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The lock-in phase in the urotropine–
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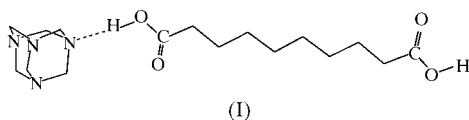
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The 1,10-decanedioic acid–1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]-decane (1/1) system, C₁₀H₁₈O₄·C₆H₁₂N₄, was studied at 215 (2) K. Its analysis provides important information with regard to the long-standing acid–carboxylate controversy in the urotropine–alkanedioic acid system. In the present structure, all the chain end-groups display a clear acid character. The asymmetric unit of this commensurate modulated phase contains two molecules of diacid as well as two molecules of urotropine. Furthermore, the chain packing suggests a possible order parameter for the lock-in transition.

Comment

In the urotropine–sebacic acid system (US), (I), an incommensurate phase has been observed at 295 K (Bussien Gaillard *et al.*, 1998). Its structure, characterized by the modulation vector $[-0.02(5), 0, 0.24(5)]$, comprises two very distinct moieties: slightly modulated layers of urotropine (U) and strongly modulated layers of sebacic acid (S). In the S layers, the planes of the two independent chains are almost at right angles to each other. The modulation requires a high number of harmonic terms or crenel functions. Another striking feature of this structure lies in its pseudo-centrosymmetric nature: both *E* statistics and systematic absences point to the superspace group $P2_1/m(\alpha 0 \gamma)0s$. Indeed, all atoms except



those of the carboxy groups fulfil the superspace symmetry *s*. However, a better model requires the non-centrosymmetric superspace group $P2_1(\alpha 0 \gamma)0$. Owing to the exceptionally large stability range of the incommensurate phase of the analogous compound urotropine suberate (Bussien Gaillard *et al.*, 1996), it was believed that the incommensurate phase of (I) persists down to liquid nitrogen temperatures.

¹ Urotropine is also called hexamethylenetetramine, hexamine and methenamine.

In this communication, we show that this is not the case. Despite the absence of all but the faintest signals in the differential scanning calorimetry curve, a lock-in phase does exist below 291 K; the oxygen disorder no longer exists and the centrosymmetric space group $P2_1/c$ is realised for the whole structure. Interestingly, the systematic absence $h0lm$ ($m = 2n$) of the incommensurate phase anticipates the absence $h0l$ ($l = 2n$) in the lock-in phase. This lock-in occurs at $[0, 0, \frac{1}{2}]$ and the transition shows mixed displacive–OD-type character (OD is order–disorder). Its enthalpy is exceedingly small and reveals the transition to be only weakly of first order. In the light of its complex nature, it has to be described by at least two order parameters. As a conclusion, we must advise that it is of crucial importance to scrutinize the calorimetric results to the fullest extent and to analyse the temperature evolution of the wave vector carefully before classifying an incommensurate phase. This is especially true for such a strongly anharmonic modulation, which can too easily be enhanced or biased by the vicinity of the lock-in phase (soliton regime).

The structure of (I) consists of (010) layers of U alternating with layers of S. The inter- and intralayer forces are due to hydrogen bonds of varying strength (Table 2 and Fig. 2). The following hydrogen-bond scheme is observed: strong O–H···N bonds link S to U and weak C–H···O bonds link U to S. Each U molecule is connected to its four U neighbours by C–H···N hydrogen bonds. The chain packing is further stabilized by van der Waals forces. The U layer in (I) closely resembles the (110) layer of pure U at 200 K (Kampermann *et*

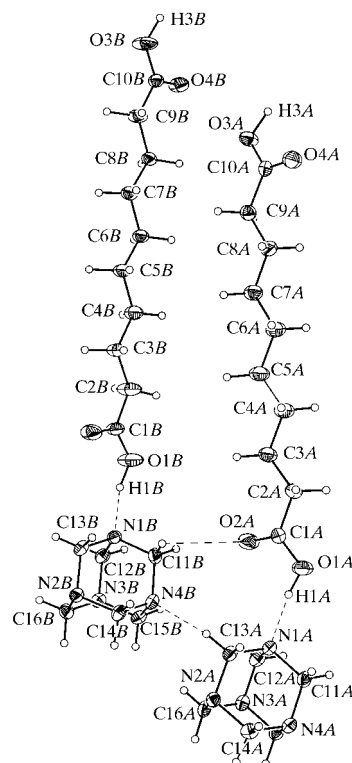


Figure 1

A view of the asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

al., 1995), except that the layer in (I) is slightly contracted along [110] and elongated along [100], and that the C—H...N hydrogen bonds are somewhat stronger (*cf.* 152° and 2.84 Å for H...N in pure U).

It is noteworthy that one of the threefold axes of U is parallel to the *a* axis in (I). In the S layers of (I), there are two chains with different orientations, *A* and *B* (Fig. 1). One of the zigzag planes of the chains lies roughly perpendicular to the (10 $\bar{4}$) plane, while the other is nearly parallel [the (10 $\bar{4}$) plane of this lock-in phase corresponds to the (10 $\bar{1}$) plane of the incommensurate structure]. The interplane angle is 80°, whereas in the incommensurate phase, a wide variation of this angle has been observed. In all urotropine–alkanedioic acid compounds, there is a wide variation of this angle. One is led to believe that it represents one of the order parameters of this system. Quite surprisingly, the two chain axes are not parallel but span an angle of 10°. They also form an angle of 30° with the [401] direction and they pack according to an *AABB*... sequence. The body of each chain lies in an almost perfect plane: the r.m.s. deviations are 0.003 and 0.007 Å for *A* and *B*, respectively. The *AABB*... sequence, the angle between the chain axes and especially the acute angle with respect to the (010) layer clearly demonstrate that the chains do not adopt as compact a packing as possible [20.5 Å², compared with 19.5 Å² in pure S (Bond *et al.*, 2001)]. The *AABB*... sequence is not only observed in the chain conformation but also in the C—H...O hydrogen-bonding scheme (Fig. 2). This feature is intrinsic to the modulated character of the structure, and

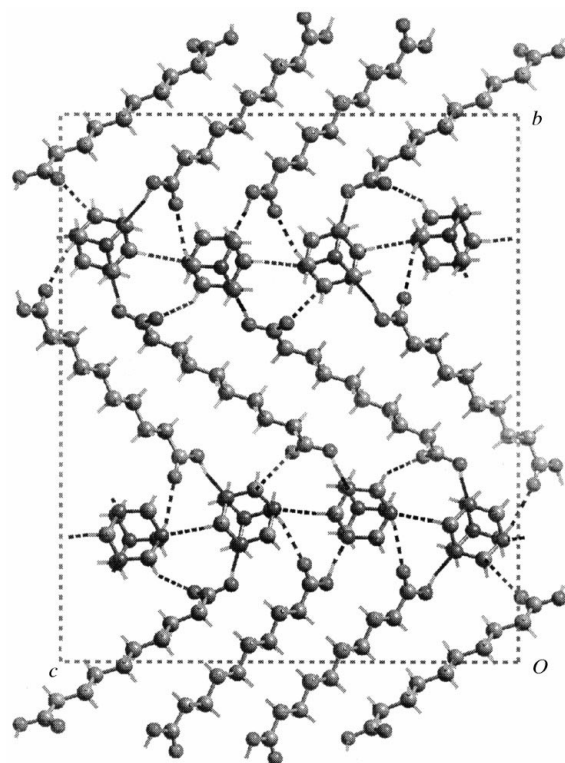


Figure 2
The projection along the *a* direction showing alternating layers of U and S in (I). Note the commensurate displacive modulation of U and the *ABBA* sequence of S along the *c* direction.

therefore the asymmetric unit contains two molecules of both moieties.

Examination of Tables 1 and 2 confirms the acid character of the chain end-groups. This acidity of the sebacic moiety will serve as a possible order parameter for many of the phase transitions in this and analogous compounds. Indeed, Bussien Gaillard *et al.* (1998) pointed out for the incommensurate phase that on one side of a chain the acid H atom was clearly attached to the chain end-group, whereas on the opposite end it was rather associated with the nearest N atom. In addition, the hydrogen bond was shared between the two O atoms. We found that during the lock-in transition, the carboxy groups reconstitute and steer towards a new potential well. Each H atom is associated with one O atom, but with a slight delocalization towards the corresponding N atom. This results in rather long O—H distances (Table 2). The carboxy groups themselves are almost planar, from analysis of the refinement, but subtend dihedral angles with the zigzag planes of between 3 and 8°. These dihedral angles are of the same order as those observed in pure S (Bond *et al.*, 2001).

The C—C and C—N bond lengths are in the ranges 1.489 (3)–1.536 (3) and 1.462 (3)–1.491 (3) Å, respectively. These values are in good agreement with those published in the *International Tables for Crystallography* (1992, Vol. C). In conclusion, we may say that both moieties retain the main features of their single-phase character, except for some (110) distortion for U and a marginally looser chain packing for S. The lock-in phase may thus be regarded as a co-crystal.

Experimental

Urotropine and sebacic acid were purchased from Fluka. Stoichiometric amounts were dissolved in ethanol, which was then removed by rotary evaporation. The resulting white powder was recrystallized by slow evaporation from acetonitrile at room temperature. The glossy colourless (010) platelets of (I) were very often twinned according to (10 $\bar{1}$) or [10 $\bar{1}$] and had to be cut to obtain single-domain crystals.

Crystal data

C₁₀H₁₈O₄·C₆H₁₂N₄
M_r = 342.44
 Monoclinic, *P*2₁/*c*
a = 5.9030 (12) Å
b = 27.549 (6) Å
c = 23.371 (5) Å
 β = 101.22 (3)°
V = 3728.0 (13) Å³
Z = 8

D_x = 1.220 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6009 reflections
 θ = 1.9–26.1°
 μ = 0.09 mm⁻¹
T = 215 (2) K
 Wedge, colourless
 0.36 × 0.24 × 0.08 mm

Data collection

Stoe IPDS diffractometer
 φ scans
 18 263 measured reflections
 6652 independent reflections
 3916 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.065
 θ_{\max} = 26.2°
h = -7 → 5
k = -34 → 34
l = -28 → 23

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.057
wR(*F*²) = 0.064
S = 1.63
 6652 reflections
 449 parameters

H atoms treated by a mixture of independent and constrained refinement
 $(\Delta/\sigma)_{\max}$ = 0.003
 $\Delta\rho_{\max}$ = 0.29 e Å⁻³
 $\Delta\rho_{\min}$ = -0.29 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1A—C1A	1.309 (3)	O1B—C1B	1.312 (3)
O2A—C1A	1.186 (3)	O2B—C1B	1.190 (2)
O3A—C10A	1.316 (3)	O3B—C10B	1.318 (3)
O4A—C10A	1.211 (3)	O4B—C10B	1.196 (2)
<hr/>			
O2A—C1A—O1A	122.3 (2)	O2B—C1B—O1B	123.10 (19)
O4A—C10A—O3A	121.4 (2)	O4B—C10B—O3B	122.32 (18)

Table 2

Hydrogen-bonding and short-contact geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1A—H1A...N1A	0.98 (3)	1.73 (3)	2.697 (2)	172 (3)
O3A—H3A...N2B ⁱ	1.07 (3)	1.68 (3)	2.693 (2)	156 (3)
O1B—H1B...N1B	1.03 (3)	1.65 (3)	2.646 (2)	163 (3)
O3B—H3B...N2A ⁱ	1.14 (3)	1.52 (3)	2.653 (2)	176 (3)
C13A—H13A...N3A ⁱⁱ	0.98	2.59	3.500 (3)	155
C13B—H13C...N4A ⁱⁱⁱ	0.98	2.66	3.574 (3)	156
C13B—H13D...N3B ⁱⁱⁱ	0.98	2.56	3.493 (3)	160
C13A—H13B...N4B	0.98	2.75	3.656 (3)	154
C11B—H11D...O2A	0.98	2.66	3.105 (3)	108
C11A—H11B...O4A ^{iv}	0.98	2.51	3.103 (3)	119
C15A—H15B...O2B ^v	0.98	2.48	3.397 (2)	157
C15B—H15D...O4B ^{vi}	0.98	2.37	3.306 (2)	161

Symmetry codes: (i) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1+x, y, z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $2-x, 1-y, 1-z$; (v) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.

H atoms bonded to the O atoms of the acid-chain end-groups were located in electron-density maps and refined isotropically. H atoms bonded to C atoms (in both U and S) were placed at calculated positions and treated as riding atoms, with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *EXPOSE* (Stoe & Cie, 1997); cell refinement: *CELL* (Stoe & Cie, 1997); data reduction: *INTEGRATE* (Stoe & Cie, 1997) and *XPREP* (Siemens, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1998); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1996) and *Cerius²* (MSI, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1054). Services for accessing these data are described at the back of the journal.

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