Trimethyl 3,3′,3′′-(benzene-1,3,5-triyl)tripropynoate

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Abstract

The title compound, $C_{18}H_{12}O_6$, crystallizes in the triclinic space group *P*-1 with one molecule in the asymmetric unit. The alkyne bonds are distorted featuring bond angles around C—C≡C—C of 173.6 (1)/179.0 (1)°, 178.1 (1)/178.4 (1)° and 174.9 (1)/175.9 (1)°, and the ester groups show interplanary angles of 3.5, 13.8 and 14.5° with reference to the plane of the central benzene ring, respectively. The molecules are connected in layers parallel to the (131)-plane by weak C—H···O hydrogen bonds giving rise to a system of new hydrogen bond ring motifs with graph sets $R^2_2(14)$ and $R^4_4(22)$. The layers are linked among each other by interactions involving C—H···O and C—H···π contacts.

Structure description

The title compound, $C_{18}H_{12}O_6$, is an interesting synthetic intermediate for the preparation of application–oriented solid materials involving both porous coordination polymers (MacGillivray, 2010) or metal-organic frameworks (Noro & Kitagawa, 2010) and crystalline inclusion hosts (Weber, 1996; Katzsch *et al.*, 2016). In the structure of the molecule (Fig. 1), the alkyne bonds are distorted which is shown by the corresponding bond angles [C2—C3—C4 173.6 (1)°, C3—C4—C13 179.0 (1)°, C6—C7—C8 178.1 (1)°, C7—C8—C15 178.4 (1)°, C10—C11—C12 174.9 (1)°, C11—C12—C17 175.9 (1)°] and the ester functions are not arranged in the benzene plane [interplanary angles: 3.5° (C2, O1, O2), 13.8° (C6, O3, O4), 14.5° (C10, O5, O10)]. The molecules are connected in layers parallel to the (131)-plane by weak C—H···O hydrogen bonds (Desiraju & Steiner, 1999) (Table 1) giving rise to new hydrogen bond ring motifs with the graph sets (Bernstein *et al.*, 1995) $R^2_2(14)$ and $R^4_4(22)$ (Fig. 2). The layers are stabilized among each other also by weak C—H···O hydrogen bonds [*d*(C1···O6) 3.438 (1) Å] and additionally by C—H···π contacts (Desiraju & Steiner, 1999) [*d*(C1···*Cg*3) 3.551 (1) Å d(C9···*Cg*1) 3.630 (1) Å].

Synthesis and crystallization

The title compound was prepared from 1,3,5-triethynylbenzene (Münch *et al.*, 2013) and methyl chloroformiate as described in the literature (Katzsch *et al.*, 2016). Colorless single crystals of prismatic shape suitable for X-ray diffraction were obtained by slow crystallization from a solvent mixture of acetone, ethyl acetate and *n*-hexane. For the synthesis of a related compound, see: Welti & Diederich (2003).

Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were included in calculated positions and treated as riding atoms.

Table 1

Experimental details

Crystal data	
Chemical formula	$C_{18}H_{12}O_6$
M_r	324.28

Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	8.5765 (2), 9.8469 (2), 10.2677 (2)
α, β, γ (°)	78.903 (1), 79.552 (1), 68.655 (1)
V (Å^3)	786.65 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.54 × 0.43 × 0.37
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *SADABS* (Sheldrick, 2004)
T_{min}, T_{max}	0.946, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16379, 2769, 2558
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.082, 1.08
No. of reflections	2769
No. of parameters	220
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.24

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table 2

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the atoms C13–C18 and Cg3 is the centroid of the atoms C7 and C8.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*C*···O6^{i}	0.98	2.70	3.4378 (15)	133
C5—H5*B*···O5^{ii}	0.98	2.66	3.4517 (15)	138
C14—H14···O2^{iii}	0.95	2.31	3.2278 (13)	162
C16—H16···O6^{iv}	0.95	2.35	3.2390 (13)	155
C1—H1*A*···*Cg*3^{v}	0.98	2.85	3.5506 (13)	130
C9—H9*A*···*Cg*1^{vi}	0.98	2.76	3.6302 (13)	148

Symmetry codes: (i) $x-1, y+1, z-1$; (ii) $x-1, y, z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+3, -y, -z+2$; (v) $x, y, z-1$; (vi) $x+1, y, z$.

Acknowledgements

This work was supported from the Deutsche Forschungsgemeinschaft (DFG) under the program SPP 1362/1.

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Figure 1

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

Figure 2

A partial view of the crystal packing of the title compound, showing the formation of the C—H···O bonded layer structure, enclosing the system of $R^2_2(14)$ and $R^4_4(22)$ ring motifs. Hydrogen bond contacts are indicated by dashed lines.

full crystallographic data

Trimethyl 3,3′,3′′-(benzene-1,3,5-triyl)tripropynoate

'Trimethyl 3,3′,3′′-(benzene-1,3,5-triyl)tripropynoate'

Crystal data

$C_{18}H_{12}O_6$
$M_r = 324.28$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.5765$ (2) Å
$b = 9.8469$ (2) Å
$c = 10.2677$ (2) Å
$\alpha = 78.903$ (1)°
$\beta = 79.552$ (1)°
$\gamma = 68.655$ (1)°
$V = 786.65$ (3) Å^3
$Z = 2$
$F(000) = 336$
$D_x = 1.369$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9912 reflections
$\theta = 2.8$–$35.9°$
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Prism, colourless
0.54 × 0.43 × 0.37 mm

Data collection

Bruker APEX-II CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 2004)
$T_{min} = 0.946$, $T_{max} = 0.963$
16379 measured reflections
2769 independent reflections
2558 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.082$
$S = 1.08$
2769 reflections
220 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
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.2206P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

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 $F^2 > 2\sigma(F^2)$ 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	0.83566 (10)	0.52293 (9)	0.16775 (8)	0.0236 (2)
O2	0.57685 (10)	0.57849 (10)	0.28339 (8)	0.0293 (2)

O3	0.65384 (9)	0.22546 (9)	1.31248 (7)	0.02084 (19)
O4	0.41386 (10)	0.31372 (9)	1.21571 (8)	0.0268 (2)
O5	1.77215 (9)	−0.03869 (9)	0.67379 (8)	0.0236 (2)
O6	1.70937 (10)	−0.04808 (10)	0.89660 (8)	0.0299 (2)
C1	0.75769 (16)	0.59765 (14)	0.04628 (11)	0.0278 (3)
H1A	0.6774	0.5528	0.0338	0.042*
H1B	0.8452	0.5882	−0.0308	0.042*
H1C	0.6982	0.7021	0.0544	0.042*
C2	0.72764 (14)	0.52404 (12)	0.27834 (11)	0.0190 (2)
C3	0.81227 (13)	0.45041 (12)	0.39566 (11)	0.0194 (2)
C4	0.86741 (13)	0.38829 (12)	0.49835 (11)	0.0185 (2)
C5	0.55244 (15)	0.23382 (15)	1.44175 (11)	0.0278 (3)
H5A	0.4759	0.3352	1.4466	0.042*
H5B	0.6263	0.2036	1.5123	0.042*
H5C	0.4865	0.1683	1.4539	0.042*
C6	0.56511 (13)	0.26911 (12)	1.20822 (11)	0.0188 (2)
C7	0.67830 (14)	0.25513 (12)	1.08442 (11)	0.0203 (2)
C8	0.77122 (13)	0.24785 (11)	0.98194 (11)	0.0188 (2)
C9	1.94875 (14)	−0.09886 (14)	0.69328 (13)	0.0277 (3)
H9A	1.9750	−0.0336	0.7404	0.042*
H9B	2.0182	−0.1071	0.6062	0.042*
H9C	1.9726	−0.1965	0.7465	0.042*
C10	1.66647 (14)	−0.01980 (12)	0.78696 (11)	0.0190 (2)
C11	1.49194 (13)	0.04128 (12)	0.76135 (10)	0.0193 (2)
C12	1.34504 (14)	0.09501 (12)	0.74997 (10)	0.0183 (2)
C13	0.93204 (13)	0.31191 (12)	0.62162 (11)	0.0175 (2)
C14	0.82157 (13)	0.31487 (12)	0.73950 (11)	0.0183 (2)
H14	0.7041	0.3661	0.7379	0.022*
C15	0.88415 (13)	0.24233 (12)	0.85995 (11)	0.0178 (2)
C16	1.05675 (14)	0.16784 (12)	0.86244 (11)	0.0180 (2)
H16	1.0992	0.1189	0.9445	0.022*
C17	1.16685 (13)	0.16532 (11)	0.74421 (11)	0.0171 (2)
C18	1.10490 (13)	0.23615 (12)	0.62325 (11)	0.0178 (2)
H18	1.1797	0.2329	0.5425	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0233 (4)	0.0293 (4)	0.0145 (4)	−0.0059 (3)	−0.0046 (3)	0.0018 (3)
O2	0.0194 (5)	0.0351 (5)	0.0271 (5)	−0.0035 (4)	−0.0074 (3)	0.0034 (4)
O3	0.0171 (4)	0.0290 (4)	0.0140 (4)	−0.0066 (3)	−0.0007 (3)	−0.0010 (3)
O4	0.0179 (4)	0.0345 (5)	0.0225 (4)	−0.0033 (4)	−0.0029 (3)	−0.0018 (3)
O5	0.0146 (4)	0.0310 (4)	0.0222 (4)	−0.0039 (3)	−0.0028 (3)	−0.0036 (3)
O6	0.0230 (4)	0.0434 (5)	0.0209 (5)	−0.0074 (4)	−0.0089 (3)	−0.0005 (4)
C1	0.0363 (7)	0.0292 (6)	0.0153 (6)	−0.0082 (5)	−0.0099 (5)	0.0038 (5)
C2	0.0204 (6)	0.0181 (5)	0.0186 (6)	−0.0061 (4)	−0.0053 (4)	−0.0007 (4)
C3	0.0162 (5)	0.0209 (5)	0.0196 (6)	−0.0046 (4)	−0.0020 (4)	−0.0025 (4)
C4	0.0153 (5)	0.0205 (5)	0.0185 (6)	−0.0050 (4)	−0.0015 (4)	−0.0026 (4)
C5	0.0248 (6)	0.0411 (7)	0.0133 (5)	−0.0097 (5)	0.0017 (4)	−0.0005 (5)
C6	0.0191 (6)	0.0179 (5)	0.0177 (5)	−0.0050 (4)	−0.0023 (4)	−0.0009 (4)
C7	0.0203 (6)	0.0211 (6)	0.0187 (6)	−0.0059 (4)	−0.0048 (5)	−0.0008 (4)
C8	0.0186 (5)	0.0191 (5)	0.0178 (6)	−0.0052 (4)	−0.0042 (4)	−0.0012 (4)

C9	0.0139 (5)	0.0309 (6)	0.0358 (7)	−0.0024 (5)	−0.0033 (5)	−0.0090 (5)
C10	0.0176 (5)	0.0185 (5)	0.0203 (6)	−0.0055 (4)	−0.0049 (4)	−0.0002 (4)
C11	0.0194 (6)	0.0225 (6)	0.0149 (5)	−0.0070 (5)	−0.0035 (4)	0.0008 (4)
C12	0.0200 (6)	0.0201 (5)	0.0151 (5)	−0.0076 (4)	−0.0034 (4)	−0.0003 (4)
C13	0.0175 (5)	0.0185 (5)	0.0163 (5)	−0.0057 (4)	−0.0044 (4)	−0.0009 (4)
C14	0.0147 (5)	0.0193 (5)	0.0199 (6)	−0.0039 (4)	−0.0037 (4)	−0.0026 (4)
C15	0.0184 (5)	0.0190 (5)	0.0166 (5)	−0.0071 (4)	−0.0020 (4)	−0.0024 (4)
C16	0.0204 (6)	0.0188 (5)	0.0157 (5)	−0.0073 (4)	−0.0055 (4)	−0.0005 (4)
C17	0.0156 (5)	0.0174 (5)	0.0188 (5)	−0.0053 (4)	−0.0046 (4)	−0.0015 (4)
C18	0.0166 (5)	0.0207 (5)	0.0162 (5)	−0.0070 (4)	−0.0013 (4)	−0.0021 (4)

Geometric parameters (Å, º)

O1—C2	1.3280 (14)	C6—C7	1.4490 (15)
O1—C1	1.4612 (13)	C7—C8	1.1961 (16)
O2—C2	1.2018 (14)	C8—C15	1.4345 (15)
O3—C6	1.3379 (13)	C9—H9A	0.9800
O3—C5	1.4478 (13)	C9—H9B	0.9800
O4—C6	1.2015 (13)	C9—H9C	0.9800
O5—C10	1.3359 (13)	C10—C11	1.4485 (15)
O5—C9	1.4478 (13)	C11—C12	1.1938 (16)
O6—C10	1.1980 (14)	C12—C17	1.4371 (15)
C1—H1A	0.9800	C13—C14	1.3931 (15)
C1—H1B	0.9800	C13—C18	1.3978 (15)
C1—H1C	0.9800	C14—C15	1.3963 (15)
C2—C3	1.4496 (15)	C14—H14	0.9500
C3—C4	1.1965 (16)	C15—C16	1.3950 (15)
C4—C13	1.4351 (15)	C16—C17	1.3945 (15)
C5—H5A	0.9800	C16—H16	0.9500
C5—H5B	0.9800	C17—C18	1.3955 (15)
C5—H5C	0.9800	C18—H18	0.9500
C2—O1—C1	114.65 (9)	H9A—C9—H9B	109.5
C6—O3—C5	114.53 (8)	O5—C9—H9C	109.5
C10—O5—C9	114.15 (9)	H9A—C9—H9C	109.5
O1—C1—H1A	109.5	H9B—C9—H9C	109.5
O1—C1—H1B	109.5	O6—C10—O5	124.66 (10)
H1A—C1—H1B	109.5	O6—C10—C11	123.62 (10)
O1—C1—H1C	109.5	O5—C10—C11	111.72 (9)
H1A—C1—H1C	109.5	C12—C11—C10	174.86 (11)
H1B—C1—H1C	109.5	C11—C12—C17	175.86 (11)
O2—C2—O1	125.16 (10)	C14—C13—C18	120.36 (10)
O2—C2—C3	122.68 (10)	C14—C13—C4	119.56 (9)
O1—C2—C3	112.16 (9)	C18—C13—C4	120.08 (10)
C4—C3—C2	173.59 (11)	C13—C14—C15	119.76 (10)
C3—C4—C13	178.97 (12)	C13—C14—H14	120.1
O3—C5—H5A	109.5	C15—C14—H14	120.1
O3—C5—H5B	109.5	C16—C15—C14	120.15 (10)
H5A—C5—H5B	109.5	C16—C15—C8	119.93 (10)
O3—C5—H5C	109.5	C14—C15—C8	119.90 (10)
H5A—C5—H5C	109.5	C17—C16—C15	119.89 (10)
H5B—C5—H5C	109.5	C17—C16—H16	120.1

O4—C6—O3	125.17 (10)	C15—C16—H16	120.1
O4—C6—C7	124.83 (10)	C16—C17—C18	120.25 (9)
O3—C6—C7	110.00 (9)	C16—C17—C12	119.01 (9)
C8—C7—C6	178.08 (11)	C18—C17—C12	120.67 (10)
C7—C8—C15	178.35 (11)	C17—C18—C13	119.58 (10)
O5—C9—H9A	109.5	C17—C18—H18	120.2
O5—C9—H9B	109.5	C13—C18—H18	120.2
C1—O1—C2—O2	1.09 (16)	C13—C14—C15—C8	178.64 (10)
C1—O1—C2—C3	−179.11 (9)	C14—C15—C16—C17	−0.29 (16)
C5—O3—C6—O4	0.66 (16)	C8—C15—C16—C17	−178.57 (9)
C5—O3—C6—C7	−179.49 (9)	C15—C16—C17—C18	−0.46 (16)
C9—O5—C10—O6	0.41 (16)	C15—C16—C17—C12	176.57 (9)
C9—O5—C10—C11	179.68 (9)	C16—C17—C18—C13	1.13 (15)
C18—C13—C14—C15	0.32 (16)	C12—C17—C18—C13	−175.85 (10)
C4—C13—C14—C15	−179.16 (10)	C14—C13—C18—C17	−1.06 (16)
C13—C14—C15—C16	0.35 (16)	C4—C13—C18—C17	178.42 (10)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the atoms C13–C18 and Cg3 is the centroid of the atoms C7 and C8.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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C9—H9*A*···*Cg*1^{vi}	0.98	2.76	3.6302 (13)	148

Symmetry codes: (i) *x*−1, *y*+1, *z*−1; (ii) *x*−1, *y*, *z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+3, −*y*, −*z*+2; (v) *x*, *y*, *z*−1; (vi) *x*+1, *y*, *z*.