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A polymorph of butobarbital with two distinct hydrogen-bonding motifs

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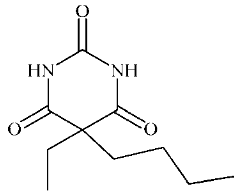
N—H···O bonding in a form of 5-butyl-5-ethylbarbituric acid (systematic name: 5-butyl-5-ethyl-1,3-diazinane-2,4,6-trione), $C_{10}H_{16}N_2O_3$, produces two distinct one-dimensional motifs, *viz.* tape and ladder. Both are different from the ribbon chain motif observed in two previously reported polymorphs of the same compound.

Comment

Butobarbital, (I), is a 5,5-disubstituted barbituric acid derivative used as a sedative hypnotic drug for severe insomnia (Soneryl®; Joint Formulary Committee, 2007). Cleverley & Williams (1959) reported the existence of four polymorphic forms, and Draguet-Brughmans *et al.* (1981) investigated the physical properties of three modifications of (I). Their form I (m.p. 397 K) is consistent with a crystal structure reported earlier by Bideau (1971). Recently, Nichol & Clegg (2005) determined the structure of a low-temperature (LT) phase, which was obtained by cooling a crystal of form I (crystallized from water) to 120 K. A subsequent data collection at room temperature showed that this phase transition is reversible. The arrangement of butobarbital molecules in these two structures is practically the same and a conformational change of the *n*-butyl groups was identified as being their main difference. Very recently, the structure of a third form of (I) was reported by Nichol & Clegg (2007*b*).



(I)

The structure of a third polymorph of (I) with a prismatic habit is reported here. Comparison with previous studies on the polymorphism of (I) (Bideau, 1971; Draguet-Brughmans *et al.*, 1981; Cleverley & Williams, 1959; Williams, 1959; Mesley & Clements, 1968; Mesley, 1969; Huang & Jerslev, 1951) shows that the data (IR spectrum and X-ray powder pattern) for this modification match closely with those given by Draguet-Brughmans *et al.* (1981) for their polymorph II.

The title structure has the $P2_1/c$ space group and four independent molecules, one of which is shown in Fig. 1. All molecules adopt the same principal geometry, and their alkyl chains exhibit the expected staggered antiperiplanar conformation. The bond lengths and angles are consistent with the corresponding parameters in the previously reported modifications of (I). The six-membered rings are not perfectly planar.

Two of the independent molecules of (I) are linked into N—H···O hydrogen-bonded tapes (Fig. 2*a* and Table 1) by employing two hydrogen-bond donor and two acceptor functions per molecule. These tapes consist of two independent $R_3^3(12)$ rings (Bernstein *et al.*, 1995), which connect three

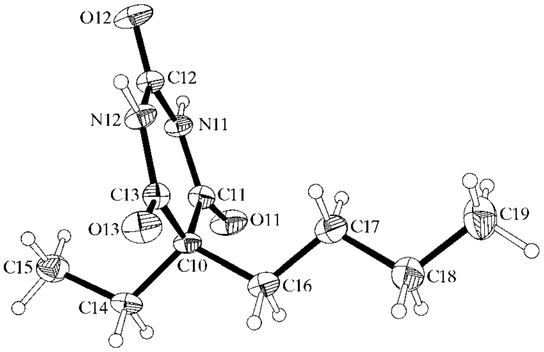


Figure 1
One of the four independent molecules of butobarbital, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

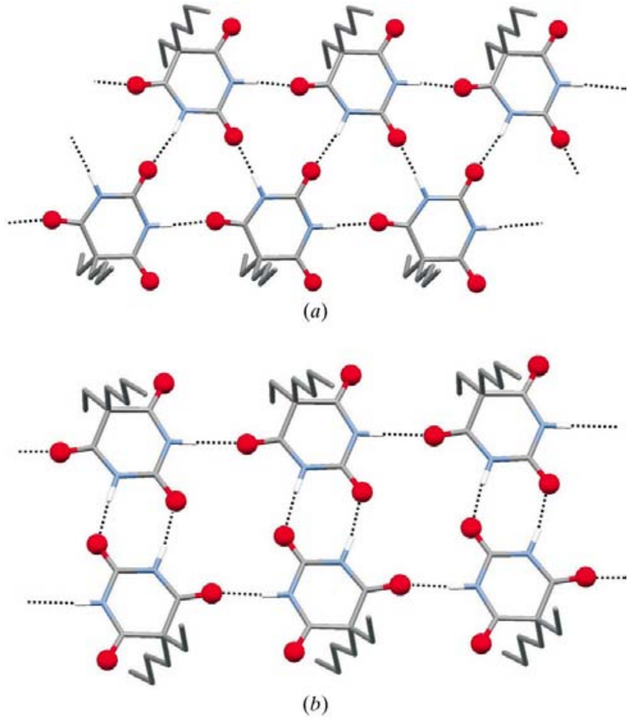


Figure 2
The one-dimensional hydrogen-bonding motifs in (I), *viz.* (*a*) tape and (*b*) ladder.

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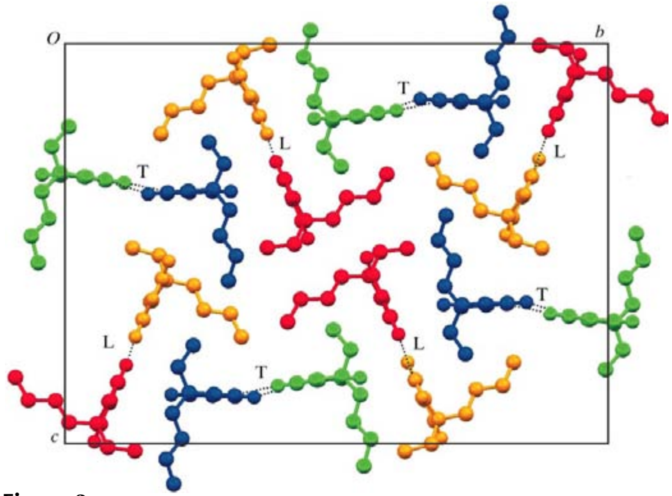

Figure 3
The packing of the hydrogen-bonded tapes (T) and ladders (L), viewed parallel to the translation vector of each chain (along the *a* axis). The four independent molecules are drawn in different colors.

molecules. The rings are edge-fused to larger $R_4^4(18)$ units. The mean plane through the alkyl fragment of (I) is approximately perpendicular with respect to the central plane of the tape defined by the C_4N_2 rings, so that angles of 87.08 (9) and 82.65 (8)° are formed. All ethyl groups point in one direction and all butyl groups in the opposite direction.

N—H···O interactions between the other two independent molecules result in the ladder motif shown in Fig. 2(*b*). Pseudocentrosymmetric dimers with $R_2^2(8)$ rings are edge-fused with pseudocentrosymmetric $R_4^4(18)$ rings connecting four molecules. Both tapes and ladders propagate parallel to the *a* axis, which implies a perfect match of their translation periods. Furthermore, the four independent molecules are arranged in separate one-dimensional stacks parallel to the *a* axis.

A closer inspection reveals a set of short dimeric C—H···O contacts (Table 1), which connect adjacent ladders related by inversion symmetry. These contacts involve a butyl CH_2 group and an O atom not engaged in classical hydrogen bonding. The packing of tapes and ladders is depicted in Fig. 3.

Ribbon chains are the most common hydrogen-bonding motif in 5,5-substituted derivatives of barbituric acid. The chains found in form I of butobarbitul and its LT form (Bideau, 1971; Nichol & Clegg, 2005) belong to this particular class. By contrast, there are only two previous examples of the tape motif shown in Fig. 2(*a*), the structures of γ-methylamobarbital (Gartland & Craven, 1971) and quinal barbitone (Nichol & Clegg, 2007*a*). The ladder motif of Fig. 2(*b*) has been observed in methylphenylbarbital (Bravic *et al.*, 1968) and barbital (Craven *et al.*, 1969). Thus, the polymorph of (I) reported here is the first example where these two rather unusual one-dimensional motifs appear simultaneously in one structure.

Experimental

Single crystals were taken from an approximately 40 year old commercial product ('Soneryl, 5-*n*-butyl-5-aethyl-barbituricum'; Interpharm Kom.-Ges. Vienna), which also contained form I described by Bideau (1971).

Crystal data

$C_{10}H_{16}N_2O_3$
$M_r = 212.25$
Monoclinic, $P2_1/c$
$a = 6.8534$ (1) Å
$b = 29.6631$ (7) Å
$c = 22.2107$ (5) Å
$\beta = 94.408$ (1)°
$V = 4501.93$ (16) Å^3
$Z = 16$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
0.20 × 0.07 × 0.07 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.896$, $T_{\max} = 0.994$
27772 measured reflections
7853 independent reflections
5428 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.138$
$S = 1.07$
7853 reflections
573 parameters
8 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O13$^{\rm i}$	0.962 (10)	1.892 (11)	2.854 (3)	178 (3)
N12—H12···O22$^{\rm ii}$	0.962 (10)	1.875 (12)	2.829 (3)	171 (3)
N21—H21···O23$^{\rm i}$	0.963 (10)	1.902 (12)	2.857 (3)	171 (3)
N22—H22···O12	0.967 (10)	1.910 (14)	2.843 (3)	161 (3)
N31—H31···O33$^{\rm ii}$	0.961 (10)	1.894 (11)	2.854 (3)	176 (3)
N32—H32···O42	0.963 (10)	1.929 (12)	2.877 (3)	167 (3)
N41—H41···O43$^{\rm i}$	0.961 (10)	1.897 (11)	2.858 (3)	178 (3)
N42—H42···O32	0.959 (10)	1.912 (12)	2.861 (3)	170 (3)
C36—H36*B*···O31$^{\rm iii}$	0.99	2.40	3.318 (4)	155

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$.

All H atoms were identified in a difference map. CH_2 H atoms were positioned geometrically (C—H = 0.99 Å). Methyl H atoms were idealized and included as rigid groups allowed to rotate but not tip (C—H = 0.98 Å). H atoms attached to N atoms were refined with restrained distances [N—H = 0.97 (1) Å]. The $U_{\rm iso}$(H) parameters were set at $1.2U_{\rm eq}$(N,C) for NH and CH_2 or at $1.5U_{\rm eq}$(C) for CH_3 H atoms.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3179). Services for accessing these data are described at the back of the journal.

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