organic compounds

Triclinic polymorph of 4-[4-(4-formyl-phenoxy)butoxy]benzaldehyde

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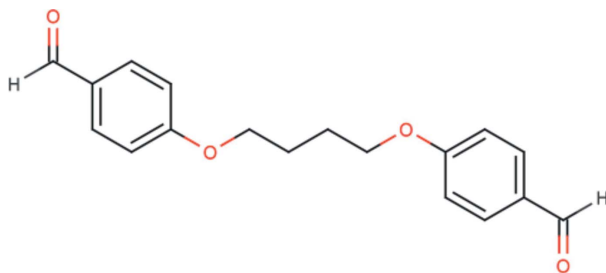
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The title compound, $C_{18}H_{18}O_4$, is a triclinic polymorph of the previously reported monoclinic polymorph [Han & Zhen (2005). *Acta Cryst.* E**61**, o4358–o4359]. In the crystal of the triclinic polymorph, molecules are linked by two pairs of C—H$\cdots$O hydrogen bonds, forming a two-dimensional network parallel to (102), and enclosing loops with graph set motifs of $R_2^2(8)$ and $R_2^2(6)$.

Related literature

For the monoclinic polymorph, see: Han & Zhen (2005). For related structures and the synthesis of similar compounds, see: Balić *et al.* (2012); Ma & Cao (2011); Dehno Khalaji *et al.* (2011); Narasimha Moorthy *et al.* (2005); Ilhan *et al.* (2007). For graph-set analysis of hydrogen bonds, see Bernstein *et al.* (1995).

Experimental

Crystal data

$C_{18}H_{18}O_4$	$\gamma = 80.903\ (5)°$
$M_r = 298.32$	$V = 374.86\ (4)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 4.4969\ (2)$ Å	Mo $K\alpha$ radiation
$b = 7.9507\ (6)$ Å	$\mu = 0.09$ mm^{-1}
$c = 11.0679\ (8)$ Å	$T = 190$ K
$\alpha = 73.854\ (6)°$	$0.59 \times 0.35 \times 0.21$ mm
$\beta = 84.788\ (5)°$	

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer	2235 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	1473 independent reflections
	1272 reflections with $I > 2\sigma(I)$
$T_{min} = 0.683$, $T_{max} = 1.000$	$R_{int} = 0.010$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	100 parameters
$wR(F^2) = 0.123$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
1473 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots$O2^i	0.95	2.58	3.4985 (16)	162
C1—H1$\cdots$O1^{ii}	0.95	2.59	3.3953 (18)	143

Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x, -y - 1, -z + 2$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *PARST97* (Nardelli, 1995) and *Mercury* (Macrae *et al.*, 2006).

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supporting information

Triclinic polymorph of 4-[4-(4-formylphenoxy)butoxy]benzaldehyde

Tomislav Balić, Berislav Marković and Ivana Balić

S1. Comment

Reacent structural studies of dialdehydes (Balić *et al.* 2012; Narasimha Moorthy *et al.* 2005), or the so called two-arm aldehydes have proposed them as potential precursors for condensation reactions with primary amines (Ilhan *et al.* 2007; Ma & Cao 2011; Dehno Khalaji *et al.* 2011). In a relation to this structural studies a new triclinic polymorph of title compound was found. Previously reported monoclinic polymorph (Han & Zhen 2005) was reported in $P2_1/c$ space group with Z=2. The new polymorph was found in $P\bar{1}$ space group (Z=1), with different intermolecular interactions (Figure 1.).

  The original polymorph crystallize in monoclinic space group $P2_1/c$, with a = 7.988 (2), b = 6.6635 (16), c= 14.260 (4) Å, β= 96.354 (4)° and Z = 2 (Han & Zhen 2005). The title compound crystallizes in the space group $P\bar{1}$ with a = 4.5749 (7), b= 7.9467 (10), c = 14.260 (4) Å, α= 73.597 (11)°, β = 83.154 (11)°, γ = 80.533 (12)° and Z = 1. In the reported structure crystallographic inversion centre lies in the center of the molecule, so the asymmetric unit comprises only one half of the molecule. The molecular structure of the title compound is shown in Figure 2. In the triclinic polymorph the molecules are linked in centrosymmetric dimers *via* weak C1— H1···O1 intermolecular interactions, as previously reported by Narasimha Moorthy *et al.* (2005) and Balić *et al.* (2012). Additional stabilization of crystal structure is accomplished by weak C4— H4···O2 (Figure 1.). In the previously reported monoclinic polymorph the dihedral angle between benzaldehyde group and four central carbon atoms is 62.82°, while in triclinic polymorph this angle is 42.07°. However, the largest difference between these two polymorphs is manifested by the presence of $R^2_2(6)$ and $R^2_2(8)$ (Bernstein *et al.* 1995) supramolecular motifs in the triclinic polymorph.

S2. Experimental

The title compound was prepared by folowing procedure: *p*-hydroxybenzaldehyde (50 mmol) and K_2CO_3 (50 mmol) were mixed in DMF and the mixture was brought to brisk reflux. 25 mmol of butane-1,4-dibrom dissolved in DMF was then added and the reaction mixture was refluxed for 5 h. After the reaction was complete, 100 ml of water was added and the resulting percipitate was filtered and washed with water. Single crystals suitable for X-ray diffraction were grown *via* slow evaporation from ethanol solution of the title compound.

S3. Refinement

All H atoms, were positioned geometrically and refined using a riding model with C—H = 0.93 - 0.97 Å and with U_{iso}(H) = 1.2 times U_{eq}(C).
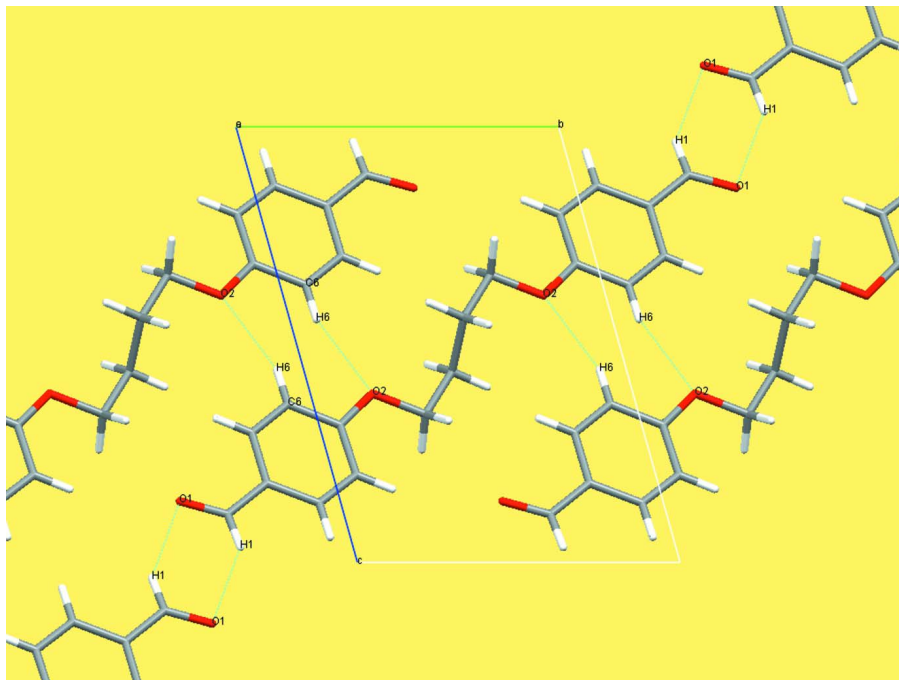
Figure 1

Crystal packing of title compound viewed down the *a* axis with dased lines representing weak C— H···O [graph set $R_2^2(6)$, $R_2^2(8)$] intermolecular interactions.
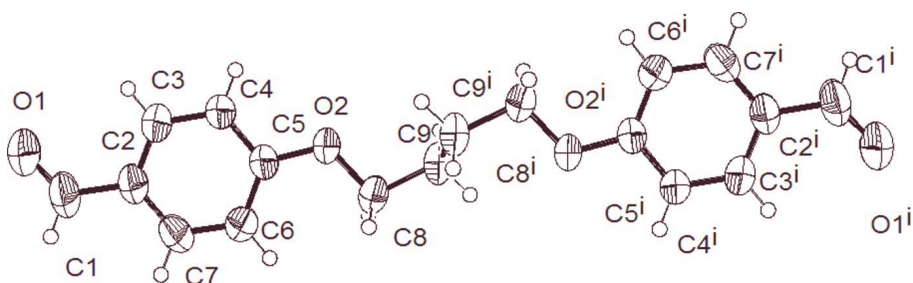
Figure 2

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

4-[4-(4-Formylphenoxy)butoxy]benzaldehyde

Crystal data

$C_{18}H_{18}O_4$	$Z = 1$
$M_r = 298.32$	$F(000) = 158$
Triclinic, $P\overline{1}$	$D_x = 1.321$ Mg m^{-3}
$a = 4.4969 (2)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
$b = 7.9507 (6)$ Å	Cell parameters from 1657 reflections
$c = 11.0679 (8)$ Å	$\theta = 4.6–28.5°$
$\alpha = 73.854 (6)°$	$\mu = 0.09$ mm^{-1}
$\beta = 84.788 (5)°$	$T = 190$ K
$\gamma = 80.903 (5)°$	Block, colourless
$V = 374.86 (4)$ Å^3	$0.59 \times 0.35 \times 0.21$ mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer	2235 measured reflections
Radiation source: Enhance (Mo) X-ray Source	1473 independent reflections
Graphite monochromator	1272 reflections with $I > 2\sigma(I)$
Detector resolution: 16.3426 pixels mm⁻¹	$R_{int} = 0.010$
ω scans	$\theta_{max} = 26.0°, \theta_{min} = 4.6°$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$h = -5\rightarrow4$
	$k = -9\rightarrow9$
$T_{min} = 0.683, T_{max} = 1.000$	$l = -13\rightarrow13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.123$	
$S = 1.04$	H-atom parameters constrained
1473 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.0807P]$ where $P = (F_o^2 + 2F_c^2)/3$
100 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.29$ e Å⁻³
	$\Delta\rho_{min} = -0.17$ e Å⁻³

Special details

Experimental. (*CrysAlis PRO RED*; Oxford Diffraction, 2009)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.2410 (3)	−0.49759 (14)	0.85962 (11)	0.0490 (4)
O2	0.8584 (2)	0.19238 (11)	0.61242 (8)	0.0289 (3)
C1	0.2367 (3)	−0.3608 (2)	0.88964 (14)	0.0377 (4)
H1	0.1248	−0.3496	0.9647	0.045*
C2	0.3920 (3)	−0.21240 (17)	0.81809 (13)	0.0283 (3)
C3	0.3932 (3)	−0.06701 (18)	0.86379 (12)	0.0308 (3)
H3	0.2870	−0.0627	0.9413	0.037*
C4	0.5460 (3)	0.07238 (17)	0.79893 (12)	0.0280 (3)
H4	0.5453	0.1711	0.8315	0.034*
C5	0.7004 (3)	0.06505 (16)	0.68513 (12)	0.0242 (3)
C6	0.6963 (3)	−0.07927 (18)	0.63690 (13)	0.0292 (3)
H6	0.7991	−0.0831	0.5586	0.035*
C7	0.5437 (3)	−0.21533 (17)	0.70273 (13)	0.0305 (3)
H7	0.5410	−0.3130	0.6694	0.037*
C8	0.8898 (3)	0.33927 (16)	0.65981 (12)	0.0268 (3)

H8A	0.9914	0.2970	0.7406	0.032*
H8B	0.6892	0.4045	0.6742	0.032*
C9	1.0762 (3)	0.45809 (17)	0.56216 (12)	0.0276 (3)
H9A	1.2708	0.3883	0.5457	0.033*
H9B	1.1206	0.5532	0.5967	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0659 (8)	0.0366 (7)	0.0488 (7)	−0.0282 (5)	0.0138 (6)	−0.0119 (5)
O2	0.0378 (5)	0.0208 (5)	0.0297 (5)	−0.0128 (4)	0.0082 (4)	−0.0076 (4)
C1	0.0431 (8)	0.0373 (8)	0.0326 (8)	−0.0182 (6)	0.0064 (6)	−0.0048 (6)
C2	0.0292 (7)	0.0262 (7)	0.0282 (7)	−0.0087 (5)	−0.0004 (5)	−0.0026 (5)
C3	0.0335 (7)	0.0356 (8)	0.0233 (6)	−0.0095 (6)	0.0045 (5)	−0.0072 (6)
C4	0.0337 (7)	0.0255 (7)	0.0271 (7)	−0.0079 (5)	0.0007 (5)	−0.0094 (5)
C5	0.0245 (6)	0.0211 (6)	0.0257 (6)	−0.0057 (5)	0.0005 (5)	−0.0032 (5)
C6	0.0342 (7)	0.0254 (7)	0.0291 (7)	−0.0087 (5)	0.0073 (5)	−0.0095 (6)
C7	0.0352 (7)	0.0235 (7)	0.0346 (7)	−0.0101 (5)	0.0047 (6)	−0.0094 (6)
C8	0.0309 (7)	0.0215 (7)	0.0301 (7)	−0.0083 (5)	−0.0009 (5)	−0.0080 (5)
C9	0.0275 (6)	0.0230 (7)	0.0328 (7)	−0.0086 (5)	−0.0023 (5)	−0.0051 (6)

Geometric parameters (Å, º)

O1—C1	1.2196 (18)	C5—C6	1.3969 (18)
O2—C5	1.3593 (15)	C6—C7	1.3704 (18)
O2—C8	1.4372 (15)	C6—H6	0.9500
C1—C2	1.4652 (18)	C7—H7	0.9500
C1—H1	0.9500	C8—C9	1.5105 (17)
C2—C3	1.3857 (19)	C8—H8A	0.9900
C2—C7	1.396 (2)	C8—H8B	0.9900
C3—C4	1.3871 (18)	C9—C9^i	1.525 (3)
C3—H3	0.9500	C9—H9A	0.9900
C4—C5	1.3933 (18)	C9—H9B	0.9900
C4—H4	0.9500		
C5—O2—C8	118.23 (10)	C7—C6—H6	120.1
O1—C1—C2	124.62 (14)	C5—C6—H6	120.1
O1—C1—H1	117.7	C6—C7—C2	120.93 (13)
C2—C1—H1	117.7	C6—C7—H7	119.5
C3—C2—C7	118.64 (12)	C2—C7—H7	119.5
C3—C2—C1	120.77 (13)	O2—C8—C9	107.25 (10)
C7—C2—C1	120.58 (13)	O2—C8—H8A	110.3
C2—C3—C4	121.52 (12)	C9—C8—H8A	110.3
C2—C3—H3	119.2	O2—C8—H8B	110.3
C4—C3—H3	119.2	C9—C8—H8B	110.3
C3—C4—C5	118.82 (12)	H8A—C8—H8B	108.5
C3—C4—H4	120.6	C8—C9—C9^i	113.78 (13)
C5—C4—H4	120.6	C8—C9—H9A	108.8

O2—C5—C4	124.74 (12)	C9^i—C9—H9A	108.8
O2—C5—C6	115.04 (11)	C8—C9—H9B	108.8
C4—C5—C6	120.22 (12)	C9^i—C9—H9B	108.8
C7—C6—C5	119.85 (12)	H9A—C9—H9B	107.7
O1—C1—C2—C3	−175.28 (14)	C3—C4—C5—C6	1.0 (2)
O1—C1—C2—C7	4.3 (2)	O2—C5—C6—C7	179.96 (11)
C7—C2—C3—C4	−1.3 (2)	C4—C5—C6—C7	−1.0 (2)
C1—C2—C3—C4	178.22 (12)	C5—C6—C7—C2	−0.2 (2)
C2—C3—C4—C5	0.2 (2)	C3—C2—C7—C6	1.4 (2)
C8—O2—C5—C4	5.11 (18)	C1—C2—C7—C6	−178.21 (12)
C8—O2—C5—C6	−175.90 (10)	C5—O2—C8—C9	179.31 (10)
C3—C4—C5—O2	179.95 (11)	O2—C8—C9—C9^i	64.84 (16)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O2^{ii}	0.95	2.58	3.4985 (16)	162
C1—H1···O1^{iii}	0.95	2.59	3.3953 (18)	143

Symmetry codes: (ii) −*x*+2, −*y*, −*z*+1; (iii) −*x*, −*y*−1, −*z*+2.