CrystEngComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *CrystEngComm*, 2018, **20**, 5123

Received 16th July 2018,
Accepted 7th August 2018

DOI: 10.1039/c8ce01169a

rsc.li/crystengcomm

Uniaxial negative thermal expansion induced by moiety twisting in an organic crystal†

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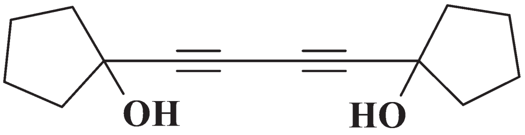
Variable temperature single-crystal X-ray diffraction reveals uniaxial negative thermal expansion (NTE) of 1,4-bis(1′-hydroxycyclopentyl)-1,3-butadiyne crystal. The length of the unit cell axis *a* decreases with increasing temperature, whereas the *b* and *c* axes increase. The mechanism of the negative thermal expansion in the organic crystal has been derived by analysis of the crystal structures at different temperatures. Steric adjustment of the molecules in the crystal structure requires twisting of the terminal cyclopentyl ring, which drives the contraction of one of the principal axes.

Expansion with increasing temperature is normal behaviour in most solid-state materials due to increased anharmonic vibration of the constituent atoms, molecules or ions. However, some materials contract along one or more directions with increasing temperature, and this phenomenon is known as negative linear thermal expansion (NTE). This anomalous behaviour is mostly confined to some metal oxides,[1–5] metal cyanides,[6–9] polymers[10–13] and zeolites.[14–19] However, there have been a number of recent reports of NTE in purely organic crystalline systems.[20–25]

Understanding the underlying mechanisms responsible for NTE is of considerable interest in the field of crystal engineering with regard to the design of new thermally-responsive materials. We now know that there is no overarching mechanism that controls the NTE observed in different materials. Indeed, a number of different mechanisms have been identified to date that vary from one material to another. These include transverse vibrations observed in some metal oxides, metal cyanides and MOFs,[1,26–29] as well as magnetic and electronic transitions in a number of other materials.[30,31] Guest-dependent NTE has been observed in FMOFs[32] and some coordination polymers.[12,33–35] In TrpGly·H_2O ordering of water molecules in the peptide channel leads to uniaxial NTE.[20] NTE was caused by steric hindrance in some organic materials,[21,36] and uniaxial NTE was recently observed in an inclusion compound due to weak host–guest interactions.[37,38] In this contribution we report uniaxial NTE in an organic crystal and explain the mechanism causing this unusual behaviour.

As part of our ongoing studies of the inclusion properties of diyn-diol molecules we prepared 1,4-bis(1′-hydroxycyclopentyl)-1,3-butadiyne (**1**) (Scheme 1). Since we have previously reported on unusually large anisotropic linear thermal expansion in (*S*,*S*)-octa-3,5-diyn-2,7-diol,[22] we were motivated to also investigate the thermal expansion properties of **1**, the shape of which was also reminiscent of a dumbbell. Before undertaking a variable-temperature single-crystal X-ray diffraction study, we first confirmed that no polymorphic phase transformation of compound **1** occurs before melting (Fig. S1 in the ESI†).

Single crystals were prepared by sublimation of as-synthesised **1** at 80–90 °C under dynamic vacuum. A suitable crystal was selected and attached by means of epoxy to the tip of a glass fibre, which was mounted on a goniometer head. Diffraction data were collected at 20 K intervals from 100 to 340 K. Data collection was not possible after 340 K owing to degradation of the single crystal, possibly due to sublimation (Fig. S2 in the ESI†). Cursory analysis of the unit cell parameters reveals that the crystallographic *a* axis shortens with increasing temperature, while the *b* and *c* axes elongate.



Scheme 1 1,4-Bis(1′-hydroxycyclopentyl)-1,3-butadiyne (**1**).

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† Electronic supplementary information (ESI) available: Details of X-ray diffraction experiments, crystal data, packing diagrams, differential scanning calorimetry, photomicrographs, molecular geometry and interaction tables, and calculations of thermal expansion coefficients. CCDC 1855339–1855351. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ce01169a

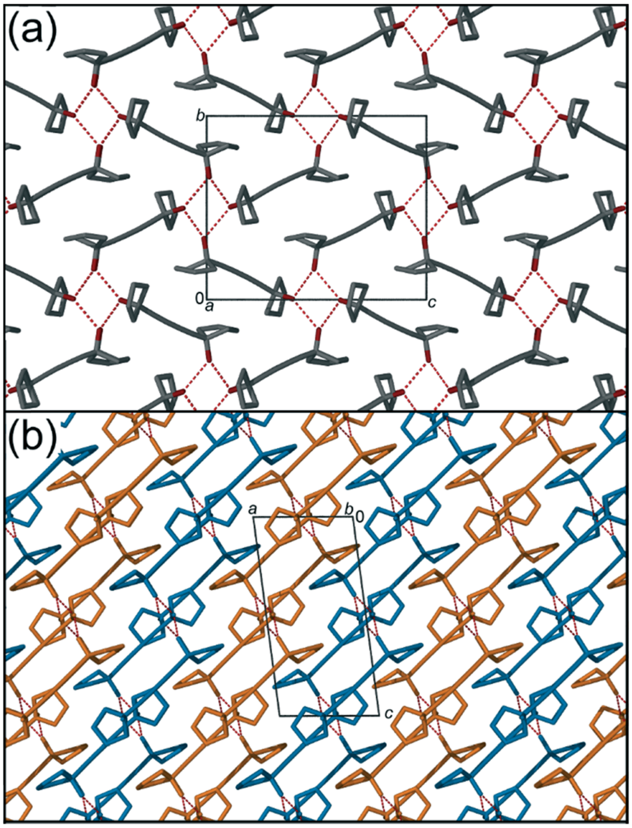

Fig. 1 (a) Hydrogen bonded tetramers forming a 2D layer, viewed along [100] and (b) stacking of 2D layers viewed along [010]. Successive layers are shown in different colours to differentiate them. Hydrogen atoms have been omitted for clarity.

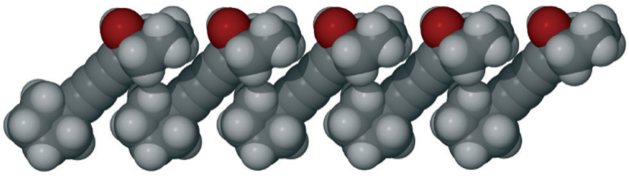

Fig. 2 Stacking of molecules along [100]. The space filling model shows how "bumps" fit hollows.

Compound **1** crystallises in the monoclinic space group $P2_1/n$, with one molecule in the asymmetric unit. The diyne spine of **1** appears to be slightly bent at all temperatures used in this study (see Table S1 in the ESI†). The crystal structure is primarily dictated by O–H⋯O hydrogen bonds (see Table S4 and Fig. S4 in the ESI† for the hydrogen bonding geometry and fingerprint plot[39] of intermolecular interactions, respectively). Each of the hydroxyl groups participates in the formation of a cyclic hydrogen bonded tetramer, thus forming 2D hydrogen bonded networks (Fig. 1a). These layers are then stacked along the crystallographic *a* axis to complete the 3D packing arrangement (Fig. 1b). The molecules are stacked along [100] in such a way that the cyclopentyl "bumps" of one layer fit into the hollows of the neighbouring layers (Fig. 2 and S5 in the ESI†).

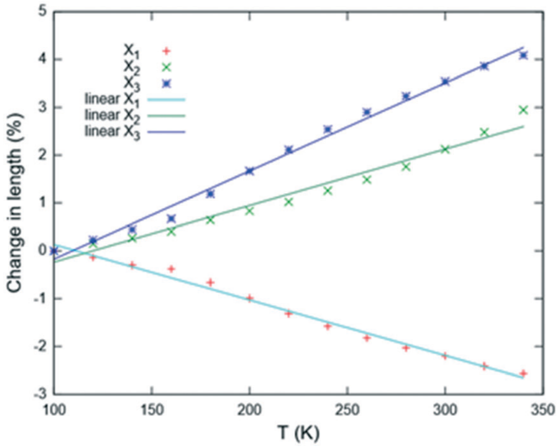

Fig. 3 Percentage changes of principal axes with temperature.

Since the crystallographic axes were not all orthogonal to one another in the monoclinic system, the program PASCal[40] was used to derive a set of orthogonal axes, with corresponding thermal expansion coefficients. The linear thermal expansion coefficients are −116(3), 118(8) and 184(5) × 10^{-6} K^{-1} along X_1, X_2 and X_3, respectively. The three principal axes are directed approximately along [−100], [010] and [001], respectively. The variations (expressed as percentage change) of the three principal axes with temperature has been shown in Fig. 3.

In order to understand the mechanism responsible for uniaxial NTE along X_1, we compare the crystal structures of **1** determined at different temperatures. The thermal ellipsoid plots of molecule **1** show normal changes of atomic displacement parameters with changing temperature (Fig. S3 in the ESI†). With the exception of O2, C13 and C14, the magnitude of U_{eq} increases monotonically with temperature (Fig. 4). The tilt angle (θ) of the molecules relative to the stacking direction [100] increases gradually from 46.5° at 100 K to 48.6° at 340 K (see Table S5 in the ESI†). Along the *a* axis the molecules move closer together as the tilt angle increases, and this leads to shrinkage of the *a* axis with increasing temperature. NTE induced by tilting of molecules has already been observed for a diyn-diol compound previously reported by our group.[22] However, the most interesting observation in

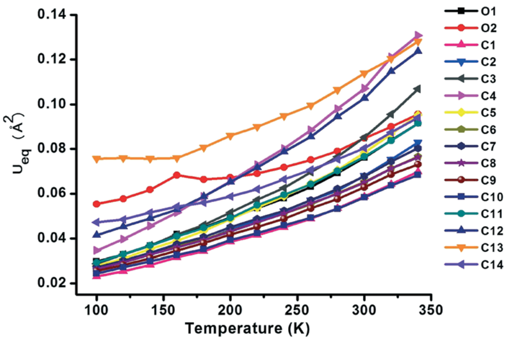

Fig. 4 Change of U_{eq} with temperature of all the non-hydrogen atoms in the molecule of compound **1**.

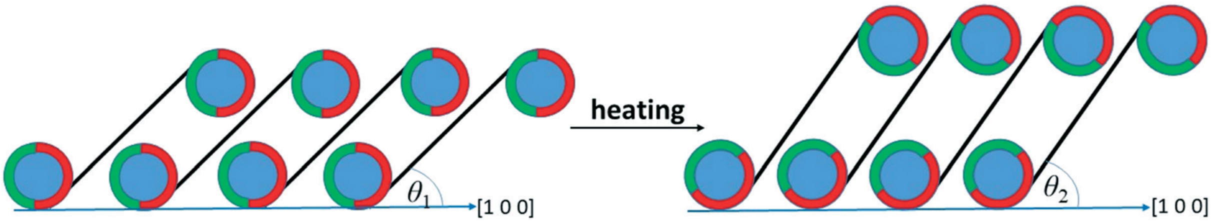

Fig. 5 Schematic representation of the mechanism of NTE in compound **1**. Cyclopentyl groups in the molecule are shown as circles with green and red arcs and diyne spines are represented by black bars. The stacking angle θ_1 along [100] increases to θ_2 as the temperature increases. Rotation of the cyclopentyl groups is shown by rotation of the coloured arcs.

the present study is that the cyclopentyl groups at the two extremities of each molecule rotate in opposite directions around the diyne spine as the temperature changes (Video S1 in the ESI†). As the footprint of each atom in the molecule of **1** increases with increasing temperature, steric hindrance arises between the molecules along the stacking direction. Since the cyclopentyl moiety fits into the hollow created in the neighbouring molecule due to its dumbbell shape, the cyclopentyl groups rotate to avoid steric hindrance, thus keeping the crystal structure intact with increasing temperature. The rotation of the cyclopentyl moiety is also evident from the change of some torsion angles with temperature (Table S3 in the ESI†). As the temperature increases from 100 to 340 K, the torsion angle C2–C3–C4–C5 increases from 16.5° to 19.5°, the torsion angle C6–C1–C2–C3 decreases from 162.8° to 155°, and the torsion angle C6–C1–C5–C4 increases from −153.9° to −144.5°. Similarly, the most significant change in the torsion angles in the other cyclopentyl moiety occurs between C11–C12–C13–C14, which decreases from 14° to 5° as the temperature increases from 100 K to 340 K.

The change in the tilt angle (θ) is related to the rotation of the cyclopentyl moiety, which creates more space along the diyn spine and brings the molecules closer to each other along the stacking direction [100], thus causing NTE along the *a* axis. The rotation of the cyclopentyl moiety and the associated change of the tilt angle are shown schematically in Fig. 5. The change in the tilt angle also induces expansion along X_2 and X_3 concertedly. The expansion along these two principal axes can also be correlated with the gradual changes in the hydrogen bonding geometry with temperature; the unique distances between the oxygen atoms within the tetramer are 2.686(2) and 2.762(2) Å at 100 K, and they increase to 2.759(3) and 2.808(3) Å at 340 K (Table S4 in the ESI†).

In conclusion, we have reported uniaxial NTE coupled with biaxial PTE of an organic crystal. Essentially, the NTE in **1** arises due to the steric adjustment of the molecules in the crystal structure with changing temperature. The steric adjustment forces the rotation of terminal cyclopentyl groups of the molecule in opposite directions relative to each other. NTE due to moiety twisting has not been reported before for an organic crystal.

We thank the National Research Foundation of South Africa and the Department of Science and Technology (SARCHI Program) for financial support. DD also acknowledges DST-PURSE, JNU for providing basic facilities for this research.

Conflicts of interest

There are no conflicts to declare.

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