MS15-P24 Large guest-dependent anisotropic thermal expansion in a series of organic inclusion compounds

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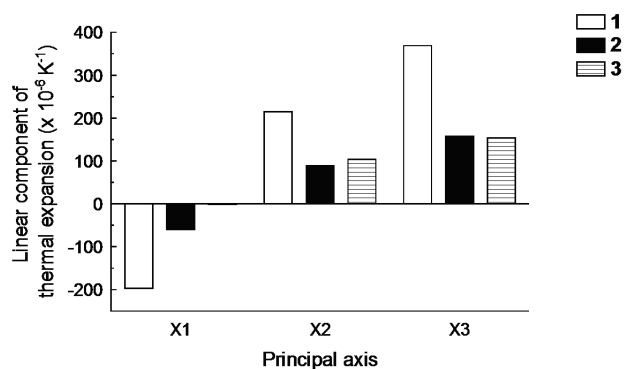
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Figure 1. Linear coefficients of thermal expansion for 1, 2 and 3 over the temperature range 180-273K.

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Most studies of extreme anisotropic thermal expansion have involved inorganic compounds.[1] In recent years, however, various examples have come to light of large anisotropic thermal expansion in organic crystals.[2] We recently reported on a nitromethane solvate of 18-crown-6 that undergoes large uniaxial negative thermal expansion with large positive expansion along the other two principal axes.[3] The present study investigated the thermal expansion behaviour of two inclusion compounds (**2** and **3**) that are analogous to the nitromethane solvate described above (**1**). The three compounds have isoskeletal crystal structures but, curiously, they exhibit drastically different thermal expansion profiles over a common temperature range of 180-273K.

Linear coefficients of thermal expansion (Figure 1) were determined using PASCal.[4] The overall trends for **1** and **2** are similar in that the expansion is negative along one axis and positive along the other two, however, the magnitude of thermal expansion is lower for **2** in all respects. Compound **3** exhibits only positive thermal expansion along two principal axes and near-zero thermal expansion along the third. The overall volumetric expansion for all three compounds is nevertheless exceptionally large for organic inclusion compounds.

The underlying mechanism of anisotropic thermal expansion in each case involves a combination of relatively weak intermolecular interactions. These were investigated computationally by calculating single-point energies and mapping electrostatic potentials.

Evidently, guest replacement is a potential strategy for greatly modifying the thermal expansion behaviour of an organic inclusion compound, even where the overall molecular packing in the crystal is unaffected.

References

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