



Crystal structure of bis(prop-2-yn-1-yl) 5-nitroisophthalate

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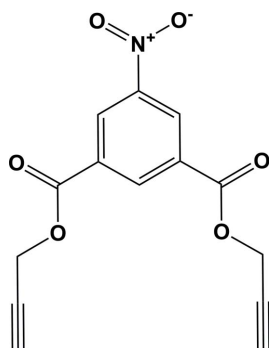
The whole molecule of the title compound, C₁₄H₉NO₆, is generated by twofold rotation symmetry; the twofold axis bisects the nitro group and the benzene ring. The nitro group is inclined to the benzene ring by 14.42 (9)°. The prop-2-yn-1-yl groups are inclined to the benzene ring by 13 (2)° and to each other by 24 (3)°; one directed above the plane of the benzene ring and the other below. In the crystal, molecules are linked *via* pairs of C—H···O hydrogen bonds, forming inversion dimers with an R₂²(18) ring motif. The dimers are linked by further C—H···O hydrogen bonds, forming sheets lying parallel to (100).

Keywords: crystal structure; 5-nitroisophthalate; prop-2-yn-1-yl; twofold rotation symmetry; C—H···O hydrogen bonding.

CCDC reference: 1402145

1. Related literature

For the biological activities of carboxylates, see: Choudhary *et al.* (2002). For the uses and properties of nitroaromatics, see: Lee *et al.* (2013); Somerville *et al.* (1995).



2. Experimental

2.1. Crystal data

C ₁₄ H ₉ NO ₆	$V = 1287.3 (12) \text{ \AA}^3$
$M_r = 287.22$	$Z = 4$
Orthorhombic, <i>Pccn</i>	Mo $K\alpha$ radiation
$a = 6.679 (5) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 11.679 (5) \text{ \AA}$	$T = 293 \text{ K}$
$c = 16.503 (5) \text{ \AA}$	$0.30 \times 0.25 \times 0.20 \text{ mm}$

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer	6369 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	1613 independent reflections
$T_{\min} = 0.965$, $T_{\max} = 0.977$	1316 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	98 parameters
$wR(F^2) = 0.136$	H-atom parameters constrained
$S = 0.73$	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
1523 reflections	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6A···O1 ⁱ	0.97	2.46	3.334 (2)	150
C6—H6B···O1 ⁱⁱ	0.97	2.57	3.313 (2)	134
C8—H8···O3 ⁱⁱ	0.93	2.50	3.251 (2)	138

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5137).

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supporting information

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S1. Comments

Carboxylates have promising activity against various antitumor cells (Choudhary *et al.*, 2002). Nitroaromatic compounds are used in the production of dyes, plastics, high explosives, pharmaceuticals, and pesticides (Somerville *et al.*, 1995). Nitrobenzene is mostly used in the synthesis of aniline and in the production of benzidine, quinolone and azobenzene (Lee *et al.*, 2013).

In the title compound, Fig. 1, the two-fold rotation bisects the benzene ring and the nitro group; atoms C1, C4, H4 and N1 lie on the two-fold rotation axis. The nitro group is inclined to the benzene ring by 14.42 (9) °. The prop-2-yn-1-yl groups are inclined to the benzene ring by 13 (2) ° and to each other by 24 (3) °; one directed above the plane of the benzene ring and the other below.

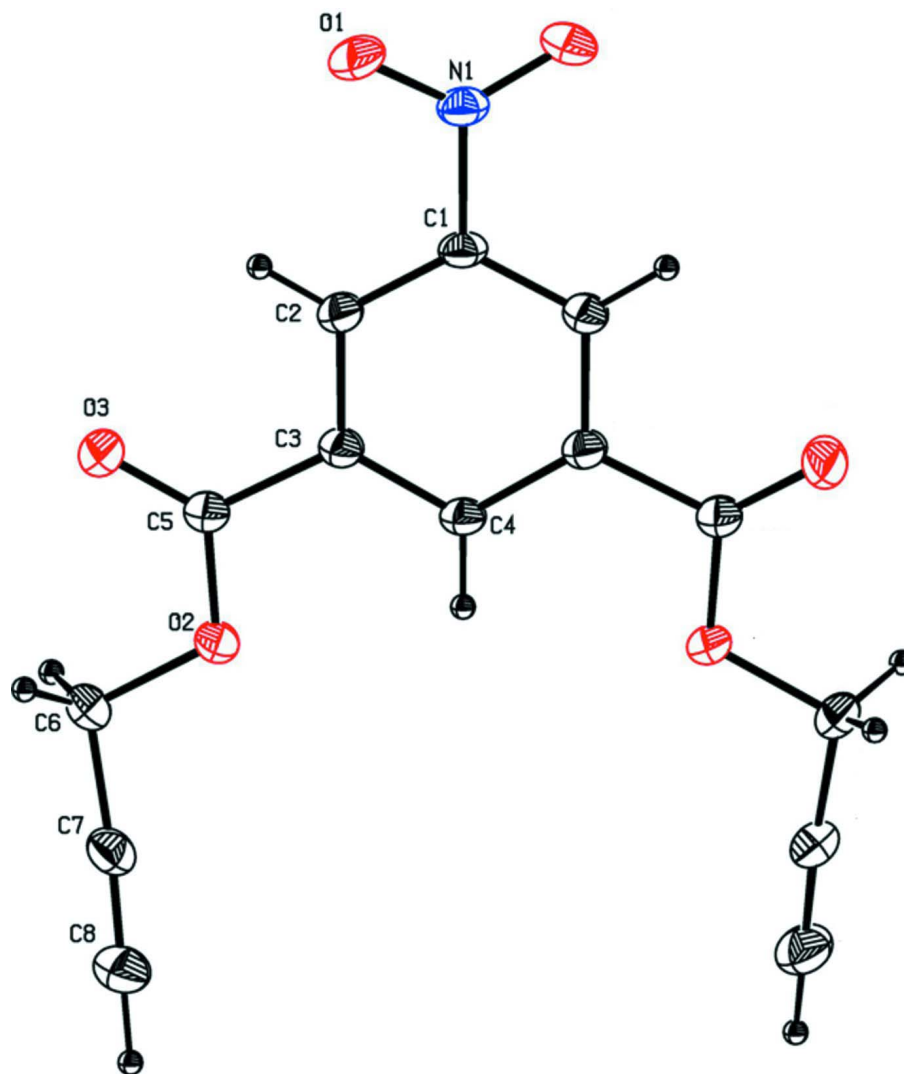
In the crystal, molecules are linked *via* pairs of C—H...O hydrogen bonds forming inversion dimers with an $R_2^2(18)$ ring motif (Table 1). The dimers are linked by further C—H...O hydrogen bonds forming sheets lying parallel to (100); see Table 1 and Fig. 2.

S2. Synthesis and crystallization

The title compound was synthesized by Steglich esterification of 5-nitro isophthalic acid (1 equiv) which together with propargyl alcohol (2.2 equiv) was added at 273 K to DMAP (2.5 equiv) and DCC (2.2 equiv) in dichloromethane (100 ml). The mixture was stirred under nitrogen at room temperature for 24 h. The white precipitate that formed was filtered off and washed with DCM (150 ml) and brine (150 ml), then dried over Na₂SO₄, filtered and evaporated to afford the title compound. It was purified by column chromatography using CHCl₃:hexane (9:1) as a eluent. Crystals were obtained by slow evaporation of the solvent.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically and treated as riding atoms: C—H = 0.93–0.97 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

**Figure 1**

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The unlabelled atoms are related to the labelled atoms by twofold rotation symmetry [symmetry code: (i) $-x + 3/2, -y + 1/2, z$].

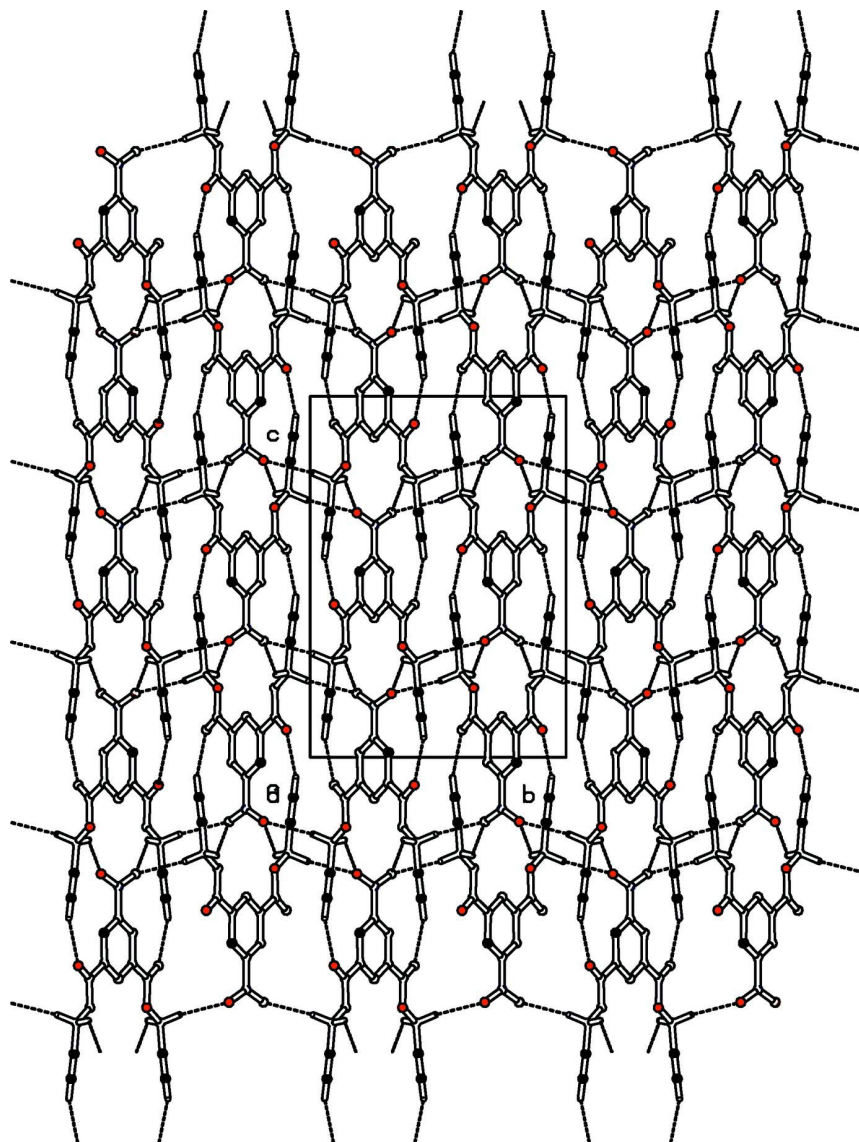


Figure 2

A view along the *a* axis of the crystal packing of the title compound. The dashed lines indicate hydrogen bonds (see Table 1 for details).

Bis(prop-2-yn-1-yl) 5-nitrobenzene-1,3-dicarboxylate

Crystal data

$C_{14}H_9NO_6$

$M_r = 287.22$

Orthorhombic, *Pccn*

Hall symbol: $-P\ 2ab\ 2ac$

$a = 6.679\ (5)\ \text{\AA}$

$b = 11.679\ (5)\ \text{\AA}$

$c = 16.503\ (5)\ \text{\AA}$

$V = 1287.3\ (12)\ \text{\AA}^3$

$Z = 4$

$F(000) = 592$

$D_x = 1.482\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

$\theta = 2.5\text{--}28.4^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.30 \times 0.25 \times 0.20\ \text{mm}$

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, 2008)
 $T_{\min} = 0.965$, $T_{\max} = 0.977$

6369 measured reflections
1613 independent reflections
1316 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 28.4^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -15 \rightarrow 7$
 $l = -12 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.136$
 $S = 0.73$
1523 reflections
98 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
 $w = 1/[\sigma^2(F_o^2) + (0.1246P)^2 + 0.5331P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.030 (5)

Special details

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7500	0.2500	0.05352 (9)	0.0336 (4)
C2	0.90289 (17)	0.30592 (10)	0.01386 (7)	0.0351 (3)
H2	1.0033	0.3433	0.0426	0.042*
C3	0.90264 (16)	0.30486 (10)	-0.07063 (7)	0.0329 (3)
C4	0.7500	0.2500	-0.11315 (9)	0.0328 (4)
H4	0.7500	0.2500	-0.1695	0.039*
C5	1.07371 (18)	0.36348 (11)	-0.11169 (7)	0.0377 (3)
C6	1.2259 (2)	0.41344 (12)	-0.23491 (7)	0.0431 (3)
H6A	1.2527	0.4888	-0.2127	0.052*
H6B	1.3450	0.3669	-0.2284	0.052*
C7	1.17465 (19)	0.42270 (11)	-0.32014 (8)	0.0412 (3)
C8	1.1422 (2)	0.43439 (16)	-0.38961 (9)	0.0565 (4)
H8	1.1166	0.4436	-0.4446	0.068*
N1	0.7500	0.2500	0.14284 (8)	0.0377 (4)
O1	0.86053 (16)	0.31731 (9)	0.17767 (6)	0.0525 (3)

O3	1.21118 (18)	0.40639 (12)	-0.07644 (6)	0.0700 (4)
O2	1.05835 (13)	0.36103 (8)	-0.19240 (5)	0.0404 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0357 (8)	0.0445 (8)	0.0205 (8)	0.0030 (6)	0.000	0.000
C2	0.0344 (6)	0.0445 (6)	0.0263 (6)	-0.0024 (4)	-0.0023 (4)	-0.0013 (4)
C3	0.0328 (6)	0.0407 (6)	0.0254 (6)	-0.0011 (4)	0.0013 (4)	0.0007 (4)
C4	0.0355 (8)	0.0411 (8)	0.0218 (7)	-0.0010 (6)	0.000	0.000
C5	0.0378 (6)	0.0483 (7)	0.0270 (6)	-0.0062 (5)	0.0000 (5)	0.0015 (5)
C6	0.0392 (7)	0.0559 (7)	0.0342 (7)	-0.0110 (5)	0.0065 (5)	0.0047 (5)
C7	0.0401 (6)	0.0463 (6)	0.0370 (7)	-0.0021 (5)	0.0090 (5)	0.0045 (5)
C8	0.0549 (8)	0.0771 (10)	0.0376 (7)	-0.0064 (7)	0.0045 (6)	0.0094 (7)
N1	0.0369 (7)	0.0529 (8)	0.0234 (7)	0.0042 (6)	0.000	0.000
O1	0.0568 (6)	0.0728 (7)	0.0278 (5)	-0.0089 (5)	-0.0065 (4)	-0.0078 (4)
O3	0.0606 (7)	0.1147 (11)	0.0345 (5)	-0.0461 (7)	-0.0069 (5)	0.0068 (6)
O2	0.0393 (5)	0.0563 (6)	0.0256 (5)	-0.0124 (4)	0.0048 (3)	-0.0012 (3)

Geometric parameters (Å, °)

C1—C2 ⁱ	1.3775 (15)	C5—O2	1.3363 (15)
C1—C2	1.3775 (15)	C6—C7	1.4517 (18)
C1—N1	1.474 (2)	C6—O2	1.4555 (15)
C2—C3	1.3944 (16)	C6—H6A	0.9700
C2—H2	0.9300	C6—H6B	0.9700
C3—C4	1.3937 (15)	C7—C8	1.175 (2)
C3—C5	1.4944 (17)	C8—H8	0.9300
C4—C3 ⁱ	1.3937 (15)	N1—O1	1.2220 (12)
C4—H4	0.9300	N1—O1 ⁱ	1.2220 (12)
C5—O3	1.1970 (17)		
C2 ⁱ —C1—C2	123.27 (14)	O2—C5—C3	112.55 (10)
C2 ⁱ —C1—N1	118.36 (7)	C7—C6—O2	108.50 (11)
C2—C1—N1	118.36 (7)	C7—C6—H6A	110.0
C1—C2—C3	118.03 (11)	O2—C6—H6A	110.0
C1—C2—H2	121.0	C7—C6—H6B	110.0
C3—C2—H2	121.0	O2—C6—H6B	110.0
C4—C3—C2	120.56 (11)	H6A—C6—H6B	108.4
C4—C3—C5	122.79 (11)	C8—C7—C6	176.19 (14)
C2—C3—C5	116.64 (10)	C7—C8—H8	180.0
C3—C4—C3 ⁱ	119.53 (14)	O1—N1—O1 ⁱ	123.89 (15)
C3—C4—H4	120.2	O1—N1—C1	118.06 (7)
C3 ⁱ —C4—H4	120.2	O1 ⁱ —N1—C1	118.06 (7)
O3—C5—O2	123.52 (11)	C5—O2—C6	114.36 (9)
O3—C5—C3	123.92 (12)		
C2 ⁱ —C1—C2—C3	-0.45 (8)	C2—C3—C5—O2	-178.24 (10)

N1—C1—C2—C3	179.55 (8)	O2—C6—C7—C8	166 (2)
C1—C2—C3—C4	0.91 (15)	C2 ⁱ —C1—N1—O1	-165.80 (8)
C1—C2—C3—C5	-178.32 (9)	C2—C1—N1—O1	14.20 (8)
C2—C3—C4—C3 ⁱ	-0.46 (8)	C2 ⁱ —C1—N1—O1 ⁱ	14.20 (8)
C5—C3—C4—C3 ⁱ	178.71 (12)	C2—C1—N1—O1 ⁱ	-165.80 (8)
C4—C3—C5—O3	-176.32 (13)	O3—C5—O2—C6	1.09 (19)
C2—C3—C5—O3	2.9 (2)	C3—C5—O2—C6	-177.80 (10)
C4—C3—C5—O2	2.56 (15)	C7—C6—O2—C5	-170.29 (11)

Symmetry code: (i) $-x+3/2, -y+1/2, z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C6—H6 <i>A</i> \cdots O1 ⁱⁱ	0.97	2.46	3.334 (2)	150
C6—H6 <i>B</i> \cdots O1 ⁱⁱⁱ	0.97	2.57	3.313 (2)	134
C8—H8 \cdots O3 ⁱⁱⁱ	0.93	2.50	3.251 (2)	138

Symmetry codes: (ii) $-x+2, -y+1, -z$; (iii) $-x+5/2, y, z-1/2$.