

isolated from a tobacco fraction (C-6) by preparative gas chromatography.<sup>2</sup>

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## A CNDO/2 Study of Some Conformational Properties in Propyl Chloride, Fluoride, Cyanide, and Ethyl Formate

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In recent years, there has been an increasing application of the semi-empirical molecular orbital method CNDO/2,<sup>1</sup> in studying structural and energetic properties of molecules.<sup>1,2</sup> Some of these calculations have been rather successful,<sup>1,3</sup> whereas others indicate that the method should be used with caution.<sup>4</sup>

In the present work the CNDO/2 method has been used to study some conformational properties of a few ethyl derivatives. Only molecules were chosen for which reliable experimental information for comparison was available. The actual molecules were propyl chloride, fluoride, cyanide, and ethyl formate. For the three first molecules rotation was considered about the C<sup>1</sup>-C<sup>2</sup> bond \* and for the last about the CH<sub>2</sub>-O bond.

*Results.* The geometries used for the calculations were obtained from recent microwave investigations.<sup>5-8</sup> The energies were calculated varying the dihedral angle from 0 to 180° in steps of 30° except around the gauche positions, where 5° intervals were used.

In Table I the calculated conformational properties of the selected molecules are presented together with experimental data. The calculations predict two stable conformations. Except for propyl chloride both dihedral angles and energy differences are in satisfactory agreement with experimental values.<sup>5-8</sup> The reason why the calculations on propyl chloride fail is not clear. Possibly, the parameters used for the third row elements are not so well fitted as for the first and second. Also the approximations inherent in the method may be less correct when the third row elements are included.

For propyl fluoride and ethyl formate the experimental *trans-gauche* barriers are well reproduced. For the *gauche-gauche*

\* The molecules are denoted C<sup>3</sup>H<sub>3</sub>-C<sup>2</sup>H<sub>2</sub>-C<sup>1</sup>H<sub>2</sub>X, where X = F, Cl, C≡N.

Table 1. Calculated and experimental conformational properties.

	Dihedral angle for stable conformation <sup>a</sup>		$\Delta E^b$ kcal/mol		trans-gauche barrier, kcal/mol		gauche-gauche barrier, kcal/mol	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
C <sub>3</sub> H <sub>7</sub> CN	0° 127°	0° <120°	1.5	~1	1.8	—	0.9	—
C <sub>3</sub> H <sub>7</sub> F	0° 125°	0° 117°	0.0	0.47 ± 0.31	2.9	4.2 ± 0.15	1.4	10.1 ± 4.4
C <sub>3</sub> H <sub>7</sub> Cl	0° 180°	0° 110°	3.0	0 ± 0.5	2.6	—	—	—
C <sub>2</sub> H <sub>5</sub> OCHO	0° 108°	0° 95°	-0.6	-0.186 ± 0.060	1.3	1.1 ± 0.25	9.8	5.2 ± 2.5

<sup>a</sup> The dihedral angle of the *trans*-form is 0°.

<sup>b</sup>  $\Delta E = E(\text{trans}) - E(\text{gauche})$

barriers, however, the calculated values are not in accordance with the experimental values. Table 2 gives the calculated and

Table 2. Calculated and experimental dipole moments.

	Dipole moment (debye)		
		Calc.	Exp.
C <sub>3</sub> H <sub>7</sub> CN	<i>trans</i>	3.12	3.46 <sup>a</sup>
	<i>gauche</i>	3.07	
C <sub>3</sub> H <sub>7</sub> F	<i>trans</i>	1.89	2.05 <sup>b</sup>
	<i>gauche</i>	1.83	
C <sub>3</sub> H <sub>7</sub> Cl	<i>trans</i>	1.95	2.04 <sup>c</sup>
	<i>gauche</i>	1.83	
C <sub>2</sub> H <sub>5</sub> OCHO	<i>trans</i>	1.37	1.98 ± 0.02 <sup>d</sup>
	<i>gauche</i>	1.21	

<sup>a</sup> Ref. 9. <sup>b</sup> Ref. 5. <sup>c</sup> Ref. 10. <sup>d</sup> Ref. 8.

experimental dipole moments.<sup>9-10</sup> It is seen that the calculated dipole moments generally are somewhat lower than the experimental values, as is often found by the CNDO-method.<sup>1</sup>

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