CONFORMATIONAL STABILITY FROM TEMPERATURE DEPENDENT FT-IR SPECTRA OF LIQUID RARE GAS SOLUTIONS AND AB INITIO CALCULATIONS FOR 1-PENTYNE

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Variable temperature studies of the infrared spectra (3500 to 400 cm^{-1}) of 1-pentyne, $CH_3CH_2CH_2CCH$, dissolved in liquid xenon (-55 to -100°C) and liquid krypton (-105 to -150°C) have been recorded. These data indicate that both the anti (methyl group trans to the acetylenic group) and gauche conformers are present in the fluid states. Utilizing seven sets of conformer pairs for the xenon solution and ten sets of conformer pairs for the krypton solution, the enthalpy has been determined to be 50 ± 6 cm^{-1} (0.60 ± 0.07 kJ/mol) and 45 ± 4 cm^{-1} (0.54 ± 0.05 kJ/mol), respectively, with the anti conformer the more stable form. Optimized geometries and conformational stabilities were obtained from ab initio MP2/6-31G(d), MP2/6-311+G(d,p), MP2/6-311+G(2d,2p) and MP2/6-311+G(2df,2pd) calculations with all of the calculations predicting the gauche rotamer to be the more stable form. The r_o adjusted structural parameters have been obtained from a combination of the microwave rotational constants and ab initio predicted parameters.