LOWERING OF KETO-ENOL TAUTOMERIZATION BARRIER OF CYCLIC DIKETONES VIA CH$\cdots$O INTERACTION

T. CHAKRABORTY, B. BANDYOPADHYAY, P. BANERJEE and P. PANDEY, *Department of Physical Chemistry, Indian Association for the cultivation of science, Calcutta 700032, India. E-mail: pctc@iacs.res.in*.

Molecular association and keto-enol tautomerization of β-cyclohexanedione (β-CHD) and analogues have been investigated in argon matrix and also in a thin solid film prepared by depositing pure β-CHD vapour on a cold (8 K) KBr window. Infrared spectra reveal that in low-pressure vapour and argon matrix, the molecules are exclusively in diketo tautomeric form. The CH$\cdots$O hydrogen bonded dimers of the diketo tautomer are produced by annealing the matrix at 28 K. No indication is found for keto-enol tautomerization of β-CHD in dimeric complexes in argon matrix within the temperature range of 8-28 K. On the other hand, in the thin film of pure diketo tautomer, the conversion initiates when the film is heated at temperatures above 165 K. The observed threshold appears to be associated with excitation of the intermolecular modes in the solid, and the IR spectra recorded at high temperatures display narrowing of vibrational bandwidths, which has been associated to re-orientations of the molecules in solid. The non-occurrence of tautomerization in the dimer is consistent with the prediction of electronic structure calculations at B3LYP/6-311++G**, M05-2X/6-311++G** and MP2/6-311++G** levels. The transition state calculation predicts that CH$\cdots$O interaction has a dramatic effect on lowering of the tautomerization barrier, from more than 60 kcal/mol of bare molecule to $\sim$35-40 kcal/mol in dimers. Details of the results on analogous systems will be discussed in the talk.

Reference

"CH$\cdots$O Interaction Lowers Hydrogen Transfer Barrier to Keto-Enol Tautomerization of β-Cyclohexanedione: Combined Infrared Spectroscopic and Electronic Structure Calculation Study", B. Bandyopadhyay, P. Pandey, P. Banerjee, A. K. Samanta, and T. Chakraborty, J. Phys. Chem A. 116,3836-3845 (2012).