Conformational Stability From Variable-Temperature Infrared Spectra Of Krypton Solutions, Ab Initio Calculations, And R(O) Structural Parameters Of Chlorocyclopentane

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Summary

The infrared spectra (3500-400 cm(-1)) of krypton solutions of chlorocyclopentane, c-C5H9Cl, at variable temperatures (-101 to -150degreesC) have been recorded and the fundamental vibrations of the axial conformer and several of those for the equatorial form have been assigned. Utilizing two pairs of fundamentals for the two conformers in the krypton solution, an enthalpy difference of 145 +/- 15 cm(-1) (1.73 +/- 0.18 kJ-mol(-1)) has been obtained with the axial conformer the more stable form. It is estimated that there is 67 +/- 2% of the axial conformer present at ambient temperature. Convincing spectroscopic evidence shows that a significant percentage of the chlorocyclopentane molecules are undergoing pseudorotation at ambient temperature. The conformational stabilities, harmonic force constants, fundamental frequencies, infrared intensities, and Raman activities have been obtained from MP2/6-31G(d) calculations with full electron correlation and 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 calculations as well as by density functional theory (DFT) by the B3LYP method with several different basis sets. 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. These new values of the structural parameters for both conformers are compared to those previously reported from electron diffraction and microwave studies. These results are compared to the corresponding quantities of some similar molecules.

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