Anisotropic thermal expansion effects in layered n-Alkyl carboxylic acid – bipyridyl cocrystals

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ABSTRACT
Co-crystallisation of butanoic acid (BA), pentanoic acid (PA), and eicosanoic acid (EA) with 4,4'-azopyridine (azp) and trans-1,2-bis(4-pyridyl)ethylene (bpe) results in 2:1 lamellar cocrystals. All cocrystals display the OH–N(pyrd) Seven-membered ring supramolecular synthon however, each cocrystal responds differently upon heating. Positive thermal expansion (PTE) occurs along the c-axis due to π–π stacking in the isostructural BA cocrystals, while the PA cocrystals are not isostructural and display a mixture of anti and gauche conformations of the acid chains because of the length mismatch with the coformer. PA₂·azp displays negative thermal expansion (NTE) of the intrasynthon C–O hydrogen bond. The two EA cocrystals both display c-axis elongation on warming due to the expansion of the distance between the alkyl chains. The expansion by more than 1 Å in EA₂·azp is highly anisotropic, however, there is much less c-axis expansion in EA₂·bpe.

Introduction
The expansion of materials in response to an increase in temperature is typically caused by an increase in the magnitude and frequency of atomic vibrations.[1, 2] On a macroscopic scale, when unit cell axes increase upon heating, this is termed positive thermal expansion (PTE). Other types of thermal response include negative thermal expansion (NTE), and zero thermal expansion (ZTE), though they are less common. [3–5] PTE and NTE can be reversible or irreversible and can also occur in the same material.[6] Whether positive or negative thermal expansion is observed depends on the type of bonds within the material. For example, fewer and weaker intermolecular interactions in molecular solids give rise to positive thermal expansion[7], while thermal contraction typically occurs due to hydrogen bond strengthening.[8,9] However, hydrogen bonding dimensionality alone is not a reliable predictor of thermal expansion behaviours[10]. In organic systems, both PTE and NTE have been reported in crystalline single component,[11], and multicomponent systems, such as inclusion compounds [1,12,13], salts [2,14,15], hydrates [16,17], solvates[18], and cocrystals [6–8,19–28]. The anisotropic expansion of lamellar solids can give rise to considerable temperature-dependent changes in crystal packing environment, even in the absence of a first-order phase change.[24]. Materials exhibiting NTE, ZTE, and PTE have applications in but are not limited to superconductors [29], ceramics[30], solar energy[31], and space science.[6].

To investigate the thermal expansion in layered cocrystalline solids, we crystallised short- and long-
chain n-alkyl carboxylic acids with two different bipyrildyl coformers to explore the cocystal response to increasing temperature in the solid state. The acids chosen represent a range of lengths to probe the relative effect of lamellar thickness as opposed to hydrogen bonded synthon. We used linear n-alkyl chains to promote lamellar packing since branched analogues are unlikely to pack efficiently side-by-side.

Results and discussion
Solution crystallisation of butanoic acid (BA), pentanoic acid (PA), and eicosanoic acid (EA) were undertaken with bifunctional pyridyl coformers 4,4’-azopyridine (azp) and trans-1,2-bis(4-pyridyl)ethylene (bpe) (Figure 1). These compounds were chosen as they are likely to form layered solids[27], and as the acid substituents are different lengths, they should affect the layer size and the layered packing arrangement of the cocystal. This kind of anisotropic structure may, in turn, result in differential thermal expansion effects. The shorter chain acid cocystals are likely to be controlled by the cocystal hydrogen OH···Npyridyl supramolecular bonded synthon, while the longer chain acid cocystal will be dominated by the packing behaviour of the long-chain alkyl substituents, in a similar way to previous work on a photoactive 25-carbon chain acid[28]. In each case, each monocarboxylic acid was combined with a pyridyl coformer in a 2:1 molar ratio, respectively, which reflects the single hydrogen bond donor group of the acids and the two hydrogen bond acceptor groups of the pyridyl coformer. The mixtures were briefly sonicated and allowed to stand to bring about slow evaporation of the solvent under ambient conditions. These experiments resulted in six cocystals characterised by single-crystal X-ray diffraction (SC-XRD) consisting of \( \text{BA}_2\text{-azp}, \ \text{BA}_2\text{-bpe}, \ \text{PA}_2\text{-azp}, \ \text{PA}_2\text{-bpe}, \ \text{EA}_2\text{-azp}, \ \text{and} \ \text{EA}_2\text{-bpe}. \)

All cocystals crystallise in the centrosymmetric, triclinic \( P\bar{1} \) space group and display OH···N hydrogen bonds from the carboxylic acid hydrogen atom of the acid to the pyridyl nitrogen atom of the coformer. A weaker CH···O interaction also occurs from the C-H of the pyridyl ring to the carbonyl oxygen atom of the acid, to complete the hydrogen-bonded dimer \( R^2_7(7) \) motif[32]. Two additional weak CH···O hydrogen bonds also occur between layers from the C-H groups of the pyridyl rings to the carbonyl oxygen atom on an adjacent acid molecule, which adds dimensionality to the cocystal layers. The cocystal hydrogen-bonded layers rest diagonally between the \( b \) and \( c \) axes, with the intermolecular hydrogen bonds within the acid-pyridyl synthon occurring along the \( b \)-axis. The cocystals were characterised at 120 K and then warmed to near room temperature to investigate their thermal response. All hydrogen bond distances reported are measured from the hydrogen bond donor atom to the hydrogen bond acceptor (O···N or C···O) and not from or to the H atom, as the position of the H atoms cannot be located with high precision in high-temperature structures.

Single crystal x-ray diffraction
\( \text{BA}_2\text{-azp} \) and \( \text{BA}_2\text{-bpe} \)

The cocystals \( \text{BA}_2\text{-azp} \) and \( \text{BA}_2\text{-bpe} \) are isostructural (Figure 2). Both materials show negligible changes in the \( a \) and \( b \)-axes, but significant PTE in the \( c \)-axis upon warming (elongation of 0.76 Å and 0.87 Å, respectively), caused by expansion in the face-to-face \( \pi \)-\( \pi \) stacking interactions aligned along the \( c \)-axis which expand on warming by 0.14 and 0.093 Å for both cocystals, respectively (Table 1). The given \( \pi \)-\( \pi \) stacking interaction distances are the distances between centroids of adjacent pyridyl rings. The positive correlation between \( \pi \)-\( \pi \) stacking direction and thermal expansion direction has been observed in similar cocystal systems [27,33]. The strong OH···N hydrogen bonds in the hydrogen-bonded sheet show insignificant PTE upon warming (0.011 and 0.0057 Å for \( \text{BA}_2\text{-azp} \) and \( \text{BA}_2\text{-bpe} \), respectively). Strong intermolecular interactions are rarely significantly perturbed on warming, unlike weaker intra- and intersynthon CH···O hydrogen bonds [9,20,24,33]. This is demonstrated by the 0.098 (within the acid-pyridyl synthon), 0.094 and 0.039 (intersynthon) Å PTE in CH···O hydrogen bonds in \( \text{BA}_2\text{-azp} \) and the 0.13 (intrasython), 0.099 and 0.042 (intersynthon) Å PTE in \( \text{BA}_2\text{-bpe} \). Therefore, in this instance, the bispyridyl coformer does not affect the thermal expansion properties of either cocystal of BA.
Unlike the cocrystals of BA, PA₂·azp and PA₂·bpe are not isostructural (Figure 3). PA₂·azp is a conformational isomorph with two conformationally different molecules of PA in the asymmetric unit. One of the PA molecules is in an anti-conformation and the other is gauche. A twist in the N=N group, causes the azp molecule to be non-planar. The presence of two independent PA molecules results in two different values for the OH···N, CH···O intra- and intersynthon hydrogen bond distances. In contrast, PA₂·bpe has only one unique molecule of PA in its asymmetric unit (Z’ = 0.5) and exists in a gauche conformation, with a planar bpe coformer situated on an inversion centre. The BA and PA cocrystals only differ by a single carbon atom however this aspect markedly affects the structures and unit cell parameters (Table 2) and seems to arise from a mismatch in the length of PA and the co-formers, whereas two BA molecules are good size match for the coformers.

Table 1. The unit cell parameters, hydrogen bond distances, and π···π stacking distances of BA₂·azp and BA₂·bpe at 120, 270 (BA₂·azp) and 296 (BA₂·bpe) K.

| Cocrystal | Temperature /K | BA₂·azp | % Change | BA₂·bpe | % Change |
|-----------|----------------|---------|----------|---------|----------|
| a-axis /Å | 120            | 6.6795(2)| 6.6930(3)| 2.6804(14)| 2.691(3)| 0.20 |
| b-axis /Å | 6.9217(2)      | 6.9135(4)| 0.12 |
| c-axis /Å | 11.3594(4)     | 12.1182(6)| 6.68 |
| Unit cell volume /Å³ | 469.70(3) | 493.66(4) | 5.10 |
| O···N /Å | 3.2191(19) | 3.317(4)| 3.04 |
| C···O intralayer /Å | 3.1407(14) and 3.323(3) and 3.00 and 1.15 | 3.3523(18) and 3.391(4) | 3.12 and 1.25 |
| C···O interlayer /Å | 3.3511 | 3.604 | 2.65 |
| π···π distance /Å | 3.533 | 3.672 | 3.93 |

PA₂·azp and PA₂·bpe

Figure 2. The X-ray structures and packing diagrams of BA₂·azp and BA₂·bpe at 120, 270 (BA₂·azp) and 296 (BA₂·bpe) K.

Figure 3. The X-ray structures and packing diagrams of PA₂·azp and PA₂·bpe at 120 K.
Table 2. The unit cell parameters, hydrogen bond distances, and π–π stacking distances of PA$_2$-azp and PA$_2$-bpe at 120 K and 293 (PA$_2$-azp) and 296 (PA$_2$-bpe) K.

| Cocyclic Parameter | PA$_2$-azp 120 K | PA$_2$-azp 293 K | % Change | PA$_2$-bpe 120 K | PA$_2$-bpe 293 K | % Change |
|-------------------|------------------|------------------|---------|------------------|------------------|---------|
| a-axis /Å         | 7.1308(5)        | 7.262(2)         | 2.74    | 7.8211(5)        | 6.7511(18)      | −1.03   |
| b-axis /Å         | 10.4524(8)       | 10.505(3)        | 0.50    | 7.1875(6)        | 7.253(2)        | 0.91    |
| c-axis /Å         | 14.8159(9)       | 15.161(5)        | 2.33    | 11.8334(10)      | 12.826(4)       | 8.39    |
| Unit cell volume /Å$^3$ | 1035.8713        | 1115.66          | 7.70    | 515.247          | 558.83          | 8.45    |
| O–N /Å            | 2.644(4) and 2.729(4) | 2.662(12) and 2.721(13) | 0.68 and 0.29 | 2.6725(15) | 2.687(4) | 0.54    |
| C–O inlayer /Å    | 3.030(4) and 3.597(4) | 3.296(14) and 3.477(13) | 0.21 and −3.34 | 3.3272(18) | 3.3725 | 2.89    |
| C–O interlayer /Å | 3.272(4) and 3.277(4) | 3.321(15) and 3.342(13) | 0.28 and 1.98 | 3.3329(13) and 3.4238(15) | 3.385(4) and 3.399(4) | 1.56 and 0.72 |
| π–π distance /Å   | 3.596            | 3.796            | 5.56    | 3.532            | 3.659           | 3.60    |

When the cocrysalts were warmed to room temperature, the crystal quality of PA$_2$-azp and PA$_2$-bpe deteriorated significantly and the resulting structure determinations are of low precision with disorder of the terminal methyl groups. However, the unit cell parameters are unambiguous and give insight into the changes in the structure on warming. For PA$_2$-azp the a-axis increases by 0.20 Å, whereas the a-axis in PA$_2$-bpe decreases slightly in length upon warming, with a NTE of −0.07 Å. The b-axis in PA$_2$-azp and PA$_2$-bpe shows almost no PTE with the axis lengths increasing on warming by 0.053 and 0.070 Å, respectively. However, PA$_2$-azp shows a much smaller PTE in the c-axis when compared to PA$_2$-bpe (with increases of 0.35 and 1.00 Å, respectively), despite the π–π stacking interaction distance increasing by a similar amount in PA$_2$-azp (0.20 Å) and PA$_2$-bpe (0.19 Å). There is a significant offset of the pyridyl rings centroids in PA$_2$-azp, with a shift distance of 0.74 Å, compared to the offset of the rings in PA$_2$-bpe with an offset of only 0.019 Å. The offset of the pyridyl ring centroids is linked to the NTE observed in the intrasynthon CH···O hydrogen bond distances in PA$_2$-azp, which contract slightly on warming. For the stronger OH···N hydrogen bond along the same axis, the interactions increase by 0.018 and 0.008 Å on warming. The weak intersynthon CH···O hydrogen bonds of PA$_2$-azp increase by 0.009 and 0.065 Å. Cocystal PA$_2$-bpe behaves differently to PA$_2$-azp in response to increasing temperature. PA$_2$-bpe has a much smaller PTE with an increase of 0.015 Å for the OH···N hydrogen bonds, 0.095 Å for intrasynthon CH···O hydrogen bonds, and PTE and NTE for the intersynthon CH···O hydrogen bonds at 0.052 and −0.025 Å.

In summary, the differences in the thermal expansion properties between PA$_2$-azp and PA$_2$-bpe on warming are due to the NTE observed in the intrasynthon CH···O hydrogen bond interactions in PA$_2$-azp, causing the centroid distances of the pyridyl rings to have a greater offset. PA$_2$-bpe does not display the same thermal expansion properties.

**EA$_2$-azp and EA$_2$-bpe**

The two long-chain EA cocrysalts, EA$_2$-azp and EA$_2$-bpe, are not isostructural, even though the alkyl chains of the acid for both cocrysalts are in an anti-conformation at both 120 K and room temperature (Figure 4). We note in passing that this is the first single-crystal diffraction study of this surfactant-like acid. On warming to room temperature, the c-axis lengths in EA$_2$-azp and EA$_2$-bpe expand by 1.04 and 0.13 Å, respectively. This represents a marked difference in two similar materials even given the temperature differences. In contrast, the a-axis length increase for EA$_2$-azp on warming is only 0.035 Å compared to 0.11 Å and for EA$_2$-bpe (Table 3). The b-axes only increase by 0.057 and 0.074 Å on warming for EA$_2$-azp and EA$_2$-bpe, respectively. The strong OH···N hydrogen bonds show negligible thermal expansion at 0.011 Å for EA$_2$-azp and 0.003 Å for EA$_2$-bpe. The intra- and intersynthon CH···O hydrogen bonds also show small PTE upon warming, with EA$_2$-azp showing CH···O bond distance changes of 0.048 (intrasynthon) and 0.038 and 0.094 Å (intersynthon), while EA$_2$-bpe has intrasynthon CH···O bond distance increases of 0.028 Å and intersynthon CH···O distances of 0.081 and 0.093 Å upon warming. No π–π stacking interactions are present in either EA cocystal, as the distances between pyridyl rings of adjacent layers are too great to form a significant interaction, therefore, π-stacking interactions cannot account for the PTE observed in the c-axis of EA$_2$-azp.

The differences in thermal expansion properties in the two EA cocrysalts must be due to differences in the coformer, even though they are of a similar size and shape. Azp and bpe are known to undergo molecular pedal motion at different temperatures, resulting in disorder that is either dynamic or static [24,26,34–37].
Interestingly, the EA₂·bpe structure displays disorder of the central ethylene group of bpe. As the site occupancies of the disordered atoms remain constant with temperature, the disorder is likely to be static [26,38]. In contrast, the EA₂·azp is ordered. The long c axis in both structures encompasses the side-by-side packing of the long alkyl chains with the EA molecular axis orientated at about 50° to this axis in each case. Interestingly, while the ordered EA₂·azp structure has almost coplanar seven-membered ring synthons and alkyl substituents, the disordered EA₂·bpe structure has a wave-like arrangement in which there is an offset of the alkyl substituents. As temperature increases, the distance between adjacent alkyl chains expands. This expansion seems to be tolerated in the wavelike bpe structure resulting in more isotropic expansion, while in the azp structure all the expansion is focused along the c axis. Increased thermal motion in hydrogen-bonded solids has been shown to result in significant thermally induced motion previously [28,39].

**Table 3.** The unit cell parameters, hydrogen bond distances, and π−π stacking distances of EA₂·azp and EA₂·bpe at 120, 270 (EA₂·bpe), and 296 (EA₂·azp) K.

| Cocystal   | EA₂·azp          | EA₂·bpe          |
|------------|------------------|------------------|
| Temperature /K | 120 K  | 296 K  | % Change | 120 K  | 270 K  | % Change |
| a-axis /Å   | 5.460(3)        | 5.4949(6)        | 0.64      | 4.8640(3) | 4.9744(6) | 2.27      |
| b-axis /Å   | 6.853(3)        | 6.9098(6)        | 0.83      | 6.8573(4) | 6.9314(8) | 1.08      |
| c-axis /Å   | 33.412(18)      | 34.451(4)        | 3.11      | 36.699(2) | 36.833(4) | 0.37      |
| Unit cell volume /Å³ | 1199.5(11) | 1259.2(2) | 4.98      | 1203.27(13) | 1252.5(3) | 4.09      |
| O−N /Å     | 2.679(4)        | 2.690(8)         | 0.41      | 2.636(3)  | 2.639(4)  | 0.11      |
| C−O intralayer /Å | 3.289(5)  | 3.337(10)       | 1.46      | 3.484(3)  | 3.512(4)  | 0.80      |
| C−O interlayer /Å | 3.191(5)  and 3.229(11) and 3.623(5) | 3.717(10) | 1.19 and 2.60 | 3.234(2) and 3.410(3) and 3.315(4) and 3.503(4) | 2.51 and 2.73 |

**Powder x-ray diffraction**

The X-ray powder diffraction (XRPD) patterns calculated from the low-temperature SC-XRD data of the cocystal structures reveal significant differences when compared to the experimental room temperature patterns of the same cocrysalts (Figures 5 and S1-5). In all cases, the calculated room temperature patterns have an improved fit to the experimental data in comparison to the patterns derived from the low-temperature data and confirm that the single crystals are representative of the bulk, although some differences remain which appear to arise from very significant preferred orientation (Table S1), particularly in...
the case of \textit{EA}_2-\textit{azp} which showed severe (110) preferred orientation (Figure 5).

**Conclusion**

Six binary pyridyl-acid cocrystals involving the OH–N\textsubscript{pyridyl} seven-membered ring supramolecular synthon have been prepared. All cocrystals crystallise in the triclinic \textit{P} \textbar \textit{1} space group and form a 2D hydrogen-bonded network via CH–O interactions. Upon warming, all cocrystals show anisotropic thermal expansion effects to different degrees. The \textit{BA} cocrystals expand in the \textit{c}-axis due to \textit{n}–\textit{n} stacking interactions that run along the same axis, while the \textit{PA} cocrystals display PTE, partly due to differences in the \textit{gauche} conformations of the \textit{PA} chains. However, \textit{PA}_2-\textit{azp} displays NTE in the intra-synthon CH–O hydrogen bonds on warming, which causes the pyridyl centroid distances to be further offset. Both \textit{EA} cocrystals show \textit{c}-axis expansion due to increased motion of the alkyl substituents that is focused almost entirely along \textit{c} for the ordered \textit{azp} cocrystal but the disordered \textit{EA}_2-\textit{bpe} shows more isotropic expansion. Therefore, in anisotropic layered solids, thermal effects can give rise to considerable differences in the expansion of each crystallographic axis. These effects, in turn, can give rise to very different experimental XRPD patterns compared to those calculated from low-temperature single-crystal data, particularly when significant preferred orientation effects are also present.

**Experimental**

All reagents and solvents were purchased from standard commercial sources and used without further purification. X-ray powder diffraction patterns were recorded on glass slides using a Bruker AXS D8 Advance diffractometer with a LynxEye Soller PSD detector, using Cu Kα radiation at a wavelength of 1.5406 Å. CHN analysis was undertaken using an Exeter CE-440 Elemental Analyser. CN analysis was undertaken using a Costech ECS 4010 Elemental Analyser. Single crystal data were collected on Bruker D8 Venture 3-circle diffractometers at various configurations (Photon 100 CMOS detector, IμS-microsource focusing mirrors/Photon III MM C14 CPAD detector, IμS-III-microsource, focusing mirrors) equipped with Cryostream (Oxford Cryostreams) open-flow nitrogen cryostats and using MoKα radiation with a wavelength of 0.71073 Å (CuKα radiation, $\lambda = 1.54178$ Å for the \textit{EA}_2-\textit{azp} high-temperature structure). All structures were solved using direct methods and refined by full-matrix least squares on \textit{F}^2 for all data using \textit{SHELXL} [40] and \textit{OLEX2} [41] software. All non-hydrogen atoms were refined with anisotropic displacement parameters. CH hydrogen atoms were placed in calculated positions and refined in riding mode. H atoms attached to oxygen atoms were located on the difference map when possible or placed in calculated positions.

Note that high-temperature data for \textit{BA}_2-\textit{azp} was recorded at 270 K because of the instability of the crystal at room temperature, similarly, the \textit{EA}_2-\textit{bpe} structure could not be determined higher than...
270 K due to decreasing crystal quality on warming. Experimental procedure and crystal details for individual cocystals at 120 K and room temperature can be found in the Supporting Information. CCDC deposition numbers: 2,171,654–2,171,666. Crystals of an impurity mono-chloro azopyridine [1] were also characterised and the structure is discussed in the supplementary information. Crystals of an impurity mono-chloro azopyridine (chlorinated azopyridined have been observed previously as impurities in azopyridine [42]) were also characterised and the structure is discussed in the supplementary information.

Acknowledgments

We thank Ashland LLC and the Engineering and Physical Sciences Research Council for studentship funding. We also thank Dr Darren R. Gröcke for the CN analysis of samples at the Stable Isotope Biogeochemistry Laboratory at Durham University.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was funded by Ashland LLC and the Engineering and Physical Sciences Research Council.

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Data Availability Statement

Electronic supplementary information (ESI) available: XRPD, preferred orientation details, and experimental details. CCDC 2171654-2171666. Other data is available from the authors.

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