

## Association complexes of cyclic diketones: Matrix isolation IR spectroscopy study

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### Summary:

Small cyclic diketones easily form association complexes in solid and liquid phases. A significant fraction of the molecules under such conditions exists in enol tautomeric form, and complexation is facilitated via OH...O hydrogen bonding involving those enol tautomers. Stability of the enol tautomers being sensitive to geometric parameters and nature of substitutions, the molecular association is profoundly influenced by those parameters. Recently, our group has investigated the keto-enol tautomerization and dimerization of 5- and 6-member cyclic diketones ( $\alpha$ ,  $\beta$  and  $\gamma$ ) using IR spectroscopy in nonpolar solutions and cold inert gas matrixes. Six-member cyclic  $\alpha$ -diketones exist exclusively in enol tautomeric form and shows no dimerization tendency. The five-member analogues show similar behaviour when left isolated, but undergo dimerization to a significant extent both in liquid and at a higher concentration in the matrix. The six-member cyclic  $\beta$ -diketones, on the other hand, exist exclusively in diketo form under matrix isolation condition and generates stable CH...O H-bonded dimer when concentration is high. In contrast, in  $\text{CHCl}_3$  solution and solid, the compound exists largely in enol form and undergoes extensive association resulting in a broad  $\nu_{\text{O-H}}$  feature in the mid IR spectra. Cooperative interaction among multiple hydrogen bonds is proposed to be the dominant factor responsible for such differing behaviour under different physical conditions. In the case of  $\gamma$ -cyclohexanedione, isomeric CH...O H-bonded dimers have been identified under matrix isolation condition wherein the molecules are exclusively in diketo form, and IR spectral data shows that such dimers are also stable in nonpolar liquids. The details will be presented in the talk.