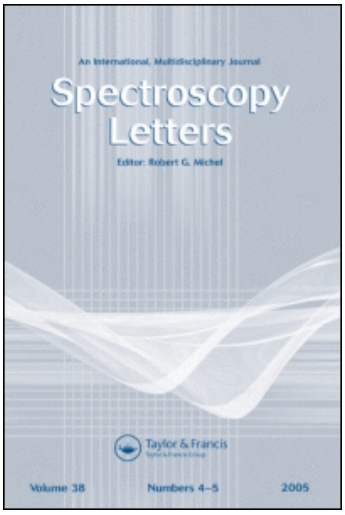

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Conformational Analysis of Some Dichloroalkanes

G. A. Crowder[a]
[a] Killgore Research Center West Texas State, University Canyon, Texas

To cite this Article Crowder, G. A.(1989) 'Conformational Analysis of Some Dichloroalkanes', Spectroscopy Letters, 22: 9, 1151 — 1160
To link to this Article: DOI: 10.1080/00387018908054012
URL: http://dx.doi.org/10.1080/00387018908054012

SPECTROSCOPY LETTERS, 22(9), 1151-1160 (1989)

CONFORMATIONAL ANALYSIS OF SOME DICHLOROALKANES

Keywords: Dichloroalkanes, Conformational analysis
Molecular mechanics calculations

G. A. Crowder
Killgore Research Center
West Texas State University
Canyon, Texas 79016

ABSTRACT

Molecular mechanics calculations were made for 1,1-dichlorobutane, 2,2-dichlorobutane, and 1,2-dichloro-2-methylpropane in order to compare the results with conclusions obtained from vibrational spectra concerning the conformational behavior of these compounds. Calculations were also made for 1,2-dichloro-2-methylbutane, although vibrational spectra are not available for this compound. The structures and relative energies of the most abundant conformers are given.

INTRODUCTION

Molecular mechanics calculations have recently been made for several monochloroalkanes that had been shown by vibrational spectroscopy to exhibit rotational isomerism.[1-3] Vibrational spectra have also been published for several dichloroalkanes that show the presence of rotational isomers.[4-10] Molecular mechanics calculations have new been made for several of those compounds in order to learn more about their conformational behavior. Included in this group of compounds are 1,1-dichlorobutane, 2,2-dichlorobutane, 1,2-dichloro-2-methyl propane, and 1,2-dichloro-2-methylbutane.

CALCULATIONS

Molecular mechanics calculations were made with the MM2 program written by Allinger and Yuh and converted by Petillo to run of a microcomputer (MICROSOFT FORTRAN v. 3.20).[11]

RESULTS

1,1-Dichlorobutane

It has been shown that 1,1-dichlorobutane exists in three spectroscopically distinguishable stable conformations, and it was concluded that the C_s conformer (See ref. 7 for drawings of the three conformers.) was the only conformer present in the crystalline solid.[7] MM2

TABLE 1

Molecular mechanics results for 1,1-dichlorobutane

Property	Value
Bond lengths (avg., Å)	
C-Cl	1.788
C-C	1.537
Angles (avg., °)	
C1-C2-C3	114.7
C2-C3-C4	112.3
C-C-Cl	111.5
Cl-C-Cl	111.0
Dihedral angles (°)	
C-C-C-Cl	
Conformer A	63, -63
Conformer B	171, -65
Conformer C	-175, 61
C-C-C-C	
Conformer A	-179
Conformer B	-177
Conformer C	62

calculations show the C_s conformer (conformer A) to be 150 cal/mole higher in energy than the most stable form, which is the one with one chlorine and all four carbons coplanar. Conformer C is 780 cal/mole higher in energy than conformer B, so the concentrations of the three conformers should be ca. 24% for conformer A, 60% for conformer B, and 16% for conformer C. Conformers B and C have mirror image forms, whereas conformer A has no equivalent form. Partial results of the MM2 calculations are given in Table 1.

2,2-Dichlorobutane

This compound was shown to exist in both possible spectroscopically distinguishable stable conformations, with the C_s conformer being the only one present in the crystalline solid.[6] Molecular mechanics calculations show the C_s conformer to be the low-energy form by ca. 620 cal/mole, which translates into a 59% concentration. The C_s conformer was also shown to be the low-energy form of 1,1-dichloropropane.[12] Other results of the calculations are given in Table 2.

1,2-Dichloro-2-methylpropane

Vibrational spectra have been published for this compound, and they were interpreted with the aid of normal coordinate calculations.[9] It was shown that two

TABLE 2

Molecular mechanics results for 2,2-dichlorobutane

Property	Value
Bond lengths (avg., Å)	
C-Cl	1.798
C-CCl_2	1.542
C-C	1.537
Angles (avg., °)	
C1-C2-C3	111.2
C2-C3-C4	115.8
C-C-Cl	108.8
Cl-C-Cl	109.8
Dihedral angles (°)	
C-C-C-Cl	
C_s conformer	61, -61
C_1 conformer	177, -64
C-C-C-C	
C_s conformer	180
C_1 conformer	58

TABLE 3

Molecular mechanics results for 1,2-dichloro-2-methylpropane

Property	Value
Bond lengths (avg., Å)	
C-Cl (1^{o})	1.789
C-Cl (2^{o})	1.542
C-C	1.537
Angles (avg., ^{o})	
C-C-C	110.7
C2-C1-Cl	114.1
C-C2-Cl	108.2
Dihedral angles (^{o})	
C3-C2-C1-Cl	
$P_X T_{XHH}$	62
$P_C T_{HHH}$	179
C4-C2-C1-Cl	
$P_X T_{XHH}$	-62
$P_C T_{HHH}$	60
Cl-C-C-Cl	
$P_X T_{XHH}$	180
$P_C T_{HHH}$	-61

conformers exist (P_CT_{HHH} and P_XT_{XHH}) in the liquid, but only the P_XT_{XHH} conformer is present in the crystalline solid. Molecular mechanics calculations show the P_XT_{XHH} conformer to be more stable than P_CT_{HHH} by ca. 1470 cal/mole, so the concentrations should be ca. 86% P_XT_{XHH} and 14% P_CT_{HHH} in the vapor at 298K. The P_CT_{HHH} conformer has a much larger dipole moment than does P_XT_{XHH}, so the concentration of P_CT_{HHH} will be larger in the liquid than in the vapor, as indicated by the relative intensities of some of the IR and Raman bands. Partial results of the calculations are given in Table 3.

1,2-Dichloro-2-methylbutane

Vibrational spectra are not available for this compound, but molecular mechanics calculations were done anyway to check the conformational behavior of this compound.

1,2-Dichloro-2-methylbutane can exist in nine spectroscopically distinguishable conformations, but two of those involve 1,3-parallel repulsion (methyl-chlorine overlap) and can be neglected. Two of the remaining seven conformers have the chlorines trans to each other, and in the other five, the chlorines are gauche. The five gauche conformers range from 1750 to 2100 cal/mole higher in energy than the most stable form, which is only ca. 280 cal/mole more stable than the other trans confor-

TABLE 4

Molecular mechanics results for

1,2-dichloro-2-methylbutane

Property	Value	
	Conformer I	Conformer II
Bond lengths (Å)		
C1-C2	1.547	1.551
C2-C3, C2-C5	1.545	1.544
C3-C4	1.536	1.536
C1-Cl	1.789	1.789
C2-Cl	1.808	1.808
Angles (°)		
C-C-C	110-116	111-116
C-C-Cl (2°, avg.)	108	108
C-C-Cl (1°)	114	114
Dihedral angles (°)		
C-C-C-C	-53,-178	178,55
C-C-C-Cl	-59,66,65	-64,-64,61
Cl-C-C-Cl	-179	178

mer. The low-energy conformer (labelled conformer I) has three carbons coplanar, with the two chlorines trans to each other and the two methyls trans to each other. The other trans conformer (labelled conformer II) has all four chain carbons coplanar. The concentrations of conformers I and II would be ca. 55% I and 34% II. The other five conformers range from 1.1 to 2.8% in abundance, with a total concentration of only ca. 11% in the vapor state. Therefore, structures are given in Table 4 only for conformers I and II. Of course, the dipole moments of the gauche conformers are larger than for the trans conformers, so those five conformers will amount to more than 11% in the liquid state.

ACKNOWLEDGEMENTS

The author is grateful to The Robert A. Welch Foundation, Houston, Texas, and to the Killgore Research Center, for financial support of this work.

REFERENCES

1. G. A. Crowder, Spectrosc. Lett. 21, 349 (1988).
2. G. A. Crowder, Spectrosc. Lett. in press.
3. S. H. Schei and R. L. Hilderbrandt, J. Mol. Struct. 128, 181 (1985).
4. G. Crowder, M. Townsend and M. Jalilian, J. Mol. Struct. 32, 403 (1976).

5. G. A. Crowder and C. Smith, J. Mol. Struct. 51, 157 (1979).

6. G. A. Crowder and W. Lin, J. Mol. Struct. 62, 1 (1980).

7. G. A. Crowder, J. Mol. Struct. 70, 193 (1981).

8. G. A. Crowder and J. K. Potter, J. Mol. Struct. 75, 161 (1981).

9. G. A. Crowder and M. T. Richardson, J. Mol. Struct. 78, 229 (1982).

10. D. L. Powell, P. Klaeboe, K. Saebo and G. A. Crowder, J. Mol. Struct. 98, 55 (1983).

11. Quantum Chemistry Program Exchange, Indiana University, Program No. QCMP010.

12. T. Rydland and R. Stølevik, J. Mol. Struct. Theochem 105, 157 (1983).

Date Received: 06/12/89
Date Accepted: 07/11/89