

The Crystal Structure of 1-Methyl-5,5-diethylbarbituric Acid (Metharbital)

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The crystal structure of 1-methyl-5,5-diethylbarbituric acid $C_9N_2O_3H_{14}$ (metharbital) has been determined from 1692 X-ray diffraction data measured on a computer controlled four-circle diffractometer using Cu $K\alpha$ radiation. The crystal data are as follows: space group $P2_1/c$ (monoclinic) $a = 6.798$ (2), $b = 11.397$ (3), $c = 13.190$ (3) Å, $\beta = 90.29$ (1)° with four molecules per unit cell. $D_m = 1.273$ g cm⁻³. The structure was solved by direct methods, the refinement converged at $R = 0.06$. Except for slight distortions, the trioxypyrimidine ring is planar and the aliphatic chains are perpendicular to it. Bond lengths and bond angles within the molecule agree with the corresponding ones in barbital, sodium barbital and sodium metharbital. Hydrogen bonds (N-H...O 2.842 Å) link the molecules to infinite ribbons parallel to the a axis. There is a distance 3.075 Å between atoms C(2)...O(2) of carbonyl groups in adjacent ribbons. These carbonyl groups are paired in antiparallel array.

Introduction

In a program of crystal structure determinations of drug-active barbiturates, the structure of 1-methyl-5,5-diethylbarbituric acid (metharbital) was investigated. Stereochemistry and packing of the molecules or ions involving hydrogen bonding, carbonyl-carbonyl dipole-dipole interactions and coordination of cations are of main interest in these structures.

In barbiturates with substituents at C(5) and without crystal water, the imino nitrogen atoms [N(1) and N(3)] in the pyrimidine ring donate or accept hydrogen bonds, the exocyclic oxygen atoms tend to accept hydrogen bonds or to show weak carbonyl-carbonyl interactions. By the methylation of N(1) in metharbital, only one hydrogen bond [N(3)-H...O] is *a priori* possible.

The intramolecular geometry of the presented structure is comparable with that of three related compounds: barbital (Craven, Vizzini & Rodrigues, 1969) containing two hydrogen bonds and intermolecular interactions between carbonyl groups; sodium barbital (Berking & Craven, 1971) with only one hydrogen bond but additional ionic interactions involving sodium ions; sodium metharbital (Berking, 1972) with a methylation of the pyrimidine ring at N(1) and ionic interactions involving sodium atoms but without any hydrogen bond.

Experimental

1-Methyl-5,5-diethylbarbituric acid ($C_9N_2O_3H_{14}$) was received from Abbott Laboratories, Chicago. By recrystallization at room temperature from an ethanol solution, transparent single crystals in the shape of needles with nearly square cross section were obtained. Systematic absence of reflections ($h0l$ with $l = 2n + 1$

and $0k0$ with $k = 2n + 1$) showed the space group to be $P2_1/c$. The crystal data at room temperature are:

$$\begin{array}{ll} a = 6.798 \text{ (2) \AA} & D_m = 1.273 \text{ g.cm}^{-3} \\ b = 11.397 \text{ (3)} & D_x = 1.289 \text{ g.cm}^{-3} \\ c = 13.190 \text{ (3)} & Z = 4 \\ \beta = 90.29 \text{ (1)^\circ} & F(000) = 424 \\ \mu = 8.2 \text{ cm}^{-1} \text{ (Cu } K\alpha) & \text{M.W. } 198.22 \end{array}$$

The crystal density was obtained by the flotation method using a mixture of n-hexane and chloroform. Lattice parameters and X-ray intensity data were measured with a four-circle automatic diffractometer (Picker FACS 1) using a graphite monochromator and Cu $K\alpha$ radiation. The crystal (dimensions 0.28, 0.32, 0.28 mm) was mounted with a parallel to the φ axis of the diffractometer. The intensities of 1692 reflections were measured by scanning in the θ - 2θ mode up to a limit of $2\theta = 130^\circ$. Of these, 174 reflections were classified to be unobserved by the criteria $I_{\text{net}} \leq 2\sigma(I)$, and their intensities were replaced by $0.5 \cdot \sigma(I)$. The standard deviation $\sigma(I)$ was defined by $\sigma(I) = [\sigma_{\text{peak}}^2 + \sigma_{\text{background}}^2 + (0.02 \cdot I_{\text{peak}})^2]^{1/2}$. Due to the low absorption coefficient, no absorption correction was applied.

During the data collection, the mechanism of the attenuators failed. Therefore a dead time correction was applied to high intensity reflections before the final refinement. The 10 strongest reflections (002, 011, 020, 023, 032, 033, 100, $11\bar{2}$, 111, $21\bar{1}$) having counting rates larger than 50,000 cps in the peak maximum were corrected by $I_c = I_o / (1 - tI_o)$. In this equation the corrected intensity I_c is given by the measured intensity I_o of the peak maximum and by the deadtime t of the scintillation counter. The data were collected in two shells (2θ limits 100, 130°) using the same standard reflections. Although there was no significant fluctuation observed in the intensities of the standards, the final refinement gave the best fit to the model using individual scale factors for both shells. There is no physical explanation for the significant difference of these scale factors (0.1115, 0.1339 respectively.)

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Structure determination and refinement

The phase problem was solved in a straightforward way using direct methods. The origin was fixed by the three phases:

No.	<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>	α
1	5	1	-7	4.13	0
11	4	8	-1	2.80	0
14	1	4	3	2.75	π

The number of interactions between these three reflections and other reflections with high |*E*| values was not large enough to determine all their phases by symbolic addition (Karle & Karle, 1966). Therefore, the phase of reflection 033 was assigned to be either 0 or π in two separate runs. Using the second set of these 4 starting phases, the tangent refinement of 184 reflections (|*E*| ≥ 1.6) converged at $R_E = \sum ||E_o| - |E_c|| / \sum |E_o| = 0.187$. In an independent determination by symbolic addition of 100 phases of reflections with $E \geq 1.97$, all phases agreed with the result of the tangent refinement.

An *E* map based on 184 phases showed all 14 non-hydrogen atoms as the highest peaks. A structure-factor calculation at this stage gave $R = \sum |\Delta F_{\text{meas}}| / \sum |F_{\text{meas}}| = 0.30$. X-ray atomic scattering factors for this structure determination were taken from *International Tables for X-ray Crystallography* (1962) for non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for hydrogen atoms. The refinement

of the atomic parameters was done by minimizing the function $\sum w(\Delta F_{\text{meas}})^2$ with the full-matrix least-squares program *ORFLS-PX* (Busing, Martin & Levy, 1962), modified for IBM 7090 by Shiono (1970).

Isotropic refinement of all 14 heavy atoms using unit weights reduced *R* to 0.21, refinement with anisotropic temperature factors converged at $R = 0.12$. At this stage, a difference electron density map clearly showed 11 hydrogen atoms; the three hydrogen atoms of the methyl group could not be located. Using a modified Cruickshank (1961) weighting scheme in a further refinement of the heavy atoms with fixed atom contributions of the 11 hydrogen atoms *R* was reduced to 0.084 (0.088) for the observed (all) reflections. Another difference electron density map showed three possible positions for H(11), H(12), H(13), although disorder can not be excluded.

Before the final refinement with 181 parameters [2 scale factors, heavy atoms anisotropic, 11 hydrogen atoms isotropic and the coordinates of H(11), H(12), H(13)] using an empirical weighting scheme $\sigma(F)^2 = 2.26 + 0.002(F)^2$, the 10 strongest reflections were corrected for dead-time losses and the unobserved reflections were weighted $w = 0$. The final *R* value is 0.057 (0.061) with $[\sum w(\Delta F)^2 / (m - n)]^{1/2} = 0.93$. The final atomic positional and thermal parameters are given in Table 1, the observed and calculated structure factors in Table 2. Fig. 1 shows the molecule with thermal parameters represented by 50% probability ellipsoids.

Table 1. Atomic parameters with *e.s.d.*'s given in parentheses and referring to the least significant figures in the parameter values

Positional parameters are given as fractions of the lattice translations. Thermal parameters are given according to the expression:

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0.2174 (2)	0.5577 (1)	0.3735 (1)	0.0055 (4)	0.0041 (1)	0.0032 (1)	-0.0007 (2)	-0.0006 (1)	-0.0004 (1)
C(1)	0.3147 (4)	0.6374 (2)	0.4453 (2)	0.0167 (6)	0.0060 (2)	0.0047 (2)	-0.0027 (3)	-0.0023 (2)	-0.0012 (1)
H(11)	0.319 (7)	0.605 (4)	0.511 (4)	10.0					
H(12)	0.459 (8)	0.639 (4)	0.427 (3)	10.0					
H(13)	0.272 (7)	0.706 (5)	0.440 (4)	10.0					
C(2)	0.0130 (3)	0.5517 (2)	0.3776 (1)	0.0068 (4)	0.0041 (2)	0.0031 (1)	0.0010 (2)	0.0007 (2)	0.0002 (1)
O(2)	-0.0816 (2)	0.6078 (1)	0.4376 (1)	0.0145 (4)	0.0063 (1)	0.0043 (1)	0.0033 (2)	0.0029 (2)	-0.0007 (1)
N(3)	-0.0761 (2)	0.4786 (2)	0.3090 (1)	0.0016 (4)	0.0076 (2)	0.0048 (1)	0.0005 (2)	0.0002 (2)	-0.0015 (1)
H(3)	-0.212 (5)	0.480 (2)	0.311 (2)	3.7 (5)					
C(4)	0.0122 (3)	0.4047 (2)	0.2419 (2)	0.0075 (5)	0.0093 (2)	0.0060 (2)	-0.0006 (3)	-0.0004 (2)	-0.0037 (2)
O(4)	-0.0867 (3)	0.3406 (3)	0.1891 (2)	0.0127 (5)	0.0209 (4)	0.0141 (2)	-0.0027 (3)	-0.0022 (2)	-0.0126 (3)
C(5)	0.2338 (3)	0.4071 (2)	0.2366 (2)	0.0073 (5)	0.0069 (2)	0.0044 (1)	0.0010 (2)	0.0009 (2)	-0.0020 (1)
C(6)	0.3290 (3)	0.4922 (2)	0.3095 (2)	0.0042 (4)	0.0053 (2)	0.0049 (1)	0.0003 (2)	0.0003 (2)	-0.0001 (1)
O(6)	0.5078 (2)	0.5024 (2)	0.3119 (2)	0.0022 (4)	0.0099 (2)	0.0102 (2)	-0.0005 (2)	0.0001 (2)	-0.0020 (1)
C(7)	0.2927 (4)	0.4400 (3)	0.1273 (2)	0.0191 (7)	0.0127 (3)	0.0046 (2)	0.0044 (4)	0.0016 (3)	-0.0010 (2)
H(71)	0.448 (5)	0.434 (3)	0.123 (2)	5.2 (7)					
H(72)	0.236 (5)	0.376 (3)	0.081 (3)	7.0 (9)					
C(8)	0.2250 (7)	0.5604 (4)	0.0924 (3)	0.0355 (12)	0.0152 (5)	0.0072 (3)	0.0056 (6)	-0.0008 (4)	0.0026 (3)
H(81)	0.080 (7)	0.552 (4)	0.086 (3)	8.1 (11)					
H(82)	0.284 (6)	0.623 (4)	0.136 (3)	7.2 (10)					
H(83)	0.258 (6)	0.577 (4)	0.015 (4)	8.8 (11)					
C(9)	0.3142 (4)	0.2827 (2)	0.2602 (2)	0.0140 (6)	0.0064 (2)	0.0068 (2)	0.0011 (3)	0.0014 (3)	-0.0025 (2)
H(91)	0.461 (5)	0.284 (3)	0.251 (2)	5.1 (7)					
H(92)	0.253 (4)	0.231 (3)	0.208 (2)	5.1 (7)					
C(10)	0.2691 (6)	0.2378 (3)	0.3656 (3)	0.0294 (9)	0.0072 (3)	0.0086 (2)	-0.0008 (4)	0.0033 (4)	0.0003 (2)
H(101)	0.119 (7)	0.239 (4)	0.379 (3)	8.0 (10)					
H(102)	0.317 (5)	0.159 (3)	0.373 (2)	6.1 (8)					
H(103)	0.308 (6)	0.300 (4)	0.422 (3)	8.7 (11)					

Table 2. Observed and calculated structure factors multiplied by 10

Unobserved reflections are indicated by asterisks. The reflections 002, 011, 020, 023, 032, 033, 100, 112, 111, 211 are corrected for dead-time losses of the scintillation counter and are marked by plus signs.

Table with multiple columns containing numerical data for structure factors, including observed and calculated values for various reflections. The table is organized into several sections, each with a header indicating the reflection indices (e.g., h k l, h k l, h k l).

Table 3. *Intra- and intermolecular distances (Å) and angles (°)*

Standard deviations for metharbital are estimated as follows:

C-N, C-O, C-C (ring)	0.002-0.003 Å	C-C-C (chain)	0.2-0.3°
C-C (aliphatic chain)	0.003-0.005	C-N-H	2
N-H, C-H	0.03-0.05	C-C-H, N-C-H	2-3
Angles at N(1), C(2), N(3), C(4), C(5), C(6)	0.2°	H-C-H	3-4

(i) Bond lengths and bond angles

	I*	II	III	IV
N(1)-C(2)	1.368	1.396	1.417	1.392
C(2)-N(3)	1.380	1.343	1.339	1.369
N(3)-C(4)	1.364	1.339	1.342	1.363
C(4)-C(5)	1.518	1.527	1.524	1.508
C(5)-C(6)	1.521	1.520	1.509	1.509
C(6)-N(1)	1.375	1.348	1.362	1.360
C(2)-O(2)	1.209	1.238	1.240	1.206
C(4)-O(4)	1.214	1.245	1.233	1.211
C(6)-O(6)	1.208	1.216	1.225	1.221
N(1)-C(1)	-	-	1.465	1.468
C(5)-C(7)	1.545	1.538	1.551	1.545
C(5)-C(9)	1.548	1.549	1.545	1.550
C(7)-C(8)	1.505	1.504	1.519	1.519
C(9)-C(10)	1.503	1.512	1.520	1.515
C(6)-N(1)-C(2)	126.7	125.5	122.6	123.8
N(1)-C(2)-N(3)	116.0	121.3	121.4	116.3
C(2)-N(3)-C(4)	126.4	119.2	121.2	127.6
N(3)-C(4)-C(5)	118.3	123.8	122.4	117.5
C(4)-C(5)-C(6)	114.1	112.4	113.3	114.0
C(5)-C(6)-N(1)	118.0	116.7	118.6	120.6

References: I, barbital I (Craven, Vizzini & Rodrigues, 1969; Craven & Gartland, 1970).

II, sodium barbital (Berking & Craven, 1971).

III, sodium metharbital (Berking, 1971).

IV, metharbital, present paper.

* The values of I are averages of three molecules.

(ii) Other bond lengths and bond angles of metharbital

C(1)-H(11) 0.94 Å	C(7)-H(72) 1.03 Å	C(9)-H(92) 0.99 Å	
C(1)-H(12) 1.02	C(8)-H(81) 0.99	C(10)-H(101) 1.04	
C(1)-H(13) 0.84	C(8)-H(82) 1.00	C(10)-H(102) 0.95	
N(3)-H(3) 0.92	C(8)-H(83) 1.06	C(10)-H(103) 1.06	
C(7)-H(71) 1.06	C(9)-H(91) 1.01	average C-H 0.99	
C(2)-N(1)-C(1)	116.9°	H(71)-C(7)-C(5)	107°
C(6)-N(1)-C(1)	119.3	H(72)-C(7)-C(5)	107
N(1)-C(2)-O(2)	122.3	H(71)-C(7)-C(8)	110
N(3)-C(2)-O(2)	121.4	H(72)-C(7)-C(8)	110
N(3)-C(4)-O(4)	120.1	H(71)-C(7)-H(72)	107
C(5)-C(4)-O(4)	122.4	H(81)-C(8)-C(7)	103
C(5)-C(6)-O(6)	120.1	H(82)-C(8)-C(7)	111
N(1)-C(6)-O(6)	119.3	H(83)-C(8)-C(7)	113
C(4)-C(5)-C(7)	108.1	H(81)-C(8)-H(82)	121
C(6)-C(5)-C(7)	109.0	H(81)-C(8)-H(83)	99
C(4)-C(5)-C(9)	109.0	H(82)-C(8)-H(83)	110
C(6)-C(5)-C(9)	108.1	H(91)-C(9)-C(5)	108
C(7)-C(5)-C(9)	108.4	H(92)-C(9)-C(5)	105
C(5)-C(7)-C(8)	115.0	H(91)-C(9)-C(10)	109
C(5)-C(9)-C(10)	114.8	H(92)-C(9)-C(10)	110
C(2)-N(3)-H(3)	114	H(91)-C(9)-H(92)	110
C(4)-N(3)-H(3)	118	H(101)-C(10)-C(9)	111
H(11)-C(1)-N(1)	112	H(102)-C(10)-C(9)	110
H(12)-C(1)-N(1)	107	H(103)-C(10)-C(9)	112
H(13)-C(1)-N(1)	111	H(101)-C(10)-H(102)	109
H(11)-C(1)-H(12)	101	H(101)-C(10)-H(103)	96
H(11)-C(1)-H(13)	117	H(102)-C(10)-H(103)	118
H(12)-C(1)-H(13)	108		

Table 3 (cont.)

(iii) Hydrogen bonding distances and angles

O(6)···H(3)	1.924 Å	N(3)-H(3)···O(6)	173°
O(6)···N(3)	2.842	N(3)···O(6)-C(6)	169
		H(3)···O(6)-C(6)	167

(iv) Other close intermolecular approaches

Symmetry code S: 1: x, y, z ; 2: $-x, -y, -z$; 3: $x, \frac{1}{2}-y, \frac{1}{2}+z$; 4: $-x, \frac{1}{2}+y, \frac{1}{2}-z$. TRL: translation in units of the cell in direction a, b, c . TRL 555 refers to the cell of the asymmetric unit listed in Table 1. Distances marked with an asterisk are less than the sum of the van der Waals radii (Pauling, 1960).

	S	TRL
N(1)···O(2)	3.263 Å	2 566
C(1)···H(103)*	3.18	2 666
C(2)···H(92)	2.95	4 555
C(2)···O(2)*	3.075	2 566
O(2)···H(103)	2.63	2 566
N(3)···H(11)	3.05	2 566
C(4)···O(6)	3.726	1 455
O(4)···H(13)	2.61	4 545
C(6)···H(3)	3.13	1 655
O(6)···H(11)	2.88	2 666
C(7)···H(102)	3.55	3 554
C(8)···H(101)*	3.12	4 555
C(9)···H(12)	3.34	4 645
C(10)···H(72)*	3.13	3 555

Discussion

(i) Molecular geometry

Intermolecular distances and angles are listed in Table 3 and are compared with corresponding values of major interest in three other structures: I, barbital (Craven, Vizzini & Rodrigues, 1969); II, sodium barbital (Berking & Craven, 1971); and III, sodium metharbital (Berking, 1971). In metharbital (IV) the bond length N(1)-C(2) is significantly longer (1.392 Å) than the three other C-N bonds, (1.369; 1.363; 1.360 Å respectively), which vary only within their e.s.d.'s. This effect was also observed in II and III, where in addition the C-N(3) bonds are shortened by the deprotonation at N(3). The C-O distances of the carbonyl groups vary in all four structures due to different effects. In IV C(6)-O(6) is slightly elongated (1.221 Å) compared with C(2)-O(2) and C(4)-O(4) (1.206, 1.211 Å respectively), which can be explained by the acceptance of the hydrogen bond, although this difference is only of the order of 4σ . In all four structures the bond lengths in the aliphatic chains differ in the same sense from the expected value of 1.526 Å (Lide, 1962); next to C(5) the bonds are elongated probably by steric hindrance, whereas the terminal bonds are shortened probably by high thermal motion. The methylation in III and IV decreases the angle at N(1) in the pyrimidine ring (122.6 and 123.8 vs. 126.7 and 125.5° in I and II). In IV this is compensated by an increase of the angles at N(3) and C(6). In II and III the deprotonation at N(3) changes additionally three angles involving the atom N(3).

The conformation of IV is shown in Fig. 1 and is very similar to those of I, II, and III. The deviations from an idealized geometry are given in Table 4(ii) in terms

of distances of atoms from least-squares planes and in Table 4(iii) and (iv) as torsion angles. The pyrimidine ring itself (plane 1) is planar within 0.022 Å, and the hydrocarbon chain C(5), C(7), C(8), C(9), C(10) forms a plane lying perpendicular to the ring. The carbonyl group C(2)–O(2) shows the largest atomic displacement from plane 1 (–0.021, –0.071 Å respectively) and participates in the carbonyl–carbonyl interaction described below. This displacement is in the sense that the intermolecular distance C=O...C is decreased. The deviation of atom N(3) from the plane 1 (+0.022 Å) may be explained by its involvement in hydrogen bonding. Both displacements increase the torsion angles around the bonding C(2)–N(3) up to 5.02°.

Table 4. *Least-squares planes and torsion angles*

Plane 1 defined by six atoms of the pyrimidine ring.
Plane 2 defined by plane 1 and O(2), O(4), O(6), C(1).
Plane 3 defined by atoms of the chain C(5), C(7), C(8), C(9), C(10).

(i) Equations of the planes with respect to the crystallographic axes.

$$\text{Plane 1: } -0.045x + 0.726y - 0.686z = 1.161$$

$$\text{Plane 2: } -0.055x + 0.730y - 0.681z = 1.185$$

$$\text{Plane 3: } 0.851x + 0.400y + 0.337z = 4.262$$

(ii) Distances (Å) of atoms from the planes. The italicised values belong to atoms *not* forming the planes.

	Plane 1	Plane 2	Plane 3
N(1)	0.005	0.015	<i>1.196</i>
C(2)	–0.021	0.005	<i>0.004</i>
N(3)	0.022	0.046	<i>–1.149</i>
C(4)	–0.007	0.002	<i>–1.273</i>
C(5)	–0.007	–0.014	<i>–0.004</i>
C(6)	0.008	0.003	<i>1.258</i>
C(7)	<i>1.237</i>	<i>1.220</i>	0.000
C(8)	<i>2.569</i>	<i>2.560</i>	0.002
C(9)	<i>–1.274</i>	<i>–1.291</i>	–0.001
C(10)	<i>–2.582</i>	<i>–2.594</i>	0.003
O(2)	<i>–0.071</i>	<i>–0.032</i>	<i>–0.020</i>
O(4)	<i>–0.030</i>	<i>–0.020</i>	<i>–2.371</i>
O(6)	<i>0.017</i>	<i>–0.001</i>	<i>2.349</i>
C(1)	<i>–0.016</i>	<i>–0.004</i>	
H(3)	<i>0.057</i>	<i>0.091</i>	

(iii) Torsion angles within the pyrimidine ring.

C(6)–N(1)–C(2)–N(3)	3.05°
N(1)–C(2)–N(3)–C(4)	5.02
C(2)–N(3)–C(4)–C(5)	–3.89
N(3)–C(4)–C(5)–C(6)	0.77
C(4)–C(5)–C(6)–N(1)	–0.77
C(5)–C(6)–N(1)–C(2)	–0.39

(iv) Torsion angles including atoms of the chain and the methyl group.

C(9)–C(5)–C(7)–C(8)	179.8°	O(2)–C(2)–N(1)–C(1)	–0.8°
C(7)–C(5)–C(9)–C(10)	179.7	O(6)–C(6)–N(1)–C(1)	–1.2
N(3)–C(4)–C(5)–C(7)	–120.7	N(3)–C(2)–N(1)–C(1)	178.9
N(3)–C(4)–C(5)–C(9)	121.7	C(5)–C(6)–N(1)–C(1)	–178.4
N(1)–C(6)–C(5)–C(7)	121.7	C(4)–C(5)–C(7)–C(8)	62.2
N(1)–C(6)–C(5)–C(9)	–120.6	C(4)–C(5)–C(9)–C(10)	–62.9
		C(6)–C(5)–C(7)–C(8)	–62.3
		C(6)–C(5)–C(9)–C(10)	61.6

(ii) *Molecular packing*

Fig. 2 shows a projection of the crystal structure of metharbital down the *b* axis. There is one intermolec-

ular hydrogen bond linking the molecules to infinite ribbons parallel to the *a* axis. The geometry of this [Table 3(iii)] agrees with that in other classes of crystal structures. In addition there is one close intermolecular approach of interest between two symmetry-related carbonyl groups forming a 'cyclic' dipole–dipole interaction (Prout & Wallwork, 1966) with two identical C...O distances of 3.075 Å, which is about the sum of the van der Waals radii of 3.1 Å (Pauling, 1960). In

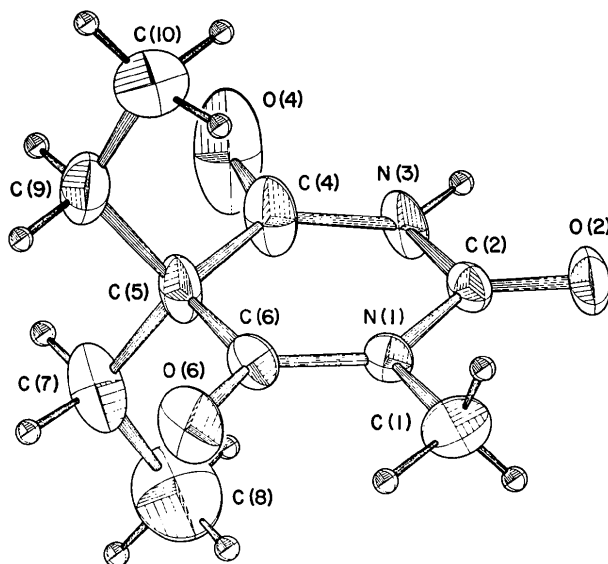


Fig. 1. The molecule of 1-methyl-5,5-diethylbarbituric acid. Except for hydrogen atoms, thermal parameters are represented by 50% probability ellipsoids (Johnson, 1965). Nomenclature according to the chemical name.

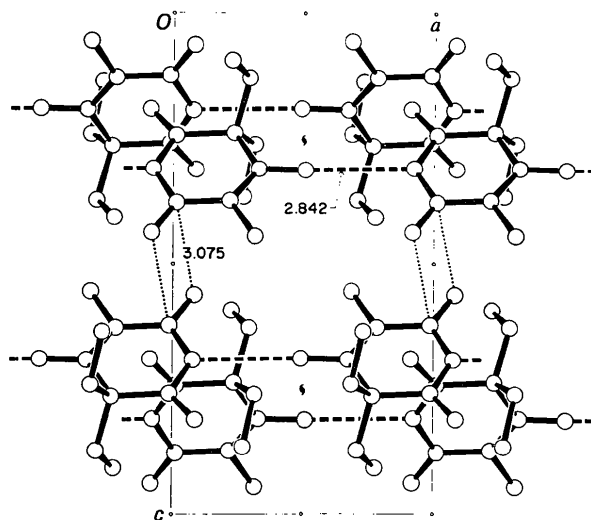
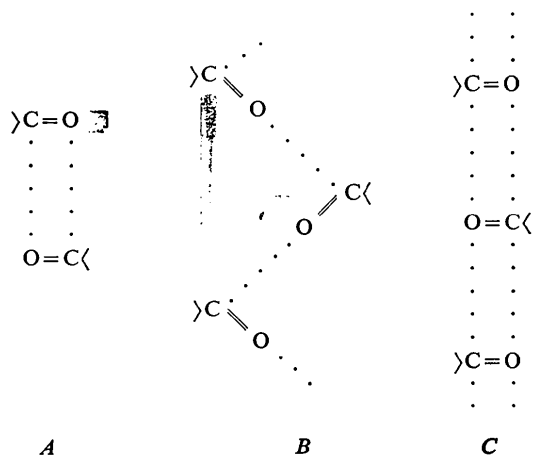


Fig. 2. The crystal structure of metharbital as a projection down the *b* axis. Symbols of the twofold screw axis in 0, 0.25C; 0, 0.75C; A, 0.25C and A, 0.75C are not shown.

this arrangement (type *A*) the carbonyl groups are anti-parallel with an angle $O(2) \cdots C(2)=O(2)$ of 82.6° ; it is thus different from the two infinite types commonly found: type *B* (e.g. Gatehouse & Craven, 1971) and type *C* (e.g. Craven & Cusatis, 1969).



Although this interaction is weak it seems to have some importance for the three dimensional packing of the molecules in the crystal structure. In metharbutal, the two other carbonyl groups are not involved in such intermolecular close approaches.

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The Crystal Structure of 1,2,3,3-Tetrachloro-4,5-dimethylspiro[2.3]hexa-1,4-diene at -65°C

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Crystals of 1,2,3,3-tetrachloro-4,5-dimethylspiro[2.3]hexa-1,4-diene ($\text{C}_8\text{H}_6\text{Cl}_4$) are triclinic, space group $P\bar{1}$; $a = 8.189$ (4), $b = 8.763$ (5), $c = 8.334$ (3) Å, $\alpha = 91.34$ (2), $\beta = 110.09$ (2), $\gamma = 106.61$ (2)°, $Z = 2$, $D_m = 1.48$ g cm $^{-3}$, $D_x = 1.52$ g cm $^{-3}$. The integrated intensities of 1979 independent reflexions were measured with an automated diffractometer, of which 1607 were used in the refinement. The data were collected at -65°C using a refrigerated goniometer. The structure was solved by direct methods and refined by full-matrix least-squares analysis to a final least-square residual of 0.072. The two rings of the molecule are mutually orthogonal and bond lengths are slightly shorter than the values reported for related cyclopropenes and cyclobutenes.

Introduction

Although the structures of some compounds containing carbon rings in a spiro arrangement have been

studied by crystallographic techniques, all of these have contained relatively large numbers of carbon atoms in the rings. The smallest spiro compound whose structure has been reported to date is spiro[4.4]nonane-1,6-