Structure of 5,5-Dimethylhydantoin*

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Abstract. $C_5H_8N_2O_2$, $P2_12_12_1$, $a = 7.2160$ (2), $b = 7.2030$ (1), $c = 13.0050$ (4) Å, $Z = 4$, $D_c = 1.254$, $D_o = 1.261$ Mg m^{-3}, $V = 676.0$ Å^3, $M_r = 128.13$, $\lambda(\text{Mo } K\bar{\alpha}) = 0.71073$ Å, $T = 299 \pm 1$ K, $F(000) = 272$. The intensity data were collected on an automated diffractometer, and the structure was solved using direct methods. The structure was refined by least squares in two blocks (non-hydrogen atoms anisotropic, hydrogens isotropic), the refinement converging on a final conventional $R(f)$ value of 4.2% (4.6% weighted) for the 777 significant data. The molecules are packed together by stacking interactions and by hydrogen bonds between N(1) and O(6) and between N(3) and O(6). O(7) apparently does not participate in hydrogen bonding.

Introduction. Structure determinations of antiepileptic drugs and their analogs are of interest in the attempt to discover a plausible molecular basis for their activity. It has been shown that, with the parent compound 5,5-diphenylhydantoin (DPH), aliphatic substitution at the C(5) position destroys the antiepileptic activity and enhances the sedative properties of the drug (Camerman & Camerman, 1970). It is of interest to determine the three-dimensional structure of 5,5-dimethylhydantoin and to examine its hydrogen-bonding properties.

Crystals of 5,5-dimethylhydantoin were obtained from the Sigma Chemical Company, St. Louis, MO, and were recrystallized from hot water. A specimen 0.1 × 0.3 × 0.5 mm was chosen for diffraction study. The space group and approximate cell dimensions were obtained from precession and Weissenberg photographs. Accurate cell dimensions were obtained by the use of least-squares refinement of the observed setting angles for sixteen Mo $K\bar{\alpha}$ reflections in the range 26 < 2θ < 42°, measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Rosenberry, 1968). The density of the crystals was measured by flotation in mixtures of cyclohexane and

dibromomethane. Intensity data were collected on the diffractometer using Nb-filtered Mo $K\bar{\alpha}$ radiation with the θ–2θ scan technique. Of the 925 reflections with $2\theta \leq 55°$, 777 were considered observed $[I > 3\sigma(I)]$. Each intensity was assigned a variance $\sigma^2(I)$ based on counting statistics plus a term $(0.04I)^2$, empirically derived during refinement. No absorption correction was applied ($\mu = 0.919$ cm^{-1}). No significant changes in two standard reflections were observed during the course of data collection.

The structure was readily solved using the direct-methods computer program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The largest absolute figure of merit indicated the correct solution. Refinement of the scale factor, the non-hydrogen atomic positions and their anisotropic temperature factors converged at an $R(f)$ value of 0.083. A difference synthesis at this point revealed the positions of the eight expected hydrogens. Further least-squares refinement, during which the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically, reduced the $R(f)$ value to 0.042. The weighted $R \{[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\}$ and σ, the goodness of fit $\{[\sum w(F_o - F_c)^2/(n - p)]^{1/2}$, where $n = 777$ reflections and $p = 115$ variables$\}$, were 0.046 and 1.15, respectively. The average shift in the final cycle of refinement was 2.3% of the corresponding standard

Table 1. *Positional and isotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms*

The isotropic temperature factor is $\exp\{-8\pi^2 U(\sin \theta/\lambda)^2\}$; the values given are the arithmetic averages of the principal components of the anisotropic temperature factors. Standard deviations in units of the last significant digits are given in parentheses.

	x	y	z	U (Å^2)
N(1)	3141 (4)	−298 (3)	3289 (2)	535 (13)
C(2)	4075 (3)	1170 (3)	2947 (2)	402 (11)
N(3)	3278 (3)	2736 (3)	3370 (2)	423 (11)
C(4)	1871 (4)	2300 (3)	4026 (2)	488 (13)
C(5)	1629 (4)	181 (3)	3986 (2)	476 (13)
O(6)	5404 (3)	1188 (2)	2358 (1)	503 (10)
O(7)	967 (3)	3368 (3)	4531 (2)	800 (15)
C(8)	−250 (5)	−282 (6)	3527 (4)	777 (25)
C(9)	1893 (7)	−694 (5)	5032 (3)	714 (21)

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deviation. The final difference map showed no features exceeding ± 0.2 e Å^{-3}.

Scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) and for the hydrogen atoms from Stewart, Davidson & Simpson (1965). All refinement was done with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final atomic parameters for the non-hydrogen atoms along with their standard deviations, estimated from the inverse of the normal-equations' matrix, are given in Table 1.*

Discussion. A drawing of the molecule, including bond distances and angles, is shown in Fig. 1. The distances and angles around the hydantoin nucleus are normal and compare well with those found in DPH (Camerman & Camerman, 1971) and allantoin (Mootz, 1965). The molecule is nearly planar, as is shown by the torsion angles presented in Table 2.

* Lists of thermal parameters, hydrogen atom parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36575 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
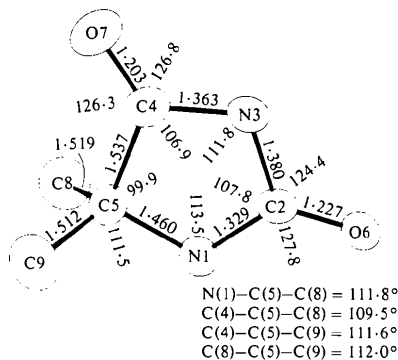

N(1)—C(5)—C(8) = 111·8°
C(4)—C(5)—C(8) = 109·5°
C(4)—C(5)—C(9) = 111·6°
C(8)—C(5)—C(9) = 112·0°

Fig. 1. Bond distances (Å) and angles (°). The boundary thermal ellipsoids are drawn at the 50% probability level. The average standard deviation in the bond lengths and angles is 0·004 Å and 0·2°, respectively. Illustrations were prepared with the aid of the computer program ORTEP (Johnson, 1965).

Table 2. *Torsion angles* (°)

The positive sense of rotation is clockwise while looking along the BC bond.

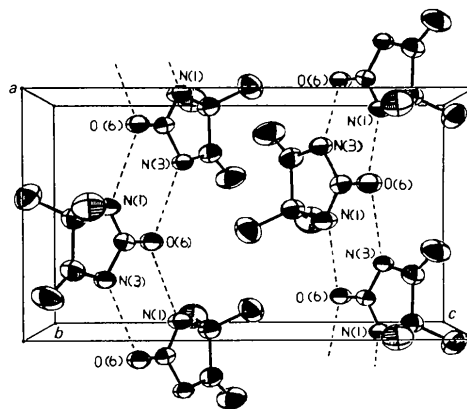| $A-B-C-D$	
N(1)—C(2)—N(3)—C(4)	2·8 (3)
C(2)—N(3)—C(4)—C(5)	−3·7 (3)
N(1)—C(5)—C(4)—N(3)	3·1 (3)
C(2)—N(1)—C(5)—C(4)	−1·6 (3)
N(3)—C(2)—N(1)—C(5)	−0·5 (3)
N(3)—C(4)—C(5)—C(8)	−114·4 (3)
N(3)—C(4)—C(5)—C(9)	121·1 (3)
C(2)—N(1)—C(5)—C(8)	114·1 (3)
C(2)—N(1)—C(5)—C(9)	−119·7 (3)

Fig. 2. Packing interactions. The dashed lines represent hydrogen bonds (ORTEP; Johnson, 1965).

The molecules are hydrogen bonded in ribbons (Fig. 2). The N(1)···O(6) and N(3)···O(6) distances are 2·870 (4) and 2·837 (3) Å, respectively; the N(1)—H(1)···O(6) and N(3)—H(3)···O(6) angles are 173·7 (3) and 168·9 (2)°, respectively. These values compare well with those tabulated by Gartland & Craven (1974). It is interesting to note that O(7) apparently does not participate in hydrogen bonding at all.

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