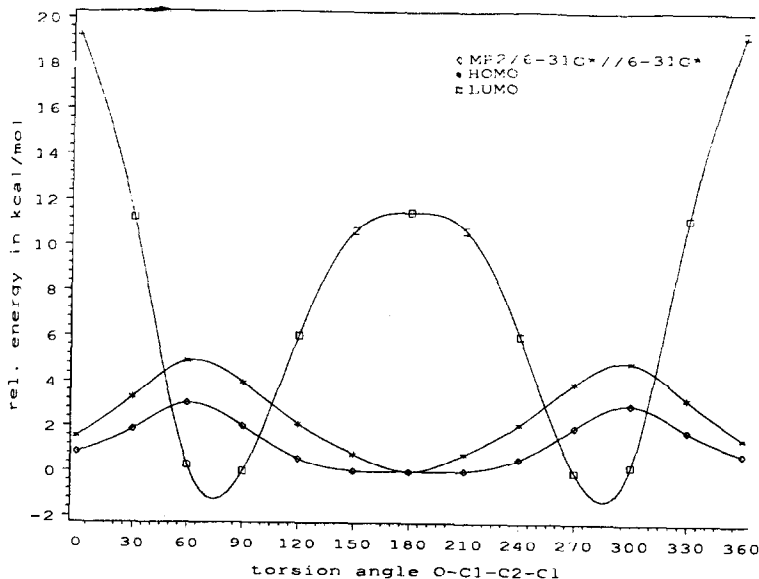


Figure 8. Calculated (MP2/6-31G(d)//HF/6-31G(d)) rotational minima 2a and 2b.

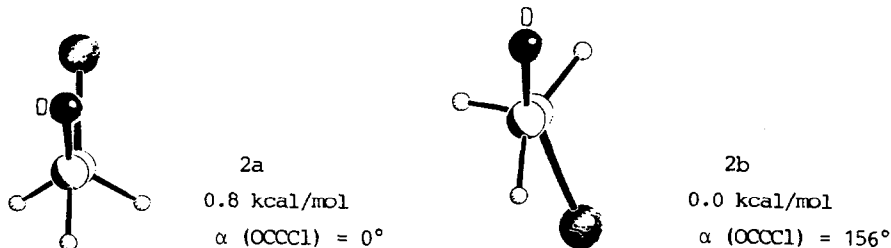


Table 3. Calculated and experimentally observed energy differences ΔE and activation barriers ΔE^* (kcal/mol) for chloroacetaldehyde 2.

$\Delta E_{\text{ecl-anti}}$	$\Delta E^*_{\text{ecl-anti}}$	$\Delta E^*_{\text{anti-anti}}$	$\Delta E^*_{\text{anti-ecl}}$	Method
0.85	2.3	0.01	3.15	Ab initio ^a
1.1	2.0	<0.1	3.1	Ab initio ^b
1.46	1.98	0.03	3.44	Ab initio ^c
		0.01		ED ^d
0.3-1.5				NMR ^e

^aMP2/6-31G(d)//HF/6-31G(d), this work. ^bMP4/4-31G(d)//HF/4-31G(d), taken from the Figure in Ref. 21a. ^cHF/6-31G(d)//HF/6-31G(d), Ref. 21b ^dRef. 22. ^eRef. 23.

2-Chloropropionaldehyde

The calculated rotational profile of 2-chloropropionaldehyde **3** is shown in Figure 9. There are three conformational minima, **3a**, **3b**, and **3c**, which are shown in Figure 10. The lowest lying conformation **3a** can be considered to be the result of favorable dipole/dipole interactions between the C=O bond and the C-Me bond,¹⁹ which are parallel like in **1a** (Figure 6), and the nearly antiparallel arrangement of C=O and C-Cl bonds as in **2b** (Figure 8). Attractive dipole/dipole interactions between the C=O and C-Cl bonds are also found in **3b**, but the C-Me bond is perpendicular to C=O which is unfavorable (see Figure 5). The least stable conformation **3c** can be understood to be the "combination" of the higher lying rotamers of propionaldehyde **1b** (Figure 6) and chloroacetaldehyde **2b** (Figure 8).

Figure 9 shows also the eigenvalue ϵ of the LUMO as function of the torsion angle α_1 . There is clearly a correlation of ϵ with α_1 . As for **2** (Figure 7), the LUMO becomes much lower in energy²⁴ when the C-Cl bond is perpendicular to C=O around $\alpha_1 = 90^\circ$ and $\alpha_1 = 270^\circ$, which corroborates the importance of $\pi^*(\text{CO}) - \sigma^*(\text{CCl})$ mixing as suggested by Anh.⁷ But in order to achieve a low-lying LUMO, **3** must be rotated around α_1 towards the conformational maxima at $\alpha_1 \sim 60^\circ$ and $\alpha_1 \sim 300^\circ$ (Figure 9).

Figure 9. Calculated (MP2/6-31G(d)//HF/6-31G(d)) rotational profile for rotation around the C-C bond and energy level of the HOMO and LUMO of 2-chloropropionaldehyde **3**.

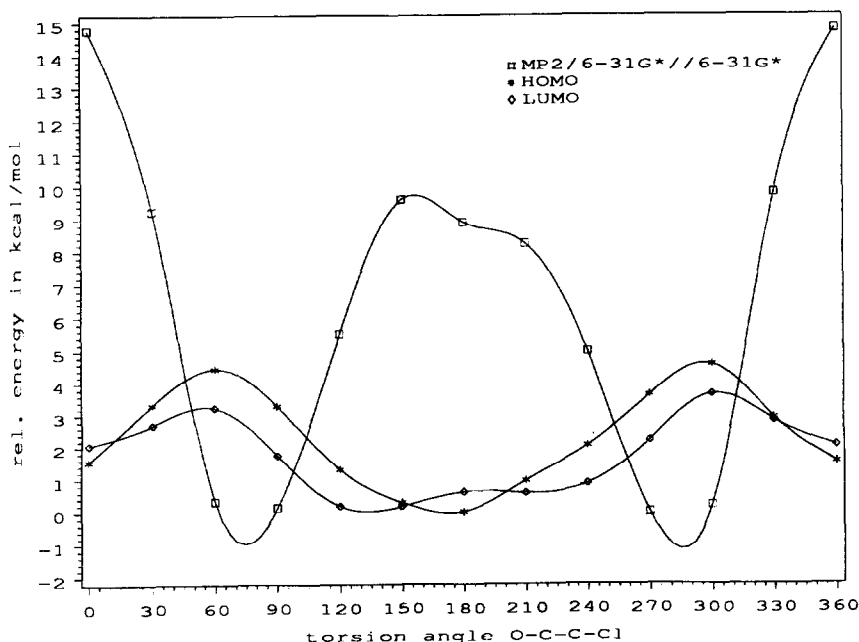
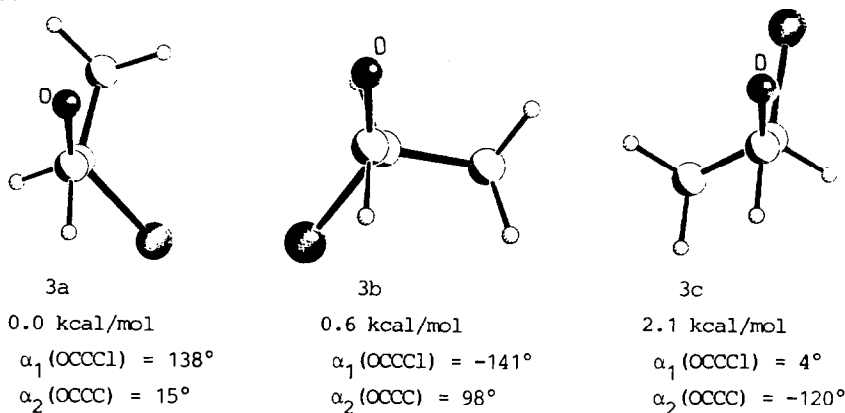


Figure 10. Calculated (MP2/6-31G(d)//HF/6-31G(d)) rotational minima 3a and 3b.



Conclusions

The theoretically predicted rotational profiles for propionaldehyde 1 and chloroacetaldehyde 2 show that 1 and 2 have two conformational minima. The lowest lying conformation of 1 has the methyl group eclipsed to the carbonyl group, which can be understood in terms of attractive dipole/dipole interactions between the C=O bond and the C-CH₃ bond. The bond moment of the C-Cl bond in 2 has the opposite orientation as the C-CH₃ bond in 2. Therefore, the lowest lying conformation of 2 has the C-Cl bond anti to the C=O bond. The LUMO of 1 and particularly 2 shows a strong correlation with the torsion angle α . The lowest lying energy value of the LUMO is calculated when the C-L bond is roughly perpendicular to the C=O bond, as postulated by the Anh⁷ model, although the minimum occurs at $\alpha -60^\circ$ for 1 and $\alpha -75^\circ$ for 2 and not at 90° . However, the lowest energy values correspond to rotational maxima of 1 and 2. The calculated rotational barriers for 1 and 2 agree with experimental data.

Three conformational minima are theoretically predicted for 2-chloropropionaldehyde 3. The most stable conformation has the C-CH₃ group nearly eclipsed with the carbonyl bond. The LUMO of 3 shows a conformational profile very similar to 2, i.e. the minimum of the LUMO is calculated near a conformational maximum. There are no experimental results available for the conformational profile of 3.

In the following paper¹³, we discuss the implications of the present results for the energies of the transition states for addition of nucleophiles to 1, 2, and 3.

Acknowledgment

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