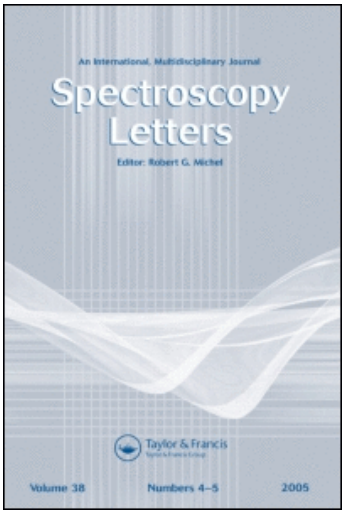

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Conformational Analysis of Some Chloro and Bromoalkanes

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CONFORMATIONAL ANALYSIS OF SOME CHLORO AND BROMOALKANES

Keywords: Bromoalkanes, chloroalkanes, molecular mechanics calculations, conformational analysis

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Rotational isomerism has been shown by vibrational spectroscopy to exist in 1-chloro-3-methylbutane,[1] 1-bromo-3-methylbutane,[2] 2-chloro-4-methylpentane,[3,4] 2-bromo-4-methylpentane,[4] 1,3-dichlorobutane,[5] and 1,3-dibromobutane.[5] In some cases, definite conclusions were drawn concerning the number and identification of the conformers present. In other cases, it was not possible to determine with certainty which conformers exist. Molecular mechanics calculations have now been made for these six compounds in order to obtain addi-

tional information about their conformational behavior, including energies and structures of the possible conformers. The calculations were done with the MM2 program written by Allinger and Yuh and converted by Petillo to run on a microcomputer.[6]

1-Chloro-3-methylbutane and 1-bromo-3-methylbutane were each shown to exist as two conformers, P_C and P_H.[1,2] The P_H conformer of 1-bromo-3-methyl butane was the only form present in the crystalline solid, but the chloro compound could not be crystallized. The MM2 calculations show the two conformers to differ in energy by only a small amount, and both should therefore be present in high concentration. It was assumed in the previous work that the C_s conformer (also P_C) would be high enough in energy to be present in only a small amount. However, MM2 calculations show that the concentration of this conformer should be 8-9% in each compound. The relative energies, C-C-C-X dihedral angles, and C-X bond lengths are given in Table 1.

2-Chloro-4-methylpentane and 2-bromo-4-methylpentane were each shown to exist as S_{HH} and S_{CH} conformers.[4,5] All other possible conformers would have 1,3-parallel repulsion (methyl-methyl or methyl-halogen) and would be at least 2.5 kcal/mole higher in energy than the other forms. The MM2 calculations show the S_{HH} conformer to be the most stable form of both compounds, and each compound[4] crystallizes in this form.

TABLE 1
Molecular Mechanics Results for Chloro and Bromoalkanes*

Compound	C-C-X dihedral angle	Relative energy (kcal/mole)	C-X bond length (Å)
X C C-C-C-C			
P_C conformer	175.9° (176.4)	0 (0)	1.788 (1.952)
P_H conformer	62.9° (64.5)	0.25 (0.26)	1.786 (1.950)
C_s conformer (P_C)	179.9° (180.0)	0.70 (0.69)	1.788 (1.952)
X C C-C-C-C			
S_{CH} conformer	178.4° (178.1)	0.45 (0.41)	1.797 (1.966)
S_{HH} conformer	61.6° (63.1)	0 (0)	1.794 (1.962)
X X C-C-C-C			
Conformer I (P_CS_{HH})	176.6°, 63.9° (176.7, 65.5)	0 (0)	1.788,1.794 (1.952,1.963)
Conformer II (P_HS_{HH})	64.7°, 63.2° (65.8, 64.2)	0.03 (0.12)	1.787,1.794 (1.951,1.963)
Conformer III (P_HS_{CH})	61.3°,178.0° (63.4,178.1)	0.81 (0.78)	1.786,1.797 (1.950,1.967)
Conformer IV (P_CS_{CH})	176.3°,177.6° (176.6,174.4)	0.98 (0.84)	1.788,1.797 (1.952,1.966)
Conformer V ($P_CS_{HH'}$)	179.6°, 64.5° (179.9, 66.5)	0.74 (0.69)	1.788,1.793 (1.953,1.962)

*Values for X = Br are in parentheses.

Some of the results of the calculations are given in Table 1.

In the previous work, five C-Br stretch bands were observed for 1,3-dibromobutane, but only three C-Cl stretch bands were observed for 1,3-dichlorobutane.[5] Normal coordinate calculations were made for several conformers of each compound, and it was concluded that 1,3-dibromobutane exists as four conformers, but that 1,3-dichlorobutane exists as only two conformers (P_HS_{HH} and P_CS_{HH}).

A molecule of 1,3-dihalobutane can exist in nine spectroscopically distinguishable conformations, but four of these involve 1,3-parallel repulsion. Molecular mechanics calculations were made for the other five conformations of each compound, and partial results are given in Table 1. The two conformations previously concluded to be the only ones present for 1,3-dichlorobutane[5] are indeed considerably lower in energy than the other three. The energy differences represent the following concentrations: P_CS_{HH} = 37% (38); P_HS_{HH} = 35% (31); P_CS_{HH}' = 11% (12); P_HS_{CH} = 10% (10); P_CS_{CH} = 7% (9). The two bands assigned to conformers III and IV for dibromobutane were both weak, compared to medium to very strong bands for conformers I and II.[5] No band was assigned solely to conformer V.

Complete results of the calculations for all the compounds are available from the author.

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