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o- and *m*-Benzenedicarbaldehyde

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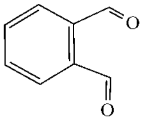
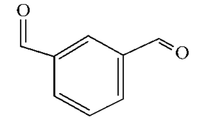
o-Benzenedicarbaldehyde (systematic name: benzene-1,2-dicarbaldehyde), $C_8H_6O_2$, exhibits a weak intramolecular hydrogen bond between an aldehyde H atom and the O atom of the adjacent aldehyde group, with a C···O distance of 2.852 (2) Å. *m*-Benzenedicarbaldehyde (systematic name: benzene-1,3-dicarbaldehyde), $C_8H_6O_2$, occurs as two different isomorphs. In all three crystals, there are intermolecular C—H···O contacts involving both aldehyde and ring H atoms.

Comment

In the structure of *p*-benzenedicarbaldehyde (Britton, 1998), there are short intermolecular C—H···O═C contacts involving the aldehyde H atoms. The structures of *o*- and *m*-benzenedicarbaldehyde, (I) and (II), respectively, have been determined in order to look for further examples of such contacts, and the results are presented here.



(I)



(II)

Views of (I) and the two isomorphs, *A* and *B*, of (II) are shown in Fig. 1. The bond lengths and angles are in the normal ranges. At the ring C atoms bonded to the aldehyde groups, the external C—C—C angles are not equal. In the *ortho* compound, (I), C7—C1—C2 [123.0 (2)°] and C8—C2—C1 [123.2 (2)°] are both 5–6° larger than C7—C1—C6 [117.1 (2)°] and C8—C2—C3 [117.8 (2)°]. This is consistent with the intramolecular hydrogen bonding forcing the groups apart (see below). In both polymorphs of the *meta* compound, (II*A*) and (II*B*), the external angles on the O side are about 2° larger than those on the H side. This can be attributed to the greater crowding between the O and ring H atoms than between the aldehyde H and ring H atoms.

There is one intramolecular C—H···O═C contact in the *ortho* compound, (I) (Fig. 2), with C8—H2···O1 = 112 (2)°, C8—H2 = 0.95 (2) Å, H2···O1 = 2.36 (2) Å, H2···O1═C7 = 98 (2)° and C8···O1 = 2.852 (2) Å. The corresponding values in naphthalene-2,3-dicarbaldehyde are 116 (2)°, 1.00 (2) Å, 2.30 (2) Å, 100 (2)° and 2.884 (2) Å (Britton, 1999). The two aldehyde groups are rotated by 13.3 (2) and 25.1 (2)° out of the plane of the benzene ring, compared with rotations of 7.2 (2) and 22.7 (2)° in the naphthalene compound. These rotations are both in the direction which increases the H···O distance, which is presumably the reason for the rotations. The smaller angles in the naphthalene compound are consistent with the longer C1—C2 length, 1.441 (2) Å *versus* 1.411 (2) Å.

In the *meta* compound, (II), where there is less intramolecular crowding, the aldehyde groups are rotated by 6.1 (2) and 6.6 (2)° in polymorph *A*, and by 4.5 (2) and 10.1 (2)° in polymorph *B*.

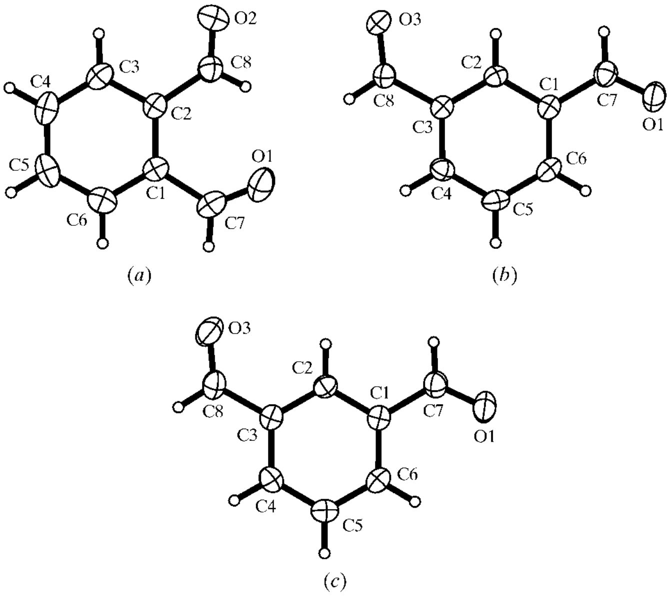


Figure 1
Views of the molecules of (*a*) (I), (*b*) polymorph *A* of (II) and (*c*) polymorph *B* of (II), showing the atom-numbering schemes. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

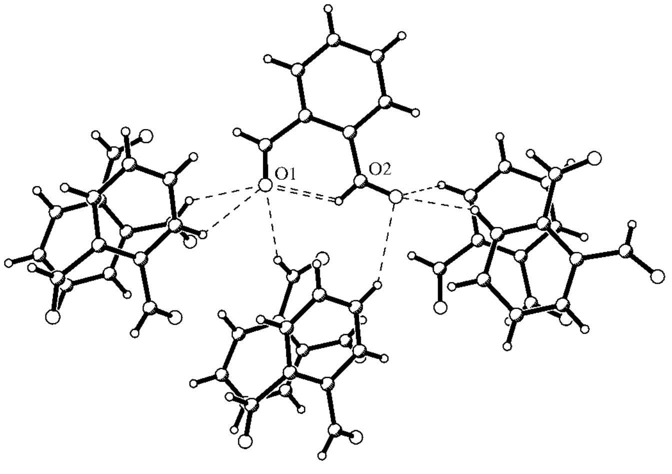


Figure 2
The contacts in (I). H···O contacts are shown as dashed lines and the intramolecular contact is shown as a double dashed line.

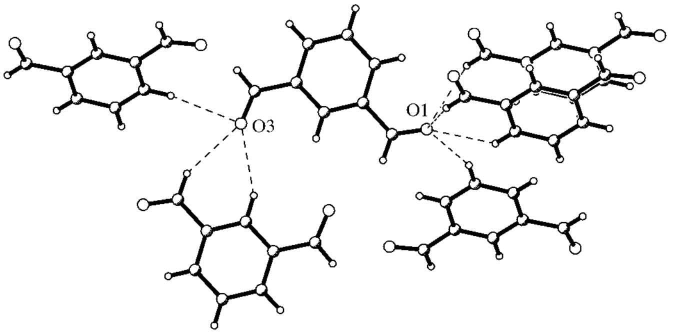


Figure 3
The H···O contacts in polymorph *A* of (II), shown as dashed lines.

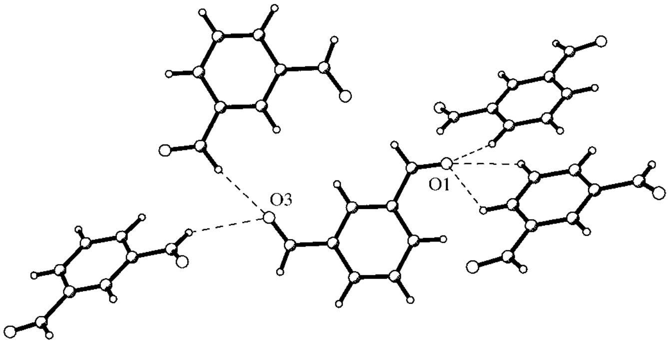


Figure 4
The H···O contacts in polymorph *B* of (II), shown as dashed lines.

The intermolecular H···O contacts shorter than 2.82 Å are listed in Table 1 for both compounds, as well as for the *para* isomer (Britton, 1998), for comparison. If approximate linearity for the C—H···O angle and an approximate trigonal angle for H···O═C are taken as indications of a good C—H···O interaction, then none of the interactions in the *ortho* and *meta* compounds are as favorable as those in the *para* compound, although there are a number of H···O distances that are as short as those in the *para* compound. Overall, the contacts involving the aldehyde H atoms are no shorter than those involving the ring H atoms, suggesting there is no noticeable difference in their abilities to form C—H···O interactions. For an extended discussion of C—H···*X* interactions, see Desiraju & Steiner (1999).

Experimental

Both title compounds were obtained from the Aldrich Chemical Co. Inc. Recrystallization of the *ortho* compound, (I), from acetone, benzene, dichloromethane or chloroform all gave similar crystals; the crystal used here was obtained from chloroform. Two polymorphs were found for the *meta* compound, (II). Sublimation, or recrystallization from benzene, dichloromethane or diethyl ether, gave crystals of polymorph *A*; the crystal used here was obtained from benzene. Recrystallization from acetone or chloroform gave crystals of polymorph *B*; the crystal used here was obtained from chloroform. Both polymorphs had the same melting point, within experimental error.

Compound (I)

Crystal data

$C_8H_6O_2$
M_r = 134.13
Orthorhombic, $Pna2_1$
a = 7.282 (2) Å
b = 13.140 (3) Å
c = 6.760 (2) Å
V = 646.8 (3) Å^3
Z = 4
D_x = 1.377 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2907 reflections
θ = 3.1–26.8°
μ = 0.10 mm^{-1}
T = 174 (2) K
Irregular prism, colorless
0.5 × 0.2 × 0.1 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min}$ = 0.97, $T_{\max}$ = 0.99
7182 measured reflections

802 independent reflections
752 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032
$\theta_{\max}$ = 27.5°
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.078
S = 1.05
802 reflections
91 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.045P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.004
$\Delta\rho_{\max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}

Compound (II*A*)

Crystal data

$C_8H_6O_2$
M_r = 134.13
Monoclinic, $P2_1/n$
a = 3.7760 (10) Å
b = 11.171 (3) Å
c = 15.229 (4) Å
β = 94.980 (10)°
V = 640.0 (3) Å^3
Z = 4

D_x = 1.392 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1982 reflections
θ = 2.7–25.3°
μ = 0.10 mm^{-1}
T = 174 (2) K
Needle, colorless
0.50 × 0.15 × 0.10 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min}$ = 0.98, $T_{\max}$ = 0.99
7258 measured reflections

1461 independent reflections
1138 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.040
$\theta_{\max}$ = 27.5°
$h = -4 \rightarrow 4$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.099
S = 1.05
1461 reflections
91 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.185P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}

Compound (II*B*)

Crystal data

$C_8H_6O_2$
$M_r = 134.13$
Monoclinic, $P2_1/n$
$a = 11.374$ (3) Å
$b = 3.8110$ (10) Å
$c = 15.721$ (4) Å
$\beta = 110.419$ (10)°
$V = 638.6$ (3) Å^3
$Z = 4$
$D_x = 1.395$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3560 reflections
$\theta = 2.7$–27.4°
$\mu = 0.10$ mm^{-1}
$T = 173$ (2) K
Needle, colorless
0.45 × 0.20 × 0.10 mm

Table 1

Comparison of the distances and angles (Å, °) for C—H···O═C contacts.

All C—H distances were fixed at 0.95 Å.

C—H···O	O	C—H···O	H···O	H···O═C	C···O
(I)					
C7^{i}—H1^{i}···O1	O1	153	2.80	132	3.670 (3)†
C8^{ii}—H2^{ii}···O1	O1	144	2.77	92	3.583 (3)†
C3^{iii}—H3^{iii}···O1	O1	131	2.66	130	3.360 (2)
C4^{iv}—H4^{iv}···O2	O2	144	2.67	103	3.482 (2)
C6^{v}—H6^{v}···O2	O2	116	2.80	98	3.323 (2)
C6^{vi}—H6^{vi}···O2	O2	137	2.57	164	3.330 (2)
(II*A*)					
C8^{vii}—H3^{vii}···O1	O1	118	2.77	130	3.318 (2)†
C8^{viii}—H3^{viii}···O1	O1	148	2.64	101	3.482 (2)†
C4^{viii}—H4^{viii}···O1	O1	143	2.72	142	3.522 (2)
C5^{ix}—H5^{ix}···O1	O1	157	2.58	124	3.470 (2)
C7^{x}—H1^{x}···O3	O3	150	2.66	154	3.517 (2)†
C2^{x}—H2^{x}···O3	O3	149	2.64	146	3.485 (2)
C6^{xi}—H6^{xi}···O3	O3	172	2.65	92	3.595 (2)
(II*B*)					
C4^{xii}—H4^{xii}···O1	O1	158	2.55	141	3.449 (2)
C5^{xiii}—H5^{xiii}···O1	O1	128	2.67	155	3.337 (2)
C6^{xiii}—H6^{xiii}···O1	O1	121	2.82	107	3.413 (2)
C7^{xiv}—H1^{xiv}···O3	O3	163	2.52	168	3.443 (2)†
C8^{xv}—H3^{xv}···O3	O3	143	2.81	117	3.606 (2)†
para compound (two independent molecules)					
C2*A*—H2*A*···O1*A*	O1*A*	119	2.81	109	3.395 (2)
C3*A*—H3*A*···O1*A*	O1*A*	129	2.62	159	3.312 (2)
C8*B*—H4*B*···O1*A*	O1*A*	160	2.67	117	3.580 (2)†
C8*B*—H4*B*···O1*A*	O1*A*	109	2.79	130	3.226 (2)†
C2*B*—H2*B*···O1*B*	O1*B*	118	2.89	111	3.457 (2)
C3*B*—H3*B*···O1*B*	O1*B*	129	2.62	161	3.327 (2)
C8*A*—H4*A*···O1*B*	O1*B*	161	2.58	131	3.521 (2)†
C8*A*—H4*A*···O1*B*	O1*B*	105	2.88	122	3.279 (2)†

† Aldehyde H-atom interactions. Symmetry codes: (i) $-x, 1-y, \frac{1}{2}+z$; (ii) $-x, 1-y, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (v) $x, y, 1+z$; (vi) $x-\frac{1}{2}, \frac{3}{2}-y, 1+z$; (vii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (viii) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (ix) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (x) $2-x, 2-y, 1-z$; (xi) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (xii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (xiii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (xiv) $1-x, 2-y, 1-z$; (xv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min} = 0.98$, $T_{\max} = 0.99$
6965 measured reflections
1452 independent reflections
1237 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -4 \rightarrow 4$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.118$
$S = 1.08$
1452 reflections
91 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

In all three cases, the H atoms were included at idealized positions, with C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ for the attached C atom. This was performed to improve the data-to-parameter ratio for the *ortho* crystal, (I), and for the sake of consistency with the *meta* crystals, (II). The *ortho* crystal, (I), is non-centrosymmetric, but with no atoms heavier than O, the correct polarity could not be determined. The Friedel pairs were averaged for the final refinement.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1394). Services for accessing these data are described at the back of the journal.

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