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Crystal structure of 3-ethynylbenzoic acid

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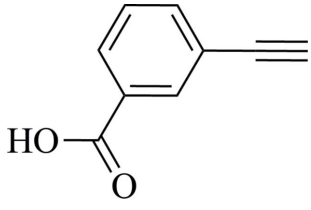
In the title compound, $C_9H_6O_2$, the carboxylic acid group is almost in the plane of the benzene ring, making a dihedral angle of 2.49 (18)°. In the crystal, molecules are linked by pairs of O—H···O hydrogen bonds, forming classical acid–acid inversion dimers, with an $R_2^2(8)$ ring motif. The dimers are linked by pairs of C—H···O hydrogen bonds forming chains, enclosing $R_2^2(16)$ ring motifs, propagating along the *c*-axis direction.

Keywords: crystal structure; 3-ethynylbenzoic acid; hydrogen bonding.

CCDC reference: 1422308

1. Related literature

For the potential applications of terminal alkynes in crystal engineering, see: Dai *et al.* (2004). For the synthesis of the title compound, see: Bischoff *et al.* (2008). For the NMR spectrum of the title compound, see: Bleisch *et al.* (2014). For other syntheses of the title compound, see: Jones *et al.* (2008); Pawle *et al.* (2011). For the crystal structure of the 4-ethynyl benzoic acid methyl ester, see: Dai *et al.* (2004).



2. Experimental

2.1. Crystal data

$C_9H_6O_2$
M_r = 146.14
Triclinic, $P\overline{1}$
a = 3.8630 (7) Å
b = 8.3000 (9) Å
c = 11.7490 (1) Å
α = 101.44°
β = 93.8°
γ = 99.83°
V = 361.84 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 K
0.9 × 0.4 × 0.1 mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.664, T_{max} = 0.745
2719 measured reflections
1317 independent reflections
1086 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.117
S = 1.08
1317 reflections
124 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	1.03 (2)	1.59 (2)	2.625 (2)	175 (2)
C9—H9···O2^{ii}	0.96 (2)	2.50 (2)	3.386 (2)	153 (2)

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

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT*; program(s) used to solve structure: *SIR2011* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5200).

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supporting information

Acta Cryst. (2015). E**71**, o750–o751 [doi:10.1107/S2056989015016515]

Crystal structure of 3-ethynylbenzoic acid

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S1. Chemical context

In recent years, the interest in compounds with an alkyne C≡CH bond has increased due to their versatility in coupling reactions such as Glaser-Hay or Sonogashira. At the same time the crystallography of terminal alkynes has become an intense field of study for the potential applications in crystal engineering (Dai *et al.*, 2004). Additionally, the presence of a carboxylate group on these compounds makes them potential candidates for the formation of metal organic frameworks *viz.* MOFs. With these applications in mind, we have synthesized the title compound and report herein on its crystal structure.The synthesis of 4-ethynylbenzoic acid has been reported previously (Jones *et al.*, 2008; Pawle *et al.*, 2011), but not its crystal structure. Only the crystal structure of the ester, 4-ethynylmethylbenzoate, has been described previously (Dai *et al.*, 2004).

S2. Synthesis and crystallization

3-ethynylbenzoic acid is commercially available. In this work it was obtained by saponification and acidification of the corresponding ester in methanol/water with lithium hydroxide, following the reported procedure (Bischoff *et al.*, 2008). Vapor diffusion of dichlomethane/hexane afforded light yellow crystals. The NMR spectrum is in agreement with the literature values (Bleisch *et al.*, 2014): ^{1}H-NMR (300 MHz, DMSO) 1H 13.22 (1H, s, O—H), 7.94-7.97 (2H, m, H6; H2), 7.73-7.71 (1H, m, H3), 7.53 (1H, t, J = 7.5 Hz, H7), 4.30 (1H, s, CHh). ^{13}C-NMR (75 MHz, DMSO) 13C 166.4 (Ci), 135.8 (Cd), 132.2 (Ca), 131.3 (Ch), 129.7 (Cb), 129.2 (Cc), 122.1 (Ce), 82.5 (Cf), 81.69 (Cg).

S2.1. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All of the H atoms were located in difference Fourier maps and freely refined.

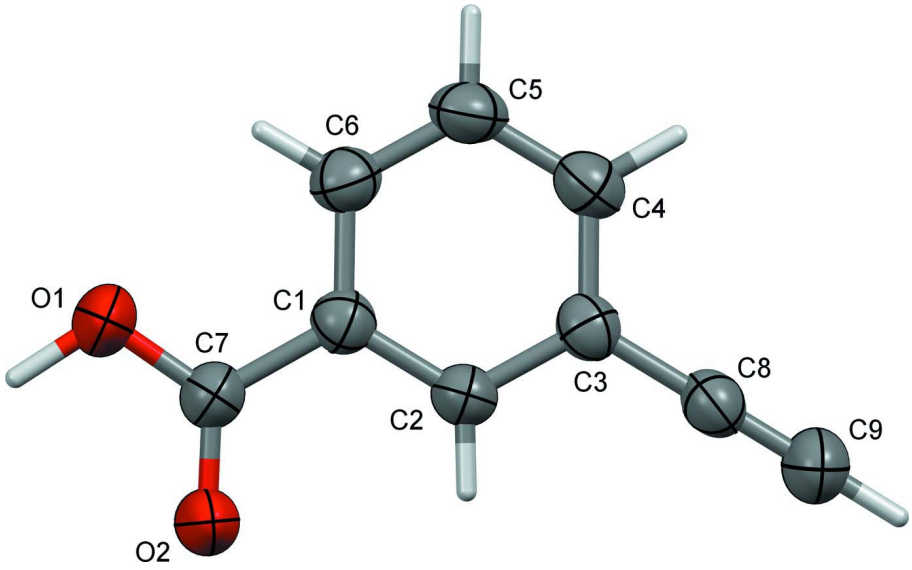

Figure 1

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

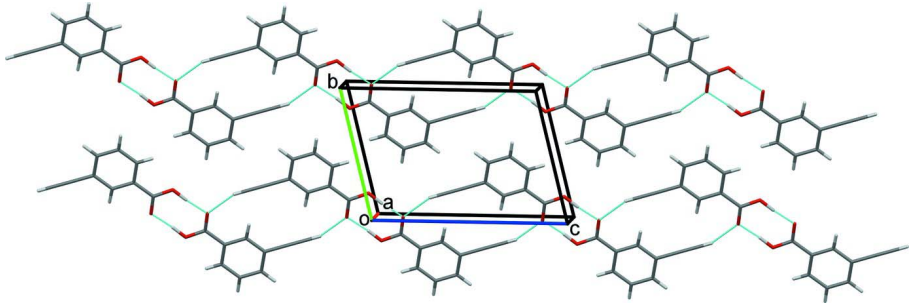

Figure 2

A view along the *a* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1).

3-Ethynylbenzoic acid

Crystal data

$C_9H_6O_2$
$M_r = 146.14$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 3.8630\ (7)$ Å
$b = 8.3000\ (9)$ Å
$c = 11.7490\ (1)$ Å
$\alpha = 101.44°$
$\beta = 93.8°$
$\gamma = 99.83°$
$V = 361.84\ (8)$ Å^3
$Z = 2$
$F(000) = 152$
$D_x = 1.341$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1127 reflections
$\theta = 2.6–26.1°$
$\mu = 0.10$ mm^{-1}
$T = 293$ K
Parallelepiped, colourless
0.9 × 0.4 × 0.1 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.664, T_{max} = 0.745
2719 measured reflections
1317 independent reflections
1086 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 26.2°, θ_{min} = 3.4°
$h = -3 \rightarrow 4$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.117
S = 1.08
1317 reflections
124 parameters
0 restraints
0 constraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 0.035P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.3420 (4)	0.18714 (15)	1.00233 (9)	0.0714 (5)
O2	0.4634 (3)	−0.00243 (13)	0.85678 (9)	0.0648 (4)
C1	0.2847 (3)	0.24041 (16)	0.81364 (11)	0.0432 (4)
C2	0.3024 (3)	0.18897 (16)	0.69499 (12)	0.0428 (4)
C3	0.2316 (3)	0.29147 (16)	0.61941 (12)	0.0434 (4)
C4	0.1418 (4)	0.44533 (18)	0.66466 (14)	0.0509 (5)
C5	0.1251 (4)	0.49579 (18)	0.78270 (14)	0.0558 (5)
C6	0.1965 (4)	0.39454 (18)	0.85767 (13)	0.0509 (5)
C7	0.3696 (4)	0.13271 (17)	0.89319 (12)	0.0477 (4)
C8	0.2570 (4)	0.23974 (16)	0.49657 (12)	0.0489 (5)
C9	0.2828 (5)	0.1985 (2)	0.39633 (14)	0.0629 (6)
H1	0.421 (7)	0.110 (3)	1.054 (2)	0.133 (9)*
H2	0.362 (4)	0.086 (2)	0.6622 (13)	0.050 (4)*
H4	0.088 (4)	0.519 (2)	0.6115 (14)	0.063 (4)*
H5	0.058 (4)	0.601 (2)	0.8124 (14)	0.069 (5)*
H6	0.188 (4)	0.429 (2)	0.9398 (16)	0.065 (5)*
H9	0.302 (5)	0.164 (2)	0.3144 (19)	0.087 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1157 (10)	0.0684 (7)	0.0382 (6)	0.0396 (7)	0.0105 (6)	0.0108 (5)
O2	0.1041 (9)	0.0569 (7)	0.0434 (6)	0.0361 (6)	0.0138 (5)	0.0146 (5)

C1	0.0424 (7)	0.0445 (7)	0.0430 (7)	0.0091 (5)	0.0044 (5)	0.0095 (5)
C2	0.0462 (8)	0.0391 (7)	0.0442 (7)	0.0111 (5)	0.0051 (5)	0.0090 (5)
C3	0.0393 (7)	0.0462 (7)	0.0459 (7)	0.0082 (5)	0.0036 (5)	0.0129 (5)
C4	0.0517 (8)	0.0463 (8)	0.0580 (9)	0.0138 (6)	0.0011 (6)	0.0165 (6)
C5	0.0599 (9)	0.0448 (8)	0.0634 (10)	0.0201 (6)	0.0027 (7)	0.0060 (7)
C6	0.0524 (8)	0.0512 (8)	0.0484 (8)	0.0155 (6)	0.0052 (6)	0.0041 (6)
C7	0.0566 (8)	0.0479 (7)	0.0399 (7)	0.0139 (6)	0.0064 (6)	0.0084 (6)
C8	0.0526 (8)	0.0485 (8)	0.0510 (9)	0.0148 (6)	0.0052 (6)	0.0189 (6)
C9	0.0827 (12)	0.0647 (10)	0.0483 (9)	0.0250 (8)	0.0116 (8)	0.0176 (7)

Geometric parameters (Å, º)

O1—C7	1.2902 (18)	C4—C5	1.376 (2)
O2—C7	1.2415 (18)	C5—C6	1.378 (2)
O1—H1	1.03 (2)	C8—C9	1.175 (2)
C1—C2	1.3845 (19)	C2—H2	0.938 (16)
C1—C6	1.389 (2)	C4—H4	0.992 (16)
C1—C7	1.4735 (19)	C5—H5	0.959 (17)
C2—C3	1.3907 (19)	C6—H6	0.955 (18)
C3—C4	1.393 (2)	C9—H9	0.96 (2)
C3—C8	1.437 (2)		
C7—O1—H1	112.4 (13)	O2—C7—C1	121.61 (12)
C2—C1—C7	119.56 (12)	O1—C7—C1	116.24 (13)
C6—C1—C7	120.24 (12)	C3—C8—C9	179.04 (17)
C2—C1—C6	120.17 (12)	C1—C2—H2	122.5 (9)
C1—C2—C3	120.08 (12)	C3—C2—H2	117.4 (9)
C2—C3—C8	120.12 (12)	C3—C4—H4	119.9 (9)
C4—C3—C8	120.72 (13)	C5—C4—H4	119.6 (9)
C2—C3—C4	119.15 (13)	C4—C5—H5	119.5 (10)
C3—C4—C5	120.48 (14)	C6—C5—H5	120.1 (10)
C4—C5—C6	120.39 (14)	C1—C6—H6	119.3 (10)
C1—C6—C5	119.73 (14)	C5—C6—H6	121.0 (10)
O1—C7—O2	122.16 (13)	C8—C9—H9	179.5 (19)
C6—C1—C2—C3	−0.05 (19)	C6—C1—C7—O2	−176.98 (14)
C7—C1—C2—C3	−178.37 (12)	C1—C2—C3—C4	−0.26 (19)
C2—C1—C6—C5	0.3 (2)	C1—C2—C3—C8	178.71 (12)
C7—C1—C6—C5	178.59 (14)	C2—C3—C4—C5	0.3 (2)
C2—C1—C7—O1	−178.90 (13)	C8—C3—C4—C5	−178.63 (14)
C2—C1—C7—O2	1.3 (2)	C3—C4—C5—C6	−0.1 (2)
C6—C1—C7—O1	2.8 (2)	C4—C5—C6—C1	−0.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	1.03 (2)	1.59 (2)	2.625 (2)	175 (2)

C9—H9···O2^{ii}	0.96 (2)	2.50 (2)	3.386 (2)	153 (2)

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