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REVIEW ARTICLE

Thermal Expansion in Organic Crystals

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Abstract | Though a large number of thermal expansion studies have been reported on inorganic systems, a considerably large number on metal–organic-based systems, but those on purely organic systems are too few. Moreover, owing to the complexity of the crystal structure of the organic systems, their thermal expansion behaviors are poorly understood. This review focuses on some interesting thermal expansion studies conducted on purely organic crystals and also on some important structure–property relationships of thermal expansion of organic crystals with intermolecular interactions, melting point of systems, guest molecules in inclusion compounds, and hydrogen bond dimensionality in the crystal structures. Most studies discussed here have been reported in recent years.

1 Introduction

Generally, materials expand on all directions when heated due to anharmonic thermal vibration of atoms.[1–3] This expansion is quantified in terms of thermal expansion coefficient. If the length of a crystal along a particular direction is L_i at T_i K and L_f at T_f K, then the linear thermal expansion coefficient, $\alpha_l = (L_f - L_i)/L_i(T_f - T_i)$ K^{-1}. Similarly, if the initial volume is V_i at T_i K and the final volume is V_f unit at T_f K, then the volumetric thermal expansion coefficient, $\alpha_v = (V_f - V_i)/V_i(T_f - T_i)$ K^{-1}.[4] The magnitude of this expansion varies for different types of materials. A typical inorganic compound generally shows α_v in the range 0–20 × 10^{-6} K^{-1}, whereas for the crystals of small organic molecules and MOF, it is usually around 100–300 × 10^{-6} K^{-1}.[5] Generally, the linear thermal expansion coefficient, α_l, is expressed along the three principal axes of thermal expansion, which are orthogonal to each other, irrespective of the crystal system.[6] If a crystal is cut into a spherical shape and then heated, it would take an ellipsoidal shape. The three principal axes of this ellipsoid are the three principal axes of the thermal expansion. Along these principal axes the material either expands or contracts in a purely linear fashion, but along the other directions some nonzero shear component is involved.[7] These principal axes are also aligned along the unique crystallographic axes of the unit cells.[5, 6] For example, in the case of monoclinic or hexagonal systems, one of the three axes would be aligned along the *b* or *c* axes, respectively, of the unit cell, and for orthorhombic, tetragonal or cubic system, the three axes would be aligned along the three mutually perpendicular crystallographic axes. But, in triclinic system, none of the three axes would be aligned along any of the three crystallographic axes. In cubic system, the thermal expansion would be isotropic, i.e., linear thermal expansion coefficients along all the three axes would be the same.[8] On the other hand, in the case of tetragonal and hexagonal systems, the α_l values would be the same along the two axes (because $a = b$).[9, 10] Several techniques are available to measure thermal expansion in a solid,[5] but the most popular method, especially among the chemists, is calculation using cell parameters obtained from single-crystal X-ray diffraction. A number of software packages, such as PASCal and STRAIN, are available for this purpose.[7, 11, 12]

Most thermal expansion studies are concerned with inorganic compounds[1–4, 8, 13–18] and quite a few on metal–organic compounds,[9, 10, 19–21] but are relatively fewer on purely organic compounds.[22–24] One reason could be that most studies were on volumetric zero or negative thermal

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expansion of materials, which are found to be among the inorganic or metal–organic systems, but so far no such example is found in the case of purely organic compounds. Nevertheless, organic compounds are good candidates for basic understanding of thermal expansion in materials and as large thermal expansion materials which find application in designing of thermomechanical actuators[25, 26].

Thermomechanical actuator: It is the component of a devise that is responsible for moving or controlling a mechanism or system by converting the thermal energy into mechanical motion.

This review aims at understanding the structure–property relationship of organic systems with their thermal expansion properties using crystal engineering[27–32] principles, such as how thermal expansion of crystals depends on interaction energy, hydrogen bond dimensionality, presence of guest molecules, polymorphism, and melting point. In addition, I also discuss several miscellaneous but interesting reports on thermal expansion studies in organic systems. If the structure–property relationship is established, crystal engineering can play a big role in designing new thermal expansion materials.

Crystal engineering: "The understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties"—G. R. Desiraju.

2 Interactions and Thermal Expansion

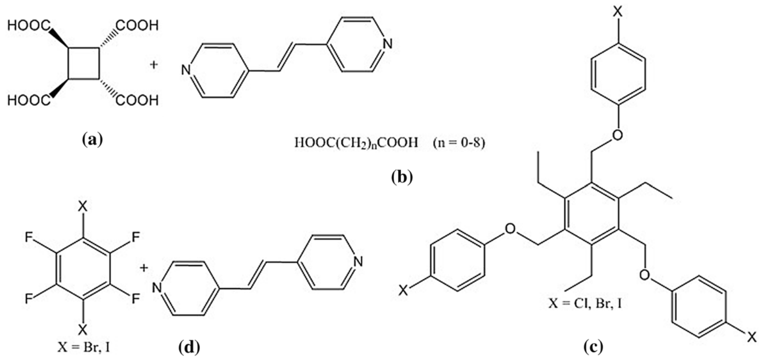
Noncovalent interactions, responsible for self-assembly process in a crystal, explain many thermal expansion properties of solids. It is known that thermal expansion decreases with increasing interaction strength.[33–35] Graphite, for example, exhibits a larger thermal expansion along the perpendicular direction to 2D sheet but there is very small expansion along this plane[36, 37] as along the plane the atoms are bonded by strong covalent bonds, whereas the interaction is much weaker π···π type along the perpendicular direction. Therefore, it is possible to control thermal expansion of an organic system by modulating its functional groups using crystal engineering approach. Indeed, some interesting studies have been reported in the literature on thermal expansion in hydrogen- and halogen-bonded[38] systems; these are shown in Scheme 1.

Based on a theoretical study, Lifshits showed that when a molecular crystal is heated, it may even contract within the layers or along the chains, whereas an expansion is observed in the perpendicular direction of the layers or chains.[39] Saha et al. have showed this phenomenon experimentally in a one-dimensional hydrogen-bonded dimorphic co-crystal system in which the molecules, 1,2,3,4-cyclobutanetetracarboxylic acid and trans-1,2-bis(4-pyridyl)ethylene (Scheme 1a) are assembled via strong O–H···N hydrogen bonds along one direction, in another via relatively weaker C–H···O interactions, and in the third via weak van der Waals contacts.[40] It has been shown that the order of thermal expansion follows the reverse order of interaction strength of these interactions, i.e., the highest expansion is observed along the weak van der Waals contacts and the lowest along the strong O–H···N hydrogen-bonded direction.

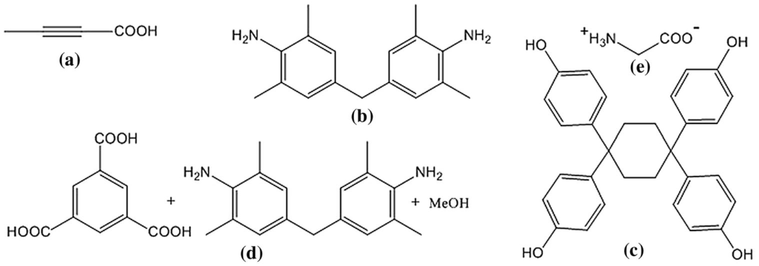
This reverse relationship between interaction strength and thermal expansion has also been found in the case of alkane dicarboxylic acids (HOOC(CH$_2$)$_n$COOH, $n = 0$–8) (Scheme 1b),[41] in which the molecules form one-dimensional hydrogen-bonded chains. Thermal expansion along the chain directions is very small and in some cases even negative but is highly positive along the perpendicular directions of the chains, in which the intermolecular interactions are of weak C–H···O type.

Thermal expansion of 2,4,6-triethyl-1,3,5-tris(4-halophenoxy)methylbenzenes (halo = Cl, Br and I) have been studied to compare different halogen···halogen interactions (Scheme 1c).[42] The guest-free forms of these three halogenated compounds are isostructural and their ethyl acetate solvates are also isostructural. In both the sets of

Isostructural: Different compounds having similar crystal structures.



Scheme 1: Systems discussed in the Sect. 2.



Scheme 2: Systems discussed in the Sect. 3.

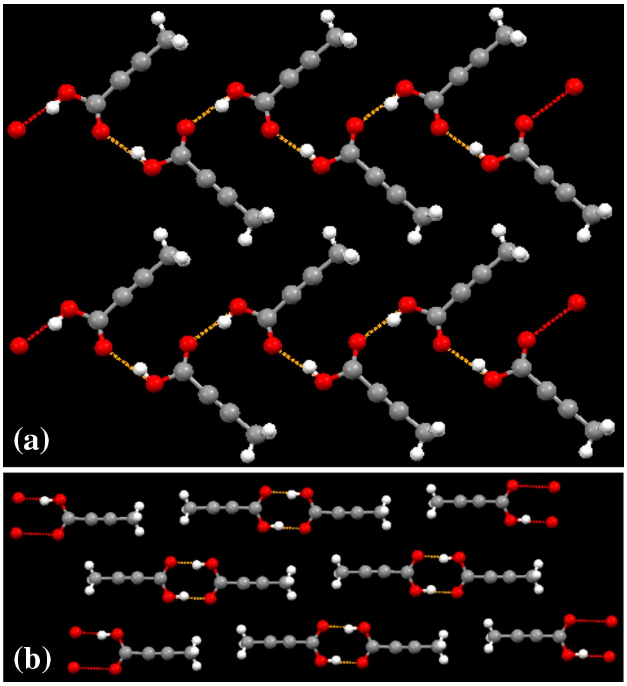


Figure 1: Tetrolic acid molecules form **a** 1D catemeric hydrogen-bonded chain in TA-1D form, and **b** centrosymmetric carboxylic acid dimer in TA-0D form.

isostructural crystals, the order of thermal expansion is found to be I···I < Br···Br < Cl···Cl. It may be noted here that the order of halogen···halogen interaction strength is known to follow as I···I > Br···Br > Cl···Cl.

Thermal expansion of halogen-bonded systems has also been studied. Resnati et al. have shown that the expansion of the stronger C–I···N interaction is smaller than that of the relatively weaker C–Br···N interaction in the co-crystals of both 1,4-diiodoperfluorobenzene and 1,4-dibromoperfluorobenzene with trans-1,2-bis(4-pyridyl)ethylene (Scheme 1d).[43] The X···N distance of these two isostructural co-crystals increased, respectively, from 2.768(8) and 2.814(2) Å to 2.820(2) and 2.873(2) for the iodo and bromo compounds when the temperature was increased from 90 to 292 K.

3 Hydrogen Bond Dimensionality and Thermal Expansion

The order of thermal expansion among the carbon allotropes is fullerene > graphite > diamond, and the covalent bond network dimensionality in them is zero (0D) in fullerene, two (2D) in graphite and three (3D) in diamond.[33–35, 44, 45] Therefore, thermal expansion decreases along with increase in the dimensionality in covalent-bonded network. Does it apply to conventional hydrogen bonds in organic crystals also? In other words, can the thermal expansion in organic crystals be controlled by changing the hydrogen bond dimensionality? It is a very pertinent question in the context of using crystal engineering strategy to control thermal expansion in organic solids. It is possible to design crystal structures with different hydrogen bond dimensionalities and if hydrogen

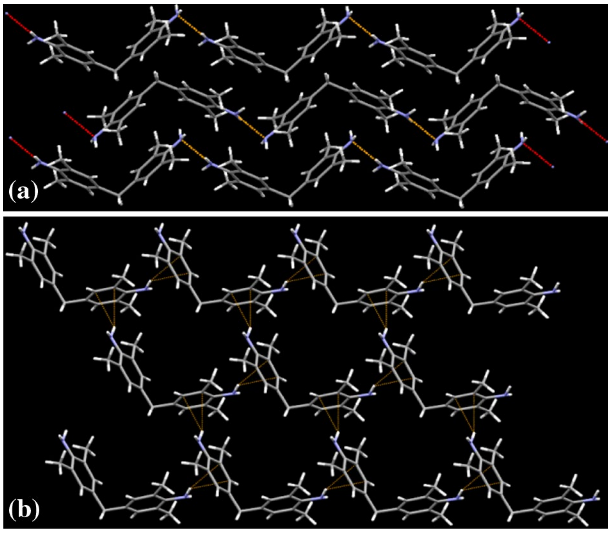


Figure 2: 4,4′-Methylenebis-(2,6-dimethylaniline) molecules form **a** 1D chain via N–H···N hydrogen bond in the MBDA-1D structure and **b** N–H···π interactions in the MBDA-0D structure by the N–H groups.

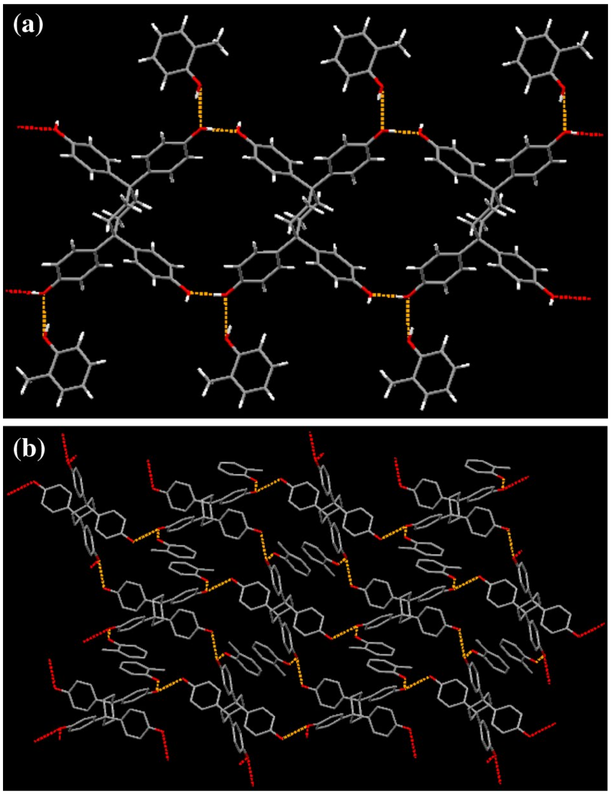
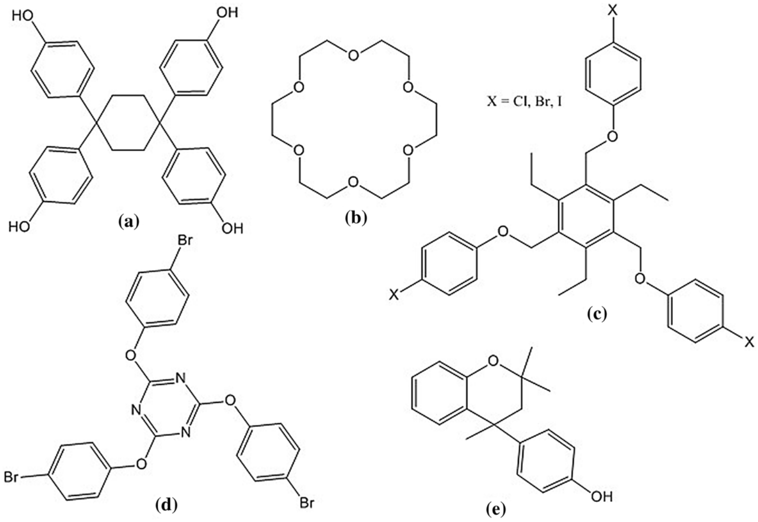


Figure 3: **a** 1D hydrogen-bonded tape structure in THPC-oc-1D form, and **b** 2D hydrogen-bonded sheet like structure in THPC-oc-2D form.

Polymorphs: Crystals with the same chemical composition but different crystal structures.

bond dimensionality can be correlated to thermal expansion, then the thermal expansion of the systems can also be controlled by varying hydrogen bond dimensionality. To answer this question, thermal expansion of some polymorphs, with different hydrogen bond dimensionality, have been studied. The systems discussed in this section are shown in Scheme 2.



Scheme 3: Host molecules discussed in the Sect. 4.

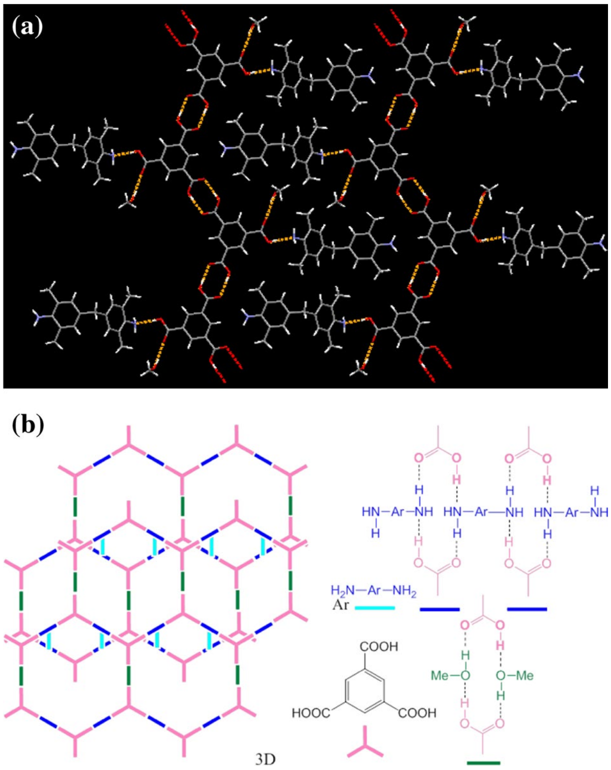


Figure 4: **a** 1D hydrogen-bonded interdigitated structure, and **b** schematic diagram of the 3D hydrogen-bonded network in the two forms of BTA.MBDA.MeOH complex.

Tetrolic acid (Scheme 2a) is reported to be dimorphic.[46] The acid molecules form catemeric 1D hydrogen-bonded chain in one crystal structure (TA-1D) (Fig. 1a) and in the other crystal structure (TA-0D) the molecules are assembled via usual centrosymmetric 0D hydrogen-bonded carboxylic acid dimers (Fig. 1b). In the TA-0D structure, the dimers also form molecular chains along the molecular axis but via weak Me···Me contacts. Saha et al. have shown that the

Dimorphic: Two different crystal structures with same chemical composition.

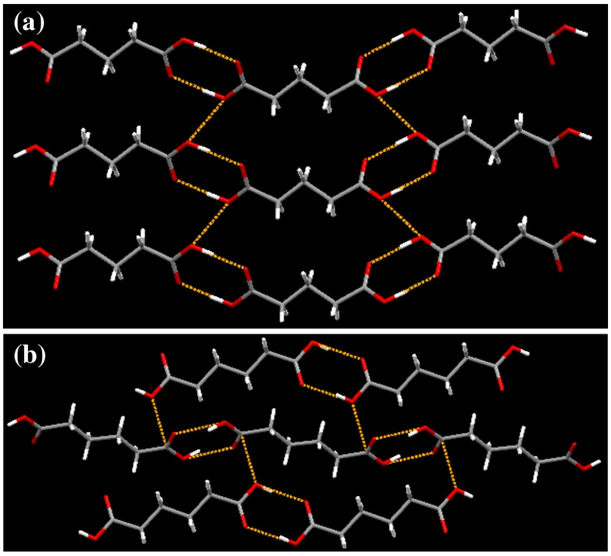


Figure 5: **a** O···O repulsive interaction in the crystal structure of $HOOC(CH_2)_3COOH$ and **b** O···C(COOH group) attractive interaction in the crystal structure of $HOOC(CH_2)_4COOH$.

volumetric thermal expansion of the TA-0D form ($\alpha_v = 332$ MK^{-1}) is much higher than the TA-1D form ($\alpha_v = 265$ MK^{-1}).[47] The difference in volumetric expansion between these two forms is mainly due to the difference in thermal expansion along the molecular chains. Due to the presence of strong hydrogen bond along the chains in the TA-1D form, the thermal expansion in this form is smaller than that in the TA-0D form in which the dimers are weakly bonded along the chain direction. These two forms are interconvertible to each other via single crystal to single-crystal phase transformation (SCSCPT). This phenomenon has also been explained in terms of thermal expansion. In the TA-1D structure, along the chain axis, the COOH terminal forms strong O–H···O hydrogen bonds, whereas the Me terminal forms weak Me···Me contact with the neighboring chains along the same direction. On the one hand, thermal expansion of strong O–H···O hydrogen-bonded side is expected to be smaller than the weak Me···Me contact side, but on the other hand, due to symmetry constrain, both the ends are supposed to expand simultaneously with equal magnitude along the chain direction. These two contradicting conditions cause phase transformation at higher temperature and system's adoption of the TA-0D structure in which both the terminals expand independently. The form with higher thermal expansion is stable at higher temperature and the one with lower thermal expansion is stable at lower temperature.

The difference between the thermal expansions of the two forms of 4,4′-methylenebis-(2,6-dimethylaniline) (Scheme 2b) has been found to be even more prominent.[48] The form which contains N–H···N hydrogen-bonded 1D molecular chain (MBDA-1D) (Fig. 2a) exhibits a volumetric thermal expansion 146(16) MK^{-1}, but the other, where such conventional hydrogen bond does not exist in the crystal structure (MBDA-0D) and the NH_2 groups are involved in N–H···π interactions, exhibits a volumetric thermal expansion as high as 235(9) MK^{-1} (Fig. 2b). Strongly vibrating Me groups caused a very high anisotropic thermal expansion (−174(8), 174(3) and 229(3) MK^{-1} along the principal axes) in the MBDA-0D form.

In contrast to the above observations, in the case of *o*-cresol solvates of an "X"-shaped host, 1,1,4,4-tetrakis(4-hydroxyphenyl)cyclohexane (THPC) (Scheme 2c), the two forms experience a very similar volumetric thermal expansion.[49] One of the two solvates is made of 1D O–H···O hydrogen- bonded tape-like structure (THPC-oc-1D) (Fig. 3a), whereas in the other structure the molecules are assembled in a 2D O–H···O hydrogen-bonded sheet (THPC-oc-2D) (Fig. 3b). The volumetric thermal expansion coefficients are found to be 124(8) and 128(3) MK^{-1}, respectively, for these two forms. The 1D form exhibits negative (−23(4) MK^{-1}), zero (−3(8) MK^{-1}) and positive (148(5) MK^{-1}) thermal expansion along the three principal axes, whereas the 2D form exhibits positive (18(3), 40(1), 69(1) MK^{-1}) thermal expansion along all the three directions. Therefore, the 1D form experiences a higher anisotropic thermal expansion than its 2D counterpart.

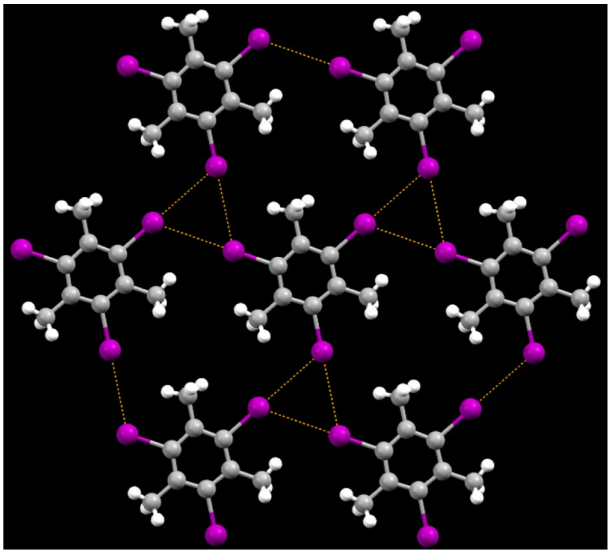
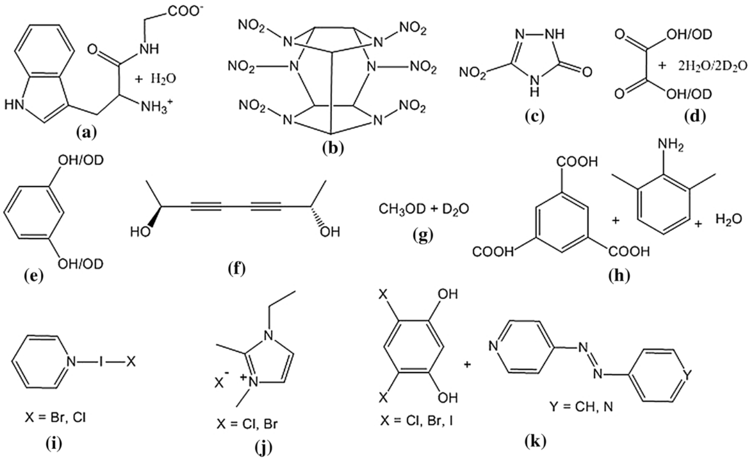


Figure 6: Packing diagram of triiodomesitylene. The molecules are assembled via iodotrimer synthon.



Scheme 4: Systems discussed in the Sect. 6.

The 1:1:1 complex of benzene-1,3,5-tricarboxylic acid (BTA), 4,4′-methylenebis(2,6-dimethylaniline) (MBDA), and methanol (Scheme 2d) is another interesting system where the two forms differ in the hydrogen-bonding dimensionality and their thermal expansion properties have been compared.[50] In one form, the molecules are assembled in an 1D hydrogen-bonded chain (Fig. 4a), whereas in the other form, the molecules are linked via 3D hydrogen-bonded network (Fig. 4b). The 1D hydrogen-bonded chains are interdigitated and the 3D hydrogen-bonded networks are interpenetrated. Interestingly, these 1D and 3D hydrogen-bonded forms exhibit comparable volumetric thermal expansion coefficients, 153(5) and 165(5) MK^{-1}, respectively. Both the forms exhibit uniaxial negative thermal expansion. In line with the above solvate structures, it was expected that the 1D form would exhibit a higher anisotropic thermal expansion compared to the 3D form. But interestingly, the 3D form exhibited a larger anisotropic thermal expansion (−35(1), 43(1), and 155(3) MK^{-1} along the principal axes), caused by sliding of layers, than the interdigitated 1D form (−7(2), 15(2), and 140(4) MK^{-1} along the principal axes).

Uniaxial negative thermal expansion: Contraction of a material along one of the three principal axes with increasing temperature.

Glycine (Scheme 2e) exists in three forms. The molecules in α form are assembled via 2D hydrogen-bonded network, whereas the β and γ forms are made up of 3D hydrogen-bonded networks.[51]

Interestingly, the α ($\alpha_v = 99(2)\ \mathrm{MK}^{-1}$) and the β ($\alpha_v = 97(2)\ \mathrm{MK}^{-1}$) forms exhibited very similar volumetric thermal expansions, whereas the γ form ($\alpha_v = 83(1)\ \mathrm{MK}^{-1}$) exhibited a relatively lower volumetric thermal expansion.[50]

4 Host–Guest Systems and Thermal Expansion

Host–guest system is one of the main streams of supramolecular chemistry.[52–56] Therefore, there is a definite interest to know whether the thermal expansion of a host lattice is affected by the guest molecules and if these molecules are capable of modulating it, then the question is the kind of influence they exert on the host lattice. There are some interesting thermal expansion studies on organic host–guest systems, as discussed below (Scheme 3).

Atomic displacement parameters: These parameters essentially give an idea about the thermal motion of the atoms.

Saha et al. have reported a thermal expansion study on a set of organic solvates, where the host was the "X"-shaped molecule, THPC (Scheme 3a) as mentioned already.[49] This molecule forms isostructural solvates with phenol (THPC-ph), *m*-cresol (THPC-mc), and *p*-cresol (THPC-pc), but with *o*-cresol it formed dimorphic solvates (mentioned above). Apart from these solvates, they were also able to study thermal expansion of the guest-free form of THPC, which was made of two-dimensional hydrogen-bonded THPC molecules. The O–H···O hydrogen bond strength was found to be the strongest in the isostructural solvates, which is followed by the guest-free form and then by the dimorphic solvates. On the other hand, the guest content was found to be the highest in the isostructural solvates (guest:host, 3:1), which is followed by dimorphic solvates (guest:host, 2:1) and no guest in the guest-free form (guest:host, 0:1). Interestingly, this is also the order of volumetric thermal expansion found in this series of systems indicating that higher guest content in closed packed solvates, in general, causes higher thermal expansion. The guest-free form possesses lowest packing fraction in this series. They also have shown that the atomic displacement parameters (ADP) of the low melting guests are larger than those of the high melting host molecule and the ADP values of the guests increase faster with increasing temperature than the host molecule. The ADP of the host molecule in the solvates is larger than that of the same molecule crystallized in the guest-free form. In another work, where thermal expansion has been studied on a dimorphic solvate, benzene-1,3,5-tricarboxylic acid·4,4′-methylenebis(2,6-dimethylaniline)·methanol (1:1:1), the average ADP values of methanol guest

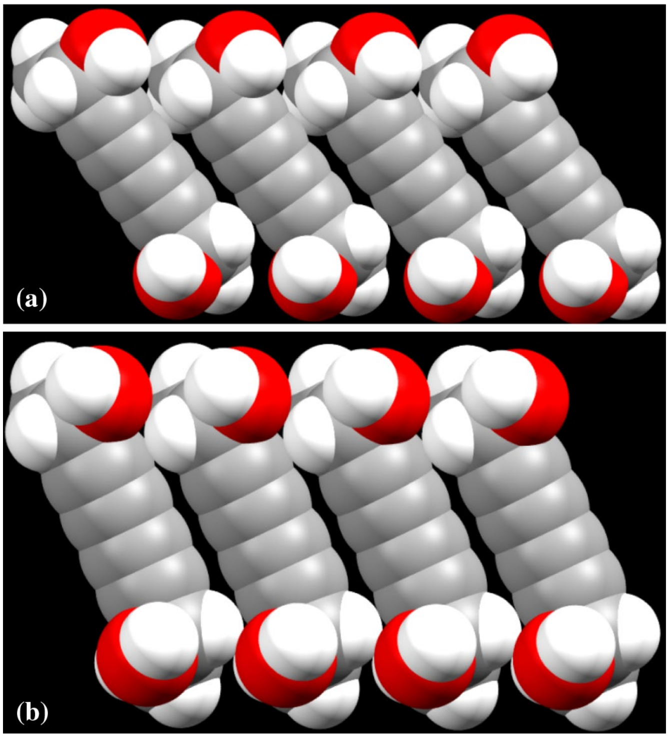


Figure 7: Stacking of the (S,S)-3,5-octadiyn-2,7-diol molecules in the **a** high- and **b** low-temperature phases. In **a**, the molecules are more tilted to the stacking propagation axis compared to those in **b**.

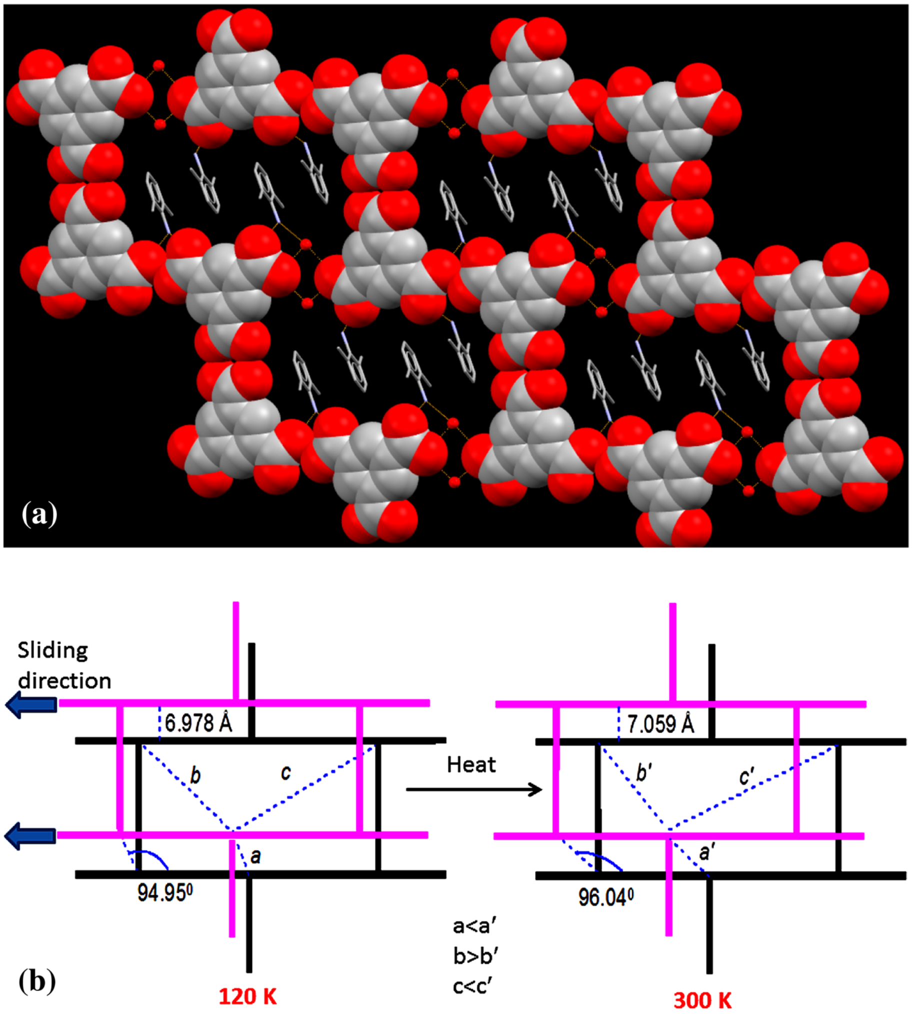


***Figure 8:* a** A single layer made of BTA (space fill model), DMA (capped stick model) and water (ball and stick model) is shown. **b** A schematic diagram of sliding of the layers is shown.

increase faster with increasing temperature compared to the other two components forming the host network.[50]

Barbour et al. have compared the thermal expansions of the isostructural nitromethane, acetonitrile, and iodomethane solvates of 18-crown-6 (Scheme 3b).[57, 58] They have shown that in spite of isostructurality, the first two solvates exhibit uniaxial negative thermal expansion, whereas the third one exhibits an uniaxial zero thermal expansion and the volumetric thermal expansion coefficients are also widely different, 378(22), 226(3), and 256(8) MK^{-1}, respectively.

In the two sets of isostructural systems of 2,4,6-triethyl-1,3,5-tris(4-halophenoxy)methylbenzene (halo = Cl, Br and I) (Scheme 3c) and their ethyl acetate solvates mentioned earlier, the volumetric thermal expansions of the three guest-free crystals were 2.8–3.4%, which is considerably smaller than the three corresponding ethyl acetate solvates (4.2–4.4%) in the temperature range 118–298 K.[42] Therefore, the presence of solvent molecules as guest causes higher thermal expansion in the host lattices.

2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (BrPOT) (Scheme 3d) crystallized in a guest-free form (BrPOT-gf) formed two concomitant inclusion compounds with each of dichloromethane (DCM), tetrahydrofuran (THF), and hexamethylbenzene (HMB).[59–63] All the three channel structures with THF (BrPOT·THF-channel), DCM(BrPOT·DCM-channel), and HMB (BrPOT·HMB-channel) are isostructural, whereas the cage structure, formed with THF (BrPOT·THF-cage I), is different from the two isostructural cage structures formed with DCM (BrPOT·DCM-cage-II) and HMB

(BrPOT·HMB-cage II). It has been shown that the host–guest systems possess higher thermal expansion than the guest-free form, except the case of BrPOT·DCM-channel crystal, which shows a comparable thermal expansion to the guest-free form. Because of high instability, a large amount of guest molecules escaped from the channel of the BrPOT·DCM-channel structure during the experiment, causing a smaller thermal expansion than expected. One more feature, noticed in these structures, is that the cage crystals exhibit higher thermal expansion than the corresponding channel counterpart. It has been argued that due to opening in the channel structure, the vibration of the guest molecules is less effective in causing thermal expansion in the host lattice.

White et al. have studied the thermal expansion properties of the isostructural guest-free form of 4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman, Dianin's compound (Scheme 3e), and its ethanol solvate.[64] Their study revealed that the solvate crystal experienced a higher thermal expansion than the corresponding guest-free form caused by increased anharmonicity in the vibrational amplitude.

5 Melting Point and Thermal Expansion

According to Lindemann's theory, the higher the thermal expansion, the lower the melting point.[65, 66] This theory works more or less well in the case of metals. But does it work in the case of complex molecular systems, such as organic molecules? Thermal expansion has been correlated in a few cases to the melting point of structurally similar organic systems.

Elastic modulus: The ratio of the force (stress) exerted upon a substance or body to the resultant deformation (strain). It is a measure of the stiffness of a solid material. It is also known as Young's modulus.

The aliphatic dicarboxylic acids, $HOOC(CH_2)_nCOOH$ ($n = 0–8$), show alternation both in melting point and in elastic moduli.[67, 68] The compounds with $n =$ odd number possess lower melting point and higher elastic modulus than the corresponding neighbor with $n =$ even number in this homologous series. It has been shown that lower melting odd diacids actually experience higher volumetric thermal expansion than the corresponding higher melting even diacids.[41] In both types of crystal structures, the molecules form parallel molecular chains via carboxylic acid dimer synthon. It has been argued that in the odd diacids, molecules repel each other along the perpendicular direction of the molecular chain due to close proximity of oxygen atoms (Fig. 5a). On the other hand, in the even diacids, the molecules experience an attractive force between the oxygen atom of one molecule and a carbon atom of the COOH group of another molecule along the perpendicular direction of the molecular chain (Fig. 5b). This interaction difference is found to be mainly responsible for alternation in thermal expansion.

The chloro, bromo, and iodo derivatives of 2,4,6-triethyl-1,3,5-tris(4-halophenoxy)methylbenzene (Scheme 3c) are found to be isostructural. As usual, the order of melting points in these three compounds is iodo (m.p. = 217–219 °C) > bromo (m.p. = 201–203 °C) > chloro (m.p. = 176–178 °C).[42] On the other hand, the order of thermal expansion in these three crystals in the temperature range 118–298 K happened to be the reverse of the order of their melting points. The chrolo crystal expands in the temperature range 118–298 K by 3.8%, which is followed by bromo crystal (3.1%), and the least expansion was found in the iodo crystal (2.8%).

There is an interesting case of correlation between melting point and thermal expansion reported in the series of trihalomesitylene (halo = Cl, Br and I).[69] These three compounds are isostructural.[70] Interestingly, the corresponding methyl derivative (hexamethylbenzene) is two-dimensionally isostructural to these three compounds.[71] In all these four structures the molecules are assembled in a two- dimensional sheet and each molecule is surrounded by six other molecules in this sheet (Fig. 6). In the case of halogenated compounds, the halogens are involved in halogen trimer synthon. In contrast to the 2,4,6-triethyl-1,3,5-tris(4-halophenoxy)methylbenzene family, the order of melting point in this series is found to be hexamethylbenzene (m.p. = 166 °C) ≪ trichloromesitylene (m.p. = 205 °C) ≈ triiodomesitylene (m.p. = 206 °C) < tribromomesitylene (m.p. = 226 °C). It is known that the halogen···halogen interactions are stronger than Me···Me interactions and also the atomic weights of the halogens are higher than the Me group. Therefore, it is not surprising that the melting point of hexamethylbenzene is much smaller than that of the halogenated derivatives. But what is interesting in this case is the melting point of triiodomesitylene, which is close to that of trichloromesitylene, instead of being the highest in this series. Thermal expansions of these compounds have been investigated and it has been found that the order of change in volume in the temperature range of 118–262 K is hexamethylbenzene > trichloromesitylene ≈ triiodomesitylene > tribromomesitylene. Therefore, compounds with higher melting point exhibit a smaller volumetric change due to thermal expansion in this series too.

6 Miscellaneous Examples

There are some discrete but interesting studies on thermal expansion in organic crystals, reported in the literature. Some of them are discussed here (Scheme 4).

Birkedal et al. have reported thermal expansion study of the monohydrate of dipeptide tryptophylglycine (Scheme 4a) crystal.[72] The molecules are arranged in a helical fashion forming channels in the crystal structure. The channels are filled with hydrogen-bonded water chains. With decreasing temperature, the hydrogen bonds become more directional and the water molecules start occupying favored sites, causing a uniaxial negative thermal expansion along the channel direction. A similar phenomenon causes lowering of density when the liquid water is condensed to ice.

Thermal expansion studies have been performed on some organic energetic materials too. In the energetic materials, γ and ε polymorphs of hexanitrohexaazaisowurtzitane (HNIW) (Scheme 4b) and β form of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) (Scheme 4c), the thermal expansion coefficients along the principal axes are $-8.8(9)$ to $-5.0(3)$, 10.5(7) to 21.1(3), 63(2) to 84.3(6) MK^{-1} for γ-HNIW, 4(2) to 19.6(6), 29(2) to 45(1), 30(2) to 53.8(7) MK^{-1} for ε-HNIW, and -4.7 to 12.3, 64.0 to 66.8, 57.7 to 90.2 for β-NTO in the temperature range 100–298 K.[73, 74] Therefore, in these energetic materials, the thermal expansion is found to be less anisotropic.

To study the effect of deuteration, thermal expansion experiments have been performed on some deuterated compounds. Comparison of thermal expansion between deuterated ($(COOD)_2.2D_2O$) vs. nondeuterated ($(COOH)_2.2H_2O$) oxalic acid dihydrate (Scheme 4d) and deuterated ($C_6H_4(OD)_2$) and non-deuterated ($C_6H_4(OH)_2$) resorcinol (Scheme 4e) shows that the thermal expansion of the deuterated crystals is slightly smaller than the corresponding nondeuterated crystals.[75] These studies show that thermal expansion can be tuned by deuteration too.

Barbour et al. performed thermal expansion studies of dimorphic (*S*,*S*)-3,5-octadiyn-2,7-diol (Scheme 4f). Both of these forms exhibit very similar hydrogen-bonding pattern and similar packing.[76, 77] They differ slightly only in the stacking angle of the molecules (Fig. 7). But, interestingly, the thermal expansion properties of these two forms have been found to be dramatically different. One of the forms shows a highly anisotropic thermal expansion (156 $MK^{-1} < \alpha_a <$ 515 MK^{-1}; -32 $MK^{-1} < \alpha_b < -85$ MK^{-1} and -48 $MK^{-1} < \alpha_c < -204$ MK^{-1}) in the temperature range 225–330 K, whereas the other form does not. This example shows how sensitive the thermal expansion could be with respect to the packing of the molecules in a crystal structure.

Fortes et al. have reported a very high volumetric thermal expansion (494(6) MK^{-1}) in $CH_3OD.D_2O$ (Scheme 4g) with linear thermal expansion coefficients 462(4) MK^{-1}, 93(4) MK^{-1} and $-61(4)$ MK^{-1} along the three principal axes in the temperature range 4.2–160 K.[78] Interestingly, this system also shows negative linear compressibility (NLC), and the direction of negative thermal expansion in this system was found to be along the NLC axis.

There is an interesting case of uniaxial negative thermal expansion due to the sliding of 2D hydrogen-bonded layers (Fig. 8).[79] In the 1:1:1 complex of 1,3,5-benzenetricarboxylic acid (BTA), 2,6-dimethylaniline (DMA), and water molecules, the BTA and DMA molecules form a 2D hydrogen-bonded layered structure, which are bridged via hydrogen-bonded water molecules (Scheme 4h). With change in temperature, the 2D layers of BTA and DMA start sliding with respect to each other, which caused an uniaxial negative thermal expansion in the system.

Energetic materials: Energetic materials, such as explosives, are a class of material that can release high amount energy which is stored as chemical energy.

Uniaxial negative thermal expansion in pyridine-IBr and pyridine-ICl (Scheme 4i) has been reported by Jones et al.[80] They have correlated this anomalous uniaxial negative thermal expansion to the weak C–H···X (X = Cl, Br) interactions in the crystal structures. As per their study, weakening of these interactions with increasing temperature caused the uniaxial negative thermal expansion in the systems.

1-Ethyl-2,3-dimethylimidazolium chloride and bromide (Scheme 4j) are isostructural.[81] The chloride system shows a high positive thermal expansion (187(2) MK^{-1}), a close to zero thermal expansion (7.03(2) MK^{-1}) and a small negative thermal expansion ($-12.8(6)$ MK^{-1}) along the three principal axes. On the other hand, the corresponding bromide system shows a biaxial negative thermal expansion ($-64.4(3)$ MK^{-1} and $-40(2)$ MK^{-1}) and a very high uniaxial positive thermal expansion (301(3) MK^{-1}). In spite of isostructurality, the two systems, interestingly, exhibit very different thermal expansion behaviors.

MacGillivray et al. have shown uniaxial zero thermal expansion in the 1:2 and 1:1 co-crystals of 2,4-dihaloresorcinol (halo = Cl, Br, I) with 4-phenylazopyridine (Scheme 4k, Y = CH) and 4,4′-azopyridine (Scheme 4e, Y = N), respectively.[82, 83] They observed pedal motion, which showed a dramatic influence on thermal expansion properties in the crystals, in the cases of 1:2 cocrystals (halo = Cl and Br). Interestingly, in the case of the 1:1 series, the co-crystal with the iodo compound (196(9) MK^{-1}) exhibited higher volumetric thermal expansion than the corresponding chloro (185(3) MK^{-1}) or bromo (181(2) MK^{-1}) compounds, and the latter two showed a comparable volumetric thermal expansion.

7 Conclusions

Thermal expansion studies on some organic systems have been discussed and some pertinent questions, such as how thermal expansion depends on interaction strength, hydrogen bond dimensionality, melting point, guest molecules in host–guest system, have been tried to answer in this mini review. It has been shown theoretically and experimentally that thermal expansion generally is smaller in the case of stronger interactions. The relationship between hydrogen bond dimensionality and thermal expansion has produced a mixed result. In some cases, systems with higher hydrogen bond dimensionality exhibit smaller thermal expansion, but in other cases they exhibit comparable thermal expansion with respect to the polymorphic form with lower hydrogen bond dimensionality. But none of the examples showed a system with higher hydrogen bond dimensionality exhibiting a significantly higher thermal expansion compared to its polymorphic form with lower hydrogen bond dimensionality. Among the solvate structures, it has been invariably shown that inclusion of solvent molecules in the organic host lattice causes higher thermal expansion in the lattice and the magnitude differs for different guests. Therefore, it is possible to tune the thermal expansion of a host lattice by changing the guest molecules. Melting point is a complex phenomenon and it depends on lots of parameters. One such parameter is thermal expansion. In this review few sets of isostructural/closely related structural systems have been chosen, which show reverse relationship between thermal expansion and melting point, i.e., system with higher melting point exhibits lower thermal expansion. Nevertheless, it should be noted that the number of examples concerning these types of studies is too small in the literature to draw any statistically meaningful conclusion. Therefore, to understand structure–property relationships discussed here more comprehensively, more studies need to be conducted; crystal engineering will play a pivotal role in understanding these relationships and will help designing new materials with desired thermal expansion properties.

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