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

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Key indicators

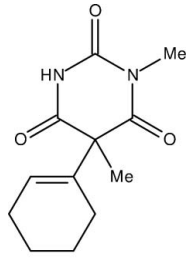
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.099
Data-to-parameter ratio = 17.5

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

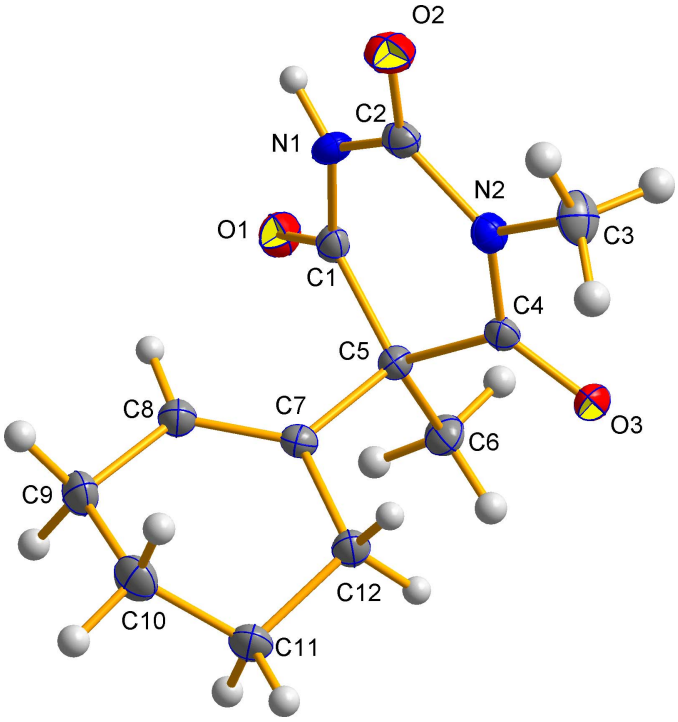


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

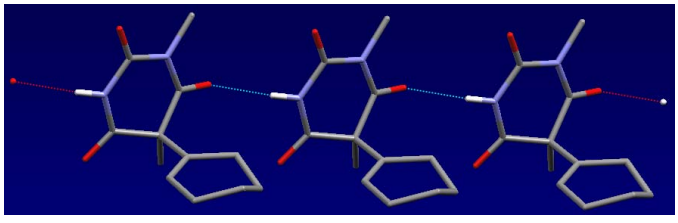


Figure 2
The hydrogen-bonding motif observed in the crystal packing of (I). Hydrogen bonds are indicated in light blue, the red dotted lines indicate the hydrogen-bond continuation and H atoms not involved in hydrogen bonding have been omitted for clarity.

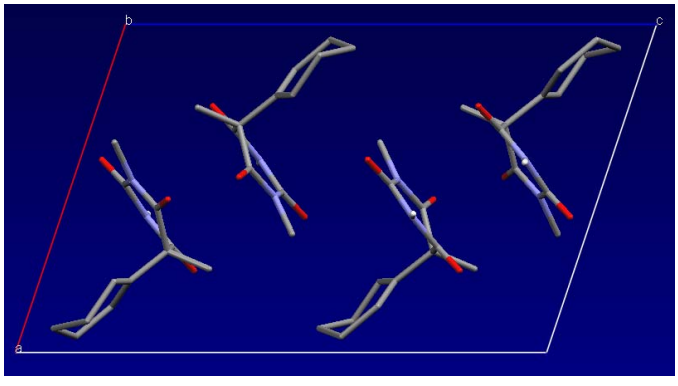


Figure 3
A projection along the *b* axis of (I). H atoms not involved in hydrogen bonding have been omitted for clarity.

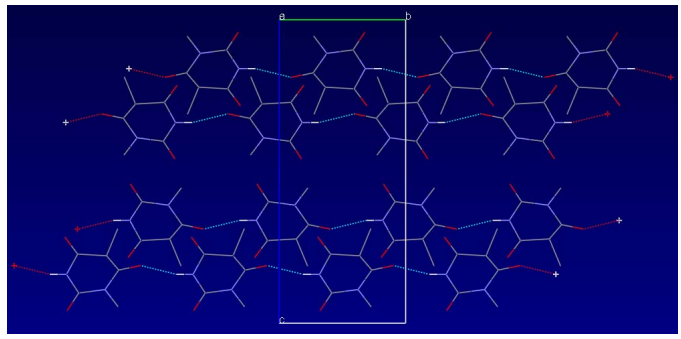


Figure 4
A projection along the *a* axis of (I). H atoms not involved in hydrogen bonding, and also the cyclohexene rings, are omitted for clarity.

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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$D_x = 1.383$ Mg m^{-3}
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Cell parameters from 8095 reflections
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Radiation source: sealed tube
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2792 independent reflections
2483 reflections with $I > 2\sigma(I)$
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$\theta_{max} = 28.9°$, $\theta_{min} = 2.0°$
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.099$
$S = 1.06$
2792 reflections
160 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
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, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.74993 (8)	0.69476 (12)	0.28400 (5)	0.02322 (19)
O2	0.41306 (8)	0.67628 (13)	0.04132 (5)	0.0274 (2)
O3	0.53405 (7)	0.09508 (11)	0.18988 (5)	0.02276 (19)
N1	0.58553 (9)	0.68113 (13)	0.16090 (6)	0.0191 (2)
H1N	0.5781 (13)	0.813 (2)	0.1613 (8)	0.023*
N2	0.47524 (8)	0.37676 (13)	0.11085 (5)	0.01796 (19)
C1	0.67870 (10)	0.59276 (15)	0.22768 (6)	0.0166 (2)
C2	0.48735 (10)	0.58421 (16)	0.09951 (6)	0.0184 (2)
C3	0.36071 (11)	0.27274 (19)	0.05388 (7)	0.0263 (2)
H3A	0.3862	0.1387	0.0395	0.039*
H3B	0.3251	0.3524	0.0021	0.039*
H3C	0.2947	0.2579	0.0821	0.039*
C4	0.56012 (9)	0.26801 (15)	0.17526 (6)	0.0161 (2)
C5	0.69146 (9)	0.36475 (15)	0.22228 (6)	0.0151 (2)
C6	0.74559 (10)	0.27562 (17)	0.31159 (6)	0.0208 (2)
H6A	0.8341	0.3256	0.3386	0.031*
H6B	0.7469	0.1276	0.3081	0.031*
H6C	0.6904	0.3166	0.3452	0.031*
C7	0.78302 (9)	0.31811 (15)	0.16946 (6)	0.0155 (2)
C8	0.85934 (10)	0.45868 (16)	0.15271 (7)	0.0198 (2)
H8	0.8551	0.5920	0.1729	0.024*
C9	0.95207 (11)	0.41939 (18)	0.10361 (8)	0.0254 (2)
H9A	1.0421	0.4209	0.1431	0.030*
H9B	0.9440	0.5297	0.0621	0.030*
C10	0.92689 (12)	0.21778 (18)	0.05710 (7)	0.0261 (2)
H10A	1.0024	0.1813	0.0389	0.031*
H10B	0.8497	0.2292	0.0060	0.031*
C11	0.90432 (11)	0.05361 (17)	0.11509 (8)	0.0242 (2)
H11A	0.9814	0.0435	0.1663	0.029*
H11B	0.8925	−0.0784	0.0856	0.029*
C12	0.78437 (10)	0.10101 (16)	0.14086 (7)	0.0197 (2)
H12A	0.7054	0.0753	0.0922	0.024*
H12B	0.7823	0.0093	0.1874	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0243 (4)	0.0205 (4)	0.0248 (4)	−0.0046 (3)	0.0078 (3)	−0.0067 (3)
O2	0.0274 (4)	0.0302 (4)	0.0230 (4)	0.0074 (3)	0.0059 (3)	0.0079 (3)
O3	0.0207 (4)	0.0142 (4)	0.0357 (4)	−0.0010 (3)	0.0123 (3)	−0.0002 (3)
N1	0.0227 (4)	0.0112 (4)	0.0240 (5)	0.0019 (3)	0.0085 (4)	0.0008 (3)
N2	0.0169 (4)	0.0185 (4)	0.0177 (4)	−0.0018 (3)	0.0045 (3)	−0.0020 (3)
C1	0.0178 (4)	0.0154 (5)	0.0193 (5)	−0.0013 (4)	0.0098 (4)	−0.0011 (4)
C2	0.0193 (5)	0.0201 (5)	0.0181 (5)	0.0033 (4)	0.0091 (4)	0.0017 (4)
C3	0.0218 (5)	0.0325 (6)	0.0216 (5)	−0.0084 (4)	0.0028 (4)	−0.0033 (4)
C4	0.0163 (4)	0.0147 (4)	0.0195 (5)	0.0007 (3)	0.0090 (4)	−0.0020 (3)
C5	0.0150 (4)	0.0134 (4)	0.0170 (4)	0.0002 (3)	0.0055 (3)	0.0006 (3)
C6	0.0219 (5)	0.0224 (5)	0.0184 (5)	0.0008 (4)	0.0067 (4)	0.0047 (4)
C7	0.0145 (4)	0.0157 (4)	0.0159 (4)	0.0020 (3)	0.0044 (3)	0.0004 (3)
C8	0.0201 (5)	0.0172 (5)	0.0241 (5)	0.0001 (4)	0.0098 (4)	−0.0003 (4)
C9	0.0251 (5)	0.0235 (5)	0.0338 (6)	−0.0013 (4)	0.0180 (5)	0.0016 (4)
C10	0.0276 (6)	0.0285 (6)	0.0274 (6)	0.0011 (5)	0.0162 (5)	−0.0020 (4)
C11	0.0246 (5)	0.0197 (5)	0.0324 (6)	0.0034 (4)	0.0147 (4)	−0.0017 (4)
C12	0.0207 (5)	0.0155 (5)	0.0252 (5)	−0.0003 (4)	0.0106 (4)	−0.0022 (4)

Geometric parameters (Å, º)

O1—C1	1.2135 (13)	C6—H6B	0.980
O2—C2	1.2103 (13)	C6—H6C	0.980
O3—C4	1.2204 (13)	C7—C8	1.3324 (14)
N1—H1N	0.876 (15)	C7—C12	1.5133 (14)
N1—C1	1.3740 (13)	C8—H8	0.950
N1—C2	1.3786 (14)	C8—C9	1.5089 (14)
N2—C2	1.3957 (14)	C9—H9A	0.990
N2—C3	1.4732 (13)	C9—H9B	0.990
N2—C4	1.3747 (13)	C9—C10	1.5220 (16)
C1—C5	1.5184 (14)	C10—H10A	0.990
C3—H3A	0.980	C10—H10B	0.990
C3—H3B	0.980	C10—C11	1.5242 (16)
C3—H3C	0.980	C11—H11A	0.990
C4—C5	1.5318 (13)	C11—H11B	0.990
C5—C6	1.5342 (14)	C11—C12	1.5284 (14)
C5—C7	1.5546 (13)	C12—H12A	0.990
C6—H6A	0.980	C12—H12B	0.990
H1N—N1—C1	117.6 (9)	H6B—C6—H6C	109.5
H1N—N1—C2	114.6 (9)	C5—C7—C8	122.23 (9)
C1—N1—C2	126.91 (9)	C5—C7—C12	116.01 (8)
C2—N2—C3	117.87 (9)	C8—C7—C12	121.72 (9)
C2—N2—C4	123.41 (9)	C7—C8—H8	117.9
C3—N2—C4	118.60 (9)	C7—C8—C9	124.12 (10)
O1—C1—N1	121.00 (9)	H8—C8—C9	117.9

O1—C1—C5	123.32 (9)	C8—C9—H9A	109.1
N1—C1—C5	115.55 (9)	C8—C9—H9B	109.1
O2—C2—N1	121.51 (10)	C8—C9—C10	112.61 (9)
O2—C2—N2	122.34 (10)	H9A—C9—H9B	107.8
N1—C2—N2	116.08 (9)	H9A—C9—C10	109.1
N2—C3—H3A	109.5	H9B—C9—C10	109.1
N2—C3—H3B	109.5	C9—C10—H10A	109.7
N2—C3—H3C	109.5	C9—C10—H10B	109.7
H3A—C3—H3B	109.5	C9—C10—C11	109.80 (9)
H3A—C3—H3C	109.5	H10A—C10—H10B	108.2
H3B—C3—H3C	109.5	H10A—C10—C11	109.7
O3—C4—N2	120.33 (9)	H10B—C10—C11	109.7
O3—C4—C5	121.74 (9)	C10—C11—H11A	109.5
N2—C4—C5	117.74 (8)	C10—C11—H11B	109.5
C1—C5—C4	110.90 (8)	C10—C11—C12	110.86 (9)
C1—C5—C6	109.72 (8)	H11A—C11—H11B	108.1
C1—C5—C7	108.50 (8)	H11A—C11—C12	109.5
C4—C5—C6	110.09 (8)	H11B—C11—C12	109.5
C4—C5—C7	106.65 (8)	C7—C12—C11	112.18 (9)
C6—C5—C7	110.94 (8)	C7—C12—H12A	109.2
C5—C6—H6A	109.5	C7—C12—H12B	109.2
C5—C6—H6B	109.5	C11—C12—H12A	109.2
C5—C6—H6C	109.5	C11—C12—H12B	109.2
H6A—C6—H6B	109.5	H12A—C12—H12B	107.9
H6A—C6—H6C	109.5		

C2—N1—C1—O1	−170.25 (10)	O3—C4—C5—C6	−29.89 (13)
C2—N1—C1—C5	13.87 (14)	O3—C4—C5—C7	90.54 (11)
C1—N1—C2—O2	−177.10 (10)	N2—C4—C5—C1	33.48 (12)
C1—N1—C2—N2	5.87 (15)	N2—C4—C5—C6	155.10 (9)
C3—N2—C2—O2	−5.63 (15)	N2—C4—C5—C7	−84.47 (10)
C3—N2—C2—N1	171.36 (9)	C1—C5—C7—C8	15.26 (13)
C4—N2—C2—O2	178.41 (9)	C1—C5—C7—C12	−167.01 (8)
C4—N2—C2—N1	−4.59 (14)	C4—C5—C7—C8	134.78 (10)
C2—N2—C4—O3	168.69 (9)	C4—C5—C7—C12	−47.49 (11)
C2—N2—C4—C5	−16.23 (14)	C6—C5—C7—C8	−105.33 (11)
C3—N2—C4—O3	−7.23 (14)	C6—C5—C7—C12	72.40 (11)
C3—N2—C4—C5	167.85 (9)	C5—C7—C8—C9	178.44 (10)
O1—C1—C5—C4	152.51 (9)	C12—C7—C8—C9	0.84 (16)
O1—C1—C5—C6	30.68 (13)	C7—C8—C9—C10	13.87 (16)
O1—C1—C5—C7	−90.66 (11)	C8—C9—C10—C11	−44.27 (13)
N1—C1—C5—C4	−31.71 (11)	C9—C10—C11—C12	62.04 (13)
N1—C1—C5—C6	−153.54 (8)	C5—C7—C12—C11	−161.76 (9)
N1—C1—C5—C7	85.11 (10)	C8—C7—C12—C11	15.98 (14)
O3—C4—C5—C1	−151.51 (9)	C10—C11—C12—C7	−47.06 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O3^{i}	0.876 (15)	2.019 (15)	2.8637 (12)	161.8 (13)

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