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Review article

Thermal Expansion in Supramolecular Organic Compounds: An Overview

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ABSTRACT

Supramolecular organic molecules are composed of molecular assemblies held collectively by non-covalent bonding or interactions. These molecules exhibited negative and positive thermal enlargement apart from traditional substances. Their thermal response arises from the dynamic and bendy nature of their molecular frameworks, regularly leading to tunable or anomalous thermal expansion behaviors. This work highlights the thermal expansion phenomenon in supramolecular organic compounds. Supramolecular organics with controlled thermal enlargement are vital for packages like close to-zero thermal growth composites in precision instruments, aerospace, and electronics. Their tunable conduct fits thermal actuators and sensors for temperature manipulation, even as their thermal houses beautify power devices like thermoelectrics and photovoltaics.

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1. Introduction

Supramolecular chemistry offers with the layout and look at of complex structures fashioned by non-covalent interactions. This subject has seen wonderful boom because of the potential of supramolecular structures to shape organized structures with precise physical and chemical properties that respond to environmental stimuli. Thermal enlargement is an essential property of materials, describing their tendency to alternate in extent or dimensions in response to temperature adjustments. While thermal growth is a highly nicely-understood phenomenon in metals and ceramics, natural supramolecular compounds exhibit awesome behaviors due to their reliance on weaker intermolecular interactions. This evaluate explores thermal expansion in supramolecular organic compounds [1-7]. The expansion conduct, the types of expansion exhibited, and the applications of these specific substances in generation and industry.

Thermal growth studies of basically organic crystals are essential for exploring the precise structure-property relationships that arise up from the complicated molecular architecture and diverse interplay types in these materials. Key elements influencing the thermal growth of natural crystals encompass intermolecular interactions, inclusive of van der Waals forces and π-π stacking, which fluctuate extensively from the ionic or metal bonds frequently present in inorganic structures [8-10]. Additionally, the melting factors of natural materials, which are typically decreased and greater variable than the ones of inorganic counterparts, can affect thermal stability and, therefore, thermal enlargement conduct. Another vital issue is the presence of visitor molecules in inclusion compounds, which could alter crystal structure, adjust thermal expansion coefficients, and introduce novel pathways for enlargement and contraction. Furthermore, the dimensionality and geometry of hydrogen bonds within natural crystal systems play an essential role, as those interactions can either restrict or promote anisotropic thermal responses depending on their orientation and strength.

Although thermal growth in materials has been substantially studied across diverse types, the research attention has predominantly been on inorganic systems, with great interest also given to metal-natural frameworks. Studies specifically concentrated on basically natural crystals, however, are rather few in quantity. Recent researches have started to deal with these factors, revealing treasured insights into how they form thermal expansion characteristics in organic systems. By inspecting those studies, we gain a clearer image of the way unique structural capabilities correlate with thermal properties, making an allowance for a more systematic know-how of the thermal behavior in organic crystals [11-14]. Such insights are vital, as they provide a foundation for advancing packages that rely upon thermal stability and responsiveness in organic substances, such as prescribed drugs, bendy electronics, and other rising technologies. The studies discussed on this assessment constitute a number of the maximum current and impactful contributions to this region, reflecting a growing interest in natural thermal enlargement and its implications for the design and application of superior natural substances.

2. Thermal Expansion

Materials upon heating generally expand along all directions. This phenomenon is known as Positive Thermal Expansion (PTE). Expansion occurs due to anharmonic vibrations of chemical bond, which can be understood by the asymmetric shape of the potential energy curve for simple diatomic molecule (Figure 1) [1]. However, there are some materials which contract upon heating and vice versa. The anomalous property of these materials called negative thermal expansion [1-3]. When a material neither contract not expands

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upon changing of temperature the phenomenon is called zero thermal expansion.3 ZTE has been observed in a very few compounds. However, ZTE can be achieved by mixing of PTE and NTE materials stoichiometrically [3,4].

Ice is an example of NTE material below 75 K. At 273K to 277K water shows enhanced density whereas below 75K ice shows NTE due to low energy transverse vibrations.5 NTE has been observed mostly in inorganic materials including metal oxides, cyanides [7], Metal-organic frameworks (MOFs). Nevertheless, many organic materials are also known for exhibiting NTE. Negative thermal expansion materials are very useful for their potential application as thermo-mechanical sensors, actuators, high precision optical instruments and high-performance explosive materials [5] Design of materials with desired NTE properties is still challenging because the mechanism of NTE varied from material to material (Fig. 1 and Fig. 2) [5-9]. Some of the mechanisms include low-frequency phonon modes, rigid unit modes (RUM), phase transitions, transverse vibration of atoms (Fig, 2), host-guest interactions, molecular packing, geometric flexibility [10-13], change of molecular conformation [14].

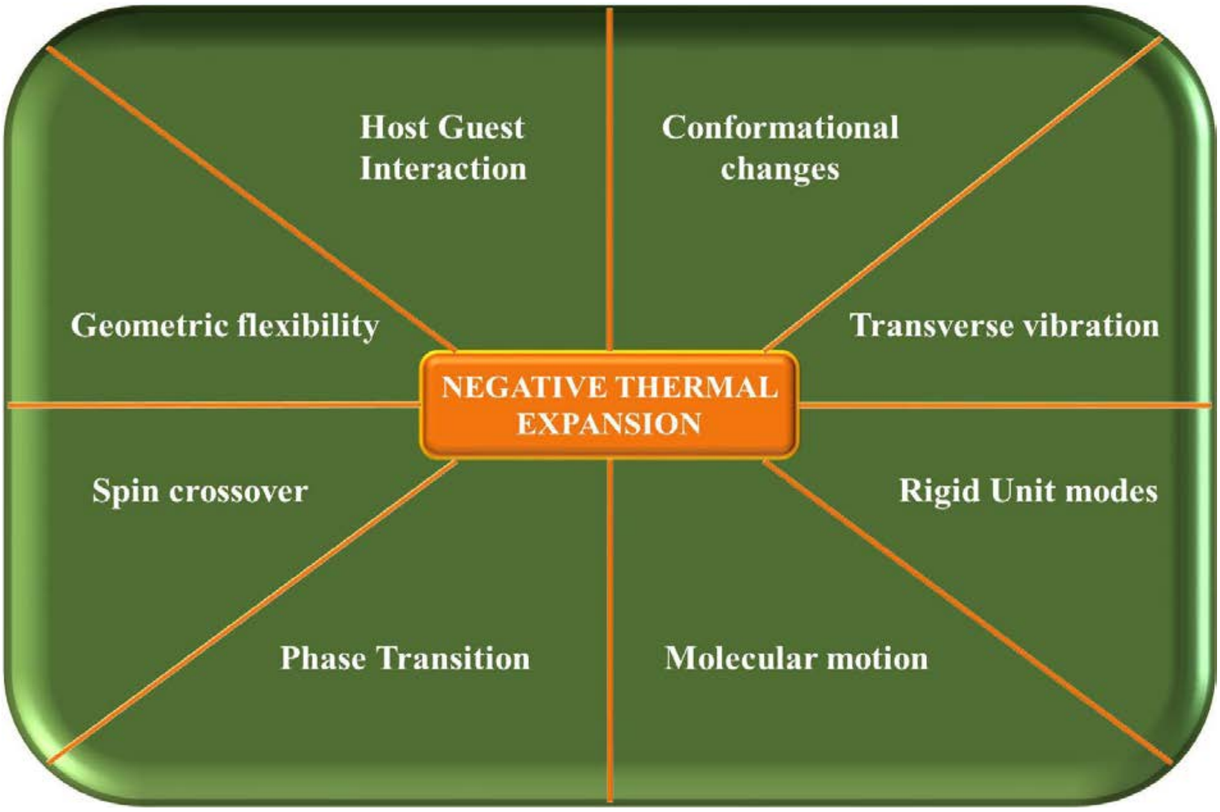


Figure 1: Different mechanisms for NTE in different materials.

Among the metal oxides ZrW2O8 is well-known compound for isotropic NTE. This material is composed of WO4 tetrahedra and ZrO6 octahedra having Zr-O-W linkage unit which induces NTE due to transverse vibration of oxygen atoms. Metal cyanides are studied by various research group for NTE property [7]. In these materials, the bridging atoms connect the metal atoms and forms a network of corner shared polyhedrons. On heating bridging atoms vibrate perpendicular to the chain resulting in shrinkage of the metal-metal distance which results in NTE behavior. MOFs, a new class of materials show greater structural flexibility and pores due to presence ofdifferent interactions like hydrogen bonds, π–π interactions in addition to covalent bonds and coordination bonds [8]. Therefore, under the external stimuli like temperature, these materials show structural changes resulting in unusual thermal expansion behavior. Thermal expansion in MOFs can be modified using different ligands. MOF-5 shows remarkable contraction in the temperature range 30 K to 293K. The organic ligand 1,4-benzenedicarboxylate in MOF-5 increases the flexibility due to the different motions of the benzene moiety resulting in NTE behavior. Kepert and coworkers showed isotropic NTE in MOF $Cu_3(BTC)_2$ (BTC=1,3,5-benzenetricarboxylate) with coefficient of thermal expansion (CTE) -4.9(1) $\times 10^{-6}$ K^{-1} in the temperature range 100K-300K. Use of elongated ligand 4,4',4''-benzene-1,3,5-triyl-tribenzoate (BTB) resulted three times more NTE behavior than $Cu(BTC)_2$. Goodwin and coworkers reported colossal thermal expansionin the flexible framework material $Ag_3[Co(CN)_6]$ in which PTE has been observed along *a* and *b* axes due to argentophilic interactions while NTE was found along the *c*-axis due to hinge like motion [7].

Thermal expansion properties have been modified by the introduction of guest molecules in framework materials. Goodwin research group have reported that the insertion of water molecule in $MPt(CN)_6$ (M= Zn, Cd) switches the thermal expansion behavior from negative to positive [7]. Presence of water molecules impedes the transverse vibrations which give rise to positive thermal expansion (PTE). Thermal expansion properties of $Cd(CN)_2$ has been modified in presence of CCl_4 guest molecules [7]. In presence of CCl_4 guest CTE is $\alpha_l = +10 \times 10^{-6}$ K^{-1} whereas in absence of guest $\alpha_l = -33\times10^{-6}$ K^{-1}. In case of prussian blue analogues such as, $YFe(CN)_6$ introduction of K^+ and water molecules enables switching from PTE to NTE volumetric thermal expansion coefficient being ($\alpha_v = +42.72 \times 10^{-6} K^{-1}$) to ($\alpha_v = -33.67\times10^{-6} K^{-1}$) [15,16].

Organic molecular crystals belong to soft materials as the supramolecular interactions such as van der Waals forces, π– π interactions, hydrogen bonds, halogen–halogen interactions involving in molecular assemblies are weak in nature [17]. These materials are more sensitive to external stimuli and have large coefficient of thermal expansion compare to inorganic and MOF materials. CSD analysis by van der Lee showed that out of the 4719 unique organic compounds 60% compounds show normal positive thermal expansion in all the directions, while 33.1% compounds show uniaxial negative thermal expansion and 5.3% compounds biaxial negative thermal expansion and about 1.5% exhibits isotropic negative thermal expansion. More recently CSD survey for organic molecular crystals by Bond reveals that uniaxial NTE is more common than biaxial NTE [11].

Mechanisms of NTE in organic molecular materials have been explained by various mechanisms such as molecular motion, transverse vibration, sliding of layers of molecules, conformational changes, steric hindrance twisting of moieties etc [16]. Das *et. al* found that the organic molecule (S,S)-octa-3,5-diyn-2,7-diol exhibits large and reversible uniaxial PTE and biaxial NTE due to concerted motion of molecules [8]. Thermal expansion of a charge transfer complex has been explained on the basis of strength of π–π interactions [9]. In host-guest system thermal expansion behavior can be tuned by varying the guest molecules. Organic inclusion compound of 18-crown-6 (nitromethane solvate) shows large anisotropic thermal expansion, while its analogue acetonitrile and iodomethane solvate does not show such huge abnormal behavior. Bhattacharya and Saha have shown different thermal expansion behavior by an organic host molecule in presence of different guest molecules due to the sliding of layers [18].

2.1 Experimental measurement of thermal expansion (α)

Thermal expansion is generally studied by variable temperature diffraction experiment such as variable temperature single crystal X-ray Diffraction (VTSCXRD), variable temperature Neutron diffraction (VTND), variable temperature powder X-ray Diffaction (VTPXRD), dilatometry. From the diffraction experiment unit cell parameters at different temperatures are determined which are used to calculate coefficient of thermal expansion (CTE) by the following equations^{2e}:

$$\alpha_L = \frac{L - L_i}{L_i(T - T_i)} \quad \text{or} \quad \alpha_L = \frac{\Delta L}{L_i \Delta T}$$

$$\alpha_V = \frac{V - V_i}{V_i(T - T_i)} \quad \text{or} \quad \alpha_V = \frac{\Delta V}{V_i \Delta T}$$

where ΔL and ΔV represents the change in length and volume of the material with respect to the change of temperature ΔT. L_i and V_i represents the initial length and volume. α_L and α_V defines the linear CTE and volumetric CTE. In case of isotropic solids $\alpha_V = 3\,\alpha_L$ while in case of anisotropic solids, magnitude and sign of CTE have different values of α_a, α_b and α_c which contributes to volumetric thermal expansion.

2.2 Co-crystals and thermal expansion

History of co-crystals dates back to 1850s when molecular co-crystal quinhydrone was synthesized [1-8]. Engineering of co-crystal has been employed by mixing of the two or more individual components to manipulate thermal expansion properties which are different from the individual components [18]. The coaching of co-crystals the use of mechanochemistry aligns with the pursuit of sustainable, green methods, at the same time as additionally exploring the development of progressive multicomponent substances—currently one of the most dynamic regions in crystal engineering. In co-crystals, the physico-chemical houses of the man or woman additives integrate, have interaction, or even transform, resulting in substances with potentially more advantageous houses. This approach holds precise promise in solid-nation chemistry applications, specifically within the pharmaceutical enterprise, wherein co-crystals offer a singular method for growing new drug formulations. These formulations may additionally improve drug solubility, stability, bioavailability, and standard performance, consequently presenting an road for optimizing current prescription drugs without altering the active elements themselves. As a result, co-crystals represent a powerful device for advancing each sustainable chemistry and pharmaceutical innovation [12,19]. Co-crystal synthesis by grinding has proved to be effective than the solution based cocrystallization strategy. Binary co-crystals are very common and reported in literature.42 Very few co-crystals of higher order are reported [19,20]. Saha and Desiraju has reported the rare quaternary co-crystal which is based on resorcinol-phenazine-tetramethylpyrazine-pyrene [21]. The acid···amide dimer heterosynthon, generally located inside the cocrystals of aromatic acids and primary amides, is a awesome structural motif characterized by means of the cooperative interplay of hydrogen bonding interactions. These interactions contain both N–H···O and O–H···O hydrogen bonds, which make contributions to the formation of a strong and directional dimeric meeting. The presence of this heterosynthon is efficiently diagnosed with the aid of unique marker peaks inside the infrared spectra. These peaks aren't simplest indicative of the person N–H···O and O–H···O hydrogen bonding interactions however additionally mirror the collective nature of the prolonged synthon framework, offering a spectral fingerprint for this supramolecular association. Organic salt and thermal expansion

Organic salts are multi-component systems in which there occurs complete transfer of proton from acid to the base [18]. The concept of a structural landscape revolves across the idea that a single natural molecule can undertake a variety of awesome crystal structures. These systems together shape a "landscape" that represents the numerous methods in which the molecule can arrange itself in a crystalline kingdom. This is not constrained to a single shape; as a substitute, it encompasses multiple sorts of crystalline preparations, which includes polymorphs, pseudopolymorphs, and solvates. Polymorphs consult with special crystal forms of the identical molecule, bobbing up from variations in molecular packing or intermolecular interactions. Pseudopolymorphs, on the other hand, consist of crystalline bureaucracy in which solvent molecules are included into the lattice, growing solvates or hydrates. In sure contexts, the structural landscape may expand to consist of multi-factor crystals, usually called co-crystals [19]. These are crystalline systems wherein the reference molecule is mixed with one or greater different molecules, ensuing in unique crystal architectures. Furthermore, the landscape can every so often expand to encompass the crystal systems of molecules which can be chemically or structurally much like the reference molecule, imparting additional perception into its crystallization conduct (Fig. 2) [22,23]. Figure 2 gives an outline of various structural behaviors in molecular substances. Panel (a) shows the capacity energy nicely of paired atoms. Panel (b) discusses mechanisms accountable for poor thermal growth (NTE) in molecular materials. Panel (c) highlights polymorphism, phase transitions, and uncommon thermal enlargement in halogen derivatives of four-phenyl substituted imidazoline. Panel (d) shows the crystal structure of the orthorhombic shape of dabcoHCl·3H2O at 270 K, showing disordered water molecules and chloride anions (left), and the temperature-structured change in its unit-cellular quantity (right).

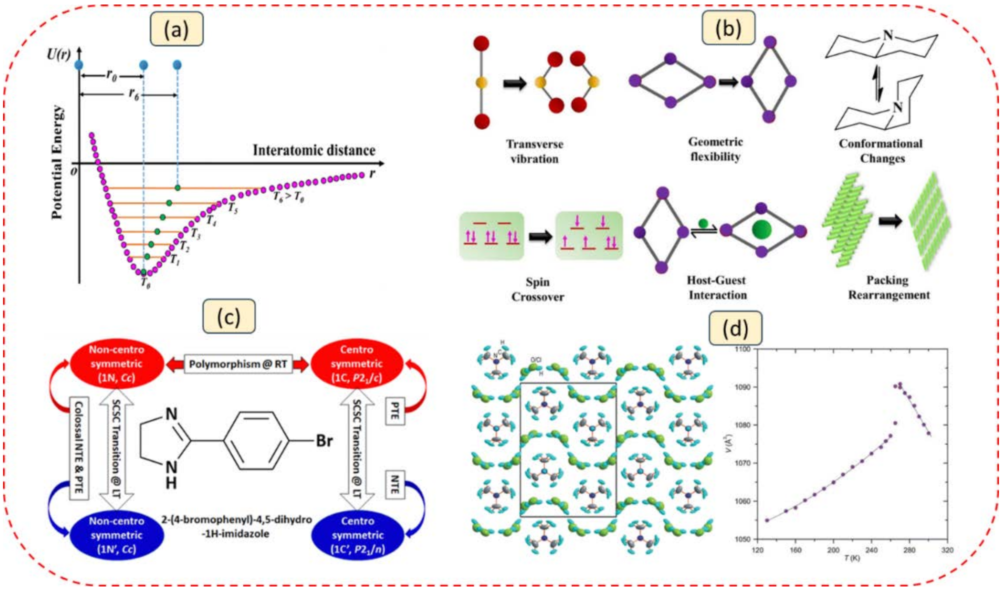
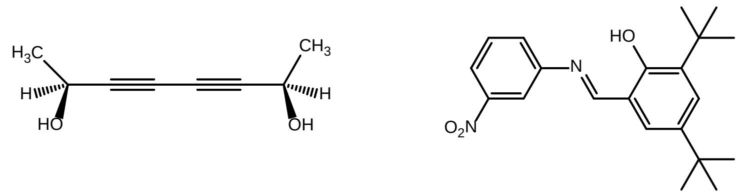
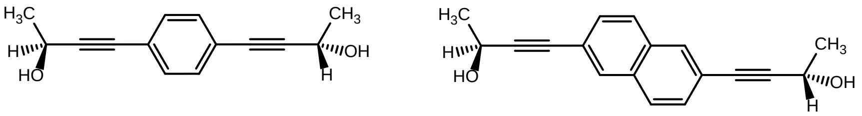


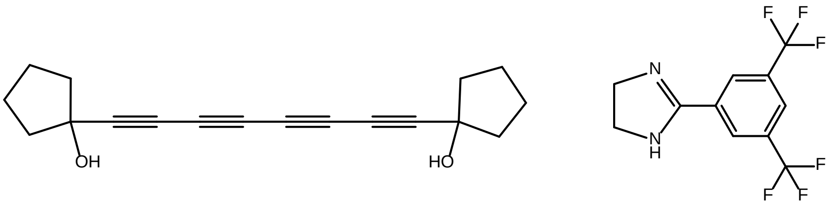
Figure 2: (a) Schematic diagram of the potential energy well of paired atoms; (b) Various mechanisms leading to negative thermal expansion (NTE) behaviour in molecular materials; (c) Polymorphism, phase transition, and unusual thermal expansion characteristics in halogen derivatives of 4-phenyl substituted imidazoline; (d) he crystal structure of the orthorhombic form of dabcoHCl·3H2O at 270 K, viewed along, showing the H-bonded disordered H2O molecules and Cl− anions (left). Temperature dependence of the unit-cell volume of dabcoHCl·3H2O (right) (Adapted from ref. [23] under CCBY, Copyright RSC 2024).



(a). (S,S)-octa-3,5-diyn-2,7-diol **(b).** ***N*-3,5-di-tert-butylsalicylide-3-nitroaniline**



(c). 1,4-Bis(S-3-butyn-2-ol)-benzene **(d). 2,6-bis(S-3-butyn-2-ol)-naphthalene**



(e). 1,1'-(octa-1,3,5,7-tetrayne-1,8-diyl)dicyclopentanol **(f). 2-(3,5-bis(trifluoromethyl)phenyl)-4,5-dihydro-1H-imidazolf**

Figure 3. Organic compounds (a-f) involved in thermal expansion properties

In order to extend to research area in 2024, Sethi & Das studied switching from PTE to NTE thermal expansion along the crystallographic a-axis in a tetrayne-diol compound such as 1,1′-(octa-1,3,5,7-tetrayne-1,8-diyl)dicyclopentanol **(e)** [24]. Interestingly, in 2024, Vikas *et. al.* reported anisotropic thermal expansion and order–and-disorder phase transition in imidazole-based novel single-component molecular crystals, 2-(3,5-bis(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazole **(f)** as shown in **figure 3**. Research particularly in this area convey several practical applications in fundamental research. The material displays PTE, ZTE, and NTE thermal expansions along a-, b-, and c-axes, respectively. The study shows isosymmetric dynamic order–disorder reversible phase transition and diverse thermal expansions along the crystallographic axes just after and before the phase transition. This study provides new perceptions into the unusual thermal behavior, thus, sustainable pure organic material can be a favorable candidate for device applications [25].

The designing of material is highly challenging which shows contraction upon heating due to varying mechanism. More interestingly, in order to convey the research in the next step, the worker considered a potential molecule imidazole for the further study, in 2024, L. Negi *et al.* reported transverse vibration and noncovalent interactions induced restricted thermal expansion of several type of organic salts made by the proper combination of imidazole and carboxylic acids as shown in **figure 4 (g-n).** Remarkably, they considered imidazolium salts of five aliphatic α, ω-alkane dicarboxylic acids and three aromatic acids for thermal expansion properties. In his study, they has been observed either uniaxial or biaxial NTE and axial zero thermal expansion (ZTE). In concisely, we can say that, the imidazolium moiety in the salts participate for the anomalous thermal expansion behaviour. The controlled thermal expansion behaviour of the salts is responsible to the H-bonding as well as transverse vibration in all the imidazolium salts [26].

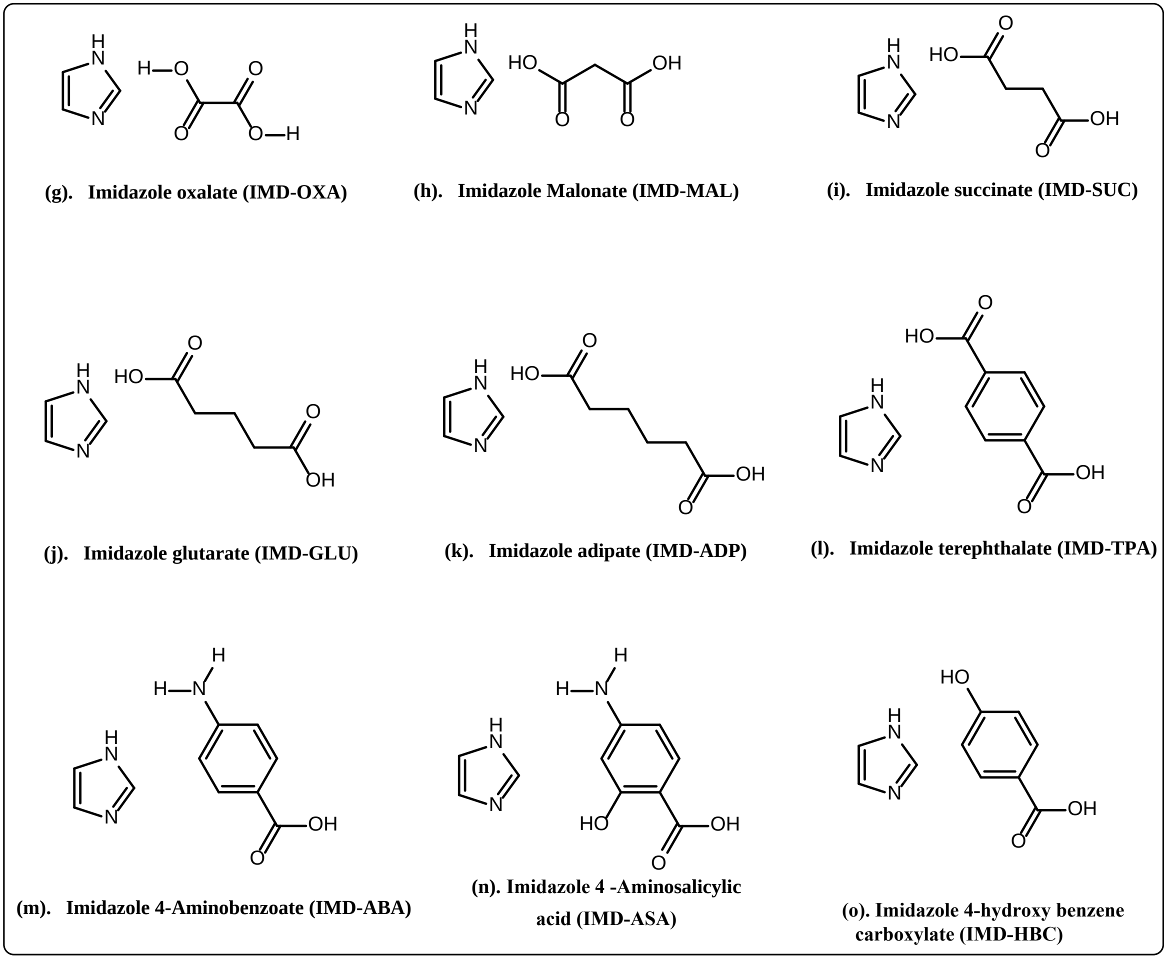
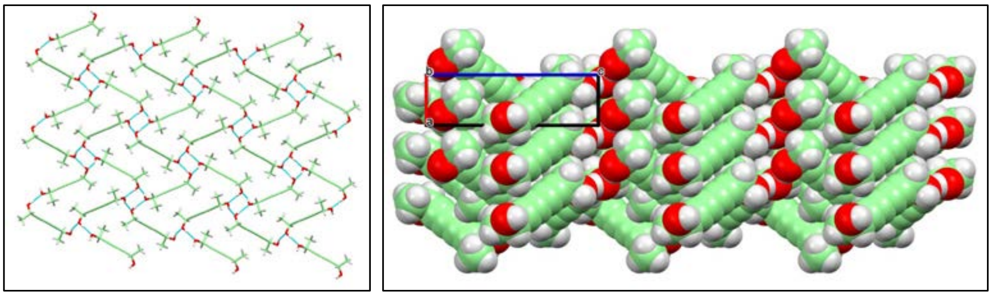
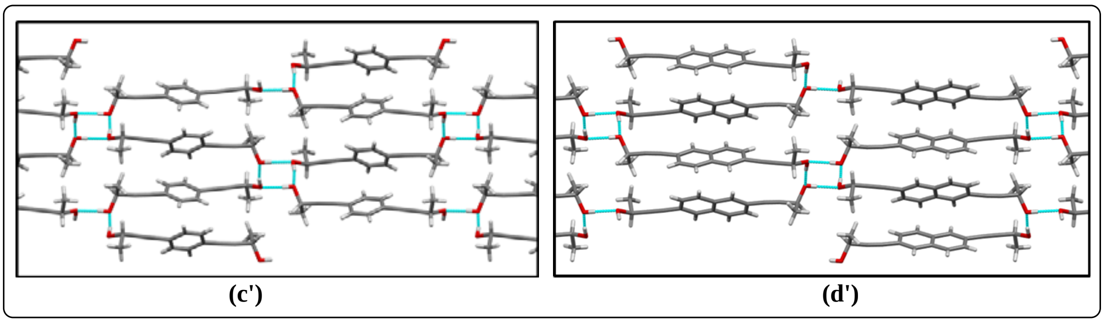

(g). Imidazole oxalate (IMD-OXA)
(h). Imidazole Malonate (IMD-MAL)
(i). Imidazole succinate (IMD-SUC)
(j). Imidazole glutarate (IMD-GLU)
(k). Imidazole adipate (IMD-ADP)
(l). Imidazole terephthalate (IMD-TPA)
(m). Imidazole 4-Aminobenzoate (IMD-ABA)
(n). Imidazole 4 -Aminosalicylic acid (IMD-ASA)
(o). Imidazole 4-hydroxy benzene carboxylate (IMD-HBC)

Figure 4. A series of organic salts (g-o) showing thermal expansion properties

In general, most of the materials usually expands in all three crystallographic axes on heating due to increasing anharmonic vibrational amplitudes of the constituent atoms, ions or molecules known as positive thermal expansion (PTE). In very rare cases, PTE, or NTE type structural peculiarities arise when lattice dimensions contract on heating. Additionally, Barbour research group had studied exceptionally NTE, PTE and packing arrangement in simple dumbbell-shaped organic molecule (S,S)-octa-3,5-diyn-2,7-diol [27] shown in **figure 5 (a)** where a cooperative mechanical response in three-dimensional framework occur nicely by changes in temperature. In the crystal structure the molecules arranged in such a way they forms square type hydrogen bonding pattern along view down a–axis as shown in **figure 5 (a')** while these molecules in the space filled model are arranged one above the other in criss-cross pattern along view down b–axis as shown in **figure 5 (a")**. This type of research area is highly essential specifically for the new design of thermomechanical actuators.


(a')
(a'')



(c') (d')

Figure 5: (a') Crystal structure Packing diagram of molecule (a) at viewed down a-axis where hydrogen bonding are shown blue dotted line. (a") Spacefilled model of molecule (a) at viewed down b-axis. Crystal structure Packing diagram of (c) and (d) molecules at viewed down a-axis whereydrogen bonding are shown blue dotted line.

In order to elaborate the research, Negi *et. al.* studied Switching from positive to negative axial thermal expansion in pure organic compounds namely 1,4-Bis(S-3-butyn-2-ol)-benzene (c), 2,6-bis(S-3-butyn-2-ol)-naphthalene [28] as shown in **figure 3 (d)**. The explanation of their crystal structure has been shown in **figure 5(c'-d')** where the molecules arranged in such a way they forms square type hydrogen bonding pattern. The expansion has been simplified based on packing of molecules and transverse thermal vibration of atoms in the molecule. The worker observed a restricted movement of molecules along c axis in the crystal structure. Subsequently, the contraction of molecular dimension with rising temperature occurs due to transverse vibration of some atoms assists to switch from PTE to NTE. The materials showing NTE, in contrast to PTE, are highly attractive and dominant for both fundamental research as well as practical applications. Interestingly, in 2024, S. Hasebe highlight NTE to PTE and PTE to NTE switching of an organic crystal ***N***-3,5-di-tert-butylsalicylide-3-nitroaniline in the enol form (enol-1) at room temperature as shown in **figure 4(b)**. On the basis of recent study 34% of organic crystals presented under NTE. The photoisomerisation and NTE–PTE switching induced by photothermal effect and around at 30 °C. Such NTE–PTE switching without a phase transition not only significant in organic crystals but also provides new policy for the designing of crystal actuators [29]. In addition, to continue the research area in 2019, Dwivedi *et. al.* studied an unusual thermal expansion property of an organic salt carboxylate (IMD-HBC), such as imidazolium 4-hydroxybenzene [30] as shown in **figure 4(o)**, which displays thermal expansion along b-axis and a-axis. The hydrogen bonding forms square grid type of the flexible network that undergoes scissor-like motion and abnormal thermal behavior during heating and cooling at different temperature (100K and 360K) by using variable temperature single Crystal X-ray diffraction analysis as shown in **figure 6**. In shortly, we can say that thermal expansion property shows colossal axial PTE and NTE. On the study of crystal structure, we conclude that an organic salt with unusual thermal expansion generates scissor-like motion from hydrogen bonded network structure.

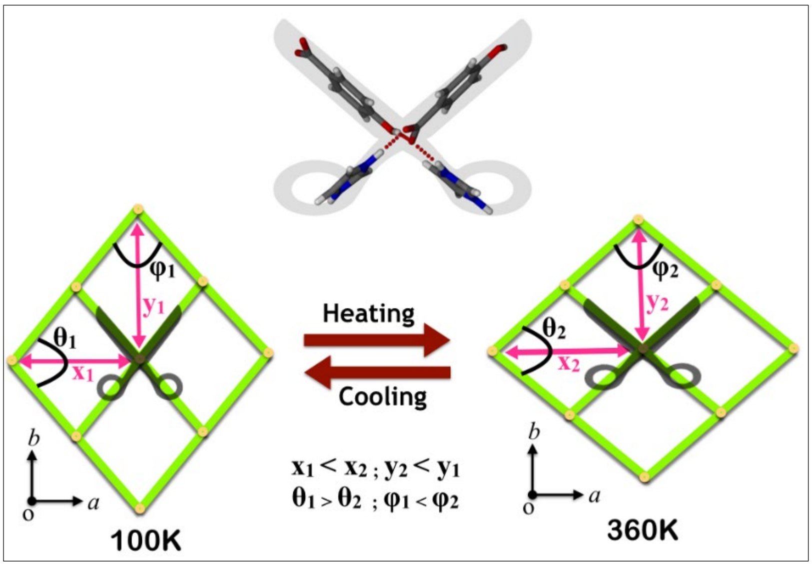


Figure 6. IMD-HBC salt showing scissor-like motion in hydrogen bonded network during colossal positive and negative axial thermal expansion (Adapted from ref. [30] with permission, Copyright ACS 2019).

Supramolecules in herbal merchandise offer a extensive range of useful applications because of their ability to shape non-covalent interactions which includes hydrogen bonding, π–π stacking, and van der Waals forces [31-33]. These interactions are relevant to the bioactivity of many natural compounds, making them precious in drug layout and shipping. Supramolecular chemistry permits the development of drug shipping structures that improve solubility, stability, and bioavailability, consisting of the usage of cyclodextrins to decorate poorly soluble pills. Additionally, supramolecular interactions in natural products are utilized to improve the efficacy of nutraceuticals, purposeful meals, and antioxidants through improving absorption. They additionally play a key position in creating sustainable, biodegradable materials from herbal materials like cellulose and chitin, and in the development of sensors for ailment detection and environmental monitoring [34-38]. However, the usage of supramolecular chemistry in natural products has big capability across medication, food technology, sustainable substances, and others.

3. Conclusion, significance and future perspectives

Organic multicomponent structures, together with co-crystals and salts, are vital for tailoring their functionality and modulating thermal expansion behaviors that range from their man or woman additives. This understanding is pivotal for designing substances with precise thermal homes, and considering that thermal expansion mechanisms can vary extensively across different compounds, continued research in diverse systems is important. The interplay of supramolecular interactions—such as hydrogen bonds, π–π interactions, and van der Waals forces—plays a key role in influencing the thermal conduct of those structures, making them treasured for a range of applications together with microscale smooth robotics, actuators, and thermal microswitches. Furthermore, polymorphism in stable-kingdom materials significantly affects their physicochemical homes and is of high-quality hobby in fields like prescription drugs, meals, and pigments.

Recent advancements in both experimental and computational techniques for polymorph discovery are increasing our know-how of how molecular interactions and crystal structures affect bulk homes. Polymorphs and inclusion compounds provide new possibilities in drug transport by means of enhancing solubility, balance, and bioavailability, whilst additionally permitting novel separation and purification methods. This assessment highlights the significance of continuing to discover the thermal enlargement conduct, polymorphism, and inclusion formation in multicomponent systems, as these regions preserve notable potential for advancing supramolecular chemistry and its applications in substances science and biological fields.

Conflict of Interest

None.

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