Conformational stability from variable temperature infrared spectra of krypton solutions, ab initio calculations, and vibrational assignment of bromocyclopentane

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Abstract: The infrared spectra from 3500 to 80 cm(-1) of krypton solutions of bromocyclopentane, c-C5H9Br, at variable temperatures (-105- -150degreesC) have been recorded and only the axial and equatorial conformers are present which supports the ab initio calculations that the twisted form is a transition state. From the temperature dependence of five conformer pairs an enthalpy difference of 233 +/- 23 cm(-1) (2.79 +/- 0.28 kJ/mol) has been obtained with the axial conformer the more stable form. From these data, it is estimated that 75 +/- 2% of the axial form is present at ambient temperature. The Raman spectra (3500-40 cm(-1)) of liquid and solid c-C5H9Br and c-C5D9Br have been recorded as well as the infrared spectrum of the normal species in the gaseous and solid states. A complete vibrational assignment is provided for the axial conformer and several of the low frequency fundamentals for the equatorial conformer have been assigned. The conformational stabilities, harmonic force constants, fundamental frequencies, infrared intensities, Raman activities, and depolarization values have been obtained from MP2/6-31G(d) calculations. These quantities have been compared to the experimental values when appropriate. The optimized geometries and conformational stabilities have also been obtained from ab initio MP2/6411 + G(d,p) calculations and from density functional theory calculations by the B3YLP method with several different basis sets. The barriers to the twisted conformer is predicted to be too large for pseudorotation. However, the predicted low frequencies for the ring twisting modes indicate many excited states are populated at ambient temperature which could explain the better fit of the radial distribution curve by a pseudorotational model in the electron diffraction study. The adjusted-r(0) structural parameters have been obtained for both conformers by combining the ab initio data with. the previously reported microwave rotational constants and the values are compared to those reported from the electron diffraction study. Many of these results are compared to the corresponding quantities of some similar molecules.