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Structure of 3-Benzoylbenzamide Oxime

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Abstract. 3-(α-Hydroxyiminobenzyl)benzamide, $C_{14}H_{12}N_2O_2$, $M_r = 240.26$, orthorhombic, *Pbca*, $a = 7.9333 (7)$, $b = 25.947 (2)$, $c = 11.855 (1)$ Å, $V = 2440.30$ Å^3, $Z = 8$, $D_x = 1.308$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.57$ cm^{-1}, $F(000) = 1008$, $T = 295$ K, $R = 0.0423$, $wR = 0.0467$ for 1487 reflections $[|F| \geq 3.92\sigma(F)]$. Intermolecular hydrogen bonds between amide and oxime groups, and between amide groups were observed.

Introduction. As part of our studies on the hydrogen-bond interactions in the packing of molecules containing both amide and oxime groups, compared with molecules containing both carboxylic acid and oxime groups, we determined the crystal structure of the title compound. The results and a comparison of the dominant packing features with those of related compounds are reported herein.

Experimental. 3-Benzoylbenzoic acid was converted to the amide oxime by treatment with $SOCl_2$ followed by aqueous ammonia and, finally, hydroxylamine hydrochloride solution. The product after recrystallization from ethanol/water solution had m.p. 466.8–467.4 K. A pale-yellow prismatic crystal of dimensions *ca* 0.42 × 0.19 × 0.17 mm was used for data collection. The lattice constants were obtained by least-squares treatment of 42 reflections with $9.48 \leq 2\theta \leq 20.53°$. 2143 unique reflections were measured at room temperature using the ω–2θ scan mode on a Syntex $P2_1$ single-crystal diffractometer to $2\theta \leq 50°$ ($0 \leq h \leq 9$, $0 \leq k \leq 30$, $0 \leq l \leq 14$). Graphite-monochromated Mo $K\alpha$ radiation was used for data collection. The systematic absences ($0kl$, k odd; $h0l$, l odd; $hk0$, h odd) indicated *Pbca* as the space group. No significant variation in the intensities of three standard reflections was observed during the data collection. The data were corrected for Lorentz–polarization effects but not for absorption or extinction. The structure was solved using the *SHELXS*86 direct-methods program (Sheldrick, 1986) and refined by use of the *SHELX*76 program (Sheldrick, 1976). All of the non-H atoms were located from an E map resulting in an agreement factor of 0.17, which decreased to 0.12 after refinement of positional and isotropic thermal parameters. Further refinement with anisotropic thermal parameters gave an R factor of 0.081. The H atoms attached to the benzene rings were located according to geometrical conditions. The amide and the oxime H atoms were located from the difference Fourier map. Refinement of a model with positional and anisotropic thermal parameters for the non-H atoms and with positional and isotropic thermal parameters for the other atoms, and the use of weights $w_i = 2.85/\sigma^2(F_i)$, resulted in $R = 0.0423$, $wR = 0.0467$ and GOF = 1.787. The peaks on the final difference map were in the range −0.19–0.16 e Å^{-3}. The ratios of shifts to e.s.d.'s in the last cycle of refinement were less than 0.005 with an average value of 0.001. The ratio of reflections to refined parameters was 1487/211 = 7.05. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B).*

Discussion. The molecular structure and the atom numbering are shown in Fig. 1. The atomic coordinates are given in Table 1. The bond lengths and angles involving the non-H atoms are listed in Table 2. The configuration of the oxime group is such that the hydroxyl group is *syn* to the benzamide ring. The oxime group does not lie in the plane of either phenyl ring. The dihedral angles between the plane defined by atoms C8, N1 and O1, and the planes of the rings C1–C6 and C9–C14 are 60.7 and 23.3°, respectively. The C3 and C9 atoms are almost copla-

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* Lists of H-atom coordinates, bond distances and angles involving H atoms, anisotropic thermal parameters, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55095 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1001]

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Table 1. *Fractional atomic coordinates and isotropic/equivalent isotropic thermal parameters* (Å^2)

U_{iso} for H atoms. $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

	x	y	z	U_{iso}/U_{eq}
O1	0.1259 (3)	0.58069 (7)	0.7497 (2)	0.057 (1)
O2	−0.3734 (2)	0.55203 (7)	0.9665 (2)	0.058 (1)
N1	0.1548 (3)	0.63414 (7)	0.7551 (2)	0.049 (1)
N2	−0.3056 (3)	0.49688 (8)	1.1031 (2)	0.051 (1)
C1	−0.0979 (3)	0.56060 (8)	1.0429 (2)	0.038 (1)
C2	−0.0522 (3)	0.59367 (9)	0.9568 (2)	0.039 (1)
C3	0.1015 (3)	0.61900 (8)	0.9566 (2)	0.040 (1)
C4	0.2097 (3)	0.6118 (1)	1.0469 (2)	0.051 (1)
C5	0.1646 (3)	0.5791 (1)	1.1344 (2)	0.058 (2)
C6	0.0128 (3)	0.5531 (1)	1.1316 (2)	0.048 (1)
C7	−0.2677 (3)	0.53586 (8)	1.0350 (2)	0.042 (1)
C8	0.1471 (3)	0.65152 (9)	0.8573 (2)	0.041 (1)
C9	0.1757 (3)	0.70778 (9)	0.8705 (2)	0.043 (1)
C10	0.1102 (3)	0.7341 (1)	0.9628 (3)	0.057 (2)
C11	0.1264 (4)	0.7873 (1)	0.9707 (3)	0.072 (2)
C12	0.2076 (5)	0.8142 (1)	0.8865 (3)	0.078 (3)
C13	0.2758 (5)	0.7884 (1)	0.7968 (3)	0.080 (2)
C14	0.2617 (4)	0.7355 (1)	0.7875 (3)	0.062 (2)
H1N	−0.227 (3)	0.4817 (8)	1.140 (2)	0.031 (6)
H2N	−0.406 (4)	0.4796 (10)	1.099 (2)	0.063 (8)
HO	0.145 (4)	0.573 (1)	0.680 (3)	0.11 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

C—H, O—H and N—H bond lengths are in the range 0.86–1.02 Å

O1—N1	1.407 (3)	O1—N1—C8	112.2 (2)
C1—C2	1.382 (3)	C2—C1—C6	118.8 (2)
C2—C3	1.385 (3)	C2—C1—C7	117.1 (2)
C3—C4	1.385 (3)	C6—C1—C7	124.0 (2)
C4—C5	1.386 (4)	C1—C2—C3	121.8 (2)
C1—C6	1.383 (3)	C2—C3—C4	118.7 (2)
C5—C6	1.381 (4)	C2—C3—C8	118.9 (2)
O2—C7	1.240 (3)	C4—C3—C8	122.4 (2)
N2—C7	1.329 (3)	C3—C4—C5	120.0 (2)
C1—C7	1.496 (3)	C4—C5—C6	120.4 (2)
N1—C8	1.294 (3)	C1—C6—C5	120.2 (2)
C3—C8	1.493 (3)	O2—C7—N2	120.2 (2)
C8—C9	1.486 (3)	O2—C7—C1	120.4 (2)
C9—C10	1.390 (4)	N2—C7—C1	119.5 (2)
C10—C11	1.390 (4)	N1—C8—C3	123.6 (2)
C11—C12	1.377 (5)	N1—C8—C9	115.7 (2)
C12—C13	1.368 (5)	C3—C8—C9	120.6 (2)
C9—C14	1.397 (4)	C8—C9—C10	120.6 (2)
C13—C14	1.382 (4)	C8—C9—C14	120.4 (2)
		C10—C9—C14	119.0 (2)
		C9—C10—C11	120.4 (3)
		C10—C11—C12	119.8 (3)
		C11—C12—C13	120.1 (3)
		C12—C13—C14	121.0 (3)
		C9—C14—C13	119.6 (3)

nar with the oxime group. The dihedral angle between the plane of the amide group and the benzene ring plane is 14.19°. The dihedral angle between the two phenyl rings is 77.7°.

A stereoview of the crystal packing down the *c* axis is shown in Fig. 2. The hydrogen bonds are marked as thin lines. The crystal structure contains three types of intermolecular hydrogen bond: a centrosymmetrically related pair of amide–amide N—H···O bonds, an O—H···O hydrogen bond between the oxime group and a carbonyl group of a molecule related by the glide along **a**, and an N—H···O hydrogen bond between the second amide H atom and an oxime O atom related by inversion and translation in the **a** direction. The observed hydrogen bonds are: N—H2N···O2 2.963 (3) Å and 161 (2)° (centrosymmetric amide–amide); O1—HO···O2 2.669 (3) Å and 164 (3)°; N—H1N···O1 3.021 (3) Å and 153 (2)°. The amide–amide hydrogen bonds are similar to those found in other structures [2.972 (2) Å in nitroacetamide (Thorup, Dreier & Simonsen, 1981); 2.933 (3) Å in benzamide (Blake & Small, 1972); 2.910 (2) Å in *p*-nitrobenzamide (Di Rienzo, Domenicano & Serantoni, 1977)]. The oxime–carbonyl O atom bond is comparable to the oxime–carboxyl distances observed in structures containing both oxime and carboxyl groups (Maurin, Paul & Curtin, 1992*a,b*; Padmanabhan, Paul & Curtin, 1989) and in 4-benzoylbutyramide oxime (Maurin, Paul & Curtin, 1992*c*). The present structure is quite different, however, from that of 4-benzoylbutyramide oxime, where polar chains linked by amide–oxime hydrogen bonds were observed.

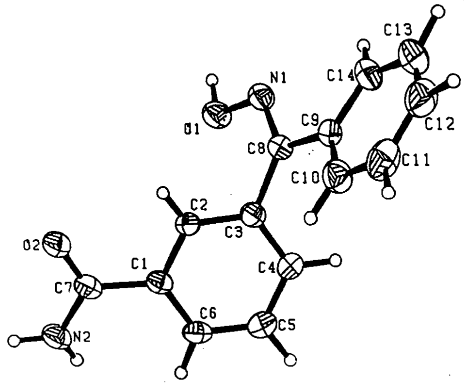

Fig. 1. Conformation of the molecule and numbering of atoms.

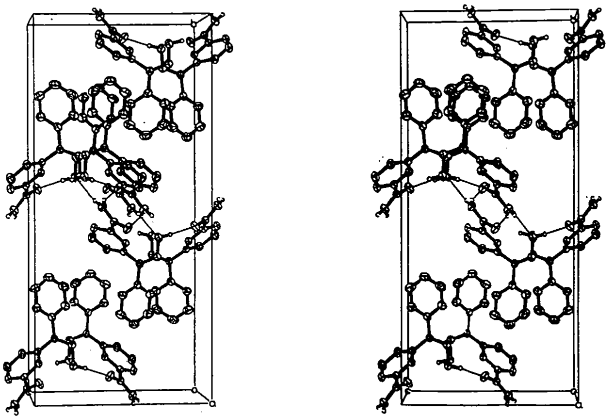

Fig. 2. Stereoview of crystal packing. Hydrogen bonds are marked as thin lines. Only those H atoms involved in hydrogen bonding are represented.

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Structures of Two Bufadienolides: Telocinobufagin (3β,5β-Dihydroxy-5β,14β-bufa-20,22-dienolide) Monohydrate and 14α-Artebufogenin (3β-Hydroxy-15-oxo-5β,14α-bufa-20,22-dienolide)

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Abstract. Telocinobufagin monohydrate (1), $C_{24}H_{34}O_5.H_2O$, $M_r = 420.55$, orthorhombic, $P2_12_12_1$, $a = 14.348\ (4)$, $b = 13.086\ (4)$, $c = 11.851\ (2)$ Å, $V = 2225\ (2)$ Å^3, $Z = 4$, $D_x = 1.255$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.83$ cm^{-1}, $F(000) = 912$, $T = 296\ (1)$ K, $R = 0.042$ for 2142 unique observed reflections. 14α-Artebufogenin (2), $C_{24}H_{32}O_4$, $M_r = 384.52$, orthorhombic, $P2_12_12_1$, $a = 7.920\ (1)$, $b = 11.507\ (1)$, $c = 22.519\ (2)$ Å, $V = 2052.3\ (6)$ Å^3, $Z = 4$, $D_x = 1.244$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 6.26$ cm^{-1}, $F(000) = 832$, $T = 296\ (1)$ K, $R = 0.047$ for 1909 unique observed reflections. The expected isostructuralism of telocinobufagin (5β-hydroxybufalin) with bufalin is hindered by an additional water molecule. Simultaneously, the δ-lactone ring assumes a different rotation about the C(17)—C(20) bond. These together result in a more complicated hydrogen-bond network than that shown by bufalin. In contrast, in 14α-artebufogenin the rotation of the lactone ring about the C(17)—C(20) bond is the same as in bufalin. However, the unusual *cis C*/*D* junction substantially alters its position relative to the other part of the rigid steroid skeleton. This results in one weak head-to-tail hydrogen bond in which the acceptor is the ether O atom of the lactone ring.

Introduction. In the course of the systematic crystal structure analysis of related bufadienolide pairs (Argay, Kálmán, Ribár, Vladimirov & Živanov-Stakić, 1987; Kálmán, Fülöp, Argay, Ribár, Lazar, Živanov-Stakić & Vladimirov, 1988) performed along with studies on the related cardenolides (Kálmán, Argay, Ribár, Vladimirov & Živanov-Stakić, 1984), a recurrent phenomenon termed as 'main-part' isostructuralism has been discovered and summarized recently by Kálmán, Argay, Scharfenberg-Pfeiffer, Höhne & Ribár (1991). The present work tries to establish why telocinobufagin (1) – in contrast with cinobufagin and cinobufotalin (Kálmán *et al.*, 1988) – cannot be isostructural with bufalin (Rohrer, Fullerton, Kitatsuji, Nambara & Yoshii, 1982). The structure determination of 14α-artebufogenin (2) reveals how the epimerization at

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