The lock-in phase in the urotropine–sebacic acid system

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The 1,10-decanedioic acid–1,3,5,7-tetraazatricyclo[3.3.1.13,7]-
decane (1/1) system, C_{10}H_{18}O_{4}C_{6}H_{12}N_{4}, 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 incom-
mensurate 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 $P_{2_1}/c(0\alpha\gamma)0s$. Indeed, all atoms except

those of the carboxy groups fulfil the superspace symmetry $s$.
However, a better model requires the non-centrosymmetric
superspace group $P_{2_1}(0\alpha\gamma)0$. 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.

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 $h0ln$
($m = 2n$) of the incommensurate phase anticipates the absence
$h0l$ ($l = 2n$) in the lock-in phase. This lock-in occurs at [0,0,1]
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 incommensu-
rate phase. This is especially true for such a strongly anhar-
monic 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

1 Urotropine is also called hexamethylenetetramine, hexamine and methen-
amine.

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.
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. 1.52 Å 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 (10Ì) plane, while the other is nearly parallel [the (10Ì) plane of this lock-in phase corresponds to the (10Ì) 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 [010] 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 C—H⋯O hydrogen-bonding scheme (Fig. 2). This feature is intrinsic to the modulated character of the structure, and 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 by rotary evaporation. The resulting white powder was recrystallized 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.

**Crystal data**

\[ \text{C}_{10}H_{18}O_4\text{C}_{6}H_{12}N_4 \]

\[ M_f = 342.44 \]

Monoclinic, \( P2_1/c \)

\[ a = 5.9030 (12) \text{ Å} \]

\[ b = 27.549 (6) \text{ Å} \]

\[ c = 23.371 (5) \text{ Å} \]

\[ \beta = 101.22 (3) ^\circ \]

\[ V = 3728.0 (13) \text{ Å}^3 \]

\[ Z = 8 \]

\[ D = 1.220 \text{ Mg m}^{-3} \]

Mo Kα radiation

Cell parameters from 6009 reflections

\[ \theta = 1.9–26.1^\circ \]

\[ \mu = 0.09 \text{ mm}^{-1} \]

\[ T = 215 (2) \text{ K} \]

Wedge, colourless

\[ 0.36 \times 0.24 \times 0.08 \text{ mm} \]

**Data collection**

Stoe IPDS diffractometer

\( \psi \) scans

18 283 measured reflections

6652 independent reflections

3916 reflections with \( I > 2\sigma(I) \)

**Refinement**

Refinement on \( F^2 \)

\[ wR(F^2) = 0.064 \]

\[ S = 1.63 \]

6652 reflections

449 parameters

H atoms treated by a mixture of independent and constrained refinement

\( \Delta \rho_{	ext{max}} = 0.29 \text{ e Å}^{-3} \)

\( \Delta \rho_{	ext{min}} = -0.29 \text{ e Å}^{-3} \)
organic compounds

Table 1
Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1A—C1A</td>
<td>1.309 (3)</td>
<td>1.73 (3)</td>
<td>2.697 (2)</td>
<td>172 (3)</td>
</tr>
<tr>
<td>O2A—C1A</td>
<td>1.186 (3)</td>
<td>1.65 (3)</td>
<td>2.646 (2)</td>
<td>163 (3)</td>
</tr>
<tr>
<td>O3A—C10A</td>
<td>1.316 (3)</td>
<td>1.52 (3)</td>
<td>2.653 (2)</td>
<td>176 (3)</td>
</tr>
<tr>
<td>O4A—C10A</td>
<td>1.211 (3)</td>
<td>1.52 (3)</td>
<td>2.658 (2)</td>
<td>176 (3)</td>
</tr>
<tr>
<td>O2A—C1A—O1A</td>
<td>122.3 (2)</td>
<td>1.190 (2)</td>
<td>3.500 (3)</td>
<td>155</td>
</tr>
<tr>
<td>O4A—C10A—O3A</td>
<td>121.4 (2)</td>
<td>1.196 (2)</td>
<td>3.512 (3)</td>
<td>155</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \( x, y, z \); (ii) \( x, y, z \); (iii) \( x, y, z \); (iv) \( x, y, z \); (v) \( x, y, z \); (vi) \( x, y, z \).

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1A—H1A···N1A</td>
<td>0.98 (3)</td>
<td>1.73 (3)</td>
<td>2.697 (2)</td>
<td>172 (3)</td>
</tr>
<tr>
<td>O3A—H3A···N2B</td>
<td>1.07 (3)</td>
<td>1.65 (3)</td>
<td>2.646 (2)</td>
<td>163 (3)</td>
</tr>
<tr>
<td>O1B—H1B···N1B</td>
<td>1.03 (3)</td>
<td>1.52 (3)</td>
<td>2.653 (2)</td>
<td>176 (3)</td>
</tr>
<tr>
<td>O3B—H3B···N2A</td>
<td>1.14 (3)</td>
<td>1.52 (3)</td>
<td>2.658 (2)</td>
<td>176 (3)</td>
</tr>
<tr>
<td>C13A—H13A···N3A</td>
<td>0.98</td>
<td>2.59</td>
<td>3.500 (3)</td>
<td>155</td>
</tr>
<tr>
<td>C13B—H13C···N4A</td>
<td>0.98</td>
<td>2.66</td>
<td>3.574 (3)</td>
<td>156</td>
</tr>
<tr>
<td>C13—H13D···N3B</td>
<td>0.98</td>
<td>2.56</td>
<td>3.493 (3)</td>
<td>160</td>
</tr>
<tr>
<td>C13A—H13B···N4B</td>
<td>0.98</td>
<td>2.75</td>
<td>3.656 (3)</td>
<td>154</td>
</tr>
<tr>
<td>C11B—H11D···O2A</td>
<td>0.98</td>
<td>2.66</td>
<td>3.105 (3)</td>
<td>108</td>
</tr>
<tr>
<td>C11A—H11B···O4A</td>
<td>0.98</td>
<td>2.51</td>
<td>3.103 (3)</td>
<td>119</td>
</tr>
<tr>
<td>C15A—H15B···O2F</td>
<td>0.98</td>
<td>2.48</td>
<td>3.397 (2)</td>
<td>157</td>
</tr>
<tr>
<td>C15B—H15D···O4F</td>
<td>0.98</td>
<td>2.37</td>
<td>3.306 (2)</td>
<td>161</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \( 2-x, \frac{1}{2}+y, \frac{1}{2}-z \); (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) \( 1-x, y, \frac{1}{2}-z \).

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 \( U_{eq}(H) = 1.2U_{eq}(C) \).

Data collection: EXPOSE (Stoe & Cie, 1997); cell refinement: CELL (Stoe & Cie, 1997); data reduction: INTEGRATE (Stoe & Cie, 1997) and XP (Siemens, 1996) and Cerius (MSI, 1997); software used to prepare material for publication: SHELXL97.

We would like to thank Dr Kurt J. Schenk for helpful advice.

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.

References