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The Crystal Structure of 5-Ethyl-5-(1-methylbutenyl)-barbituric Acid

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Three crystalline forms of 5-ethyl-(1-methylbutenyl)-barbituric acid (vinbarbital) have been reported. The crystal structure of one of these (m.p. 164°C) is monoclinic with $a=14{\cdot}359$, $b=6{\cdot}822$, $c=12{\cdot}540$ Å and $\beta=107°34'$, space group $P2_1/c$ and four molecules in the unit cell. The structure has been determined from three-dimensional X-ray intensity data (Cu $K\alpha$ radiation) obtained by the use of an automatic four-circle diffractometer. There were 2259 reflections measured of which 452 were unobservably weak. The phase problem was solved by a straightforward application of the direct method. Full-matrix least-squares refinement of atomic positional parameters, including anisotropic thermal parameters for the heavier atoms and positional parameters only for the hydrogen atoms, gave convergence at $R=0{\cdot}05$. The terminal butenyl methyl group is *gauche* with respect to rotation about the C–C single bond adjacent to the double bond. Both hydrogen bonding and van der Waals interactions between the non-polar alkyl groups are important cohesive factors in the crystal structure. The hydrogen bonding is of a type not previously found in barbiturates. One carbonyl group, C(6)–O(6), forms two NH···OC hydrogen bonds while the other two carbonyl groups are not hydrogen bonded.

Introduction

The crystal structure determination of 5-ethyl-5-(1-methylbutenyl)-barbituric acid (vinbarbital, see Fig. 1) was undertaken as part of a program for the study of molecular interactions in barbiturates. In addition to being pharmacologically active, vinbarbital contains the isoprenoid grouping which is a structural subunit of such natural products as rubber. Although the crystal structure of several compounds containing the isoprenoid unit have been reported (*e.g.* geranylamine hydrochloride, Jeffrey, 1945; harunganin, Alden, Stout, Krout & High, 1964) including rubber itself (Nyburg, 1954), surprisingly little is known of the preferred conformation of the isoprenoid unit in the solid state.

It is of interest that drug-active barbiturates are commonly polymorphous in their crystal structure. Brandstätter-Kuhnert & Vlachopoulos (1967) reported three polymorphs of vinbarbital (m. p. 165, 129 and 106°C for I, II and III respectively). Attempts to grow single crystals of polymorphs II and III either from solution at different temperatures, by the use of different solvents, or by sublimation, were unsuccessful. Because of super-cooling problems, crystals of these polymorphs of vinbarbital could not be obtained even from the melt, using the method described by Brandstätter-Kuhnert & Vlachopoulos (1967). Vinbarbital is thus markedly different from barbital and amobarbital, for which different polymorphs were readily obtained by evaporation of their respective alcoholic solutions (Craven, Vizzini & Rodrigues, 1969; Craven & Vizzini, 1969).

Experimental

Single crystals of vinbarbital I were obtained from aqueous solution by slow evaporation at room temperature. The crystal density was measured at room temperature by flotation. Lattice parameters (Table 1) and X-ray intensity data (Table 2) were measured using a Picker four-circle automatic diffractometer with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). Intensity measurements were made by scanning reflections in the $\theta:2\theta$ mode at a rate of 2°min^{-1} with scans of 2° and a background count of 20 seconds at each of the scan limits. Data were collected for 2259 reflections for which 2θ was less than 130° ($\sin\theta/\lambda$ = 0·59 Å^{-1}). An integrated intensity, I, was assumed to be unobservably weak if I was less than 1·5 $\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation (e.s.d) in I, as determined from counting statistics. These reflections numbering 452, were assigned an intensity of 0·5 $\sigma(I)$. X-ray absorption corrections were neglected.

Table 1. *Crystal data for vinbarbital* I ($C_{11}H_{16}N_2O_3$)

Melting point	164°C
Crystal system	Monoclinic
Habit	Rectangular plates
Space group	$P2_1/c$
a	$14{\cdot}395\pm0{\cdot}005$ Å
b	$6{\cdot}822\pm0{\cdot}003$
c	$12{\cdot}540\pm0{\cdot}007$
β	$107°26\pm2'$
Z	4
D_m	$1{\cdot}273\pm0{\cdot}007$ g.cm^{-3}
D_x	$1{\cdot}266$ g.cm^{-3}
Cleavage plane	(100)
Absorption coefficient (Cu $K\alpha$ radiation)	7·8 cm^{-1}

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Determination of the crystal structure

The three-dimensional Patterson function showed the approximate ring plane and the three possible ring orientations within this plane. Attempts to solve the structure in the **b** projection by considerations of hydrogen bonding and packing of hydrocarbon chains were unsuccessful, because the kind of hydrogen bonding present in this structure was unexpected and an appropriate structure model was not tested.

The structure was finally solved by a straightforward application of the direct method of phase determination using Beurskens' (1963) procedure. The signs of 287 normalized structure factors with $E_{(hkl)} > 1·0$ were determined in terms of one symbolic sign. The first assumption made for the undetermined sign was correct, giving a three-dimensional Fourier synthesis with E coefficients in which all atoms were readily recognized in spite of the presence of some spurious peaks.

The refinement of atomic parameters

The carbon, oxygen and nitrogen atomic positional parameters and individual isotropic thermal parameters were refined by a full-matrix least-squares procedure. The X-ray atomic scattering factors were taken from *International Tables for* X-*ray Crystallography*, (1962). The refinement was interrupted at an R value of 0·16. All the hydrogen atoms were then located in a three-dimensional difference Fourier synthesis. Full-matrix refinement was resumed, including the hydrogen atoms. At this stage, anisotropic thermal parameters were varied for the heavier atoms. Cruickshank's (1961) weighting scheme was used with

$$\sigma^2(F) = 1·0 + 0·015F + 0·010F^2.$$

Refinement criteria are given in Table 2. The observed and calculated structure factors are shown in Table 3 and the final atomic positional parameters and individual anisotropic thermal parameters are presented in Table 4. The thermal parameters in the ellipsoidal representation are shown in Fig. 2.

Discussion

In the crystal structures of the 5,5-dialkylbarbituric acids which have been previously determined, two carbonyl groups are each involved in one NH···O=C hydrogen bond, while the third carbonyl group is not hydrogen bonded. In vinbarbital I, however, the carbonyl group C(6)–O(6) is involved in two hydrogen bonds, while the other two carbonyl groups are not hydrogen bonded (see Fig. 3). Hydrogen bonding distances and angles are given in Table 5. The hydrogen bonding links molecules to form complex sheets extending parallel to the (100) plane, with a thickness of d_{100} (13·7 Å).

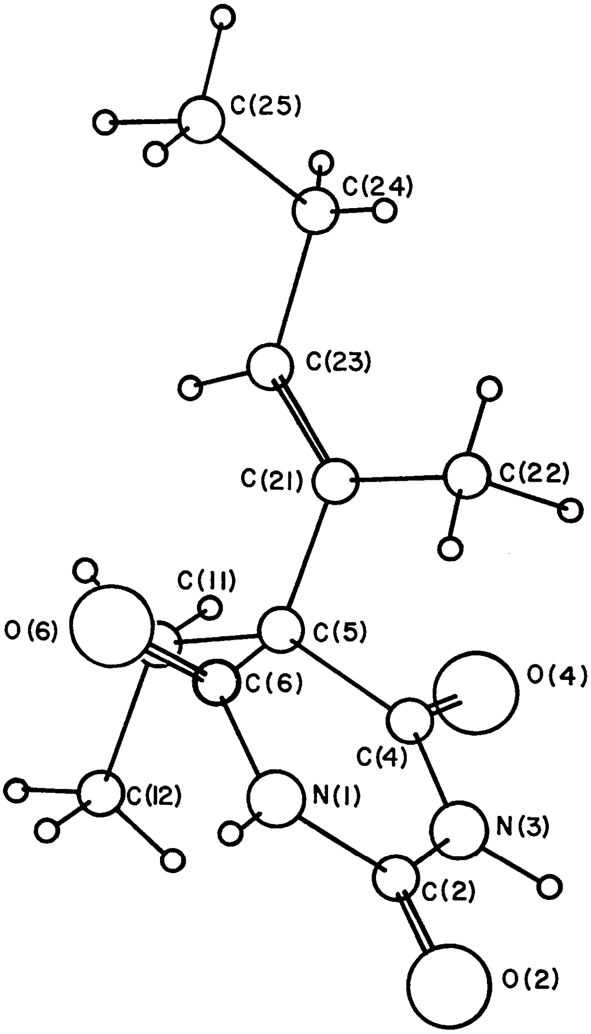

Fig. 1. The molecular structure and atomic nomenclature of vinbarbital.

Table 2. X-*ray intensity data and refinement criteria*

Crystal dimensions	b=0·20 mm c=0·17 a=0·14
Crystal axis parallel to diffractometer φ-axis	c^*
Number of independent reflections	2259
Number of unobserved reflections	452
R, including unobserved	5·4 per cent
R, excluding unobserved	4·8 per cent
Standard deviation in observation of unit weight	0·67

Table 3. *Observed and calculated structure factors*

Columns are: h index, $10|F_{\rm obs}|$, $10F_{\rm calc}$.

The carbonyl groups which are not hydrogen bonded differ markedly in their crystal environments. The carbonyl groups C(2)–O(2) are stacked along **b** in approximately antiparallel array. This type of arrangement has been observed in other barbiturates (*e.g.* violuric acid monohydrate, Craven & Mascarenhas, 1964) where dipole-dipole interactions between carbonyl groups were postulated (Bolton, 1964). However, in vinbarbital I, these interactions are weak with C$\cdots$O intermolecular distances 3·45 and 3·48 Å, which are con-

Table 4. *Atomic parameters with e.s.d.'s*

Positional parameters are given as fractions of the lattice translations. Thermal parameters are given according to the expression: $T=\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. The e.s.d.'s given 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}
N(1)	0·4465 (1)	−0·1516 (3)	0·3706 (1)	0·0035 (1)	0·0233 (4)	0·0055 (1)	−0·0021 (1)	0·0015 (1)	−0·0026 (2)
H(1)	0·507 (2)	−0·091 (4)	0·413 (2)						
C(2)	0·4453 (1)	−0·2414 (3)	0·2710 (1)	0·0046 (1)	0·0220 (4)	0·0060 (1)	−0·0010 (1)	0·0020 (1)	−0·0024 (2)
O(2)	0·5166 (1)	−0·2437 (2)	0·2396 (1)	0·0051 (1)	0·0390 (5)	0·0034 (1)	−0·0030 (2)	0·0039 (1)	−0·0069 (2)
N(3)	0·3584 (1)	−0·3261 (2)	0·2128 (1)	0·0040 (1)	0·0240 (4)	0·0053 (1)	−0·0006 (1)	0·0014 (1)	−0·0028 (1)
H(3)	0·358 (2)	−0·388 (4)	0·139 (2)						
C(4)	0·2746 (1)	−0·3314 (2)	0·2429 (1)	0·0041 (1)	0·0175 (4)	0·0053 (1)	−0·0001 (2)	0·0003 (1)	−0·0003 (2)
O(4)	0·2034 (1)	−0·4165 (2)	0·1840 (1)	0·0046 (1)	0·0280 (4)	0·0073 (1)	−0·0028 (1)	0·0007 (1)	−0·0054 (2)
C(5)	0·2729 (1)	−0·2260 (3)	0·3496 (1)	0·0033 (1)	0·0168 (4)	0·0044 (1)	−0·0004 (1)	0·0009 (1)	0·0002 (2)
C(6)	0·3699 (1)	−0·1331 (2)	0·4120 (1)	0·0037 (1)	0·0149 (4)	0·0042 (1)	−0·0004 (1)	0·0008 (1)	0·0010 (2)
O(6)	0·3801 (1)	−0·0431 (2)	0·4994 (1)	0·0042 (1)	0·0214 (3)	0·0040 (1)	−0·0016 (1)	0·0011 (1)	−0·0017 (1)
C(11)	0·2508 (1)	−0·3827 (3)	0·4282 (2)	0·0050 (1)	0·0197 (5)	0·0064 (1)	−0·0018 (2)	0·0017 (1)	−0·0013 (2)
H(111)	0·237 (2)	−0·305 (4)	0·492 (2)						
H(112)	0·186 (2)	−0·439 (5)	0·382 (2)						
C(12)	0·3298 (2)	−0·5372 (4)	0·4661 (2)	0·0087 (2)	0·0212 (6)	0·0084 (2)	0·0012 (3)	0·0020 (2)	0·0040 (3)
H(121)	0·347 (3)	−0·594 (5)	0·407 (3)						
H(122)	0·394 (2)	−0·488 (5)	0·515 (3)						
H(123)	0·311 (2)	−0·637 (5)	0·519 (3)						
C(21)	0·1978 (1)	−0·0593 (3)	0·3152 (1)	0·0040 (1)	0·0195 (4)	0·0048 (1)	0·0006 (1)	0·0021 (2)	0·0048 (3)
C(22)	0·2147 (2)	0·0748 (4)	0·2284 (2)	0·0080 (2)	0·0227 (6)	0·0089 (2)	0·0035 (3)	0·0021 (2)	0·0048 (3)
H(222)	0·191 (2)	0·003 (5)	0·143 (3)						
H(223)	0·177 (2)	0·182 (5)	0·216 (3)						
C(23)	0·1259 (2)	−0·0384 (4)	0·3604 (2)	0·0045 (1)	0·0338 (7)	0·0077 (2)	0·0027 (2)	0·0011 (1)	−0·0006 (3)
H(23)	0·124 (2)	−0·133 (5)	0·417 (3)						
C(24)	0·0488 (2)	0·1180 (6)	0·3342 (3)	0·0061 (2)	0·0488 (1)	0·0107 (2)	0·0076 (3)	0·0013 (2)	−0·0024 (4)
H(241)	0·066 (3)	0·204 (6)	0·290 (3)						
H(242)	−0·019 (3)	0·045 (5)	0·321 (3)						
C(25)	0·0473 (2)	0·2367 (5)	0·4338 (3)	0·0077 (2)	0·0296 (7)	0·0137 (3)	−0·0001 (3)	0·0044 (2)	−0·0033 (4)
H(251)	0·043 (3)	0·160 (6)	0·498 (3)						
H(252)	0·113 (3)	0·301 (6)	0·475 (3)						
H(253)	−0·006 (3)	0·334 (6)	0·417 (3)						

Table 5. *Intermolecular distances and angles*

Atoms not in the crystal chemical unit (*i.e.* not listed in Table 4) are specified by a subscript. The four-digit subscript denotes how the atomic parameters can be derived from the corresponding atom in the crystal chemical unit. The first three digits 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 refers to one of the following symmetry operations:

$$1\colon x,y,z \qquad 2\colon \bar{x},\bar{y},\bar{z} \qquad 3\colon x,\tfrac{1}{2}-y,\tfrac{1}{2}+z \qquad 4\colon \bar{x},\tfrac{1}{2}+y,\tfrac{1}{2}-z.$$

(i) Hydrogen-bond distances and angles

O(6)$\cdots$N(1)$_{6462}$	2·866 (2) Å	C(6)–O(6)$\cdots$N(1)$_{6562}$	126·2 (1)°
$\cdots$N(3)$_{5453}$	2·924 (2)	$\cdots$H(1)$_{6562}$	127·7 (7)
$\cdots$H(1)$_{6462}$	1·90 (2)	$\cdots$N(3)$_{5453}$	130·4 (1)
$\cdots$H(3)$_{5453}$	1·93 (3)	$\cdots$H(3)$_{5453}$	132·9 (7)
		N(3)–H(3)$\cdots$O(6)$_{5443}$	166 (2)
		N(1)–H(1)$\cdots$O(6)$_{6562}$	175 (2)
		H(1)$_{6562}\cdots$O(6)$\cdots$H(3)$_{5453}$	86 (1)

(ii) Other close intermolecular approaches

Intermolecular distances listed are those which are the closest in terms of the sum of the appropriate van der Waals' radii (Pauling, 1960).

N(3)$\cdots$H(111)$_{5443}$	2·94 (3) Å	H(111)$\cdots$H(222)$_{5453}$	2·75 (5) Å
H(3)$\cdots$H(111)$_{5443}$	2·50 (3)	H(252)$\cdots$H(222)$_{5453}$	2·46 (5)
C(4)$\cdots$H(111)$_{5443}$	3·17 (3)	H(251)$\cdots$H(251)$_{5562}$	2·52 (6)
O(4)$\cdots$H(223)$_{5451}$	2·81 (3)	H(112)$\cdots$H(252)$_{5651}$	2·52 (5)
O(4)$\cdots$H(242)$_{5451}$	2·65 (4)		

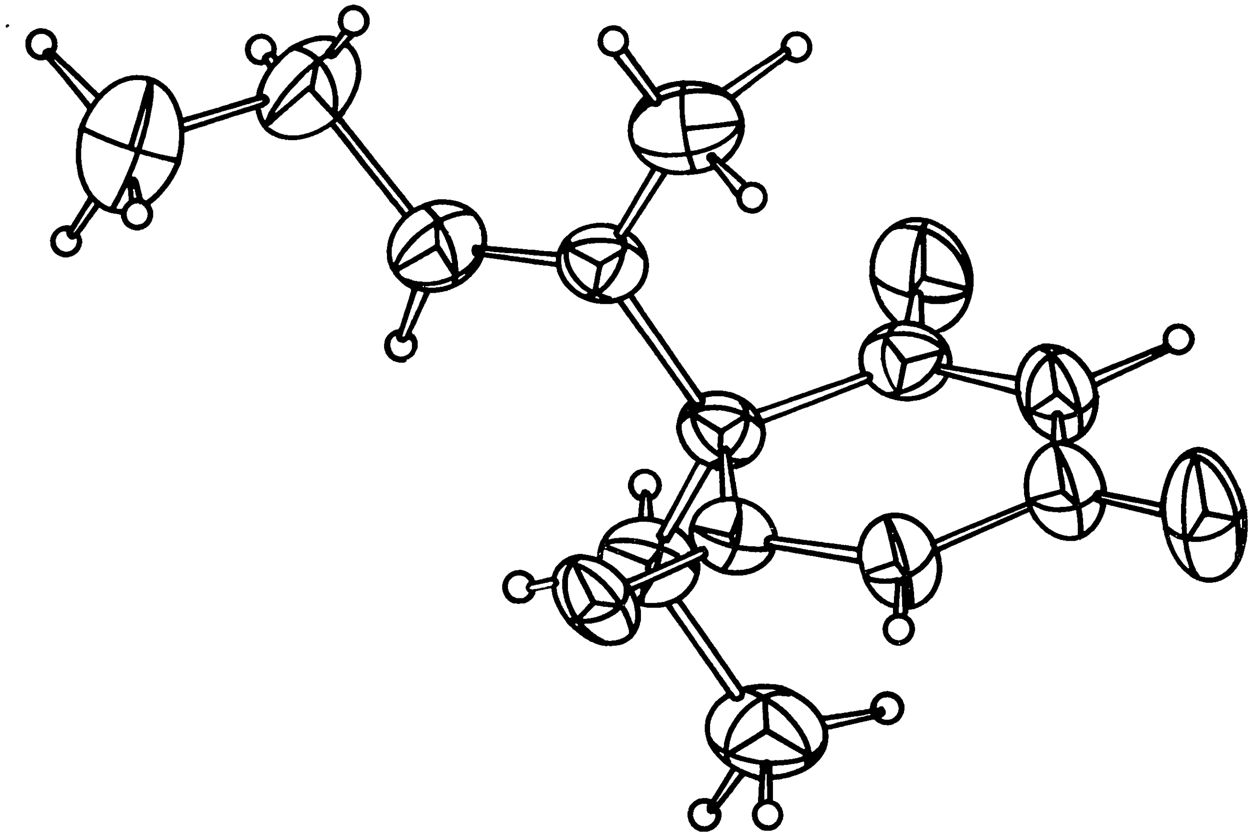

Fig. 2. Ellipsoidal representation of thermal parameters.

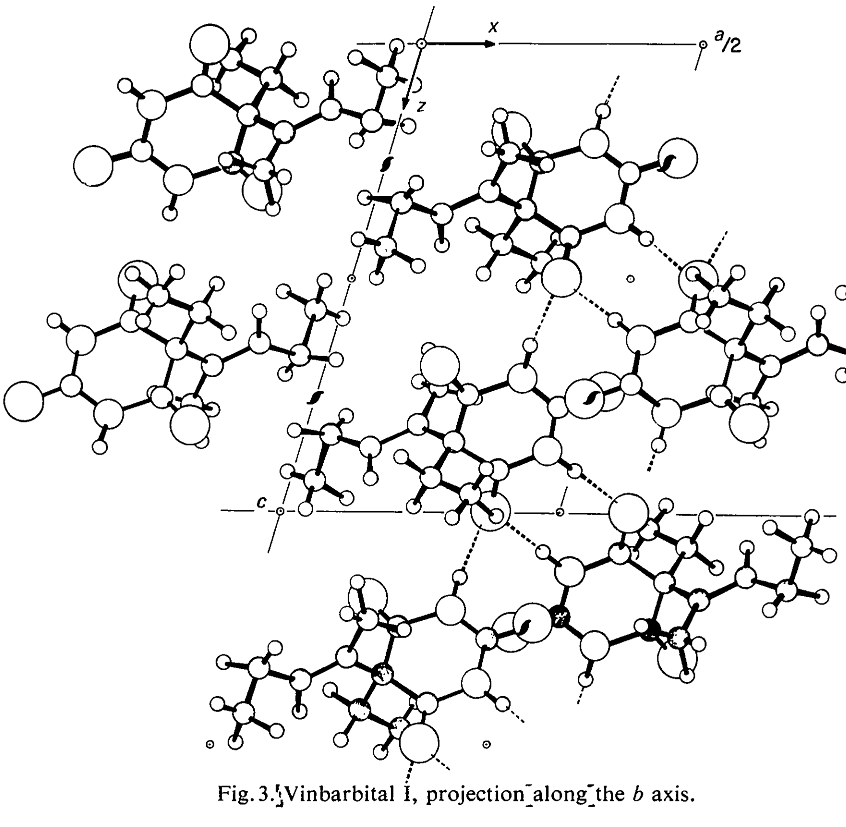

Fig. 3. Vinbarbital I, projection along the *b* axis.

siderably greater than the sum of the appropriate van der Waals radii (3·1 Å). The carbonyl group C(4)-O(4) is in van der Waals contact with hydrogen atoms of neighboring alkyl groups (see Table 5).

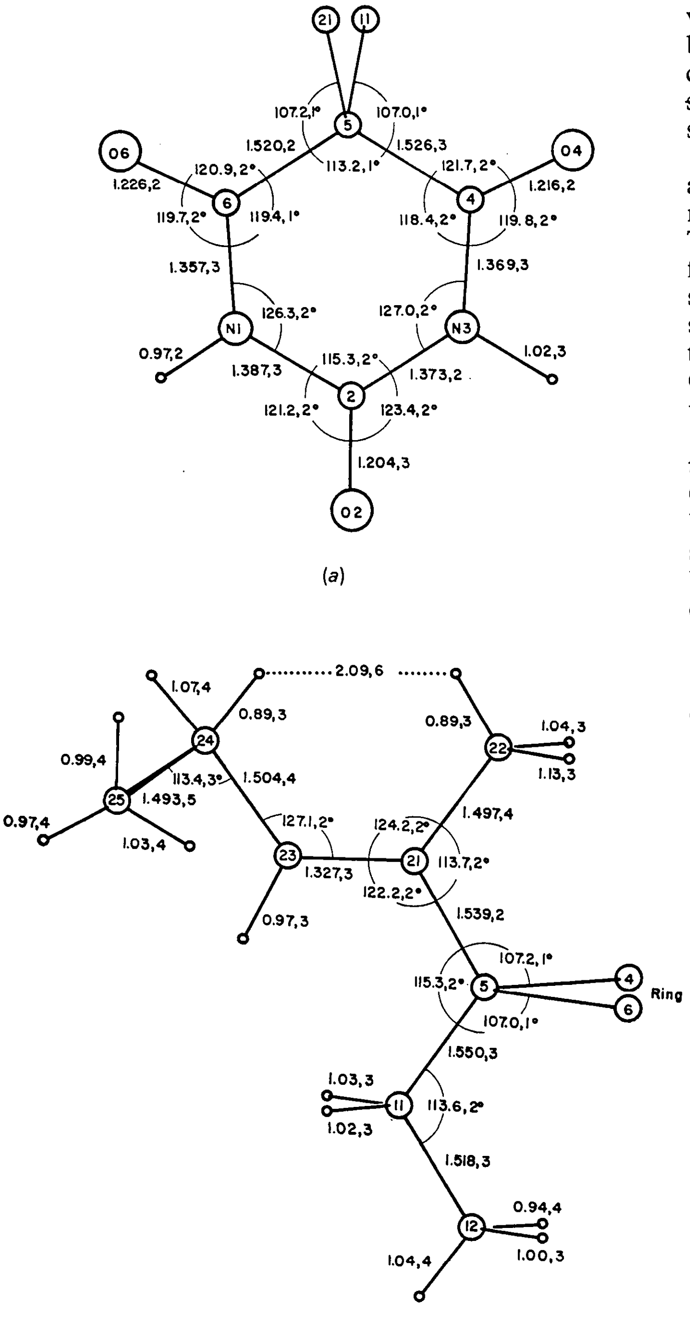

Fig. 4. (*a*) Bond angles and bond lengths for the ring. The e.s.d.'s given after the commas refer to the least significant figures in the parameter values. (*b*) Bond angles and bond lengths for the hydrocarbon chains.

The packing together of the alkyl groups in this crystal structure is particularly efficient. The ethyl group is embedded within the hydrogen bonded sheet structure, yet is in a predominantly nonpolar environment, consisting of projecting methyl groups C(12), C(22) and C(25) from neighboring molecules. Adjacent hydrogen bonded sheet structures are held together by van der Waals interactions involving the 1-methyl butenyl groups (see Fig. 3 and Table 5). The observed crystal cleavage parallel to (100) presumably corresponds to the separation of these hydrogen bonded sheets.

The intramolecular bond lengths and bond angles are shown in Fig. 4. These values have not been corrected for the effect of anisotropic thermal motion. The corrections will not be serious, except possibly for the C-C bonds of terminal groups, *e.g.* the observed bond lengths C(24)–C(25) and C(11)–C(12) are somewhat shorter than the normal value (1·53 Å, Bartell & Kohl, 1963). The bond lengths C(5)–*C*(11) and C(5)–C(21) are 0·02 and 0·03 Å longer than normal values of sp^3–sp^3 and sp^2–sp^3 carbon–carbon bonds (Lide, 1962). This is attributed to steric repulsions between the bulky substituents at C(5). The small variations in C–N and C–O bond lengths in vinbarbital I and similar barbiturate crystal structures appear to be related in a systematic way to the mode of intermolecular hydrogen bonding. These effects are discussed in more detail elsewhere (Craven, Cusatis, Gartland & Vizzini, 1969).

The pyrimidine ring is almost planar. The biggest atomic displacement from the best least-squares plane is for the atom N(1) (0·038 Å, with an e.s.d. of 0·002 Å). The ring may be regarded as slightly folded along the N(1)–C(4) line, with a dihedral angle of 2·6° (see Table 6). The carbon atoms in the hydrocarbon chains are very nearly coplanar, except C(25). The biggest atomic displacement from this best least-squares plane is for the atom C(11) (0·091 Å). The atoms of the ethylenic group are coplanar within experimental error. The twist of the C(25) methyl group from this plane is shown in Fig. 5. In the observed configuration there is a close intramolecular contact (2·1 Å) between hydrogen atoms bonded to C(22) and C(24).

The existence of a different l-methylbutenyl group conformation from that found in vinbarbital I is suggested by consideration of the single crystals which have been obtained from a solid solution of approximately 25 per cent vinbarbital in amobarbital (Craven & Cusatis, unpublished). The 'average' crystal structure for the solid solution is closely related to that of amobarbital II (Craven & Vizzini, 1969). In the latter structure such a large proportion of amobarbital molecules can be replaced by vinbarbital only if the corresponding 5-isoamyl group of amobarbital and the 5-(1-methylbutenyl) group of vinbarbital are closely related in shape and size. This requirement is not satisfied in the molecular conformation observed in vinbarbital I. However, inspection of a space filling molecular model shows that a suitable conformation can be

Table 6. *Least-squares planes and dihedral angles*

Plane 1: The plane passing through the atoms N(1), C(2), O(2), N(3), C(4), O(4), C(5), C(6) and O(6).
Plane 2: The plane passing through the atoms N(1), C(2), O(2), N(3) and C(4).
Plane 3: The plane passing through the atoms C(4), C(5), C(6), O(6) and N(1).
Plane 4: The plane passing through the atoms C(12), C(11), C(5), C(21), C(22), C(23) and C(24).

(i) Equations of planes

The equations of these planes are in the form $AX+BY+CZ=D$, referred to the crystallographic axes, with X,Y,Z in Å units.

Plane	A	B	C	D
1	−0·14679	0·84662	−0·44406	1·93120
2	−0·15236	0·85902	−0·42063	2·03762
3	−0·12319	0·84539	−0·45894	1·97000
4	0·38235	0·55629	0·58934	6·97890

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

The e.s.d.'s given in brackets refer to the least significant digit of the distances quoted.

	$d(1)$	$d(2)$	$d(3)$	$d(4)$
Atoms forming the plane				
N(1)	−0·038 (2) Å	0·000 (2) Å	−0·002 (2) Å	
C(2)	0·000 (2)	0·002 (2)		
O(2)	0·011 (2)	−0·003 (2)		
N(3)	0·019 (2)	0·003 (2)		
C(4)	−0·002 (2)	−0·003 (2)	0·001 (2)	
O(4)	−0·016 (2)			
C(5)	0·015 (2)		−0·003 (2)	0·044 (2) Å
C(6)	0·000 (2)		0·003 (2)	
O(6)	0·011 (2)		0·000 (2)	
C(11)				−0·091 (2)
C(12)				0·038 (2)
C(21)				0·010 (2)
C(22)				−0·031 (2)
C(23)				0·027 (2)
C(24)				0·003 (2)
Atoms not forming the plane				
H(1)	−0·05 (2)	0·00 (2)	0·00 (2)	
H(3)	0·07 (2)	0·03 (2)		
O(4)		−0·035 (2)	−0·025 (2)	
O(2)			0·096 (2)	
C(25)				1·181 (2)

(iii) Dihedral angles

(2) ∧ (3) 2·6° fold along C(4)···N(1) line.

obtained by a 120° rotation of the 1-methylbutenyl group about the bond C(5)–C(21).

The conformation about C–C single bonds adjacent to a *cis*-substituted C=C double bond is an important factor in determining the stereochemistry of certain biomolecular species, such as glycerides incorporating *cis*-unsaturated fatty acids and natural products such as rubber. The 1-methylbutenyl group of vinbarbital contains this system. In Table 7, the *gauche* conformation of the terminal methyl group C(25) in vinbarbital I is shown to be similar to that observed for related groupings in several other crystal structure determinations. Evidence for the conformation of this system in simple molecules in the gaseous state appears to be sparse. Microwave spectral data for *cis*-2-butene have given a low barrier to the rotation between *gauche* and *trans* configurations (750 cal.mole^{-1}, Sarachmann, 1963; *cf.* 3000 cal.mole^{-1} for the barrier in ethane). Electron diffraction data for *cis*-2-butene were not interpreted in terms of a conformational equilibrium (Pauling & Brockway, 1937). While crystal structure determinations suggest that the *gauche* conformation is preferred about C–C bonds which are adjacent to a *cis*-ethylenic group, further evidence is needed before any firm conclusion can be drawn.

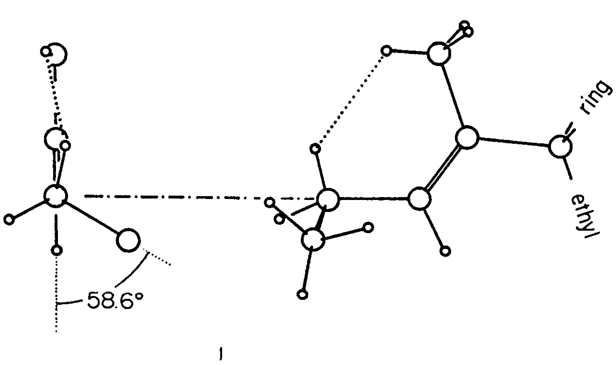

Fig. 5. Conformation about the C(24)–C(23) bond.

Table 7. *Torsion angles about* C(24)–C(23) *in vinbarbital and in analogous systems in other crystal structures**

Atoms in the several molecules being compared with vinbarbital are numbered according to the conventions adopted by the respective authors. The torsion angles are defined in the same way as shown in Fig. 5.

Compound	Atoms	Angle
Vinbarbital	C(24)–C(23)	58·6°
Geranylamine hydrochloride†	C(6)—C(5)	47
Harunganin‡	C(26)–C(16)	60
	C(31)–C(16)	51
Rubber§	C(4)—C(6)	48·7
	C(9)—C(1)	49·7
Oleic acid‖	C(8)—C(7)	48·6
	C(11)–C(12)	51·5

* This is not an exhaustive table

† Jeffrey (1945)

‡ Alden, *et al.* (1964)

§ Nyburg (1954)

‖ Abrahamsson & Ryderstedt-Nahringbauer (1962)

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NH_4LiSO_4: A Variant of the General Tridymite Structure

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The crystal structure of the pseudohexagonal form of NH_4LiSO_4 has been determined and refined to an R index of 5.0% with 364 counter-diffractometer measured reflections. The space group is $P2_1cn$ with $a = 5.280$ (2), $b = 9.140$ (7), $c = 8.786$ (6) Å and $Z = 4$. SO_4 and LiO_4 tetrahedra share corners to form a framework enclosing large cavities which contain the NH_4 groups. The tetrahedral framework differs from that of $KLiSO_4$ (a tridymite derivative structure) by inversion of two tetrahedra in each of the six-membered rings of tetrahedra. The inversion of these tetrahedra leads to the formation of chains of four-membered rings of tetrahedra and modification of the shape of the large cavity, relative to the $KLiSO_4$ structure.

Introduction

Ammonium lithium sulfate, NH_4LiSO_4, is reported (Wyrouboff, 1890), to be polymorphous. The form crystallizing from an aqueous solution above room temperature is orthohombic, pseudohexagonal, and based on its morphological cell and pseudosymmetry is evidently related to the hexagonal compounds $KLiSO_4$ and $RbLiSO_4$. The crystal structure of $KLiSO_4$ (Bradley, 1925) shows that it is a derivative structure of tri-