

### A THEORETICAL STUDY OF DIFFUSE SCATTERING FROM LIBRATING AND VIBRATING GLOBULAR MOLECULES IN SOLIDS

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Molecular crystals with globular molecules have interesting properties and form systems amenable to theoretical modelling with some degree of realism. The hardest behaviour to incorporate in a model is the large amplitude librations of the molecules. This study introduces a method of calculating the effect of large angle librational behaviour on the X-ray scattering produced by such molecules. The technique could be extended to other molecular solids. We have applied the method to illustrate the scattering from SF<sub>6</sub>, adamantane (C<sub>10</sub>H<sub>16</sub>) and Buckminsterfullerene (C<sub>60</sub>), using librational amplitudes derived from molecular dynamic simulation and other sources. The results illustrate nicely how increasing angles of libration smear out the molecular specific features of the scattering. Adding in the effect of vibrational smearing through the influence of the Debye-Waller term enables one to see how realistic scattering contours in reciprocal space are built-up from the sum total of the processes contributing to the scattering.

**Keywords:** MOLECULAR CRYSTALS DIFFUSE SCATTERING LIBRATIONS

### NEW INSIGHTS INTO THE [2+2] PHOTODIMERIZATION OF *o*-ETHOXY-TRANS-CINNAMIC ACID

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*o*-Ethoxy-trans-cinnamic acid (OETCA) has been found to form two polymorphs (the  $\alpha$  and  $\gamma$  polymorphs) and two solvate structures (the  $\beta$  polymorph(s))<sup>[1,2,3]</sup>. These have been studied using single crystal and powder X-ray diffraction techniques as well as DSC and TGA. CH...O interactions have been found to be very dominant in these structures with hydrogen bonding playing a minor role. Also the solid-state products on exposing the various crystals to U.V. light are those expected from the lattice control of the reaction process. However, though the product obtained from the alpha polymorph of OETCA is the one that is predicted from crystallographic measurements, the distance between the two reacting double bonds in the two reacting molecules are too far apart (4.6Å) to allow the reaction to occur via the conventional topochemical [2,2] photodimerization pathways and is thought to be aided by defects in the structure<sup>[3]</sup>. The  $\beta$  polymorph is really a solvate containing benzene (Schmidt's original polymorph). It is also possible to grow this polymorph using thiophene. Here we present new insights including a possible mechanism for the photodimerization reaction of the  $\alpha$  polymorph. In addition the crystal structures of the  $\alpha$  and  $\beta$  polymorph photodimerization products will be presented as well as an updated overall scheme for the photodimerization of the polymorphs of OETCA.

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### ATOMIC THERMAL MOTIONS IN CRYSTALLINE *m*-DINITROBENZENE IN RELATION TO ITS SECOND ORDER NON-LINEAR RESPONSE

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The meta-dinitrobenzene crystal structure has been determined at several temperatures in the 100 K - 300 K temperature range. The thermal expansion coefficients were calculated from the temperature variation of the lattice parameters. The rigid-body analysis with the correlation of the internal motions of large amplitude provided the T, L and S tensors' values at temperatures studied and was used to characterise the torsional motion of two nitro groups in the molecule. The translation and libration normal modes and the nitro groups' torsion frequencies from the rigid-body analysis were compared with the wave numbers at the maximum of bands of the low-frequency Raman and IR spectra. Our results point to very large, and strongly increasing with temperature, amplitudes of the nitro groups' torsional vibrations. The ab initio calculations were performed in order to assess the contribution from the internal motions to the static first-order hyperpolarizability of the *m*-dinitrobenzene molecule. The results indicate that the vibrational component, which originates from the nitro groups' torsional vibrations, is about 8 times larger than the electronic one. The intermolecular interactions in the crystal consist of numerous very weak CH...O hydrogen bonds between the molecules situated near the (ab) plane and short (3.0 to 3.4 Å) contacts between the oxygen atoms along the polar *c* axis. The interactions may enhance the non-linear response of the material due to cooperativity and tuning of the oxygen atoms' vibrations of large amplitude.

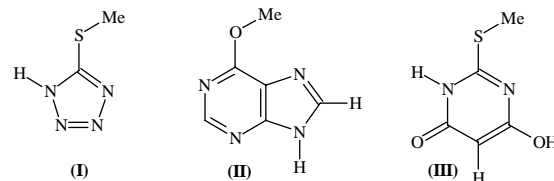
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### INTERMOLECULAR METHYL MIGRATION

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The combination of supramolecular architecture in solids together with the ability of molecules to undergo intermolecular reactions make such systems valuable for the study of cooperative bulk phenomena. We have studied the solid-state intermolecular methyl transfer in cyanurates and thiocyanurates. All the studied compounds undergo solid-state methyl rearrangements. In some cases the rearrangement was topochemically controlled, in other cases the rearrangement was not topochemically controlled and in all other cases the rearrangement took place in the melt. The next step in this study is to find out to what extent these types of intermolecular methyl migration are general. Few compounds possessing the moieties that enable intermolecular methyl migration was analyzed by differential scanning calorimeter (DSC) and their crystal structures were determined. Compounds (I) and (II) undergo methyl rearrangement in the liquid-state. Compound (II) crystallizes with three non-equivalent molecules of water that leave the crystal upon heating at different temperatures. The crystal structures of the two compounds show that topochemically controlled solid-state methyl rearrangement is not possible. Compound (III) on the other hand undergoes methyl rearrangement in the solid-state. The DSC thermograph indicates that the solid compound undergoes three phase transitions before the rearrangement takes place in the solid.



**Keywords:** METHYL MIGRATION SOLID-STATE REACTION METHYL REARRANGEMENT