Conformational Stability from Variable-Temperature Infrared Spectra of Krypton Solutions, Ab Initio Calculations, and ro Structural Parameters of Chlorocyclopentane.

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Abstract

The IR spectra (3500-400 cm-1) of krypton solns. of chlorocyclopentane, c-C5H9Cl, at variable temps. (-101 to -150 °C) 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 soln., 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 estd. that there is 67±2% of the axial conformer present at ambient temp. Convincing spectroscopic evidence shows that a significant percentage of the chlorocyclopentane mols. are undergoing pseudorotation at ambient temp. The conformational stabilities, harmonic force consts., fundamental frequencies, IR intensities, and Raman activities have been obtained from MP2/6-31G(d) calcns. with full electron correlation and these quantities have been compared to the exptl. values when appropriate. The optimized geometries and conformational stabilities have also been obtained from ab initio MP2 calcns. as well as by d. functional theory (DFT) by the B3LYP method with several different basis sets. The adjusted r0 structural parameters have been obtained for both conformers by combining the ab initio data with the previously reported microwave rotational consts. 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 mols.