TORSIONAL ANALYSIS OF PHENYLCYCLOPENTENES

JOSH J. NEWBY, CHRISTIAN MÜLLER, CHING-PING LIU[a] and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2804*.

The excitation and emission spectra of phenylcyclopentene (PCP), phenylcyclopentadi-1,3-ene (PCP3D) and phenylcyclopentadi-1,4-ene (PCP4D) in the S_0-S_1 region have been recorded in a supersonic jet environment. Low-frequency vibronic structure can be assigned to torsional motion of the six- and five-membered rings relative to one another. Analysis of these spectra leads to quantitative torsional potentials for all three molecules in ground and excited states. The excited state torsional potentials of all three molecules are quite similar, involving symmetric single well potentials with varying degrees of anharmonicity. The ground state potentials, on the other hand, vary substantially between the three close structural analogs due to a delicate balance between conjugative effects that favor planarity of the two rings and steric effects which disfavor the same. PCP3D has a planar heavy-atom structure with a flat-bottomed well, while PCP4D is a symmetric double well with an inter-ring angle of about 30°. On the other hand, the torsional potential for PCP is asymmetric about the planar minimum with a potential energy 'shelf' about 200 cm^{-1} above the global minimum. *Ab initio* calculations were carried out for both the ground and excited states to aid in the analysis of torsion potentials of all three species.

[a]Current Address: Department of Biological Science and Technology, National Chiao Tung University, Hsinchu, 30050 Taiwan.