CONFORMATIONAL ISOMERIZATION OF *bis*-(4-HYDROXYPHENYL)METHANE IN A SUPERSONIC JET EXPANSION, PART I: LOW BARRIER POTENTIAL ENERGY SURFACE IN THE S_0 STATE.

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The bichromophore *bis*-(4-hydroxyphenyl)methane, has been studied using single, double and triple resonance laser based spectroscopic methods in a supersonic jet expansion. This molecule consists of two identical chromophores (phenol moieties) linked through a methylene group with torsional flexibility along the two $Ph - CH_2$ bonds. Existence of three conformational isomers in the jet expansion has been established using fluorescence excitation spectroscopy, UV-UV holeburning and fluorescence dip IR spectroscopic methods. S_0–S_1 electronic origins of the three conformers are within $25\,\mathrm{cm}^{-1}$(0.3 kJ/mol) of one another, with the red most origin at $35184\,\mathrm{cm}^{-1}$. Direct experimental determination of the isomerization barriers separating the three conformers were probed using stimulated emission pumping-population transfer spectroscopy. Experimental barriers between conformations are remarkably low, with a highest barrier of no more than $45\,\mathrm{cm}^{-1}$(0.54 kJ/mol) from the zero-point level. Quantum chemical calculations carried out using density functional theory (B3LYP/6-311G**) also support the three minimum energy conformations with near-identical stabilities. The calculated potential energy surfaces of the ground state along the phenyl torsional coordinates show that the minimum energy pathways to isomerization lie along the asymmetric phenyl torsional vibrational mode. Furthermore, the predicted torsional energy barriers are comparable in size to the experimentally determined thresholds.