

The Crystal Structure of Calcium Barbital Trihydrate

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The crystal structure of calcium 5,5-diethylbarbiturate (calcium barbital) trihydrate, $\text{Ca}(\text{C}_8\text{N}_2\text{O}_3\text{H}_{11})_2 \cdot 3\text{H}_2\text{O}$, has been determined from 8237 X-ray diffraction data measured on an automatic diffractometer using $\text{Cu } K\alpha$ radiation. Crystal data are: space group $P\bar{1}$, $a = 16.999$ (4), $b = 9.122$ (2), $c = 16.780$ (4) Å, $\alpha = 77.29$ (1), $\beta = 89.36$ (1), $\gamma = 74.86$ (1)°, $Z = 4$, $D_x = 1.250$ g.cm⁻³. Final R is 0.046. The structure shows some pseudosymmetrical features; 49% of the scattering density lies in a sheet close to $y = \frac{1}{2}$. Deprotonation of the four crystallographically independent pyrimidine rings causes changes in bond lengths and internal bond angles. The greater part of the formal negative charge seems to be equally distributed between the two oxygen atoms adjacent to the deprotonated nitrogen atom. There are conformational differences in the barbiturate rings: one is flat and three are puckered with the quaternary carbon, C(5), out of plane. Deprotonated nitrogen atoms are involved either in hydrogen bonds or in coordination with the calcium ions. Centrosymmetrically related barbital ions form doubly hydrogen-bonded ($\text{NH} \cdots \text{O}=\text{C}$) dimers which are isolated with respect to having no hydrogen bonds with other barbital ions. Dimers are linked by hydrogen bonds *via* water molecules and calcium ions to form ribbons along **b** and sheets perpendicular to **b***. The two calcium ions are sevenfold coordinated by six oxygen and one nitrogen atom at the corners of irregular pentagonal bipyramids. These coordination polyhedra are not interconnected, but they interact with the anions in the ribbons and sheets establishing a three-dimensional packing.

Introduction

This work is part of a program to study the tautomeric form, stereochemistry, and intermolecular interactions in barbituric acids and their salts. So far, a series of some 40 crystal structures involving barbiturates has been determined in which the main interest is the pharmacological activity that some barbiturates possess *in vivo*: they block the excitation of membrane nerves. There is controversy about whether the free acids (Blaustein, 1968) or the anionic forms (Sharpless, 1968) of barbiturates are more potent, and whether barbiturates interfere with the binding of calcium to phospholipids (Kripp, Bianchi & Suárez-Kürtz, 1969). Thus, the interactions of barbiturate molecules and anions with calcium cations and water molecules are of great interest. The crystal structure of calcium 5,5-diethylbarbiturate (calcium barbital) trihydrate, $\text{Ca}(\text{C}_8\text{N}_2\text{O}_3\text{H}_{11})_2 \cdot 3\text{H}_2\text{O}$, was determined to gain information about these interactions in the crystalline state.

In all salts of barbital, proton loss is necessarily from an imine nitrogen atom. In sodium barbital (Berkling & Craven, 1971), the nondeprotonated nitrogen atom is involved in an $\text{NH} \cdots \text{O}=\text{C}$ hydrogen bond through which infinite chains of barbital anions are formed, whereas the deprotonated nitrogen atom is involved neither in hydrogen bonding nor in coordination polyhedra. In calcium barbital trihydrate, the water molecules and the coordination need of the calcium cations would be expected to break the predominating $\text{NH} \cdots \text{O}=\text{C}$ hydrogen-bonding scheme found in sodium barbital and many other barbiturates.

Experimental and crystallographic data

Calcium barbital was prepared from an aqueous solution of sodium barbital and calcium chloride. A mixture of crystals was obtained in which some crystals were single crystals of barbital II (Craven, Vizzini & Rodrigues, 1969), identified by Weissenberg photographs, and transparent single crystals of calcium barbital trihydrate.

The crystal data of calcium barbital trihydrate are: Space group $P\bar{1}$ (proved by the final crystal structure) M.W. 460.6.

$$\begin{aligned} a &= 16.999 \text{ (4)}, & b &= 9.122 \text{ (2)}, & c &= 16.780 \text{ (4)} \text{ \AA}. \\ \alpha &= 77.29 \text{ (1)}, & \beta &= 89.36 \text{ (1)}, & \gamma &= 74.86 \text{ (1)}^\circ. \\ V &= 2447.6 \text{ \AA}^3, & Z &= 4. \\ D_x &= 1.250 \text{ g.cm}^{-3}. \end{aligned}$$

With space group $P\bar{1}$ and $Z = 4$, the asymmetric unit contains two calcium cations, four barbital anions, and six water molecules. Weissenberg photographs showed a high degree of pseudosymmetry; intensities $I(hkl)$ were similar to $I(h\bar{k}l)$ and reflections $h00$ were strong for $h = 2n$, $00l$ strong for $l = 2n$, $hk0$ strong for $h = 2n$, revealing pseudosystematic variations. There was no indication that the crystal structure belongs to a higher symmetry system.

Lattice parameters and X-ray intensities were measured on a Picker FACS I automatic diffractometer using Ni-filtered $\text{Cu } K\alpha$ radiation and θ - 2θ scanning mode. A crystal of dimensions $0.3 \times 0.3 \times 0.3$ mm was mounted with **b** along the diffractometer ϕ axis. Intensities for 8237 independent reflections were measured

Table 1. |F_o| and F_c multiplied by 10

Unobserved reflections are indicated by *; reflections affected by extinction and not included in the final refinement are indicated by +.

Table with 10 columns of numerical data representing |F_o| and F_c values for various reflections. The table is organized into rows corresponding to different reflection indices, with some values marked with asterisks or plus signs to indicate specific characteristics.

Table 1 (cont.)

Table of crystallographic data with multiple columns containing numerical values and symbols, representing diffraction pattern parameters.

B. BERKING

Table 1 (cont.)

10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

Table 1 (cont.)

Table of numerical data with multiple columns and rows, likely representing reflection indices and intensities.

up to 2θ=130°. Of these, 1434 reflections were considered to be 'unobserved' because their net intensities did not exceed twice the standard deviation of the counting statistics. Absorption corrections were not applied.

Structure determination and refinement

Calcium atoms were located from the (E^2 - 1) Patterson function. Structure-factor calculations for this partial structure (R=0.69), using 230 reflections with |E| ≥ 2.2, gave the first set of phases. A tangent refinement, including these 230 phases and an additional 233 reflections with |E| ≥ 1.9, converged easily with

R_E = (sum of |E_o| - |E_c|) / sum of |E_o| = 0.138. An E map based on this

total of 463 phased reflections yielded 26 more atoms (R=0.56). All 60 nonhydrogen atoms were located after several steps of conventional structure-factor and electron-density calculations (R=0.34). The structure was refined using the block-diagonal and the full-matrix least-squares programs of the X-ray 63 system (Stewart & High, 1963) and also the program versions of Shiono (1966). X-ray atomic scattering factors were taken from International Tables for X-ray Crystallography (1962) for heavy atoms and from Stewart, Davidson & Simpson (1965) for hydrogen atoms. The calcium ion was treated as an atom with Z=20 without

anomalous dispersion corrections. The function minimized was sum w delta F^2 using the weighting scheme 1/w = sigma^2(F) = 1.5 + 0.008 F^2. All mentioned R values are defined as R = sum |delta F_meas| / sum |F_meas|.

The block-diagonal least-squares refinement, using isotropic thermal parameters, converged after four cycles with R=0.24. However, with full-matrix methods, one cycle of refining three blocks of 20 atoms each (atoms related by pseudosymmetry were within the same block) reduced R to 0.17. Using anisotropic thermal parameters, seven cycles of block-diagonal refinement reduced R to 0.105, and one more cycle of full-matrix refinement with three 20-atom blocks gave R=0.068. At this stage, most hydrogen atoms could be located from a difference map, but five that are located close to the plane y = 1/2 (where 49% of the scattering density is positioned) and the positions of which should be predictable, did not appear. However, all missing hydrogen atoms were found after nine reflections were removed from the data set. These reflections showed difference between observed and calculated structure amplitudes that might be due to extinction effects.

To justify this procedure, the influence of the extinction-affected reflections on the significance of the difference Fourier peaks was calculated for one case. If only the three reflections (010, 020 and 030) are removed, the electron density near the plane y = 1/2 increases about 0.1 e. A^-3. This corresponds to an increase of 20 to 25% in peak height for the hydrogen atoms.

Table 2. Final atomic parameters with e.s.d.'s

Positional parameters are given as fractions of lattice translations. Thermal parameters are given according to the expression:
 $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

E.s.d.'s given in parentheses refer to the least significant figures in the parameter values. In all nonhydrogen-atom names with two indices occurring in the text, the first denotes the barbitol ion, the second denotes the atom within the ion.

	x	y	z	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Anion 1								
N(1)	0-1110 (1)	-0-0104 (2)	-0-0196 (2)	0-0023 (1)	0-0040 (2)	-0-0014 (1)	0-0002 (1)	-0-0022 (1)
H(1)	0-072 (2)	-0-059 (4)	-0-021 (2)	3-5 (0-7)	0-0076 (3)	-0-0009 (2)	0-0001 (1)	-0-0016 (1)
C(2)	0-0832 (2)	0-1367 (3)	-0-0006 (2)	0-0025 (1)	0-0031 (1)	-0-0009 (2)	0-0007 (1)	-0-0029 (1)
O(2)	0-0116 (1)	0-1749 (2)	0-0171 (1)	0-0022 (1)	0-0050 (1)	-0-0012 (1)	0-0003 (1)	-0-0021 (1)
N(3)	0-1327 (1)	0-2315 (2)	-0-0057 (2)	0-0025 (1)	0-0041 (1)	-0-0010 (1)	0-0000 (1)	-0-0015 (2)
C(4)	0-2109 (2)	0-1821 (3)	-0-0219 (2)	0-0026 (1)	0-0037 (1)	-0-0011 (2)	0-0005 (1)	-0-0028 (1)
O(4)	0-2569 (1)	0-2700 (2)	-0-0284 (2)	0-0025 (1)	0-0063 (1)	-0-0021 (1)	0-0002 (1)	-0-0026 (2)
C(5)	0-2506 (2)	0-0138 (3)	-0-0299 (2)	0-0023 (1)	0-0046 (1)	-0-0011 (2)	0-0001 (1)	-0-0013 (2)
C(6)	0-1877 (2)	-0-0727 (3)	-0-0375 (2)	0-0024 (1)	0-0033 (1)	-0-0009 (2)	0-0001 (1)	-0-0033 (1)
O(6)	0-2066 (1)	-0-1990 (2)	-0-0571 (1)	0-0032 (1)	0-0050 (1)	-0-0014 (1)	0-0007 (1)	-0-0020 (3)
C(7)	0-3041 (2)	-0-0736 (4)	0-0485 (3)	0-0039 (1)	0-0068 (2)	-0-0003 (2)	-0-0020 (1)	
H(71)	0-348 (3)	-0-021 (6)	0-055 (3)	7-0 (1-0)				
H(72)	0-334 (2)	-0-194 (6)	0-040 (3)	6-4 (1-0)				
C(8)	0-2574 (3)	-0-0908 (6)	0-1271 (3)	0-0084 (3)	0-0049 (2)	0-0003 (4)	-0-0022 (2)	-0-0022 (3)
H(81)	0-288 (3)	-0-150 (6)	0-173 (3)	8-8 (1-3)				
H(82)	0-222 (3)	0-019 (6)	0-136 (3)	7-0 (1-1)				
H(83)	0-209 (3)	-0-146 (6)	0-121 (3)	8-3 (1-2)				
C(9)	0-3036 (2)	0-0156 (4)	-0-1055 (3)	0-0031 (1)	0-0073 (2)	-0-0020 (2)	0-0020 (1)	-0-0042 (3)
H(91)	0-350 (3)	0-075 (5)	-0-099 (3)	6-5 (1-0)				
H(92)	0-338 (3)	-0-095 (5)	-0-106 (3)	6-6 (1-0)				
C(10)	0-2573 (3)	-0-0983 (6)	-0-1864 (3)	0-0070 (2)	0-0058 (2)	-0-0034 (4)	0-0025 (2)	-0-0037 (4)
H(101)	0-222 (3)	0-206 (6)	-0-187 (3)	8-4 (1-2)				
H(102)	0-219 (3)	0-041 (6)	-0-201 (3)	6-0 (1-0)				
H(103)	0-297 (3)	0-074 (6)	-0-228 (3)	8-0 (1-2)				

Table 2 (cont.)

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Anion 2									
N(1)	0.5054 (1)	0.4996 (3)	0.1088 (1)	0.0016 (1)	0.0231 (6)	0.0022 (1)	-0.0023 (2)	0.0003 (1)	-0.0028 (2)
H(1)	0.469 (2)	0.513 (5)	0.068 (2)	3.7 (0.8)					
C(2)	0.5864 (2)	0.4821 (4)	0.0911 (2)	0.0016 (1)	0.0155 (6)	0.0023 (1)	-0.0018 (2)	0.0002 (1)	-0.0019 (2)
O(2)	0.6057 (1)	0.4788 (3)	0.0194 (1)	0.0017 (1)	0.0218 (5)	0.0020 (1)	-0.0020 (1)	0.0004 (1)	-0.0028 (1)
N(3)	0.6435 (1)	0.4696 (3)	0.1470 (1)	0.0018 (1)	0.0192 (5)	0.0024 (1)	-0.0023 (2)	0.0004 (1)	-0.0028 (2)
C(4)	0.6243 (2)	0.4732 (5)	0.2246 (2)	0.0022 (1)	0.0239 (8)	0.0025 (1)	-0.0028 (2)	0.0003 (1)	-0.0034 (2)
O(4)	0.6786 (1)	0.4605 (4)	0.2763 (2)	0.0025 (1)	0.0435 (9)	0.0029 (1)	-0.0047 (2)	0.0001 (1)	-0.0064 (2)
C(5)	0.5376 (2)	0.4898 (5)	0.2524 (2)	0.0023 (1)	0.0238 (8)	0.0020 (1)	-0.0032 (2)	0.0005 (1)	-0.0027 (2)
C(6)	0.4769 (2)	0.5052 (5)	0.1840 (2)	0.0020 (1)	0.0220 (7)	0.0024 (1)	-0.0024 (2)	0.0003 (1)	-0.0026 (2)
O(6)	0.4043 (1)	0.5210 (4)	0.1946 (1)	0.0019 (1)	0.0363 (8)	0.0028 (1)	-0.0037 (2)	0.0008 (1)	-0.0045 (2)
C(7)	0.5115 (2)	0.6378 (7)	0.2884 (3)	0.0035 (2)	0.0320 (5)	0.0047 (2)	-0.0029 (3)	0.0010 (1)	-0.0077 (4)
H(71)	0.555 (2)	0.621 (5)	0.334 (2)	4.8 (0.8)					
H(72)	0.452 (2)	0.656 (5)	0.301 (2)	5.5 (0.9)					
C(8)	0.5107 (5)	0.7876 (8)	0.2282 (5)	0.0076 (3)	0.0263 (11)	0.0112 (5)	-0.0041 (5)	0.0008 (3)	-0.0075 (6)
H(81)	0.569 (3)	0.777 (6)	0.216 (3)	8.6 (1.2)					
H(82)	0.470 (3)	0.796 (7)	0.179 (7)	8.5 (1.3)					
H(83)	0.496 (4)	0.899 (7)	0.239 (4)	10.6 (1.4)					
C(9)	0.5359 (2)	0.3441 (7)	0.3195 (2)	0.0035 (1)	0.0304 (9)	0.0029 (1)	-0.0038 (3)	0.0000 (1)	-0.0007 (3)
H(91)	0.479 (2)	0.356 (5)	0.336 (2)	4.8 (0.8)					
H(92)	0.577 (2)	0.341 (5)	0.359 (2)	5.2 (0.8)					
C(10)	0.5579 (5)	0.1966 (8)	0.2914 (4)	0.0097 (4)	0.0253 (11)	0.0066 (3)	-0.0048 (5)	0.0002 (3)	0.0003 (5)
H(101)	0.612 (3)	0.169 (6)	0.265 (3)	8.1 (1.2)					
H(102)	0.523 (3)	0.206 (6)	0.249 (3)	8.2 (1.2)					
H(103)	0.563 (4)	0.108 (7)	0.328 (4)	9.9 (1.3)					
Anion 3									
N(1)	0.0005 (1)	0.5333 (4)	0.3884 (1)	0.0019 (1)	0.0254 (7)	0.0020 (1)	-0.0035 (2)	0.0004 (1)	-0.0021 (2)
H(1)	-0.032 (2)	0.525 (5)	0.432 (2)	4.8 (0.8)					
C(2)	0.0800 (2)	0.5254 (4)	0.4087 (2)	0.0018 (1)	0.0156 (6)	0.0023 (1)	-0.0020 (2)	0.0002 (1)	-0.0018 (2)
O(2)	0.1012 (1)	0.5051 (3)	0.4823 (1)	0.0020 (1)	0.0241 (5)	0.0018 (1)	-0.0028 (2)	0.0002 (1)	-0.0020 (2)
N(3)	0.1356 (1)	0.5361 (4)	0.3532 (1)	0.0017 (1)	0.0191 (5)	0.0020 (1)	-0.0023 (2)	0.0002 (1)	-0.0017 (2)
C(4)	0.1142 (2)	0.5606 (6)	0.2733 (2)	0.0026 (1)	0.0257 (8)	0.0023 (1)	-0.0038 (2)	0.0004 (1)	-0.0022 (2)
O(4)	0.1672 (1)	0.5640 (6)	0.2223 (1)	0.0028 (1)	0.0520 (11)	0.0023 (1)	-0.0066 (3)	0.0011 (1)	-0.0043 (2)
C(5)	0.0264 (2)	0.5954 (5)	0.2428 (2)	0.0024 (1)	0.0237 (8)	0.0019 (1)	-0.0027 (2)	0.0002 (1)	-0.0013 (2)
C(6)	-0.0299 (2)	0.5599 (5)	0.3109 (2)	0.0020 (1)	0.0213 (7)	0.0024 (1)	-0.0022 (2)	0.0001 (1)	-0.0021 (2)
O(6)	-0.1003 (1)	0.5602 (4)	0.2970 (1)	0.0023 (1)	0.0331 (7)	0.0027 (1)	-0.0046 (2)	0.0001 (1)	-0.0028 (2)
C(7)	0.0190 (2)	0.5038 (6)	0.1777 (2)	0.0031 (1)	0.0305 (9)	0.0024 (1)	-0.0029 (3)	-0.0001 (1)	-0.0034 (3)
H(71)	-0.039 (2)	0.544 (5)	0.154 (2)	4.2 (0.7)					
H(72)	0.057 (2)	0.532 (5)	0.133 (2)	4.7 (0.8)					
C(8)	0.0414 (4)	0.3286 (8)	0.2080 (4)	0.0065 (3)	0.0338 (13)	0.058 (2)	-0.0007 (5)	-0.0012 (2)	-0.0073 (5)
H(81)	0.095 (3)	0.301 (6)	0.221 (3)	7.6 (1.2)					
H(82)	0.030 (3)	0.287 (7)	0.165 (4)	9.3 (1.3)					
H(83)	0.025 (3)	0.290 (7)	0.258 (3)	7.9 (1.2)					
C(9)	-0.0038 (3)	0.7708 (7)	0.2031 (3)	0.0049 (2)	0.0238 (7)	0.0043 (2)	-0.0039 (4)	-0.0006 (1)	0.0010 (3)
H(91)	-0.061 (2)	0.797 (5)	0.183 (2)	4.7 (0.8)					
H(92)	0.031 (3)	0.785 (6)	0.156 (3)	7.0 (1.1)					
C(10)	0.0022 (5)	0.8792 (8)	0.2589 (6)	0.0105 (5)	0.0226 (11)	0.00113 (6)	-0.0034 (6)	-0.0019 (4)	-0.0016 (7)
H(101)	0.057 (3)	0.879 (7)	0.277 (4)	9.4 (1.3)					
H(102)	-0.022 (3)	0.964 (6)	0.234 (3)	7.9 (1.1)					
H(103)	-0.051 (4)	0.857 (8)	0.305 (4)	13.6 (1.6)					

Table 2 (cont.)

	x	y	z	β_{11} or β_B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Anion 4									
N(1)	0-3881 (2)	0-0239 (3)	0-4809 (2)	0-0026 (1)	0-0086 (4)	0-0051 (1)	-0-0015 (1)	-0-0004 (1)	-0-0024 (2)
H(1)	0-424 (2)	0-072 (5)	0-494 (2)	3-7 (0-7)					
O(2)	0-4213 (2)	-0-1314 (4)	0-4752 (2)	0-0026 (1)	0-0078 (4)	0-0042 (1)	-0-0008 (2)	-0-0004 (1)	-0-0016 (2)
C(2)	0-4964 (1)	-0-1797 (3)	0-4831 (2)	0-0023 (1)	0-0094 (4)	0-0065 (1)	-0-0008 (1)	-0-0004 (1)	-0-0026 (2)
N(3)	0-3733 (2)	-0-2207 (3)	0-4632 (2)	0-0027 (1)	0-0085 (4)	0-0056 (1)	-0-0010 (1)	-0-0005 (1)	-0-0023 (2)
C(4)	0-2929 (2)	-0-1595 (4)	0-4523 (2)	0-0030 (1)	0-0084 (5)	0-0055 (2)	-0-0012 (2)	-0-0007 (1)	-0-0022 (2)
O(4)	0-2468 (1)	-0-2421 (3)	0-4426 (2)	0-0029 (1)	0-0086 (3)	0-0087 (2)	-0-0014 (1)	-0-0012 (1)	-0-0030 (2)
C(5)	0-2514 (2)	0-0111 (4)	0-4477 (3)	0-0028 (1)	0-0086 (5)	0-0065 (2)	-0-0007 (2)	-0-0012 (1)	-0-0027 (2)
C(6)	0-3083 (2)	0-0976 (4)	0-4702 (2)	0-0030 (1)	0-0074 (4)	0-0041 (1)	-0-0008 (2)	-0-0003 (1)	-0-0015 (2)
O(6)	0-2836 (1)	0-2322 (2)	0-4775 (2)	0-0033 (1)	0-0082 (3)	0-0063 (1)	-0-0009 (1)	-0-0005 (1)	-0-0030 (2)
C(7)	0-1795 (3)	0-0242 (6)	0-5074 (5)	0-0031 (2)	0-0167 (8)	0-0165 (6)	-0-0019 (3)	0-0018 (2)	-0-0095 (6)
H(71)	0-140 (3)	-0-016 (6)	0-481 (3)	8-0 (1-2)					
H(72)	0-159 (3)	0-124 (6)	0-511 (3)	7-5 (1-1)					
C(8)	0-2072 (6)	-0-0501 (9)	0-5958 (5)	0-0126 (6)	0-0328 (14)	0-0106 (5)	-0-0083 (8)	0-0068 (5)	-0-0054 (7)
H(81)	0-244 (4)	0-003 (7)	0-621 (4)	9-9 (1-4)					
H(82)	0-214 (4)	-0-164 (8)	0-611 (4)	13-1 (1-5)					
H(83)	0-165 (4)	-0-015 (7)	0-642 (4)	10-2 (1-4)					
C(9)	0-2206 (4)	0-0902 (6)	0-3583 (4)	0-0085 (3)	0-0123 (7)	0-0089 (4)	0-0004 (4)	-0-0059 (3)	-0-0026 (4)
H(91)	0-181 (3)	0-030 (6)	0-350 (3)	7-0 (1-0)					
H(92)	0-185 (3)	0-196 (6)	0-354 (3)	6-5 (1-0)					
C(10)	0-2850 (6)	0-0940 (9)	0-2993 (4)	0-0167 (7)	0-0271 (13)	0-0050 (3)	-0-0005 (8)	-0-0033 (4)	-0-0031 (5)
H(101)	0-335 (3)	0-076 (6)	0-308 (3)	8-3 (1-2)					
H(102)	0-304 (4)	-0-023 (7)	0-291 (4)	10-4 (1-4)					
H(103)	0-264 (4)	0-161 (7)	0-248 (4)	10-0 (1-4)					
Cations and water molecules									
Ca(1)	0-2523 (1)	0-4987 (1)	0-4564 (1)	0-0015 (1)	0-0076 (1)	0-0023 (1)	-0-0010 (1)	0-0000 (1)	-0-0016 (1)
Ca(2)	0-2424 (1)	0-5357 (1)	-	0-0016 (1)	0-0070 (1)	0-0024 (1)	-0-0012 (1)	0-0005 (1)	-0-0018 (1)
O(1)	0-3894 (1)	0-4639 (2)	0-4964 (2)	0-0020 (1)	0-0083 (3)	0-0065 (1)	-0-0010 (1)	-0-0007 (1)	-0-0018 (2)
H(11)	0-430 (2)	0-392 (6)	0-501 (3)	5-8 (0-9)					
H(12)	0-399 (2)	0-536 (5)	0-490 (2)	4-9 (0-8)					
O(2)	-0-1081 (1)	0-4536 (2)	0-0131 (1)	0-0020 (1)	0-0084 (3)	0-0052 (1)	-0-0013 (1)	0-0012 (1)	-0-0028 (1)
H(21)	-0-066 (2)	0-391 (5)	0-015 (2)	4-3 (0-7)					
H(22)	-0-102 (3)	0-529 (6)	0-007 (3)	5-8 (1-0)					
O(3)	0-2636 (1)	0-5106 (4)	0-0934 (1)	0-0025 (1)	0-0275 (6)	0-0026 (1)	-0-0032 (2)	0-0007 (1)	-0-0034 (2)
H(31)	0-225 (2)	0-527 (5)	0-122 (2)	4-9 (0-8)					
H(32)	0-309 (2)	0-502 (5)	0-113 (2)	5-2 (0-9)					
O(4)	0-2362 (1)	0-4743 (5)	0-5989 (1)	0-0033 (1)	0-0379 (8)	0-0027 (1)	-0-0063 (2)	0-0006 (1)	-0-0052 (2)
H(41)	0-265 (2)	0-494 (5)	0-623 (2)	5-1 (0-8)					
H(42)	0-194 (3)	0-467 (6)	0-625 (3)	7-2 (1-1)					
O(5)	0-1846 (1)	0-5706 (5)	-0-1846 (1)	0-0026 (1)	0-0345 (8)	0-0032 (1)	-0-0045 (2)	0-0002 (1)	-0-0042 (2)
H(51)	0-146 (2)	0-547 (5)	-0-208 (2)	5-0 (0-8)					
H(52)	0-226 (3)	0-553 (6)	-0-213 (3)	6-8 (1-1)					
O(6)	0-3038 (1)	0-5056 (6)	0-3244 (2)	0-0023 (1)	0-0530 (10)	0-0029 (1)	-0-0056 (3)	0-0009 (1)	-0-0045 (3)
H(61)	0-262 (3)	0-522 (6)	0-290 (3)	6-5 (1-0)					
H(62)	0-344 (2)	0-500 (6)	0-302 (3)	5-6 (0-9)					

A final two-cycle block-diagonal refinement, using anisotropic thermal parameters for heavy atoms and isotropic ones for hydrogen atoms, reduced R to 0.046 (0.057) for the observed (all) reflections and R_w to 0.069 (0.069) with $[\sum_w(\Delta F)^2/(m-n)]^{1/2}=0.25$. Observed and calculated structure amplitudes are given in Table 1. Final atomic positional and thermal parameters are given in Table 2. In Fig. 1, the thermal parameters are represented as 50% probability ellipsoids (ORTEP, Johnson, 1965).

The best least-squares fit of atomic anisotropic thermal parameters, U_{ij} , to a rigid-body motion (Schomaker & Trueblood, 1968) was calculated both for each of the four individual independent barbitol anions, and for each of the four independent dimers formed through double hydrogen-bonding between two centrosymmetrically related anions. Hydrocarbon-chain atoms C(7), C(8), C(9), C(10) were omitted from the calculations. As might be expected, the better rigid-body fit is for the individual barbitol anions, e.g., in anion 1 the root-mean-square of $\Delta U_{ij} = [\sum\{U_{ij}(\text{meas}) - U_{ij}(\text{calc})\}^2 / (n-s)]^{1/2}$, is 0.0025 Å² compared with 0.0042 Å² for the dimer. However, the rigid-body model for the dimers seems to be satisfactory. Therefore, the dimers can with some respect, be considered as structural units.

The pseudosymmetry in the reciprocal lattice can be explained by the transformation $\frac{1}{2}-x, -y, \frac{1}{2}+z$ being nearly obeyed in the direct lattice. This transformation relates the two calcium ions to each other, the barbitol anions 4 to 1 and 3 to 2, and the water molecules $W(1)$ to $W(2)$, $W(3)$ to $W(4)$ and $W(5)$ to $W(6)$. Separations of up to 1.6 Å are found between ideally coincident positions. However, the pseudosymmetry element $P2_1$ cannot be implied because α differs too much from 90° to allow a pseudomonoclinic structure.

Discussion

Geometry of barbitol anions

As in the barbitol molecule (Craven *et al.*, 1969) and the barbitol ion of the sodium salt (Berking & Craven, 1971), the conformation of all four barbitol ions is such that the rings are nearly planar, and the ethyl groups together with C(5) form hydrocarbon chains

that are nearly in the all *trans* configuration. Axes of the chains are perpendicular (90.7, 89.1, 91.6, 90.0°, respectively) to the ring planes. Deviations from this idealized geometry are given in Table 3 as atomic displacements from the best least-squares planes and torsion angles about covalent bonds. There are two different conformations in the four barbiturate rings: the ring of anion 2 is essentially flat and the other three puckered, with the tetrahedrally surrounded atom C(5) out of plane (Fig. 2). The puckering is possibly due to a need to relieve the angular strain induced by the ring closure. Variations within the four barbitol rings cannot be explained by the nature of the C(5) substituents (which in other barbiturates play a role; Craven, 1970), because here all substituents are identical. Therefore, intermolecular interactions may be important in controlling the mode of puckering.

Table 3. Least-squares planes, torsion angles, and dihedral angles

Key to planes in:

- 1: planes through the six pyrimidine ring atoms.
- 2: planes through N(1), C(2), N(3), C(4), C(6).
- 3: planes through the atoms of the chains C(7), C(8), C(5), C(9), C(10).
- 4: plane through atoms of coordination-pentagon of atom Ca(1).
- 5: plane through atoms of coordination-pentagon of atom Ca(2).

As the structure is centrosymmetric, the sign may be changed for each barbitol ion in (b) and (c).

(a) Equations of the planes:

Anions	Planes	
1	1:	0.159x - 0.122y + 0.971z = -0.049
	2:	0.208x - 0.128y + 0.959z = 0.043
	3:	0.134x + 0.980y + 0.104z = 1.577
2	1:	-0.147x + 0.965y - 0.209z = 5.359
	2:	-0.145x + 0.964y - 0.213z = 5.356
	3:	0.946x + 0.193y + 0.200z = 10.714
3	1:	-0.218x + 0.972y - 0.017z = 6.012
	2:	-0.228x + 0.968y - 0.061z = 5.711
	3:	0.949x + 0.177y - 0.318z = 0.321
4	1:	-0.169x - 0.102y + 0.991z = 6.312
	2:	-0.138x - 0.105y + 0.993z = 6.520
	3:	0.076x + 0.983y + 0.130z = 4.131
4	4:	-0.179x + 0.973y - 0.122z = 5.440
	5:	-0.191x + 0.969y - 0.134z = 4.978

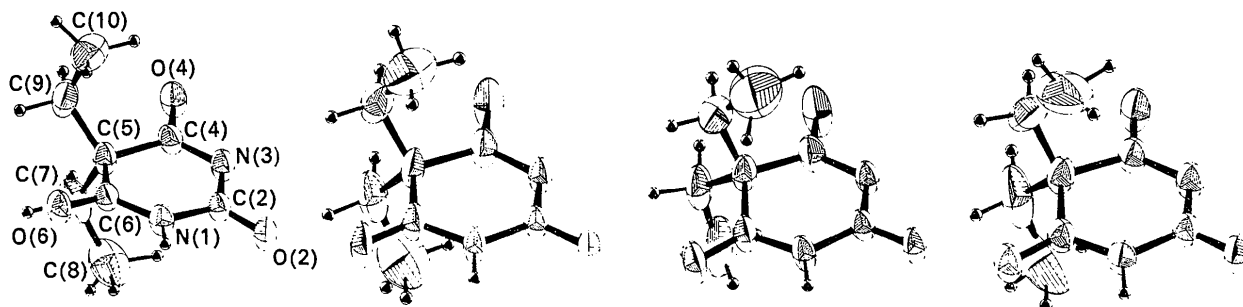


Fig. 1. The 50% probability ellipsoidal representation of atomic thermal parameters of the four crystallographically independent barbitol ions and nomenclature within the ions. Directions of the four projections are defined by corresponding intramolecular vectors.

Bond lengths and angles for the four barbitol anions of calcium barbitol are listed in Table 4 and, if relevant, are compared with those of the barbitol anion of sodium barbitol (where the deprotonated nitrogen atom has no intermolecular interactions) and with those of the barbitol molecule. Within the pyrimidine rings not all corresponding values agree within 3σ . With one exception [C(4)–C(5)], the values within anion 1 are close to those of anion 4 and the values of anion 2 are close to those of anion 3. This is possibly explained by the kind of intermolecular interactions of the ring atom N(3); in anions 1 and 4 it accepts a hydrogen bond, in anions 2 and 3 it coordinates a calcium ion. However, the values show common tendencies; thus, for further discussion average values may be used. They show the same characteristic features for deprotonation (Singh, 1965) that have been found in sodium barbitol; the internal ring angle at N(3), which is the deprotonation site, closes from 126.4° in the barbitol molecule to 120.1° in the barbitol ion (119.2 in sodium barbitol, $\sigma=0.3^\circ$), whereas the adjacent internal ring angles at C(2) and C(4) open by approximately 5° , more than compensating for the decrease at N(3). The two C–N bonds at the deprotonated nitrogen atoms are almost equal in length and are significantly shorter (here 1.333 and 1.339 Å, in sodium barbitol 1.343 and 1.339 Å, $\sigma=0.002$ Å) than the corresponding bonds in barbitol (1.36 and 1.38 Å, $\sigma=0.004$ Å). The C–N bond lengths at the nondeprotonated nitrogen atom N(1) differ significantly (here: 1.392 vs 1.347 Å; in sodium barbitol 1.395 vs 1.348 Å), whereas in barbitol (1.368 and 1.375 Å) they are, of course, comparable with those of N(3).

Three more crystal structures involving barbitol ions have been determined, all showing the same effects of deprotonation: barbitolguanidine dihydrate (McClure & Craven, 1971) in which the deprotonated nitrogen atom accepts two hydrogen bonds, and the bis-barbitol-bis-imidazole complexes of cobalt(II) and zinc(II) (Wang & Craven, 1971) in which N(3) coordinates the metal ions.

In discussing the C–O bond lengths, one has to be aware of the effect of hydrogen bonding on bond lengths, which may result in an increase of the order of 0.01 Å (Craven, 1970). Table 5 lists the intermolecular and ionic interactions involving barbitol oxygen atoms. Owing to pseudosymmetry, the oxygen atoms of anions 1 and 4 are involved in corresponding interactions, as are atoms of anions 2 and 3. Within both groups the three C–O bond lengths agree within 2σ ($\sigma=0.004$ Å); however, significant differences exist between both groups. For example, C(2)–O(2) bond lengths are 1.228 and 1.235 Å in the first group in which the O(2) atoms each accept two hydrogen bonds, and 1.248 and 1.251 Å in the second group where the O(2) atoms each accept one hydrogen bond and coordinate one calcium cation.

Except in C(12)–O(12) (1.228 Å), the C(2)–O(2) and C(4)–O(4) bonds (average 1.245 Å), which are adjacent to the deprotonated nitrogen atoms, are significantly

longer than the remote C(6)–O(6) bond (average 1.223 Å). Also, they are longer than the corresponding C(2)–O(2) and C(4)–O(4) bonds in barbitol, whose average is 1.211 Å. The same effect of increase in C–O bonds (1.238 and 1.245 vs. 1.216 Å with e.s.d.'s of 0.002 Å) has been found in the crystal structure of sodium barbitol. The decrease of the N(3)–C bonds, the increase of the two C–O bonds, and the symmetry around the atoms N(3) indicate that the greatest part of the formal negative charge on the barbitol ions is equally distributed between the O(2) and O(4) oxygen atoms.

The C–C bonds and angles at C(5) and in the ethyl groups are within expected ranges, except for two bonds: C(29)–C(210) and C(49)–C(410) with values of 1.48 and 1.47 Å respectively and with e.s.d.'s of

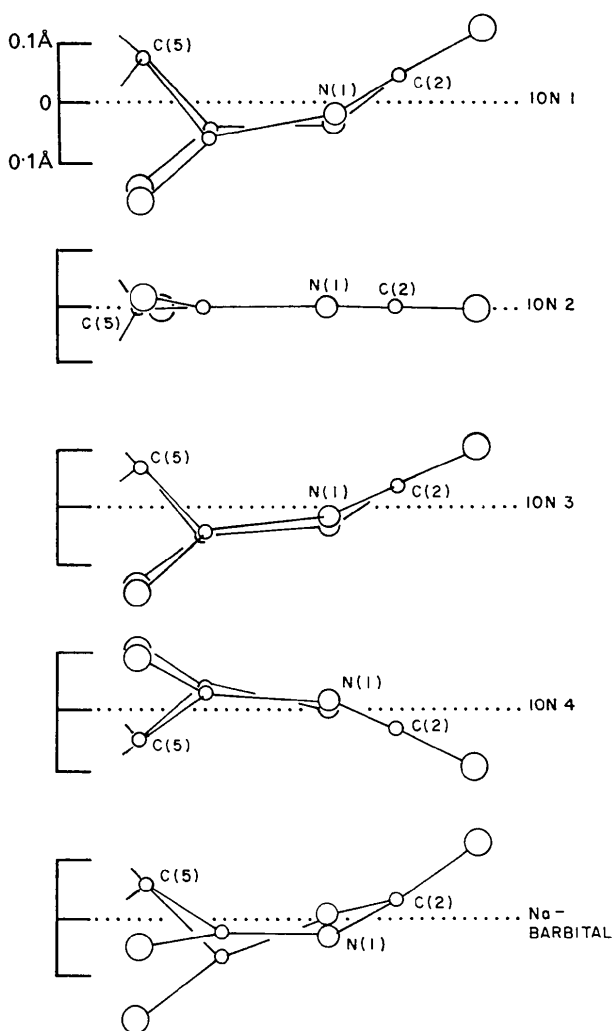


Fig. 2. Conformations of the trioxypyrimidine rings of the four symmetrically independent ions in calcium barbitol trihydrate and the ring in sodium barbitol. Dotted lines are the traces of the best least-squares planes through the six ring atoms. Scale in the vertical direction is about six times that in the horizontal. Ion 4 is drawn as enantiomorph of ion 3, but, because of the center of symmetry, ions 1, 3, and 4 do not differ significantly.

0.01 Å. A correction for the high degree of anisotropic thermal motion increases the values, but the discussed rigid-body model does not seem appropriate for atoms of the ethyl groups. All bond distances and angles involving hydrogen atoms are in expected ranges: average values are 0.90 Å for 4 N-H distances, 0.99 Å for 40 C-H distances and 0.80 Å for 12 C-O distances.

Ionic interactions of calcium ions

Both calcium ions are sevenfold coordinated in the same way: by three barbital oxygen atoms, three water

oxygen atoms, and one deprotonated barbital nitrogen atom. The coordination can be pictured as being distorted pentagonal bipyramids around the calcium ions. Interesting distances and angles are shown in Figs. 3 and 4, and the least-squares planes for the pentagons and corresponding displacements are listed in Table 3(a). The polyhedra are not connected to each other. The sevenfold coordination of calcium atoms by pentagonal bipyramids has been found in the crystal structures of 1,3-diphosphorylimidazole (Beard & Lenhart, 1968) and calcium 1-naphthyl phosphate trihydrate (Li

Table 4. *Interatomic distances and angles*

Standard deviations are estimated as follows:

0.004–0.005 Å:	C–N, C–O, C–C bonds within the rings, Ca–O, and Ca–N distance
0.010:	C–C bonds in aliphatic chains
0.08:	O–H, N–H, C–H bonds
0.6°:	angles between heavy atoms in and at the rings
1.0:	C–C–C angles in the chain
5–7:	angles with hydrogen atoms

In atom names with two indices, the first denotes the barbital ion, the second denotes the atom within the ion.

(a) Bond lengths within barbital anions

	Anions				Average	Na-barbital	Barbital
	1	2	3	4	of four	*	Molecule†
C(6)–N(1)	1.340 Å	1.355 Å	1.352 Å	1.343 Å	1.347 Å	1.348 Å	1.375 Å
N(1)–C(2)	1.407	1.381	1.376	1.405	1.392	1.396	1.368
C(2)–N(3)	1.345	1.323	1.326	1.340	1.333	1.343	1.380
N(3)–C(4)	1.333	1.343	1.349	1.332	1.339	1.339	1.364
C(4)–C(5)	1.542	1.520	1.512	1.517	1.522	1.527	1.518
C(5)–C(6)	1.506	1.510	1.517	1.495	1.507	1.520	1.521
C(2)–O(2)	1.228	1.248	1.251	1.235	–	1.238	1.209
C(4)–O(4)	1.247	1.240	1.238	1.254	–	1.245	1.214
C(6)–O(6)	1.229	1.219	1.222	1.223	–	1.216	1.208
C(5)–C(7)	1.543	1.557	1.539	1.568	1.552	1.538	1.545
C(5)–C(9)	1.548	1.548	1.541	1.546	1.546	1.549	1.548
C(7)–C(8)	1.531	1.507	1.512	1.512	1.516	1.504	1.505
C(9)–C(10)	1.515	1.478	1.525	1.469	1.497	1.512	1.503
N(1)–H(1)	0.89	0.89	0.91	0.90	0.90	0.93	0.90

(b) Bond angles within barbital anions:

C(6)–N(1)–C(2)	124.6°	123.8°	124.1°	124.1°	124.2°	125.5°	126.7°
N(1)–C(2)–N(3)	120.6	122.4	122.6	121.2	121.7	121.3	116.0
C(2)–N(3)–C(4)	120.4	120.6	119.7	119.6	120.1	119.2	126.4
N(3)–C(4)–C(5)	122.8	122.3	122.3	123.7	122.8	123.8	118.3
C(4)–C(5)–C(6)	111.9	113.1	112.8	112.7	112.6	112.4	114.1
C(5)–C(6)–N(1)	118.0	117.8	116.9	118.0	117.7	116.7	118.0
N(1)–C(2)–O(2)	116.6	118.1	119.0	116.0	–	117.4	122.4
N(3)–C(2)–O(2)	122.7	119.5	118.4	122.8	–	121.3	121.6
N(3)–C(4)–O(4)	120.9	119.7	119.3	120.5	–	118.9	119.9
C(5)–C(4)–O(4)	116.3	117.9	118.4	115.8	–	117.2	121.7
C(5)–C(6)–O(6)	121.1	122.5	122.1	121.5	–	122.2	122.7
N(1)–C(6)–O(6)	120.8	119.7	121.0	120.5	–	121.1	120.0
C(4)–C(5)–C(7)	108.3	108.5	111.0	109.3	109.2	109.3	–
C(4)–C(5)–C(9)	109.9	108.9	108.4	108.6	109.0	108.5	108.1
C(6)–C(5)–C(7)	107.5	108.6	109.0	108.5	108.4	108.2	108.8
C(6)–C(5)–C(9)	109.3	108.3	107.3	106.3	107.8	108.1	–
C(7)–C(5)–C(9)	110.0	109.5	108.2	111.5	109.8	110.3	109.4
C(5)–C(7)–C(8)	114.8	114.2	115.1	113.2	114.3	113.3	115.3
C(5)–C(9)–C(10)	114.7	114.2	115.0	114.9	114.7	114.7	114.8
C(6)–N(1)–H(1)	122	118	122	121	121	119	119
C(2)–N(1)–H(1)	114	119	114	115	116	115	114

* Berking & Craven (1971).

† Average values of three molecules: barbital I (Craven *et al.*, 1969) and the 2:1 complex of barbital and caffeine (Craven & Gartland, 1970).

& Caughlan, 1965). However, in both structures, all seven coordinating atoms are oxygen atoms; calcium and the other alkaline-earth metal ions are known for their coordination by oxygen atoms instead of coordination by nitrogen atoms. Here, in both polyhedra, the distances from the calcium ions to the two barbitol-oxygen atoms forming the apices of the bipyramids are shortest (average 2.31 Å); the distances to the three water oxygen atoms within the pentagon planes are next shortest (average 2.37 Å). Distances to the two barbitol atoms O(32) and N(33) in the case of ion Ca(1), and to O(22) and N(23) in the case of Ca(2), both atoms of the same barbitol anion respectively, range from 2.52 to 2.60 Å, forming angles O(2)–Ca–N(3) of only 51° (instead of 72° for an ideal pentagon). Reduction of this angle from the ideal value may be due to the intramolecular O(2)–N(3) distances, which are too short to allow more regular pentagons. The coordination can also be described by fairly regular octahedra in which one corner is replaced by an intramolecular O–C–N group. Thus, the Ca–N interaction might not be due to the actual coordination need of the Ca²⁺ ion itself, but to intramolecular groupings. Only a few structures are reported to have Ca ions coordinated by nitrogen atoms: in the hexahydrated calcium salt of hexacyanoisobutylene (sixfold coordination; Bekoe, Gantzel & Trueblood, 1967) where the Ca–N distance

Table 5. Intermolecular interactions involving barbitol-oxygen atoms, deprotonated barbitol-nitrogen atoms, and water molecules

Barbitol oxygen atom	Accepts H-bond from	Coordinates cation
O(12)	N(11), O(2)	
O(14)		Ca(2)
O(16)		Ca(2)
O(22)	N(21)	Ca(2)
O(24)	O(4), O(5)	
O(26)	O(3), O(6)	
O(32)	N(31)	Ca(1)
O(34)	O(3), O(6)	
O(36)	O(4), O(5)	
O(42)	N(41), O(1)	
O(44)		Ca(1)
Barbitol nitrogen atom		
O(46)		Ca(1)
N(13)	O(2)	
N(23)		Ca(2)
N(33)		Ca(1)
N(43)	O(1)	
Water oxygen atom	Donates H-bond to	Coordinates cation
O(1)	N(43), O(42)	Ca(1)
O(2)	N(13), O(12)	Ca(2)
O(3)	O(26), O(34)	Ca(2)
O(4)	O(24), O(36)	Ca(1)
O(5)	O(24), O(36)	Ca(2)
O(6)	O(26), O(34)	Ca(1)

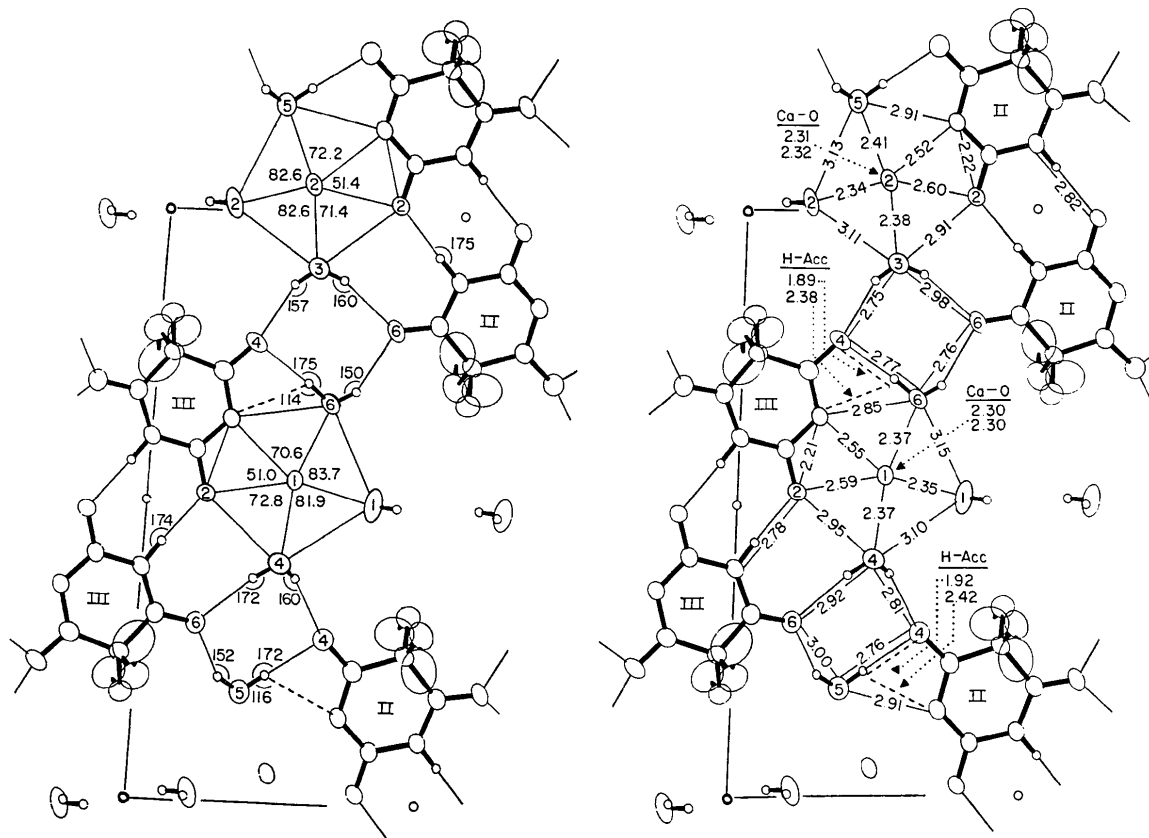
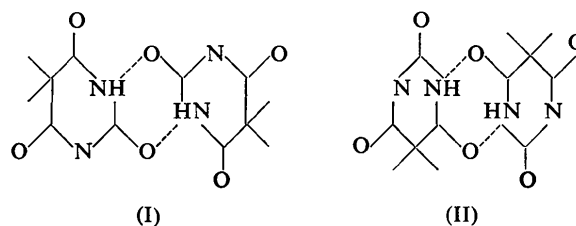


Fig. 3. Distances and angles describing the coordination of the calcium ions by distorted pentagonal bipyramids and the hydrogen bonding in which barbitol ions 2 and 3 are involved to form an infinite two-dimensional sheet perpendicular to b^* .

is very long (2.79 Å); in calcium dipicolinate (eightfold coordination; Strahs & Dickerson, 1968) where the situation is similar to that in this work, *i.e.*, the nitrogen atom and other coordinating oxygen atoms are near neighbors within one anion.

Hydrogen-bonding scheme

Distances and angles describing the hydrogen-bonding scheme are shown in Figs. 3 and 4. All four barbital anions form double-linked N(1)–H...O(2)=C(2) hydrogen-bonded dimers with anions related by a center of symmetry. For convenience, the dimer formed from two anions 1 is called dimer 1, *etc.* The pyrimidine rings within dimers 2 and 3 are oriented nearly parallel to the *ac* plane, while those of dimers 1 and 4 are almost perpendicular to this plane. All four independent dimers are isolated with respect to having no hydrogen bonds to other barbital anions, whereas in most other crystal structures of barbiturates, the barbiturate molecules or ions have extended hydrogen-bond interactions with one another. Two different double-linked kinds of barbiturate dimers (and a hybrid) are possible:



So far, one structure has been reported to form hydrogen-bonding scheme (II): 1-methyl-5-phenyl-5-ethyl-barbituric acid (Bideau, Morly & Housty, 1969). No other structure except the one reported here (calcium barbital trihydrate), is known to form isolated dimers with hydrogen-bonding scheme (I).

All other hydrogen bonding makes use of the water molecules and is of the type C=O...H–O–H...O=C or N...H–O–H...O=C. Because of the structural pseudosymmetry, the ways in which the dimers are connected are corresponding for dimers 1 and 4 (Fig. 4) and for dimers 2 and 3 (Fig. 3) respectively. Dimers 1 form two-dimensional ribbons along *b* at *z*=0.0. The linkage is accomplished by two independent

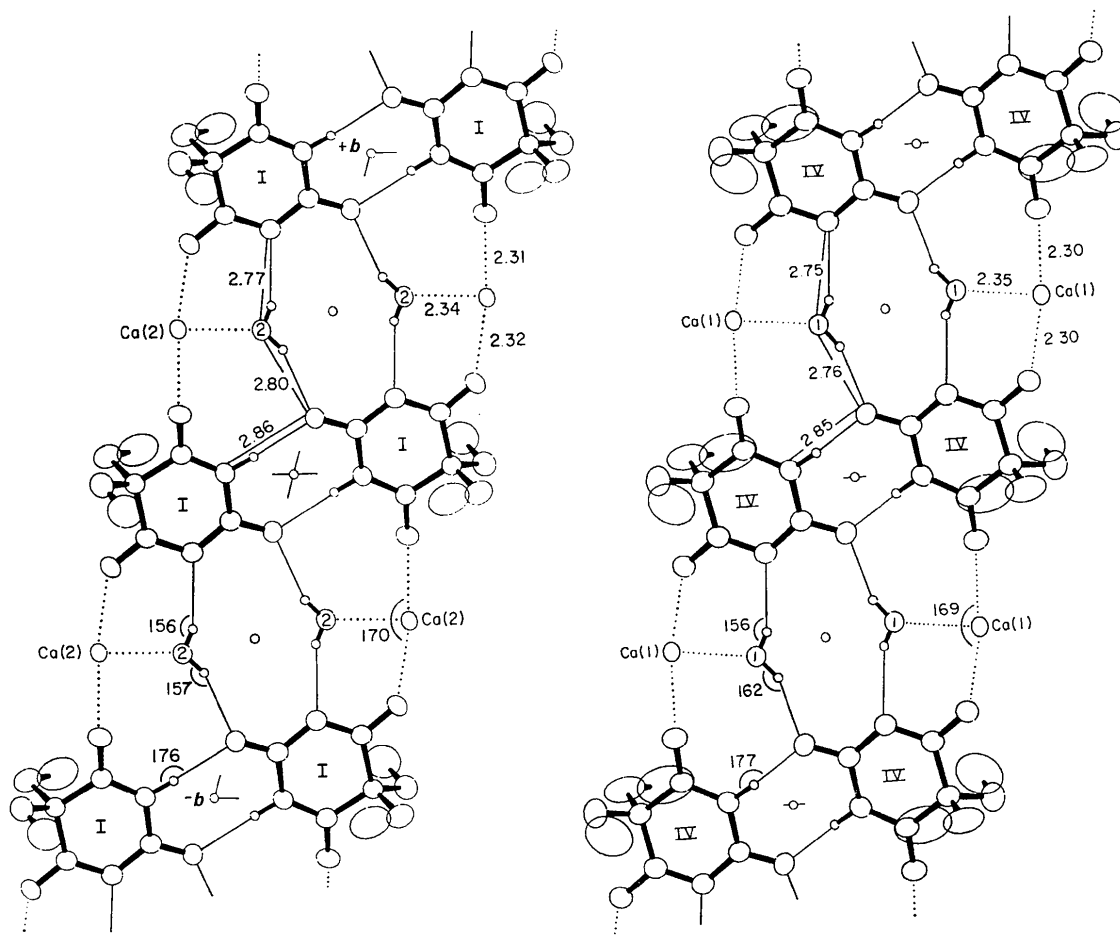


Fig. 4. Projection along *c*, describing the geometry in the ribbons which are formed from dimers 1 and 4, respectively. Short Ca–O distances (2.30–2.32 Å) point to the apices of the pentagonal bipyramids, whose bases are shown in Fig. 3.

hydrogen bonds *via* water molecule 2: N(13)···HO(21)–O(2)–HO(22)···O(12'). Similarly, dimers 4 form two-dimensional ribbons at $z=0.5$ which are separate from, and parallel to, those of dimers 1. Linkage is by two independent hydrogen bonds *via* water molecule 1: N(43)···HO(12)–O(1)–HO(11)···O(42'). In both dimers the deprotonated nitrogen atom plays the role of an acceptor. Ribbons are stabilized by coordination bonds between calcium ions and apices of the bipyramids.

The pyrimidine rings of dimers 2 and 3 together with the two Ca ions and the six water molecules form a layer close to the plane $y=\frac{1}{2}$. Fig. 5 shows the way in which an infinite two-dimensional sheet is formed. This sheet consists of an assembly of loops, having a gap to host the calcium ions and to let the ribbons formed by barbitol dimers 1 and 4 pass through. The loops contain both dimers 2 and 3, linked by water molecules $W(3)$, $W(4)$, $W(5)$ and $W(6)$. The only interactions between the ribbons and the nearly perpendicular sheets are by calcium ions. Four out of seven coordination bonds point to atoms belonging to the loops; the remaining three bonds point to atoms belonging to the ribbons (two barbitol oxygen atoms at the apices and one oxygen atom of the isolated water molecules in Fig. 5).

Crystal packing with such weak three-dimensional interactions allows a high degree of anisotropic thermal motion. The principal axes of the probability ellipsoids (Fig. 6) have main components perpendicular to the sheet at $y=\frac{1}{2}$ for dimers 2 and 3, which are part of the sheet, and perpendicular to the ribbons at $z=0$ and $z=\frac{1}{2}$ for dimers 1 and 4 which form the ribbons.

Each of the four oxygen atoms of water molecules $W(3)$, $W(4)$, $W(5)$, and $W(6)$ is involved in five distances to nonhydrogen atoms which are less than 3.15 Å. For example, in the case of water molecule $W(3)$ coordination bond O(3)–Ca(2) is 2.38 Å, pentagon vector O(3)–O(2) is 3.11 Å, hydrogen bond O(3)–O(34) is 2.75 Å, and the two distances O(3)–O(22') and O(3)–O(26) are 2.91 and 2.98 Å long respectively. If the exact position of the hydrogen atom was not known, the latter two distances would wrongly suggest bifurcated hydrogen bonding. However, the corresponding hydrogen–acceptor distances would be 2.60 *vs.* 2.20 Å, and the angles: donor–hydrogen atom–acceptor, would be 101° *vs.* 160°. This indicates that the hydrogen bond is unambiguously between O(3) and O(26), even if a small interaction along the shorter distance might take place. Moreover, there might be a repulsive interaction between the calcium ion and the hydrogen atom by which hydrogen bonding to O(26) is favored.

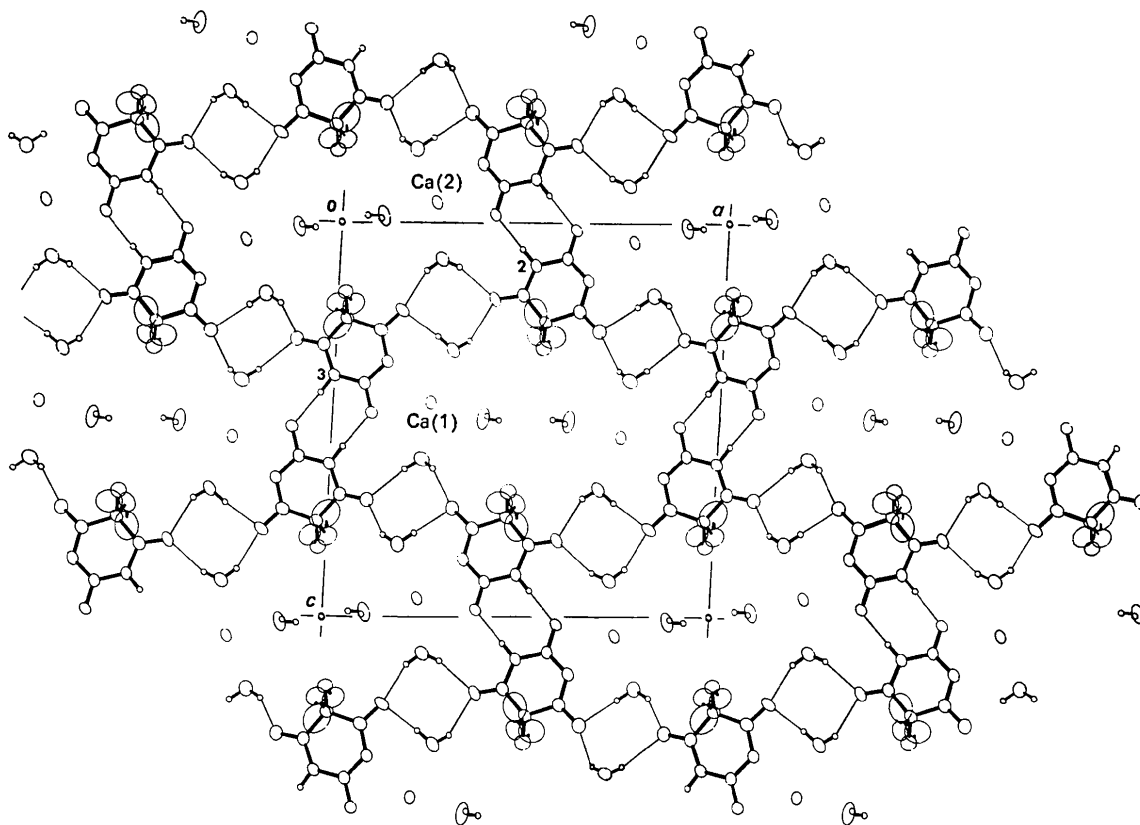


Fig. 5. Projection along b . All included atoms except ethyl groups are located in a sheet close to $y=\frac{1}{2}$. The two ribbons of hydrogen-bonded dimers 1 and dimers 4, which are omitted in this drawing, intersect the sheet in the gaps which contain calcium ions and isolated water molecules. These water molecules are part of the ribbons.

Packing of alkyl groups

The diethyl groups of anions 1 and 4 are oriented nearly parallel to each other, as are those of anions 2 and 3. This allows a regular way of packing: the groups of anions 2 lie in infinite channels parallel to the *b* axis and those of anions 3 are arranged in a similar way. Alternating groups from anions 1 and 4 are located in infinite channels parallel to the *c* axis (Fig. 6). Gaps between the diethyl groups within the channels (determined by closest intermolecular H-H distances) range from 2.56 to 3.26 Å.

Atoms of the diethyl groups have only few close intermolecular interactions: four H-H distances are smaller than 2.5 Å and six more are smaller than 2.75 Å. Atom H(471) has no intermolecular distance smaller than 4.0 Å. The lack of close van der Waals contacts ($d=2.4$ Å for an H-H approach; Pauling, 1960) explains the high thermal motion of the ethyl groups, and indicates that efficient alkyl-group packing is not as important for the crystal packing as it is in some other barbiturates (Gartland & Craven, 1971). The crystal packing is dominated by one- and two-dimensional hydrogen bonding and three-dimensional coordination interactions of the calcium ions.

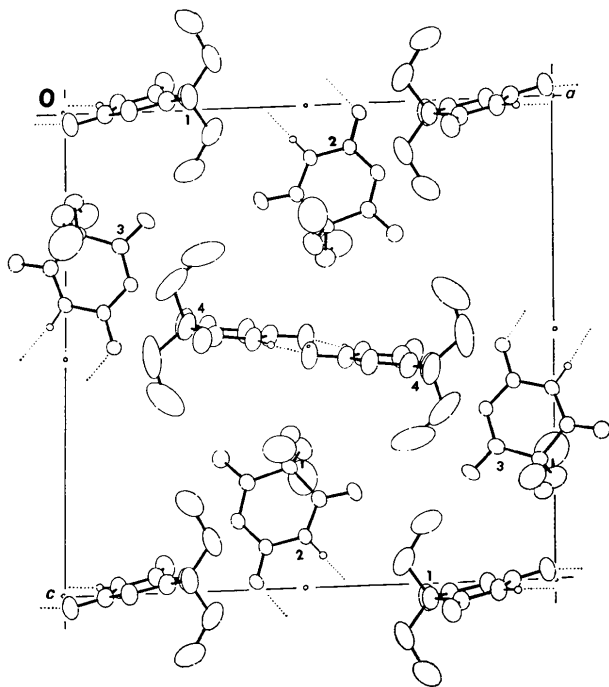


Fig. 6. Projection along *b*, containing only the barbital ions. Each ion forms a dimer with a centrosymmetrically related ion. Thermal-motion ellipsoids have main components perpendicular to pyrimidine ring planes.

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