

# A CNDO/2 Study of Rotational Isomerism and Barriers to Internal Rotation of Acetaldehyde and Some of its Chloro- and Fluoro-Derivatives

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Acetaldehyde derivatives of the  $\text{CH}_2\text{Y}-\text{CXO}$  type are generally found to possess one or more of the conformations I–IV of Fig. 1 as stable energy minima. Accurate experimental information is now available for several  $\text{CH}_3-\text{CXO}$  molecules. For example, acetaldehyde,<sup>1</sup> acetyl fluoride,<sup>2</sup> and acetyl chloride<sup>3</sup> have all been shown by the microwave substitution method to possess the *trans* form as the

stable equilibrium conformation with  $\theta = 60^\circ$  corresponding to the maximum of the threefold barrier to internal rotation. The barrier heights of these three molecules vary only slightly from approximately 1.0 to 1.2 kcal/mol.<sup>1–3</sup>

The potential functions of the  $\text{CH}_2\text{Y}-\text{CXO}$  ( $\text{Y} = \text{F}, \text{Cl}, \text{X} = \text{H}, \text{F}, \text{Cl}$ ) compounds are much more complicated than the simple threefold barriers of the  $\text{CH}_3-\text{CXO}$  molecules. Some experimental information is at present available for such compounds. Fluoroacetyl fluoride,<sup>4</sup> for example, has two stable conformations, a *trans* form and a *cis* form, the former being more stable by about 0.9 kcal/mol. The energetically favoured form of  $\text{CH}_2\text{Cl}-\text{CClO}$  is the *trans* with a less stable rotamer intermediate between the *gauche* and the *cis* forms<sup>5,6</sup> ( $\theta$  about  $150^\circ$ ).

Little theoretical work has appeared on the  $\text{CH}_3-\text{CXO}$  and  $\text{CH}_2\text{Y}-\text{CXO}$  type molecules with the exception of acetaldehyde for which an elaborate LC (Hartree-Fock) AO MO-SCF study has demonstrated that the threefold rotational barrier is controlled by attractive forces between non-bonded atoms.<sup>7</sup> It is not expected in the near future that such complete calculations as this one will be carried out for the majority of molecules studied here because they would be much more lengthy than in the case of acetaldehyde. The more simple CNDO/2 results presented here seem to be in relatively good agreement with experiments when available, and it is therefore hoped that the predictions made are meaningful.

**Results and discussion.** The computations were carried out using the CNDO/2 (complete neglect of differential overlap) method described in Refs. 8 and 9. The structures reported in the literature were

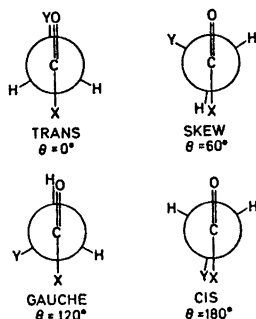


Fig. 1. Newman projections of possible stable forms of molecules of the general type  $\text{CH}_2\text{Y}-\text{CXO}$ .

Table 1. Experimental and computed barriers to internal rotation and dipole moments of stable conformations of some  $\text{CH}_3-\text{CXO}$  molecules.

Molecule	Barrier <sup>a</sup>		Dipole moment		Ref.
	Exp. (cal/mol)	CNDO/2 (cal/mol)	Exp. (D)	CNDO/2 (D)	
$\text{CH}_3-\text{CHO}$	$1143 \pm 30$	720	2.69	2.51	1
$\text{CH}_3-\text{CFO}$	$1041 \pm 6$	627	2.96	2.53	2
$\text{CH}_3-\text{CClO}$	$1296 \pm 30$	407	2.38	2.79	3,11 <sup>b</sup>

<sup>a</sup> Stable conformation is the *trans* form. <sup>b</sup> Dipole moment.

Table 2. Results of potential function calculations.

Molecule	Stable conformations	Maxima of potential curve	Energy differences
CH <sub>2</sub> F-CHO	<i>trans</i> ( $\theta=0^\circ$ ) and <i>cis</i> ( $\theta=180^\circ$ )	$\theta=90^\circ$ , 4.35 kcal/mol above <i>cis</i>	<i>cis</i> 0.11 kcal/mol more stable than <i>trans</i>
CH <sub>2</sub> Cl-CHO	<i>trans</i> ( $\theta=0^\circ$ ) and <i>gauche</i> ( $\theta=115^\circ$ )	$\theta=52^\circ$ , 0.92 kcal/mol above <i>gauche</i> and $\theta=180^\circ$ , 0.95 kcal/mol above <i>gauche</i>	<i>gauche</i> 0.34 kcal/mol more stable than <i>trans</i>
CH <sub>2</sub> F-CFO	<i>trans</i> ( $\theta=0^\circ$ ) and <i>cis</i> ( $\theta=180^\circ$ )	$\theta=101^\circ$ , 4.5 kcal/mol above <i>trans</i>	<i>trans</i> 1.0 kcal/mol more stable than <i>cis</i>
CH <sub>2</sub> Cl-CFO	<i>trans</i> ( $\theta=0^\circ$ ) and <i>gauche</i> ( $\theta=110^\circ$ )	$\theta=43^\circ$ , 0.98 kcal/mol above <i>gauche</i> and $\theta=180^\circ$ , 0.47 kcal/mol above <i>gauche</i>	<i>gauche</i> 0.82 kcal/mol more stable than <i>trans</i>
CH <sub>2</sub> F-CClO	<i>trans</i> ( $\theta=0^\circ$ ) and <i>cis</i> ( $\theta=180^\circ$ )	$\theta=91^\circ$ , 4.3 kcal/mol above <i>cis</i>	<i>cis</i> 0.62 kcal/mol more stable than <i>trans</i>

used. In those cases where a structure has not been determined, plausible structural parameters were transferred from related compounds. The dihedral angle  $\theta$  was varied in intervals of  $20^\circ$  keeping the other structural parameters fixed. The results are shown in Tables 1-3. The calculations were repeated for some of the molecules varying the C-C bond length within reasonable limits, but very little change in the potential functions resulted.

The CNDO/2 method correctly predicts the stable conformation of the CH<sub>3</sub>-CXO

type molecules to be the *trans* form where one hydrogen atom of the methyl group eclipses the carbonyl oxygen, but the rotational barriers are too low by 0.4-0.8 kcal/mol. The results for CH<sub>3</sub>-CHO and CH<sub>3</sub>-CFO are closer to the experimental values than in the case of CH<sub>3</sub>-CClO. But the dipole moments are in all these cases close to the experimentally determined ones.

The most important results of the calculated potential functions of the CH<sub>2</sub>Y-CXO compounds are summarized in Tables 2 and 3. The results for CH<sub>2</sub>Cl-CClO is not included in Table 2 because the erroneous result (see Refs. 5 and 6) that the *cis* conformation was approximately 10 kcal/mol more stable than the *trans* form was obtained, but the dipole moments computed for the two stable forms of this molecule given in Table 3 appear to be reasonable.

The potential functions of this type of molecules are characterized by having two minima which means that two stable conformations exist. The energy difference between the two forms are small, usually less than about 1 kcal/mol. The

Table 3. Calculated dipole moments of stable conformers.

Molecule	$\theta$	$\mu$ (debye)	$\theta$	$\mu$ (debye)
CH <sub>2</sub> F-CHO	$0^\circ$	3.65	$180^\circ$	0.67
CH <sub>2</sub> Cl-CHO	$0^\circ$	3.55	$115^\circ$	1.97
CH <sub>2</sub> F-CFO	$0^\circ$	2.68	$180^\circ$	1.79
CH <sub>2</sub> Cl-CFO	$0^\circ$	2.65	$110^\circ$	2.18
CH <sub>2</sub> F-CClO	$0^\circ$	2.59	$180^\circ$	1.72
CH <sub>2</sub> Cl-CClO	$0^\circ$	2.55	$150^\circ$	1.91

energy maxima separating the two rotamers are computed to have energies of less than 5 kcal/mol higher than those of the stable forms. Molecules possessing the  $\text{CH}_2\text{F}$ -moiety are seen to possess stable *trans* and *cis* forms, whereas those substances having a  $\text{CH}_2\text{Cl}$ -group have stable *trans* and *gauche* rotamers.

Unfortunately, incomplete experimental data are available to check the calculations performed on the  $\text{CH}_2\text{Y}$ -CXO compounds. Moreover, the existing experimental information has been derived from "bottoms" of the potential wells, and virtually no complete potential curve has been determined experimentally. The most exhaustive study available appears to be one performed by Saegebarth and Wilson<sup>4</sup> on  $\text{CH}_2\text{F}$ -CFO as mentioned in the introduction. As can be seen from Table 2 there is very good agreement between their results and the present computations regarding the relative stability of the two forms. Insufficient information was available to draw a complete potential function for this molecule, but the one suggested by Saegebarth and Wilson<sup>4</sup> closely resembles the CNDO/2 result of Table 2. The dipole moments of the two forms<sup>4</sup> are  $2.67 \pm 0.05$  D for *trans* and  $2.05 \pm 0.06$  D for *cis* which compare well to the computed values of 2.68 D and 1.79 D, respectively.

The existence of two forms of  $\text{CH}_2\text{Cl}$ -CHO has now been experimentally established.<sup>10</sup> This is in agreement with the present findings.

For  $\text{CH}_2\text{F}$ -CHO,  $\text{CH}_2\text{F}$ -CClO, and  $\text{CH}_2\text{Cl}$ -CFO no experimental data have been found in the literature. By comparing the calculated potential curves of these molecules to those for which experimental information is available, a few interesting features are observed. *E.g.*, the  $\text{CH}_2\text{F}$ -CHO potential function resembles that of  $\text{CH}_2\text{F}$ -CFO, with the difference that the *cis* form is relatively more stable for the former molecule. This seems quite plausible for steric reasons because there is probably a slight repulsion<sup>4</sup> between the fluorine atoms in *cis*  $\text{CH}_2\text{F}$ -CFO, whereas steric conditions are probably more favourable in *cis*  $\text{CH}_2\text{F}$ -CHO. For  $\text{CH}_2\text{F}$ -CClO and  $\text{CH}_2\text{Cl}$ -CFO virtually no experimental data exist to check the computational results.

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## Synthesis of 3,4-Stilbenequinones

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3,4-Stilbenequinoid structures are of considerable interest as possible chromophoric constituents of sulfite and sulfate pulps.<sup>1</sup> Apparently, the instability of this particular type of chromophoric system has hitherto handicapped the preparation of representative models. Our efforts to synthesize models of this type employing familiar routes such as oxidation with potassium nitrosodisulfonate (Fremy-salt),<sup>2</sup>