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Anisotropy in the mechanical properties of organic crystals: temperature dependence

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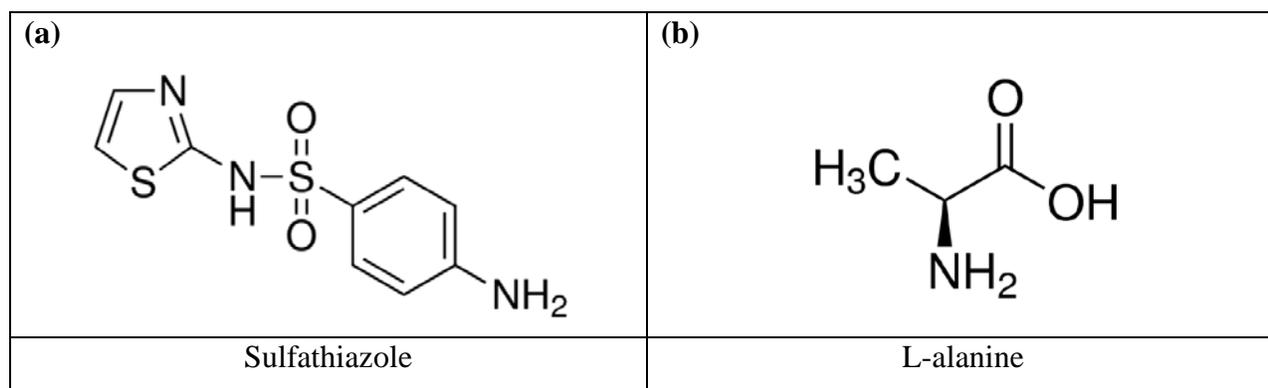
Abstract

The nanoindentation technique has recently been utilized for quantitative evaluation of the mechanical properties of molecular materials successfully, including their temperature (T) dependence. In this paper, we examine as to how the mechanical anisotropy varies with T in saccharin and L-alanine single crystals. Our results show that elastic modulus (E) decreases linearly in all the cases examined, with the T -dependence of E being anisotropic. Correspondence between directional dependence of the slopes of the E vs. T plots and the linear thermal expansion coefficients was found. The T -dependence of hardness (H), on the other hand, was found to be nonlinear and drastic when (100) of saccharin and (001) of L-alanine are indented. While the anisotropies in E and H of saccharin and E of L-alanine enhance with T , the anisotropy in H of L-alanine was found to reduce with T . Possible mechanistic origins of these variations are discussed.

1. Introduction

Interest in measuring the mechanical properties of molecular materials and correlating those properties with the crystal structural features has increased considerably in the recent past.¹⁻¹⁰ This is due mainly to the utilization of the nanoindentation technique as it allows for the measurement of properties even when the volume of the material available is considerably small.¹¹⁻¹² In particular, it is particularly suited for extracting properties of organic and inorganic single crystals.¹³⁻³³ This has paved way for understanding a number of phenomena such as shear

stability of polymorphs,³⁴ identification of intergrowth polymorphism,³⁵ solid state mechanochromism,³⁶ etc. Most of the nanoindentation studies performed hitherto on molecular materials were conducted at room temperature (RT, ~293 K).¹² However, extending such studies to higher temperatures can open new avenues for research. Further such studies can also be utilized for understanding solid state phenomenon such as temperature-dependent phase transformations.³⁷ They can also be useful in industrial practice of pharmaceutical manufacturing.³⁸⁻⁴⁷ Keeping this in view, we have recently conducted an experimental study wherein the mechanical properties of the major faces of saccharin, sulfathiazole (form 2), and L-alanine (scheme 1) crystals were probed with a nanoindenter as a function of temperature, T , between 283 and 343 K.³¹ Our results established that both the elastic modulus, E , and the hardness, H , are strongly sensitive to T . In this article, we extend this work to examine as to how the mechanical anisotropy varies with T in saccharin and L-alanine. Further, we examine if the mechanical anisotropy is related to the anisotropy in the thermal expansion behavior of the single crystals, α . In particular, we are interested in seeing if the variation in the thermal expansion coefficient, α , with the crystallographic direction can be correlated with the slope of the E vs. T data. This is because both E and α depend on the same structural factors, namely the number and strength of intermolecular interactions.



Scheme 1. Chemical structure of (a) sulfathiazole and (b) L-alanine

2. Materials and experiments

Large single crystals of saccharin (melting point, $T_m = 502$ K) and L-alanine ($T_m = 588$ K) with rhombic and plate morphologies respectively, were examined in this study. Commercially

available compounds (saccharin: Loba Chemie, India; L-alanine: Sigma-Aldrich) were utilized for crystallization in conical flasks by slow evaporation of saturated solutions of different solvents (ethanol for saccharin and water for L-alanine) at RT over a period of 2-3 weeks. The as-grown crystals were dried first and then washed with paraffin oil to remove any small crystals that might have gotten attached to the surface. Defect-free single crystals were carefully chosen after viewing them through an optical microscope, which is supported by rotatable polarizing stage, and were subjected first to single crystal X-ray diffraction (XRD) at 150 K on a Rigaku Mercury 375R/M CCD⁴⁸ (XtaLAB mini) diffractometer using graphite monochromated Mo-K α radiation, equipped with a Rigaku low temperature gas spray cooler. The Rigaku CrystalClear software⁴⁸ was used to process the XRD data. The structure solution was performed by direct methods, and refinements were performed by using SHELX97⁴⁹ and WinGX suite.⁵⁰ Face indexing of good quality single crystals was performed with the Rigaku CrystalClear software and the major faces were assigned.

The selected single crystals (average size: $2.5 \times 1.5 \times 1 \text{ mm}^3$) were firmly mounted on a stud using a thin layer of cyanoacrylate glue before the nanoindentation experiments, which were performed on (100) and (011) faces of saccharin and (001) and (101) faces of L-alanine. A nanoindenter (Triboindenter of Hysitron, Minneapolis, USA) equipped with a heating/cooling stage and zircon Berkovich tip (end radius $\sim 100 \text{ nm}$) was utilized. To ensure accuracy in the measured data, a thermocouple was placed on the sample surface to accurately determine the temperature of crystal. The crystal surfaces were imaged prior to indentation using the same indenter tip, which serves also as an atomic force microscope, so as to identify flat and smooth regions for the experiment, the. Nanoindentation tests were performed from temperatures, T of 283 to 343 K with 10 K intervals, and the load, P , vs. displacement, h , responses were recorded. In all cases, the loading and unloading rates were 0.5 mN/s and the hold time at the peak load (5 mN) was 30 s. A minimum of 20 indentations were performed on each crystal at each T to ensure reproducibility. The P - h curves obtained were analyzed using the standard Oliver-Pharr (O-P) method^{51,52} to determine E and hardness, H .

Defect free single crystals of saccharin and L-alanine were subjected to variable temperature single crystal X-ray diffraction over a temperature range of 298 to 98 K, through gradual cooling of the crystal using liquid nitrogen. Data was collected at each 50 K interval. The

estimated interplanar spacings, d_{hkl} , in different crystallographic orientations were utilized to compute the linear thermal expansion coefficients, α , using the following equation⁵³⁻⁵⁵:

$$\alpha = \frac{1}{d_{hkl}(98K)} \left(\frac{\Delta d_{hkl}}{\Delta T} \right) \quad (1)$$

where Δd_{hkl} is the increase in the interplanar spacing for a given temperature increment, ΔT data.

3. Structural features

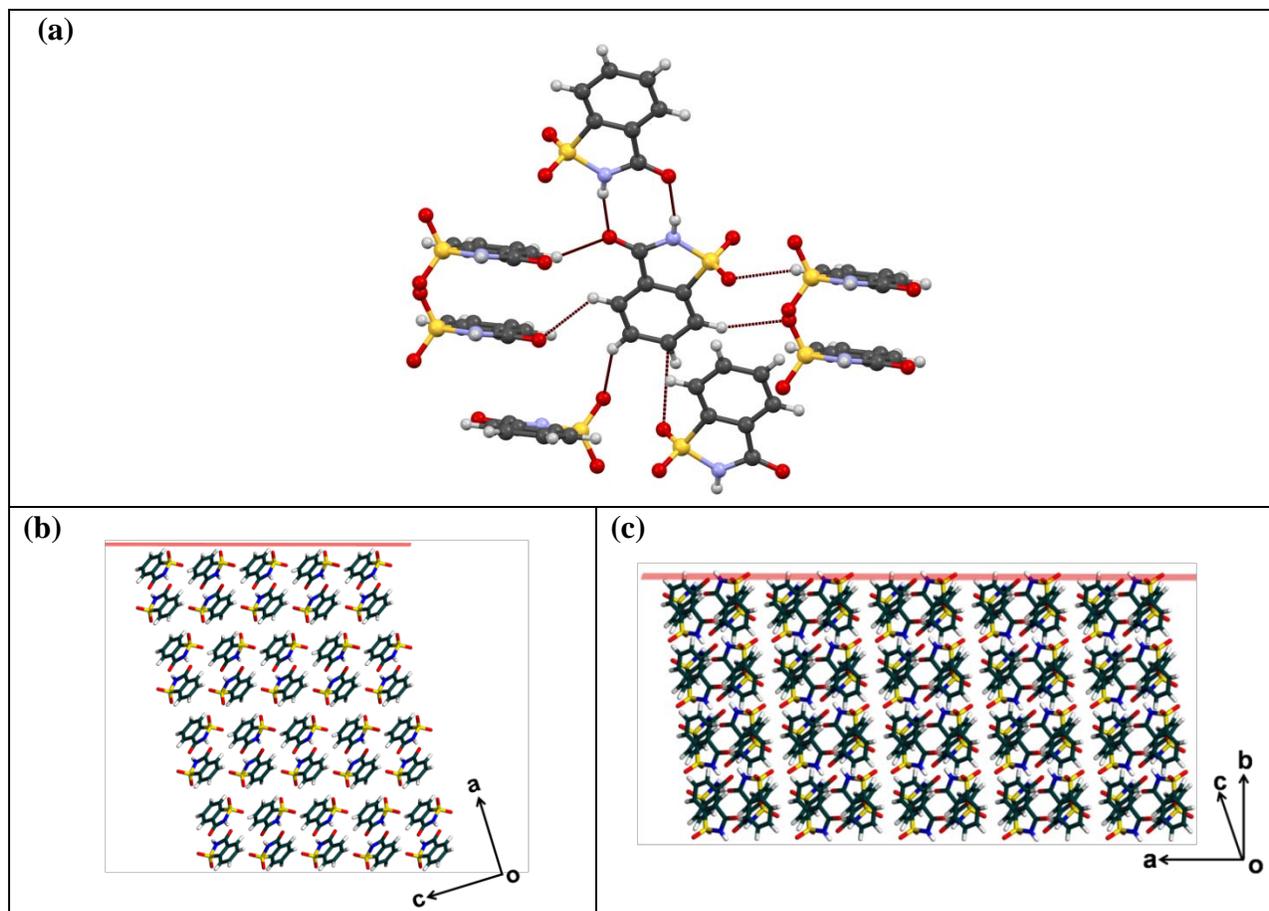


Figure 1. (a) Hydrogen bond pattern and (b) and (c) crystallographic projections of structural features along various planes in saccharin. The red lines represent traces of (100) in (b) and (011) in (c). The indentation directions are normal to these traces on the respective facets.

The crystal structures of both the compounds examined in this work are reported in literature; therefore only the relevant structural features are briefly demonstrated.^{56,57} On the major face of saccharin (100), the molecules form stack strong centrosymmetric N–H \cdots O hydrogen bonds along [100], inclined oblique angle to the face normal, which is also the indentation direction

(Figs. 1b and c).⁵⁶ Within a stack, the molecules are stabilized by nondirectional van der Waals ($\pi \cdots \pi$) interactions and adjacent stacks are connected by C–H \cdots O hydrogen bonds (Fig. 1b). From Fig. 1(b) it is seen that the saccharin molecules make a bilayer arrangement, and only weak interactions persist between the bilayers. In the case of the (011) plane, the dimers, formed via strong N–H \cdots O interactions, are stacked in the [011] direction at an oblique angle, and several weak C–H \cdots O interactions normal to the plane of indentation exist (Fig. 1c) An important (and distinguishing feature vis-à-vis that seen on (100)) is that the adjacent molecules from the dimers criss-cross to form weak C–H \cdots O interactions in the two other directions.

In L-alanine (Fig. 2), an amino acid, which crystallize as zwitterions,⁵⁷ there are several strong N–H \cdots O and weak C–H \cdots O hydrogen bonds that connect the molecules into puckered layers in *a-c* plane that are stacked along *b* axis of the crystal. This arrangement results in a three-dimensional hydrogen bond network structure (Fig. 2a). Consequently, the crystals of L-alanine are characterized by multitude of strong hydrogen bonds that are present in all the three directions (isotropic) whereas saccharin, in contrast, has comparatively fewer hydrogen bonds, that are also highly directional (anisotropic). Herein, we want to investigate as to how the anisotropy in the mechanical behavior of isotropic and anisotropic molecular materials changes within the temperature range of 283 and 343 K.

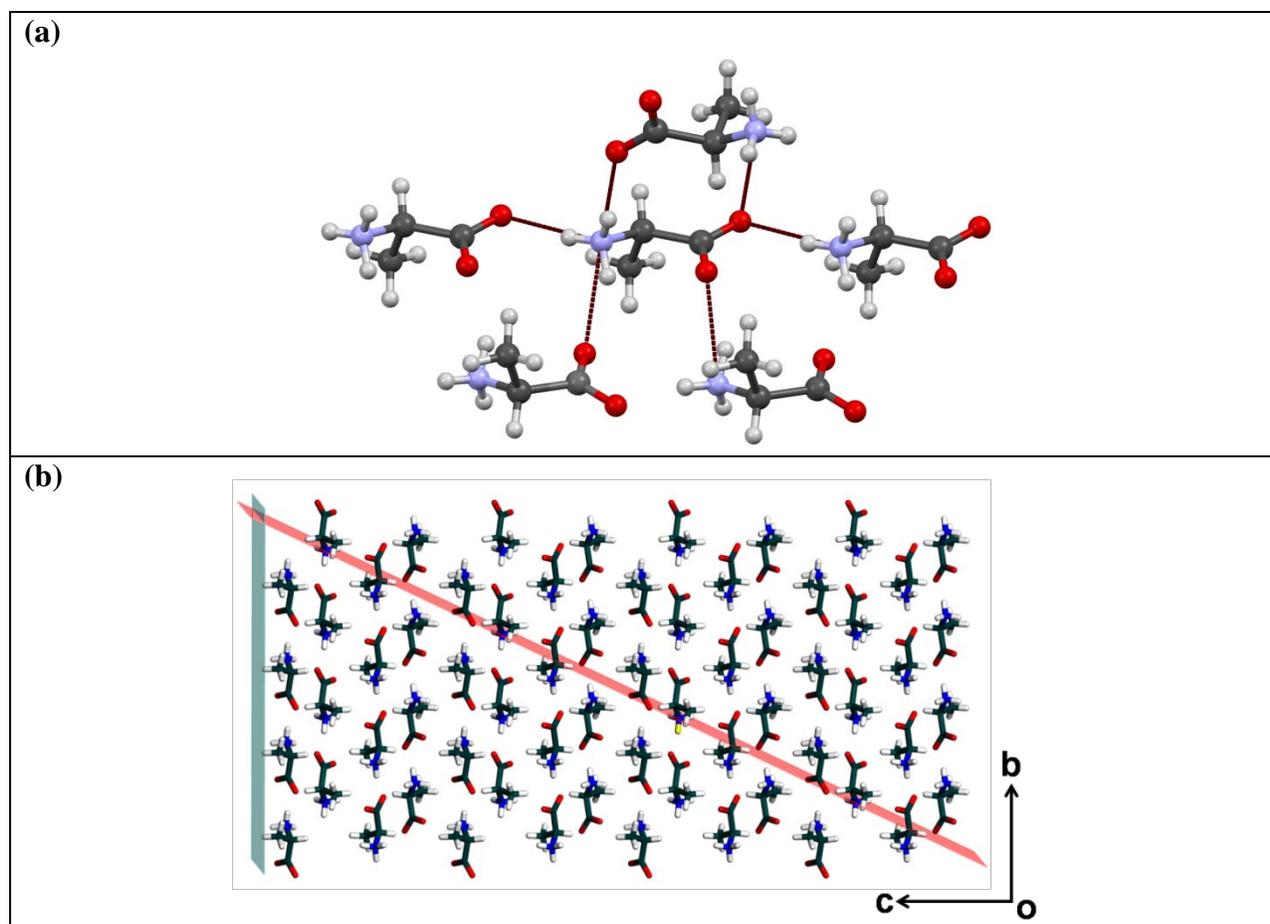


Figure 2. (a) Hydrogen bond pattern and (b) Molecular arrangements in L-alanine. The green line represents the trace of (001) plane whereas the red line represents (101) plane. Nanoindentation was performed on these planes such that the plane normals coincide with the indentation axis.

4. Mechanical properties and anisotropy

Representative P - h curves, obtained on various crystallographic faces of saccharin and L-alanine, at different T are displayed in Figure S1, in supplementary information (SI). The P - h responses measured on both the faces of L-alanine are smooth, indicating to continuous plasticity. In contrast, the P - h curves obtained on saccharin, especially the (100) face of the crystals, exhibit pronounced serrations. These features persist at all the examined T , indicating that the plastic deformation mechanism does not change in any significant manner within the range of T examined; possibly because of the relatively small range of T examined in this work. In an earlier paper, Kiran et al. have examined the nanoindentation responses on (100) and (011) faces of saccharin at RT and made similar observations.⁵⁸ They have discussed in detail the

reasons for the observation of pop-ins only on the (100) face and conclude that they are a result of the intermittent yielding of the layered stacked columns (see Figure 1) when indented along [100]. The absence of pronounced pop-ins on the loading part of the P - h curves obtained during the indentation on (011) was argued as due to the availability of the favorably oriented slip planes, which allow for smooth sliding of the molecular layers past each other, for strain accommodation. See Kiran et al.'s paper for a detailed discussion on the mechanics involved.⁵⁸

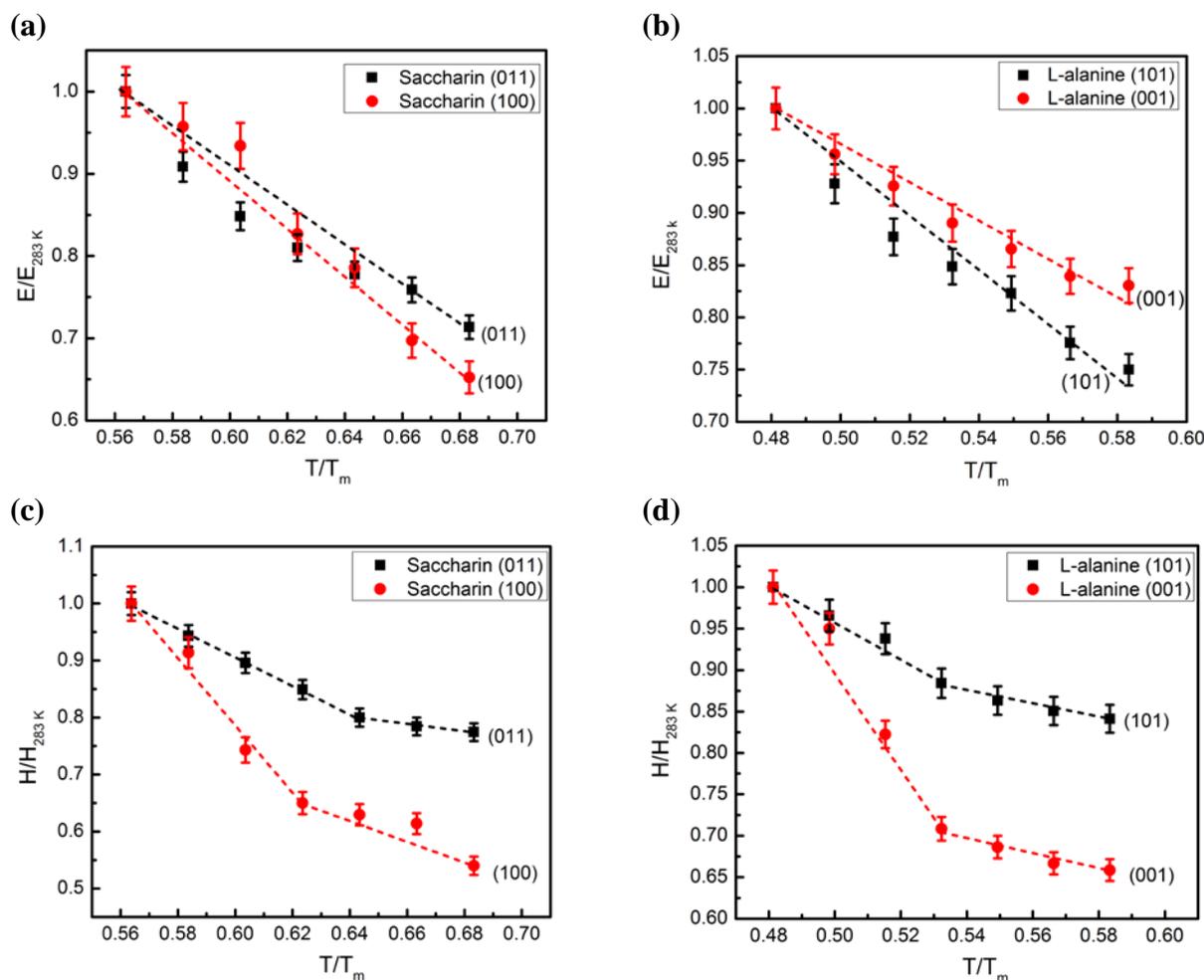


Figure 3. Variations in elastic modulus, E , and hardness, H , as a function of homologous temperature, T/T_m , in saccharin, (a) and (c), and L-alanine, (b) and (d). Here, E and H are normalized with the corresponding values measured at 283 K, the lowest T at which nanoindentation were made, so that the relative changes can be seen directly. Note that the dashed lines in (c) and (d) are only for the purpose of guiding the eye. Individual and non-normalized variations are displayed in Figures S2 and S3 of SI.

Table 1. Summary of the mechanical and thermal properties measured in this study.

Substance	Face	Elastic modulus at 293 K, E_{293} (GPa)	Hardness at 293 K, H_{293} (MPa)	E_0 (GPa)	ψ	α ($10^{-6}/\text{K}$)
Saccharin	(100)	13.9 ± 0.40	530.0 ± 3.0	40.0	1.12	65.3
	(011)	14.0 ± 0.03	501.3 ± 2.3	34.0	1.0	26.7
L-alanine	(001)	25.1 ± 0.28	1140 ± 4.8	47.2	0.94	38.3
	(101)	19.2 ± 0.54	943.4 ± 3.1	43.4	1.11	13.63

Note: The α values correspond to the direction normal to the plane listed.

The P - h responses were utilized to extract values of E and H at various T , which are plotted in Figs. 3 (a) through (d) for both the compounds. In these, the mechanical properties are normalized with the respective values measured at 283 K, so that the relative variations with T become apparent. The temperature is normalized with respective T_m . The E vs. T data plotted in Figures 3(a) and (b) indicate that the variation of E with T is linear in all the cases examined in this work. The following equation, which is generally used to describe T -dependence of elastic properties of crystals, is utilized to fit the data:

$$E(T) = E_0 \left[1 - \psi \left(\frac{T}{T_m} \right) \right]. \quad (2)$$

Here, E_0 is the intercept of the linear fit with the ordinate and ψ is slope which reflects the temperature-sensitivity of E .^{59,60} From Table 1, it is seen that the estimated values of ψ in all four cases are relatively high (ranging between 0.94 and 1.1.2), indicating to a strong T -sensitivity. As discussed in a recent paper by us, such high sensitivity is due to the relatively weak intermolecular interactions in organic crystals vis-à-vis the metallic and ionic bonds that prevail in inorganic materials.⁶¹⁻⁶⁷

Since the same factors, especially the strength of the interaction, also play a role in determining thermal expansion behavior, we have made an attempt to see if any correlation exists between ψ and α . Measured values of α are listed in Table 1. It is seen that they range between 13 and $65 \times 10^{-6} \text{ K}^{-1}$. These are relatively high values in comparison to metals (for example, Fe: $12 \times 10^{-6} \text{ K}^{-1}$; Mg: $25 \times 10^{-6} \text{ K}^{-1}$; Al: $22 \times 10^{-6} \text{ K}^{-1}$) and oxides (examples, Alumina: $5.4 \times 10^{-6} \text{ K}^{-1}$, and silica: $0.55 \times 10^{-6} \text{ K}^{-1}$) and are comparable to those measured for polymers that range between 30 to $200 \times 10^{-6} \text{ K}^{-1}$.⁵³⁻⁵⁵ Thus, the larger values of α measured for the two organic crystals are consistent with the high values of ψ observed in them. In the context of the present

paper, and most importantly, significant anisotropy in α values can be seen. For example, the measured α value for [100] of saccharin is more than twice that measured for [011]. Such large anisotropies are not seen in metals or ceramics, which is due to the close packing in them. Further, we note that for a given compound, there appears to be some correlation between ψ and α ; higher the α , higher is ψ . Further and more comprehensive studies are essential to ascertain the exact relationships between these two fundamental properties, both of which depend on lattice vibrations and their sensitivity to thermal variations.

Turning attention to the H variations with T , from Figures 3 (c) and (d), we note that the reductions in H with increasing T are not only nonlinear but also quite anisotropic, i.e. the reductions are not similar in different orientations. In L-alanine, for example, H of (101) decreases by ~15% when T is increased from 283 to 343 K. In contrast, a ~35% drop is seen on (001) for the same T range. In the case of saccharin, we note a massive drop of ~45% on (100), but only ~20% on (011). Interestingly, most of the reduction appears to occur between the temperatures of 283 and 313 K, whereas above 313 K, the reduction in H is relatively smaller. It may be noted that 313 K corresponds to T/T_m of 0.53 for L-alanine and 0.62. Typically, time-dependent deformation (creep) mechanisms start becoming prominent above T/T_m of 0.5.⁶⁸ However, we can discount those in the context of the current study for the following reasons. (a) The nanoindentation experiments were performed at rather higher rates of loading and unloading (and the hold time at the peak load was also minimum). Therefore, there might not be sufficient time for the contribution of creep to the overall deformation for it to become significant. (b) As seen from Figure 3, the rate of decrease in H is smaller at higher T , i.e., above 313 K. If creep was to dictate the deformation response of the crystals, the rate of decrease in H should increase with increase in T and not decrease. (c) The fact that the change in the slopes of the H variations with T occur at different homologous temperatures, also indicates that some other mechanism other than creep is possibly responsible for this transition. It is interesting to note that the variations of H with T can be approximately described as bilinear. Then, it is possible that the first segments of these linear reductions are due to the same reasons as those for the observed reduction in E with T , namely softening of the lattice with the increase in T .

In table 1, the measured values of E and H of various faces of the two compounds at room temperature (293 K) are listed, so that the reader can appreciate the mechanical anisotropy

that prevails in these crystals. From this data, it is seen that at 293 K, (100) and (011) planes of saccharin have similar E values whereas H measured on (011) is slightly (by about 6%) lower. These observations are consistent with those reported earlier by Kiran et al.⁵⁸ although their H values are relatively higher, which is possibly because of the higher maximum depth of penetration they have used for their nanoindentation measurements. In contrast, the mechanical anisotropy in L-alanine is more pronounced; the E and H values measured on (101) are higher by ~31% and 21% respectively, vis-à-vis those of (001). With increase in T , the anisotropy in E appears to get more pronounced. In the case of saccharin, the anisotropy in E at 343 K increases to ~16% whereas at 293 it is nearly-zero. In the case of L-alanine also, the anisotropy in E increases from 31% to 41%. However, no such generalization can be made with respect to anisotropy in H . In the case of saccharin, anisotropy increases with T ; it is 31.4% at 343 K as compared to only 6% at 293 K. In L-alanine, in complete contrast, the anisotropy decreases to 4% at 343 K from 21% at 293 K, i.e., at 343 K, the plastic response of L-alanine is more or less isotropic.

Although the precise mechanistic reasons for the changes observed in the mechanical anisotropy variations are difficult to ascertain without complementary modeling efforts, we offer some tentative explanations in the following. On the (011) face of saccharin, various weak C–H...O intermolecular interactions are arranged in such a way that they are perpendicular to the indentation direction whereas the stacked dimmers, formed via strong N–H...O interactions, are effectively inclined to the indentation direction. Therefore, one can anticipate that (011) face of saccharin to be stiffer than (100). On the other hand, the slip plane (100) is nearly perpendicular along to [100] and almost parallel to [011]. So, it is reasonable to expect that plastic deformation through slip of molecular planes over each other can occur with relative ease when (011) is indented. Indeed, both E and H measurements are in agreement with these expectations. Coming to L-alanine, its (001) face has several strong N–H...O and weak C–H...O hydrogen bonds connect the molecules into puckered layers that are normal to the indentation direction results high E values than (101). In case of indentation along [001], the slip plane (001) is 90° as it is almost parallel to [101]. Therefore, (001) is harder than (101) of L-alanine. Further, L-alanine is much stiffer as compared to saccharin due to the present of several strong three-dimensional hydrogen bond network structures (isotropic). The slip planes in L-alanine are interconnected via strong hydrogen bonds, which in turn provide higher friction for shear sliding,

which results higher H as compared to saccharin where weak interactions are present between the slip planes.

Since the anisotropies in α and ψ appear to be correlated, we utilize the rationalizations offered in the literature for the anisotropy in α for the hydrogen bonded complexes such as saccharin and L-alanine as means to explain anisotropy in ψ . According to the Kitaigorodsky principle, α of molecular crystals is determined by the weaker and lesser number of intermolecular interactions, specifically the presence of the hydrogen bond in the crystal structure.⁶⁹ For example, Bhattacharya et al,⁷⁰ who examined the relationship between the interaction strength and thermal expansion behavior of molecular solids, observe that smaller expansions occur in directions along which the interactions are strong in nature.⁷¹ Taking cue from it, we examine our results. On the (011) face of saccharin, various weak C–H...O intermolecular interactions exist via a dimer of strong N–H...O interactions, which are oriented along [011]. However, on (100), only weak C–H...O hydrogen bonds and nondirectional van der Waals ($\pi\cdots\pi$) interactions are present. Therefore, it is not surprising that α measured along [011] is less as compared to [100], and so was ψ in saccharin. In the case of L-alanine, as mentioned already, multitudes of strong and weak hydrogen bonds are present in all the three directions, which make the material somewhat isotropic in nature. However, the numbers of strong N–H...O and weak C–H...O hydrogen bonds are more in the direction perpendicular to the (101) plane as compared to that of the (001) plane. This causes α along [101] to be lesser the α along [001]. Further, in saccharin, the higher anisotropy in the intermolecular interactions results the higher anisotropy in the thermal expansion on (100) and (011) faces whereas in L-alanine, due to the isotropic nature of the interactions, the anisotropy in α is relatively small. These observations qualitatively explain not only the differences in ψ in various directions of a given molecular crystal, but also the differences between both α and ψ values of saccharin and L-alanine. Since, H was also observed to vary linearly with T , we presume the same factors determine its variation with T . However, we do not yet know the reasons for the bilinear dependence of H on T or the mechanistic reasons for the precipitous reduction in H above certain T . Further and detailed experiments coupled with modeling efforts are necessary to understand these.

5. Summary and conclusions

Nanoindentation technique was employed to investigate as to how the anisotropy in the mechanical behavior of molecular materials changes within the temperature range of 283 and 343 K. Two facets each of single crystals of saccharin and L-alanine were probed. Experimental results show that indeed the anisotropy could vary significantly, especially that of hardness. The anisotropy in the slope of the linear variation of elastic modulus with T , correlates with that of the linear thermal expansion coefficient, suggesting that the same structural features, namely number and strength of the intermolecular interactions, govern the modulus variations. Results of this preliminary study indicate that there is a large scope for studying the mechanical properties of organic crystals as a function of temperature, and in turn utilize them for fine-tuning the pharmaceutical manufacturing processes as well throwing new light on thermally activated processes such as phase transformations,³⁷ thermosalient effects,^{24,72,73} thermally reversible mechanochromic luminescence,^{36,74} thermal expansion,^{55,70,71} etc. to understand the structure-property relationship for designing future smart materials.

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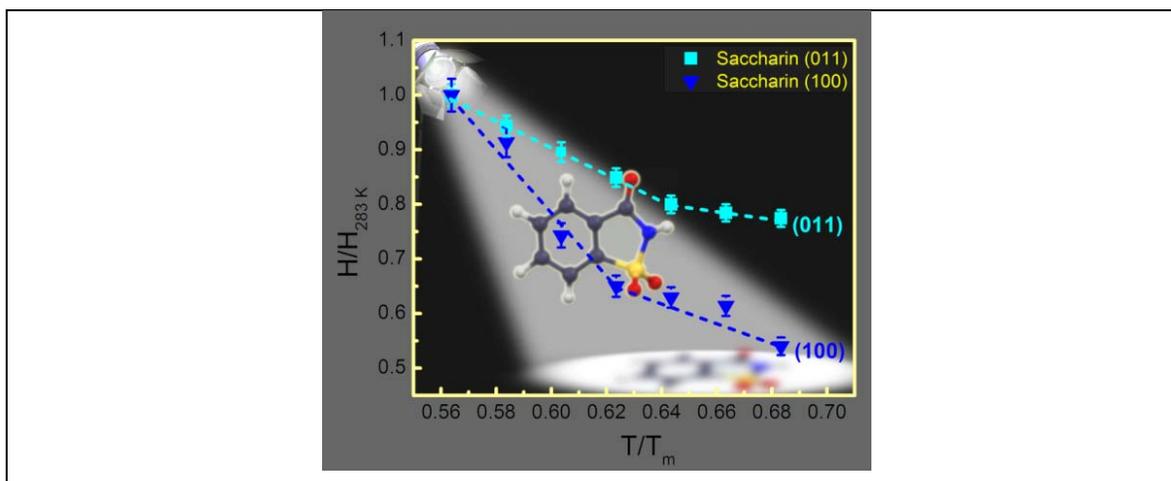
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Table of contents (TOC)/graphical abstract



Nanoindentation technique was employed on organic molecular crystals to investigate as to how the anisotropy in the mechanical behavior changes within the temperature range of 283 and 343 K.