C2	0.8121 (3)	0.0137 (3)	0.2717 (2)	0.0476 (8)
C3	0.7479 (3)	−0.0540 (3)	0.3377 (2)	0.0444 (8)
C4	0.7911 (3)	−0.0387 (3)	0.4311 (2)	0.0465 (8)

Table 2. *Selected geometric parameters (Å, °)*

N—C4	1.477 (4)	C3—C4	1.529 (4)
C1—C2	1.519 (4)	C1—O1	1.231 (3)
C2—C3	1.505 (4)	C1—O2	1.248 (3)
C1—C2—C3	112.0 (2)	C2—C1—O1	120.5 (2)
C2—C3—C4	112.9 (3)	C2—C1—O2	117.1 (2)
C3—C4—N	112.2 (2)	O1—C1—O2	122.4 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N—H1A···O2^{i}	0.87 (4)	1.94 (4)	2.797 (3)	172 (3)
N—H1A···O1^{i}	0.87 (4)	2.63 (3)	3.274 (3)	131 (2)
N—H1B···O1^{ii}	0.89 (4)	1.88 (4)	2.764 (3)	178 (4)
N—H1C···O2^{iii}	0.93 (3)	1.85 (3)	2.769 (3)	169 (3)

Symmetry codes: (i) $x, -y, \frac{1}{2}+z$; (ii) $1-y, x-\frac{1}{2}, \frac{1}{4}+z$; (iii) $\frac{1}{2}-y, 1-x, \frac{1}{4}+z$.

Scan widths were $(1.52 + 0.30\tan\theta)^\circ$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment and systematic absences led to unique assignment of the space group as $I4_1cd$ (No. 110); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions.

The maximum effect of extinction was 6.3% of F_o for 220. The maximum peak in the final difference map occurred ~0.9 Å from C2 and C3; the maximum negative peak occurred ~1.0 Å from H1C and ~1.2 Å from N.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

It is a pleasure to acknowledge partial support provided to AJD by a National Needs Fellowship. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3078-3081

2-Acetylbenzoic Acid: Phthalide Form

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(*Received 14 June 1996; accepted 5 August 1996*)

Abstract

In the structure of the phthalide form of 2-acetylbenzoic acid, $C_9H_8O_3$, there is a single type of hydrogen bond. Each molecule donates one and accepts one hydrogen bond. The hydrogen-bonded molecules form sets of puckered ribbons running along the **c** direction which are not crosslinked to each other. The dihedral angle between the planes of adjacent molecules along a hydrogen-bonded ribbon is 77.4 (1)°.

Comment

This study of 2-acetylbenzoic acid is one of a continuing series on hydrogen bonding in carboxylic acids. As expected on the basis of the organic chemical literature, this acid crystallized in its phthalide form, (I). The only previous report on this structure (Gupta & Prasad, 1970) gave somewhat approximate cell parameters and a space-group assignment in agreement with the present results, but provided no atomic coordinates or structural analysis.

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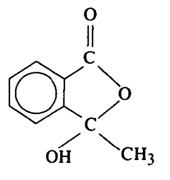
Acta Crystallographica Section C
ISSN 0108-2701 © 1996



(I)

In the phthalide form of the molecule (Fig. 1), the carboxyl atom O1 has transferred its H atom to the acetyl-O atom, O3, and forms a bond with C8 to complete a heterocyclic five-membered ring C1,C7,O1,C8,C2. The single type of hydrogen bond observed in this structure has O3 as donor and $O2^{i}$ [(i) = $1/2 - x, -y, \frac{1}{2} + z$] as acceptor. Thus, each molecule participates in two hydrogen bonds: once as donor and once as acceptor. As shown in Fig 2, the hydrogen bonds occur in sets of puckered ribbons, running along the **c** direction, which are not crosslinked to each other.

The average deviation of atoms C1–C6 from the best-fit plane through them is 0.006 (2) Å, the maximum deviation being 0.010 (2) Å. For the heterocyclic five-membered ring, the corresponding values are 0.008 (2) Å and 0.014 (2) Å. Since the dihedral angle between these two planes is only 1.1 (1)°, the two rings are essentially coplanar; the average deviation of the involved atoms from the best-fit plane through both rings is 0.010 (2) Å while the maximum deviation is 0.026 (2) Å. The dihedral angle between these molecular planes for adjacent molecules along a hydrogen-bonded ribbon is 77.4 (1)°.

With respect to the geometry of the heterocyclic ring, a close analog for comparison is the phthalide of 2-(trifluoroacetyl)benzoic acid for which partial structural results are cited by Prabhu, Eapen & Tamborski (1984); while severe decomposition of the crystal during X-ray data collection limits such comparison, there is general agreement of corresponding bond distances within approximately ±0.03 Å. A second close analog is 3-(*p*-bromophenyl)phthalide whose structure has been determined by Kalyani & Vijayan (1969) using photographic data. The mean deviation of corresponding distances in the five-membered ring between that study and the present study is 0.02 Å, and 1° in the corresponding angles.

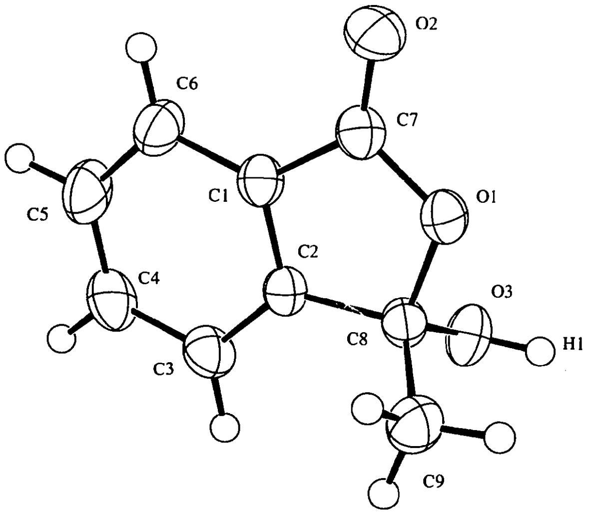


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of 2-acetylbenzoic acid in the phthalide form showing our numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small.

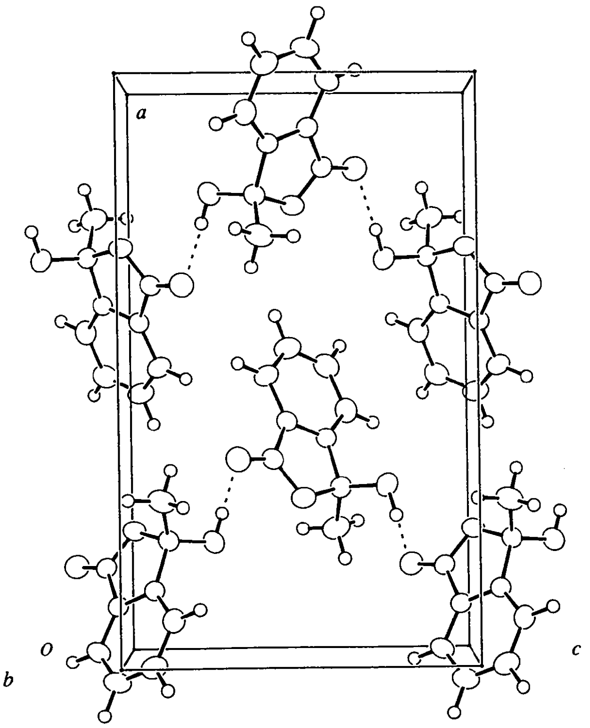


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of the packing of the phthalide form of 2-acetylbenzoic acid. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small. Hydrogen bonds are shown as dashed lines.

In (I), the only intermolecular approach which falls significantly short of the corresponding sum of the Bondi (1964) radii involves the carbonyl at C7 and $H1^{i}$ which forms a hydrogen bond with the (acceptor) O2 atom bonded to C7.

Experimental

2-Acetylbenzoic acid from Pfaltz and Bauer, Inc. was dissolved in ether, treated with Norit-A decolorizing carbon and filtered. Slow evaporation of the filtrate at room temperature produced suitable crystals.

Crystal data

$C_9H_8O_3$
$M_r = 164.16$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
$P2_12_12_1$
$a = 15.962\,(2)$ Å
$b = 5.218\,(2)$ Å
$c = 9.613\,(2)$ Å
$V = 800.7\,(4)$ Å^3
$Z = 4$
$D_x = 1.362$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 15.0$–$17.3°$
$\mu = 0.096$ mm^{-1}
$T = 296$ K
Cut rod
0.39 × 0.35 × 0.35 mm
Light amber

Data collection

AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2125 measured reflections
1123 independent reflections
845 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.022$

$\theta_{\rm max} = 27.50°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 6$
$l = -12 \rightarrow 12$
6 standard reflections monitored every 150 reflections
intensity decay: −5.70%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.034$
$S = 1.40$
845 reflections
114 parameters
$w = 1/\sigma_F^2$
$(\Delta/\sigma)_{\rm max} = < 0.01$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.11$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $19\,(7) \times 10^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965), (H); Cromer & Waber (1974), (C, O)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.21629 (8)	0.1316 (3)	0.0110 (1)	0.0391 (4)
O2	0.14854 (8)	−0.0427 (3)	−0.1688 (2)	0.0483 (4)
O3	0.19662 (9)	0.2189 (3)	0.2459 (1)	0.0449 (4)
C1	0.0867 (1)	0.3014 (4)	−0.0337 (2)	0.0334 (5)
C2	0.1173 (1)	0.4369 (4)	0.0776 (2)	0.0317 (4)
C3	0.0709 (1)	0.6329 (5)	0.1374 (2)	0.0423 (5)
C4	−0.0081 (1)	0.6793 (5)	0.0819 (2)	0.0493 (6)
C5	−0.0389 (1)	0.5394 (5)	−0.0296 (2)	0.0529 (6)
C6	0.0082 (1)	0.3495 (5)	−0.0905 (2)	0.0446 (6)
C7	0.1497 (1)	0.1109 (4)	−0.0742 (2)	0.0348 (5)
C8	0.2023 (1)	0.3340 (4)	0.1169 (2)	0.0340 (5)
C9	0.2742 (1)	0.5198 (5)	0.1039 (2)	0.0495 (6)
H1	0.247 (1)	0.151 (5)	0.270 (3)	0.079 (9)

Table 2. *Selected geometric parameters (Å, °)*

O1—C7	1.347 (2)	C2—C3	1.388 (3)
O1—C8	1.484 (2)	C2—C8	1.506 (3)
O2—C7	1.212 (2)	C3—C4	1.389 (3)
O3—C8	1.381 (2)	C4—C5	1.387 (3)
C1—C2	1.373 (2)	C5—C6	1.375 (3)
C1—C6	1.389 (2)	C8—C9	1.508 (3)
C1—C7	1.466 (3)		
C7—O1—C8	110.8 (1)	C1—C6—C5	117.1 (2)
C2—C1—C6	122.3 (2)	O1—C7—O2	121.4 (2)
C2—C1—C7	108.2 (2)	O1—C7—C1	109.0 (2)
C6—C1—C7	129.5 (2)	O2—C7—C1	129.6 (2)
C1—C2—C3	120.8 (2)	O1—C8—O3	108.4 (2)
C1—C2—C8	109.4 (2)	O1—C8—C2	102.6 (1)
C3—C2—C8	129.8 (2)	O1—C8—C9	106.6 (2)
C2—C3—C4	117.0 (2)	O3—C8—C2	108.8 (2)
C3—C4—C5	121.8 (2)	O3—C8—C9	113.8 (2)
C4—C5—C6	121.0 (2)	C2—C8—C9	115.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O2$^{\rm i}$	0.90 (2)	1.86 (2)	2.761 (2)	174 (2)

Symmetry code: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

Scan widths were $(1.58 + 0.35\tan\theta)°$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and the lack of centrosymmetry indicated by the intensity statistics led to the unique assignment of the space group as $P2_12_12_1$ (No. 19); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. In the latter stages of refinement all H atoms except H1 were made canonical with C—H distance = 0.98 Å and $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached atom. H1 was refined isotropically.

The maximum effect of extinction was 4.2% of F_o for $20\bar{1}$. The maximum peak in the final difference map occurred approximately 0.8 Å from C8 and C9; the maximum negative peak occurred near the center of the C1–C6 ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3081-3083

Coumarin-3-carboxylic Acid

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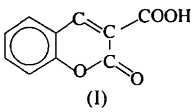
(*Received 25 June 1996; accepted 5 September 1996*)

Abstract

In the structure of the title compound, $C_{10}H_6O_4$, there is a single intramolecular hydrogen bond. In addition, there are a number of significant intermolecular C—H···O attractive interactions. These interactions account in part for the rather high density for an ordinary monocarboxylic acid, 1.522 Mg m^{-3}.

Comment

Coumarin-3-carboxylic acid, (I), was apparently first described over a century ago by Stuart (1886) who synthesized it from salicylaldehyde and malonic acid in glacial acetic acid. This structural study of the acid is one of a continuing series on hydrogen bonding in carboxylic acids. In this structure, there is a single intramolecular hydrogen bond which is depicted in Figs. 1 and 2 and whose geometric parameters are given in Table 3. In addition, as discussed below, there are a number of significant intermolecular C—H···O attractive interactions.



(I)

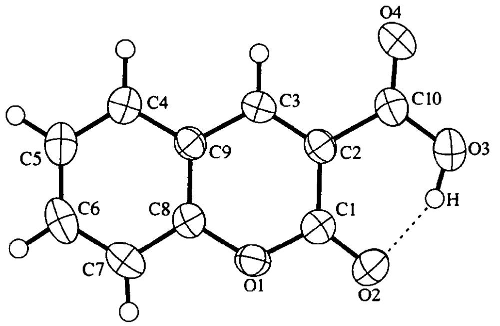


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of coumarin-3-carboxylic acid showing our numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms, for which they have been set artificially small. The intramolecular hydrogen bond is shown as a dashed line.

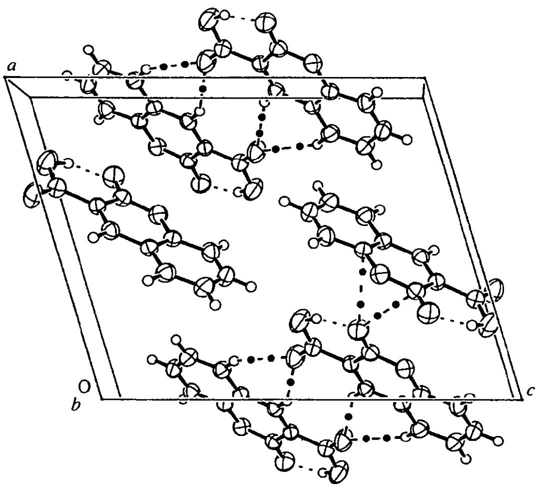


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of coumarin-3-carboxylic acid. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms, for which they have been set artificially small. Dashed lines represent hydrogen bonds while the dot-dashed lines represent the closest intermolecular approaches among the depicted molecules.

As is apparent from the figures, the molecule as a whole is nearly planar. The average deviation of the non-H atoms from the best-fit plane describing them is 0.030 (2) Å; the maximum deviation is 0.110 (2) Å. These molecular planes adopt two orientations in the cell, the dihedral angle between them being 60.31 (4)°. The coumarin core of the molecule (C1–C9, O1, O2) is more nearly planar, the average deviation of these atoms from the best-fit plane describing them being 0.019 (2) Å with a maximum deviation of 0.037 (2) Å. The dihedral angle between this plane and the plane of the carboxyl group is 4.2 (1)°.

For geometrical comparisons, data for the reasonably comparable 3-(bromoacetyl)coumarin (Vasudevan, Puttaraja & Kulkarni, 1991) are available. From those data, we calculate an average deviation of the coumarin core atoms from the best-fit plane describing them to be 0.036 Å, the maximum deviation being 0.097 Å. Thus, coumarin-3-carboxylic acid is the more nearly planar. The dihedral angle between the best-fit plane for the bromoacetyl group and the best-fit coumarin core plane is given by Vasudevan *et al.* (1991) as 4.5 (8)°, a value very similar to the analogous dihedral angle cited above for the present structure. For corresponding bond distances in the coumarin cores, the average difference is

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ISSN 0108-2701 © 1996