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5-(1-Cyclohexen-1-yl)-1,5-dimethylbarbituric acid (hexobarbitone): a low-temperature redetermination

Gary S. Nichol and William Clegg*

School of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail: w.clegg@ncl.ac.uk

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Key indicators

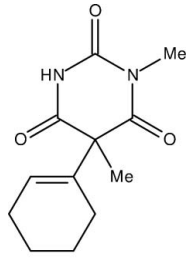
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.099
Data-to-parameter ratio = 17.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

A low-temperature redetermination of the title compound, $C_{12}H_{16}N_2O_3$, more commonly known as hexobarbitone, is reported, with significantly improved precision. The crystal packing reveals an infinite hydrogen-bonded hexobarbitone chain linked by a single N—H···O interaction, an extremely rare motif in barbiturate crystal packing. Unlike some other barbiturate crystal structures, there is no phase transition on cooling to 150 K.

Comment

As part of our research on *s*-block complexes of barbituric acid and its derivatives, we have redetermined the crystal structures of the various ligands of interest at low temperatures for the purpose of having reference structures that are more precise than those previously published, most of which are over 30 years old. We found that at least two of these compounds actually undergo a phase transition at low temperatures (Nichol & Clegg, 2005*a*,*b*). We redetermined the structure of hexobarbitone at 150 K, but in this case no phase transition occurs.



(I)

The crystal structure of hexobarbitone [5-(1-cyclohex-en-1-yl)-1,5-dimethylbarbituric acid], (I), was reported by Bideau *et al.* (1970). The structure refined to a final R = 0.09. The authors were unable to locate from a difference Fourier synthesis any H atoms; those which could be placed in calculated positions by means of well established geometry were added to the model; however, others (such as the methyl H atoms) were omitted. We have redetermined the crystal structure of compound (I) at 150 K. The structure refines to a final R value of 0.036. The precision of the structure is improved markedly. The unit-cell volume decreases by *ca* 34 Å^3, as expected for a low-temperature determination. Molecular dimensions are unexceptional and are in general agreement with the room-temperature structure.

Compound (I) crystallizes from water in the space group $P2_1/c$ with one molecule in the asymmetric unit and no solvent molecules (Fig. 1). The steric hindrance of the *N*-methyl group prevents hydrogen bonding on that side of the molecule so, in contrast to the crystal structures of many other barbiturate

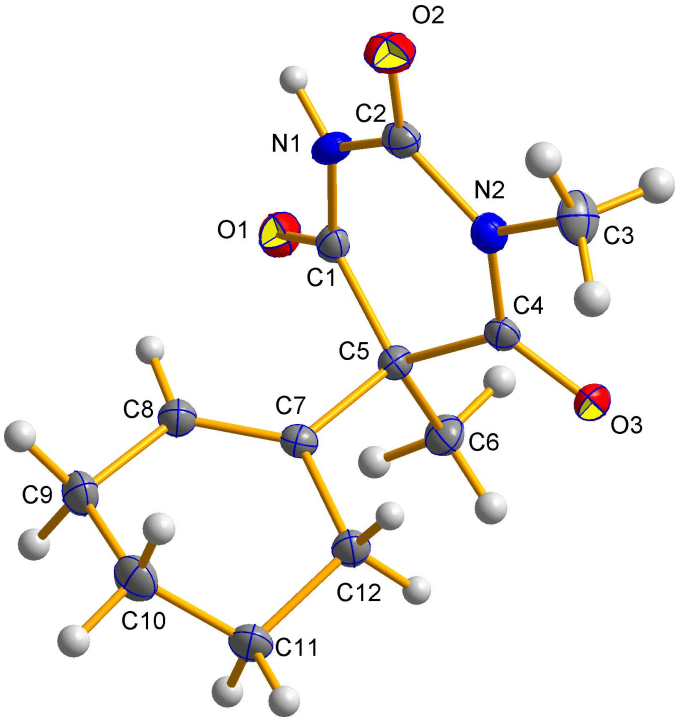


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

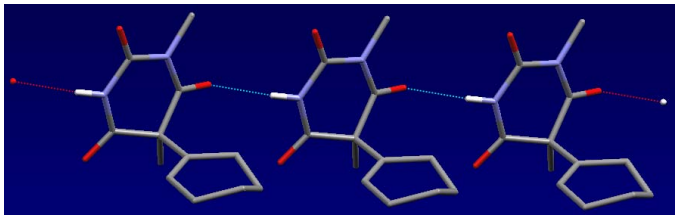


Figure 2
The hydrogen-bonding motif observed in the crystal packing of (I). Hydrogen bonds are indicated in light blue, the red dotted lines indicate the hydrogen-bond continuation and H atoms not involved in hydrogen bonding have been omitted for clarity.

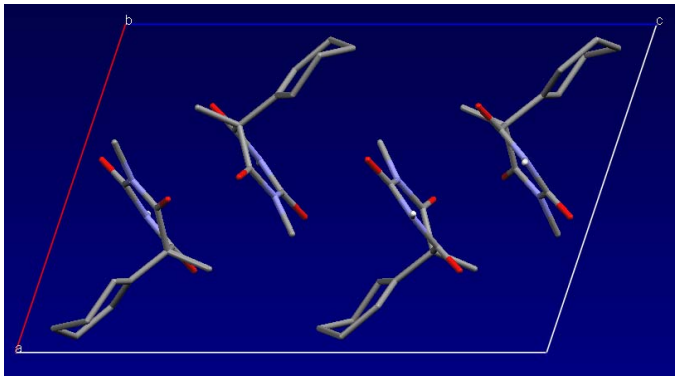


Figure 3
A projection along the *b* axis of (I). H atoms not involved in hydrogen bonding have been omitted for clarity.

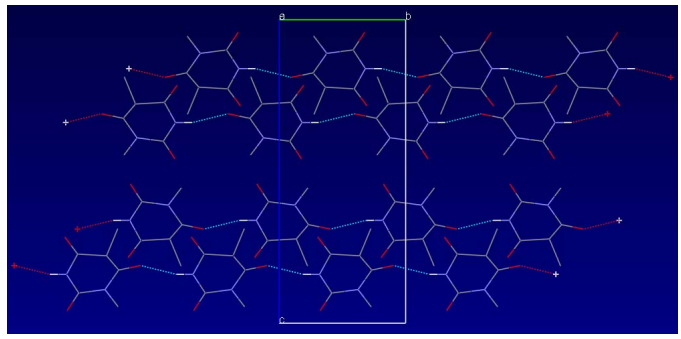


Figure 4
A projection along the *a* axis of (I). H atoms not involved in hydrogen bonding, and also the cyclohexene rings, are omitted for clarity.

compounds, there is only one hydrogen bond observed. This forms an infinite chain (Fig. 2) and two of the three carbonyl groups are not involved in hydrogen bonding. Such hydrogen-bonding geometry is highly unusual in barbiturate crystal packing. A search of the Cambridge Structural Database (Version 5.26, plus one update; Allen, 2002) shows there to be only two other 5,5-disubstituted barbiturate chains formed by a single N—H···O interaction. These are for 1-methyl-5,5-diethylbarbituric acid (Wunderlich, 1973) and 1-methyl-5-isopropyl-5-β-bromoallylbarbituric acid (Wilhelm & Fischer, 1976). Fig. 3 shows the positions of the chains relative to one another and the orientation of the cyclohexenyl rings in the crystal packing. The barbiturate rings are staggered rather than overlapping, as shown in Fig. 4.

Experimental

Hexobarbitone was obtained as a commercial crystalline compound and was not recrystallized.

Crystal data

$C_{12}H_{16}N_2O_3$
M_r = 236.27
Monoclinic, $P2_1/c$
a = 10.8604 (5) Å
b = 6.6081 (3) Å
c = 16.6771 (8) Å
β = 108.553 (1)°
V = 1134.66 (9) Å^3
Z = 4
D_x = 1.383 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8095 reflections
θ = 2.8–28.8°
μ = 0.10 mm^{-1}
T = 150 (2) K
Block, colourless
0.50 × 0.50 × 0.50 mm

Data collection

Bruker SMART 1K CCD diffractometer
Thin-slice ω scans
Absorption correction: none
9831 measured reflections
2792 independent reflections
2483 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.9°
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.06
2792 reflections
160 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.4078P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.011 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O3^{i}	0.876 (15)	2.019 (15)	2.8637 (12)	161.8 (13)

Symmetry code: (i) $x, 1+y, z$.

All H atoms were found in a difference map. Methyl H-atom positions were then idealized (C—H = 0.98 Å) and refined as riding, with free rotation about the C—C bond, and with U_{iso}(H) = 1.5U_{eq}(C). CH_2 H atoms were also positioned geometrically (C—H = 0.99 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). The H atom bonded to C8 was positioned geometrically (C—H = 0.95 Å) and also refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). The N—H H-atom position was refined freely, with U_{iso}(H) = 1.2U_{eq}(N).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND 3* (Brandenburg & Putz, 2004) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL* and local programs.

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