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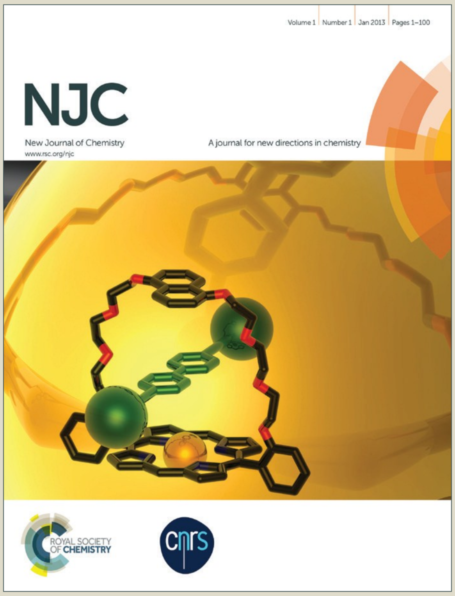

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

NJC

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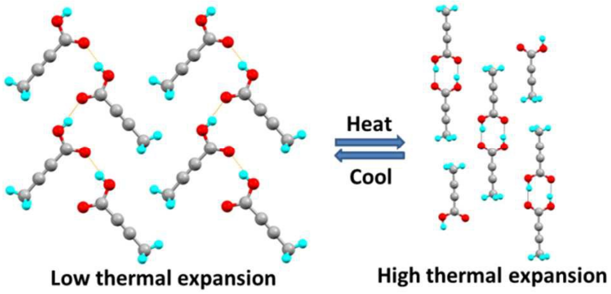

Higher dimensional (1-D) hydrogen bonded form shows smaller thermal expansion than lower dimensional (0-D) hydrogen bonded form of 2-butynoic acid.

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LETTER

Can the thermal expansion be controlled by varying hydrogen bond dimensionality in polymorphs?

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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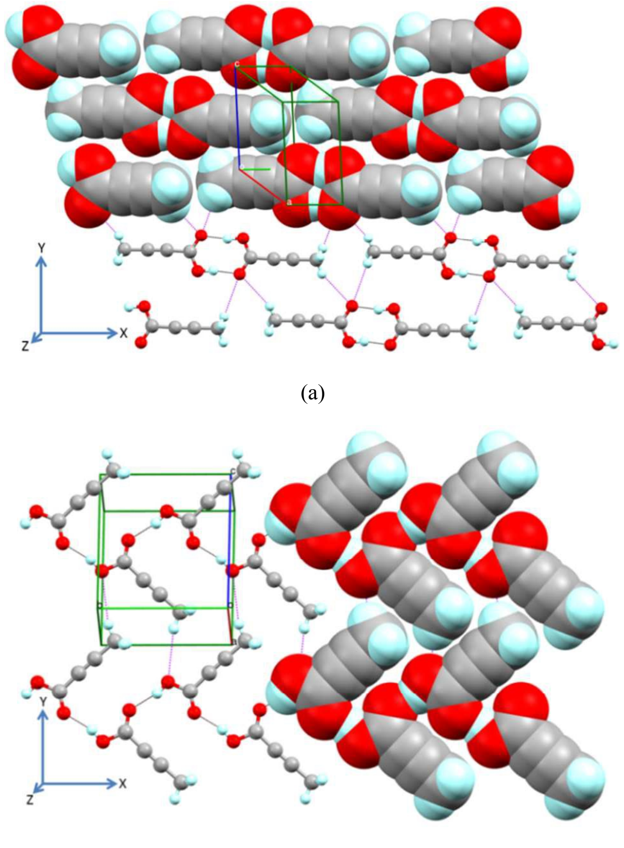
2-Butynoic acid exists in two enantiotropically related polymorphic forms. The monoclinic form, containing one dimensional hydrogen bond in the structure, exhibits a smaller volumetric thermal expansion coefficient than the triclinic form which has a zero dimensional hydrogen bond. The phase transformation 1D → 0D has been correlated to the different thermal expansion abilities of the groups present in the molecule and the crystal packing in these two forms.

Polymorphs are different crystalline forms of a solid material which exhibit different crystal packing features.[1] The properties which depend on crystal packing *e.g.* solubility, color, particle size, hardness, reactivity *etc.* could be different for different polymorphic forms of a material.[2] Structure – property correlation studies, conducted on polymorphic systems[3], thus can provide more relevant information on the influence of solid state crystal packing in directing solid state properties which would facilitate a more systematic approach to materials designing.

Thermal expansion of a material is intimately related to the type of molecules or ions, interactions and symmetry in the solid state architecture.[4] Contrary to the regular expansion along all directions (positive thermal expansion or PTE) the solid state framework of a particular system could bring about substantial anomalies in thermal expansion of the material *viz.* contraction of the material along one or more directions (negative thermal expansion or NTE)[5] or no effective expansion in material (zero thermal expansion or ZTE)[6] on application of heat. Such anomalous instances of thermal expansion have been widely studied and systems exhibiting such phenomenon have been found to have profound applications in materials science and biomedical field.[7] Very large thermal expansion materials also have potential applications in designing thermomechanical actuators.[8] Explanations have been reported in the context of structural deformation, transverse vibration, magnetic transition, rigid unit mode *etc.* as probable causes for such anomalies.[9] However, systematic designing of materials exhibiting such properties, with the existing knowledge, is still a challenge.

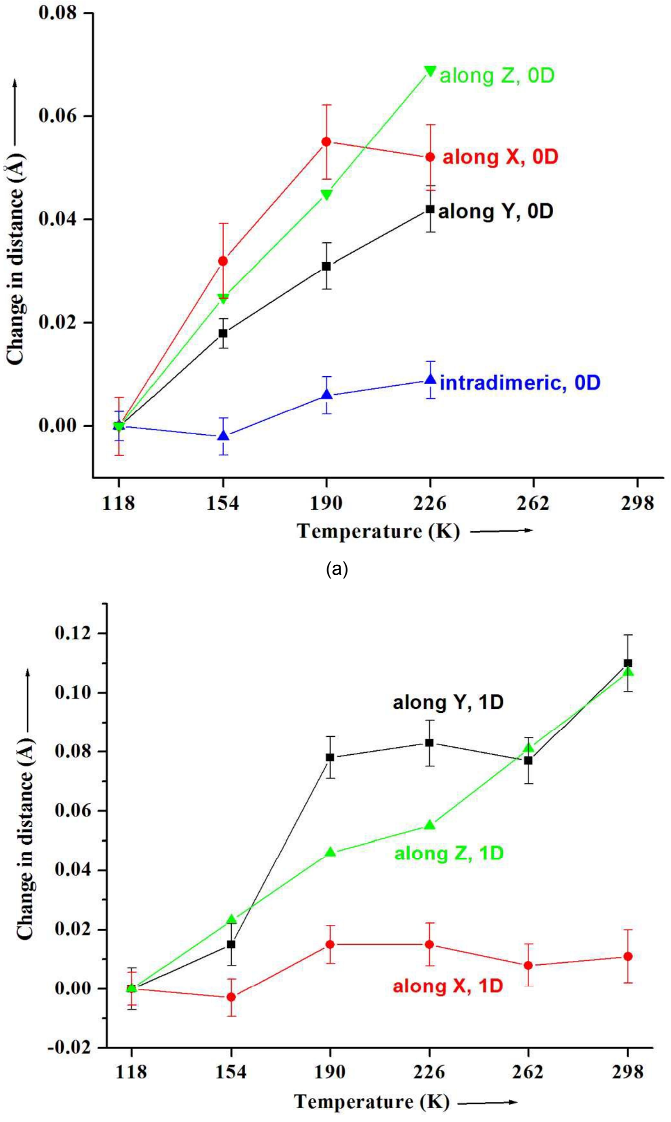


(a)

(b)

Fig 1. One layer of molecular packing (a) on the $(2\bar{4}2)$ plane in **0D** and (b) on the (101) plane in **1D** structures are shown. The COOH groups form dimer in **0D** but catemer in **1D** crystal structures. Directions of the X (along chain/dimer axis), Y (on the plane and perpendicular to chain/dimers axis) and Z (perpendicular to the plane) axes are shown.

Earlier, we have reported a dimorphic system, where both the forms were made of one dimensional hydrogen bonded parallel chains, showed similar thermal expansion properties due to similar hydrogen bonding topologies.[10] Therefore, we were interested to know what would happen to the relative thermal expansion properties if the hydrogen bond dimensionalities are different in two polymorphic forms. Would the higher dimensional hydrogen bonded solid exhibit a lower thermal expansion coefficient than the lower dimensional hydrogen bonded counterpart? Herein, we have studied thermal expansion properties of 2-butynoic acid which crystallizes in two forms, with one dimensional (1-D) and zero dimensional (0-D) hydrogen bonded synthons.[11] Here, we have attempted to study thermal expansion properties of a polymorphic organic system where the hydrogen bonding dimensionalities are different in different forms and phase transition[12] has also been explained in terms of the differences in their thermal expansion behaviours.



(a)

(b)

Fig 2. Change in distances along different directions with increasing temperature in (a) 0D and (b) 1D structures are shown. Along X axes the distances were calculated between (a) two consecutive dimeric units for 0D and (b) two consecutive translationally related molecules for 1D. Along Y and Z axes the distances were calculated between two consecutive parallel chains and between two consecutive parallel layers respectively.

The plate shaped crystals of the 0-D hydrogen bonded form (**0D**) were obtained *via* slow evaporation of the solvent from a hexane solution of the compound at 5 °C. It crystallized in $P\overline{1}$ space group with one molecule in the asymmetric unit. The molecules form usual 0-D centrosymmetric carboxylic acid dimer synthon (Fig. 1a). The dimer axes are parallel to the [321] axis and the inter dimer contacts, along this axis, are through the methyl groups (Me···Me). These dimers are further assembled *via* weak C−H···O interactions on the crystallographic $(2\overline{4}2)$ plane which is coplanar to the COOH groups. The interactions, present between two consecutive planes, are of weak C−H···O and C···O (with the carbonyl carbon) types. On the other hand, the block shaped crystals of 1-D hydrogen bonded form (**1D**) were produced, using slow evaporation method, from a cyclohexane solution of the compound at 5 °C. It was solved in $P2_1$ space group with one molecule in the asymmetric unit. In this crystal structure, the carboxylic acid groups form a catemeric 1-D hydrogen bonded chain, propagating along the *b* axis (Fig. 1b). These chains assemble in a herringbone pattern *via* weak C−H···O and C−H···π interactions on the crystallographic (101) plane and the COOH groups are coplanar to this plane. These two dimensional sheets are stacked *via* weak C−H···O and C···O interactions in the third dimension.

According to Kitaigorodsky, weaker and lesser number of interactions cause larger thermal expansion in a solid.[13] There are some interesting studies where anisotropy of thermal expansion in the crystals have been correlated to the hydrogen bonds present in the systems.[14] From a theoretical study, Lifshits proposed that in a molecular crystal the maximum expansion of the structures on heating is expected to occur in the perpendicular directions to the chains or the layers where as a contraction is expected along the chains or within the layers.[15] In one of our previous works on a one dimensional hydrogen bonded dimorphic pair, we demonstrated an interaction strength−thermal expansion relationship.[10] In both the structures, smaller expansions occurred in those directions along which molecules were bound *via* stronger interactions. This result prompted us to study the present system where the hydrogen bond dimensionality is different in different forms. In the process of variable temperature data collection, good diffraction quality crystals of both the forms were employed and data were collected at 36 K interval starting at 118 K (Fig. S1). In case of the **1D** system, a set of six data was collected within the temperature range of 118 – 298 K, whereas, for the **0D** form we were able to collect only four data till 226 K and at 262 K the **0D** crystal got converted to the **1D** form (**1D**^{t} (262 K) in Fig. S1 and Table S3) *via* a single crystal to single crystal phase transition (SCSCPT) process. Calculation of volumetric thermal expansion coefficients using PASCal[16] program suggests that expansion in the lower dimensional hydrogen bonded **0D** form (α_v = 332(12)

MK^{-1}) is 25 % higher than that in the higher dimensional hydrogen bonded **1D** form (α_v = 265(9) MK^{-1}). Fig. 2a shows that, even though, the change in distance, with increasing temperature, between two acids within a dimer (intradimeric, 0D) is very small due to the presence of strong carboxylic acid dimer synthon, the change in distance along the X axis is quite high. It is because the interdimer contact along the X axis in the **0D** form is of very weak Me···Me type. Due to the presence of strong 1-D hydrogen bonded chain, the distance change along the X axis is relatively smaller in the **1D** form (Fig. 2b). In both the forms, along Y and Z directions the thermal expansions are controlled by weak C−H···O, C−H···π or C···O types of interactions. Comparison in % thermal expansion along these three orthogonal directions suggests that the expansions are more or less similar in these two forms along the Y and Z axes, but along X direction the expansion is always lesser in the **1D** form than that in the **0D** form (Fig. 3). This explains why the volumetric thermal expansion in **0D** is found to be larger than that in the **1D** form.

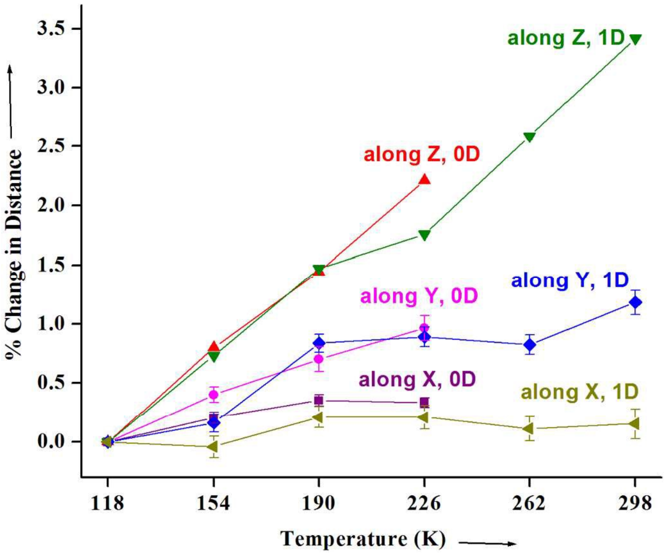


Fig 3. % changes in distances along different directions in the two structures are shown.

The 2-butynoic acid is a low melting (melting point 76 - 78 °C) solid. During our variable temperature diffraction experiments we did not observe any phase transition for the **1D** crystal in the temperature range 118-298 K, but with **0D** crystals a SCSCPT (**0D** → **1D**) was observed at above 226 K. The SCSCPT is interesting in this particular case because of the presence of large structural differences between the two forms. In the **0D** structure, the acid molecules are assembled in a parallel arrangement, whereas, in the **1D** form the molecular axes are tilted by around 85°. In spite of this large structural change, the system retains the single crystallinity in the process of phase transformation! Previous report suggests that there is a phase transition from **1D** → **0D** at around 56-58 °C,[11] though it did not mention explicitly if the transformation occurred *via* a SCSCPT process. The compound is hygroscopic and it also sublimes easily, which did not allow us to detect the phase obtained after the transformation at this temperature range. However, the DSC experiment showed an endotherm at around 56 °C suggesting a probable phase transformation from **1D** → **0D** (Fig. S2a). Therefore, these two forms are enantiotropically related to each other where **0D** → **1D** conversion occurs at low temperature and the **1D** → **0D** conversion occurs at high temperature. Moreover, the density of the **1D** form is slightly higher than the **0D** form (Fig. S2b). These observations suggest that the **1D** form is stable at or below room temperature, whereas the **0D** form is stable at higher temperature. We have made an attempt to correlate the phase transformation to the thermal expansion properties in these two forms. If we consider two end groups of the molecule, the COOH group forms O−H···O hydrogen bond, but the methyl group is involved in Me···Me contact in both the structures. It is known that with increasing temperature the stronger O−H···O hydrogen bonds would expand slowly compared to the weaker Me···Me contact. But in the **1D** structure, both the interactions are propagating along the X axis (Fig. 1b) and hence expansions must be same in both the terminals along this direction. On the other hand, these expansions are independent in the case of **0D** structure. Therefore, at higher temperature (56 °C), when the expansion along X axis in the Me end is considerably higher than that in the COOH end, the **1D** structure does not sustain further and gets converted to the **0D** structure where they can expand independently. It should also be noted that the average equivalent isotropic displacement parameter (mean Ueq) value and the change of this quantity with temperature are higher for the **0D** structure compared to the **1D** structure (Fig. S2b and S2c).

In summary, here we have shown that volumetric thermal expansion in the lower dimensional (0-D) hydrogen bonded form (**0D**) is more than that in the higher dimensional (1-D) hydrogen bonded polymorphic form (**1D**) of 2-butynoic acid crystal due to lesser expansion along the O−H···O chain direction in the **1D** form. We also have demonstrated that the different thermal expansion behavior along the strong hydrogen bonded chain and weak Me···Me contact causes phase transformation from **1D** to **0D** at higher temperature. Though there are several parameters that control the thermal expansion in a material, this work suggests that hydrogen bond dimensionality is an important parameter which could be used as an important tool to control the thermal expansion in a material.

B.K.S thanks CSIR, India for research funding (No. 02(0026)/11/EMR-II, dated 16/12/11). We gratefully thank DST, India for SXRD facility. V.G.S thanks to UGC for fellowship. SB thanks CSIR, India for Senior Research Fellowship.

Experimental

Crystallization: Single crystal of both forms of 2-butynoic acid, **0D** and **1D** were produced by slow evaporation of the solvent from hexane and cyclohexane solutions of the compound respectively at 5 °C.

Variable temperature single crystal X-Ray diffraction: In case of the **1D** form, six data sets were collected at an interval of 36 K by gradually heating the crystal from 118 K to 298 K and for the

0D form, four data sets were collected from 118 K to 226 K at a 36 K interval. Temperature was controlled by an Oxford Cryojet HT instrument. Above 226 K the **0D** crystal was found to get converted to the **1D** form via a single crystal to single crystal transformation and a data was further recorded for the transformed crystal (**1D**$^{\mathbf{t}}$**, 262 K**). X-ray crystal data were collected on Xcalibur Eos, Agilent Technologies Ltd. with Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption correction using spherical harmonics, implemented inn SCALE3 ABSPACK scaling algorithm were applied.[17] Structure solution and refinement were performed with SHELXS-97[18a] and XL[18b] respectively in Olex 2.1-2 package[19]. In all the structures carbon bonded hydrogen atoms have been placed at calculated positions and hydrogen atoms of the carboxylic acid groups (except for transformed **1D**$^{\mathbf{t}}$**, 262 K**) have been isotropically refined. Only in case of the data for the **0D→1D** transformed crystal data collected at 262 K, the hydrogen atoms of the carboxylic group has been placed at calculated position.

Notes and references

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Electronic Supplementary Information (ESI) available: Thermal ellipsoid plots at 50% probability, DSC plot of **1D** form, plots for variation of density, mean Ueq and change in mean Ueq for the systems, variable temperature geometry of hydrogen bonds, variable temperature geometry of important contacts present in the systems, crystallographic parameters of the systems at different temperatures. CCDC 1040237−1040247. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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