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The Crystal Structure of 5-Ethyl-5-(3, 3-dimethylbutyl)-barbituric Acid (γ-Methylamobarbital)

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The crystal structure of 5-ethyl-5-(3,3-dimethylbutyl)barbituric acid (γ-methylamobarbital) is monoclinic with lattice parameters $a=9{\cdot}478$ (2), $b=6{\cdot}793$ (1), $c=21{\cdot}489$ (8) Å, $\beta=96{\cdot}66$ (3)°, space group $P2_1/c$ and four molecules in the cell. The structure has been determined from 2310 three-dimensional X-ray intensity data (Cu $K\alpha$ radiation) measured with an automatic four-circle diffractometer. The phase problem was solved by direct methods. Least-squares refinement of heavier-atom positional and anisotropic thermal parameters and of hydrogen-atom positional parameters was concluded with $R=0{\cdot}093$. The molecule is in the 2,4,6-trioxo tautomeric form. The barbiturate ring is almost planar, with the ethyl and t-hexyl substituents at C(5) forming a hydrocarbon chain extending nearly perpendicular to the ring. N–H···O–C hydrogen bonds join each molecule to four neighbors, forming ribbons along **b**. It is unusual that in all hydrogen bonds, the four atoms N–H···O–C are almost collinear. Hydrogen-bonded ribbons are stacked together so that the projecting alkyl chains are loosely packed with their axes all nearly parallel. Each ethyl group has five lateral alkyl group near-neighbors, while each *t*-hexyl group has seven.

Introduction

The pharmacologically active 5,5-dialkylbarbituric acids have molecular structures with both a polar portion (trioxopyrimidine ring), which has considerable hydrogen-bonding capability, and a non-polar hydrocarbon portion. The crystal structures of some of these barbiturates are dominated by hydrogen bonding (*e.g.*, barbital, polymorph II; Craven, Vizzini & Rodrigues, 1969), while in others (*e.g.*, vinbarbital; Craven & Cusatis, 1969) the requirements of efficient alkyl-group packing may also assume importance. The two crystalline forms of amobarbital* (Craven & Vizzini, 1969) have structures of the first kind. In both amobarbital I and II, the same hydrogen-bonded structural unit (the so-called 'double ribbon') is found, and the crystal structures differ only in the way in which the double ribbons are assembled. The 5-isoamyl groups project from the double ribbons in loose association, so that the terminal carbon atoms have large apparent thermal motions (root-mean-square amplitudes of ~0·5 Å). It was considered possible that 5-ethyl-5-(3,3-dimethylbutyl) barbituric acid (in which the hydrogen atom at the γ position of the isoamyl group of amobarbital is replaced by a bulkier methyl group) would also crystallize with double-ribbon hydrogen bonding. However, the presently reported crystal-structure determination of this compound, hereafter called γ-methylamobarbital (Fig. 1), shows this is not the case. Indeed, the mode of hydrogen bonding is of a type not previously found in barbiturate crystal structures. Although γ-methylamobarbital is not a commonly used drug, its preparation has been reported (Whitmore & Thorpe, 1939), and Dixit & Abraham (1969) have shown that it is a more potent and longer-acting hypnotic than amobarbital.

* Generic, trade, and systematic barbiturate names are given in Table 1.

Table 1. 5-R-5-*ethylbarbituric acids*

Generic name	Trade name	R
Barbital	Veronal	Ethyl
Butabarbital	Butisol	1-Methylpropyl (sec-butyl)
Amobarbital	Amytal	3-Methylbutyl (isoamyl)
Pentobarbital	Nembutal	1-Methylbutyl (sec-amyl)
Vinbarbital	Delvinal	1-Methyl-1-butenyl
γ-Methylamobarbital	–	3,3-Dimethylbutyl
Heptabarbital	Medomin	1-Cycloheptenyl

Crystal data and experimental

Dr D. J. Abraham (University of Pittsburgh) kindly provided a sample of γ-methylamobarbital, and monoclinic prismatic crystals were obtained from an aqueous ethanol solution by slow evaporation at room temperature. The crystals were colorless, with well-developed forms: {100} and {$\bar{1}$02}. Crystal density was found by flotation in a mixture of benzene and carbon tetrachloride. Lattice parameters and X-ray diffracted intensities were measured using a Picker four-circle automatic diffractometer with nickel-filtered Cu $K\alpha$ radiation. Crystal dimensions were approximately $0{\cdot}4\times0{\cdot}3\times0{\cdot}3$ mm. Lattice parameters were refined by least-squares methods, giving the values and estimated standard deviations (e.s.d.'s) quoted below:

γ-Methylamobarbital ($C_{12}H_{20}O_3N_2$);
M.W. 240·3; m.p. 190–192 °C.
Monoclinic; space group $P2_1/c$;
$Z=4$ molecules per cell.
$a=9{\cdot}478$ (2), $b=6{\cdot}793$ (1), $c=21{\cdot}489$ (8) Å,
$\beta=96{\cdot}66$ (3)°.
$D_m=1{\cdot}156$, $D_x=1{\cdot}161$ g.cm^{-3}. $\mu_{\mathrm{Cu}\,K\alpha}=6{\cdot}93$ cm^{-1}.

Table 2. *Observed and calculated structure factors*

Columns are l index, $10|F_{obs}|$, $10F_{calc}$.

Intensity data were collected for $\sin\theta/\lambda \leq 0{\cdot}59$ Å^{-1} ($\theta \leq 65°$) with the crystal symmetry axis b along the φ axis of the instrument. Scanning was in the θ:2θ mode at a rate of 2°/min with background counts of 20 sec at each of the 2° scan limits. If I_H is the integrated intensity for the Bragg reflection H and $\sigma(I_H)$ is its e.s.d. obtained from counting statistics, then reflections for which $I_H < 1{\cdot}5\sigma(I_H)$ were assumed to be unobservably weak. Such reflections – 281 of the 2310 reflections examined – were assigned intensities of $\sigma(I_H)/2$, thereby giving $|F_H| = \sigma(F_H)$. No corrections were made for possible sources of systematic error such as X-ray absorption, extinction, or multiple diffraction.

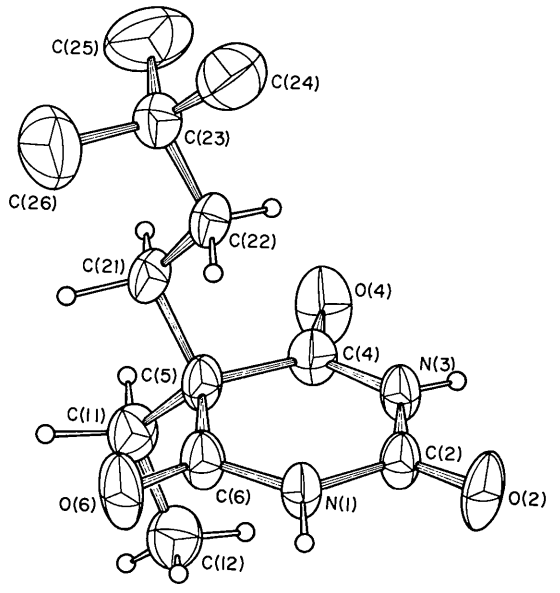

Fig. 1. γ-Methylamobarbital molecule with atomic labelling. Thermal-motion ellipsoids are scaled for 50% probability. Hydrogen atoms for the methyl carbons C(24), C(25), and C(26) were not located.

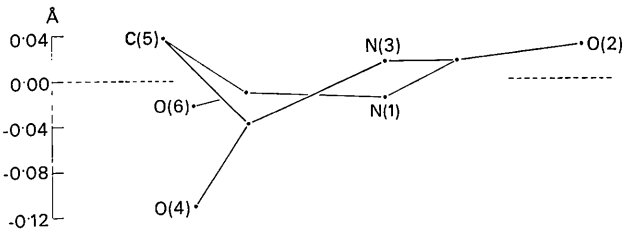

Fig. 2. Conformation of the trioxopyrimidine ring. Dotted line is the trace of the best least-squares plane through the six ring atoms. Scale in the vertical direction is about 11 times that in the horizontal.

Structure analysis

A direct method of phase determination was applied using the sign-correlation procedure of Beurskens (1963). Signs of 200 of the 250 largest normalized structure factors, E_H, were determined in terms of one symbolic sign. However, each of two E_H-Fourier syntheses,

Table 3. *Atomic parameters* ($\times 10^2$) *for γ-methylamobarbital*

Positional parameters are given as fractions of unit translations. Thermal parameters are given according to the expression: $T = \exp(-\sum_i \sum_j \beta_{ij} h_i h_j)$. E.s.d.'s given in parentheses refer to the least significant figures in the parameter values.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	18·81 (2)	42·61 (3)	36·75 (1)	1·30 (3)	1·08 (5)	0·195 (6)	0·00 (3)	−0·15 (1)	− 0·02 (1)
H(1)	17·2 (6)	28·0 (8)	36·6 (3)						
C(2)	11·05 (3)	52·48 (4)	32·01 (1)	1·10 (3)	1·34 (6)	0·194 (6)	0·03 (3)	−0·11 (1)	− 0·04 (1)
O(2)	3·55 (3)	44·06 (4)	27·89 (1)	1·57 (3)	2·23 (6)	0·273 (6)	−0·03 (3)	−0·30 (1)	− 0·27 (1)
N(3)	12·10 (2)	72·69 (3)	32·21 (1)	1·16 (3)	1·22 (5)	0·158 (5)	0·16 (3)	−0·16 (1)	0·02 (1)
H(3)	6·9 (6)	78·8 (8)	29·8 (2)						
C(4)	19·83 (3)	83·41 (4)	36·71 (1)	1·33 (4)	0·89 (6)	0·203 (7)	−0·06 (3)	−0·10 (1)	0·02 (1)
O(4)	19·17 (3)	101·16 (3)	36·55 (1)	2·42 (5)	1·02 (6)	0·313 (7)	0·04 (3)	−0·24 (1)	0·02 (1)
C(5)	29·49 (3)	72·71 (4)	41·74 (1)	1·10 (3)	1·55 (6)	0·144 (6)	−0·17 (3)	−0·12 (1)	− 0·06 (1)
C(6)	27·87 (3)	50·54 (4)	41·60 (1)	1·26 (3)	1·34 (6)	0·192 (6)	0·06 (3)	−0·10 (1)	0·05 (1)
O(6)	34·24 (3)	40·05 (3)	45·43 (1)	2·15 (4)	1·75 (6)	0·273 (6)	0·20 (3)	−0·35 (1)	0·17 (1)
C(11)	26·25 (3)	80·14 (5)	48·24 (1)	1·37 (4)	2·40 (8)	0·182 (6)	−0·23 (4)	−0·06 (1)	− 0·17 (2)
H(111)	28·4 (7)	95 (1)	48·3 (3)						
H(112)	35·3 (7)	73·7 (8)	51·8 (3)						
C(12)	11·21 (4)	75·93 (6)	49·71 (2)	1·58 (5)	3·1 (1)	0·255 (8)	0·01 (5)	0·03 (2)	− 0·10 (2)
H(121)	10·7 (7)	64 (1)	49·2 (3)						
H(122)	4·2 (8)	81 (1)	46·7 (3)						
H(123)	10·7 (8)	79 (1)	53·6 (3)						
C(21)	45·10 (3)	77·76 (5)	40·86 (1)	1·13 (4)	2·28 (8)	0·196 (7)	−0·36 (4)	−0·09 (1)	− 0·06 (2)
H(211)	45·5 (6)	93·6 (9)	41·5 (3)						
H(212)	51·4 (7)	72·1 (9)	45·0 (3)						
C(22)	49·64 (3)	71·32 (5)	34·67 (1)	1·22 (4)	2·69 (9)	0·189 (7)	−0·34 (4)	−0·09 (1)	− 0·06 (2)
H(221)	47·7 (6)	57 (1)	34·6 (3)						
H(222)	43·9 (7)	77·4 (9)	31·9 (3)						
C(23)	65·40 (4)	74·31 (5)	33·75 (2)	1·39 (4)	2·71 (9)	0·208 (7)	−0·23 (4)	−0·04 (1)	0·02 (2)
C(24)	67·53 (5)	66·95 (9)	27·26 (2)	1·76 (6)	5·2 (2)	0·28 (1)	−0·59 (8)	0·13 (2)	− 0·18 (3)
C(25)	68·67 (6)	96·3 (1)	34·02 (3)	2·51 (8)	4·6 (2)	0·49 (2)	−1·7 (1)	0·28 (3)	− 0·32 (4)
C(26)	74·82 (5)	63·0 (1)	38·68 (2)	1·67 (6)	8·0 (3)	0·34 (1)	0·7 (1)	0·00 (2)	0·35 (5)

corresponding to the two solutions for the undetermined sign, gave many peaks forming extended hexagonal patterns in the ($\bar{2}04$) plane. A sharpened three-dimensional Patterson synthesis, using $|E_H|^2$ coefficients, confirmed that the barbiturate ring does lie in a plane almost parallel to ($\bar{1}02$). Considerations of molecular packing and possible hydrogen-bonding modes led to only a few suitable positions for the ring in the ($\bar{2}04$) hexagonal mesh. These positions differed mainly by translations along **b**, suggesting that the structure could first be determined in the projection down **b**. Proceeding through successive (010) Fourier projections and difference syntheses, two-dimensional positional and isotropic thermal parameters were adjusted, yielding an agreement index R of 0·18 for $h0l$ data. Returning to the direct method, but incorporating the known E_{h0l} signs, the solution of the phase problem in three dimensions was obtained without difficulty.

Atomic positional and isotropic thermal parameters were refined by least-squares methods until the R value was reduced to 0·21. Hydrogen atoms, except those bonded to atoms C(24), C(25), and C(26) were located in a difference Fourier synthesis in which only reflec-

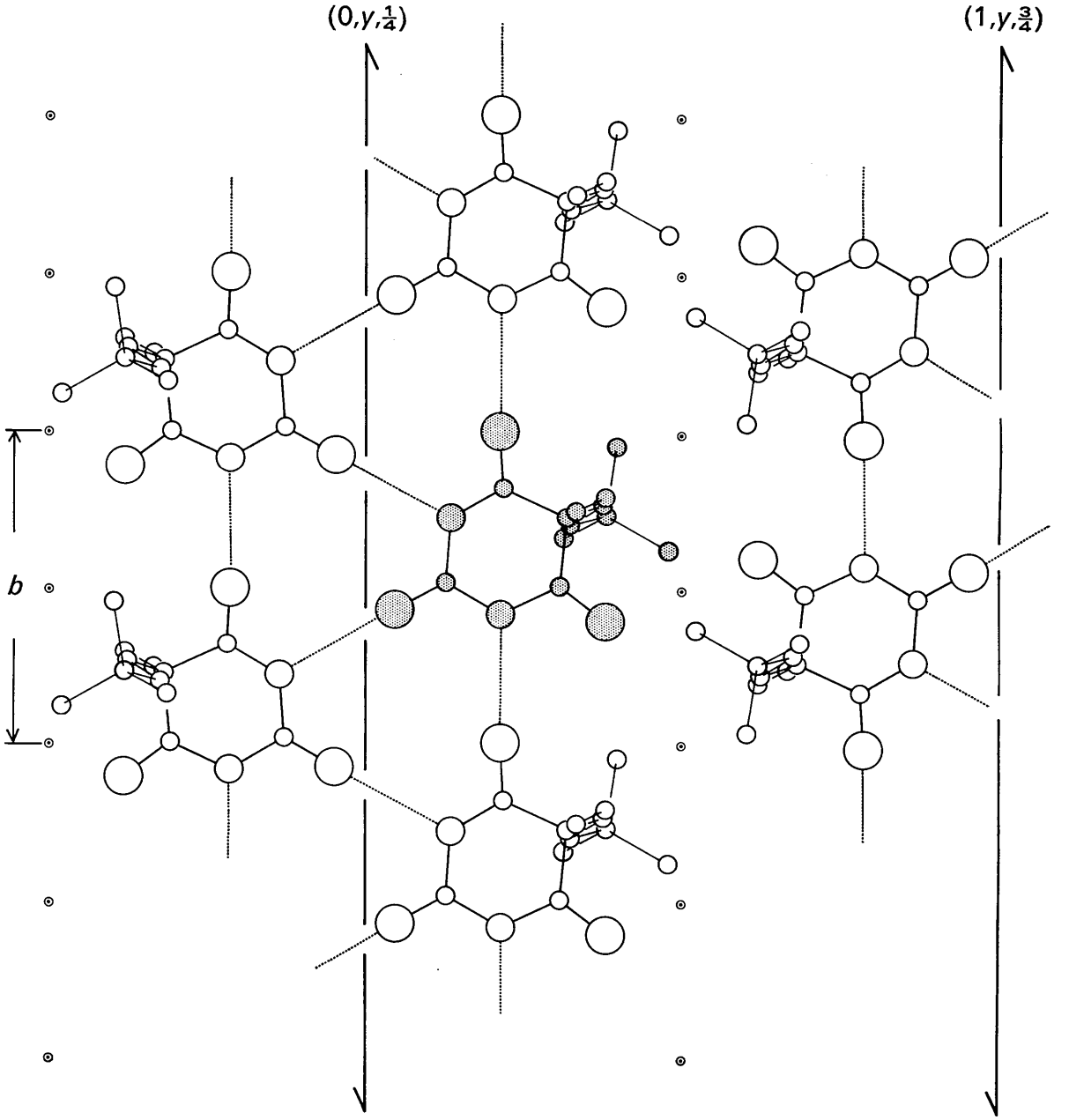

Fig. 3. Hydrogen-bonded ribbons as seen in a projection normal to the ($\bar{1}02$) plane.

tions with $\sin\theta<0{\cdot}7$ were used. Peaks corresponding to hydrogen atoms bonded to C(12), however, were so ill-defined that they were omitted from calculations until confirmed by a later difference map following a cycle of anisotropic least-squares.

Full-matrix least-squares refinement was resumed with a variation of anisotropic thermal parameters. Hydrogen positional parameters were adjusted separately using a block-diagonal approximation. Following common practice, the parameter residuals calculated by the block-diagonal method were divided by two before recycling (see *e.g.*, Christofferson, Sparks & McCullough, 1958). Temperature factors for the hydrogen atoms were assumed to be the same as for the atoms to which they are covalently bonded. For the final cycles of anisotropic refinement, the standard errors of observations were assumed to be given by the expression:

$$\sigma^2(F_H)=A+B|F_H|+C|F_H|^2$$

(Cruickshank, 1961), with $A=1{\cdot}54\times10^{-1}$, $B=8{\cdot}97\times10^{-2}$, $C=6{\cdot}80\times10^{-3}$. Coefficient values were chosen to give constant averages of $w_H[|F_H^o|-|F_H^c|]^2$ in groups of increasing $|F_H^o|$. A change in the sum of weighted squares of residuals, $\sum w_H[|F_H^o|-|F_H^c|]^2$, from 2052 to 2015 for the last two cycles suggested that further refinement would be unprofitable, and termination was effected with $R=0{\cdot}093$. Before the last cycle, seven intense reflections with $F_{obs}<F_{calc}$ (those marked by asterisks in Table 2) were given zero weight. Final atomic parameters with e.s.d.'s are listed in Table 3.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), except for H, which was taken from Stewart, Davidson & Simpson (1965).

Molecular structure

As with other 5,5-dialkylbarbiturates, γ-methylamobarbital molecules are in the triketo tautomeric form (Fig. 1) in the crystal structure. The isolated γ-methylamobarbital molecule presumably has point symmetry *m*. The mirror plane passes through the C(5)···C(2) axis of the planar trioxopyrimidine ring and also through the carbon-atom backbone of the extended alkyl groups. Small but real departures from this geometry exist in the crystal structure. The pyrimidine ring is almost planar, but with a significant degree of puckering (Fig. 2). The asymmetries of the ring puckering in this and other alkyl substituted barbiturate crystal structures are remarkably alike, although the molecular environments in these crystals are in some cases quite different (Craven, Cusatis, Gartland & Vizzini, 1971). Both the ethyl and t-hexyl groups have extended conformations, except for small twists about C–C bonds. The largest twists are 5·2° about C(21)–C(22) and 7·3° about C(11)–C(12). The seven carbon atoms of the hydrocarbon backbone, including C(5), are coplanar to within 0·05 Å. Least-squares planes through the pyrimidine ring and the hydrocarbon backbone make a dihedral angle of 90·0°.

Bond distances and angles are given in Table 4. These have not been corrected for thermal-motion effects. Ring bond lengths and angles agree closely with those of other barbiturates. There are differences in bond lengths between pairs of ring C–N and carbonyl bonds which would be symmetry-related in the isolated molecule. These differences are significant for C–N bond pairs and possibly significant for the C=O pair. The possibility of a correlation of such variations with the particular mode of hydrogen bonding has been suggested (Craven *et al.*, 1971). The C(5)–C(11) and C(5)–C(21) bonds are longer by 0·023 and 0·025 Å than an accepted tetrahedral carbon–carbon value (1·526 Å, Lide, 1962). This lengthening of C(5)–C(α) bonds is also reported in the polymorphs of barbital (Craven *et al.*, 1969) and amobarbital (Craven & Vizzini, 1969); it has been attributed to steric repulsion between the bulky C(5) substituents. There is increasing uncertainty in the detailed geometry of the alkyl chains in progressing from C(5), due to the greater apparent thermal vibrations and to the possibility of conformational disorder at the 'free' end of the t-hexyl chain. The nine methyl hydrogen atoms associated with atoms C(24), C(25), and C(26) were not located.

Table 4. *Bond lengths and angles in γ-methylamobarbital*

Atoms are numbered as in Fig. 1. E.s.d.'s given in parentheses refer to the least significant figures in tabulated values.

C(6)—N(1)	1·380 (3) Å	N(1)—C(2)—O(2)	122·2 (3)°
N(1)—C(2)	1·361 (3)	N(1)—C(2)—N(3)	115·9 (2)
C(2)—N(3)	1·376 (3)	N(3)—C(2)—O(2)	121·8 (3)
N(3)—C(4)	1·355 (3)	C(2)—N(3)—C(4)	126·1 (2)
		N(3)—C(4)—O(4)	119·6 (3)
C(6)—O(6)	1·197 (4)	N(3)—C(4)—C(5)	118·8 (2)
C(2)—O(2)	1·213 (4)	C(5)—C(4)—O(4)	121·6 (2)
C(4)—O(4)	1·208 (4)	C(4)—C(5)—C(6)	114·3 (2)
		C(5)—C(6)—O(6)	122·5 (3)
C(5)—C(4)	1·517 (4)	C(5)—C(6)—N(1)	117·1 (2)
C(5)—C(6)	1·513 (4)	N(1)—C(6)—O(6)	120·4 (3)
C(5)—C(11)	1·549 (4)	C(6)—N(1)—C(2)	127·4 (2)
C(5)—C(21)	1·551 (4)	C(4)—C(5)—C(11)	108·6 (2)
		C(4)—C(5)—C(21)	108·3 (2)
C(11)–C(12)	1·522 (5)	C(6)—C(5)—C(21)	108·3 (2)
C(21)–C(22)	1·509 (4)	C(6)—C(5)—C(11)	108·1 (2)
		C(11)—C(5)—C(21)	109·2 (2)
C(22)–C(23)	1·542 (5)	C(5)—C(11)–C(12)	114·5 (3)
C(23)–C(24)	1·518 (6)	C(5)—C(21)–C(22)	114·6 (2)
C(23)–C(25)	1·528 (7)	C(21)—C(22)–C(23)	117·0 (3)
C(23)–C(26)	1·511 (7)	C(22)—C(23)–C(24)	107·9 (3)
		C(22)—C(23)–C(25)	108·6 (3)
N(1)—H(1)	1·00 (6)	C(22)—C(23)–C(26)	110·2 (3)
N(3)—H(3)	0·79 (5)	C(24)—C(23)–C(25)	108·0 (4)
		C(24)—C(23)–C(26)	110·3 (4)
C(11)–H(111)	1·01 (6)	C(25)—C(23)–C(26)	111·7 (4)
C(11)–H(112)	1·16 (6)	C(6)—N(1)—H(1)	119 (3)
C(21)–H(211)	1·08 (6)	C(2)—N(1)—H(1)	114 (3)
C(21)–H(212)	1·09 (6)	C(4)—N(3)—H(3)	116 (4)
C(22)–H(221)	0·98 (6)	C(2)—N(3)—H(3)	117 (4)
C(22)–H(222)	0·86 (6)	H(111)–C(11)–H(112)	103 (5)
		H(121)–C(12)–H(122)	106 (7)
C(12)–H(121)	0·83 (7)	H(121)–C(12)–H(123)	111 (7)
C(12)–H(122)	0·95 (7)	H(122)–C(12)–H(123)	117 (6)
C(12)–H(123)	0·87 (7)	H(211)–C(21)–H(212)	104 (5)
		H(221)–C(22)–H(222)	111 (6)

Hydrogen bonding and molecular packing

In the crystal structure of γ-methylamobarbital, molecules are linked to form hydrogen-bonded ribbons (Fig. 3) that extend along the **b** direction, in a plane close to (2̄04).* The crystal structure is obtained by the stacking together of sheets of these ribbons with an interplanar spacing of $d(\bar{1}02)=7{\cdot}50$ Å (Fig. 4). Each molecule is hydrogen-bonded with four neighbors so that the atoms N–H···O–C in each hydrogen bond are almost collinear (Table 5). Almost-collinear hydrogen bonds have been reported before (Donohue, 1968) and are quite common in barbiturate crystal structures, *e.g.*, barbital I, 5-methyl-5-phenylbarbituric acid (Bravic, Housty & Bideau, 1968), sodium barbital (Berthou, Cavelier, Marek, Rérat & Rérat, 1962; Berking & Craven, 1971), vinbarbital I, and heptabarbital (Bideau, Leroy & Housty, 1969). This type of hydrogen bonding occurs between two barbiturate molecules that are joined by only one hydrogen bond. The almost-col-

* Covariant components of the normal to the best least-squares plane through the atoms of the oxopyrimidine ring are (−2·144, 0·038, 3·799).

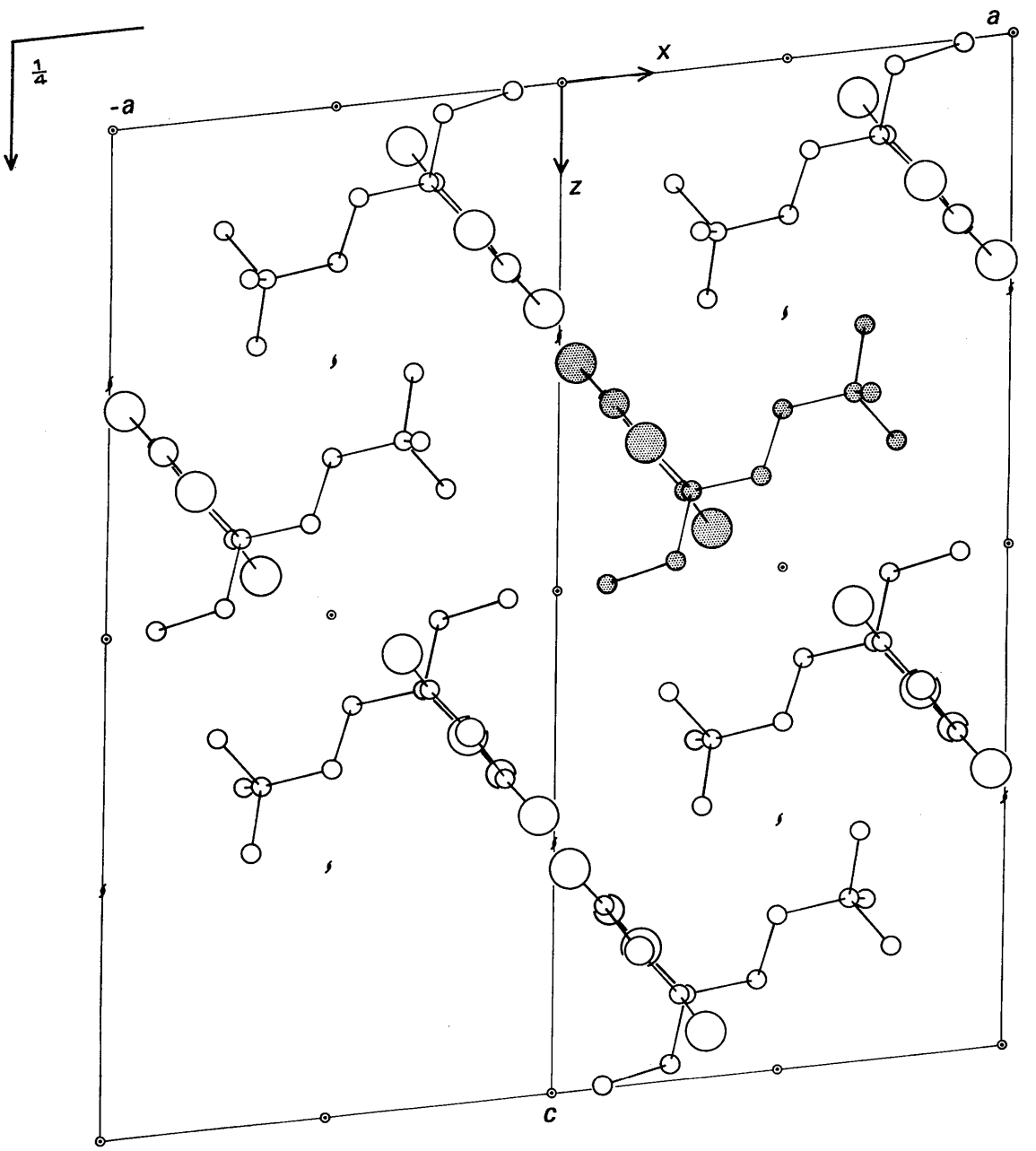

Fig. 4. Crystal structure as viewed down **b**.

linear geometry is attributed to intermolecular repulsions of non-bonded atoms flanking those involved in the hydrogen bond. The crystal structure of γ-methylamobarbital is the first barbiturate in which all hydrogen bonds are of the collinear type.* In the other structures listed above, there are also molecules linked by pairs of NH···O–C hydrogen bonds, such that the N···O–C angle is close to 128°. Two molecules hydrogen-bonded in this way, and sometimes related by a center of symmetry, have often been described as a 'cyclic dimer'. Cyclic-dimer type hydrogen bonding also occurs exclusively in some barbiturate crystal structures, *e.g.*, barbital II, and amobarbital I and II.

Table 5. *Hydrogen-bond distances and angles*

Parameters for atoms not in the crystal chemical unit (as listed in Table 3) may be derived from those in Table 3 by operations specified by the subscripts i,j,k,l. The first three digits code a lattice translation of $(i-5)a+(j-5)b+(k-5)c$. The last digit denotes one of the following symmetry operations: $l=1$: x,y,z; $l=2$: $-x,\frac{1}{2}+y,\frac{1}{2}-z$; $l=3$: $-x,-y,-z$; $l=4$: $x,\frac{1}{2}-y,\frac{1}{2}+z$. E.s.d.'s given in parentheses refer to the least significant figures in tabulated values.

N(1)···O(4)$_{5451}$	2·816 (3) Å
H(1)···O(4)$_{5451}$	1·83 (6)
N(3)···O(2)$_{5552}$	2·876 (3)
H(3)···O(2)$_{5552}$	2·09 (5)
N(1)·····O(4)$_{5451}$–C(4)$_{5451}$	176·8 (2)°
H(1)·····O(4)$_{5451}$–C(4)$_{5451}$	176 (2)
N(1)–H(1)···O(4)$_{5451}$	166 (5)
H(1)–N(1)···O(4)$_{5451}$	9 (3)
N(3)·····O(2)$_{5552}$–C(2)$_{5552}$	175·1 (2)
H(3)·····O(2)$_{5552}$–C(2)$_{5552}$	172 (1)
N(3)–H(3)···O(2)$_{5552}$	169 (5)
H(3)–N(3)···O(2)$_{5552}$	8 (4)

The 5-ethyl-5-alkylbarbituric acids in which the alkyl group is 1-methylpropyl, or 1-methylbutyl, or 3-methylbutyl (see Table 1) crystallize with closely related structures that are based on a double-ribbon hydrogen-bonded framework (Craven & Vizzini, 1969). The alkyl groups are arranged with chain axes almost parallel, and are separated by about 5·3 Å. This distance is determined by the periodicity of the double-ribbon hydrogen-bonded framework in which all linkages are of the cyclic-dimer type. In the crystal structure of γ-methylamobarbital, the alkyl groups are also arranged with chain axes almost paralleling each other and perpendicular to the ribbon plane. However, by adopting a more open framework in which the hydrogen bonds are all of collinear type, the axes of hydrocarbon chains attached to the same ribbons are further apart. The shortest distance between such chain axes is 6·8 Å. No unusually short interatomic distances exist between chains (Table 6). Presumably, the difference in ribbon structure in amobarbital and γ-methylamobarbital arises from the greater bulk of the t-hexyl group.

Table 6. *Some non-bonded intermolecular approaches*

All distances within 0·2 Å of the sum of the appropriate van der Waals radii (Pauling, 1960), are listed. Asterisks indicate distances that also appear in Fig. 5. Atomic subscripts are defined in Table 5. E.s.d.'s given in parentheses refer to the least significant figures in tabulated values.

*C(11)···C(25)$_{6763}$	4·110 (7) Å
C(11)···C(26)$_{6663}$	4·072 (7)
*C(12)···C(12)$_{5663}$	4·124 (5)
*C(12)···C(12)$_{5763}$	3·909(5)
C(12)···H(122)$_{5763}$	3·37 (7)
*C(12)···C(26)$_{4551}$	4·047 (7)
*C(12)···C(26)$_{6663}$	3·770 (7)
C(21)···O(6)$_{6663}$	3·554 (4)
H(212)···O(6)$_{6663}$	2·47 (6)
C(24)····C(2)$_{6552}$	3·854 (6)
C(24)····O(2)$_{6552}$	3·582 (5)
C(24)····O(4)$_{6452}$	3·522 (5)
*C(24)····C(25)$_{6452}$	4·203 (8)
C(26)····H(121)$_{6663}$	3·33 (7)
C(26)····H(122)$_{6551}$	3·34 (7)

The view down the axis of the hydrocarbon chains in γ-methylamobarbital (Fig. 5) shows that the smaller ethyl group has five neighboring alkyl groups, and the bulkier t-hexyl group has seven. This is an unusual departure from the hexagonal arrangement of close-packed alkyl chains in crystal structures of long-chain aliphatic carboxylic acids (Abrahamsson, 1959; von Sydow, 1956), and in the barbiturates such as amobarbital, which have double-ribbon type crystal structures.

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* The geometry observed for each barbiturate ring together with its nearest screw-related neighbors is similar to the disposition of hydrogen-bonded bases in the proposed structure for triply stranded polyinosinic acid (Rich, 1958).

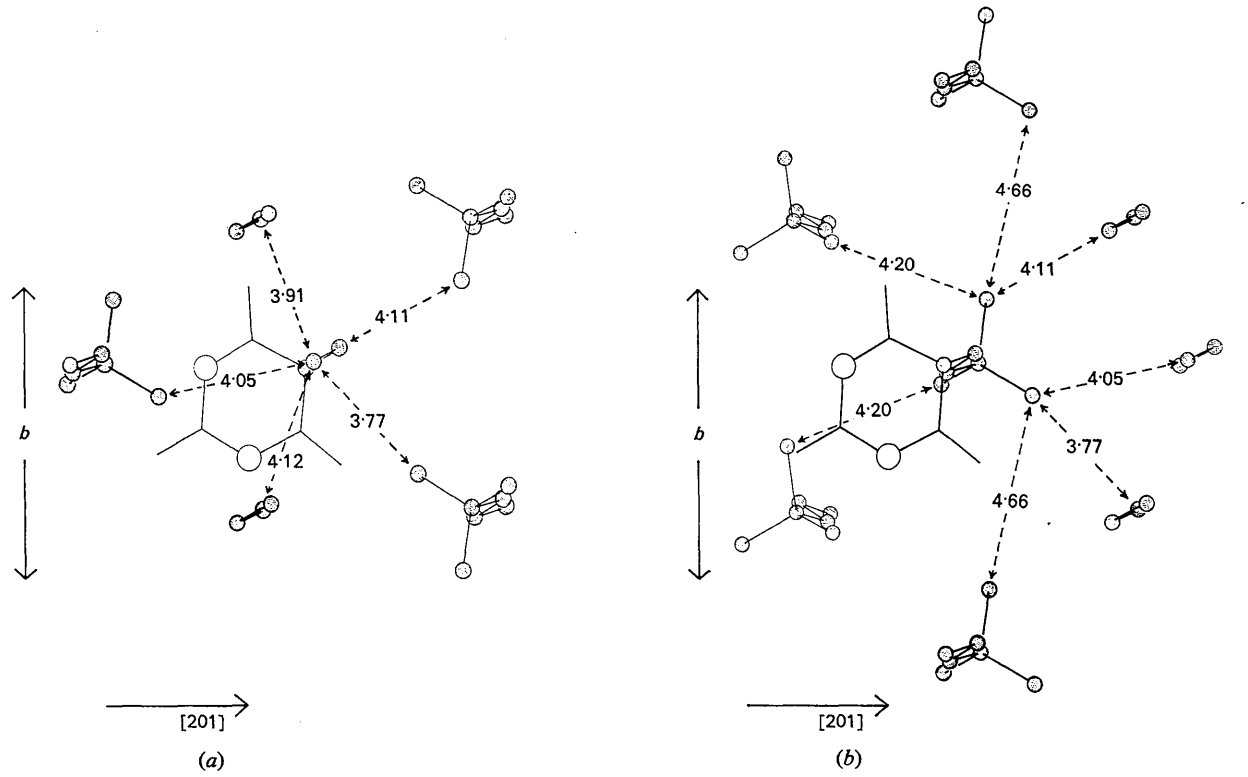

Fig. 5. Near-neighbor alkyl groups of (*a*) ethyl and (*b*) *t*-hexyl groups. These projections are along the same direction as in Fig. 3.

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