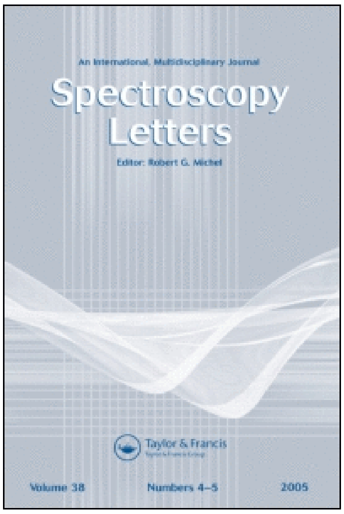

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Conformational Analysis of Some Monochloroalkanes

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CONFORMATIONAL ANALYSIS OF SOME MONOCHLOROALKANES

Keywords: Chloroalkanes, molecular mechanics calculations, conformational analysis

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ABSTRACT

Molecular mechanics calculations were made for 2-chloro-2,3-dimethylbutane, 2-chloro-2,4-dimethylpentane, and 2-chloro-2,5-dimethylhexane in order to compare the results with conclusions obtained from vibrational spectra concerning the conformational behavior of these compounds. The structures, relative energies, and heats of formation were also calculated.

INTRODUCTION

Vibrational spectra have been published for quite a few alkyl chlorides that show the presence of rotational isomers.[1-14] Molecular mechanics calculations have verified the existence of rotational isomerism in some of these compounds.[15-18] The present work was done in order to compare the results of molecular mechanics calculations with conclusions drawn from vibrational spectra for additional alkyl chlorides and to calculate structures and relative energies of the possible conformers. The compounds included in the present work are 2-chloro-2,3-dimethylbutane, 2-chloro-2,4-dimethylpentane, and 2-chloro-2,5-dimethylhexane.

CALCULATIONS

The molecular mechanics program was written by Allinger and Yuh and was converted by Petillo to run on a microcomputer (MICROSOFT FORTRAN v. 3.20).[19]

2-Chloro-2,3-dimethylbutane

This compound was shown to exist as a mixture of T_{HHH} and T_{CHH} conformers, with T_{HHH} being the only conformer present in the crystalline solid.[14] The present calculations show the T_{HHH} conformer to be the low-energy form by 455 cal (neglecting excess charges). The concentrations of T_{HHH} and T_{CHH} are therefore 68%

and 32%, respectively. This is, of course, for the vapor state, but since the dipole moment is essentially the same for the two conformers, the concentrations in the liquid state should be about the same as for the vapor. The liquid-state infrared spectrum shows the C-Cl stretching band of the T_{CHH} conformer (612 cm^{-1}) to be a little more intense than that of the T_{HHH} conformer (568 cm^{-1}), so the absorption coefficient must be larger for T_{HHH}. The 568 cm^{-1} Raman band is a little stronger than that at 612 cm^{-1}.[14] Partial results of the molecular mechanics calculations are given in Table 1.

2-Chloro-2,4-dimethylpentane

This compound was shown to exist in a T_{CHH} conformation and at least one of the two possible T_{HHH} conformations, but it could not be determined if one or both T_{HHH} conformers exist.[14] One of the T_{HHH} conformers was the only form present in the crystalline solid. Molecular mechanics calculations show that all three conformers should exist in the following amounts: T'_{HHH}, 59%; T_{HHH}, 36%; T_{CHH}, 5% (See ref. 14 for a ball and stick drawing of the three conformers). The greater stability of the T_{HHH} conformer seems reasonable because this conformer has a methyl group overlapping the chlorine in 1,3-parallel repulsion, whereas the other two conformers have methyl-methyl repulsion.

TABLE 1

Partial molecular mechanics results for 2-chloro-2,3-dimethylbutane

Property	Value
Bond length (avg., Å)	
C-Cl	1.806
C-C	1.542
C_2C-CC_2	1.554
Dihedral angle	
C-C-C-C	
T_{HHH} conformer	177,-57,57,-177°
T_{CHH} conformer	177, 53,54,-70°
C-C-C-Cl	
T_{HHH}	63,-63°
T_{CHH}	170,-65°
Relative energy (Kcal/mole)	
T_{HHH}	0
T_{CHH}	0.46
ΔH_f (Kcal/mole)	-52.74

One difference in the spectra of the butane and pentane is that the C-Cl stretching band of T_{CHH} (629 cm^{-1}) is considerably less intense than that of the T_{HHH} conformer (573 cm^{-1}) of the pentane. Even so, the 629 cm^{-1} band is more intense than might be expected for

TABLE 2

Partial molecular mechanics results for 2-chloro-2,5-dimethylpentane

Property	Value
Bond length (avg., Å)	
C-Cl	1.806
C-C	1.542
Dihedral angle	
C-C-C-Cl	
T_{HHH}	77°
T'_{HHH}	66°
T_{CHH}	163°
C-C-C-C	
T_{HHH}	-165,174,-64,-44°
T'_{HHH}	-177,-143,95,-55°
T_{CHH}	-175,-81,45,63°
Relative energy (Kcal/mole)	
T_{HHH}	0
T'_{HHH}	0.28
T_{CHH}	1.42
ΔH_f (Kcal/mole)	-57.85

only a 5% concentration, but this can be explained by a larger absorption coefficient of T_{CHH}, as was the case for the butane. Some additional results of the calculations are given in Table 2.

2-Chloro-2,5-dimethylhexane

A molecule of 2-chloro-2,5-dimethylhexane can exist in a large number of conformations, but only nine do not involve 1,3-parallel repulsion. These nine will be at least 2 kcal/mole more stable than the others, so those others can be neglected because their concentrations will be very low. Included in the nine conformers considered here are four mirror image pairs, so there are five spectroscopically distinguishable conformers to be considered. The previous work considered only the three conformers with carbons 2 through 6 coplanar.[14] Ball and stick drawings of these three conformers are shown in ref. 14. The two conformers omitted in that work have both methyl groups that are bonded to carbon 5 out of the skeletal plane. Conformer IV is formed from conformer I (T'_{HHH}) or II by internal rotation about C4-C5 by 120^{o} so that both methyls are out of the plane. Conformer V is formed from III (T_{CHH}) by rotation about C4-C5 by 120^{o}. Conformer V has C_s symmetry, whereas the other four have C_1 symmetry. Molecular mechanics calculations were made for all five conformers,

TABLE 3

Partial molecular mechanics results
for 2-chloro-2,5-dimethylhexane

Property	Value
Bond length (avg., Å)	
C-Cl	1.804
C-C	1.541
Dihedral angle	
C-C-C-Cl	
Conformer I	-66°
Conformer II	-64°
Conformer III	179°
Conformer IV	-65°
Conformer V	180°
C-C-C-C	
Conformer I	176,172,-174,64,55°
Conformer II	179,-178,173,-64,58°
Conformer III	-174,175,61,-64,64°
Conformer IV	177,177,62,-64,56°
Conformer V	62,180,63,-63,-62°
Relative energy (Kcal/mole)	
Conformer I	0
Conformer II	0.15
Conformer III	0.67
Conformer IV	0.81
Conformer V	1.42
ΔH_f (Kcal/mole)	-64.68

resulting in the following concentrations: I, 42%; II, 32%; III, 13%; IV, 11%; V, 2%.

In the previous work, it was concluded that one of the two T_{HHH} conformers was the only one present in the crystalline solid. Although normal coordinate calculations were not made for conformer IV, which is also T_{HHH}, it is improbable that this is the one present in the solid. The C-Cl stretch band would undoubtedly overlap that of conformers I and II, but some of the skeletal bending frequencies should be different. Indeed, a weak band observed at 534 cm^{-1} left unassigned in ref. 14 could be due to conformer IV. Partial results of the MM2 calculations are given in Table 3. Complete results for all three compounds are available from the author.

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