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The Crystal Structures of Two Polymorphs of 5-Ethyl-5-isoamylbarbituric Acid (Amobarbital)

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Two crystalline forms of 5-ethyl-5-isoamylbarbituric acid (amobarbital) are known. Three-dimensional X-ray crystal structure determinations of these are reported. The crystal data are: I (monoclinic, m.p. 154–156 °C) $a=21{\cdot}480$, $b=11{\cdot}590$, $c=10{\cdot}370$ Å, $\beta=97°4'$, space group $C2/c$ with 8 molecules per cell; II (monoclinic, m.p. 160–162 °C) $a=10{\cdot}281$, $b=22{\cdot}601$, $c=11{\cdot}679$ Å, $\beta=109°6'$, space group $P2_1/c$ with 8 molecules per cell. The X-ray intensity data (1861 and 4139 reflections in I and II) were collected with a four-circle automatic diffractometer and Cu $K\alpha$ radiation. Refinement of atomic positional and anisotropic thermal parameters was by a least-squares procedure, resulting in final R values of 9·6 and 7·2 per cent for all reflections or 6·9 and 7·1 per cent excluding unobserved and extinction affected reflections. The positions of the three isoamyl terminal atoms are not well-defined in either I or II because of unusually large amplitudes of thermal vibration and possibly some degree of conformational disorder. Hydrogen atoms were found except for those associated with the isoamyl terminal groups. The molecules are in the 2,4,6-trioxo tautomeric form. Variations of 0·012 Å in C–N ring bond lengths are observed which appear to be systematic and may be correlated with the effects of hydrogen bonding. The main difference between I and II is in the mode of assembly of the same structural unit, the so-called double ribbon. A single ribbon is formed from (NH···OC) hydrogen bonded barbiturate rings with all isoamyl groups projecting on one side and all ethyl groups on the other. In the double ribbon, the two component ribbons are interlocked with their ethyl group surfaces in close contact.

Introduction

A study of polymorphism in drug-active barbiturates has been undertaken in this laboratory.* In this paper, the crystal structure determinations of the two polymorphs of 5-cthyl-5-isoamyl barbituric acid, or amobarbital (Fig. 1) are reported.

Experimental

Single crystals of amobarbital I and II were obtained from the same aqueous ethanol solution by slow evaporation at room temperature. The melting points, crystal morphology, and infrared spectra of these two forms as presently observed are in agreement with those previously reported (Williams, 1959; Cleverley & Williams, 1959; Brandstätter-Kuhnert & Aepkers, 1962). The crystal data are listed in Table 1.

The intensity data were collected in the same way as for barbital (Craven, Vizzini & Rodrigues, 1969). For both forms I and II, the crystals were oriented with the symmetry axis b along the φ axis of the diffractometer. X-ray absorption corrections were applied only to the data for amobarbital I.

* See the previous paper (Craven, Vizzini & Rodrigues, 1969).

Determination of the crystal structures

A transformation of the lattice translations of amobarbital I ($\mathbf{a}'=\mathbf{c}_I$, $\mathbf{b}'=2\mathbf{b}_I$, $\mathbf{c}'=-(\mathbf{a}_I+\mathbf{c}_I)/2$ gives parameters $a'=10{\cdot}37$, $b'=23{\cdot}18$, $c'=11{\cdot}33$ Å and $\beta'=109°50'$ which are very similar to the lattice parameters of amobarbital II. This transformation suggested a close relationship which was later established by the determination of these two crystal structures.

(*a*) *Amobarbital* I

The space group was assumed to be $C2/c$ rather than Cc because the statistical distribution of normalized structure amplitudes, $|E_{hkl}|$, gave a strong indication favoring a centrosymmetric crystal structure (Karle, Hauptman & Christ, 1958). An initial attempt to apply the direct method of structure determination by Beurskens' (1963) procedure was unsuccessful because of incorrect sign indications in the early stages. The sharpened three-dimensional Patterson function with E^2_{hkl} as coefficients was then calculated. This showed, in the region close to the section $v=0$, the characteristic hexagonal pattern of peaks associated with vectors between barbiturate ring atoms. This established the approximate tilt of the barbiturate ring and the orientation of the ring within this plane as one of three possibilities. One of these was consistent with the requirements of NH---OC hydrogen bonding, thus leading to a trial structure in the projection down *b*. After this was confirmed by obtaining reasonable agreement ($R=0{\cdot}30$) between observed and calculated structure factors F_{h0l}, the trial structure was extended to the third dimension and refinement was attempted by several cycles of structure factors and three-dimensional Fourier syntheses of electron density. This procedure gave convergence at a false solution of the structure with $R=0{\cdot}40$. Returning to the direct method, but this time assuming the phases for F_{h0l} as determined above, the true solution to the phase problem was obtained. It was found that no atom in the false structure was further than 0·5 Å from its position in the true structure. The major difference between the two structures lay in a relative molecular tilt of about 5° about the axis N(3)–C(6).

(*b*) *Amobarbital* II

The direct method of phase determination was applied by the use of Beurskens' (1963) procedure. A total of 815 signs were determined, of which 234 corresponded to normalized structure amplitudes (F_{hkl}) greater than 2·0. These were used in a Fourier synthesis with F_{hkl} coefficients, which showed the positions of all atoms except for ambiguities concerning the three terminal carbon atoms of each of the isoamyl groups. These atoms, subsequently located by several cycles of Fourier refinement, were found to be subject to considerable thermal vibration. This is probably the reason for their not being located in a straightforward manner from the *E* map.

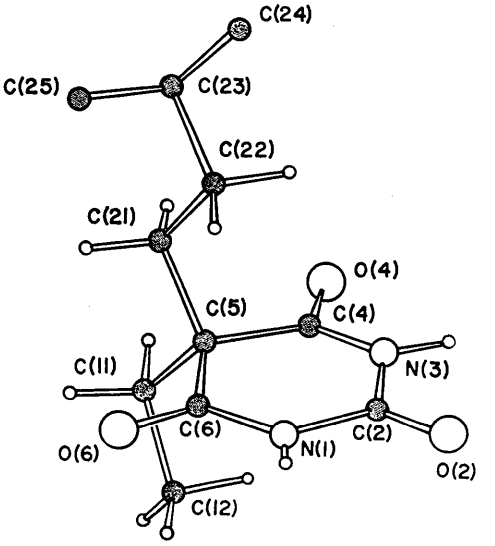


Fig. 1. Molecular formula of amobarbital. The hydrogen atoms attached to C(23), C(24), and C(28) were not found in the crystal structure determinations and are not shown here.

Table 1. *The crystal data for amobarbital* I *and* II

	I	II
Melting point	154–156°C	160–162°C
Crystal system	Monoclinic	Monoclinic
a	21·480 (10) Å	10·281 (6) Å
b	11·590 (6)	22·601 (10)
c	10·370 (6)	11·679 (6)
β	97°4(2)′	109°6(2)′
Z	8	8
Space group	$C2/c$ (by crystal structure determination)	$P2_1/c$
D_m	1·167 (7) g.cm^{-3}	1·185 (7) g.cm^{-3}
D_x	1·171	1·178
Cleavage plane	(100)	—
Crystal habit	Plates developed on {100}, exhibiting also {010}, {011}.	Needles elongated along *b*
Absorption coefficient (Cu $K\alpha$ radiation)	7·14 cm^{-1}	7·14 cm^{-1}
Dimensions of crystal used for data collection, with *b* dimensions given second	0·1 × 0·6 × 0·6 mm^3	0·25 × 0·20 × 0·18 mm^3

The refinement of atomic parameters

(*a*) *Amobarbital* I

The full-matrix least-squares refinement procedure was similar to that used in the case of barbital. Refinement was interrupted at an R value of 0·15. Hydrogen atoms, except those bonded to atoms C(23), C(24) and C(25), were then found in a three-dimensional difference Fourier synthesis and refinement was resumed, including the hydrogen atoms. At this stage anisotropic thermal parameters were varied for the heavier atoms. In the final three cycles of refinement, reflections with observed structure amplitudes greater than 70 and the unobservably weak reflections were given zero weight. The former were found to be systematically smaller than the calculated values, perhaps as a result of extinction effects. The refinement converged (Table 2) giving a structure with unusually large anisotropic thermal parameters for the terminal carbon atoms of the isoamyl group. The largest principal component of the β_{ij} tensor for atom C(25) corresponded to a root mean square amplitude of vibration of 0·6 Å, in the direction of a twisting motion about the C(22)–C(23) bond. The three-dimensional Fourier synthesis [Fig. 2,I] was then calculated. The electron density peaks were progressively more diffuse along the carbon chain from C(21) to C(23), with very diffuse peaks for C(24) and C(25).

It was considered possible that the crystal structure might be better described in terms of the lower symmetry space group *Cc*. In this case, there would be two non-symmetry related molecules differing in the conformation of their isoamyl groups by a twist of about 90° around the C(22)–C(23) bond. This possibility was rejected when the noncentrosymmetrical trial structure, after least-squares refinement, exhibited unreasonable C–C bond lengths (1·7 Å) and a wide range of isotropic atomic thermal parameters (0·4 to 27·7 Å^2) in the isoamyl groups.

A trial structure was then assumed in the space group *C*2/*c*, with a random disordering of the isoamyl group between the two conformations which were tested in the ordered *Cc* trial structure. Fractional atoms for C(23), C(24) and C(25) were placed in fixed sites which gave the best agreement with the observed electron density [Fig. 2,I] and were consistent with C–C bond distances and angles of 1·50 Å and 112°. Least-squares refinement of site occupancy factors gave values of 0·7 and 0·1 for the two conformations, the former corresponding to the atomic positions shown in Fig. 2,I. There was no improvement in the structure factor agreement.

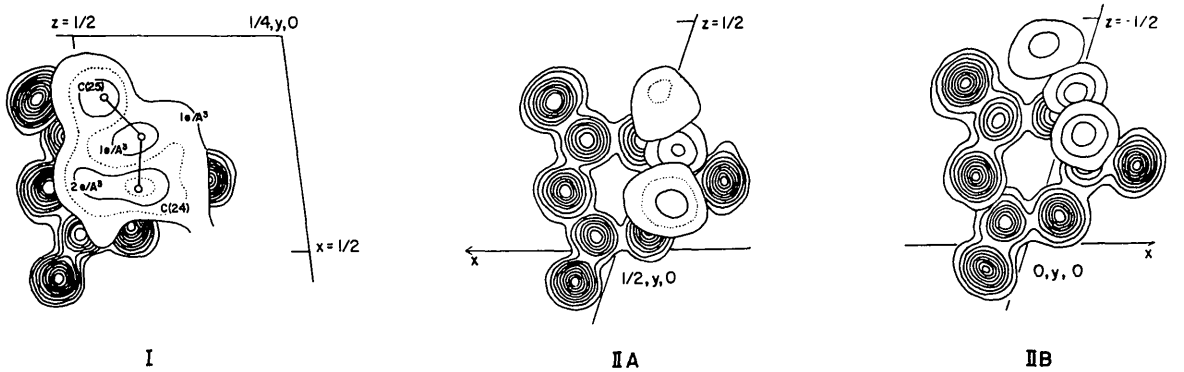
The atomic parameters and estimated standard deviations for amobarbital I which are given in Table 4 are those derived from the first conventional least-squares refinement in which all atoms are assumed to be ordered and executing harmonic anisotropic thermal motion.

(*b*) *Amobarbital* II

In this case, full-matrix least-squares refinement of carbon, nitrogen and oxygen atomic positional parameters and anisotropic thermal parameters was carried out until the R value was 0·09. A three-dimensional difference Fourier synthesis then revealed all hydrogen atoms except those of the terminal methyl groups of the isoamyl side chain in both the non-symmetry-related molecules. With the inclusion of the hydrogen atomic

Table 2. *Intensity data and refinement indices for amobarbital* I *and* II

	I	II
Total no. of reflections	1861	4139
No. of unobservably weak reflections	306	652
R index including all reflections	9·6%	7·2%
R index excluding unobserved reflections	8·6%	7·1%
R index excluding zero-weight reflections	6·9%	



I IIA IIB

Fig. 2. Observed electron density in sections of the three-dimensional Fourier synthesis normal to the crystallographic *b* axis. Unbroken contours are at intervals of 1 e.Å^{-3} beginning with the 1 e.Å^{-3} contour. Peaks corresponding to ring atoms and the terminal atoms of the isoamyl group are shown, except for C(23) in I.

Table 3. *Observed and calculated structure factors*

The listing for II begins after the horizontal double line. Columns are: for amobarbital I, h index, $10|F_o|$, $10F_c$; for amobarbital II, l index, $10|F_o|$, $10F_c$.

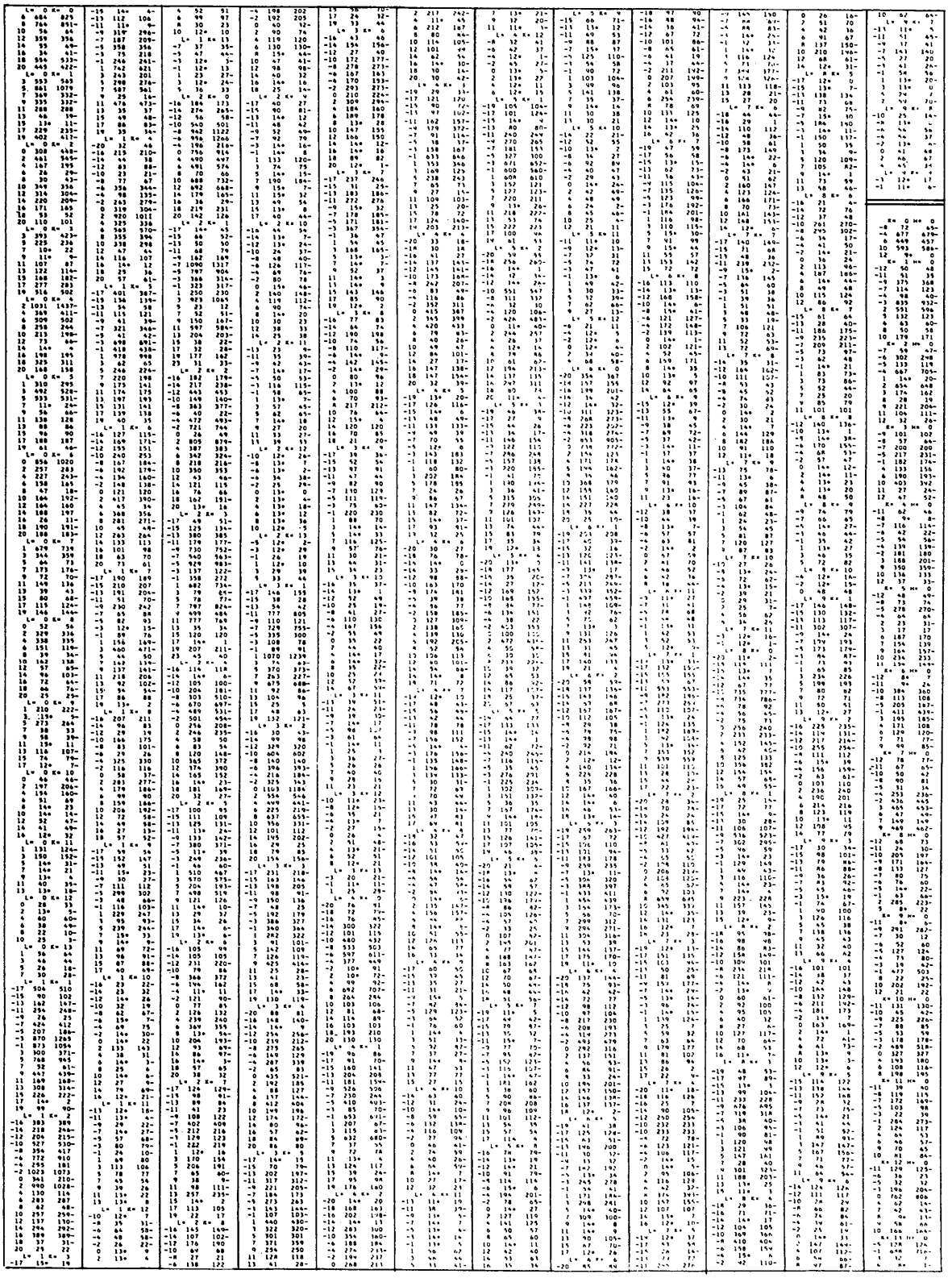


Table 3 (*cont.*)

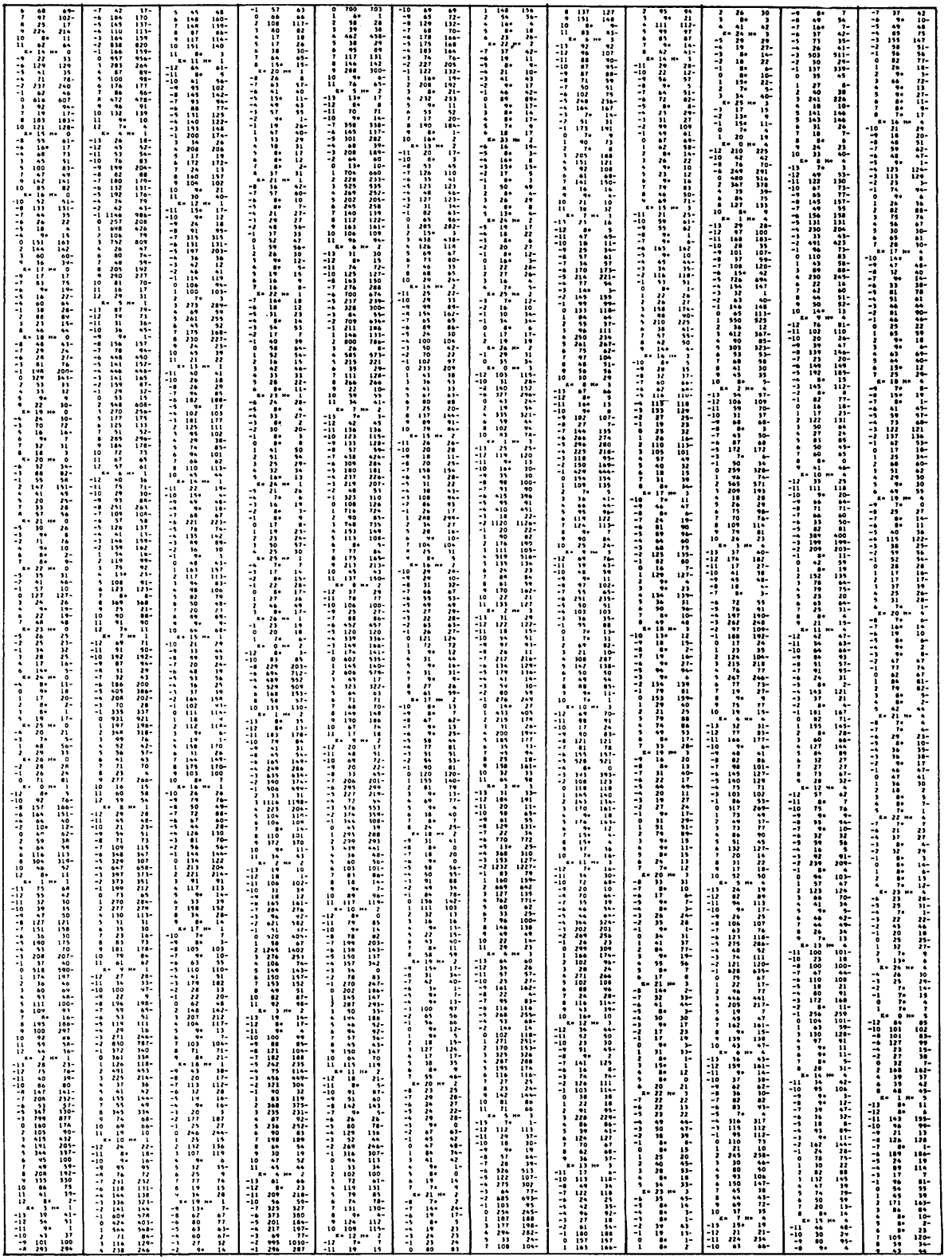
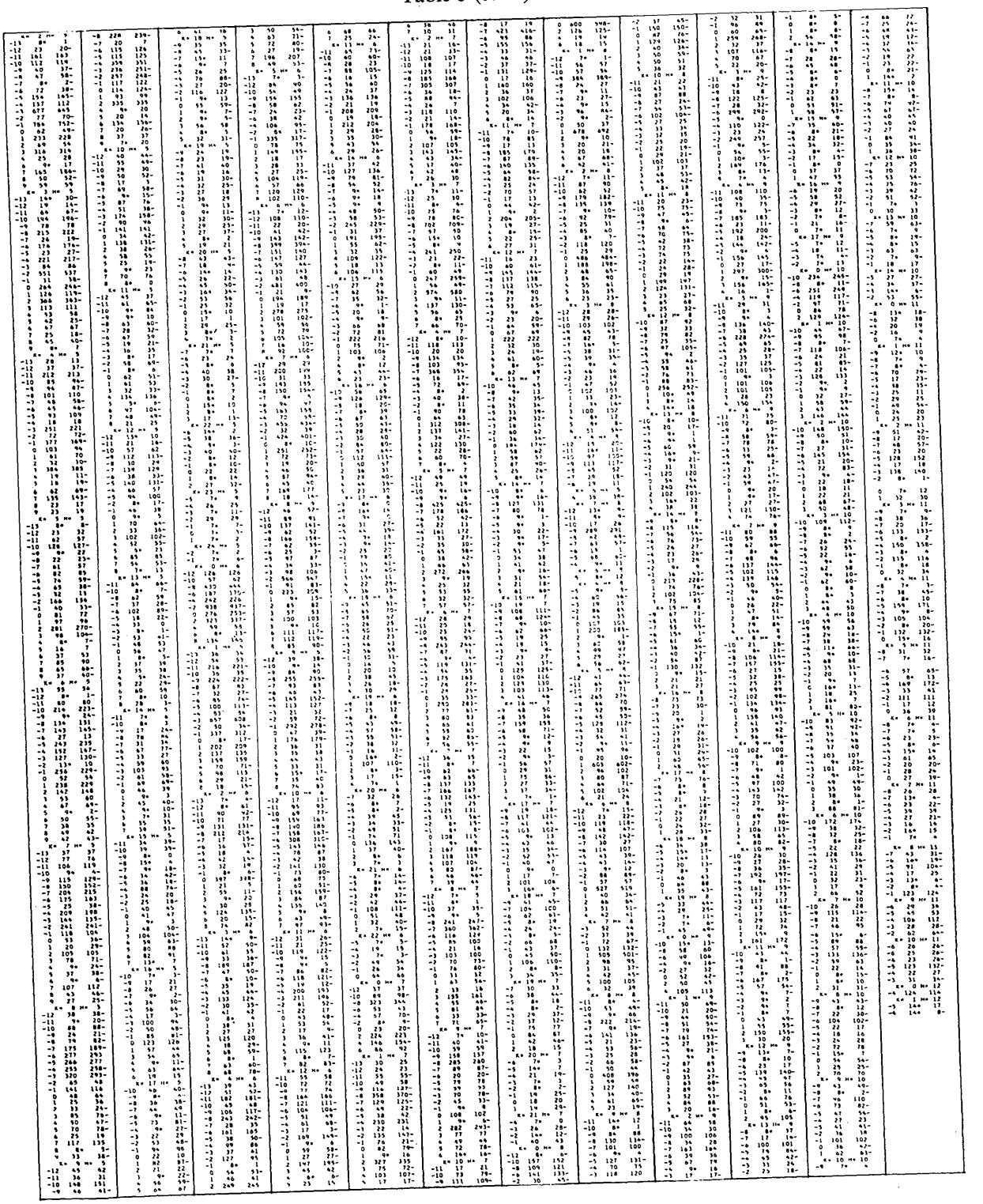


Table 3 (*cont.*)



positional parameters, computer program limitations prohibited a continuation of full-matrix least-squares refinement.

Refinement was completed with the block-diagonal least-squares procedure of the '*X-ray* 63' series of programs (Stewart, 1964). Convergence was obtained

after five cycles of calculations, with a damping factor of 0·5 applied to the calculated parameter changes.

As in the case of amobarbital I, the terminal atoms of the isoamyl groups in both molecules *A* and *B* of form II have large anisotropic thermal motion parameters and correspond to diffuse peaks in the final three-dimensional Fourier synthesis of observed electron density (Fig. 2). The ellipsoidal representation of atomic

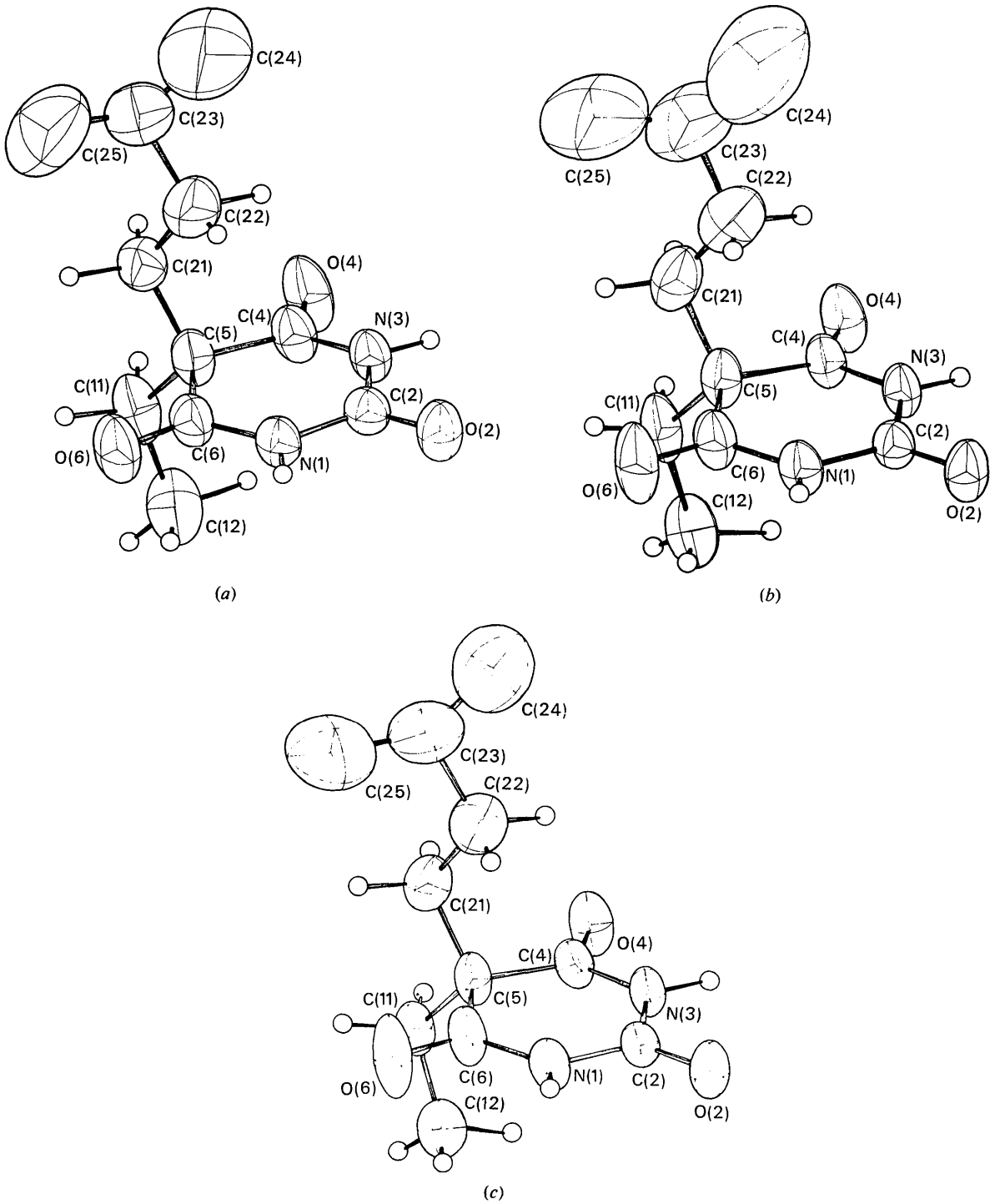


Fig. 3. The ellipsoidal representations of atomic thermal parameters (Johnson, 1965). (*a*) Amobarbital I. (*b*) Amobarbital II, molecule *A*. (*c*) Amobarbital II, molecule *B*.

Table 4. *Atomic parameters with e.s.d.'s for amobarbital* I *and* II

For each parameter, the values given are for amobarbital I (on top), amobarbital II molecule *A* (in middle), amobarbital II molecule *B* (at bottom). Positional parameters are given as fractions of the lattice translations. Thermal parameters are given corresponding to the expression:

$$T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

E.s.d.'s shown in brackets 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}
	0·4287 (1)	0·6533 (2)	0·6102 (2)	0·00203 (6)	0·0097 (2)	0·0062 (3)	0·0005 (1)	0·0009 (1)	0·0003 (2)
N(1)	0·6755 (2)	0·5876 (1)	0·1289 (2)	0·0060 (2)	0·00302 (6)	0·0065 (2)	−0·0005 (1)	0·0022 (2)	−0·0003 (1)
	−0·1821 (2)	0·5787 (1)	−0·1502 (2)	0·0057 (2)	0·00295 (6)	0·0059 (2)	0·0003 (1)	0·0021 (2)	−0·0003 (1)
	0·436 (2)	0·646 (3)	0·691 (4)						
H(1)	0·737 (3)	0·589 (1)	0·120 (2)						
	−0·243 (3)	0·583 (1)	−0·137 (2)						
	0·4818 (1)	0·6410 (2)	0·5514 (3)	0·00198 (8)	0·0078 (2)	0·0075 (3)	0·0002 (1)	0·0004 (1)	−0·0003 (2)
C(2)	0·5675 (2)	0·5757 (1)	0·0269 (2)	0·0073 (2)	0·00214 (5)	0·0060 (2)	−0·0001 (1)	0·0022 (2)	−0·0003 (1)
	−0·0724 (2)	0·5741 (1)	−0·0474 (2)	0·0069 (3)	0·00197 (6)	0·0052 (2)	0·0000 (1)	0·0017 (2)	−0·0003 (1)
	0·5328 (1)	0·6240 (2)	0·6122 (2)	0·00201 (5)	0·0136 (2)	0·0080 (2)	0·0010 (1)	0·0002 (1)	0·0000 (2)
O(2)	0·5675 (2)	0·5670 (1)	−0·0710 (2)	0·0087 (2)	0·00392 (6)	0·0065 (1)	−0·0006 (1)	0·0034 (1)	−0·0012 (1)
	−0·0828 (2)	0·5725 (1)	0·0524 (2)	0·0082 (2)	0·00364 (6)	0·0054 (2)	0·0003 (1)	0·0027 (2)	0·0002 (1)
	0·4743 (1)	0·6484 (2)	0·4185 (2)	0·00162 (6)	0·0104 (2)	0·0068 (3)	0·0003 (1)	0·0009 (1)	0·0000 (2)
N(3)	0·4399 (2)	0·5742 (1)	0·0400 (2)	0·0064 (2)	0·00264 (5)	0·0051 (2)	−0·0006 (1)	0·0012 (1)	0·0006 (1)
	0·0551 (2)	0·5715 (1)	−0·0632 (2)	0·0065 (2)	0·00250 (5)	0·0046 (2)	0·0002 (1)	0·0012 (2)	−0·0001 (1)
	0·508 (2)	0·638 (3)	0·386 (4)						
H(3)	0·375 (2)	0·566 (1)	−0·024 (2)						
	0·126 (3)	0·568 (1)	0·008 (2)						
	0·4189 (1)	0·6586 (3)	0·3402 (3)	0·00177 (7)	0·0125 (3)	0·0080 (4)	0·0001 (1)	0·0006 (2)	0·0001 (2)
C(4)	0·4123 (2)	0·5804 (1)	0·1458 (2)	0·0070 (2)	0·00284 (6)	0·0051 (2)	−0·0001 (1)	0·0018 (2)	−0·0002 (1)
	0·0791 (2)	0·5700 (1)	−0·1711 (2)	0·0069 (3)	0·00246 (7)	0·0054 (2)	−0·0001 (1)	0·0017 (2)	−0·0004 (1)
	0·4175 (1)	0·6502 (3)	0·2228 (2)	0·00212 (6)	0·0240 (4)	0·0057 (3)	0·0003 (1)	0·0007 (1)	−0·0003 (2)
O(4)	0·2954 (2)	0·5734 (1)	0·1470 (2)	0·0066 (2)	0·00480 (7)	0·0063 (2)	−0·0007 (1)	0·0023 (1)	−0·0003 (1)
	0·1958 (2)	0·5628 (1)	−0·1727 (2)	0·0070 (2)	0·00440 (7)	0·0067 (2)	0·0005 (1)	0·0027 (1)	−0·0005 (1)
	0·3601 (1)	0·6860 (3)	0·4025 (3)	0·00158 (7)	0·0123 (3)	0·0082 (3)	0·0004 (1)	0·0007 (1)	0·0005 (2)
C(5)	0·5282 (2)	0·5995 (2)	0·2583 (2)	0·0071 (3)	0·00337 (7)	0·0059 (2)	−0·0007 (1)	0·0023 (2)	−0·0010 (2)
	−0·0413 (2)	0·5799 (1)	−0·2868 (2)	0·0077 (3)	0·00287 (8)	0·0047 (2)	0·0001 (1)	0·0019 (2)	−0·0003 (1)
	0·3694 (1)	0·6765 (3)	0·5490 (3)	0·00191 (8)	0·0100 (2)	0·0090 (4)	0·0005 (1)	0·0013 (1)	0·0001 (2)
C(6)	0·6686 (3)	0·6007 (2)	0·2415 (2)	0·0078 (3)	0·00330 (8)	0·0063 (2)	−0·0007 (1)	0·0017 (2)	−0·0006 (1)
	−0·1795 (3)	0·5835 (2)	−0·2662 (2)	0·0076 (3)	0·00345 (8)	0·0053 (2)	0·0005 (1)	0·0011 (2)	−0·0002 (1)
	0·3266 (1)	0·6902 (3)	0·6128 (2)	0·00237 (6)	0·0187 (3)	0·0100 (3)	0·0013 (1)	0·0021 (1)	0·0011 (2)
O(6)	0·7720 (2)	0·6120 (1)	0·3240 (2)	0·0084 (2)	0·00610 (11)	0·0077 (2)	−0·0024 (1)	0·0013 (2)	−0·0018 (1)
	−0·2857 (2)	0·5898 (2)	−0·3488 (2)	0·0078 (2)	0·00733 (10)	0·0057 (2)	0·0016 (1)	0·0005 (2)	0·0001 (1)
	0·3069 (2)	0·6035 (3)	0·3489 (4)	0·00189 (9)	0·0156 (4)	0·0123 (5)	−0·0004 (1)	0·0010 (1)	−0·0024 (3)
C(11)	0·5355 (3)	0·5567 (2)	0·3634 (2)	0·0097 (3)	0·00443 (7)	0·0049 (2)	−0·0008 (1)	0·0018 (2)	−0·0002 (1)
	−0·0471 (3)	0·5292 (1)	−0·3775 (2)	0·0105 (3)	0·00284 (10)	0·0049 (2)	−0·0002 (1)	0·0024 (2)	−0·0005 (1)
	0·304 (2)	0·613 (4)	0·244 (4)						
H(111)	0·595 (3)	0·572 (2)	0·437 (3)						
	−0·115 (3)	0·543 (1)	−0·462 (2)						

Table 4 (*cont.*)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	0·267 (2)	0·636 (4)	0·381 (4)						
H(112)	0·448 (3)	0·559 (2)	0·373 (2)						
	−0·048 (3)	0·525 (1)	−0·385 (2)						
	0·3175 (2)	0·4775 (4)	0·3892 (6)	0·00287 (11)	0·0132 (4)	0·0275 (8)	−0·0004 (2)	0·0020 (2)	−0·0057 (5)
C(12)	0·5824 (4)	0·4941 (2)	0·3491 (3)	0·0172 (5)	0·00394 (9)	0·0082 (3)	−0·0014 (2)	0·0027 (3)	0·0005 (1)
	−0·0877 (4)	0·4693 (2)	−0·3428 (3)	0·0172 (5)	0·00309 (11)	0·0081 (3)	−0·0007 (2)	0·0031 (3)	0·0003 (1)
	0·275 (2)	0·426 (4)	0·356 (5)						
H(121)	0·571 (3)	0·472 (2)	0·416 (3)						
	−0·093 (4)	0·443 (2)	−0·408 (3)						
	0·359 (2)	0·471 (4)	0·338 (5)						
H(122)	0·517 (3)	0·477 (2)	0·262 (3)						
	−0·034 (3)	0·460 (2)	−0·257 (3)						
	0·326 (2)	0·479 (4)	0·497 (6)						
H(123)	0·662 (4)	0·497 (2)	0·339 (3)						
	−0·166 (3)	0·471 (2)	−0·325 (3)						
	0·3411 (2)	0·8121 (3)	0·3674 (4)	0·00219 (9)	0·0132 (4)	0·0129 (4)	0·0007 (1)	0·0008 (1)	0·0039 (3)
C(21)	0·4964 (3)	0·6628 (2)	0·2900 (3)	0 0123 (4)	0·00391 (7)	0·0101 (3)	−0·0008 (1)	0·0047 (3)	−0·0021 (1)
	−0·0178 (3)	0·0389 (2)	−0·3433 (3)	0·0134 (4)	0·00280 (10)	0·0078 (3)	0·0003 (2)	0·0040 (3)	0·0004 (1)
	0·330 (2)	0·821 (4)	0·271 (5)						
H(211)	0·420 (3)	0·658 (2)	0·310 (3)						
	−0·090 (3)	0·648 (1)	−0·425 (3)						
	0·298 (2)	0·829 (4)	0·400 (4)						
H(212)	0·566 (3)	0·674 (2)	0·368 (3)						
	0·069 (3)	0·633 (1)	−0·360 (3)						
	0·3900 (2)	0·9012 (4)	0·4119 (6)	0·00287 (12)	0·0122 (4)	0·0294 (9)	0·0003 (2)	0·0001 (2)	0·0050 (5)
C(22)	0·4768 (4)	0·7084 (2)	0·1921 (4)	0·0196 (5)	0·00344 (8)	0·0154 (4)	−0·0005 (2)	0·0069 (4)	−0·0017 (1)
	−0·0058 (4)	0·6931 (2)	−0·2648 (3)	0·0190 (5)	0·00272 (11)	0·0117 (5)	0·0005 (2)	0·0050 (4)	−0·0001 (1)
	0·433 (3)	0·886 (4)	0·388 (6)						
H(221)	0·413 (4)	0·695 (2)	0·114 (3)						
	−0·079 (4)	0·693 (2)	−0·233 (3)						
	0·406 (3)	0·893 (5)	0·488 (6)						
H(222)	0·554 (4)	0·711 (2)	0·175 (3)						
	0·062 (4)	0·689 (2)	−0·185 (3)						
	0·3692 (3)	1·0244 (5)	0·3711 (8)	0·00428 (16)	0·0126 (5)	0·0449 (14)	0·007 (2)	0·0038 (4)	0·0037 (6)
C(23)	0·4409 (8)	0·7694 (3)	0·2212 (6)	0·0430 (7)	0·00327 (9)	0·0273 (6)	0·0000 (2)	0·0113 (5)	−0·0019 (2)
	0·0054 (5)	0·7508 (2)	−0·3285 (5)	0·0251 (14)	0·00267 (13)	0·0197 (9)	0·0001 (3)	0·0079 (9)	0·0005 (3)
	0·4262 (4)	1·1010 (7)	0·3959 (18,	0·0071 (3)	0·0151 (8)	0·129 (5)	−0·0019 (4)	0·0019 (10)	0·0148 (16)
C(24)	0·4152 (11)	0·8122 (3)	0·1085 (4)	0·064 (1)	0·0035 (1)	0·0370 (10)	0·0026 (3)	0·0147 (10)	0·0011 (3)
	0·0473 (7)	0·8014 (2)	−0·2347 (6)	0·037 (2)	0·0045 (2)	0·0278 (14)	0·0030 (5)	− 0·0012 (15)	0·0035 (4)
	0·3187 (4)	1·0613 (7)	0·4384 (8)	0·0088 (3)	0·0237 (9)	0·035 (1)	0·0043 (5)	0·0033 (5)	0·0006 (9)
C(25)	0·5232 (14)	0·7338 (4)	0·3240 (10)	0·083 (1)	0·0051 (2)	0·0421 (10)	−0·0053 (4)	0·0098 (10)	−0·0062 (3)
	−0·1288 (8)	0·7640 (3)	−0·4328 (7)	0·309 (3)	0·0030 (3)	0·0285 (18)	−0·0006 (7)	0·0091 (20)	−0·0020 (6)

Table 5. *Best least-squares planes through the selected atomic groupings for amobarbital* I *and* II

Equations of planes are in the form $Ax+By+Cz=D$, referred to the crystallographic axes with x, y, z in Å. The e.s.d.'s given in parentheses refer to the least significant digit of the distance quoted.

Plane 1: Plane through the six pyrimidine ring atoms, all atoms being equally weighted.
Plane 2: Plane through the atoms N(1), C(2), N(3), C(4)
Plane 3: Plane through the atoms N(1), C(4), C(5), C(6).
Plane 4: Plane through the atoms C(5), C(11), C(21), C(22), C(23).

(*a*) Amobarbital I

(i) Equations of planes

Plane	*A*	*B*	*C*	*D*
1	0·17147	0·98430	0·02023	9·19189
2	0·11036	0·99330	0·02020	8·65670
3	0·22511	0·97350	0·01214	9·50670
4	−0·51696	0·09869	0·90743	0·57567

(ii) Distances $d(i)$ (Å) of atoms from the ith plane

	Atoms forming the plane				Atoms not forming the plane				
	d(1)	*d*(2)	*d*(3)	*d*(4)		*d*(1)	*d*(2)	*d*(3)	*d*(4)
N(1)	−0·031 (2)	0·009 (2)	0·012 (2)		N(1)				
C(2)	0·011 (2)	−0·020 (2)			C(2)			0·122 (2)	
N(3)	0·041 (2)	0·021 (2)			N(3)			0·153 (2)	
C(4)	−0·064 (2)	−0·010 (2)	−0·010 (2)		C(4)				
C(5)	0·042 (2)		0·020 (2)	−0·003 (2)	C(5)		0·176 (2)		
C(6)	0·001 (2)		−0·022 (2)		C(6)		0·122 (2)		
C(11)				−0·010 (3)	O(2)	0·017 (2)	0·082 (2)	0·184 (2)	
C(21)				0·023 (3)	O(4)	−0·190 (2)	−0·135 (2)	−0·127 (2)	
C(22)				0·000 (3)	O(6)	0·014 (2)	0·192 (2)	−0·066 (2)	
C(23)				−0·011 (4)	C(12)				0·107 (4)
					C(24)				−0·324 (6)

(iii) Dihedral angles

(2) ∧ (3) 6·7° (3) ∧ (4) 89·2°

(*b*) Amobarbital II

(i) Equations of planes

	Molecule *A*				Molecule *B*			
Plane	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*
1	−0·06440	0·97145	−0·19456	12·19196	0·07174	0·99440	0·04970	12·81448
2	−0·06473	0·98242	−0·14416	12·37452	0·06773	0·99726	0·00582	12·89946
3	−0·06932	0·95919	−0·23621	11·89364	0·07829	0·98984	0·08641	12·64585
4	0·89170	0·21172	0·08544	7·96291	0·92818	−0·11021	0·03130	−1·91048

(ii) Distances $d(i)$ (Å) of atoms from the ith plane

	Atoms forming the plane				Atoms not forming the plane				
	d(1)	*d*(2)	*d*(3)	*d*(4)		*d*(1)	*d*(2)	*d*(3)	*d*(4)
					Molecule *A*				
N(1)	−0·030 (2)	0·007 (2)	0·009 (2)		N(1)				
C(2)	0·012 (2)	−0·014 (2)			C(2)			0·109 (2)	
N(3)	0·033 (2)	0·015 (2)			N(3)			0·130 (2)	
C(4)	−0·053 (2)	−0·007 (2)	−0·007 (2)		C(4)				
C(5)	0·034 (2)		0·014 (2)	0·006 (2)	C(5)		0·151 (2)		
C(6)	0·004 (2)		−0·015 (2)		C(6)		0·111 (2)		
C(11)				−0·027 (3)	O(2)	0·034 (2)	0·052 (2)	0·180 (2)	
C(21)				0·050 (3)	O(4)	−0·132 (2)	0·087 (2)	−0·079 (2)	
C(22)				−0·010 (3)	O(6)	−0·002 (2)	0·155 (2)	−0·070 (2)	
C(23)				−0·018 (4)	C(12)				0·089 (4)
					C(24)				0·955 (6)
					Molecule *B*				
N(1)	−0·030 (2)	0·007 (2)	0·002 (2)		N(1)				
C(2)	0·006 (2)	−0·014 (2)			C(2)			0·091 (2)	
N(3)	0·033 (2)	0·015 (2)			N(3)			0·119 (2)	
C(4)	−0·044 (2)	−0·007 (2)	−0·002 (2)		C(4)				
C(5)	0·021 (2)		0·004 (2)	−0·032 (2)	C(5)		0·122 (2)		
C(6)	0·014 (2)		−0·004 (2)		C(6)		0·110 (2)		
C(11)				0·004 (3)	O(2)	0·021 (2)	−0·050 (2)	0·149 (2)	
C(21)				0·024 (3)	O(4)	−0·122 (2)	−0·090 (2)	−0·072 (2)	
C(22)				0·032 (3)	O(6)	0·027 (2)	0·170 (2)	−0·034 (2)	
C(23)				−0·028 (4)	C(12)				−0·221 (4)
					C(24)				0·279 (6)

(iii) Dihedral angles

Molecule *A*				Molecule *B*			
(2) ∧ (3)	5·8°	(3) ∧ (4)	88·2°	(2) ∧ (3)	5·2°	(3) ∧ (4)	89·7°

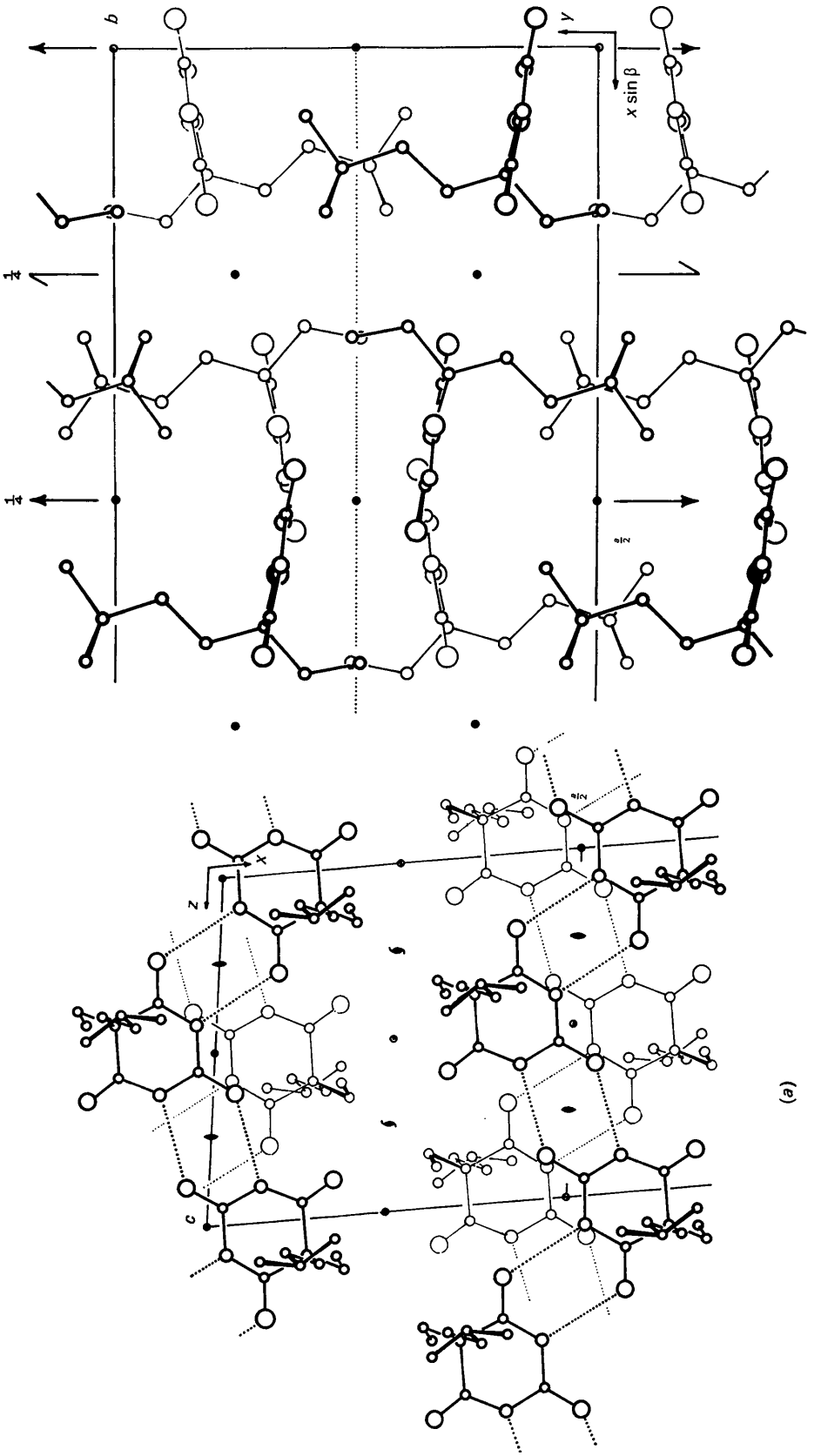


Fig. 4. The crystal structure of amobarbital I. (*a*) The projection down the *b* axis. (*b*) the projection down the *c* axis.

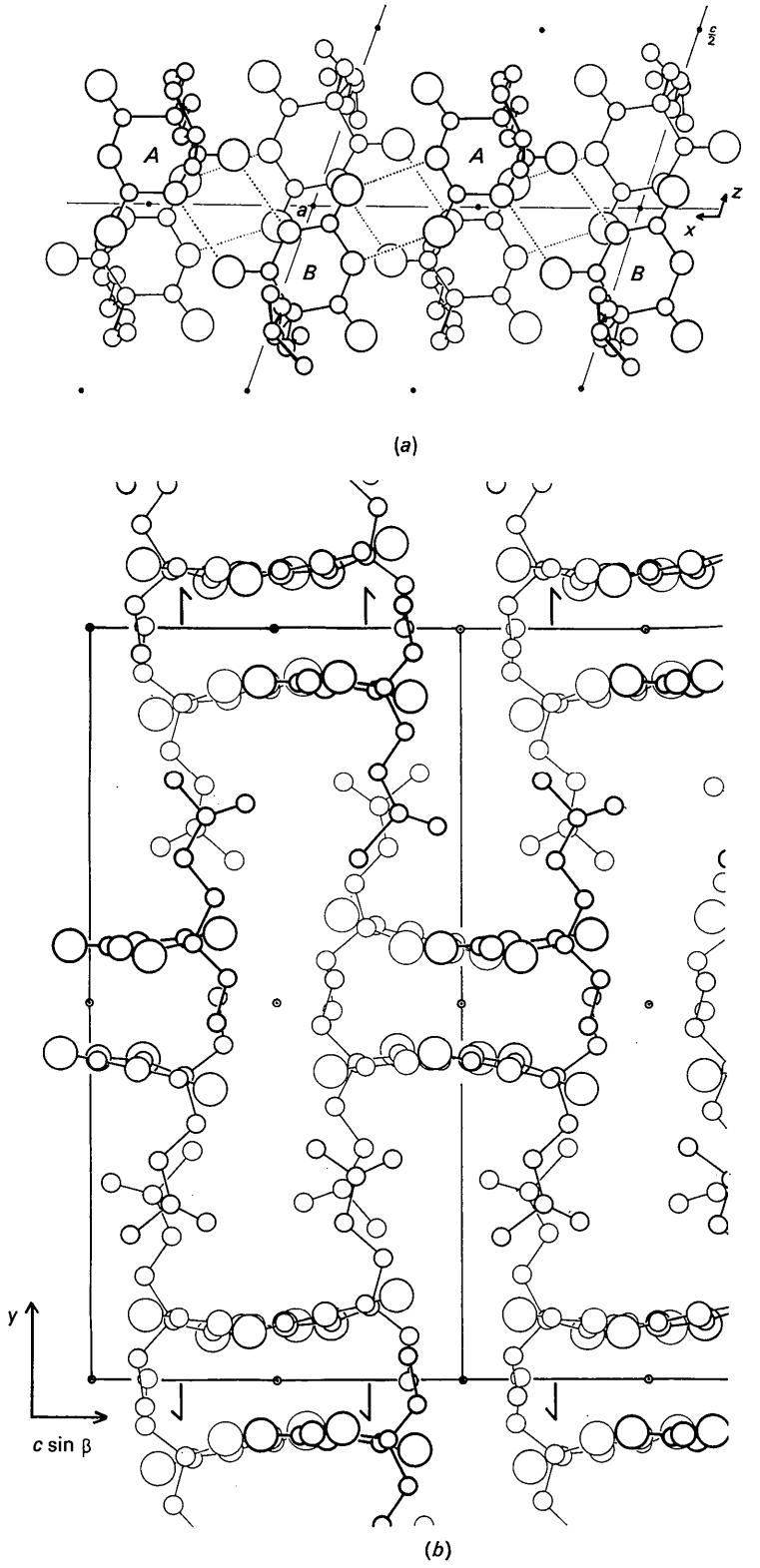


Fig. 5. The crystal structure of amobarbital II. (*a*) The projection of a double ribbon of hydrogen bonded molecules down the *b* axis. There are twofold screw axes at $(0,y,\frac{1}{4})$, $(\frac{1}{2},y,\frac{1}{4})$ *etc.* These generate partially overlapping additional double ribbons which are not shown. (*b*) The projection down the *a* axis.

thermal parameters is shown in Fig. 3 for all three molecules.*

The observed and calculated structure factors are listed in Table 3 and final values of atomic parameters with e.s.d.'s are listed in Table 4.

The molecular structure of amobarbital

The amobarbital molecules I, II*A* and II*B* are all in the trioxopyrimidine tautomeric form (Fig. 1).

For an isolated molecule, the barbiturate ring atoms should be coplanar and the hydrocarbon chain consisting of the ethyl and isoamyl groups and the atom C(5) should be normal to the ring plane with a fully extended conformation except for a *gauche* configuration of either atom C(24) or C(25). The best least-squares planes through the appropriate atomic groupings (Table 5) and the Newman projections along the C–C hydrocarbon bonds (Vizzini, 1968) show that there are small but real departures from idealized geometry, and that these deviations are much the same in the three molecules I, II*A* and II*B*. Such a result is consistent with the similarity in molecular environments.

The pyrimidine rings are slightly folded along the N(1)---C(4) diagonal with dihedral angles of 6·7°, 5·8° and 5·2° in I, II*A* and II*B*. This fold is along the diagonal which separates the hydrogen-bonded ring positions 1 through 4 from the non-hydrogen-bonded positions, 5, 6. A similar folding (4·5°) is found in barbital I (Craven, Vizzini & Rodrigues, 1969).

The hydrocarbon chains have spines of carbon atoms which are very nearly coplanar, from atoms C(11) through to C(23) (Table 5). There is a twist about the C(5)–C(11) bond of 5·8°, 6·7°, 7·5° in the same sense in molecules I, II*A*, II*B* as a result of an attractive van der Waals interaction between the C(12) terminal methyl group and the oxygen atom O(2) of a neighbouring molecule (Table 8). This interaction helps to stabilize the double ribbon hydrogen-bonded structure which is discussed in the section below. Although there are uncertainties in the detailed conformations of the isoamyl terminal groups because of their considerable apparent thermal vibrations, it appears that the carbon atoms C(24) and C(25) favor approximately the same *gauche* configuration of C(24) with respect to a twist about the C(22)–C(23) bond in all three molecules.

The apparent deviations in C–C isoamyl bond lengths (Table 6) from the expected value of 1·53 Å (Bartell & Kohl, 1963) may also be attributed to the effects of apparent thermal motion. The appropriate corrections cannot be made. However, the minimum and maximum corrected bond lengths, assuming the observed atomic thermal parameters (Busing & Levy, 1964) indicate that there are no significant differences from 1·53 Å in bond lengths involving C(23), C(24) and C(25) in any of the three molecules. Thus in molecule II*A*, the uncorrected bond length C(23)–C(25) is 1·34 Å while the minimum and maximum corrected values are 1·35 and 1·62 Å.

The bond lengths and angles in the oxopyrimidine rings have been determined with a precision approaching that obtained for barbital. There is agreement, within experimental error, among the corresponding bond lengths and angles in the amobarbital molecules I, II*A* and II*B* (Table 6). The pattern of variation in C–N and also C–O bond lengths in each molecule is similar to that observed in barbital I, thus providing further support for the suggestion that these variations are related to the mode of barbiturate hydrogen bonding (Craven, Cusatis, Gartland & Vizzini, 1968).

The hydrogen bonding and the double ribbon structure in amobarbital I and II

The barbiturate rings are hydrogen bonded in the same way in forms I and II [Figs. 4(*a*) and 5(*a*)]. Each molecule is hydrogen bonded to two neighbouring molecules so that the barbiturate rings form a slightly puckered ribbon extending along the **c** direction in I and along the **a** direction in II. The ribbon periodicities are nearly the same (10·37 and 10·28 Å in I and II). In I, crystallographic twofold rotation axes related each molecule to its hydrogen-bonded neighbours. In II, this symmetry relationship is not exact, so that in each hydrogen-bonded ribbon, nonsymmetry related molecules *A* and *B* alternate. The N(3)–H(3)---O(4) and N(1)–H(1)---O(2) hydrogen bonds which are formed in both crystal structures have very similar interatomic distances and angles (Table 7), but are not otherwise remarkable. The carbonyl groups C(6)–O(6) are not hydrogen-bonded.

The alkyl groups which flank a hydrogen-bonded ribbon of barbiturate rings project from both sides of the ribbon in directions more or less normal to the ribbon plane. It should be noted that the isoamyl groups all project from the same side of a ribbon, with all the ethyl groups on the other side.

A compact crystal structural unit, referred to hereafter as a double ribbon, is formed by bringing together two of the ribbons described above, one of which is inverted with respect to the other across centers of symmetry, so that the ribbon surfaces on the sides of the ethyl groups are in close proximity. An isolated double ribbon is shown in Fig. 5(*a*). The separations between the best least-squares planes of the pyrimidine rings which superimpose in a double ribbon are 3·22, 3·21 and 3·26 Å for molecules I, II*A* and II*B* respectively. These values are within the range observed for the stacking separation of flat molecules in other oxopyrimidine crystal structures (3·05 Å in violuric acid monohydrate, Craven & Mascarenhas, 1964; 3·30 Å in dialuric acid monohydrate, Craven & Sabine, 1969). In the double-ribbon structure, the ethyl

* See Vizzini (1968) for a table of mean square amplitudes of atomic thermal vibrations as tensor components referred to the same molecular axes for all three molecules.

Table 6. *Bond lengths and angles in amobarbital* I *and* II

For the atomic numbering system, see Fig. 1. The e.s.d.'s are shown in brackets and refer to the least significant digit in the distance or angle.

(*a*) Bond lengths

	I	II*A*	II*B*
C(6)–N(1)	1·378 (4) Å	1·372 (4) Å	1·369 (4) Å
N(1)–C(2)	1·366 (4)	1·363 (3)	1·355 (3)
C(2)–N(3)	1·370 (4)	1·370 (3)	1·383 (3)
N(3)–C(4)	1·361 (4)	1·363 (4)	1·361 (4)
C(6)–O(6)	1·207 (3)	1·205 (3)	1·205 (3)
C(2)–O(2)	1.211 (3)	1.213 (3)	1.206 (3)
C(4)–O(4)	1·218 (4)	1·217 (3)	1·217 (3)
C(5)–C(4)	1·520 (4)	1·519 (3)	1·520 (3)
C(5)–C(6)	1·511 (4)	1·519 (4)	1·519 (4)
C(5)–C(11)	1·540 (4)	1·545 (4)	1·548 (4)
C(5)–C(21)	1·551 (5)	1·540 (5)	1·542 (4)
C(11)–C(12)	1·527 (6)	1·522 (6)	1·510 (5)
C(21)–C(22)	1·505 (6)	1·502 (6)	1·511 (5)
C(22)–C(23)	1·54 (1)	1·50 (1)	1·53 (1)
C(23)–C(24)	1·51 (1)	1·56 (1)	1·54 (1)
C(23)–C(25)	1·43 (1)	1·34 (1)	1·51 (1)
N(1)–H(1)	0·85 (4)	0·68 (3)	0·70 (3)
N(3)–H(3)	0·84 (4)	0·84 (2)	0·91 (2)
C(11)–H(111)	1·08 (4)	0·94 (3)	1·05 (2)
C(11)–H(112)	1·01 (4)	0·94 (3)	1·01 (3)
C(21)–H(211)	0·99 (5)	0·90 (3)	1·02 (3)
C(21)–H(212)	1·03 (5)	0·99 (3)	0·98 (3)
C(22)–H(221)	1·00 (6)	0·98 (3)	0·95 (3)
C(22)–H(222)	0·80 (6)	0·88 (4)	0·97 (3)
C(12)–H(121)	1·10 (5)	0·87 (4)	0·90 (4)
C(12)–H(122)	1·08 (5)	1·09 (3)	1·00 (3)
C(12)–H(123)	1·11 (6)	0·97 (4)	0·96 (4)

(*b*) Bond angles

N(1)—C(2)—O(2)	122·4 (3)°	122·8 (2)°	123·1 (2)°
N(1)—C(2)—N(3)	116·2 (3)	116·3 (2)	115·9 (2)
N(3)—C(2)—O(2)	121·4 (3)	120·9 (2)	121·5 (2)
C(2)—N(3)—C(4)	126·2 (3)	126·2 (2)	126·2 (2)
N(3)—C(4)—O(4)	120·1 (3)	119·8 (2)	119·7 (2)
N(3)—C(4)—C(5)	118·4 (3)	118·4 (2)	118·6 (2)
C(5)—C(4)—O(4)	121·5 (3)	121·7 (3)	121·7 (2)
C(4)—C(5)—C(6)	113·5 (3)	113·8 (2)	113·5 (2)
C(5)—C(6)—O(6)	121·8 (3)	121·8 (3)	122·0 (3)
C(5)—C(6)—N(1)	118·5 (3)	118·0 (2)	118·3 (2)
C(6)—N(1)—C(2)	126·2 (3)	126·7 (2)	127·0 (2)
N(1)—C(6)—O(6)	119·7 (3)	120·2 (3)	119·7 (3)
C(4)—C(5)—C(11)	109·7 (3)	109·2 (2)	109·8 (2)
C(4)—C(5)—C(21)	107·7 (3)	107·7 (2)	108·1 (2)
C(6)—C(5)—C(21)	107·5 (3)	107·5 (3)	107·9 (2)
C(6)—C(5)—C(11)	108·6 (3)	108·2 (2)	108·6 (2)
C(11)—C(5)—C(21)	109·7 (3)	110·4 (3)	108·8 (2)
C(5)—C(11)–C(12)	114·4 (4)	115·4 (3)	115·6 (3)
C(5)—C(21)–C(22)	115·0 (3)	116·1 (3)	115·7 (3)
C(21)—C(22)–C(23)	113 (1)	116 (1)	114 (1)
C(22)—C(23)–C(24)	107 (1)	111 (1)	110 (1)
C(22)—C(23)–C(25)	111 (1)	117 (1)	111 (1)
C(24)—C(23)–C(25)	113 (1)	112 (1)	113 (1)
C(6)—N(1)—H(1)	121 (3)	119 (2)	121 (2)
C(2)—N(1)—H(1)	112 (3)	114 (2)	111 (2)
C(4)—N(3)—H(3)	121 (3)	119 (2)	120 (2)
C(2)—N(3)—H(3)	113 (3)	115 (2)	113 (2)
H(111)–C(11)–H(112)	110 (4)	104 (3)	108 (2)
H(121)–C(12)–H(122)	120 (4)	112 (3)	123 (3)
H(121)–C(12)–H(123)	110 (4)	121 (3)	113 (3)
H(122)–C(12)–H(123)	117 (4)	103 (3)	92 (3)
H(211)–C(21)–H(212)	101 (3)	103 (3)	106 (3)
H(221)–C(22)–H(222)	85 (5)	101 (3)	92 (3)

groups from one ribbon extend into indentations bordered by oxygen atoms in the complementary ribbon. An improved fit and tighter interlocking of complementary ribbons is obtained by the intramolecular twisting of the C(12) terminal methyl groups by about 6° about the C(5)–C(11) bond. This twist relieves a close contact (3·1 Å) with oxygen atom O(2) and tends to equalize the C(12)---O(4) and C(12)---O(6) distances [3·537 and 3·373 Å, Table 8(*a*)].

The hydrocarbon chain packing in amobarbital I and II

The relationship between the two crystal structures is shown in Figs. 4(*b*) and 5(*b*), and diagrammatically in Fig. 6 in the projections down the length of the double ribbons (the **c** and **a** directions in I and II, respectively). The cross section of a double ribbon is represented as an H-like symbol in which the uprights represent hydrocarbon chains and the cross bars represent barbiturate rings. The isoamyl and ethyl groups are not resolved in this symbol, but it should be remembered that the ethyl groups flank the cross bars, while the isoamyl groups extend above and below. For the purpose of emphasizing the existence of the double ribbons as structural units, the H-symbols are shown without overlap, although this is not actually the case [Figs. 4(*b*) and 5(*b*)]. In both crystal structures isoamyl groups intermesh with those attached to adjacent double ribbons so that there is an end-to-end alignment of hydrocarbon chains along **b**, with an ethyl group of one molecule next to an isoamyl group of the next.

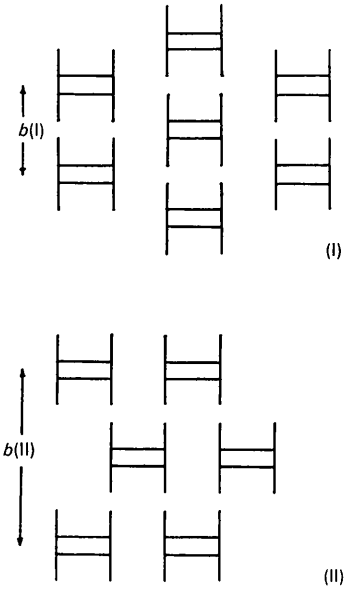


Fig. 6. Diagrammatic representation of the crystal structures of amobarbital I and II showing the arrangement of hydrogen bonded double ribbons. The projection is down the length of a ribbon (*c* axis for amobarbital I, *a* axis for amobarbital II).

Table 7. *Hydrogen bond distances and angles in amobarbital* I *and* II

Parameters for atoms not in the crystal chemical unit (*i.e.* not listed in Table 4) may be derived from those in Table 4 by operations specified by the subscript. The first three digits of the subscript code a lattice translation, *e.g.* 564 means a translation of $(5-5)a+(6-5)b+(4-5)c$ or $b-c$. The fourth digit specifies a symmetry operation which is space group dependent. In amobarbital I, these are

1:	x, y, z	3:	$\bar{x}$, y, $\frac{1}{2}-z$
2:	$\bar{x}$, $\bar{y}$, $\bar{z}$	4:	x, $\bar{y}$, $\frac{1}{2}+z$
5:	$\frac{1}{2}+x$, $\frac{1}{2}+y$, z	6:	$\frac{1}{2}-x$, $\frac{1}{2}-y$, $\bar{z}$
7:	$\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$	8:	$\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$

In amobarbital II, these are

1	x, y, z	3:	$\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$
2:	$\bar{x}$, $\bar{y}$, $\bar{z}$	4:	x, $\frac{1}{2}-y$, $\frac{1}{2}+z$

Amobarbital I		Amobarbital II	
N(1)···O(2)$_{6563}$	2·915 (3) Å	N(1*A*)···O(2*B*)$_{6551}$	2·923 (3) Å
H(1)···O(2)$_{6563}$	2·08 (4)	H(1*A*)···O(2*B*)$_{6551}$	2·27 (4)
N(3)···O(4)$_{6553}$	2·890 (4)	N(3*A*)···O(4*B*)	2·907 (4)
H(3)···O(4)$_{6553}$	2·07 (4)	H(3*A*)···O(4*B*)	2·08 (4)
N(1)—H(1)···O(2*B*)$_{6563}$	172 (4)°	N(1*A*)—H(1*A*)···O(2*B*)$_{6551}$	163 (4)°
H(1)···O(2)$_{6563}$–C(2)$_{6563}$	131 (1)	H(1*A*)···O(2*B*)$_{6551}$–C(2*B*)$_{6551}$	132 (1)
N(1)···O(2)$_{6563}$–C(2)$_{6563}$	128·6 (2)	N(1*A*)···O(2*B*)$_{6551}$–C(2*B*)$_{6551}$	130·3 (2)
N(3)—H(3)···O(4)$_{6553}$	163 (2)	N(3*A*)—H(3*A*)···O(4*B*)	168 (3)
H(3)···O(4)$_{6553}$–C(4)$_{6553}$	129 (1)	H(3*A*)···O(4*B*)—C(4*B*)	126 (1)
N(3)···O(4)$_{6553}$–C(4)$_{6553}$	125·7 (2)	N(3*A*)···O(4*B*)—C(4*B*)	123·7 (2)
N(1)···O(2*A*)$_{4551}$	2·883 (3) Å		
H(1*B*)···O(2*A*)$_{4551}$	2·21 (3)		
N(3*B*)···O(4*A*)	2·857 (3)		
H(3*B*)···O(4*A*)	1·96 (3)		
N(1*B*)—H(1*B*)···O(2*A*)$_{4551}$	162 (3)°		
N(1*B*)—H(1*B*)···O(2*A*)$_{4551}$	132 (1)		
N(1*B*)···O(2*A*)$_{4551}$–C(2*A*)$_{4551}$	131·2 (2)		
N(3*B*)—H(3*B*)···O(4*A*)	169 (2)		
H(3*B*)···O(4*A*)—C(4*A*)	128 (1)		
N(3*B*)···O(4*A*)—C(4*A*)	124·9 (2)		

The notable difference between the two modes of assembly of double ribbons (Fig. 6) is that in amobarbital I, simple stacking along **b** produces two-dimensional sheet-like structures with only weak interactions between sheets, whereas in II, a three-dimensionally interlocking structure is obtained. Crystals of form I cleave along (100), which is the plane parallel to the sheet structures.

In projecting down *b*, which is close to the end-on view of the hydrocarbon chains, the chain arrangement is found to conform closely to a regular periodic network which is remarkably similar in both structures, in spite of the two different modes of assembly of the double ribbons. In amobarbital I, the net translations are 5·2 and 5·7 Å at an angle of 110°. The corresponding values for amobarbital II are 5·1, 5·8 Å and 109°.

The side-by-side spacing of hydrocarbon chains in amobarbital I and II is determined by the geometry of the double ribbon. The resulting cross sectional area per chain is 28 Å^2 which is greater than that found in the crystal structures of aliphatic long chain carboxylic acids. In the polymorphs of stearic acid

$$CH_3[CH_2]_{17}COOH$$

and in several of its *C*-methyl derivatives, the chain cross sectional areas are close to 20 Å^2 (calculated from data tabulated by Abrahamsson, 1959). In these crystal structures chain branching does not increase the cross sectional area because the methyl substituents are tucked between end groups of neighbouring chains. It is more appropriate to compare the chain cross sectional areas in amobarbital I and II with those determined from compressed monolayers of carboxylic acid molecules on an aqueous surface. The chain area for isostearic acid $(CH_3)_2CH[CH_2]_{15}COOH$ is reported to be considerably greater than for stearic acid itself (31·6 *vs.* 20·3 Å^2; Ries & Cook, 1954). Although the detailed structure of the isostearic acid monolayer and the extent of molecular disorientation are unknown, the cross sectional area per chain is close to that found in amobarbital I and II, suggesting an efficiency of chain packing which is nearly the same, but which is considerably less efficient than the packing of unbranched chains.

It is not surprising that unusually large thermal parameters are observed in the isoamyl groups of amobarbital I and II.

The double ribbon in barbiturate crystal structures

The hydrogen bonded double ribbon forms a structural framework which is expected to occur in other barbiturate crystal structures if the 5-alkyl substituents satisfy steric requirements which allow the assembly of double ribbons in a periodic way. The effective cross sectional area per chain must be close to 28 Å^2 as in amobarbital. This could well be the case in 5-ethyl-5-

Table 8. *Intermolecular distances in amobarbital* I *and* II

Distances marked 'v' lie within 0·2 Å of the sum of the appropriate van der Waals radii (Pauling, 1960). Atomic subscripts are as defined in Table 7.

(*a*) Distances within a hydrogen bonded double ribbon

Amobarbital I		Amobarbital II			
N(1)···O(4)$_{5654}$	3·724 (6) Å	N(1*A*)···O(4*B*)$_{6652}$	3·623 (6) Å	N(1*B*)···O(4*A*)$_{5652}$	3·634 (6) Å
C(2)···O(2)$_{6662}$	3·504 (4)	C(2*A*)···O(2*A*)$_{6652}$	3·679 (4)	C(2*B*)···O(2*B*)$_{5652}$	3·685 (4)
···N(3)$_{6662}$	3·488 (4)	···N(3*A*)$_{6652}$	3·473 (4)	···N(3*B*)$_{5652}$	3·517 (4)
O(2)···N(3)$_{6662}$	3·175 (5)	O(2*A*)···N(3*A*)$_{6652}$	3·228 (4)	O(2*B*)···N(3*B*)$_{5652}$	3·265 (5)
C(4)···O(2)$_{6662}$	3·452 (6)	C(4*A*)···O(2*A*)$_{6652}$	3·451 (6)	C(4*B*)···O(2*B*)$_{5652}$	3·502 (6)
O(6)···H(121)$_{5654}$	3·18 (4)	O(6*A*)···H(121*B*)$_{6652}$	3·35 (4)	O(6*B*)···H(121*A*)$_{5652}$	3·11 (4)
···H(122)$_{5654}$	3·01 (4)	···H(122*B*)$_{6652}$	3·45 (4)	···H(122*A*)$_{5652}$	3·24 (4)
C(12)···O(2)$_{6662}$	3·426 (6)v	C(12*A*)···O(2*A*)$_{6652}$	3·422 (6)v	C(12*B*)···O(2*B*)$_{5652}$	3·402 (6)v
···O(4)$_{5654}$	4·117 (6)	···O(4*B*)$_{6652}$	3·765 (6)	···O(4*A*)$_{5652}$	3·731 (6)
···O(6)$_{5644}$	3·488 (6)v	···O(6*B*)$_{5652}$	3·591 (6)v	···O(6*A*)$_{5652}$	3·674 (6)
H(122)···O(2)$_{6662}$	2·58 (4)v	H(122*A*)···O(2*A*)$_{6652}$	2·35 (4)v	H(122*B*)···O(2*B*)$_{5652}$	2·41 (4)v

(*b*) Other intermolecular distances

O(6)···H(212)$_{5666}$	2·67 (7)v	O(6*A*)···H(111*B*)$_{6561}$	2·86 (7)	O(6*B*)···H(111*A*)$_{4541}$	2·43 (7)v
···C(21)$_{5666}$	2·633 (5)	···C(21)B_{6561}	3·826 (5)	···C(21*A*)$_{4541}$	4·399 (5)
···C(11)$_{5666}$	3·792 (5)	···C(11*B*)$_{6561}$	3·856 (5)	···C(11*A*)$_{4541}$	3·345 (5)v
C(11)···C(23)$_{5457}$	4·27 (1)	C(11*A*)···C(11*A*)$_{6662}$	4·34 (1)	C(11*B*)···C(11*B*)$_{5642}$	3·56 (1)v
···C(25)$_{5457}$	3·80 (1)v	···C(12*A*)$_{6662}$	4·09 (1)v	···C(12*B*)$_{5642}$	3·94 (1)v
···C(25)$_{5666}$	4·15 (1)v			···C(12*A*)$_{4541}$	4·17 (1)v
H(111)···C(25)$_{5457}$	3·10 (1)v	H(111*A*)···H(111*B*)$_{6561}$	2·90 (4)	H(111*B*)···H(123*A*)$_{4541}$	2·88 (4)
H(112)···H(212)$_{5666}$	2·84 (8)	H(112*A*)···H(121*A*)$_{6662}$	2·63 (4)	H(112*B*)···H(121*B*)$_{5642}$	2·70 (4)
C(12)···C(25)$_{5457}$	4·31 (1)	C(12*A*)···C(12*B*)$_{6561}$	4·10 (1)v	C(12*B*)···C(24*B*)$_{5443}$	3·89 (1)v
···C(25)$_{5666}$	3·64 (1)v	···C(24*A*)$_{6453}$	4·14 (1)v		
C(21)···O(6)$_{5666}$	3·633 (5)	C(21*A*)···C(24*A*)$_{5654}$	4·11 (1)v		
C(22)···C(24)$_{6762}$	4·20 (1)v	C(22*A*)···C(25*A*)$_{5644}$	4·48 (1)	C(22*B*)···C(25*B*)$_{5654}$	4·56 (1)
C(23)···C(25)$_{5744}$	4·59 (1)	C(23*A*)···C(23*B*)$_{5654}$	4·35 (1)		
C(24)···C(24)$_{6553}$	4·64 (1)	C(24*A*)···C(25*A*)$_{5644}$	4·52 (1)	C(24*B*)···O(6*A*)$_{4644}$	3·69 (1)
···C(24)$_{6762}$	4·30 (1)	···O(6*B*)$_{6654}$	3·69 (1)		
		C(25*A*)···C(25*B*)$_{6561}$	3·83 (1)v		

sec-butyl and 5-ethyl-5-(1-methylbutyl) barbituric acids. Crystals of these compounds have been shown to have structures which closely resemble amobarbital II (Craven & Cusatis, unpublished). However, it is unlikely that barbiturates substituted with unbranched chains at C(5) could have a double ribbon structure because the chain packing would be very inefficient. A double ribbon structure is not found in barbital I, II or IV* (Craven, Vizzini & Rodrigues, 1969). More work is needed to determine the extent to which chain length in a C(5) substituent affects the occurrence of double ribbons in barbiturate crystal structures. It is probable that length is a less critical factor than cross sectional area.

Solid solutions and molecular complex formation have been reported in many binary systems of 5,5'-dialkylbarbiturates (Brandstätter-Kuhnert & Vlachopoulos, 1967). This suggests the existence of hydrogen bonded frameworks in the solid state which are not greatly perturbed when one barbiturate is substituted for another. The double ribbon structure is well suited to this role, and in fact occurs in solid solutions in at least one such binary system (amobarbital/vinbarbital; Craven & Cusatis, unpublished).

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* The crystal structure of barbital IV has not yet been determined, but the lattice translations are incompatible with a double ribbon structure.

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A Neutron-Diffraction Study of Perdeuteronaphthalene

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The crystal structure of perdeuteronaphthalene, $C_{10}D_8$, is very similar to that of $C_{10}H_8$. The space group is $P2_1/a$ with $a=8{\cdot}266\pm0{\cdot}008$, $b=5{\cdot}968\pm0{\cdot}006$, $c=8{\cdot}669\pm0{\cdot}008$ Å; $\beta=122{\cdot}92\pm0{\cdot}02°$. 331 independent observations give an R value of 5·2% in a refinement where the anisotropic temperature factors were fixed at the best values obtained with the use of the rigid-body thermal-motion constraint, and the positional parameters were constrained to the *mmm* symmetry of the free molecule. Statistical tests showed that no significant improvement is possible on removing the constraints. Consequently, the molecular geometry resulting from the constrained refinements was better determined than it would have been from a conventional unconstrained refinement.

Introduction

The present investigation of the crystal structure of perdeuteronaphthalene, $C_{10}D_8$, is part of the study of the lattice dynamics of molecular crystals. Measurement of phonon frequencies is best done with neutron inelastic coherent scattering. Hydrogen is a very strong incoherent scatterer, and for this reason fully deuterated crystals are preferred.

Calculations have been made of phonon frequencies in naphthalene by Pawley (1967), with the use of the crystal structure of $C_{10}H_8$ as determined by X-ray dif-