Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

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

Coumarin-3-carboxylic Acid

Allison J. Dobson and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

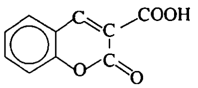
(*Received 25 June 1996; accepted 5 September 1996*)

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)

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)°.

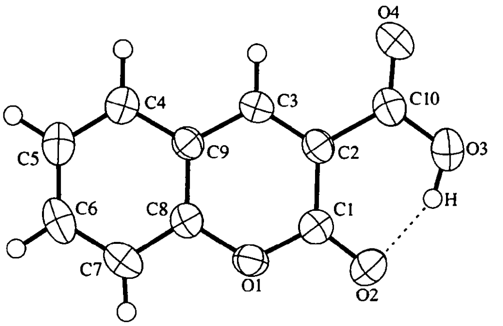


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of coumarin-3-carboxylic acid showing our numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms, for which they have been set artificially small. The intramolecular hydrogen bond is shown as a dashed line.

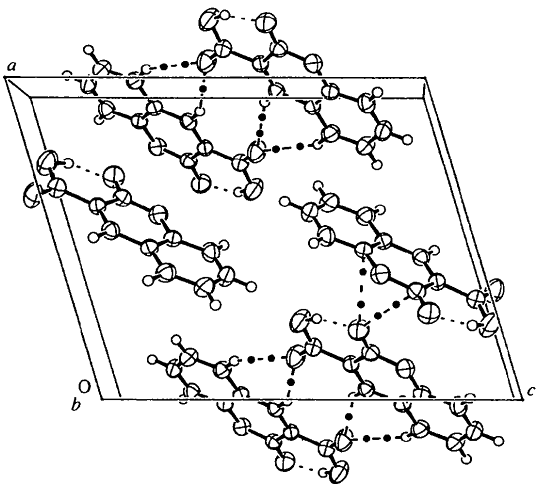


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of coumarin-3-carboxylic acid. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms, for which they have been set artificially small. Dashed lines represent hydrogen bonds while the dot-dashed lines represent the closest intermolecular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

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

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

0.009 Å and the maximum difference 0.016 Å; representative e.s.d.'s are 0.007 Å for the Vasudevan *et al.* (1991) bond distances, 0.003 Å for the present data. Thus the core geometries show good agreement.

The intramolecular hydrogen-bond parameters for this molecule are strikingly similar to those for 2-hydroxybiphenyl-3-carboxylic acid (Dobson & Gerkin, 1996): donor···acceptor distances 2.589 (2) and 2.612 (3) Å, H atom···acceptor distances 1.72 (3) and 1.72 (3) Å, donor–H atom···acceptor angle 153 (3) and 153 (3)°, respectively.

The closest intermolecular approaches in coumarin-3-carboxylic acid involve O2···C1^{i}, O2···C8^{i} [(i) = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$], O4···H3^{ii}, O4···H4^{ii} [(ii) = $-x, -1 - y, 1 - z$] and H3···O4^{ii}, H4···O4^{ii}. These distances, shown in Fig. 2, fall short of the corresponding Bondi (1964) radius sums by amounts from 0.12 to 0.19 Å. The shape and disposition of molecules in this structure and the rather high density (1.522 Mg m^{-3}; values for analogous molecules typically lie in the range 1.34–1.42 Mg m^{-3}) suggest that these close approaches are produced by attractive interactions rather than as a consequence of minimizing repulsive effects elsewhere on the molecule. Indeed, the four C—H···O atom groupings involving the O4···H close approaches cited above satisfy the criteria elucidated by Taylor & Kennard (1982) for significant attractive interaction ('C—H···O hydrogen bonds'): the C···O distances, 3.386 (3) and 3.475 (3) Å, fall near the middle of Taylor & Kennard's suggested 3–4 Å range, while the relevant C—H···O angles, 151 (2) and 147 (2)°, are greater than those in 30 of their 59 tabulated exemplars (in which this angle ranges from 90.7 to 176.7°). Significant C—H···O interactions have also been invoked for other reasonably similar coumarin structures: for example, for 3-(bromoacetyl)coumarin (Vasudevan *et al.*, 1991) and for ethyl furo[3,2-*g*]-coumarin-3-carboxylate (Delettré, Delaitre, Vigny & Bisagni, 1986). Moreover, our calculations based on the data of Gavuzzo, Mazza & Giglio (1974) for coumarin itself show that in that structure the O2—H3* and O2—H4* (present atomic numbering; * = $\frac{1}{2} - x, 1 + y, z - \frac{1}{2}$ in space group $Pca2_1$) distances fall short of the Bondi radius sums and that the relevant C—H···O parameters satisfy the Taylor & Kennard (1982) criteria (C···O distances 3.50 and 3.48 Å, C—H···O angles 156 and 148°) for significant attractive interaction. [While Gavuzzo *et al.* (1974) state that O2 'is involved in many intermolecular contacts and is probably the atom which contributes most to the stabilization of the crystal lattice by means of van der Waals interactions', they do not mention C—H···O interactions in particular.]

In the absence of an atomic charge analysis for the title molecule, it is not possible to assert that the two O2···C close approaches depicted in Fig. 2 are also due to attractive effects, though this appears likely.

Experimental

Coumarin-3-carboxylic acid obtained from Aldrich Chemical Company was dissolved in ether. Evaporation of the solution at room temperature produced crystals in the form of irregular hexagonal plates and columns.

Crystal data

$C_{10}H_6O_4$
$M_r = 190.16$
Monoclinic
$P2_1/n$
$a = 11.342$ (1) Å
$b = 5.517$ (1) Å
$c = 13.823$ (1) Å
$\beta = 106.39$ (1)°
$V = 829.8$ (2) Å^3
$Z = 4$
$D_x = 1.522$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.4$–17.2°
$\mu = 0.112$ mm^{-1}
$T = 296$ K
Hexagonal plate
0.39 × 0.31 × 0.19 mm
Colorless

Data collection

AFC-5*S* diffractometer
ω scans
Absorption correction: none
2215 measured reflections
2113 independent reflections
1100 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.016$

$\theta_{\rm max} = 27.50$°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 7$
$l = -17 \rightarrow 17$
6 standard reflections monitored every 150 reflections
intensity decay: −2.1%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.045$
$S = 1.50$
1100 reflections
152 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = < 0.01$

$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 20 (4) × 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)

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

	x	y	z	$U_{\rm eq}$
O1	0.1009 (1)	0.1922 (3)	0.74577 (10)	0.0426 (4)
O2	0.2271 (1)	0.2965 (3)	0.6589 (1)	0.0547 (5)
O3	0.2593 (2)	0.0251 (4)	0.5156 (1)	0.0694 (6)
O4	0.1430 (2)	−0.2979 (3)	0.4725 (1)	0.0629 (6)
C1	0.1536 (2)	0.1470 (4)	0.6709 (2)	0.0398 (6)
C2	0.1179 (2)	−0.0717 (4)	0.6114 (1)	0.0366 (5)
C3	0.0350 (2)	−0.2237 (4)	0.6311 (2)	0.0383 (6)
C4	−0.1011 (2)	−0.3323 (4)	0.7380 (2)	0.0453 (6)
C5	−0.1444 (2)	−0.2780 (5)	0.8186 (2)	0.0522 (7)
C6	−0.1054 (2)	−0.0706 (5)	0.8743 (2)	0.0528 (7)
C7	−0.0236 (2)	0.0878 (5)	0.8506 (2)	0.0478 (7)
C8	0.0194 (2)	0.0316 (4)	0.7690 (1)	0.0373 (5)
C9	−0.0167 (2)	−0.1770 (4)	0.7120 (1)	0.0362 (5)
C10	0.1736 (2)	−0.1267 (4)	0.5273 (2)	0.0458 (6)

Table 2. *Geometric parameters (Å, °)*

O1—C1	1.357 (2)	C5—C6	1.381 (4)
O1—C8	1.382 (2)	C6—C7	1.380 (3)
O2—C1	1.216 (2)	C7—C8	1.384 (3)
C1—C2	1.452 (3)	C8—C9	1.390 (3)
C2—C3	1.344 (3)	C2—C10	1.501 (3)
C3—C9	1.425 (3)	C10—O3	1.328 (3)
C4—C5	1.372 (3)	C10—O4	1.199 (3)
C4—C9	1.404 (3)		
C1—O1—C8	121.8 (2)	C6—C7—C8	117.8 (2)
O1—C1—O2	116.5 (2)	O1—C8—C7	117.2 (2)
O1—C1—C2	118.2 (2)	O1—C8—C9	120.6 (2)
O2—C1—C2	125.3 (2)	C7—C8—C9	122.2 (2)
C1—C2—C3	120.2 (2)	C3—C9—C4	123.5 (2)
C1—C2—C10	119.7 (2)	C3—C9—C8	118.3 (2)
C3—C2—C10	120.1 (2)	C4—C9—C8	118.2 (2)
C2—C3—C9	120.9 (2)	C2—C10—O3	116.7 (2)
C5—C4—C9	120.0 (2)	C2—C10—O4	122.6 (2)
C4—C5—C6	120.2 (2)	O3—C10—O4	120.7 (2)
C5—C6—C7	121.5 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H···O2	0.93 (3)	1.72 (3)	2.589 (2)	153 (3)

Scan widths were $(1.60 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetry indicated by the intensity statistics led to unique assignment of the space group as $P2_1/n$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The final refined C—H distances ranged from 0.94 (2) to 1.02 (2) Å, with a mean value of 0.97 (2) Å.

The maximum effect of extinction was 8.4% of F_o for 202. The maximum peak in the final difference map occurred ~0.8 Å from C2 and ~0.9 Å from C1; the maximum negative peak occurred near the center of the C4—C9 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*.

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, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Delettré, J., Delaitre, M.-E., Vigny, P. & Bisagni, E. (1986). *Acta Cryst.* C**42**, 1849–1851.
Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**. 3088-3091.
Gavuzzo, E., Mazza, F. & Giglio, E. (1974). *Acta Cryst.* B**30**, 1351–1357.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
Stuart, C. M. (1886). *J. Chem. Soc.* **49**, 365–367.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Vasudevan, K. T., Puttaraja & Kulkarni, M. V. (1991). *Acta Cryst.* C**47**, 775–777.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1996). C**52**, 3083–3086

4-(2-Naphthyl)butanoic Acid

Allison J. Dobson and Roger E. Gerkin

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

(*Received 9 May 1996; accepted 15 July 1996*)

Abstract

4-(2-Naphthyl)butanoic acid, $C_{14}H_{14}O_2$, crystallizes in the centrosymmetric space group $P2_1/a$. The single type of hydrogen bond forms cyclic dimers about inversion centers. The carboxylic-O atoms are ordered as is the acid-H atom. The structure comprises double layers of aromatic rings in a herringbone array separated by double layers of hydrogen-bonded aliphatic strings, a pattern seen previously in related substances.

Comment

This investigation of 4-(2-naphthyl)butanoic acid, (I), is part of a continuing series on hydrogen bonding in carboxylic acids. Also of interest was the packing of the ring (naphthalene), the string (the butyl chain) and the terminal carboxyl group of the molecule for comparison with the structural results from the (2-naphthyl)ethanoic acid analog.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996