

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) \cdots O(15ⁱ) 2.89 (1), H(11) \cdots O(15ⁱ) 2.09 (1) Å, N(1)—H(11) \cdots O(15ⁱ) 166 (1), C(2)—O(15) \cdots H(11ⁱ) 98 (1) $^\circ$ [(i) symmetry element: $1-x, 2-y, 1-z$];

N(3) \cdots O(16ⁱⁱ) 2.86 (1), H(31) \cdots O(16ⁱⁱ) 1.99 (1) Å, C(4)—O(16) \cdots H(31ⁱⁱ) 120 (1), N(3)—H(31) \cdots O(16ⁱⁱ) 168 (1) $^\circ$ [(ii) symmetry element: $1-x, 1-y, 1-z$]. There is a short O(14) \cdots 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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Structure of the Z Isomer of 5-Benzylidene-1-methylhydantoin

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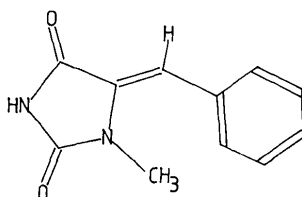
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Abstract. 5-Benzylidene-1-methyl-2,4-imidazolidinedione, $C_{11}H_{10}N_2O_2$, $M_r = 202.21$, monoclinic, $P2_1/c$, $a = 8.640(7)$, $b = 15.340(9)$, $c = 7.550(7)$ Å, $\beta = 109.0(2)^\circ$, $U = 946.1$ Å³, $Z = 4$, $D_m = 1.33(5)$, $D_x = 1.42$ 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

hydrogen bonds are observed in the molecule they are not as extensive as in the case where both imine H atoms in the imidazolidine ring are unsubstituted.

Introduction. Compounds of 2,4-imidazolidinedione (also known as hydantoin) are well known (*Kirk-Othmer Encyclopedia of Chemical Technology*, 1980), except for those with a methylene linkage at the 5-position which are relatively uncommon. In a previous structure determination (Drew, Mok, Ang & Tan, 1987a) it was reported that the *Z* isomer of 5-[(4-methoxyphenyl)methylene]-2,4-imidazolidinedione was flat within 0.30 Å despite the presence of strain caused by the proximity of two H atoms: the imine H atom at the 1-position of the five-membered ring and the *ortho*-position H atom in the phenyl ring. The effect of the presence of a methyl group at the 1-position in the related molecule 5-benzylidene-1-methyl-2,4-imidazolidinedione is now reported.



Experimental. Compound prepared as described elsewhere (Ang, Tan & Fong, 1986). Density measured by flotation in CCl_4 /ligroin. Precession photograph established preliminary cell constants. Crystal of approximate size 0.4 × 0.6 × 0.6 mm mounted on Stoe Stadi-2 diffractometer to rotate about the *a* axis. Cell dimensions by measurement of about 20 high-angle axial reflections (θ range 30 to 40°). Intensity data collected *via* variable-width ω scan, background counts 20 s, step-scan rate 0.033° s⁻¹, width (1.5 + sin μ /tan θ). Absorption and extinction corrections not applied. Standard reflections *h*22 measured every 2 θ measurements for each layer: no significant variation in intensity. 1999 data measured with 2 θ_{max} 50° (0 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 18, -8 ≤ *l* ≤ 8). 1286 unique data with *I* > 3 σ (*I*) used in subsequent calculations, R_{int} = 0.06. Structure solved by using *SHELX76* (Sheldrick, 1976), which was also used for subsequent refinements (on *F*) and calculations. Non-H atoms refined anisotropically before placing H atoms in tetrahedral or trigonal positions. Methyl group refined as rigid group. Thermal parameters of H atoms in imine and methylene groups allowed to refine individually; those on phenyl ring and methyl group constrained to refine with common parameters. Weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$, $\sigma(F)$ taken from counting statistics. Final *R* 0.057 (wR 0.064, *S* 1.00) and final shift/e.s.d. ratio < 0.01. In final difference map, max. and min. peaks 0.16, -0.25 e Å⁻³. Scattering factors

from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1, interatomic distances and angles in Table 2.*

Discussion. It has been noted that the imidazolidine ring is planar in most hydantoins which are mono- or disubstituted at the 5-position, with the N(1)–C(5) and C(4)–C(5) distances and N(1)–C(5)–C(4) bond angle in the ranges 1.45 to 1.48, 1.51 to 1.55 Å and 99 to 101° respectively (Camerman & Camerman, 1971; Florencio, Smith-Verdier & Garcia-Blanco, 1978; Fujiwara & Van der Veen, 1979; Koch, Germain, Declercq & Dusauso, 1975; Smith-Verdier, Florencio & Garcia-Blanco, 1977, 1979). However, these corresponding values shift to about 1.38, 1.47 Å and 105°

* 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 43619 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	<i>x</i>	<i>y</i>	<i>z</i>	\bar{U} (Å ² × 10 ³)*
N(1)	7552 (2)	330 (1)	4837 (3)	60 (2)
C(2)	7874 (3)	1006 (2)	6061 (3)	60 (3)
N(3)	8580 (3)	1650 (1)	5302 (3)	66 (2)
C(4)	8798 (3)	1400 (1)	3672 (3)	59 (2)
C(5)	8141 (3)	507 (1)	3347 (3)	57 (2)
C(6)	8141 (3)	47 (2)	1851 (3)	63 (2)
C(7)	7321 (3)	-756 (2)	1076 (3)	58 (2)
C(8)	5720 (3)	-919 (1)	1045 (3)	63 (2)
C(9)	4893 (3)	-1637 (2)	161 (3)	63 (2)
C(10)	5653 (3)	-2203 (2)	-728 (3)	67 (3)
C(11)	7227 (3)	-2052 (2)	-716 (3)	80 (3)
C(12)	8058 (3)	-1335 (2)	169 (3)	71 (2)
C(13)	7118 (3)	-508 (2)	5411 (4)	77 (3)
O(14)	7602 (3)	1040 (1)	7539 (3)	91 (3)
O(15)	9385 (2)	1822 (1)	2677 (2)	73 (2)

$$* \bar{U} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j U_{ij}$$

Table 2. Molecular dimensions, distances in Å, angles in °

N(1)–C(2)	1.355 (3)	C(5)–C(6)	1.332 (3)
N(1)–C(5)	1.404 (3)	C(6)–C(7)	1.446 (3)
N(1)–C(13)	1.445 (3)	C(7)–C(8)	1.399 (3)
C(2)–N(3)	1.380 (3)	C(7)–C(12)	1.395 (3)
C(2)–O(14)	1.214 (3)	C(8)–C(9)	1.363 (3)
N(3)–C(4)	1.360 (3)	C(9)–C(10)	1.386 (3)
C(4)–C(5)	1.472 (3)	C(10)–C(11)	1.377 (4)
C(4)–O(15)	1.220 (3)	C(11)–C(12)	1.365 (3)
C(2)–N(1)–C(5)	110.5 (2)	N(1)–C(5)–C(6)	132.6 (2)
C(2)–N(1)–C(13)	119.5 (2)	C(4)–C(5)–C(6)	121.9 (2)
C(5)–N(1)–C(13)	127.6 (2)	C(5)–C(6)–C(7)	131.2 (2)
N(1)–C(2)–N(3)	106.6 (2)	C(6)–C(7)–C(8)	120.8 (2)
N(1)–C(2)–O(14)	127.0 (2)	C(6)–C(7)–C(12)	119.9 (2)
N(3)–C(2)–O(14)	126.5 (2)	C(8)–C(7)–C(12)	119.0 (2)
C(2)–N(3)–C(4)	112.6 (2)	C(7)–C(8)–C(9)	120.7 (2)
N(3)–C(4)–C(5)	104.7 (2)	C(8)–C(9)–C(10)	119.2 (2)
N(3)–C(4)–O(15)	128.0 (2)	C(9)–C(10)–C(11)	121.0 (2)
C(5)–C(4)–O(15)	127.3 (2)	C(10)–C(11)–C(12)	120.0 (2)
N(1)–C(5)–C(4)	105.5 (2)	C(7)–C(12)–C(11)	120.1 (2)

respectively when there is a methylene linkage at the 5-position (Drew *et al.*, 1987a; Thieme & Haedicke, 1978). In this molecule the five-membered ring is also planar and the corresponding values are 1.404 (3), 1.472 (3) Å and 105.5 (2)° respectively. Otherwise the bond lengths and angles in both the imidazolidine and the phenyl rings are normal. The C(6)–C(7) bond length at 1.446 (3) Å is shorter than expected for a single bond but much longer than that for a double bond.

In the *Z* isomer of a 5-arylmethylenehydantoin molecule with no substitutions at the N(1) atom and the *ortho* positions of the phenyl ring, it is possible for the molecule to be planar as found in the case of 5-[4-methoxyphenyl)methylene]hydantoin (Drew *et al.*, 1987a). In the present molecule the large methyl group at the N(1) position makes it impossible to have a

Table 3. *Least-squares planes for molecule*

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

Plane 1. N(1) –0.02 (1), C(2) 0.02 (1), N(3) –0.01 (1), C(4) 0.01 (1), C(5) 0.01 (1), C(6)* 0.02 (1), C(13)* 0.27 (1), O(14)* 0.08 (1), O(15)* –0.02 (1)

Plane 2. C(6)* –0.14 (1), C(7) 0.00 (1), C(8) 0.00 (1), C(9) 0.00 (1), C(10) 0.00 (1), C(11) 0.00 (1), C(12) 0.00 (1).

Angle between plane 1 and plane 2: 45.9 (3)°

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

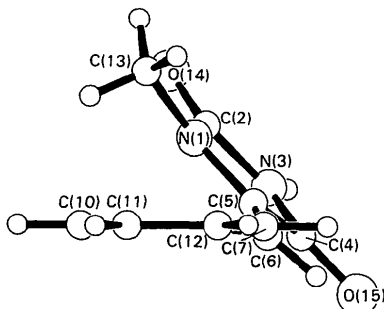


Fig. 1. View of the molecule along the plane of the benzene ring.

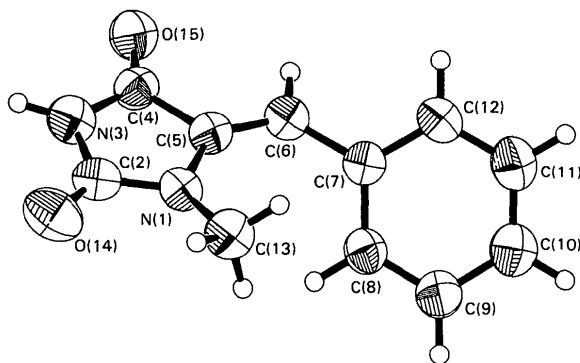


Fig. 2. The structure of the molecule with numbering scheme. Thermal ellipsoids are shown at 50% probability.

Table 4. *Angles around the C(5) atom in two 5-arylmethylenehydantoin* (°)

	(1)	(2)
N(1)–C(5)–C(4)	105.5 (2)	105.1 (2)
N(1)–C(5)–C(6)	132.6 (2)	131.8 (2)
C(4)–C(5)–C(6)	121.9 (2)	123.0 (2)

(1) This molecule.

(2) *Z* isomer of 5-[4-methoxyphenyl)methylene]-2,4-imidazolidinedione (Drew *et al.*, 1987a).

planar structure; as a result the benzene ring is rotated 45.9 (3)° with respect to the imidazolidine ring as shown in Fig. 1 (see Table 3). This means there are two equivalent conformations for the *Z* isomer with both present in the crystal as required by the centrosymmetric space group. The molecule is shown in Fig. 2. The twisted structure probably reduces efficient molecular packing and results in a lower melting point (408–409 K) compared to that for the *E* isomer (460–461 K) which is relatively flat (Drew, Mok, Ang & Tan, 1987b) with an angle of intersection of 5.7 (3)°.

One interesting feature in the structure of this molecule concerns the C(5) atom. The N(1)–C(5)–C(4) angle in the five-membered ring is around 105° in the 5-arylmethylenehydantoin as mentioned earlier and is 105.5 (2)° in the present molecule. The N(1)–C(5)–C(6) and C(4)–C(5)–C(6) angles in this molecule are 132.6 (2) and 121.9 (2)° but these values are reversed in the *E* isomer. The sum of the three angles around the C(5) atom is close to 360° in each case; thus the C(5) atom has a distorted trigonal environment. The difference between the angles in the *Z* and *E* isomers must be due to interatomic repulsions between the methyl group and the phenyl ring despite the rotation of 45.9 (3)° in this molecule. These values are compared in Table 4.

Intermolecular hydrogen bonds are observed, although not as extensively as in the case of 5-[4-methoxyphenyl)methylene]hydantoin. The N(3)–H(31)···O(15ⁱ) and H(31)···O(15ⁱ) distances are 2.90 (1) and 2.04 (3) Å respectively while the N(3)–H(31)···O(15ⁱ) angle is 168 (3)° [symmetry code (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$].

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Structures of *O*-Palmitoyl Benzophenone Oxime (I) and (*E*)-*O*-Palmitoyl Phenyl 2-Pyridyl Ketone Oxime (II)

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Abstract. (I): diphenylmethyleamino palmitate, $C_{29}H_{41}NO_2$, $M_r = 435.7$, triclinic, $P\bar{1}$, $a = 5.764$ (4), $b = 8.997$ (3), $c = 25.576$ (7) Å, $\alpha = 81.79$ (2), $\beta = 84.62$ (3), $\gamma = 86.78$ (4)°, $V = 1305.7$ Å³, $Z = 2$, $D_m = 1.100$, $D_x = 1.108$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.0735$ mm⁻¹, $F(000) = 476$, $T = 296$ K, $R = 0.058$ for 4545 observed reflections. (II): phenyl-(2-pyridyl)methyleamino palmitate, $C_{28}H_{40}N_2O_2$, $M_r = 436.6$, monoclinic, $P2_1/n$, $a = 8.195$ (2), $b = 54.46$ (1), $c = 5.800$ (1) Å, $\beta = 96.78$ (2)°, $V = 2570.4$ Å³, $Z = 4$, $D_m = 1.125$, $D_x = 1.128$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 0.554$ mm⁻¹, $F(000) = 952$, $T = 296$ K, $R = 0.060$ for 2731 observed reflections. The C=N part of the molecule is nearly coplanar with the *trans*-zigzag palmitoyl plane for both (I) and (II). (II) has an unusual eclipsed form about the N–O–C(=O)–C bond in contrast to the *anti* form of (I). The C=N distances are 1.280 (3) Å for (I) and 1.273 (5) Å for (II), and the N–O distances are 1.435 (2) Å for (I) and 1.439 (2) Å for (II). The palmitoyl chains of (I) are packed in a T'' subcell, while those of (II) are packed in a new type of subcell hybridizing the T'' and M'' packings.

Introduction. (*E*)-Phenyl 2-pyridyl ketone *O*-acyl oximes and their related compounds were synthesized to study their selective reactions for different classes of amines. The selective reactions for primary and *N*-methyl secondary amines are of special interest in relation to their molecular recognition by epinephrine derivatives at their receptor sites (Miyasaka, Noguchi, Taga, Kajiwara & Fuji, 1986). Molecular dimensions of oxime groups in crystalline states have been discussed

in connection with their intermolecular hydrogen bonds formed by the oxime OH group (Bertolasi, Gilli & Veronese, 1982; Jerslev, 1983), but structures of *O*-substituted oximes have been determined for only a few crystals, e.g. 4,4'-dibromobenzophenone oxime *O*-picryl ether (McCullough, Paul & Curtin, 1972) and *O*-(4-bromobenzoyl) 1,2-benzisoxazol-3-yl phenyl ketone oxime (Sax, Pletcher, Scholtz, Gerkin & Pinkus, 1971). This paper describes two structures of the title *O*-palmitoyl oximes, X-ray studies of which were undertaken in order to elucidate the structural properties of the *O*-substituted oxime moieties. The pyridine group in (II) is changed to a phenyl group in (I), and the effects of this change of aromatic groups on the molecular structure and on the molecular packing are discussed.

Experimental. Colourless crystals, (I) 0.2 × 0.2 × 0.3 mm and (II) 0.2 × 0.2 × 0.2 mm, on a Rigaku AFC-5RU; lattice parameters (I) from 20 reflections ($21.7 < 2\theta < 31.0^\circ$) with Mo $K\alpha$ and (II) from 25 reflections ($46.6 < 2\theta < 56.6^\circ$) with Cu $K\alpha$; densities by flotation method. Intensities collected in an ω -2 θ scanning mode; (I) 7197 measured reflections (h 0→8, k -12→12, l -34→34) within $2\theta = 60^\circ$ using Mo $K\alpha$, and (II) 4068 measured reflections (h -9→9, k 0→39, l 0→6) within $2\theta = 120^\circ$ using Cu $K\alpha$; three standard reflections recorded every 56 reflections, no change greater than 2% in intensity; Lorentz-polarization corrections applied, no absorption correction. Both structures solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-matrix least-squares refinement minimizing $\sum w(|F_o| -$