5,6-Dihydro-1,3-dimethyl-5,6-bis-[1',3'-dimethyl-2',4',6'-trioxo-pyrimid(5',5')yl]furo[2,3-*d*]uracil

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Abstract. $C_{18}H_{18}N_6O_9$, m.p. 370–373° dec., orthorhombic, space group *Pbca*, $a = 13 \cdot 236$ (1), $b = 15 \cdot 931$ (1), $c = 19 \cdot 584$ (2) Å, $Z = 8$, $M = 462 \cdot 37$, $D_x = 1 \cdot 487$, $D_m = 1 \cdot 492$ g cm^{-3}. The title compound is a trimeric form of 1,3-dimethylbarbituric acid with two spiro linkages and a central dihydrofuran ring. The bond between the two quaternary carbons C(12)–C(22) is $1 \cdot 612$ Å.

Introduction. The title compound represents a novel trimeric structure synthesized from 1,3-dimethylbarbituric acid by electrochemical oxidation. A preliminary report of this structure has been published (Kato, Poling, van der Helm & Dryhurst, 1974).

Table 1. *Positional parameters for* C, O, *and* N *atoms*

Calculated standard deviations are given in parentheses.

	x	y	z
C(11)	687 (1)	5856 (1)	2068 (1)
C(12)	672 (1)	4956 (1)	2353 (1)
C(13)	−78 (1)	4840 (1)	2933 (1)
C(14)	6 (2)	6352 (1)	3155 (1)
C(15)	599 (2)	7359 (1)	2311 (1)
C(16)	−867 (2)	5431 (1)	3952 (1)
O(11)	937 (1)	5999 (1)	1490 (1)
O(12)	−436 (1)	4162 (1)	3065 (1)
O(13)	−165 (2)	6929 (1)	3534 (1)
N(11)	451 (1)	6481 (1)	2525 (1)
N(12)	−254 (1)	5537 (1)	3332 (1)
C(21)	2406 (1)	5447 (1)	2834 (1)
C(22)	1794 (1)	4695 (1)	2593 (1)
C(23)	1740 (1)	4006 (1)	3135 (1)
C(24)	1870 (1)	5101 (1)	4000 (1)
C(25)	2686 (2)	6445 (1)	3757 (1)
C(26)	1314 (2)	3687 (1)	4314 (1)
O(21)	2910 (1)	5863 (1)	2452 (1)
O(22)	1750 (1)	3274 (1)	2983 (1)
O(23)	1785 (1)	5310 (1)	4586 (1)
N(21)	2249 (1)	5652 (1)	3508 (1)
N(22)	1615 (1)	4298 (1)	3789 (1)
C(31)	1492 (1)	4065 (1)	1604 (1)
C(32)	572 (1)	4338 (1)	1777 (1)
C(33)	−270 (1)	4181 (1)	1345 (1)
C(34)	914 (1)	3361 (1)	622 (1)
C(35)	2708 (2)	3229 (1)	929 (1)
C(36)	−850 (2)	3463 (2)	300 (1)
O(31)	2259 (1)	4337 (1)	2004 (1)
O(32)	−1130 (1)	4441 (1)	1432 (1)
O(33)	1071 (1)	2916 (1)	132 (1)
N(31)	1701 (1)	3577 (1)	1063 (1)
N(32)	−25 (1)	3689 (1)	771 (1)

The compound was recrystallized from methanol. An orthorhombic crystal, $0 \cdot 125 \times 0 \cdot 291 \times 0 \cdot 581$ mm, was used for data collection and unit-cell determination. The unit-cell dimensions were determined at 27 °C from the $+2\theta$ and -2θ values of 14 reflections distributed through all octants of reciprocal space, with Cu $K\alpha_1$ radiation ($\lambda = 1 \cdot 54051$ Å). The data showed systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$ which uniquely determine space group *Pbca*. The intensities of 3705 reflections [3285 reflections had $I > 2\sigma(I)$] with $2\theta < 135°$ were measured with Ni-filtered Cu $K\bar{\alpha}$ radiation ($\lambda = 1 \cdot 5418$ Å) and θ–2θ scans on a Nonius CAD-4 automatic diffractometer. Lorentz and polarization corrections were applied; no absorption corrections were made. The crystal structure was determined by direct methods with the *MULTAN* (Germain, Main & Woolfson, 1971) program. The structure was refined by block-diagonal least-squares techniques (Ahmed, 1966) with anisotropic temperature factors for the non-H atoms and isotropic temperature factors for the H atoms. The refinement was terminated when all shifts for the non-H atoms were less than $0 \cdot 7$ of the corresponding estimated standard deviation. Scattering factors for C, O, and N were taken from *International Tables for X-ray Crystallography* (1962) and those for H from Stewart, Davidson & Simpson (1965). R for all data (3705) based on the final parameters (Table 1) $(R = \sum ||kF_o| - |F_c||/\sum |kF_o|)$ was 0·043.† The weights of F in the least-squares calculation were calculated from $\sigma(I)$ determined from counting statistics (van der Helm, Ealick & Burks, 1975).

Discussion. An *ORTEP* drawing (Johnson, 1965) of a single molecule with thermal ellipsoids is given in Fig. 1, bond lengths in Fig. 2, and bond angles in Fig. 3. The range of C–H bonds is 0·83 to 1·07 Å with an average value of 0·96 Å. Apparently it is energetically unfavorable in the electrochemical oxidation to form a cyclopropane ring with C(12), C(22) and C(32), but instead a central dihydrofuran ring is formed with C(12), C(22)

† A list of structure factors, the coordinates for the H atoms and the thermal parameters for all the atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31939 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
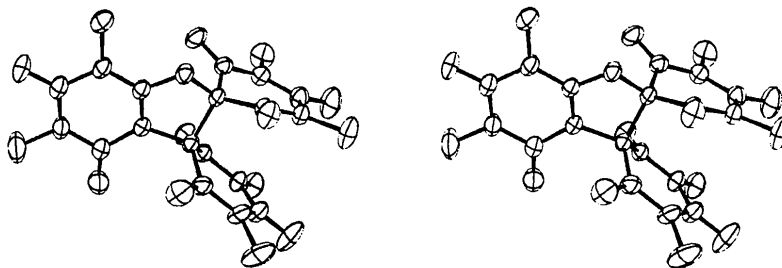
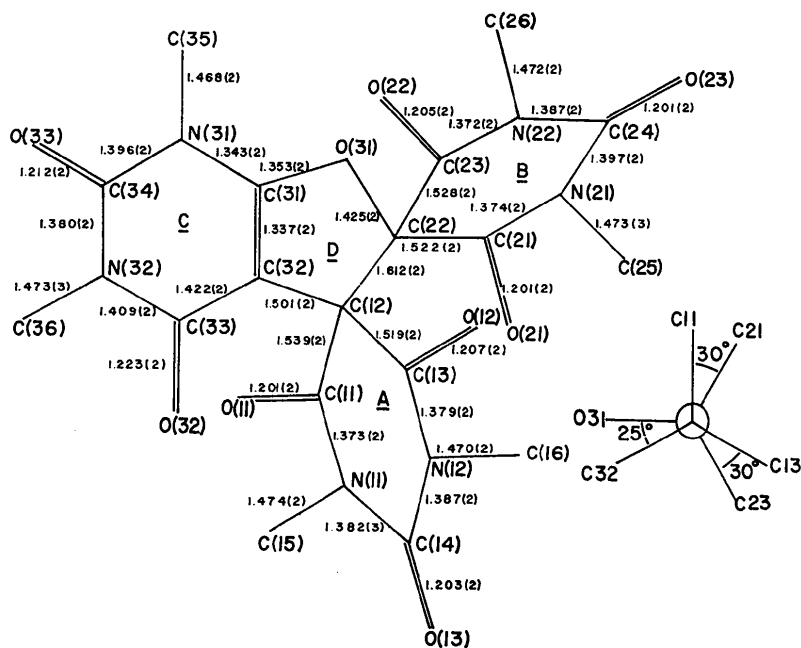Fig. 1. Stereo view of a single molecule (Johnson, 1965).
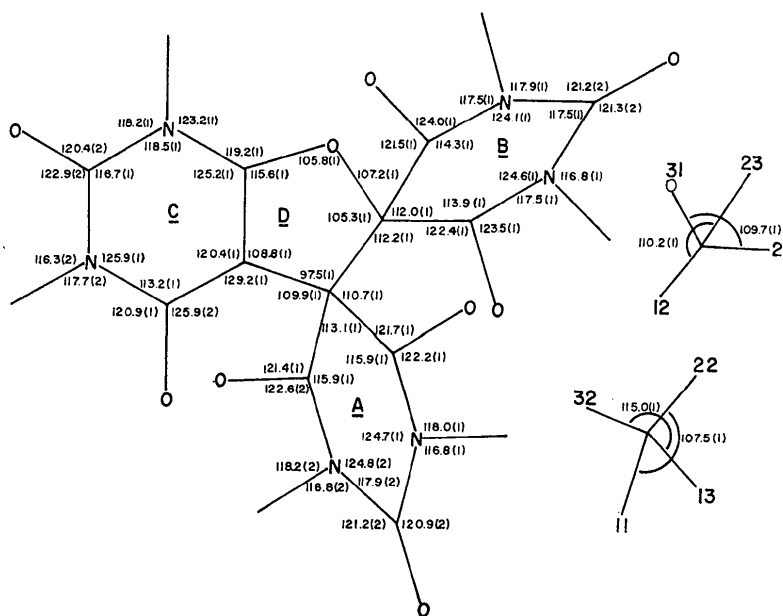
Fig. 2. Bond distances and numbering scheme.
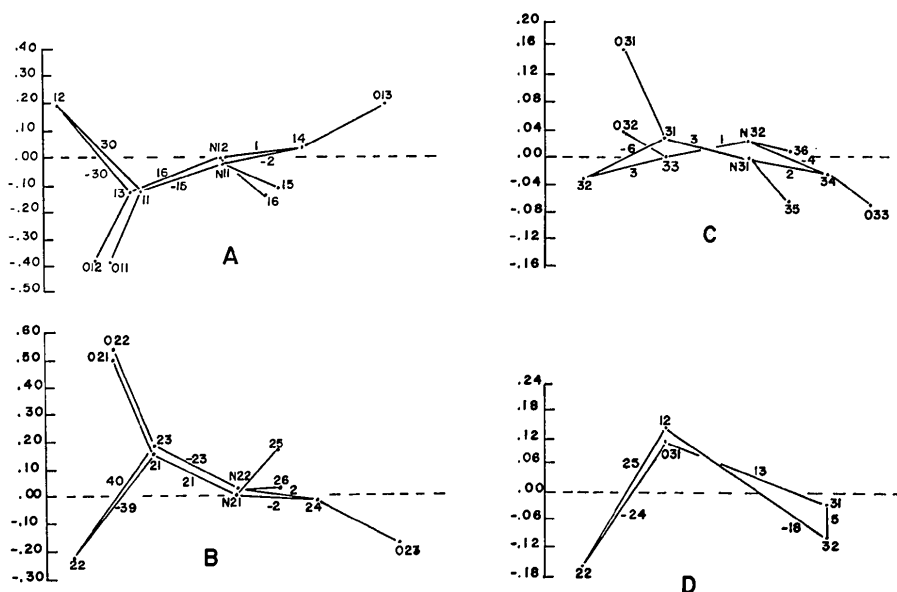
Fig. 3. Bond angles.

Fig. 4. Ring conformations and least-squares planes. The equations of the least-squares planes are: (A) $11·593x - 0·655y + 9·415z = 2·484$; (B) $12·394x - 5·340y + 2·029z = 0·484$; (C) $2·511x + 13·141y - 10·429z = 4·019$; (D) $2·647x + 13·043y - 10·541z = 4·023$. Vertical scale in Å.

and three atoms of the third barbiturate molecule. The bond distance between the C atoms of the two spiro-linked barbiturate molecules [C(12)–C(22)] is quite long, 1·612 Å. The Newman projection in Fig. 2 shows the half-eclipsed configuration of the substituents on these quaternary atoms. Similarly long bonds have been previously observed involving adjacent quaternary C atoms with partially eclipsed substituents (McCandlish, 1974; Birnbaum, 1972).

Distances of the atoms in the five- and six-membered rings from least-squares planes passing through the ring atoms are given in Fig. 4. The five-membered ring is in an envelope conformation. The barbiturate ring C is almost planar. The small puckering observed is the asymmetric one of two common types of nonplanarity found in barbiturate crystals (Craven, Cusatis, Gartland & Vizzini, 1973). Rings A and B show much larger deviations from planarity; they assume a half-chair conformation. Rings A and B approximately face each other; the angle between the normals to their least-squares planes is 27·9°. They are approximately at right angles to ring C, with 82·9° for A–C and 81·9° for B–C (angles between normals to the least-squares planes).

The molecules are closely packed in the crystal structure, which is indicated by the fact that there are six intermolecular distances from 2·89 to 3·00 Å. The contacts (2) are between N and O atoms, an O atom and the C atom of a methyl group (1), and an O atom of a carbonyl group (3). The latter three distances are 2·986, 2·971 and 2·897 Å. Only the shortest one, $C(21)\cdots O(32)$ $(\frac{1}{2}+x, y, \frac{1}{2}-z)$, seems to be an example of a close $O\cdots C{=}O$ contact in which the C atom is

displaced out of the plane of the carbonyl group towards the nearby O atom (Bürgi, Dunitz & Shefter, 1974). The displacement for C(21) is 0·031 Å, while the $O\cdots C{=}O$ angle is 102·6°. The displacements of the C atoms involving the two longer distances are only 0·006 Å and are not significant.

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