

differ significantly. They lie considerably below the range for C—S single bonds [1.76–1.83 Å (Rademacher, 1987)] but agree completely with the values 1.659 (2) and 1.666 (2) Å observed in the related zwitterionic compound $S_2C-C[N(CH_3)_2]_2$ (Ziegler, Weber, Nuber & Serhadle, 1987). The same is true for the N—C(methyl) distances which correspond clearly to single bonds. The C1—C2 bond length [1.495 (3) Å] is a little shorter than the average of experimental values for carboxylic anions [1.520 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. The dithioacetate fragment is planar; the only significant deviation from the plane through its four atoms is 0.014 (2) Å for C1. It is tilted to the exactly planar formamidine group $C=N(CH_3)_2$ by 87.6°. The benzene ring has standard dimensions [C—C = 1.382 (11) Å, C—C—C = 120.0 (5)°]. The angle between its plane and the approximately planar fragment defined by atoms C1··C5 and N [with maximum deviations from the least-squares plane of 0.084 (4) Å for C3 and 0.066 (3) Å for C4] amounts to 49.3°.

The molecular packing of (2a) is shown in Fig. 2. All intermolecular contacts are consistent with van der Waals radii.

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Structure of *p*-Acetylbenzoic Acid Oxime

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Abstract. 4-(1-Hydroxyiminoethyl)benzoic acid, $C_9H_9NO_3$, $M_r = 179.18$, orthorhombic, *Pbca*, $a = 7.137$ (1), $b = 14.438$ (3), $c = 16.110$ (3) Å, $V = 1660.0$ (5) Å³, $Z = 8$, $D_x = 1.434$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.02$ cm⁻¹, $F(000) = 752$, $T = 295$ K, $R = 0.0474$, $wR = 0.0493$, for 1268 reflections [$|F| > 3.92\sigma(F)$]. The structure is formed from infinite polar chains of molecules held together by pairs of strong hydrogen bonds between the carboxyl and oxime groups. There are no strong interactions between the approximately antiparallel chains.

Introduction. As part of a study of molecules that crystallize in space groups with polar axes (Curtin &

Paul, 1981), the crystal structure of (–)-(1*S*)-pinonic acid β -oxime was determined in our laboratory (Padmanabhan, Paul & Curtin, 1989). The packing was dominated by chains of pinonic acid oxime molecules held together by hydrogen bonds between the carboxyl and oxime groups. In an attempt to establish how generally this type of hydrogen bonding occurs, we have determined the crystal structures of several molecules containing both the carboxyl and oxime groups. In this paper, we report the structure of *p*-acetylbenzoic acid oxime.

Experimental. The title compound was synthesized by the reaction of *p*-acetylbenzoic acid with

hydroxylamine hydrochloride in alkaline solution. Crystals were obtained from ethanol/water solution by slow evaporation. The melting point was 488.4–490.4 K. A colorless prismatic crystal of dimensions $ca\ 0.23 \times 0.26 \times 0.35\text{ mm}$ was used for data collection. The unit-cell parameters were obtained by least-squares treatment of 21 reflections with $9.5 \leq 2\theta \leq 20^\circ$. The systematic absences ($0kl$, k odd; $h0l$, l odd; $hk0$, h odd) indicated *Pbca* as the space group. 1557 unique reflections were measured using the ω - 2θ -scan mode on a Syntex *P2*₁ single-crystal diffractometer to $2\theta \leq 56^\circ$ ($0 \leq h \leq 8$, $0 \leq k \leq 19$, $0 \leq l \leq 21$). Four low-order reflections of very high intensity could not be measured reliably and were not included in any further calculations. No significant variation in intensities of three standard reflections was detected during data collection. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved using the *SHELXS86* direct-methods program (Sheldrick, 1990), and refined by use of *SHELX76* (Sheldrick, 1976). All of the non-H atoms were located from an *E* map. Least-squares refinement on *F* with anisotropic displacement parameters gave $R = 0.084$. All H atoms were located from a $\Delta\rho$ map. The observation of six maxima of comparable height instead of three in the methyl-group region indicated a rotational disorder around the C—CH₃ bond. The site occupancy factors for both orientations of the methyl group were refined to 0.47 (4) and 0.53 (4), respectively, and a common isotropic thermal parameter for methyl-group H atoms was varied. The final values of *R* and *wR* were 0.0474 and 0.0493, with weights $w_i = 9.4/$

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for the non-H atoms

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
N1	0.1017 (3)	0.5585 (1)	-0.29674 (9)	0.0423 (8)
O1	0.0976 (3)	0.48552 (9)	-0.35478 (9)	0.0578 (9)
O2	0.1094 (2)	0.89671 (9)	0.01270 (8)	0.0540 (8)
O3	0.1005 (2)	0.78503 (9)	0.10849 (8)	0.0504 (8)
C1	0.0998 (3)	0.6033 (1)	-0.1561 (1)	0.0361 (9)
C2	0.0559 (4)	0.6948 (1)	-0.1747 (1)	0.047 (1)
C3	0.0587 (4)	0.7628 (1)	-0.1140 (1)	0.045 (1)
C4	0.1022 (3)	0.7398 (1)	-0.0321 (1)	0.0364 (9)
C5	0.1427 (3)	0.6486 (1)	-0.0128 (1)	0.044 (1)
C6	0.1428 (3)	0.5809 (1)	-0.0739 (1)	0.045 (1)
C7	0.1005 (3)	0.5299 (1)	-0.2211 (1)	0.039 (1)
C8	0.0964 (6)	0.4295 (2)	-0.1979 (2)	0.061 (2)
C9	0.1047 (3)	0.8147 (1)	0.0310 (1)	0.0386 (9)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for the non-H atoms

C—H and O—H bond lengths are in the range 0.87–1.05 \AA

O1—N1	1.409 (2)	O1—N1—C7	112.8 (1)
C1—C2	1.395 (2)	C2—C1—C6	119.0 (2)
C2—C3	1.386 (3)	C2—C1—C9	118.5 (2)
C3—C4	1.390 (3)	C6—C1—C9	122.5 (2)
C4—C5	1.398 (2)	C1—C2—C3	120.1 (2)
C1—C6	1.383 (3)	C2—C3—C4	121.2 (2)
C5—C6	1.386 (3)	C3—C4—C5	118.2 (2)
N1—C7	1.286 (2)	C3—C4—C7	121.7 (2)
C4—C7	1.491 (2)	C5—C4—C7	120.1 (2)
C7—C8	1.497 (3)	C4—C5—C6	120.6 (2)
O2—C9	1.221 (2)	C1—C6—C5	120.8 (2)
O3—C9	1.320 (2)	N1—C7—C4	115.9 (2)
C1—C9	1.484 (2)	N1—C7—C8	123.2 (2)
		C4—C7—C8	120.8 (2)
		O2—C9—O3	122.9 (2)
		O2—C9—C1	122.8 (2)
		O3—C9—C1	114.3 (2)

$[\sigma^2(F_o) + 0.00015F_o^2]$, and $S = 1.98$. The peaks on the final $\Delta\rho$ map were in the range -0.21 – 0.21 e \AA^{-3} . In the last cycle of refinement $(\Delta/\sigma)_{\text{max}}$ was 0.01 with an average value of 0.001. The ratio of reflections/refined parameters was 7.8. 163 parameters were refined. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).*

Discussion. The conformation of the molecule and the numbering of the atoms are shown in Fig. 1. The atomic coordinates are given in Table 1. The bond lengths and angles involving the non-H atoms are given in Table 2. A stereoview of the unit-cell contents is shown in Fig. 2. The dihedral angles between the carboxyl (O2—C9—O3) and oxime (C7—N1—O1) substituent planes and the plane of the six atoms of the benzene ring are 16.4 (2) and 15.8 (1) $^\circ$, respectively. The atoms of both substituents lie almost in the same plane.

* Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55291 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0273]

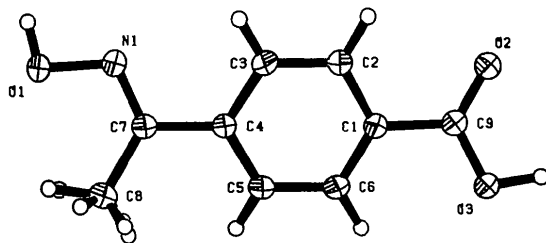


Fig. 1. Conformation of the molecule and the numbering of the atoms.

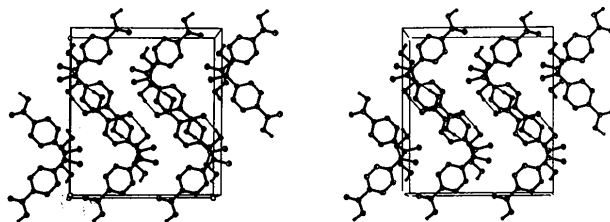


Fig. 2. Stereoview of the unit cell along the *a* axis with *b* across and *c* down the diagram. Only H atoms involved in hydrogen-bond formation are included.

The molecules are almost parallel to the (100) plane in the crystal (Fig. 2). Two strong intermolecular hydrogen bonds, O1—HO1...O2 and O3—HO3...N1, are observed between the carboxyl and oxime groups. The O1...O2 and O3...N1 lengths are 2.731 (2) and 2.727 (2) Å, and the O1—HO1...O2 and O3—HO3...N1 angles are 169 (3) and 176 (2)°, respectively. For a comparison of hydrogen-bond lengths with those observed in carboxylic acid dimers and oxime dimers see Maurin, Paul & Curtin (1992). No other close contacts were observed.

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Structure of 3-Benzoylbenzoic Acid Oxime

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Abstract. 3-(α -Hydroxyiminobenzyl)benzoic acid, C₁₄H₁₁NO₃, $M_r = 241.25$, monoclinic, $P2_1/n$, $a = 9.169$ (1), $b = 9.370$ (1), $c = 13.883$ (2) Å, $\beta = 92.028$ (4)°, $V = 1192.0$ (2) Å³, $Z = 4$, $D_x = 1.345$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.89$ cm⁻¹, $F(000) = 504$, $T = 295$ K, $R = 0.0426$, $wR = 0.0454$ for 1538 reflections [$|F| \geq 3.92\sigma(F)$]. Infinite chains of molecules held together by pairs of strong hydrogen bonds between carboxyl and oxime groups were observed.

Introduction. 3-Benzoylbenzoic acid oxime is the third oxime structure solved in our laboratories (Padmanabhan, Paul & Curtin, 1989; Maurin, Paul & Curtin, 1992), which contains the carboxyl as the second functional group. Structures of different complexity are being studied to determine whether the preference for carboxyl–oxime hydrogen-bond formation is a general rule for this type of compound.

Experimental. The title compound was synthesized by the reaction of 3-benzoylbenzoic acid with hydroxylamine hydrochloride in alkaline solution. The recrystallization of the solid product from ethanol/water solution gave prismatic crystals with a melting point of 475.5–476.4 K. A crystal with dimensions ca 0.22 × 0.10 × 0.55 mm was used for the data collection. The crystal lattice parameters

were obtained by a least-squares treatment of 27 reflections within a 2θ range of 9.84–20.15°. The systematic absences (0 k 0, k odd; h 0 l , $h + l$ odd) indicated $P2_1/n$ as the space group. 2091 unique reflections were measured at room temperature using the ω - 2θ scan mode on a Syntex $P2_1$ single-crystal diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used for data collection. Intensities were collected to $2\theta \leq 50^\circ$ ($0 \leq h \leq 16$, $0 \leq k \leq 11$, $-10 \leq l \leq 10$). Four low-order reflections of very high intensity could not be measured reliably and were not included in any further calculations. No significant variation in the intensities of three standard reflections was observed during data collection. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved using the *SHELXS86* program (Sheldrick, 1990), and refined by use of *SHELXL76* (Sheldrick, 1976). All of the non-H atoms were located from an E map. Least-squares refinement on F with anisotropic displacement parameters gave $R = 0.081$. All H atoms were located from a $\Delta\rho$ map. The inclusion of the H atoms in the model, refinement of their positional and isotropic displacement parameters, and the use of weights $w_i = 1.0/[\sigma^2(F_i) + 0.0001F_i^2]$ gave final values of $R = 0.0426$ and $wR = 0.0453$; $S = 1.720$. The peaks on the final $\Delta\rho$ map were in the range -0.24 – 0.17 e Å⁻³.