

SHELXL97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC (Canada). RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1331). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 2140–2142

Network of C—H···O interactions in 4-benzyloxy-3-methoxybenzaldehyde (vanillin benzyl ether)

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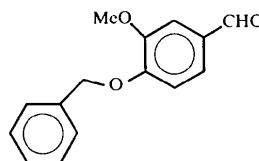
(Received 24 May 1999; accepted 2 July 1999)

Abstract

The title aldehyde, C₁₅H₁₄O₃, crystallized in the centrosymmetric space group *P2₁/c* with one molecule in the asymmetric unit. Six significant intermolecular C—H···O interactions have C···O distances ranging from 3.405 (2) to 3.802 (2) Å and C—H···O angles ranging from 121 to 162°. These six intermolecular interactions link a molecule directly to six neighbors and form a three-dimensional network. The dihedral angle between the best-fit planes of the benzene rings within a molecule is 78.1 (1)°. The dihedral angle between the carboxaldehyde-group plane and the best-fit plane of the ring to which it is attached is 3 (1)°.

Comment

This report on the title aldehyde, (I), is one of a series on hydrogen bonding in organic solids. It follows our reports on two other aldehydes with additional O atoms as potential acceptors, dibenzofuran-4-carboxaldehyde (Fitzgerald *et al.*, 1991) and 2,2'-dihydroxy-5,5'-dimethoxybiphenyl-3,3'-dicarboxaldehyde [hereafter, (II)] (Gerkin, 1999). (I) crystallized in the centrosymmetric space group *P2₁/c* with one molecule in the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. Six intermolecular C—H···O interactions have parameter values falling well within



(I)

the criteria of Taylor & Kennard (1982) for significantly attractive interactions; a recent comprehensive analysis of such interactions is given by Steiner & Desiraju (1998). Geometric details for these are given in Table 2. Altogether these interactions link a molecule directly to six neighbors; in (II), 11 intermolecular interactions link a molecule directly to eight neighbors. The results

of graph-set analysis (Bernstein *et al.*, 1995) of these six interactions, labeled *a–f* for this purpose in the order of their appearance in Table 2, are given in Table 3. (Second-level descriptors in extended form for *a*, *c* and *d* would include, in appended brackets, the descriptors for the corresponding first-level rings.) Among these 21 patterns, 15 are chains and six are rings. The chains propagate variously along [010], [001], [101] and [203], generating a three-dimensional network. If inclusion of C—H···O interactions is restricted to the two having H···O distances less than the sum of the corresponding Bondi (1964) van der Waals radii (eliminating entries *c–f* in Table 3), chains of only types [010] and [203] appear and the network becomes two-dimensional. Interestingly, each of the three first-level rings occurs about a center of symmetry. It may be noted that if interaction *c*, the weaker component of a bifurcated arrangement involving H12, is excluded, the remaining interactions still form a three-dimensional network. A packing diagram of the structure is presented in Fig. 2.

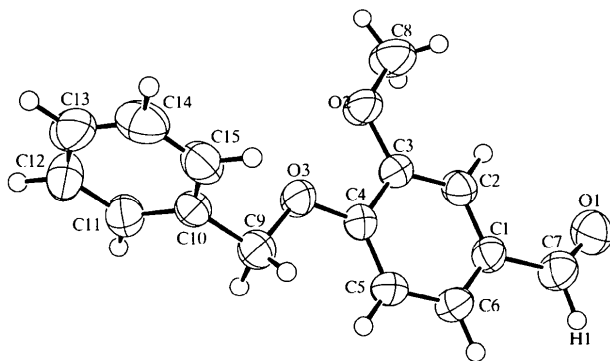


Fig. 1. ORTEP (Johnson, 1976) drawing of (I), showing the labelling scheme. Displacement ellipsoids are drawn for 50% probability for non-H atoms; spheres of arbitrary small radius depict H atoms.

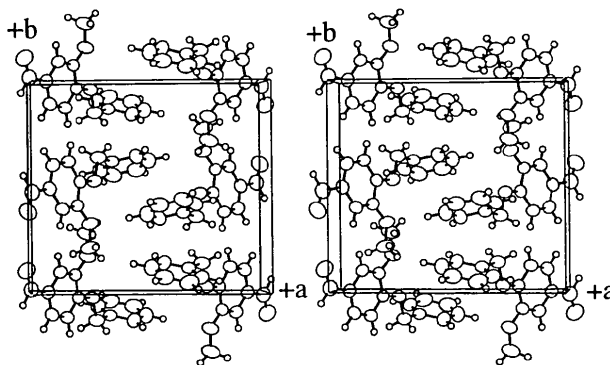


Fig. 2. ORTEP (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 20% probability for non-H atoms; spheres of arbitrary small radius depict H atoms.

The benzene rings in (I) are nearly planar, the maximum deviation of any of their atoms from the best-fit planes describing them being 0.012 (2) and

0.004 (2) Å, while the average deviations are 0.006 (2) and 0.003 (2) Å. These values are quite similar to the corresponding maximum and average deviations found, *e.g.* in the above-cited dialdehyde, (II): 0.014 (2) and 0.007 (2) Å, and 0.008 (2) and 0.005 (2) Å, respectively. The dihedral angle between the best-fit benzene-ring planes within a molecule in (I) is 78.1 (1)°. In (I), the dihedral angle between the plane of the carboxaldehyde group and the plane of the ring to which it is attached is 3.0 (10)°, which may be compared with the corresponding values for the two carboxaldehyde groups of (II): 4.7 (10) and 2.6 (10)°, and with that for the other cited carboxaldehyde, 3.2 (7)°.

Selected distances and angles are given in Table 1. All distances and angles fall within normal ranges. Excluding pairs of atoms involved in C—H···O interactions, the closest intermolecular approaches are between C7 and C7^{vi} [symmetry code: (vi) $-x, 2-y, 2-z$], and are 0.06 Å less than the corresponding Bondi radius sum.

Experimental

The title aldehyde was obtained from a sample in Dr D. J. Hart's chemical collection as a pale yellow chunk. This was cut to provide the experimental sample. This compound is commercially available from, *e.g.*, Lancaster Synthesis Inc.

Crystal data

C₁₅H₁₄O₃
M_r = 242.27
 Monoclinic
*P*2₁/*c*
a = 13.035 (1) Å
b = 11.600 (1) Å
c = 8.668 (1) Å
 β = 81.230 (9)°
V = 1295.3 (2) Å³
Z = 4
D_x = 1.242 Mg m⁻³
D_m not measured

Data collection

AFC-5S diffractometer
 ω scans
 Absorption correction: none
 3115 measured reflections
 2991 independent reflections
 1590 reflections with
 $I > 2\sigma I$
R_{int} = 0.023
 θ_{\max} = 27.56°

Refinement

Refinement on *F*²
R(*F*) = 0.050
 $wR(F^2)$ = 0.068
S = 1.61

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 16.0–17.4°
 μ = 0.086 mm⁻¹
T = 296 K
 Cut chunk
 0.35 × 0.31 × 0.31 mm
 Pale yellow

h = 0 → 16
k = 0 → 15
l = -11 → 11
 6 standard reflections
 every 150 reflections
 intensity variation: ±2.2%
 (average maximum relative intensity)

$w = 1/[\sigma_c^2 + (0.006\lambda)^2]$
 $(\Delta/\sigma)_{\max} = 0.0004$
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{Å}^{-3}$

2988 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement

Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.212 (2)	O3—C4	1.358 (2)
O2—C3	1.366 (2)	O3—C9	1.442 (2)
O2—C8	1.419 (2)		
C3—O2—C8	117.5 (1)	C4—O3—C9	117.1 (1)

Table 2. Intermolecular C—H...O interactions (Å, °)

No s.u.'s are given for quantities involving fixed H atoms.

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12...O2'	0.98	2.58	3.460 (2)	150
C6—H6...O1 ⁱⁱ	0.98	2.60	3.420 (2)	142
C12—H12...O3'	0.98	2.79	3.405 (2)	121
C9—H9B...O1 ⁱⁱⁱ	0.98	2.79	3.570 (2)	137
C8—H8B...O1 ^{iv}	0.98	2.83	3.778 (2)	162
C8—H8A...O2'	0.98	2.89	3.802 (2)	154

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $-x, 2 - y, 1 - z$; (iv) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (v) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Table 3. Basic first- and second-level graph-set descriptors involving interactions designated a–f in order as given in Table 2

	a	b	c	d	e	f
a	R ₂ ² (18)	C ₂ ² (18)	R ₁ ² (5)	C ₂ ² (12)	C ₂ ² (15)	C ₁ ² (12)
b		C(5)	C ₂ ² (17)	C ₁ ² (8)	R ₂ ² (18)	R ₁ ² (28)
c			R ₂ ² (12)	C ₂ ² (13)	C ₂ ² (18)	C ₂ ² (15)
d				R ₂ ² (18)	C ₂ ² (9)	C ₂ ² (14)
e					C(8)	C ₂ ² (9)
f						C(3)

The aldehyde H atom (H7) was refined isotropically [C7—H7 = 1.03 (2) Å]; all other H atoms were allowed for as riding atoms.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

I acknowledge with pleasure the provision of the sample by Dr David J. Hart and my use of the departmental X-ray crystallographic facility, which is supervised by Dr J. C. Gallucci. The diffractometer system was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1220). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 2142–2145

Hydrogen bonding and C—H...O interactions in bis(4-carboxyquinolinium) sulfate monohydrate

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(Received 10 June 1999; accepted 3 August 1999)

Abstract

The title substance, 2C₁₀H₈NO₂⁺·SO₄²⁻·H₂O, crystallized in the centrosymmetric space group *P* $\bar{1}$ with two organic cations, one sulfate ion and one water molecule in the asymmetric unit. Seven leading intermolecular hydrogen bonds are formed in this structure: two N—H...O bonds have N...O distances of 2.592 (3) and 2.650 (3) Å, while five O—H...O bonds have O...O distances ranging from 2.493 (2) to 3.072 (3) Å. All of the potential donors are involved in these bonds, but three of the potential nine acceptors are not. The H and O atoms in all these hydrogen bonds are ordered. The hydrogen bonds form a three-dimensional network. In addition, there are nine significant C—H...O interactions for which the H...O distances are less than the corresponding van der Waals radii sum. The dihedral angle between the best-fit quinoline core plane and the carboxyl group plane is 35.2 (3)° for one of the organic cations and 6.4 (4)° for the other.