

An examination of the thermal expansion of urea using high-resolution variable-temperature X-ray powder diffraction

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Variable-temperature high-resolution capillary-mode powder X-ray diffraction is used to assess changes in unit-cell dimensions as a function of temperature over the range 188–328 K. No evidence was found for any polymorphic transformations over this temperature range and thermal expansion coefficients for urea were found to be $\alpha_a = (5.27 \pm 0.26) \times 10^{-5} \text{ K}^{-1}$ and $\alpha_c = (1.14 \pm 0.057) \times 10^{-5} \text{ K}^{-1}$.

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1. Introduction

Despite being of fundamental importance in many areas, information about the solid-state properties of molecular materials still remains surprisingly limited (Desiraju, 2003). In particular, detailed knowledge of the thermal expansion tensor for many low-symmetry organic materials is not always available, this despite the fact that structural change as a function of temperature can have ramifications for particle properties.

In the case of crystals not undergoing any polymorphic change, the effect of temperature on crystal structure is well described in terms of a linear thermal expansion coefficient. More specifically, in the case of anisotropic crystals such as urea, thermal expansion can be described by a linear thermal expansion coefficient along its primary crystallographic axes:

$$\alpha = \frac{1}{L_0} \frac{dl}{dT}, \quad (1)$$

where L_0 is a given cell parameter of the material (reference length) in a given direction and at a given temperature T_0 (reference temperature).

In this short note, we report the determination of the thermal expansion coefficients of urea using temperature-programmed high-resolution X-ray powder diffraction. Urea, $\text{O}=\text{C}(\text{NH}_2)_2$, has applications in agrochemistry and nonlinear optics and is one of the simpler organic molecules. Urea is an unusual compound, having only eight atoms yet existing in a solid form under ambient conditions. Because of its simplicity, the crystal structure of urea was one of the first among the organic crystals to be determined by X-ray crystallographic methods (Vaughan & Donohue, 1952, and references therein), being found to crystallize in the highly symmetrical tetragonal space group $P4_21m$ with two molecules in the unit cell of dimensions $a = 5.661$ and $c = 4.712 \text{ \AA}$. Urea crystal chemistry is dominated by hydrogen-bonding chains associated with a network of six strong intermolecular hydrogen bonds, four intrachain along the c axis and two interchain along the ab axis in its first coordination sphere (see Docherty *et al.*, 1993), and is noteworthy for having its carbonyl group as an acceptor for four hydrogen bonds.

2. Experimental details

The calculation of the linear thermal expansion was carried out by monitoring the changes in the a and c cell parameters of a polycrystalline sample of urea, as determined using a Siemens D5000 high-resolution powder X-ray diffractometer equipped with an Oxford Instruments Cryocool liquid-nitrogen cold-flow cryostatic temperature controller. The urea powder, finely ground in a pestle and mortar and loaded into a 1 mm capillary, was examined over a temperature range from 188 to 328 K.

The resultant powder data were analysed with the lattice parameters calculated using the program *DICVOL* (Boultif & Louer, 1991). The quality of the lattice parameters derived was cross-checked through full-pattern fitting using the program *GSAS* (Larson & von Dreele, 1994). Using the values obtained from *DICVOL* during pattern indexing resulted in a comparatively low value for R_{wp} (9%), and hence the change of lattice parameters after the refinement was not found to be significant, reflecting a difference between the refined and the experimental values of about 0.01%. Hence, the *DICVOL* data was found to be of sufficient quality for calculation of the thermal expansion coefficient.

The thermal expansion was calculated along the a and c axes *via* equation (1) with reference temperature and cell parameters from previous studies (Swaminathan *et al.*, 1984), from which the parameters at 150 K are $a = 5.59$ and $c = 4.69 \text{ \AA}$.

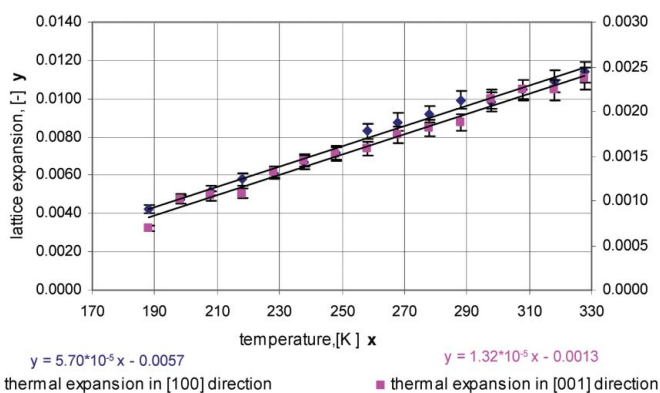
3. Results and discussion

The lattice expansion as a function of temperature is given in Fig. 1. No significant variation in cell parameters, reflecting polymorphic variation, was found to occur, confirming previous observations on the polymorphic behaviour of urea. The thermal expansion coefficient over the temperature range 188–328 K was measured to be $(5.27 \pm 0.26) \times 10^{-5} \text{ K}^{-1}$ in the ab direction, and $(1.14 \pm 0.057) \times 10^{-5} \text{ K}^{-1}$ in the c direction, which correlates well with the values determined from previously published data over a temperature range of 12–123 K (Swaminathan *et al.*, 1984). In this range, the coefficients of thermal expansion, calculated in the same way as used for the data

Table 1

Results of a literature survey on previously measured coefficients of thermal expansion for some related organic crystals.

Compound	Coefficient of thermal expansion (K^{-1})	Reference
α -Chloroacetic acid (nonlinear)	7.7×10^{-5}	Hoseneder & Hartel (2001)
MODPA (4,5-methyl-1,3,4-oxadiazin-2-yl- <i>N,N</i> -dimethylphenylamine)	1.8×10^{-4}	Franco & Reck (2002)
DPO (2,5-diphenyl-1,3,4-oxadiazine)	1.9×10^{-4}	Franco & Reck (2002)
L-Alanine	1.64×10^{-7} , 12.07×10^{-7}	Misoguti (1996)
Hexamine	6×10^{-7}	Fomo (1974)
UDT (urea- <i>d</i> -tartaric acid)	5.23×10^{-5} , 3.86×10^{-5} , 3.57×10^{-5}	Meng & Lu (1998)
Benzophenone	1.77×10^{-7} , 3.00×10^{-7} , 1.48×10^{-7}	Girdwood (1998)
Urea	5.27×10^{-5} , 1.14×10^{-5}	This work

**Figure 1**

The lattice expansion $[(l - l_0)/l_0]$, dimensionless is represented as a function of the temperature. The coefficient of thermal expansion was determined from the slope of the straight line used to fit the experimental data.

presented here, were found to be $(3.74 \pm 0.187) \times 10^{-5} K^{-1}$ in the *ab* direction and $(1.21 \pm 0.0605) \times 10^{-5} K^{-1}$ in the *c* direction.

Examining the above results, it is noteworthy that the coefficient of thermal expansion in the *ab* direction is larger, for both temperature regions examined, compared with that in the *c* direction. This is expected, reflecting weaker intermolecular interactions associated with the hydrogen bonds along *ab* axis (interchain) compared with those along the *c* axis (intrachain) (Docherty *et al.*, 1993), and hence the *ab* axis allows for the greater thermal expansion. The comparison of the expansion coefficient for the two different temperature ranges, *i.e.* this study and that of Swaminathan *et al.*, indicates a larger change of the thermal expansion coefficient in the *ab* direction for the higher temperature range, again reflecting the weaker nature of the intermolecular interactions associated with the hydrogen bonding compared with the stronger ones along the *c* direction. In contrast, the change of the coefficient of thermal expansion in the *c* direction

for the two temperature ranges is quite similar, being within the range of the error for these studies.

A literature survey (Table 1) of thermal expansion data for organic crystals reveals that available data are limited for this class of materials. The thermal expansion of urea is comparable with other urea-based compounds (Meng & Lu, 1998) but is larger than other aromatic hydrocarbons such as benzophenone (Girdwood, 1998). This is not unexpected given the dominance of the van der Waals and hydrogen-bonding contribution to the crystal lattice energy.

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