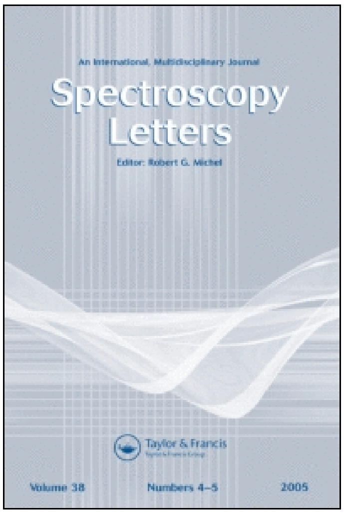

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CONFORMATIONAL ANALYSIS OF meso-1,2,4,5-TETRABROMOPENTANE

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Vibrational spectra have been obtained for quite a few monobromo[1-15] and dibromoalkanes[16-32], most of which were shown to exhibit rotational isomerism. However, very few tribromo[23,33,34] and tetrabromoalkanes[28,35,36] have been studied. Therefore, IR spectra have been obtained for 1,2,4,5-tetrabromopentane (TBP), and molecular mechanics calculations have been made for the six spectroscopically distinguishable conformers of this molecule that have all five carbons coplanar, in order to learn something about the molecule's conformational behavior. The calculations were made with the MM2 program written by Allinger and Yuh and converted by Petillo to run on a microcomputer.[37] The six conformers of TBP can be represented by the following skeletal formulas, where a + indicates a bromine on one side of the plane of carbons and a - indicates a bromine on the other side of that plane:

Conformer I: Br^{+}-C1-C2(Br)$^{-}$-C3-C4(Br)$^{+}$-C5-Br^{-}
Conformer II: Br^{-}-C1-C2(Br)$^{-}$-C3-C4(Br)$^{+}$-C5-Br^{-}
Conformer III: Br -C1-C2(Br)$^{-}$-C3-C4(Br)$^{+}$-C5-Br^{-}
Conformer IV: Br^{-}-C1-C2(Br)$^{-}$-C3-C4(Br)$^{+}$-C5-Br^{+}
Conformer V: Br^{-}-C1-C2(Br)$^{-}$-C3-C4(Br)$^{+}$-C5-Br
Conformer VI: Br -C1-C2(Br)$^{-}$-C3-C4(Br)$^{+}$-C5-Br

Conformers I, IV, and VI have C_2 symmetry, whereas the other three conformers have no symmetry (C_1).

This compound is a solid at room temperature, and the IR spectrum shows the solid to be crystalline. Therefore, only one conformer is expected to be present in the solid. The solid-state spectrum shows only three bands in the C-Br stretch region, at 558, 580, and 640 cm^{-1}. IR spectra of solutions of TBP in CS_2, CCl_4, and CH_3CN show the appearance of several bands that were absent for the solid. In the region 400-700 cm^{-1}, additional bands were observed at 496, 544, 632, and 669

cm^{-1}, all of which lie in normal C-Br stretching regions. For 1,2-dibromobutane, C-Br stretching bands were observed at 645 and 563 cm^{-1} for the P_XS_{XH} conformer, 663 and 537 cm^{-1} for the P_CS_{HH} conformer, and at 587 and 509 cm^{-1} for the P_HS_{HH} conformer.[38] Applying this nomenclature to conformers I-VI of TBP gives the following: conformer I = $(P_XS_{XH})_2$; conformer II = $P_HS_{HH}P_XS_{XH}$; conformer III = $P_CS_{HH}P_XS_{XH}$; conformer IV = $(P_HS_{HH})_2$; conformer V = $P_HS_{HH}P_CS_{HH}$; conformer VI = $(P_CS_{HH})_2$. The solid-state C-Br stretching frequencies fit the expected values for conformer I.

Molecular mechanics calculations were made for conformers I-VI in order to check their relative stabilities and structures. Table 1 gives the relative energies of the six conformers in the vapor state.

Since conformer I is the low-energy form, it is not surprising that it is the form present in the crystalline solid, although the low-energy form is not always the one present in the crystals. It should be pointed out that the concentrations given in Table 1 do not apply to the solutions, because the more polar conformers are stabilized more in solution than are the less polar conformers, relative to the vapor state. Even though the relative amount of conformer VI present in the vapor may be very low, it could be much higher in the liquid.

Since conformer I seems to be the one present in the solid and it is the low-energy form, partial results of

TABLE 1

MM2 results for $CH_2BrCHBrCH_2CHBrCH_2Br$

Conformer	Relative energy (kJ/mole)	Concentration (%)	Dipole moment (D)
I	0	67.4	0.38
II	5.31	15.8	2.78
III	5.90	12.5	2.78
IV	9.16	1.7	0.88
V	10.4	2.0	2.28
VI	11.8	0.5	3.55

(note: There are two spectroscopically equivalent forms of conformers II, III, and V, excluding mirror image forms. Therefore, the concentration of V is greater than that of IV, even though V is higher in energy than IV.)

calculated geometries are given only for this conformer in Table 2. Complete results of the MM2 calculations are available from the author.

The six conformers included in the MM2 calculations can be interchanged by internal rotation about the C1-C2 and C4-C5 bonds. The only difference among the conformers is in the position of the bromines bonded to carbons 1 and 5. There are several conformers in which the carbons are not all coplanar that could be relatively stable, but these all have the same skeletal structure.

TABLE 2

Molecular mechanics geometry for conformer I

Property	Value
Bond lengths (Å)	
C1-C2	1.542
C2-C3	1.545
C3-C4	1.545
C-Br (1°)	1.954
C-Br (2°)	1.968
Angles (°)	
C1-C2-C3	113.2
C2-C3-C4	116.9
C2-C1-Br (C4-C5-Br)	112.6
C1-C2-Br (C5-C4-Br)	108.4
C3-C2-Br (C3-C4-Br)	110.1
Dihedral angles (°)	
C1-C2-C3-C4	173.7
C2-C3-C4-C5	174.0
C3-C2-C1-Br (C3-C4-C5-Br)	-68.5
C2-C3-C4-Br (C4-C3-C2-Br)	-64.6
Br-C1-C2-Br (Br-C4-C5-Br)	169.0

They are formed from the other conformers by internal rotation by 120° about C2-C3 and C3-C4 so that carbons 1 and 5 are on opposite sides of the C2-C3-C4 plane. As with conformers I-VI, these conformers differ only in the position of the two end bromines and are interconverted by rotation about C1-C2 and C4-C5. The most stable of these should be the one analogous to conformer I, with the bromines on adjacent carbons being trans to each other. MM2 calculations show this conformer to be 19.9 kJ higher in energy than conformer I, so all these conformers can be neglected.

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