Supporting information for article:

A survey of thermal expansion coefficients for organic molecular crystals in the Cambridge Structural Database

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Routines for extracting the volumetric and principal expansion coefficients were implemented using Python (v3), for compatibility with the CSD Python API. The methodology largely follows the implementation of PASCal (Cliffe & Goodwin, 2012), except where highlighted below.

S1. Extracting the volumetric expansion coefficient

Since the unit-cell volume is directly available for each CSD entry, the volumetric expansion coefficient can be extracted from the linear LS fit of $V$ vs $T$. The gradient defines $\Delta V/\Delta T$, but it is necessary to choose a reference value for $V$. For consistency across the large range of structure families, the reference volume is extrapolated to 298 K, as calculated by the parameters of the LS fit.

$$\alpha_V = 1 \times 10^6 \times \frac{\text{LS gradient}}{V\text{(298 K)}} \text{ ppm K}^{-1} \text{ for the plot of } V \text{ vs } T.$$  

The $\alpha_V$ value calculated by PASCal is based on an LS fit of $T$ vs $V$ (since this enables weights to be applied conveniently to the $T$ values). For good linear fits, there is little difference between a fit of $V$ vs $T$ and $T$ vs $V$. For data sets deviating significantly from linearity, however, the value obtained from $T$ vs $V$ can differ substantially from that obtained using $V$ vs $T$. A consistent approach with $T$ as the independent variable is applied in this paper and recommended for comparison of $\alpha_V$ to the presented distributions. See ABELAU below for an example.

S2. Calculating the strain tensor

Calculation of the strain tensor follows the description given for PASCal. At the heart of the method is the transformation matrix to yield Cartesian axes from the crystal axes, which depends on the convention chosen. Schlenker (1978), PASCal and the Bilbao Crystallographic Server all choose the Institute of Radio Engineers (IRE) convention: $z$(cart) parallel to crystal $c$, $x$(cart) parallel to crystal $a^*$, and $y$(cart) perpendicular to $x$(cart) and $z$(cart). The same convention was implemented in the Python code, and the resulting strain tensors were validated against the STRAIN module of the Bilbao server.

S3. Calculating the principal expansion coefficients

The three principal strains, $\Delta L/L$, are obtained as the eigenvalues of the strain tensors. For each data point above the minimum temperature, the strain tensor is calculated relative to the lowest temperature, then a linear LS fit is applied. As for PASCal, the eigenvalues at each step are sorted by magnitude and assumed to be in the same sequence through the range. The resulting $\alpha_L$ values are relative to $L$ at the minimum temperature in the supplied range. For consistency with the approach applied to the volume fit, the values are re-scaled to refer to $L$ at $T = 298$ K.

$$\alpha_L = 1 \times 10^6 \times \frac{\text{LS gradient}}{1 + \Delta L/L(298 \text{ K})} \text{ ppm K}^{-1} \text{ for the plot of each eigenvalue vs } T.$$


S4. Calculating errors

Standard uncertainties are calculated using heteroscedasticity-consistent standard errors, defined at: https://en.wikipedia.org/wiki/Heteroscedasticity-consistent_standard_errors. For $\alpha_V$, the quoted standard uncertainty is the standard error on the gradient of $V$ vs $T$, divided by the reference volume extrapolated to 298 K. For $\alpha_L$, the quoted standard uncertainty is the standard error on the gradient of $\Delta L/L$ vs $T$, divided by the reference value of $\Delta L/L$ extrapolated to 298 K.

S5. Fitting of the distributions

Histograms were produced using EXCEL, with bin ranges chosen to provide a smooth representation of the distribution. Continuous distributions were fitted to the derived histogram values using the SOLVER within EXCEL. For the volumetric coefficient, a normal distribution was applied. Three parameters (scale, mean, $su$) were optimised so as to minimise the sum of the squared differences between the normal distribution and the value in each histogram bin. The temperature points for the fit were taken to be the midpoint of each bin. For the principal coefficients and the anisotropy measure, the histogram was initially fitted using a skew normal distribution (https://en.wikipedia.org/wiki/Skew_normal_distribution), defined in EXCEL as follows:

$$\text{scale} \times \text{NORM.DIST}(T, \text{mean}, \text{su}, \text{FALSE}) \times \text{NORM.DIST}(\alpha T, \alpha \times \text{mean}, \text{su}, \text{TRUE})$$

The first term is a symmetrical normal distribution and the second term is a cumulative normal distribution, multiplied by the skew parameter $\alpha$. Four parameters (scale, mean, $su$, $\alpha$) were optimised so as to minimise the sum of the squared differences between the normal distribution and the value in each histogram bin. The resulting continuous skew normal distribution was then approximated by two half normal distributions, defined with a common mean, but individual standard deviations and a single scale parameter linked by the ratio ($su(R)/su(L)$). The four parameters defining these two half normal distributions were optimised so as to minimise the squared differences relative to the continuous skew normal distribution over the full range of the plot, with this sum of squares including the lower half of the left distribution and the upper half of the right distribution. The values quoted in the paper are rounded to integers, to avoid any false indication of precision.
### S6. Chemical diagrams for the structures referred to in the text

| ABELAU | AHEJAZ | BIJWAS |
|--------|--------|--------|
| ![Chemical diagram for ABELAU](image) | ![Chemical diagram for AHEJAZ](image) | ![Chemical diagram for BIJWAS](image) |

| BOQHOE | DPANTH | FOCGOT |
|--------|--------|--------|
| ![Chemical diagram for BOQHOE](image) | ![Chemical diagram for DPANTH](image) | ![Chemical diagram for FOCGOT](image) |

| GLYALB | HACTPH | JETRIJ |
|--------|--------|--------|
| ![Chemical diagram for GLYALB](image) | ![Chemical diagram for HACTPH](image) | ![Chemical diagram for JETRIJ](image) |

| JOGVEJ | METNAM | MEZKEH |
|--------|--------|--------|
| ![Chemical diagram for JOGVEJ](image) | ![Chemical diagram for METNAM](image) | ![Chemical diagram for MEZKEH](image) |
| MNPYDO | PBPACB | RALLAU |
|--------|--------|--------|
| ![MNPYDO](image1) | ![PBPACB](image2) | ![RALLAU](image3) |
| TEDAPC | TEJKUO | TETROL |
| ![TEDAPC](image4) | ![TEJKUO](image5) | ![TETROL](image6) |
| UROBUA | XIWREA | ZZZAOS |
| ![UROBUA](image7) | ![XIWREA](image8) | ![ZZZAOS](image9) |
| ZZZKAY | | |
S7. Selected examples

S7.1. ABELAU (MacGillivray et al., 2000; Hutchins et al., 2018b)

Table S1  This is noted in the text to be an example of a family containing a significant outlier at 173 K.

| Refcode  | T(K) | a (Å)  | b (Å)  | c (Å)  | α (°)  | β (°)  | γ (°)  | V (Å³)  |
|----------|------|--------|--------|--------|--------|--------|--------|---------|
| ABELAU   | 173  | 9.749  | 11.367 | 14.273 | 111.668| 90.000 | 90.000 | 1469.926|
| ABELAU01 | 190  | 9.749  | 11.324 | 14.245 | 111.822| 90.000 | 90.000 | 1459.897|
| ABELAU02 | 210  | 9.753  | 11.316 | 14.248 | 111.746| 90.000 | 90.000 | 1460.435|
| ABELAU03 | 230  | 9.770  | 11.322 | 14.267 | 111.713| 90.000 | 90.000 | 1466.124|
| ABELAU04 | 250  | 9.776  | 11.314 | 14.269 | 111.658| 90.000 | 90.000 | 1466.780|
| ABELAU05 | 270  | 9.789  | 11.314 | 14.283 | 111.607| 90.000 | 90.000 | 1470.797|
| ABELAU06 | 291  | 9.802  | 11.312 | 14.292 | 111.539| 90.000 | 90.000 | 1474.028|

Figure S1  [Blue line shows the LS fit to all data points; red line shows LS fit excluding ABELAU at 173 K]

Table S2  **Python code**: including all structures in the fit of $V$ vs $T$ ($R^2 = 0.3729$):

| Reporting T | $\alpha_L$ (1) (ppm K$^{-1}$) | $\alpha_L$ (2) (ppm K$^{-1}$) | $\alpha_L$ (3) (ppm K$^{-1}$) | $\Sigma \alpha_L$ | $\alpha_V$ (ppm K$^{-1}$) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0           | $-23$ (20)      | 26 (12)         | 49 (5)          | 52              | 52 (37)         |
| 173         | $-23$ (20)      | 26 (12)         | 49 (5)          | 52              | 52 (37)         |
| 298         | $-23$ (20)      | 26 (11)         | 49 (5)          | 52              | 51 (36)         |
**Python code:** omitting ABELAU from the fit of $V$ vs $T$ ($R^2 = 0.9633$):

| Reporting $T$ | $\alpha_l (1)$ (ppm K$^{-1}$) | $\alpha_l (2)$ (ppm K$^{-1}$) | $\alpha_l (3)$ (ppm K$^{-1}$) | $\Sigma \alpha_l$ | $\alpha_V$ (ppm K$^{-1}$) |
|--------------|-------------------------------|-------------------------------|-------------------------------|-----------------|-----------------------------|
| 0            | −12 (3)                       | 56 (4)                        | 57 (2)                        | 101             | 102 (8)                     |
| 190          | −12 (3)                       | 56 (4)                        | 56 (2)                        | 100             | 100 (8)                     |
| 298          | −12 (3)                       | 55 (4)                        | 56 (2)                        | 99              | 99 (8)                      |

**PASCal (unit weights on $T$):** including ABELAU:

| Reporting $T$ | $\alpha_l (1)$ (ppm K$^{-1}$) | $\alpha_l (2)$ (ppm K$^{-1}$) | $\alpha_l (3)$ (ppm K$^{-1}$) | $\Sigma \alpha_l$ | $\alpha_V$ (ppm K$^{-1}$) |
|--------------|-------------------------------|-------------------------------|-------------------------------|-----------------|-----------------------------|
| 173          | −23 (17)                      | 26 (10)                       | 49 (4)                        | 52              | 136 (51)                    |

For this case, with the poor linear fit to all of the points, the volumetric coefficient derived from a fit of $T$ vs $V$ is significantly different from the sum of the principal coefficients.

**PASCal (unit weights on $T$):** omitting ABELAU:

| Reporting $T$ | $\alpha_l (1)$ (ppm K$^{-1}$) | $\alpha_l (2)$ (ppm K$^{-1}$) | $\alpha_l (3)$ (ppm K$^{-1}$) | $\Sigma \alpha_l$ | $\alpha_V$ (ppm K$^{-1}$) |
|--------------|-------------------------------|-------------------------------|-------------------------------|-----------------|-----------------------------|
| 190          | −13 (2)                       | 55 (3)                        | 56 (1)                        | 98              | 102 (7)                     |

S7.2. MNYPDO

**Table S3**  The largest identified structure family, and noted in the text to contain a clear outlier at 296 K. The orthorhombic structure permits an independent check on $\Delta L/L$ calculations and extrapolation of $\alpha_L$ to 298 K, by a direct plot of $L$ vs $T$.

| Refcode     | $T$ (K) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | $V$ (Å$^3$) |
|-------------|---------|---------|---------|---------|--------------|-------------|--------------|-------------|
| MNPYDO01    | 106     | 5.135   | 6.094   | 20.890  | 90.000       | 90.000      | 90.000       | 653.704     |
| MNPYDO04    | 120     | 5.133   | 6.109   | 20.953  | 90.000       | 90.000      | 90.000       | 657.090     |
| MNPYDO05    | 135     | 5.134   | 6.111   | 20.992  | 90.000       | 90.000      | 90.000       | 658.589     |
| MNPYDO06    | 150     | 5.134   | 6.113   | 21.022  | 90.000       | 90.000      | 90.000       | 659.795     |
| MNPYDO07    | 165     | 5.134   | 6.114   | 21.059  | 90.000       | 90.000      | 90.000       | 661.102     |
| MNPYDO08    | 180     | 5.135   | 6.116   | 21.098  | 90.000       | 90.000      | 90.000       | 662.587     |
| MNPYDO09    | 195     | 5.136   | 6.116   | 21.132  | 90.000       | 90.000      | 90.000       | 663.867     |
| MNPYDO10    | 210     | 5.137   | 6.119   | 21.172  | 90.000       | 90.000      | 90.000       | 665.542     |
| MNPYDO11    | 225     | 5.138   | 6.120   | 21.216  | 90.000       | 90.000      | 90.000       | 667.173     |
| MNPYDO12    | 240     | 5.139   | 6.122   | 21.260  | 90.000       | 90.000      | 90.000       | 668.856     |
| MNPYDO30    | 255     | 5.141   | 6.123   | 21.300  | 90.000       | 90.000      | 90.000       | 670.507     |
| MNPYDO13    | 270     | 5.143   | 6.126   | 21.343  | 90.000       | 90.000      | 90.000       | 672.455     |
| MNPYDO14    | 285     | 5.146   | 6.128   | 21.383  | 90.000       | 90.000      | 90.000       | 674.310     |
| MNPYDO26    | 296     | 4.986   | 6.001   | 20.343  | 90.000       | 90.000      | 90.000       | 608.622     |
Figure S2 [Blue line shows the LS fit to all data points; red line shows LS fit excluding MNPYDO26 at 296 K]

Table S4  

| Reporting T (K) | $\alpha_L(1)$ (ppm K$^{-1}$) | $\alpha_L(2)$ (ppm K$^{-1}$) | $\alpha_L(3)$ (ppm K$^{-1}$) | $\Sigma\alpha_L$ | $\alpha_V$ (ppm K$^{-1}$) |
|-----------------|-------------------------------|-------------------------------|-------------------------------|------------------|--------------------------|
| 0               | -45 (50)                      | -37 (53)                      | 53 (66)                       | -29              | -26 (164)                |
| 106             | -45 (51)                      | -37 (53)                      | 52 (66)                       | -30              | -26 (165)                |
| 298             | -46 (51)                      | -37 (53)                      | 52 (65)                       | -31              | -27 (166)                |

**Python code**: including all structures in the fit of $V$ vs $T$ ($R^2 = 0.0045$):

| Reporting T (K) | $\alpha_L(1)$ (ppm K$^{-1}$) | $\alpha_L(2)$ (ppm K$^{-1}$) | $\alpha_L(3)$ (ppm K$^{-1}$) | $\Sigma\alpha_L$ | $\alpha_V$ (ppm K$^{-1}$) |
|-----------------|-------------------------------|-------------------------------|-------------------------------|------------------|--------------------------|
| 106             | 12 (2)                        | 23 (4)                        | 129 (2)                       | 164              | 166 (5)                  |
| 135             | 12 (2)                        | 23 (4)                        | 127 (2)                       | 162              | 163 (5)                  |
| 150             | 12 (2)                        | 23 (4)                        | 124 (2)                       | 159              | 158 (5)                  |

**Python code**: omitting MNPYDO26 from the fit of $V$ vs $T$ ($R^2 = 0.9933$):

| Reporting T (K) | $\alpha_L(1)$ (ppm K$^{-1}$) | $\alpha_L(2)$ (ppm K$^{-1}$) | $\alpha_L(3)$ (ppm K$^{-1}$) | $\Sigma\alpha_L$ | $\alpha_V$ (ppm K$^{-1}$) |
|-----------------|-------------------------------|-------------------------------|-------------------------------|------------------|--------------------------|
| 106             | 12 (2)                        | 23 (4)                        | 127 (2)                       | 162              | 164 (5)                  |

**PASCal (unit weights on $T$)**: omitting MNPYDO26:

| Reporting T (K) | $\alpha_L(1)$ (ppm K$^{-1}$) | $\alpha_L(2)$ (ppm K$^{-1}$) | $\alpha_L(3)$ (ppm K$^{-1}$) | $\Sigma\alpha_L$ | $\alpha_V$ (ppm K$^{-1}$) |
|-----------------|-------------------------------|-------------------------------|-------------------------------|------------------|--------------------------|
| 106             | 12 (2)                        | 23 (4)                        | 127 (2)                       | 162              | 164 (5)                  |

**Check using a linear fits of $V$ vs $T$ and $L$ vs $T$ (calculations in EXCEL)**:

| $T$ (K) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | LS fit ($a$) | LS fit ($b$) | LS fit ($c$) | LS fit ($V$) |
|---------|---------|---------|---------|-------------|--------------|--------------|--------------|--------------|
| 106     | 5.135   | 6.094   | 20.890  | 653.704     | 5.1318       | 6.1039       | 20.9032      | 654.781      |
| 120     | 5.133   | 6.109   | 20.953  | 657.090     | 5.1326       | 6.1058       | 20.9404      | 656.273      |
| 135     | 5.134   | 6.111   | 20.992  | 658.589     | 5.1336       | 6.1079       | 20.9803      | 657.872      |
| 150     | 5.134   | 6.113   | 21.022  | 659.795     | 5.1345       | 6.1100       | 21.0202      | 659.471      |
Gradients and extrapolated values for $L$ and $V$ based on the linear fits:

| $T$ (K) | Gradient * 1e6 | Intercept (= value at 0 K) | Value at 106 K | Value at 298 K |
|--------|----------------|---------------------------|----------------|----------------|
| 225    | 5.1318         | 6.1039                    | 20.9032        | 21.4136        |
| 240    | 5.1437         | 6.1305                    | 21.4136        | 21.3790        |
| 255    | 5.1411         | 6.1223                    | 21.3000        | 21.2993        |
| 270    | 5.1437         | 6.1305                    | 21.3433        | 21.3392        |
| 285    | 5.1411         | 6.1223                    | 21.3000        | 21.2993        |

Calculated coefficients based directly on the LS fitted values of $L$ and $V$:

| $T$ (K) | $\alpha_L$ (1) (ppm K$^{-1}$) | $\alpha_L$ (2) (ppm K$^{-1}$) | $\alpha_L$ (3) (ppm K$^{-1}$) | $\alpha_V$ (ppm K$^{-1}$) |
|--------|-----------------|------------------|-----------------|-----------------|
| 0      | 12.12           | 22.81            | 128.91          | 165.64          |
| 106    | 12.10           | 22.75            | 127.17          | 162.78          |
| 298    | 12.08           | 22.66            | 124.14          | 157.85          |

S7.3. AHEJAZ (Das et al., 2010)

Table S5 This example is noted in the text to be an exceptional case reported in the literature. The orthorhombic structure has principal axes aligned with the crystal axes, which permits independent checks on $\Delta L/L$ calculations, and extrapolation of $\alpha_L$ to 298 K, by a direct plot of $L$ vs $T$. 

| Refcode | $T$ (K) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | $V$ (Å$^3$) |
|---------|---------|---------|---------|---------|-------------|-------------|-------------|------------|
| AHEJAZ  | 225     | 4.616   | 11.699  | 15.191  | 90.000      | 90.000      | 90.000      | 820.335    |
| AHEJAZ01| 240     | 4.686   | 11.656  | 15.089  | 90.000      | 90.000      | 90.000      | 824.109    |
| AHEJAZ02| 255     | 4.743   | 11.638  | 15.025  | 90.000      | 90.000      | 90.000      | 829.313    |
| AHEJAZ03| 270     | 4.785   | 11.618  | 14.965  | 90.000      | 90.000      | 90.000      | 831.988    |
| AHEJAZ04| 285     | 4.819   | 11.615  | 14.938  | 90.000      | 90.000      | 90.000      | 836.189    |
| AHEJAZ05| 300     | 4.845   | 11.607  | 14.905  | 90.000      | 90.000      | 90.000      | 838.196    |
| AHEJAZ06| 315     | 4.868   | 11.607  | 14.883  | 90.000      | 90.000      | 90.000      | 840.984    |
| AHEJAZ07| 330     | 4.880   | 11.596  | 14.873  | 90.000      | 90.000      | 90.000      | 841.589    |
[Shaded rows are not used for the primary analysis (restricted to the range 90–300 K), but mentioned below when comparing to the results reported by Das et al.]

**Figure S3**  
Python code: fit of \( V \) vs \( T \) \( (R^2 = 0.9868) \):  

| Reporting \( T \) | \( \alpha_L (1) \) (ppm K\(^{-1}\)) | \( \alpha_L (2) \) (ppm K\(^{-1}\)) | \( \alpha_L (3) \) (ppm K\(^{-1}\)) | \( \Sigma \alpha_L \) | \( \alpha_L \) (ppm K\(^{-1}\)) |
|-------------------|--------------------------------|--------------------------------|--------------------------------|----------------|----------------|
| 0                 | –231 (31)                      | –96 (21)                        | 766 (79)                        | 439            | 319 (19)      |
| 225               | –244 (33)                      | –98 (21)                        | 653 (68)                        | 311            | 298 (18)      |
| 298               | –249 (34)                      | –99 (22)                        | 623 (64)                        | 275            | 291 (17)      |

**PASCal (unit weights on \( T \)):**  

| Reporting \( T \) | \( \alpha_L (1) \) (ppm K\(^{-1}\)) | \( \alpha_L (2) \) (ppm K\(^{-1}\)) | \( \alpha_L (3) \) (ppm K\(^{-1}\)) | \( \Sigma \alpha_L \) | \( \alpha_L \) (ppm K\(^{-1}\)) |
|-------------------|--------------------------------|--------------------------------|--------------------------------|----------------|----------------|
| 225               | –244 (27)                      | –98 (17)                        | 654 (55)                        | 312            | 300 (13)      |

**Check using a linear fits of \( V \) vs \( T \) and \( L \) vs \( T \) (calculations in EXCEL):**  

| \( T \) (K) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( V \) (Å\(^3\)) | \( \text{LS fit (a)} \) | \( \text{LS fit (b)} \) | \( \text{LS fit (c)} \) | \( \text{LS fit (V)} \) |
|------------|-------------|-------------|-------------|----------------|----------------|----------------|----------------|----------------|
| 225        | 4.616       | 11.699      | 15.191      | 820.335        | 4.6357         | 11.6819        | 15.1576        | 820.863        |
| 240        | 4.686       | 11.656      | 15.089      | 824.109        | 4.6810         | 11.6647        | 15.1021        | 824.527        |
| 255        | 4.743       | 11.638      | 15.025      | 829.313        | 4.7263         | 11.6474        | 15.0466        | 828.190        |
| 270        | 4.785       | 11.618      | 14.965      | 831.988        | 4.7717         | 11.6302        | 14.9911        | 831.853        |
| 285        | 4.819       | 11.615      | 14.938      | 836.189        | 4.8170         | 11.6130        | 14.9356        | 835.517        |
| 300        | 4.845       | 11.607      | 14.905      | 838.196        | 4.8623         | 11.5958        | 14.8800        | 839.180        |

Gradients and extrapolated values for \( L \) and \( V \) based on the linear fits:  

| \( a \) | \( B \) | \( c \) | \( V \) |
|---------|---------|---------|---------|
| \( \text{Gradient } \times 1\text{E}6 \) | 3020.95 | –1148.57 | –3700.95 | 244228.6 |
Intercept (= value at 0 K)

|   |   |   |   |
|---|---|---|---|
|   | 3.9560 | 11.9403 | 15.9903 | 765.912 |

Value at 225 K

|   |   |   |   |
|---|---|---|---|
|   | 4.6357 | 11.6819 | 15.1576 | 820.863 |

Value at 298 K

|   |   |   |   |
|---|---|---|---|
|   | 4.8562 | 11.5981 | 14.8874 | 838.692 |

Calculated coefficients based directly on the LS fitted values of $L$ and $V$:

| $T$ (K) | $\alpha_i (1)$ (ppm K$^{-1}$) | $\alpha_i (2)$ (ppm K$^{-1}$) | $\alpha_i (3)$ (ppm K$^{-1}$) | $\alpha_V$ (ppm K$^{-1}$) |
|---------|------------------------------|------------------------------|------------------------------|--------------------------|
| 0       | 3020.95 / 763.6               | -1148.57 / -96.2             | -3700.95 / -231.5            | 244228.6 / 318.9         |
| 225     | 3020.95 / 651.7               | -1148.57 / -98.3             | -3700.95 / -244.2            | 244228.6 / 297.5         |
| 298     | 3020.95 / 622.1               | -1148.57 / -99.0             | -3700.95 / -248.6            | 244228.6 / 291.2         |

Comparison of values calculated in this paper to the values reported in Das et al., 2010

The coefficients reported by Das et al. are calculated directly from the (orthorhombic) cell parameters, relative to the values at 330 K, e.g. $\alpha_i = 1/(330 - T) * (L(330) - L(T))$.

| $T$ (K) | $\alpha_i$ (ppm K$^{-1}$) | $\alpha_b$ (ppm K$^{-1}$) | $\alpha_c$ (ppm K$^{-1}$) | $\alpha_V$ (ppm K$^{-1}$) |
|---------|--------------------------|--------------------------|--------------------------|--------------------------|
| 225     | 514.9                    | -84.6                    | -203.6                   | 241.0                    |
| 240     | 441.7                    | -57.5                    | -161.4                   | 231.0                    |
| 255     | 374.3                    | -48.3                    | -136.3                   | 194.9                    |
| 270     | 322.4                    | -31.6                    | -103.1                   | 190.1                    |
| 285     | 274.6                    | -36.4                    | -97.1                    | 142.6                    |
| 300     | 237.0                    | -31.6                    | -71.7                    | 134.7                    |
| 315     | 155.7                    | -63.2                    | -44.8                    | 47.5                     |
| 330     | 0                        | 0                        | 0                        | 0                        |

This corresponds to taking a sequence of linear approximations between each lower temperature and the upper temperature of 330 K:
The results are then quoted as ranges: the expansion coefficients (ppm K\(^{-1}\)) of the axes lie in the range 156 < \(\alpha_a\) < 515; –32 < \(\alpha_b\) < –85 and –48 < \(\alpha_c\) < –204 over the temperature range 225–330 K.

The approach in this current paper is to assume linearity of the plot of \(V\) (or \(L\)) against \(T\) (recalling that this is a necessity to deal with the vast majority of the data set extracted from the CSD), thereby producing a single fitted value for the gradient. Considering the full data range for AHEJAZ (225–330 K), this produces the following plots and coefficients:
| Reference T | $\alpha_a$ (ppm K$^{-1}$) | $\alpha_b$ (ppm K$^{-1}$) | $\alpha_c$ (ppm K$^{-1}$) | $\alpha_V$ (ppm K$^{-1}$) |
|-------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 298 K       | 509                      | $-$73                    | $-$194                   | 251                      |
| 330 K       | 501                      | $-$73                    | $-$195                   | 249                      |