

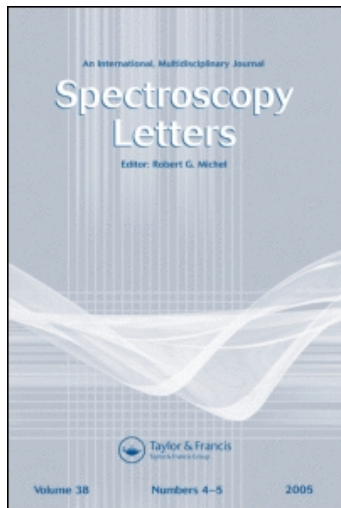
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CONFORMATIONAL ANALYSIS OF 1,2-DICHLOROBUTANE

Keywords: 1,2-Dichlorobutane, Conformational analysis,
Normal coordinate calculations, Molecular
mechanics calculations

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Vibrational spectra have been published and normal coordinate calculations have been made for 1,2-dichlorobutane.^{1,2} Those calculations were limited to the three conformers that had all four carbon atoms coplanar. Molecular mechanics calculations have now shown a conformer that was omitted to be the second most abundant conformer. Therefore, normal coordinate calculations have been made for this conformer and

molecular mechanics calculations have been made for all possible conformers.

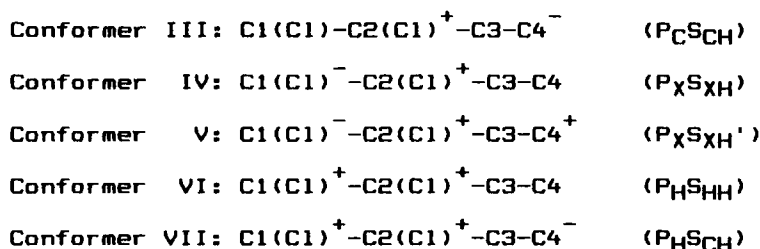
Normal coordinate calculations were made with a Prime 9955 computer. The programs written by Schachtschneider^{3,4} were used for calculation of the G matrix (GMAT) and for solution of the vibrational secular equation (VSEC). Molecular mechanics calculations were done with the MM2 program written by Allinger and Yuh and modified by Petillo⁵ to run on a microcomputer (MICROSOFT FORTRAN v3.20).

1,2-Dichlorobutane can exist in nine possible conformations that result from internal rotations about the C1-C2 and C2-C3 bonds so that the primary chlorine and methyl can be in or out of the C1-C2-C3 plane. However, two of those conformations involve 1,3-parallel repulsion (methyl-chlorine overlap) and would be present only in very small amounts. The other seven conformers can be distinguished by writing the skeletal formula in the following ways, where a + indicates a chlorine or methyl on one side of the C1-C2-C3 plane, and a - indicates a chlorine or methyl on the other side of that plane:

Conformer I: C1(C1)-C2(C1)⁺-C3-C4 (PCSHH)*

Conformer II: C1(C1)-C2(C1)⁺-C3-C4⁺ (PCSHH')

*See ref. 6 for a description of conformer notation.



The previous normal coordinate calculations were done only for conformers I, IV, and VI.² MM2 calculations showed conformer V to be lower in energy than all others except IV, which was shown to be the conformer present in the crystalline solid.¹ Relative energies of the seven conformers and their concentrations are given

TABLE 1
Partial MM2 results for 1,2-dichlorobutane

Conformer	Relative energy (kcal/mole)	Abundance (%)	dipole moment
I	1.36	5.9	3.05
II	1.99	2.1	3.02
III	2.05	1.8	3.09
IV	0.00	59.4	0.30
V	0.56	23.0	0.19
VI	1.41	5.5	3.04
VII	1.93	2.3	3.00

TABLE 2
Observed and calculated wavenumbers for
1,2-dichlorobutane conformer V

obs. cm ⁻¹	calc. cm ⁻¹	obs. cm ⁻¹	calc. cm ⁻¹
1465	1462	--	980
1454	1457	943	950
1436	1445	855	860
1436	1434	814	814
1377	1377	732	721
1356	1360	659	679
--	1331	552	534
1295	1295	388	385
1295	1288	298	290
1230	1228	-	254
1188	1189	-	219
--	1134	172	179
1076	1080	-	144
1038	1039	-	84

TABLE 3
Molecular mechanics results for
1,2-dichlorobutane conformers IV and V

Property	Calculated value
<u>Bond length, avg. (Å)</u>	
C-Cl (1°)	1.788
C-Cl (2°)	1.797
C-C	1.539
<u>Bond angles (°)</u>	
C-C-C	
Conf. IV	113.4
Conf. V	115.3
C-C-Cl	
Conf. IV	108-112
Conf. V	109-112
<u>Dihedral angles (°)</u>	
Cl-C1-C2-C3	
Conf. IV	-66
Conf. V	-61
Cl-C2-C3-C4	
Conf. IV	-64
Conf. V	68
Cl-C1-C2-Cl	
Conf. IV	172
Conf. V	175
C-C-C-C	
Conf. IV	174
Conf. V	-56

in Table 1. Conformers IV and V comprise 82% of the total, so it was concluded that a vibrational assignment was needed for conformer V. The other three conformers that had been excluded from the previous normal coordinate calculations are in such small amounts that additional normal coordinate calculations were made only for V. The calculated wavenumbers and the observed values to which they were assigned are given in Table 2. The force constants obtained previously² were used unchanged for this calculation. There is, of course, some speculation about some of the band assignments.

Additional MM2 results are given in Table 3 only for conformers IV and V. Complete results of the calculations are available from the author.

The MM2 results reported here are for the vapor state at 298K. It can be seen that the dipole moment is around 0.2D for conformers IV and V, but it is around 3.0 for the other five conformers. The net dipole moment for the equilibrium mixture in the vapor state would be 1.03 D. The concentrations of the five less stable conformers will be larger in the liquid state than in the vapor, and the dipole moment of the compound in the liquid will therefore be larger than 1.03D.

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