STRUCTURAL, CONFORMATIONAL AND VIBRATIONAL STUDIES OF ISOCYANOCYCLOPENTANE FROM INFRARED, RAMAN SPECTRA AND AB INITIO CALCULATIONS

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The infrared and Raman spectra (3200 to 50 cm^{-1}) of the gas, liquid or solution, and solid have been recorded of isocyanocyclopentane, $_c$-C_5H_9NC. FT-microwave studies have also been carried out and 23 transitions were recorded for the envelope-axial (Ax) conformer. Variable temperature (-55 to -100°C) studies of the infrared spectra (3200 to 400 cm^{-1}) dissolved in liquid xenon have been carried out. From these data, both the Ax and envelope-equatorial (Eq) conformers have been identified and their relative stabilities obtained. The enthalpy difference has been determined to be 102 $\pm 10 cm^{-1}$ (1.21 $\pm 0.03 kJmol^{-1}$) with the Ax conformer the more stable form. The percentage of the Eq conformer is estimated to be 38 $\pm$ 1% at ambient temperature. The conformational stabilities have been predicted from ab initio calculations by utilizing several different basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been made for the observed bands for both conformers with initial predictions by MP2(full)/6-31G(d) ab initio calculations to obtain harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for both conformers. The heavy atom distances ($\AA$): C≡N = 1.176 ; C-N≡C= 1.432; C-C_β,$C_\beta{}'$ = 1.534; C_β-C_γ, $C_\gamma{}'$ = 1.542; C_γ-$C_\gamma{}'$ = 1.554 and angles (°):∠C-N= 177.8; ∠C_βC-N= 110.4; ∠C_βC$C_\beta{}'$= 102.9; ∠C$C_\beta C_\gamma$ = 103.6; ∠$C_\beta C_\gamma C_\gamma{}'$ = 105.9. The results are discussed and compared to the corresponding properties of some related molecules.