

We thank the Natural Sciences and Engineering Research Council of Canada for operating grants to CCL and to RJB and BER. We also thank the Canadian International Development Agency for support of YL and the University of Regina for computing time.

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Acta Cryst. (1987). **C43**, 743–745

Structure of the Z Isomer of 5-[(4-Methoxyphenyl)methylene]imidazolidine-2,4-dione

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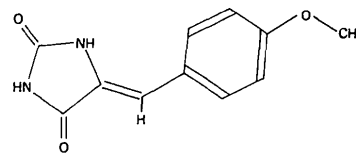
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(Received 16 September 1986; accepted 3 November 1986)

Abstract. $C_{11}H_{10}N_2O_3$, $M_r = 218.22$, triclinic, $P\bar{1}$, $a = 5.350$ (7), $b = 10.327$ (7), $c = 10.073$ (7) Å, $\alpha = 78.7$ (2), $\beta = 78.0$ (2), $\gamma = 105.6$ (3)°, $U = 505.4$ Å³, $Z = 2$, $D_m = 1.40$ (3), $D_x = 1.43$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.66$ cm⁻¹, $F(000) = 228$, room temperature, final $R = 0.078$ for 1217 [$I > 3\sigma(I)$] independent observed reflections. The molecule is planar to within 0.30 (1) Å apart from two of the H atoms of the methoxy group. The bond lengths and angles are as expected except for the C–O bond between the methoxy group and the phenyl ring at 1.353 (5) Å, which is shorter than a normal single bond. The two O atoms of the imidazolidine ring are involved in intermolecular hydrogen bonding [O...H–N 2.86 (1) and 2.89 (1) Å].

Introduction. Substituted compounds of imidazolidine-2,4-dione (also known as hydantoin) are well documented (*Kirk-Othmer Encyclopedia of Chemical Technology*, 1980). Many have physiological activities and are proprietary preparations, especially those disubstituted at the 5-position, a well-known class of which is the spiro-5-hydantoin. Compounds with a methylene linkage at the 5-position are relatively uncommon and no structure determination has so far

been reported. The title compound is a member of this class.



Experimental. Compound prepared as reported elsewhere (Tan, Ang & Fong, 1986). Density measured by flotation in CCl_4 /ligroin. Precession photograph established preliminary cell constants. Crystal of approximate size 0.2 × 0.2 × 0.4 mm mounted on Stoe Stadi-2 diffractometer to rotate about the a axis. Cell dimensions by measurement of about 20 high-angle axial reflections (2θ range 30 to 40°). Intensity data collected via variable-width ω scan, background counts every 20 s, step-scan rate 0.033° s⁻¹, width $(1.5 + \sin\mu/\tan\theta)$. Absorption and extinction corrections not applied. Standard reflections $h2l$ measured every 20 measurements for each layer: no significant variation in intensity. 1737 unique data measured with $2\theta_{\text{max}} 50^\circ$ ($0 \leq h \leq 6$, $-12 \leq k \leq 11$, $-11 \leq l \leq 12$). 1217 data

with $I > 3\sigma(I)$ used in subsequent calculations. Structure solved with the *SOLV* routine of *SHELX86* (Sheldrick, 1986) on the Cray computer at the University of London Computer Centre; other methods tried but unsuccessful. Subsequent refinements and calculations used *SHELX76* (Sheldrick, 1976). Non-hydrogen atoms refined anisotropically before placing H atoms in tetrahedral or trigonal positions. Thermal parameters of H atoms allowed to refine individually except those on methyl group constrained to refine as rigid group with common parameter. Weighting scheme $w = 1/[\sigma^2(F) + 0.002F^2]$, $\sigma(F)$ taken from counting statistics. Final $R(F)$ 0.078 (wR 0.080, S 1.00) and final shift/e.s.d. < 0.05 ; the relatively high R value considered satisfactory in view of the weak diffracting power of the crystals. In final difference map, max. and min. peaks 0.35, -0.38 e \AA^{-3} . Scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j U_{ij}$$

	x	y	z	$U_{eq}(\text{\AA}^2 \times 10^3)$
N(1)	2592 (7)	8129 (4)	5602 (4)	65 (4)
C(2)	4970 (8)	8098 (4)	4803 (4)	65 (5)
N(3)	4693 (7)	6725 (3)	4888 (4)	61 (4)
C(4)	2281 (8)	5874 (4)	5785 (4)	56 (4)
C(5)	855 (7)	6804 (4)	6261 (4)	55 (4)
C(6)	-1573 (8)	6338 (5)	7178 (4)	57 (5)
C(7)	-3286 (7)	7037 (4)	7833 (4)	53 (4)
C(8)	-2696 (8)	8459 (4)	7588 (5)	65 (5)
C(9)	-4415 (9)	9039 (5)	8291 (5)	68 (5)
C(10)	-6769 (7)	8201 (4)	9277 (4)	59 (4)
C(11)	-7424 (8)	6789 (4)	9539 (5)	62 (5)
C(12)	-5700 (8)	6217 (5)	8813 (5)	60 (5)
C(13)	-10700 (10)	8072 (6)	10981 (5)	97 (6)
O(14)	-8291 (6)	8882 (3)	9908 (3)	77 (4)
O(15)	6946 (6)	9077 (3)	4154 (4)	88 (4)
O(16)	1562 (5)	4612 (3)	6130 (3)	69 (4)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

N(1)—C(2)	1.369 (5)	C(7)—C(8)	1.376 (6)
N(1)—C(5)	1.373 (5)	C(7)—C(12)	1.384 (6)
C(2)—N(3)	1.369 (5)	C(8)—C(9)	1.377 (6)
C(2)—O(15)	1.203 (5)	C(9)—C(10)	1.371 (6)
N(3)—C(4)	1.360 (5)	C(10)—C(11)	1.362 (6)
C(4)—C(5)	1.468 (5)	C(10)—O(14)	1.353 (5)
C(4)—O(16)	1.210 (5)	C(11)—C(12)	1.384 (6)
C(5)—C(6)	1.328 (6)	C(13)—O(14)	1.420 (5)
C(6)—C(7)	1.445 (5)		
C(2)—N(1)—C(5)	110.9 (3)	C(6)—C(7)—C(8)	125.5 (4)
N(1)—C(2)—N(3)	106.8 (3)	C(6)—C(7)—C(12)	117.7 (4)
N(1)—C(2)—O(15)	127.3 (4)	C(8)—C(7)—C(12)	116.8 (4)
N(3)—C(2)—O(15)	125.9 (4)	C(7)—C(8)—C(9)	121.6 (4)
C(2)—N(3)—C(4)	111.2 (3)	C(8)—C(9)—C(10)	120.3 (4)
N(3)—C(4)—C(5)	105.7 (3)	C(9)—C(10)—C(11)	119.6 (4)
N(3)—C(4)—O(16)	125.6 (3)	C(9)—C(10)—O(14)	115.3 (4)
C(5)—C(4)—O(16)	128.6 (3)	C(11)—C(10)—O(14)	125.2 (3)
N(1)—C(5)—C(4)	105.2 (3)	C(10)—C(11)—C(12)	119.6 (4)
N(1)—C(5)—C(6)	131.8 (4)	C(7)—C(12)—C(11)	122.0 (4)
C(4)—C(5)—C(6)	123.0 (4)	C(10)—O(14)—C(13)	117.9 (3)
C(5)—C(6)—C(7)	132.7 (4)		

Atomic coordinates are given in Table 1, interatomic distances and angles in Table 2.*

Discussion. In most hydantoin which are mono- or disubstituted at the 5-position, the imidazolidine ring is planar with the N(1)—C(5) and C(4)—C(5) distances in the range 1.45–1.48 and 1.51–1.55 \AA respectively; the N(1)—C(5)—C(4) bond angle is 99–101 $^\circ$ (Camerman & Camerman, 1971; Florencio, Smith-Verdier & Garcia-Blanco, 1978*a,b*; Fujiwara & Van der Veen, 1979; Koch, Germain, Declercq & Dusausoy, 1975; Smith-Verdier, Florencio & Garcia-Blanco, 1977, 1979). The five-membered ring in the present molecule is also planar but the corresponding values are 1.373 (5), 1.468 (5) \AA and 105.2 (3) $^\circ$ respectively, which are closer to those observed for a 2-thiohydantoin with a double-bond linkage at the 5-position (Thieme & Haedicke, 1978). The larger angle is most likely due to the shorter bond lengths, which in turn are due to sp^2 hybridization at C(5) and an increase in the π -electron delocalization arising from the methylene linkage at the 5-position. Bond lengths and angles in the phenyl ring are normal. The C(6)—C(7) and C(10)—O(14) bond lengths at 1.445 (5) and 1.353 (5) \AA are shorter than expected for single bonds but not as short as those for double bonds. Partial double-bond character is indicated.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43509 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Least-squares planes for the molecule

Distances of atoms from the two planes are given in \AA . Atoms not contributing to the plane are marked with an asterisk.

Plane 1. N(1) -0.01 (1), C(2) 0.02 (1), N(3) -0.02 (1), C(4) 0.01 (1), C(5) 0.03 (1), C(6)* 0.05 (1), O(15)* 0.08 (1), O(16)* 0.07 (1).
Plane 2. C(7) 0.01 (1), C(8) 0.00 (1), C(9) -0.01 (1), C(10) 0.01 (1), C(11) 0.00 (1), C(12) -0.01 (1), C(6)* 0.06 (1), C(13)* 0.07 (1), O(14)* 0.00 (1).

Angle between plane 1 and plane 2: 5.4 (3) $^\circ$.

Note: Plane 1 is that of the imidazolidine ring and 2 the benzene ring.

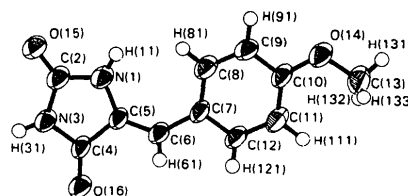


Fig. 1. The structure of the molecule with numbering scheme. Thermal ellipsoids are shown at 50% probability.

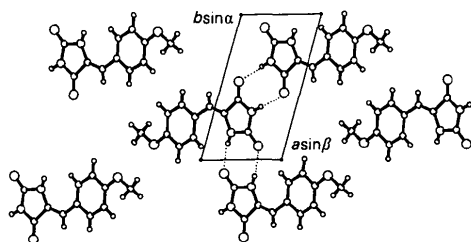


Fig. 2. Packing diagram of one layer of the molecules in the *c* projection. Hydrogen bonds are shown as dotted lines.

The most unusual feature of the molecule is its virtual flatness. The molecule is essentially made up of two planes of atoms (the imidazolidine-2,4-dione ring and the benzene ring) with an angle of $5.4(3)^\circ$ between them (least-squares planes in Table 3). This implies there are two possible conformers but both are present in the crystal as required by the $P\bar{1}$ symmetry. The near coplanarity of all the non-hydrogen atoms could be due to extensive conjugation in the molecule as well as packing interactions in the crystal. One important consequence of this is that there are two possible orientations of the C(13)—O(14) bond, giving rise to two conformers. This molecule is one of the two possible *Z* isomers and the structure is shown in Fig. 1.

Extensive hydrogen bonding is present in the crystal with the participation of N-hydrogen and oxygen atoms of the imidazolidine ring, as is common to many hydantoin. Bond distances and angles are as follows: N(1)···O(15ⁱ) 2.89(1), H(11)···O(15ⁱ) 2.09(1) Å, N(1)—H(11)···O(15ⁱ) 166(1), C(2)—O(15)···H(11ⁱ) 98(1) $^\circ$ [(i) symmetry element: $1-x, 2-y, 1-z$];

N(3)···O(16ⁱⁱ) 2.86(1), H(31)···O(16ⁱⁱ) 1.99(1) Å, C(4)—O(16)···H(31ⁱⁱ) 120(1), N(3)—H(31)···O(16ⁱⁱ) 168(1) $^\circ$ [(ii) symmetry element: $1-x, 1-y, 1-z$]. There is a short O(14)···O(14ⁱⁱⁱ) distance of 3.32(1) Å [(iii) symmetry element: $-2-x, 2-y, 2-z$] but no other intermolecular distances of note. Fig. 2 shows these intermolecular hydrogen bonds.

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Acta Cryst. (1987). C43, 745–748

Structure of the *Z* Isomer of 5-Benzylidene-1-methylhydantoin

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Abstract. 5-Benzylidene-1-methyl-2,4-imidazolidinedione, C₁₁H₁₀N₂O₂, $M_r = 202.21$, monoclinic, $P2_1/c$, $a = 8.640(7)$, $b = 15.340(9)$, $c = 7.550(7)$ Å, $\beta = 109.0(2)^\circ$, $U = 946.1$ Å³, $Z = 4$, $D_m = 1.33(5)$, $D_x = 1.42$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.60$ cm⁻¹,

$F(000) = 424$, room temperature, final $R = 0.057$ for 1286 [$I > 3\sigma(I)$] independent observed reflections. The molecule consists of two planar groups (the 2,4-imidazolidinedione and benzene rings) with an angle of $45.9(3)^\circ$ between them. Although intermolecular