

*Can hydrogen bond dimensionality be used to control thermal expansion?*Saraswatula Viswanadha Ganesh<sup>1</sup>, Binoy K. Saha<sup>1</sup><sup>1</sup>Department Of Chemistry, Pondicherry University, Pondicherry, India

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In general, most of the materials expand on heating. This phenomenon is called positive thermal expansion (PTE). In few instances some materials are found to be contracted on heating or expanded on cooling. This phenomenon is called negative thermal expansion (NTE). Some cases the materials neither expand nor contract with application of external heat energy. This phenomenon is known as zero thermal expansion (ZTE). Materials with zero thermal expansion have considerable applications in high precision optical mirrors, electronic devices and ceramics. Zero thermal expansion materials can be prepared by mixing positive and negative thermal expansion materials.

Thermal expansions studies on polymorphs reported in the literature are very less. Polymorphs are suitable for structure-property relationship because the molecules are same but their three dimensional arrangements differ. Whether it is possible to control thermal expansion by changing hydrogen bond dimensionality, we have compared the thermal expansion properties between the polymorphs that differ in hydrogen bonding dimensionality. Three polymorphic systems are studied here- i) tetrolic acid (2-butynoic acid), which exists in two polymorphic forms with zero and one dimensional (0-D & 1-D) hydrogen bonded chain;1 ii) o-cresol solvate of 1,1,4,4-tetrakis(4-hydroxyphenyl)cyclohexane (THPC.o-cresol) polymorphs, which shows one and two dimensional (1-D & 2-D) hydrogen bonded networks;2 iii) a dimorphic methanol solvate of the organic complex of benzene-1,3,5-tricarboxylic acid (BTA) and 4,4'-methylenebis(2,6-dimethylaniline) (MBDA) (BTA.MBDA.MeOH), which forms one and three dimensional (1-D & 3-D) hydrogen bonded networks.3 In the case of tetrolic acid, the lower dimensional (0-D) form exhibits higher volumetric thermal expansion, but in THPC.o-cresol, the two forms showed comparable volumetric thermal expansion, whereas in the case of BTA.MBDA.MeOH polymorphs, the higher dimensional (3-D) form exhibits marginally higher volumetric thermal expansion than the 1-D form.

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