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3-Methoxy-4-(prop-2-yn-1-yloxy)benzaldehyde

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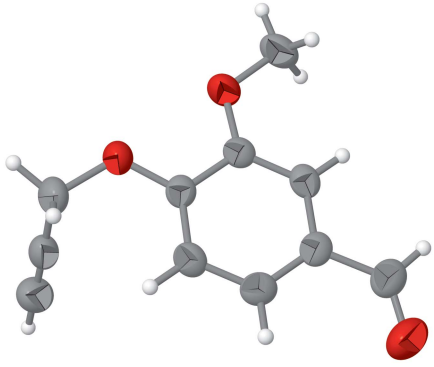
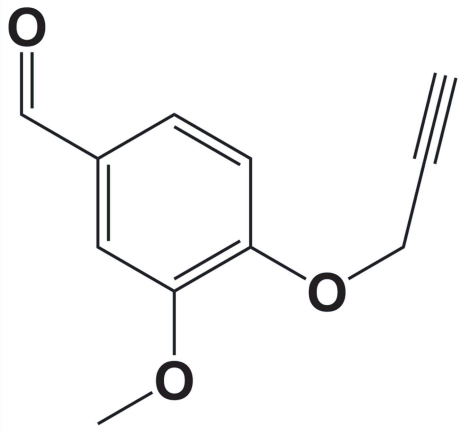
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{11}H_{10}O_3$, the prop-2-yn-1-yl group is inclined to the benzene ring by 69 (7)°. In the crystal, molecules are linked by a pair of C—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(12)$ ring motif. The dimers are linked by a second C—H···O hydrogen bond, forming sheets parallel to the (102) plane. The sheets stack along the *c*-axis direction with a separation of *ca* 3.4 Å.

3D view



Chemical scheme



Structure description

Vanillin and vanillin derivatives are used in food and non-food applications, in fragrances and as flavouring agents for pharmaceutical products (Hocking, 1997; Walton *et al.*, 2003). Synthetic vanillin is used as an intermediate in chemical and pharmaceutical industries for the production of herbicides, antifoaming agents and drugs, such as papaverine, L-dopa and L-methyldopa, as well as antimicrobial agents such as trimethoprim (Fitzgerald *et al.*, 2005). In the past few years, 1,2,3-triazole molecules have been synthesized which can be employed as chemotherapeutic agents for various diseases (Wang *et al.*, 2008). In particular, vanillin when treated with propargyl bromide forms propargyloxybenzaldehyde which is linked *via* a 1,2,3-triazole ring with an alkane side arm (Ahmed Kamal *et al.*, 2011). We report herein on the synthesis and crystal structure of a new vanillin derivative.

The molecular structure of the title compound is illustrated in Fig. 1. The prop-2-yn-1-yl group (C1≡C2—C3) is inclined to the benzene ring by 69 (7)°.

In the crystal, molecules are linked by a pair of C—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(12)$ ring motif (Table 1 and Fig. 2). The dimers are linked by a second C—H···O hydrogen bond, involving the propynyl group (H1), forming sheets parallel to plane (102); see Table 1 and Fig. 2. The sheets stack along the *c*-axis direction, with a separation of *ca* 3.4 Å, but with no significant intermolecular interactions being present.

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O2^{i}	0.97	2.42	3.374 (2)	166
C1—H1···O3^{ii}	0.93	2.39	3.274 (2)	158

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

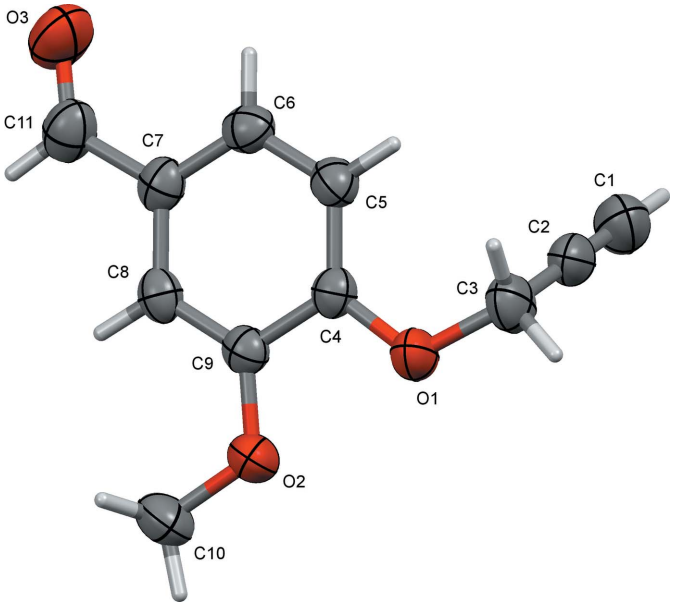


Figure 1
The molecular structure of the title compound, showing the atom labelling and 50% probability displacement ellipsoids.

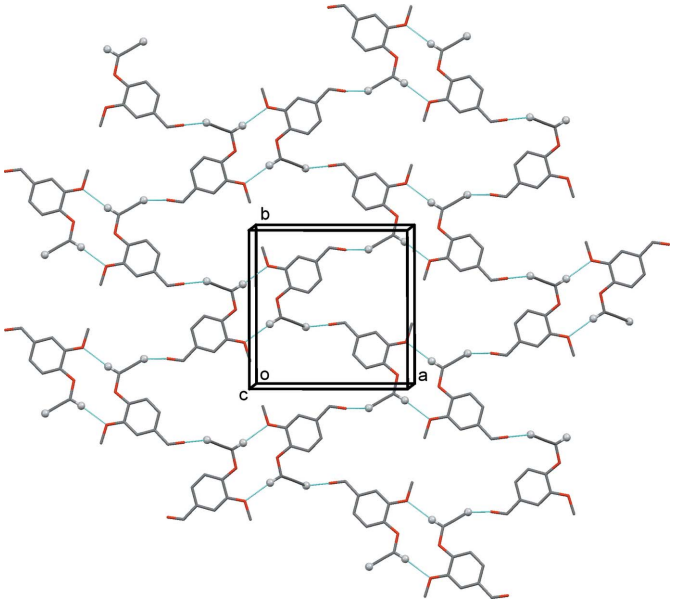


Figure 2
The crystal packing of the title compound, viewed along the c axis. Hydrogen bonds are shown as dashed lines (see Table 1) and, for clarity, only H atoms H1 and H3A (grey balls) have been included.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{10}O_3$
M_r	190.19
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	11.8560 (6), 11.8836 (6), 6.8348 (4)
β (°)	92.044 (1)
V (Å^3)	962.36 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.35 × 0.30 × 0.25
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.961, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10764, 1896, 1528
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.093, 1.07
No. of reflections	1896
No. of parameters	129
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.13

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

Synthesis and crystallization

4-Hydroxy-3-methoxybenzaldehyde (0.378 g, 2.48 mmol) and anhydrous K_2CO_3 (0.414 g, 3.0 mmol) were dissolved in 15 ml of dry DMF and propargyl bromide (1 g, 2.48 mmol) was added. The reaction mixture was stirred at room temperature for 24 h, and then poured into 100 ml of water and extracted with $CHCl_3$. The organic phases were combined and washed with water, brine solution, dried over anhydrous sodium sulfate and the solvent evaporated under vacuum. The crude product was purified by column chromatography using silica gel (hexane/ethyl acetate = 4:1 v/v) and the title compound was obtained as a yellow solid (yield 0.915 g, 78%; m.p. 458 K). The compound was dissolved in acetone and slowly evaporated to give brown block-like crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161919 [https://doi.org/10.1107/S2414314616019192]

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Crystal data

$C_{11}H_{10}O_3$
M_r = 190.19
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.8560 (6) Å
b = 11.8836 (6) Å
c = 6.8348 (4) Å
β = 92.044 (1)°
V = 962.36 (9) Å^3
Z = 4
$F(000)$ = 400
D_x = 1.313 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4115 reflections
θ = 2.4–28.4°
μ = 0.10 mm^{-1}
T = 296 K
Block, brown
0.35 × 0.30 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.961, T_{max} = 0.980
10764 measured reflections
1896 independent reflections
1528 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 26.0°, θ_{min} = 2.4°
h = −14→14
k = −14→14
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.093
S = 1.07
1896 reflections
129 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.2349P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0104 (19)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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}
C1	0.25864 (14)	0.36251 (15)	−0.2945 (3)	0.0699 (5)
H1	0.2947	0.3419	−0.4077	0.084*
C2	0.21334 (12)	0.38838 (13)	−0.1523 (3)	0.0539 (4)
C3	0.15648 (13)	0.41756 (12)	0.0269 (2)	0.0547 (4)
H3A	0.0865	0.3755	0.0317	0.066*
H3B	0.2039	0.3955	0.1390	0.066*
C4	0.22014 (11)	0.60814 (11)	0.06716 (18)	0.0383 (3)
C5	0.33237 (11)	0.57799 (12)	0.09667 (19)	0.0433 (3)
H5	0.3527	0.5024	0.0997	0.052*
C6	0.41399 (11)	0.65991 (12)	0.12150 (19)	0.0445 (3)
H6	0.4893	0.6394	0.1408	0.053*
C7	0.38435 (11)	0.77230 (11)	0.11782 (18)	0.0416 (3)
C8	0.27149 (11)	0.80274 (11)	0.09066 (18)	0.0403 (3)
H8	0.2516	0.8784	0.0902	0.048*
C9	0.18929 (11)	0.72245 (11)	0.06453 (18)	0.0379 (3)
C10	0.04141 (14)	0.85726 (13)	0.0341 (3)	0.0610 (4)
H10A	0.0620	0.8914	0.1576	0.091*
H10B	−0.0390	0.8607	0.0131	0.091*
H10C	0.0773	0.8969	−0.0691	0.091*
C11	0.46886 (14)	0.86149 (14)	0.1404 (2)	0.0579 (4)
H11	0.4424	0.9352	0.1418	0.069*
O1	0.13206 (8)	0.53520 (8)	0.03999 (15)	0.0511 (3)
O2	0.07696 (8)	0.74270 (8)	0.03513 (15)	0.0518 (3)
O3	0.56883 (10)	0.84848 (12)	0.1572 (2)	0.0815 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0562 (10)	0.0683 (12)	0.0853 (13)	−0.0013 (8)	0.0054 (9)	−0.0240 (10)
C2	0.0445 (8)	0.0405 (8)	0.0762 (11)	−0.0023 (6)	−0.0035 (7)	−0.0097 (7)
C3	0.0559 (9)	0.0348 (8)	0.0739 (10)	−0.0050 (6)	0.0070 (8)	−0.0006 (7)
C4	0.0421 (7)	0.0379 (7)	0.0349 (6)	−0.0026 (6)	0.0015 (5)	−0.0017 (5)
C5	0.0475 (8)	0.0389 (7)	0.0431 (7)	0.0049 (6)	−0.0024 (6)	−0.0015 (6)
C6	0.0402 (7)	0.0542 (9)	0.0390 (7)	0.0019 (6)	−0.0016 (5)	−0.0036 (6)
C7	0.0464 (8)	0.0466 (8)	0.0321 (6)	−0.0061 (6)	0.0052 (5)	−0.0040 (6)
C8	0.0513 (8)	0.0358 (7)	0.0341 (6)	−0.0002 (6)	0.0054 (5)	−0.0016 (5)

C9	0.0410 (7)	0.0407 (7)	0.0320 (6)	0.0030 (6)	0.0020 (5)	−0.0019 (5)
C10	0.0585 (9)	0.0513 (9)	0.0729 (11)	0.0178 (8)	−0.0019 (8)	−0.0047 (8)
C11	0.0568 (10)	0.0608 (10)	0.0568 (10)	−0.0121 (8)	0.0107 (7)	−0.0090 (7)
O1	0.0439 (6)	0.0375 (5)	0.0720 (7)	−0.0023 (4)	0.0033 (5)	−0.0072 (5)
O2	0.0434 (6)	0.0431 (6)	0.0684 (7)	0.0068 (4)	−0.0034 (5)	−0.0062 (5)
O3	0.0540 (8)	0.0867 (10)	0.1042 (10)	−0.0200 (7)	0.0096 (7)	−0.0199 (8)

Geometric parameters (Å, º)

C1—C2	1.168 (2)	C6—H6	0.9300
C1—H1	0.9300	C7—C8	1.3921 (19)
C2—C3	1.460 (2)	C7—C11	1.463 (2)
C3—O1	1.4311 (17)	C8—C9	1.3711 (18)
C3—H3A	0.9700	C8—H8	0.9300
C3—H3B	0.9700	C9—O2	1.3612 (16)
C4—O1	1.3647 (16)	C10—O2	1.4251 (17)
C4—C5	1.3858 (18)	C10—H10A	0.9600
C4—C9	1.4068 (18)	C10—H10B	0.9600
C5—C6	1.3789 (19)	C10—H10C	0.9600
C5—H5	0.9300	C11—O3	1.1968 (19)
C6—C7	1.3812 (19)	C11—H11	0.9300
C2—C1—H1	180.0	C8—C7—C11	118.51 (13)
C1—C2—C3	178.47 (18)	C9—C8—C7	120.80 (12)
O1—C3—C2	112.64 (13)	C9—C8—H8	119.6
O1—C3—H3A	109.1	C7—C8—H8	119.6
C2—C3—H3A	109.1	O2—C9—C8	125.69 (12)
O1—C3—H3B	109.1	O2—C9—C4	115.16 (11)
C2—C3—H3B	109.1	C8—C9—C4	119.15 (12)
H3A—C3—H3B	107.8	O2—C10—H10A	109.5
O1—C4—C5	125.57 (12)	O2—C10—H10B	109.5
O1—C4—C9	114.47 (11)	H10A—C10—H10B	109.5
C5—C4—C9	119.96 (12)	O2—C10—H10C	109.5
C6—C5—C4	120.10 (13)	H10A—C10—H10C	109.5
C6—C5—H5	120.0	H10B—C10—H10C	109.5
C4—C5—H5	120.0	O3—C11—C7	126.07 (16)
C5—C6—C7	120.23 (13)	O3—C11—H11	117.0
C5—C6—H6	119.9	C7—C11—H11	117.0
C7—C6—H6	119.9	C4—O1—C3	118.26 (11)
C6—C7—C8	119.76 (12)	C9—O2—C10	117.21 (11)
C6—C7—C11	121.73 (13)		
C1—C2—C3—O1	−174 (100)	C5—C4—C9—O2	−179.79 (11)
O1—C4—C5—C6	179.69 (12)	O1—C4—C9—C8	179.94 (11)
C9—C4—C5—C6	−0.66 (19)	C5—C4—C9—C8	0.26 (18)
C4—C5—C6—C7	0.2 (2)	C6—C7—C11—O3	2.6 (2)
C5—C6—C7—C8	0.6 (2)	C8—C7—C11—O3	−176.98 (15)
C5—C6—C7—C11	−178.98 (12)	C5—C4—O1—C3	−4.62 (19)

C6—C7—C8—C9	−0.97 (19)	C9—C4—O1—C3	175.72 (12)
C11—C7—C8—C9	178.59 (12)	C2—C3—O1—C4	−69.00 (17)
C7—C8—C9—O2	−179.39 (11)	C8—C9—O2—C10	−0.92 (19)
C7—C8—C9—C4	0.55 (18)	C4—C9—O2—C10	179.13 (12)
O1—C4—C9—O2	−0.11 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···O2^{i}	0.97	2.42	3.374 (2)	166
C1—H1···O3^{ii}	0.93	2.39	3.274 (2)	158

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