

**THE HIGH ENERGY *S-TRANS* CONFORMERS OF CH<sub>3</sub>COOH AND CH<sub>3</sub>COOCH<sub>3</sub>: A MOLECULAR MECHANICS AND VIBRATIONAL STUDY OF CH<sub>3</sub>COCl, CH<sub>3</sub>COOH AND CH<sub>3</sub>COOCH<sub>3</sub>**

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ABSTRACT

Structural and vibrational properties of CH<sub>3</sub>COCl, CH<sub>3</sub>COOH and CH<sub>3</sub>COOCH<sub>3</sub> have been determined by combined molecular mechanics and vibrational studies. New data for the high energy *s-trans* conformers of CH<sub>3</sub>COOH and CH<sub>3</sub>COOCH<sub>3</sub> are reported and the torsional mode of CH<sub>3</sub>COCl is identified.

INTRODUCTION

In a previous paper [1], we developed a molecular mechanics force field for acyl chlorides, carboxylic acids and esters. We now apply the force field obtained to CH<sub>3</sub>COCl, CH<sub>3</sub>COOH and CH<sub>3</sub>COOCH<sub>3</sub>. While these molecules have been considered in the past, they are studied herein with a new method, which combines molecular mechanics and vibrational spectroscopy to assess conformational effects. In the case of CH<sub>3</sub>COOH and CH<sub>3</sub>COOCH<sub>3</sub>, new data concerning high energy *s-trans* conformers are reported; for CH<sub>3</sub>COCl, the identification of the torsional mode is considered.

EXPERIMENTAL

All the details of the molecular mechanics force field have been reported [1].

Raman spectra have been recorded on a Cary 82 spectrometer using an Ar<sup>+</sup> Spectra Physics laser (model 164-05) whose output at 514.5 nm was adjusted to provide 200–250 mW at the sample position.

We used the photon counting mode with sensitivities adjusted in the 10<sup>3</sup>–10<sup>5</sup> counts s<sup>-1</sup> range to provide reasonable signal-to-noise ratios. The spectrometer operated with spectral slitwidths (*s*) of 4 cm<sup>-1</sup>. The pen period (*τ*) was set at 0.5 or 1.0 s and the monochromators scanning speed (*v*(cm s<sup>-1</sup>)) adjusted so that  $v \leq s/(4\tau)$ .

Spectroscopic grade CH<sub>3</sub>COCl was obtained commercially and distilled prior to recording spectra.

## RESULTS AND DISCUSSION

 $CH_3COCl$ 

The force field developed in [1] yields a single minimum energy conformation, when the oxygen and one of the hydrogen atoms are eclipsed (Fig. 1). This result agrees with electron diffraction data [2] (see Table 1). The conformation of maximum energy shows the chlorine and one of the hydrogen atoms eclipsed, and exhibits a larger H—C—C angle due to steric repulsions between the chlorine and the *syn*-periplanar hydrogen atoms.

The calculated threefold energy barrier ( $\text{kJ mol}^{-1}$ ) around the C—C bond (5.250) agrees very well with experimental values obtained for the gaseous state (5.273 [4], 5.372 [5], 5.424 [6]).

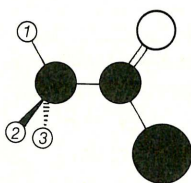
Fig. 1. Conformer of  $CH_3COCl$ .

TABLE 1

Structural parameters for acetylchloride

Parameter	Experimental values [2, 3]	Calculated values	Parameter	Experimental values [2, 3]	Calculated values
<i>Bond lengths (pm)</i>			<i>Moments of inertia (<math>10^{-23}</math> (kg mol<sup>-1</sup>) m<sup>2</sup>)</i>		
C—C	150.75(53)	151.02	$I_a$	49.7453	49.8391
C—H <sub>1</sub>	110.70 <sup>a</sup>	109.61	$I_b$	102.1965	104.5013
C—H <sub>2,3</sub>	110.70 <sup>a</sup>	109.65	$I_c$	148.9893	151.1179
C=O	118.74(28)	118.59	<i>Rotational constants (MHz)</i>		
C—Cl	179.83(29)	180.17	A	10162.39	10140.46
<i>Angles (degrees)</i>			B	4946.66	4836.22
C—C—H <sub>1</sub>	110.35 <sup>a</sup>	109.47	C	3393.07	3344.35
C—C—H <sub>2,3</sub>	110.35 <sup>a</sup>	110.44			
C—C=O	127.45(88)	126.93			
C—C—Cl	112.17(85)	112.99			
H <sub>1</sub> —C—H <sub>2,3</sub>	108.58 <sup>a</sup>	108.61			
H <sub>2</sub> —C—H <sub>3</sub>	108.58 <sup>a</sup>	109.24			
O=C—Cl	120.32(63)	120.08			
O=C—C—H <sub>1</sub>	0.00	0.00			
C—C(=O)—Cl	180.00 <sup>a</sup>	180.00			

<sup>a</sup> Assumed value.

The IR [7, 8] and Raman [8, 9] spectra of this compound have been studied both in the gaseous and condensed phases. The spectra of the pure liquid have also been recorded. In this case, a weak Raman band was detected at ca.  $150 \text{ cm}^{-1}$ , deeply buried in the Rayleigh wing. This band, which has not been referred to in the literature, is herein ascribed to the torsional mode, as the corresponding calculated frequency has been evaluated at  $145 \text{ cm}^{-1}$ . A comparison of calculated and experimental vibrational frequencies is presented in Table 2.

 $CH_3COOH$ 

The structure of the monomer of acetic acid has been determined by electron diffraction [10] and microwave spectroscopy [11–14] for the more stable *s-cis* conformation. While an *s-trans* conformer has also been predicted [15, 16] (see Fig. 2), only the *s-cis* form has been studied both from the structural and vibrational point of view [10–14, 17].

As can be seen from Table 3, the calculated and observed structures of the *s-cis* form agree well. Only the calculated O=C—O and C—C—O angles deviate from the experimental values [14]. Table 3 also presents the calculated structure of the *s-trans* form, for which no structure was found for comparison. A close proximity between the carboxylic hydrogen atom and two of the methyl hydrogen atoms causes an increase in the C—C—O and C—O—H angles (Table 3).

TABLE 2

Experimental and calculated vibrational frequencies ( $\text{cm}^{-1}$ ) for acetylchloride

Observed		Calculated (mol. mechanics)	Approximate description and symmetry species	
Raman (liq.)	IR (gas) [8]			
3021	3029	3045	CH <sub>3</sub>	anti. stretch A'
2995 dp	3029	3045	CH <sub>3</sub>	anti. stretch A''
2935	2950	2931	CH <sub>3</sub>	sym. stretch A'
1804	1822	1824	C=O	stretch A'
	1432	1429	CH <sub>3</sub>	anti. deform. A'
1423	1432	1423	CH <sub>3</sub>	anti. deform. A''
1362	1370	1415	CH <sub>3</sub>	sym. deform. A'
1100	1109	1101	C—C	stretch A'
1030 dp	1029	945	CH <sub>3</sub>	rock. A''
957	958	897	CH <sub>3</sub>	rock. A'
593	608	610	C—Cl	stretch A'
520 dp	514	505	C=O	rock. A''
440	436	440	O=C—Cl	deform. A'
354	348	360	C—C=O	deform. A'
150 dp?	—	145	C—C	torsion A''

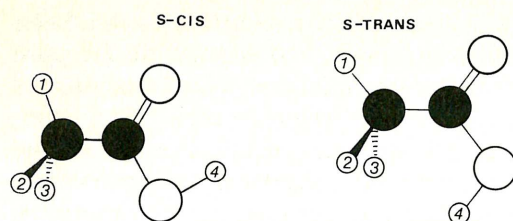
Fig. 2. Conformers of  $\text{CH}_3\text{COOH}$ .

TABLE 3

Structural parameters for acetic acid

Parameter	Experimental values [18]	Calculated values	
		( <i>s-cis</i> )	( <i>s-trans</i> )
<i>Bond lengths (pm)</i>			
C—C	149.4(10)	150.6	151.4
C—H	109.0(4)		109.6
C=O	120.9 (6)		120.1
C—O	135.7(5)	133.7	134.3
O—H	97.0(3)		97.0
<i>Angles (degrees)</i>			
C—C—H	109.5 <sup>a</sup>		109.9
C—C=O	126.2(7)	125.9	124.5
C—C—O	112.0(6)	108.4	110.3
H—C—H	109.5(5)		109.0
O=C—O	121.8(12)	125.8	125.2
C—O—H	105.9(5)		106.8
O=C—C—H <sub>1</sub>	0.0		0.0
O=C—O—H	0.0	0.0	180.0
C—C(=O)—O	180.0 <sup>a</sup>		180.0
<i>Moments of inertia (10<sup>-23</sup> (kg mol<sup>-1</sup>)m<sup>2</sup>)</i>			
<i>I<sub>a</sub></i>	44.5838	45.0754	46.7132
<i>I<sub>b</sub></i>	53.3176	51.9182	50.7322
<i>I<sub>c</sub></i>	94.9081	93.7778	94.2257
<i>Rotational constants (MHz)</i>			
<i>A</i>	11335.47	11212.13	10819.82
<i>B</i>	9478.60	9734.38	9961.94
<i>C</i>	5324.91	5389.24	5363.62

<sup>a</sup> Assumed value.

The calculated energy barrier ( $\text{kJ mol}^{-1}$ ) for the rotation around the C—C bond in the *s-cis* conformer ( $\Delta E(60^\circ-0^\circ) = 1.185$ ) is somewhat smaller than the experimental value ( $\Delta E(60^\circ-0^\circ) = 2.021 \pm 0.105$  [13]), a result which is probably correlated with details of the force field parameterization [1]. On the other hand, the energy values calculated for the rotation around the C—O bond ( $\Delta E(s\text{-trans} - s\text{-cis}) = 24.858$  and  $\Delta E(90^\circ-0^\circ) = 44.308$ ) are in excellent agreement with the experimental values ( $\Delta E(s\text{-trans} - s\text{-cis}) = 24.984$  and  $\Delta E(90^\circ-0^\circ) = 43.398$ , [15]).

The vibrational frequencies of the *s-cis* form [17] are compared in Table 4 with the calculated values. The results for the *s-trans* form are also shown.

 $\text{CH}_3\text{COOCH}_3$ 

Previous studies [15, 18, 19] have shown that the methyl acetate molecule can exist in two stable conformations (Fig. 3), despite the fact that the detailed structure and properties of the *s-trans* conformer have not been experimentally determined. In our calculations, we have also obtained two energy minima, the *s-cis* conformer (Table 5) showing good general agreement with experimental structures [20, 21]. It is interesting to note that the

TABLE 4

Experimental and calculated vibrational frequencies ( $\text{cm}^{-1}$ ) for acetic acid

Observed IR (gas) [17]	Calculated (mol. mechanics)		Approximate description and symmetry species
	( <i>s-cis</i> )	( <i>s-trans</i> )	
3566	3556	3552	O—H stretch $A'$
3051	3046	3046	$\text{CH}_3$ anti. stretch $A'$
2996	3044	3045	$\text{CH}_3$ anti. stretch $A''$
2944	2929	2930	$\text{CH}_3$ sym. stretch $A'$
1779	1793	1784	C=O stretch $A'$
1439	1421	1424	$\text{CH}_3$ anti. deform. $A'$
1434	1422	1425	$\text{CH}_3$ anti. deform. $A''$
1380	1454	1492	$\text{CH}_3$ sym. deform. $A'$
1280	1330	1372	C—O stretch $A'$
1181	1200	1220	C—O—H deform. $A'$
1044	933	931	$\text{CH}_3$ rock. $A''$
987	903	909	$\text{CH}_3$ rock. $A'$
847	769	779	C—C stretch $A'$
639	618	558	C—O torsion $A''$
581	631	640	O=C—O deform. $A'$
535	397	267	C=O rock. $A''$
428	448	481	C—C=O deform. $A'$
(92) <sup>a</sup>	69	118	C—C torsion $A''$

<sup>a</sup> Calculated.

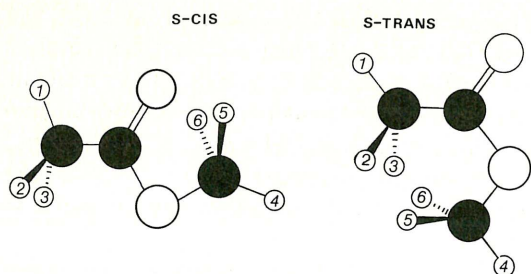
Fig. 3. Conformers of  $\text{CH}_3\text{COOCH}_3$ .

TABLE 5

Structural parameters for methyl acetate

Parameter	Experimental values [21, 22]	Calculated values	
		( <i>s-cis</i> )	( <i>s-trans</i> )
<b>Bond lengths (pm)</b>			
C—C	152.0	150.6	151.4
C—H	108.6		109.6
C=O	120.0		120.0
C—O	133.4	133.8	134.6
O—C	143.7	143.8	144.2
<b>Angles (degrees)</b>			
C—C—H <sub>1</sub>	108.2	109.9	109.1
C—C—H <sub>2,3</sub>	108.2	109.8	110.8
C—C=O	125.1	125.7	123.4
C—C—O	109.0	108.2	111.7
H <sub>1</sub> —C—H <sub>2,3</sub>	110.7	109.0	108.1
H <sub>2</sub> —C—H <sub>3</sub>	110.7	109.2	109.9
O=C—O	125.9	126.0	124.9
C—O—C	114.8	116.2	121.0
O—C—H <sub>4</sub>	108.2	108.8	107.9
O—C—H <sub>5,6</sub>	108.2	108.6	109.6
H <sub>4</sub> —C—H <sub>5,6</sub>	110.7	110.3	109.4
H <sub>5</sub> —C—H <sub>6</sub>	110.7	110.2	110.9
O=C—C—H <sub>1</sub>	0.0		0.0
O—C—O—C	0.0	0.0	180.0
C—O—C—H <sub>4</sub>	180.0		180.0
C—C(=O)—O	180.0		180.0
<b>Moments of inertia (<math>10^{-23}</math> (kg mol<sup>-1</sup>)m<sup>2</sup>)</b>			
<i>I<sub>a</sub></i>	49.3213	50.4469	53.2105
<i>I<sub>b</sub></i>	121.1852	120.2027	116.1533
<i>I<sub>c</sub></i>	164.2684	164.1777	162.8405
<b>Rotational constants (MHz)</b>			
<i>A</i>	10246.60	10018.27	9497.95
<i>B</i>	4170.28	4204.49	4351.07
<i>C</i>	3076.53	3078.32	3103.60

calculations predict the  $\text{C}_\alpha\text{—C—O}$  and  $\text{C—O—C}$  angles to be a few degrees larger in the less stable *s-trans* conformer than in the *s-cis* form (Table 5).

The calculated energy difference ( $\text{kJ mol}^{-1}$ ) between conformers (32.622) agrees with a previous value (32.643, [15]). In addition, the energy barrier is ca.  $63 \text{ kJ mol}^{-1}$  and occurs at a  $\text{O=C—O—C}$  dihedral angle of  $100^\circ$ . In the more stable *s-cis* conformer, the barriers of internal rotation around the  $\text{C}_\alpha\text{—C}$  (1.190) and  $\text{O—C}$  (5.089) bonds are also in excellent agreement with experimental values (1.254 and 5.055 [20], respectively).

The orientation of the methoxy methyl group corresponding to minimum energy has been calculated to occur at a  $\text{C—O—C—H}$  dihedral angle of  $60^\circ$ .

The vibrational frequencies of the *s-cis* form [17] are compared in Table 6 with calculated values and the results of the *s-trans* form are shown.

TABLE 6

Experimental and calculated vibrational frequencies ( $\text{cm}^{-1}$ ) for methyl acetate

Observed IR (gas) [17]	Calculated (mol. mechanics)		Approximate description and symmetry species		
	( <i>s-cis</i> )	( <i>s-trans</i> )			
3028	3047	3045	$\text{OCH}_3$	anti. stretch	$A'$
	3046	3043	$\text{CCH}_3$	anti. stretch	$A'$
3003	3047	3048	$\text{OCH}_3$	anti. stretch	$A''$
	3044	3044	$\text{CCH}_3$	anti. stretch	$A''$
2964	2925	2925	$\text{OCH}_3$	sym. stretch	$A'$
2950	2929	2930	$\text{CCH}_3$	sym. stretch	$A'$
1769	1766	1763	$\text{C=O}$	stretch	$A'$
1469	1436	1466	$\text{OCH}_3$	anti. deform.	$A'$
1462	1436	1449	$\text{OCH}_3$	anti. deform.	$A''$
1447	1422	1432	$\text{CCH}_3$	anti. deform.	$A''$
1440	1486	1416	$\text{OCH}_3$	sym. deform.	$A'$
1437	1422	1430	$\text{CCH}_3$	anti. deform.	$A'$
1372	1400	1474	$\text{CCH}_3$	sym. deform.	$A'$
1246	1325	1351	$\text{C—O}$	stretch	$A'$
1194	953	936	$\text{OCH}_3$	rock	$A'$
1160	922	922	$\text{OCH}_3$	rock	$A''$
1058	993	1054	$\text{O—CH}_3$	stretch	$A'$
(1053) <sup>a</sup>	941	942	$\text{CCH}_3$	rock	$A''$
976	888	914	$\text{CCH}_3$	rock	$A'$
840	771	698	$\text{C—C}$	stretch	$A'$
636	610	568	$\text{O=C—O}$	deform.	$A'$
603	603	519	$\text{C=O}$	rock	$A''$
438	410	501	$\text{C—C=O}$	deform.	$A'$
295	298	384	$\text{C—O—C}$	deform.	$A'$
(185) <sup>a</sup>	163	313	$\text{C—O}$	torsion	$A''$
(136) <sup>a</sup>	129	165	$\text{O—CH}_3$	torsion	$A''$
(73) <sup>a</sup>	68	87	$\text{C—C}$	torsion	$A''$

<sup>a</sup>Calculated.

## CONCLUSIONS

As was shown above, vibrational spectra [7-9, 17] indicate a single conformer for  $\text{CH}_3\text{COCl}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOCH}_3$  molecules. In the cases of the acid and the ester molecules, molecular mechanics suggest two conformers resulting essentially from rotation around the C-O bond, but the high energy *s-trans* forms do not have significant populations at room temperature.

A comparison of the calculated barriers of rotation around the  $\text{C}_\alpha\text{-C}$  bond reveals the influence of steric interactions in the case of  $\text{CH}_3\text{-COCl}$ .

The energy differences between *s-trans* and *s-cis* conformers in acetic acid and its methyl ester show an increase of approximately  $8 \text{ kJ mol}^{-1}$  in the latter molecule. In addition, the barrier in  $\text{CH}_3\text{C(=O)-OCH}_3$  is predicted to be greater than in  $\text{CH}_3\text{C(=O)-OH}$ , by approximately  $20 \text{ kJ mol}^{-1}$ . Also, the maximum of the barrier does not seem to occur at  $90^\circ$  in the ester molecule, as it should be predicted if only mesomeric effects were operating in the  $\text{O=C-O}$  group, but at  $100^\circ$ . These increases in the energy differences and in the angle of maximum potential energy may be ascribed to steric repulsions between the acetyl and methoxyl groups. This interpretation gets further support from the fact that the calculated  $\text{C}_\alpha\text{-C-O}$  and  $\text{C-O-C}$  angles are larger in the less stable conformer than in the more stable form (Table 5).

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