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Competition of interactions and a new high-temperature phase of selenourea

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The aggregation of molecules is usually associated with a specific type of interaction, which can be altered by thermodynamic conditions. Under normal conditions, the crystal structure of selenourea, SeC(NH₂)₂, phase α is trigonal, space group $P3_1$, Z = 27. Its large number of independent molecules ($Z_{\alpha}' = 9$) can be associated with the formation of an NH···N hydrogen bond substituting one of 36 independent NH···Se hydrogen bonds, which prevail among intermolecular interactions. Phase α approximates the trigonal structure with a threefold smaller unit cell (Z = 9), which in turn approximates another still threefold smaller unit cell (Z = 3). The temperature-induced transformations of selenourea have been characterized by calorimetry and by performing 21 single-crystal X-ray diffraction structural determinations as a function of temperature. At 381.0 K, phase α undergoes a first-order displacive transition to phase γ , with space group P3₁21 and Z reduced to 9, when the NH···N bond is broken and an $NH \cdots Se$ bond is formed in its place. Previously, an analogous competition was observed between $NH \cdots N$ and $NH \cdots O$ hydrogen bonds in high-pressure phase III of urea. The lattice vectors along the (001) plane in lowand high-temperature phases of selenourea are related by a similarity rule, while the lattice dimensions along direction c are not affected. This similarity rule also applies to the structures of phase γ and hypothetical phase δ (Z = 3). The thermally controlled transition between enantiomorphic phases of selenourea contrasts with its high-pressure transition at 0.21 GPa to a centrosymmetric phase β , where both the NH···Se and NH···N bonds are present. The compression and heating reduce the number of independent molecules from Z' =9 in phase α , to Z' = 2 in phase β and to Z' = 1.5 in phase γ .

1. Introduction

Selenourea is an important metabolite and chemical agent (Hariharan & Dharmaraj, 2020; Koketsu & Ishihara, 2006; Zheng et al., 2002). Its polymorph α , which is stable under normal conditions, is unique due to the complex structure comprising nine independent molecules (Z' = 9) in the asymmetric unit (Roszak & Katrusiak, 2021; Luo & Dauter, 2017; Rutherford & Calvo, 1969). The recently revealed polymorph β , stable above 0.21 GPa, contains two independent molecules (Z' = 2). The recrystallization under high pressure also induces a partial stochastic hydration in phase α ; the recrystallization from the aqueous solution above 0.21 GPa favors the formation of duotritohydrate $3SeC(NH_2)_2 \cdot 2H_2O$, unknown under normal conditions (Roszak & Katrusiak, 2021). Meanwhile, relatively little is known about the thermal behavior of $SeC(NH_2)_2$. Two crystal structures determined at 100 K (Luo & Dauter, 2017) and 173 K (Rutherford & Calvo, 1969) are both consistent with phase α (*i.e.* space group P3₁, Z' = 9) (Roszak & Katrusiak, 2021; Rutherford & Calvo, 1969). Our differential scanning calorimetry (DSC) measurements revealed a first-order phase

transition at 381.0 K and a new solid selenourea phase γ stable below the melting point at 473 K (Fig. 1). The structural mechanism of this transition involves intermolecular hydrogen bonds NH···Se and NH···N, aggregating the molecules into helices and the helices into a three-dimensional framework. The lattice projections along **c** of selenourea phases α and γ are related by a similarity transformation, which is connected with the qualitative differences between intermolecular interactions in the structures of these phases and to the origin of the large number of independent molecules in phase α .

2. Experimental

2.1. Calorimetric measurements

Several differential scanning calorimetry (DSC) heating and cooling runs were measured between 160 K and 473 K. They clearly showed the phase transition between phases α and γ at $T_c = 381.0$ K, as well as a partial decomposition of selenourea at the melting point at $T_{mp} = 473$ K (Fig. S1b) and the full decomposition immediately above T_{mp} (Fig. S1c). DSC was performed for the samples sealed in aluminium capsules in N₂ atmosphere on a Setsys 1200 Setaram instrument at a scan speed of 5 K min⁻¹ (see Figs. 1 and S1).

2.2. Single-crystal X-ray diffraction

A single crystal of SeC(NH₂)₂ was mounted on an Oxford Diffraction SuperNova diffractometer with a Cu $K\alpha$ microsource and then on an Xcalibur diffractometer equipped with an EOS-CCD detector and a graphite-monochromator from a fine-focus X-ray Mo $K\alpha$ tube. The single-crystal diffraction data were measured at 21 temperature points in the range



Figure 1

Differential scanning calorimetry signal for selenourea at ambient pressure measured at the rate of 5 K min⁻¹ (*cf.* Fig. S1). The insets show: (top) the enhanced region of the transition between phases α and γ ; (bottom) the selenourea molecule with its atom labels (letters a/b distinguish H atoms *anti/syn*, respectively).

Table 1

Selected crystal data of SeC(NH₂)₂ phases α and γ , all determined at ambient pressure.

See *Experimental* for information about the racemic twins and Table S1 for detailed information about 21 single-crystal determinations.

Phase	α -SeC(NH ₂) ₂	γ-SeC(NH ₂) ₂
Temperature (K)	373	383
Space group	P31	P3 ₁ 21
a (Å)	15.3619 (8)	8.8551 (4)
<i>c</i> (Å)	13.0768 (6)	13.0694 (7)
$V(Å^3)$	2672.5 (2)	887.50 (7)
Z, Z'	27, 9	9, 1.5
$D_x (\mathrm{g} \mathrm{cm}^{-3})$	2.064	2.072

110–393 K on the same single-crystal sample (Table 1). The low-temperature data collections were performed with Cu $K\alpha$ radiation, while for the high-temperature experiments the





Unit-cell dimensions of SeC(NH₂)₂ crystal: (*a*) molecular volume and (*b*) the unit-cell dimensions, as a function of temperature. The 100 K/0.1 MPa points were determined by Luo & Dauter (2017). The molecular volume of phase β (the open circle) is also indicated for its lowest limit of pressure range at 0.21 GPa (Roszak & Katrusiak, 2021). Where not indicated, the estimated standard deviations are smaller than the plotted symbols.

Mo $K\alpha$ radiation was used, because in high temperature the selenourea crystals sublimate and the shorter radiation allows quicker data collections (due to the more compact reciprocal lattice); we additionally applied shorter exposition time, of five seconds per image compared to 30 seconds per image for the experiments with Cu radiation. These measures allowed us to reduce the effects of the sample-crystal sublimation, although they also reduced the accuracy of measurements, apparent from Fig. 2 and Tables S1 and S2. Our nitrogen gas-flow Oxford Cryosystem low-temperature attachments stabilize temperature within 0.1 K. The CrysAlisPro software (Rigaku Oxford Diffraction, 2015) controlled the diffraction measurements and the preliminary data reduction. The crystal structures were solved by direct methods with the program SHELXT (Sheldrick, 2015a) and refined by least-squares with SHELXL (Sheldrick, 2015b), both operated under OLEX2 (Dolomanov et al., 2009) software. As indicated by the Flack parameter, the structures were refined as twins of enantiomorphs. All refinements converged to the racemic-twin compounds, with the 50:50 composition of enantiomorphs (hence the twins of enantiomorphic space groups $P3_1$ and $P3_2$ in phase α , and space groups $P3_121$ and $P3_221$ in phase γ). For simplifying the description, only the symmetry of space groups $P3_1$ and $P3_121$ are discussed below. Anisotropic displacement factors were generally applied for non-hydrogen atoms. The H atoms in selenourea were located from the molecular geometry (N-H distance 0.86 Å) and their U_{iso} parameters constrained to $1.2U_{eq}$ of their carrier atoms. Structural drawings were prepared using program Mercury 4.0 (Macrae et al., 2020).

3. Results and discussion

The clear abrupt shrinking of the crystal volume and of all unit-cell dimensions (Fig. 2) fully confirm the transition between phases α and γ marked by the DSC endothermic peak at 381.0 K in the heating run and exothermic peak at 380.7 K in the cooling run (Fig. 1). This hysteresis of about 0.3 K and the shapes of the DSC peaks are characteristic of a first-order phase transition. We noted that the hysteresis depends on the rate of temperature changes. Its entropy change ΔS of 2.4 J mol⁻¹ K⁻¹ corresponds to Rln1.33 (R is the gas constant) is consistent with the displacive character of the structural transformation (Salje, 1992; Dove, 1997). We have performed for phases α and γ a series of 21 single-crystal diffraction structural determinations at different temperature points (Tables 1 and S1). Both phases α and γ are trigonal, but the space-group type changes from $P3_1$ to $P3_121$. The unit-cell size is reduced in phase γ according to matrix equation $A_{\nu} = MA_{\alpha}$:

$$\begin{pmatrix} \mathbf{a}_{\gamma} \\ \mathbf{b}_{\gamma} \\ \mathbf{c}_{\gamma} \end{pmatrix} = \begin{pmatrix} \frac{1}{3} - \frac{1}{3} & 0 \\ \frac{1}{3} & \frac{2}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_{\alpha} \\ \mathbf{b}_{\alpha} \\ \mathbf{c}_{\alpha} \end{pmatrix},$$
(1)

where A_{α} and A_{γ} are metric matrices of lattices versors of phases α and γ , respectively [equation (1)]. The unit-cell volume change is equal to det $M = \frac{1}{3}$.

The reverse transformation $A_{\alpha} = M^{-1}A_{\gamma}$ has the form:

$$\begin{pmatrix} \mathbf{a}_{\alpha} \\ \mathbf{b}_{\alpha} \\ \mathbf{c}_{\alpha} \end{pmatrix} = \begin{pmatrix} 2 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_{\gamma} \\ \mathbf{b}_{\gamma} \\ \mathbf{c}_{\gamma} \end{pmatrix},$$
(2)

where matrix M^{-1} is the inverse of M in equation (1).

The $\alpha - \gamma$ transition in selenourea can be connected with crystal cohesion forces and, in particular, with NH···Se hydrogen bonds linking the molecules into helices along direction **c**, as shown in Figs. 3 and 4. In phase α , the NH···Se hydrogen bonds along the helices involve H atoms in the syn positions (Figs. 1 and 4), the helices in turn are interconnected approximately perpendicular to direction **c** by hydrogen bonds NH···Se and NH···N, involving the *anti*-H atoms. In phase γ hydrogen bons NH···N are broken. In phase α there are five independent helices labeled A₉, A₈, A₇, B₆₅₄ and B₃₂₁ (the subscripts list the numbers labeling nine independent molecules in the helix): helix A₉ consists of molecules labeled with number 9 (i.e. all molecules in this helix are symmetry dependent) related by the screw axis 3_1 at x = 0 and y = 0; helix A₈ consists of molecules labeled with number 8 related by the screw axis 3_1 at $x = \frac{1}{3}$ and $y = \frac{2}{3}$; helix A₇ consists of molecules labeled with number 7 related by the screw axis 3_1 at $x = \frac{2}{3}$ and $y = \frac{1}{3}$; helix B₆₅₄ consists of independent molecules labeled with numbers 6, 5, 4 approximating a 3_1 axis at $x = \frac{1}{3}$ and y = 0; helix B₃₂₁ consists of three independent molecules labeled with numbers 3, 2, 1 located about a pseudo-3₁ axis at $x = \frac{1}{3}$ and $y = \frac{1}{3}$ $\frac{1}{3}$.

When phase α transforms to phase γ , helices A₉, A₈ and A₇ become translationally dependent, in accordance with the lattice transformation described by equation (1), and they also acquire the symmetry of twofold axes aligned parallel to directions [100], [010] and $[\overline{110}]$, as well as to the C—S bonds of the selenourea molecules. This transformation requires that the molecules in helices, shifted by a_{γ} and b_{γ} , be equally elevated along axis **z**, *i.e.* their relative elevation Δz is 0 Å and the corresponding molecules be equally oriented, *i.e.* their relative orientation $\Delta \varphi$ is 0°. For the structure in phase α , Table 2 compares the distances between helices, d; displacements Δd_{xy} from the idealized distances [either a or $a(3^{1/2})$] along **x**,**y**; elevations Δz along axis **z** relative to helix A₉; and the mean orientation of molecules in one helix, φ , relative to the closest x,y and [110] directions; as well as the deviation of three φ angles within one helix, σ_{φ} , calculated for each helix as $\frac{1}{3}\sum_{i=1}^{3} |\bar{\varphi} - \varphi_i|$. For the ideal threefold symmetric helices their $\sigma_{\varphi} = 0^{\circ}$; for helices B₆₅₄ and B₃₂₁ the σ_{φ} parameter indicates in degrees the average angular distortion from the ideal screw axis 3_1 .

In phase γ , two independent helices A_1 and B_2 acquire the ideal symmetry of screw axes 3_1 , and in helix A_1 the molecules lie on twofold axes. These two independent helices A_1 and B_2 are located at (x, y) positions: (0,0) and $(\frac{1}{3}, \frac{2}{3})$, respectively. The ideally 3_1 -symmetric helices A_9 , A_8 and A_7 of phase α become symmetry dependent in phase γ (the ideal 3_1 -helix A_1 with molecules located on twofold axes); while distorted helices B_{654} and B_{321} of phase α become in phase γ ideally 3_1 -symmetric and they are shifted to the positions of the screw



Figure 3

Crystal structure of selenourea phase α projected down the 3_1 axes along **c**. The unit-cell contours of phases α (red/green/black), γ (purple) and δ (cyan) as well as the labels of helices (red capital letters with indices 1–9 labeling independent molecules in the helix) are indicated (see Fig. S2); in phase γ two independent helices labeled A and B are located along screw axes 3_1 (see the purple unit-cell contour). In hypothetical phase δ all 3_1 -symmetric helices are located at the cyan unit-cell corners. The competing hydrogen bonds N27–H27a···N16 and N27–H27a···Se5 are shown by blue and green dotted lines for one helix A₇ and one helix B₆₅₄, respectively.



Figure 4

(Left) γ -Selenourea structure with two independent helices A_1 and B_2 of $NH \cdots$ Se hydrogen-bonded molecules. Atoms H_{anti} and H_{syn} are distinguished by letters 'a' and 'b', respectively. Distances $H \cdots$ Se are given in Å. (Right) Bonds $NH_{anti} \cdots O$ and $NH_{syn} \cdots O$ clearly distinguished in urea phase I between crystal directions z and x, y, respectively. The graph descriptors (Etter *et al.*, 1990) of hydrogen-bonded patterns are indicated.

$\frac{\Delta d(\text{\AA})}{d(\text{\AA})}$	helix A9	helix A ₈	helix A ₇	helix B ₆₅₄	helix B ₃₂₁	Δz (Å)	$\Delta \bar{\varphi}(^{\circ})$	$\sigma_{\varphi}(^{\circ})$
helix A ₉	a _a	0	0	0.026	-0.027	0	0	0
helix A ₈	$a_{\alpha}/\sqrt{3}$	a_{α}	0	0.082	0.094	1.732	7.16	0
helix A ₇	$a_{\alpha}/\sqrt{3}$	$a_{\alpha}/\sqrt{3}$	a_{α}	0.056	-0.066	-0.066	17.84	0
helix B ₆₅₄	5.118	5.010	5.148	$a_{\alpha}/\sqrt{3}$	0.012	0.4947	3.86	6.67
helix B ₃₂₁	5.065	5.186	5.026	5.104	$a_{\alpha}/\sqrt{3}$	1.1027	1.49	4.80

Table 2Positions of helices A9, A8, A7, B654 and B321 in α -selenourea at 293 K/ambient pressure†.

[†] Distances between helices are expressed in blue as the unit-cell parameter $a_{\alpha} = 15.2757$ (6) Å. Parameter Δd (in red, Å) is the difference between distances d between helices and distances d_0 between the closest screw axis 3_1 . Helices A_9 , A_8 and A_7 are ideally located at [00z], $[\frac{1}{3}\frac{2}{3}z]$ and $[\frac{2}{3}\frac{1}{3}z]$, respectively, while helix B_{654} is close to $[0\frac{1}{3}z]$ and helix B_{321} is close to $[\frac{1}{3}\frac{1}{3}z]$; Δz is the elevation along **c** relative to helix A_9 . $\Delta \overline{\varphi} = \overline{\varphi} - \overline{\varphi}_{A9}$ is the average rotation of helices relative to helix A_9 , where $\overline{\varphi} = (\varphi_1 + \varphi_2 + \varphi_3)/3$ is the average of three smallest angles between Se=C bonds in one helix and directions [100], [010] and [110]. σ_{φ} is the standard deviation of $\overline{\varphi}$.

Table 3 Relative positions of helices in γ -selenourea at 383 K/0.1 MPa.

 $a_{\gamma} = 8.8551$ (4) Å (*cf.* Table 2, but in phase γ angles $\varphi_1 = \varphi_2 = \varphi_3 = \varphi$ and all σ_{φ} parameters in γ -selenourea are equal to zero). Δd values are given in red, d (Å) values are given in blue.

$\frac{\Delta d(\text{\AA})}{d(\text{\AA})}$	helix A ₁	helix B ₂	Δz (Å)	φ̄(°)
helix A ₁	ay	0	0	0
helix B ₂	$a_{\gamma}/\sqrt{3}$	ay	-0.5541	8.14

axis B₂. Table 3 lists the distances between two independent helices, their elevations Δz and orientations in phase γ . These displacements Δz and φ of independent helice are comparable in magnitudes to those in phase α (Table 2). It suggests that at still higher temperature another transformation of phase γ is possible. Such a transition to hypothetical phase δ has not been observed (see DSC measurements in Fig. S1) below the melting temperature.

The application of matrix M [equation (1)] to the lattice of phase γ would result in a threefold smaller unit cell of hypothetical phase δ . Phase δ would contain one helix per one unit cell, and there would be three molecules per unit cell (Z = 3) in this structure of space group $P3_1$, $P3_112$ or $P3_121$. The lattices of phases α , γ and δ can be considered as three consecutive elements in the series of transitions according to the similarity relation described by matrix M: $A_{\delta} = MA_{\gamma}$ and $A_{\gamma} = MA_{\alpha}$. The direct transformation between metric matrices of phases α and δ is $A_{\delta} = M^2A_{\alpha}$, as specified in equation (3):

$$\begin{pmatrix} \mathbf{a}_{\delta} \\ \mathbf{b}_{\delta} \\ \mathbf{c}_{\delta} \end{pmatrix} = \begin{pmatrix} 0 & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{1}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_{\alpha} \\ \mathbf{b}_{\alpha} \\ \mathbf{c}_{\alpha} \end{pmatrix}.$$
 (3)

The consecutive elements of these transformations are rotated, translated and rescaled according to the similarity rule. In crystal structures, such a transformation cannot be precisely fulfilled due to the fixed atomic and molecular dimensions. The lattices of selenourea phases α and γ exemplify the similarity-type of crystal-lattice transformations. Between phases α and γ , the lattices are rotated by 30°, and

dimensions perpendicular to the z axis are rescaled linearly by $3^{-1/2}$, while the shape of the lattice along plane (001) and the trigonal crystal symmetry are preserved. The hypothetical phase δ fulfills the same similarity relation, described by equation (1) (toward reduced dimensions) and equation (2) (up the scale). In mathematical terms, one can infinitely apply this transformation for abstract lattices, however, in the structure of real materials the down-scaling similarity is limited to the molecular dimensions. The hypothetical selenourea phase δ most likely cannot be obtained due to the previous melting of the compound.

The series of similarity transformations in selenourea lattices is illustrated in Fig. 3 and this transformation applied to a related geometric composition is exemplified in Fig. 5.

The structural origin of the phase transition between $SeC(NH_2)_2$ phases α and γ can be considered as an interplay between different types of NH····Se and NH····N hydrogen bonds. The hydrogen bonds involving the *syn*-H atoms (with respect to atom Se, *i.e.* where torsion angle Se-C-N-H_{syn} is close to 0°) connect the molecules into helices along direction **c**; *anti*-H atoms (torsion angle Se-C-N-H_{anti} is close to 180°) are involved in the hydrogen bonds linking neighboring helices (Fig. 6). In the three-dimensional framework of hydrogen bonds NH_{syn}···Se and NH_{anti}···Se in selenourea, one can discriminate the directions and patterns, described by $R_2^2(8)$ and $R_2^1(6)$ graph sets (Etter *et al.*, 1990), respectively, as



Figure 5

Similarity transformations described in equations (1) and (2) applied to the lattices of selenourea phases α (black contour), γ (purple) and δ (cyan), as well as to an abstract geometrical figure (see Fig. 3).

Table 4

Connectivity map in selenourea phase α at 293 K.

Hydrogen-bonding distances (Å) N···Se and N···N for molecules within helices (diagonal colored blocks) and between helices (off-diagonal white fields). Hydrogen bonds NH_{syn} ···Se are given in red, NH_{anti} ···Se are given in black and NH_{anti} ···N are given in blue. The labels of atoms and helices are listed in Table S2. Note the long N27···Se5 distance due to the presence of the N27H···N16 bond (see Figs. 6 and 7).

helix		B ₃₂₁			B654			A ₇	A_8	A9
۷	donor	Se1	Se2	Se3	Se4	Se5	Se6	Se7	Se8	Se9
	N11		3.579(2)					3.798(2)		
	N21			3.637(3)				3.719(5)		
321	N12	3.577(2)				3.738(2)				
B	N22			3.566(4)		3.507(2)				
	N13	3.519(2)					3.545(5)			
	N23		3.629(2)				3.700(2)			
	N14			3.605(2)			3.636(2)			3.430(4)
	N24					3.574(2)				3.636(7)
654	N15				3.596(6)				3.751(2)	
B	N25						3.641(6)		3.684(6)	
	N16		3.742(2)			3.571(5)				
	N26		3.537(5)		3.533(6)					
4	<u>N17</u>					3.459(5)	3.400(6)	3.5190(5)		
4	N27					4.218(7)		3.515(3)		
8	N18			3.490(6)	3.745(6)				3.503(5)	
1	N28				3.714(7)				3.470(4)	
67	N19	3.6230(8)								3.532(5)
A	N29	3.599(2)								3.501(2)
helix	donor	N11/N12	N21/N22	N13/N23	N14/N24	N15/N25	N16/N26	N17/N27	N18/N28	N19/N29

Table 5Selenourea phase γ at 383 K.

Distances (Å) of bonds NH_{syn} · · ·Se are given in red, NH_{anti} · · ·Se are given in black (see Table S2).

helix ->		B_2	A ₁
¥	H-donor	Se2	Se1
B ₂	N21	3.5127(6)	3.7732(3)
	N22	3.5679(6)	3.7026(6)
A_1	N11	3.7952(6)	3.6221(6)

illustrated for phase γ in Fig. 4. In phase α there are 36 independent NH···Se bonds and their number in phase γ is reduced to 6. As shown in Fig. 6, in phase α most of the 18 independent NH_{syn} · · · Se bonds are shorter than NH_{anti} · · · Se hydrogen bonds, but there are three NH_{anti} · · ·Se bonds which are on average shorter by 0.3 Å compared to the other NH_{anti}···Se. Moreover, the shortest of all hydrogen bonds in phase α involves the *anti*-H atom of group N17H₂ while the longest of NH···Se contact involves the *anti*-H atom of group $N27H_2$ in the same molecule labeled with number 7 (see Fig. S3). This longest contact is longer than the sum of van der Waals radii of H and Se atoms (Fig. 6). Instead, atom H27a forms hydrogen bond N27-H27a···N16ⁱ (symmetry code: 1 -x + y, 1 - x, $-\frac{1}{3} + z$; the length of this hydrogen bond NH···N, unique in the structure of phase α , is plotted in Fig. 7. The hydrogen-bonding connectivity between molecules in selenourea phases α and γ is also presented in Tables 4 and 5. Table 4 shows that the arbitrary labeling of nitrogen atoms N11/N21 and N13/N23 in phase α does not correspond to the

increased symmetry of phase γ . Table 4 indicates a likely origin of missing hydrogen bond N29H_{anti}···Se (black), which may be due to the involvement of this H atom in four-center hydrogen bond N29–H29_{anti}···Se9. According to Table 4, the H-acceptor capability of selenium atoms varies between three and six. In phase γ Se1 is the H-acceptor of six hydrogen bonds and Se2 of five hydrogen bonds.

The transition to phase γ eliminates the unique structural features connected to the long contact N27-H27A···Se5 and the presence of hydrogen bond N27–H27a···N16ⁱ. Above 381.0 K, the unique NH···N bond is broken and elongated by about 0.4 Å (Fig. 7). The symmetry of phase γ increases and the unit cell becomes smaller [equation (1)]. In the structure of phase γ there are six NH···Se hydrogen bonds; all three NH_{syn} ··· Se bonds are longer by about 0.25 Å than NH_{anti} ··· Se bonds. At the same time, the spread of angles $NH \cdot \cdot Se$ of the strongest hydrogen bonds, which in phase α are between 150° and 172°, become much narrower, between 164 and 167°, in phase γ (Fig. 8). These systematic changes of NH···Se bonds confirm their dominant role for the structural transformations of selenourea phases. The averaged positions of molecules in phase γ induce some internal strain in the crystal structure, which reduces the lengths of the longest NH···Se hydrogen bonds and elongates the shortest of the NH···Se bonds, compared to their dimensions in phase α , as shown in Fig. 6. Only in phase γ do all NH···Se contacts meet the hydrogenbond criterion (Jeffrey & Saenger, 1991), based on the sum of van der Waals radii of atoms H and Se.

In phase γ , the average lengths of hydrogen bonds (see Fig. S5) become marginally longer for $NH_{syn} \cdots Se$ bonds, but $NH_{anti} \cdots Se$ bonds become significantly longer, by about

0.07 Å, which reflects the incorporation of the longest contact N27H27a···Se16ⁱ of phase α . The increased lengths of hydrogen bonds NH···Se and of NH···N contacts show that the anomalous shrinking of the crystal along **x**, **y** and **z** and the anomalous volume drop at the transition to phase γ (Fig. 2) cannot be connected with the dimensions of hydrogen bonds, as was observed in KH₂PO₄-type (KDP-type) phase transitions induced by H disordering in OH····O bonds (Katrusiak, 1993, 1995) and in H₂O ice at 80 K due to the gradual triggering of molecular tumbling (Katrusiak, 1996). Consequently, the contraction of the selenourea crystal dimensions on its transition to phase γ can be associated with thermally activated librations of molecules and the so-called riding model of atoms (Cruickshank, 1961). Indeed, the averaged intramolecular dimensions and, in particular, the average C-N and C-Se bond distances decrease in phase γ (see Fig. S7). These strong vibrations of the hydrogen-bonded atoms are



Figure 6

Distances H_{anti} . Se and N. Se involving *anti*-H (open circles) and *syn*-H atoms (full circles) in selenourea phases α and γ as a function of temperature. Horizontal dashed lines indicate the sums of van der Waals radii (vdW_H = 1.2 Å, vdW_N = 1.55 Å, vdW_{Se} = 1.9 Å) (Bondi, 1964).

'projected' onto the hydrogen bonds, which in the timedependent function are strongly inclined to the average positions of the donor (N) and acceptor (Se) atoms. This riding model of hydrogen bonds was proposed for explaining the exceptionally high-volume drop, of -3 Å^3 per ionic pair, observed in guanidinium nitrate, [C(NH₂)₃]⁺NO₃⁻, for its giant-strain phase transition at 296 K (Katrusiak & Szafrański, 1996). Another transition in guanidinium nitrate, at 384 K, is associated with a smaller volume drop, of 0.4 Å³, which was connected, apart from the riding model of hydrogen bonds, with the activated motion and centering positions of the protons (Szafrański & Katrusiak, 2004). It is plausible that in selenourea in its phase transition at 381.0 K (similar to that in guanidinium nitrate), both these effects take place, and also the significant shifts in atomic positions and changed types of hydrogen bonds contribute to the volume change.

The structural mechanism leading to different molecular packing in the crystals of urea, thiourea and selenourea, and also to the α - γ phase transition in selenourea, involves the anisotropy of electrostatic potential of the chalcogen atoms and, consequently, the directional preferences of their hydrogen bonds. It is characteristic of all NH···Se bonds in selenourea phases α and γ that the H atoms approach the Se atoms at angles close to 90° (Fig. S4). It strongly suggests that the electrostatic potential on the rim of the Se atom surface perpendicular to the Se=C bond is more negative compared to the surface at the extension of the Se=C bond. Similar geometries of hydrogen bonds were observed in thiourea phase V (stable at ambient conditions), where the NH_{syn}···S bonds with their H_{syn}···S=C angles close to 100° are signifi-





Three shortest NH···N (empty symbols) and N···N (filled symbols) in selenourea phases α and γ as a function of temperature: N27–H27a···N16ⁱ (circles), N18–H18a···N23 (triangles) and N14–H14a···N19 (squares). Horizontal dashed lines indicate the relevant sums of van der Waals radii: vdW_H = 1.2 Å and vdW_N = 1.55 Å (Bondi, 1964).



One shortest distance (a) H···Se, (b) N···Se and (c) the relevant N–H···Se angle in selenourea phases α and γ as a function of temperature. The dimensions involving *syn*-H atoms are indicated with full symbols and those involving *anti*-H atoms with open symbols. The same code of colors is applied in plots (a)–(c) for molecules in helices A₉, A₈, A₇ (purple, navy blue, blue triangles), B₆₅₄ (pink, green, red diamonds) and B₃₂₁ (orange, cyan, light-green circles), respectively.

cantly shorter compared to hydrogen bonds NH_{anti} ...S bonds with their H_{anti} ...S=C angles close to 165°; in thiourea phase VI above 0.34 GPa the lengths of these hydrogen bonds become more similar (Tomkowiak & Katrusiak, 2018). This observation is analogous to the charge distribution on halogen atoms, where the negative rims and σ -hole are present and their net charges increase in the series from Cl to Br and to I. Likewise, the van der Waals anisotropy increases in the chalcogen series of O, S and Se atoms (Eramian *et al.*, 2013; Nyburg & Faerman, 1985). The same patterns of H_{syn} and H_{anti} hydrogen bonds can be found in all phases of selenourea, thiourea and urea (see Fig. 4). In both urea high-pressure phases III and IV, NH···N hydrogen bonds are promoted (Roszak & Katrusiak, 2017), while no NH···N hydrogen bonds were found in thiourea phases.

The similarity transformation between the lattices of selenourea crystal phases α and γ , as well as of the hypothetical phase δ , subdivides the unit cell and the number of independent molecules. The phase transitions involving analogous similarity transformations of lattices, retaining the crystallographic system and even the space-group type, were observed also for other crystals. For example, on lowering temperature, a Dianin clathrate (Frampton *et al.*, 2017) of space-group type $R\bar{3}$ undergoes a series of two transitions between phases α , β and γ , which retain the space-group type but the unit-cell parameters transform according to the rule:

$$\begin{pmatrix} a_{\gamma} \\ b_{\gamma} \\ c_{\gamma} \end{pmatrix} = M \begin{pmatrix} a_{\beta} \\ b_{\beta} \\ c_{\beta} \end{pmatrix} = M^2 \begin{pmatrix} a_{\alpha} \\ b_{\alpha} \\ c_{\alpha} \end{pmatrix} \text{ where } M = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This rule is clearly different from that revealed for selenourea [equations (1)–(3)], due to the interplay between the similarity and crystal symmetry. The crystal phases undergoing such transitions intrinsically display a considerable rate of three-dimensional isostructurality (Fábián & Kálmán, 2004). The structures of selenourea phases α and γ shed new light on the

microscopic origin of such structure–superstructure transformations and on the origin of a large number of independent molecules. In selenourea phase α , NH···N hydrogen bonds are present in a very small proportion (1:35 NH···Se bonds), which lowers the symmetry of the crystal.

4. Conclusions

The transformation of phase α to phase γ has been connected with the $N-H \cdots N$ bond breaking and substituting it by another bond NH···Se, after which hydrogen bonds N-H...Se fully dominate the structure of phase γ . An analogous process, of the competition between hydrogen bonds NH···O and $NH \cdots N$, was observed in high-pressure phase III of urea (Roszak & Katrusiak, 2017), but no hydrogen bonds NH···N were formed in thiourea ambient-pressure phase V nor highpressure phase VI/VII (Tomkowiak & Katrusiak, 2018). The new structures of selenourea phases illustrate the possible structural mechanisms of solid-state transformations in a large group of urea analogs. These structural features can be connected with the large number of independent molecules in selenourea phase α . The one hydrogen bond NH···N per 35 hydrogen bonds NH···Se leads to the large Z' number, as well as shifts and rotations, which accommodate the different intermolecular contacts. High temperature averages the molecular positions and leads to the higher symmetry phase γ , with a smeller unit cell and the smaller Z' number.

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