# Weak C—H···O hydrogen bonds in anisaldehyde, salicylaldehyde and cinnamaldehyde

**Michael T. Kirchner,[a] Dieter Bläser,[a] Roland Boese,[a]\* Tejender S. Thakur[b] and Gautam R. Desiraju[b]**

[a]Faculty of Chemistry, University Duisburg–Essen, Universitätsstrasse 7, D-45117 Essen, Germany, and [b]Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Correspondence e-mail: roland.boese@uni-due.de

*In situ* cryocrystallization has been employed to grow single crystals of 4-methoxybenzaldehyde (anisaldehyde), $C_8H_8O_2$, 2-hydroxybenzaldehyde (salicylaldehyde), $C_7H_6O_2$, and (2*E*)-3-phenylprop-2-enal (cinnamaldehyde), $C_9H_8O$, all of which are liquids at room temperature. Several weak C—H···O interactions of the types $C_{aryl}$—H···O, $C_{formyl}$—H···O and $Csp^3$—H···O are present in these related crystal structures.

## Comment

Experimental sophistication and developments in theoretical methodologies have improved the reliability of studies of weaker and lesser known intermolecular interactions (Desiraju & Steiner, 1999). As a result, weakly bound complexes such as those involving C—H···O interactions are being extensively studied, and the nature and strength of these interactions are being assessed. The formyl C—H···O hydrogen bond in small-molecule aldehydes is one such example. Many simple aldehydes are liquids, so not many structural reports are available for these compounds. Even if solid, there are not many crystal structure determinations for aldehydes. [There are 37 simple aromatic aldehydes in the Cambridge Structural Database (CSD, Version 5.32, November 2010 update; Allen, 2002) with refcodes ANTHAL, AYOHAL, BARFOT, DEWLOH, DPEDAL, FATVUS, FAXXEI, FEDSAJ, FIXHIE, FIXHOK, FIYQOT, FOMZUD, FORBZA, HEQXOR, HODMAP, IHEMAJ, IHEMIR, IZALAW, JULZAR, KATKIA, KERKOI, LOSGOQ, MASBUD, NARZUC, OKUHEH, PHBALD10, RAJKOC, RAFJOC, SAZQIT, SOCHAT, SUNDUA, TEBBOR, WASLOS, XAMVUJ, XAMVEN, XAYCIJ and XIGWAM; four *α,β*-unsaturated aldehydes with refcodes JAZLAX, SIPKEH, WOBJOM and WOBJUS; and nine salicylaldehyde derivatives with refcodes KOYTOH, MAYWEO, NEJJOB, OVANIL, RAPLAW, XEVRUL, YIQYIH, YOMXOO and YOMXUU.] Therefore, we chose to investigate the nature and type of intermolecular interactions in the crystal structures of some very simple aldehydes.
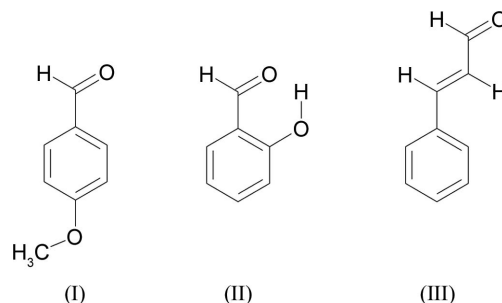


Anisaldehyde (4-methoxybenzaldehyde), (I), salicylaldehyde (2-hydroxybenzaldehyde), (II), and cinnamaldehyde [(2*E*)-3-phenylprop-2-enal], (III), are liquids with melting points of 272, 266 and 265.5 K, respectively. These compounds are widely used in the chemical industry as intermediates in the preparation of perfumes, flavouring agents, dyes, pharmaceuticals and agrochemicals. The interesting feature of these compounds is that they do not possess any strong hydrogen-bonding functionalities. In salicylaldehyde, the OH group is bound intramolecularly to the aldehyde C=O group. The possible intermolecular interactions in these three compounds are of the types $C_{aryl}$—H···O, $C_{formyl}$—H···O, $Csp^2$—H···O, $Csp^3$—H···O, C—H···$\pi$ and $\pi$–$\pi$. The formyl C—H···O interaction is known to be very weak, owing to the poor electropositive character of the formyl H atom (Breneman & Wiberg, 1990; Williams, 1988). Despite this, short $C_{formyl}$—H···O contacts are frequently observed in the crystal structures of aliphatic aldehydes (Thakur *et al.*, 2011). The stabilizing nature of these $C_{formyl}$—H···O contacts has also been confirmed by computations on formaldehyde clusters; these calculations show a gradual increase in the electropositive nature of the formyl H atom on going from an isolated gas-phase environment to the crystal. X-ray crystallographic studies of aromatic aldehydes by Moorthy and Venugopalan also established that formyl C—H···O interactions are relevant to crystal packing (Moorthy *et al.*, 2003, 2004, 2005; Lo
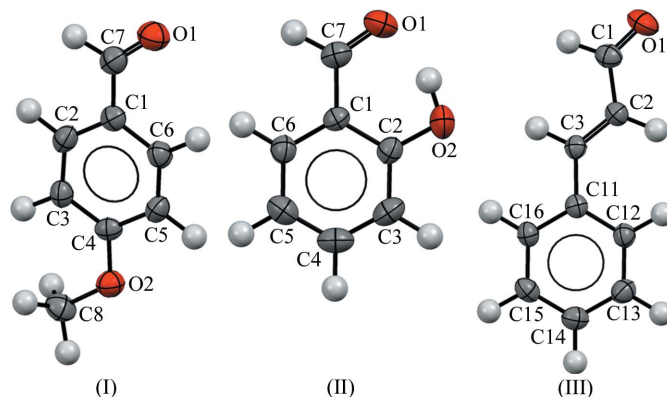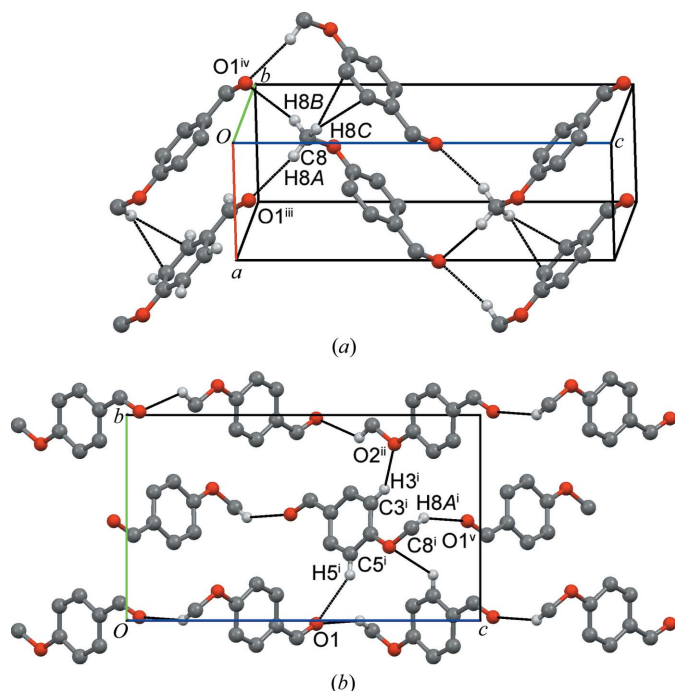


**Figure 1**
The asymmetric units of the crystal structures of (I), (II) and (III). Displacement ellipsoids are drawn at the 50% probability level.

# organic compounds



(a)

(b)

**Figure 2**
The crystal packing in (I), with intermolecular interactions shown as thin lines. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (v) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$.]

Presti *et al.*, 2006). However, in the case of aromatic aldehydes, the $C_{formyl}$—H$\cdots$O interactions have to compete with $C_{aryl}$—H$\cdots$O interactions involving a relatively more acidic H atom. With our ongoing interest in the study of C—H$\cdots$O hydrogen bonds in aldehydes, we report here the crystal structures of (I), (II) and (III) (Fig. 1). Crystals were obtained in each case by means of *in situ* cryocrystallization.

Compound (I) crystallizes in the space group $P2_12_12_1$ with $Z' = 1$. The formyl and methoxy groups lie slightly out of the plane of the benzene ring by 4.3 (4) and −2.9 (3)°, respectively (torsion angles O1—C7—C1—C6 and C3—C4—O2—C8). The $C_{aryl}$—$C_{formyl}$ bond [1.455 (3) Å] is slightly shorter than a normal C—C single-bond distance (Allen *et al.*, 1987). This is possibly a result of extended conjugation between the aldehyde group and the aromatic ring. There are several weak C—H$\cdots$O hydrogen bonds (Table 1). Molecules are arranged in zigzag chains along the *c* axis and are held together by weak $Csp^3$—H$\cdots$O hydrogen bonds between atom H8*A* of the methoxy group and the carbonyl O atom of a neighbouring molecule. The chains are stacked along the *a* axis *via* weak $Csp^3$—H$\cdots\pi$ interactions (Fig. 2a). Molecules in adjacent chains (along the *b* axis) are held together by weak $C_{aryl}$—H$\cdots$O interactions, *viz.* C3—H3$\cdots$O2$^i$ and C5—H5$\cdots$O1$^{ii}$ (Fig. 2b; symmetry codes as in Table 1). The formyl H atom is not engaged in a directed intermolecular interaction (Ribeiro-Claro *et al.*, 2002).

Compound (II) crystallizes in the space group $P2_1/c$ with $Z' = 1$. The hydroxy group is intramolecularly hydrogen bonded to the formyl O atom (O2—H2$\cdots$O1), as expected. A shorter $C_{aryl}$—$C_{formyl}$ bond [1.449 (2) Å] and a slightly elon-



(a)

(b)
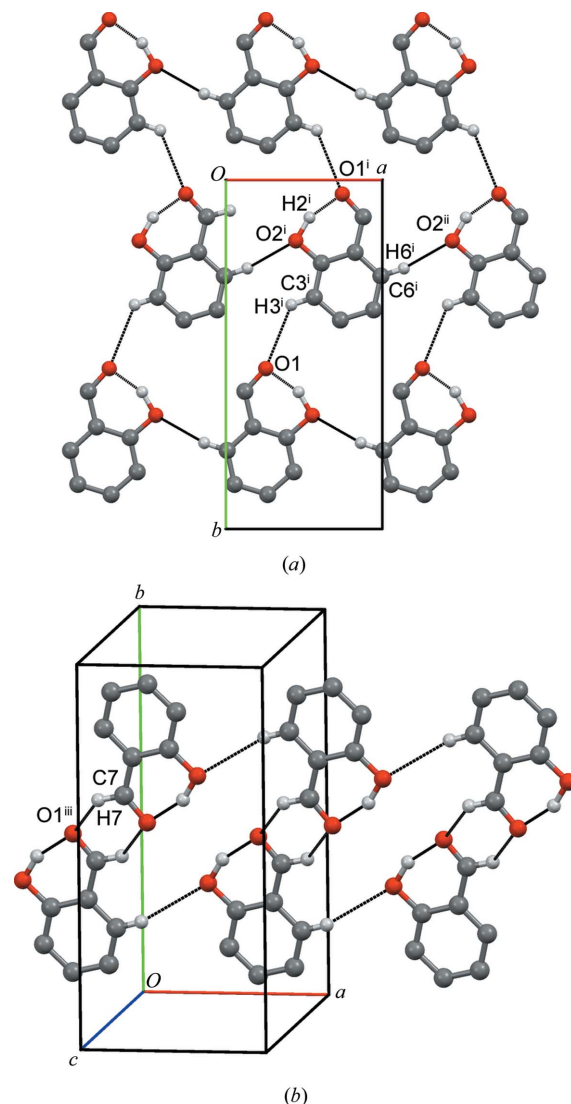
**Figure 3**
(a) The crystal packing in (II), viewed down the *c* axis, showing the layers formed by the $C_{aryl}$—H$\cdots$O interactions. (b) The $C_{formyl}$—H$\cdots$O interactions between the molecules of adjacent layers. The interactions are shown as thin lines. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x, -y + 1, -z + 1$.]

gated C=O bond [1.230 (2) Å] are observed. Molecules in (II) are linked by weak $C_{aryl}$—H$\cdots$O hydrogen bonds (Table 2): C3—H3 and C6—H6 interact with the carbonyl O atom (O1) and hydroxy O atom (O6), respectively, of different neighbouring molecules (Fig. 3a). Additionally, a weak $C_{formyl}$—H$\cdots$O interaction is also observed [C7—H7$\cdots$O1($-x, -y + 1, -z + 1$); Fig. 3b].

Compound (III) crystallizes in the space group $P2_1/c$ with $Z' = 1$. The propenal fragment lies out of the plane of the benzene ring by −9.36 (18)° (torsion angle C2—C3—C11—C12), with a $C_{aryl}$—$Csp^2$ bond length of 1.4656 (16) Å. This indicates poor resonance between the propenal fragment and the aromatic ring. The molecules are arranged in linear chains arranged in a head-to-tail fashion *via* C14—H14$\cdots$O1($x + 1, y, z + 1$) hydrogen bonds (Table 3 and Fig. 4). The carbonyl O atom has weak C—H$\cdots$O interactions with one $C_{aryl}$—H
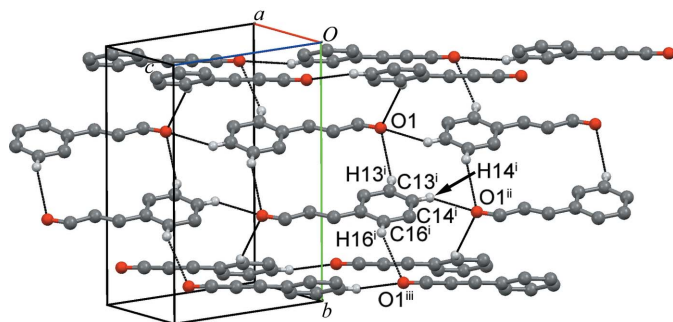
**Figure 4**
The crystal packing in (III), with intermolecular interactions shown as thin lines. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x - 1, -y + 1, -z - 1$; (iii) $-x - 1, y + \frac{1}{2}, -z - \frac{1}{2}$.]

group (C13—H13 or C16—H16) from each of two adjacent chains. Despite the high acidity of the $Csp^2$—H group relative to the $C_{aryl}$—H groups, no $Csp^2$—H···O hydrogen bonds (between the carbonyl O atom and aliphatic fragment) are observed. However, such interactions have been observed frequently in the crystal structures of some substituted cinnamaldehydes (CSD refcodes CUBNUJ, LUJTEQ, CUBJUJ and QODVAH).

## Experimental

Crystallization was performed on the diffractometer using a miniature zone-melting procedure with focused IR laser radiation, according to Boese & Nussbaumer (1994). The temperature of crystallization was 263 K for (I), 253 K for (II) (Fluka) and 248 K for (III) (Fluka, 98%, lot No. 1222882 24005132). The first crystal of (I) obtained was of low quality. Therefore, only a reduced set of frames was collected, but afterwards no better crystals could be obtained. For (I)–(III), the low coverage of the reflection data resulted from the orientation of the cylindrical crystal and the chosen scan mode, both due to the *in situ* crystal-growing technique. Any other mounting of the crystal or different scan mode would lead to melting of the crystals.

## Compound (I)

*Crystal data*

$C_8H_8O_2$
$M_r = 136.14$
Orthorhombic, $P2_12_12_1$
$a = 4.970$ (4) Å
$b = 9.034$ (9) Å
$c = 15.544$ (14) Å

$V = 697.9$ (11) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm$^{-1}$
$T = 203$ K
$0.30 \times 0.30 \times 0.30$ mm

*Data collection*

Siemens SMART three-axis goniometer with an APEXII area-detector system
2015 measured reflections

885 independent reflections
705 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 24.0°$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.071$
$S = 0.94$
885 reflections

92 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.12$ e Å$^{-3}$
$\Delta\rho_{min} = -0.13$ e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °) for (I).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···O2$^i$ | 0.96 | 2.75 | 3.603 (4) | 149 |
| C5—H5···O1$^{ii}$ | 0.96 | 2.70 | 3.447 (4) | 135 |
| C8—H8$A$···O1$^{iii}$ | 0.97 | 2.71 | 3.582 (4) | 150 |
| C8—H8$B$···O1$^{iv}$ | 0.97 | 2.75 | 3.434 (4) | 128 |

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

## Compound (II)

*Crystal data*

$C_7H_6O_2$
$M_r = 122.12$
Monoclinic, $P2_1/c$
$a = 6.3945$ (3) Å
$b = 13.8939$ (9) Å
$c = 6.9172$ (4) Å
$\beta = 103.262$ (3)°

$V = 598.17$ (6) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm$^{-1}$
$T = 233$ K
$0.3 \times 0.3 \times 0.3$ mm

*Data collection*

Siemens SMART three-axis goniometer with an APEXII area-detector system
8643 measured reflections

1853 independent reflections
1002 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 36.2°$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.185$
$S = 1.00$
1853 reflections

82 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ e Å$^{-3}$

## Compound (III)

*Crystal data*

$C_9H_8O$
$M_r = 132.15$
Monoclinic, $P2_1/c$
$a = 5.9626$ (2) Å
$b = 12.9977$ (3) Å
$c = 9.2522$ (2) Å
$\beta = 94.282$ (2)°

$V = 715.04$ (3) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm$^{-1}$
$T = 173$ K
$0.3 \times 0.3 \times 0.3$ mm

*Data collection*

Siemens SMART three-axis goniometer with an APEXII area-detector system
7349 measured reflections

1775 independent reflections
1648 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 31.8°$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.125$
$S = 1.06$
1775 reflections

92 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.28$ e Å$^{-3}$
$\Delta\rho_{min} = -0.17$ e Å$^{-3}$

H atoms of the methoxy group were idealized with tetrahedral angles in a combined rotating and rigid-group refinement, with C—H = 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. All other C-bound H atoms were refined using a riding model starting from idealized geometries, with C—H = 0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The hydroxy H-atom position in (II) was taken from a Fourier map and also refined as a riding atom, with $U_{iso}(H) = 1.5U_{eq}(O)$.

**Table 2**
Hydrogen-bond geometry (Å, °) for (II).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|---|---|---|---|
| O2—H2···O1 | 1.07 | 1.61 | 2.6231 (18) | 156 |
| C3—H3···O1$^{\text{i}}$ | 0.96 | 2.76 | 3.460 (2) | 130 |
| C7—H7···O1$^{\text{ii}}$ | 0.96 | 2.73 | 3.443 (2) | 132 |
| C6—H6···O2$^{\text{iii}}$ | 0.96 | 2.70 | 3.513 (2) | 143 |

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

**Table 3**
Hydrogen-bond geometry (Å, °) for (III).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|---|---|---|---|
| C13—H13···O1$^{\text{i}}$ | 0.96 | 2.81 | 3.5982 (18) | 140 |
| C14—H14···O1$^{\text{ii}}$ | 0.96 | 2.63 | 3.304 (2) | 128 |
| C16—H16···O1$^{\text{iii}}$ | 0.96 | 2.73 | 3.3880 (17) | 126 |

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

For all compounds, data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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