Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

5-Cyano-1,3-phenylene diacetate

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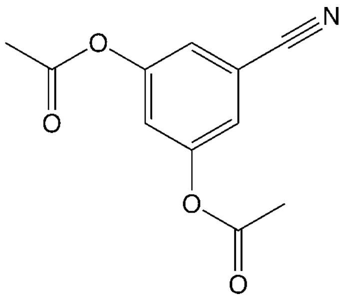
Received 2 May 2014; accepted 16 May 2014

Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.092; data-to-parameter ratio = 15.8.

In the title molecule, $C_{11}H_9NO_4$, the two acetoxy groups are twisted from the plane of the benzene ring by 67.89 (4) and 53.30 (5)°. Both carbonyl groups are on the same side of the aromatic ring. In the crystal, weak C—H$\cdots$O hydrogen bonds link molecules into layers parallel to the ac plane. The crystal packing exhibits π–π interactions between the aromatic rings, indicated by a short intercentroid distance of 3.767 (3) Å.

Related literature

For background to thermoreversible organogelator compounds, see: Carr (2008). For background to the synthesis, see: Ellis *et al.* (1976). For a review of the dehydration of amides to nitriles, see: Bhattacharyya *et al.* (2012). For the crystal structure of a related compound, see: Haines & Hughes (2009).



Experimental

Crystal data

$C_{11}H_9NO_4$
M_r = 219.19
Monoclinic, $P2_1/c$
a = 6.2293 (5) Å
b = 21.1153 (17) Å
c = 8.5989 (7) Å
β = 109.171 (1)°
V = 1068.32 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 200 K
0.22 × 0.16 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.977, T_{max} = 0.990
14252 measured reflections
2340 independent reflections
2067 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.092
S = 1.01
2340 reflections
148 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$A\cdots$O2^{i}	0.95	2.54	3.3495 (14)	143
C10—H10$A\cdots$O2^{ii}	0.98	2.48	3.3738 (15)	151

Symmetry codes: (i) $x+1, y, z$; (ii) $x+1, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

This research was funded by a chemistry department grant from the Welch Foundation (AD-0007). X-ray data were collected at the University of North Texas using a Bruker APEXII CCD diffractometer.

Supporting information for this paper is available from the IUCr electronic archives (Reference: CV5455).

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supplementary materials

Acta Cryst. (2014). E**70**, o712 [doi:10.1107/S1600536814011374]

5-Cyano-1,3-phenylene diacetate

Bahar Abbassi, Michela Brumfield, Lloyd M. Jones, Vladimir N. Nesterov and Andrew J. Carr

1. Comment

In the synthesis of a class of organogelators, it was necessary to shorten the synthesis of 3,5-dialkoxybenzyl amine derivatives by utilizing 5-cyano-1,3-phenylene diacetate as an intermediate. Typical synthesis of these benzyl amine derivatives started at the alkylation of methyl 3,5-dihydroxybenzoate, followed by several synthetic steps that required lithium aluminium hydride (LAH), and sodium azide (Carr, 2008). By forming the nitrile and catalytically reducing it, the hazardous chemicals (LAH, NaN_3) are removed from the synthetic scheme creating a greener process. The 3-acetoxy-5-carbamoylphenyl acetate is dehydrated using cyaniuric acid chloride in dimethylformamide (Bhattacharyya *et al.*, 2012). The crude solid nitrile is isolated by diluting the reaction mixture with bicarbonate solution and vacuum filtration. Samples of crystaline 5-cyano-1,3-phenylene diacetate are obtained from the slow evaporation of the recytallizing solvent (acetone with 10%water).

Investigated compound (Fig. 1) crystallized in the monoclinic crystal system and the molecule occupies a general position in the unit cell. Both acetoxy groups are planar and form dihedral angles with the mean plane of the Ph-ring equal to 67.89 (4) and 53.30 (5) °, respectively and have similar geometry found in the structure of benzene-1,3,5-triyl triacetate (Haines & Hughes, 2009). In the crystal, the molecules (I) form centrosymmetric dimers through partial π-π stacking interactions between aromatic rings. Such mutual orientation of the molecules is a reason of the existance of weak intermolecular C···C contacts with distances from 3.532 Å (C1···C2) to 3.464 Å (C1···C3) that are slightly bigger than their sum of the van der Waals radii. At the same time, two weak intermolecular C—H···O hydrogen bonds with H···O distances of 2.54 and 2.48 Å (Table 1), respectively, link molecules into layers parallel to *ac* plane. The crystal packing exhibits π–π interactions between the aromatic rings proved by short intercentroid distance of 3.767 (3) Å.

2. Experimental

In a 250 ml round bottom flask equipped with a stir bar, 8.50 g (35.7 mmol) 3,5-diacetoxybenzamide was suspended in 25 ml of dry *N*,*N*-dimethylformamide (DMF). The reaction was placed under nitrogen. A solution of 4.40 g (23.8 mmol) 2,4,6- trichloro[1,3,5]triazine (TCT) in 15 ml of dry DMF was generated. After the TCT solution turned yellow (10 min.), it was added drop wise to the amide suspension over a period of 15 min. After 30 min. all amide dissolved. The reaction was stirred at room temperature overnight. At which time, 150 ml of 0.5 *M* sodiumbicarbonate solution was added slowly with vigorous stirring. A white solid was collected by vacuum filtration. The solid was washed with a copious amount of water and left to air dry, producing 7.9 g (97% yield) of 3-acetoxy-5-cyanophenyl acetate. m.p. 350 K (Ellis *et al.*, 1976): ^{1}H NMR(300 MHz, $CDCl_3$): 7.31 (d, J = 2.4 Hz, 2H). 7.20 (t, J = 2.4 Hz, 1H), 2.27 (s,CH_3, 6H): ^{13}C NMR (75 MHz $CDCl_3$): 168.4, 151.4, 122.8, 120.8, 117.2, 113.8, 21.1

The nitrile was then recrystallized from the slow evaporation of acetone with 10% water, giving X-ray quality crystals.

3. Refinement

C-bound H atoms were placed in idealized positions (C—H = 0.95 – 0.98 Å) and allowed to ride on their parent atoms. Their positions were constrained so that the U_{iso}(H) was equal to 1.2Ueq and 1.5 U_{eq} of their respective parent atoms.

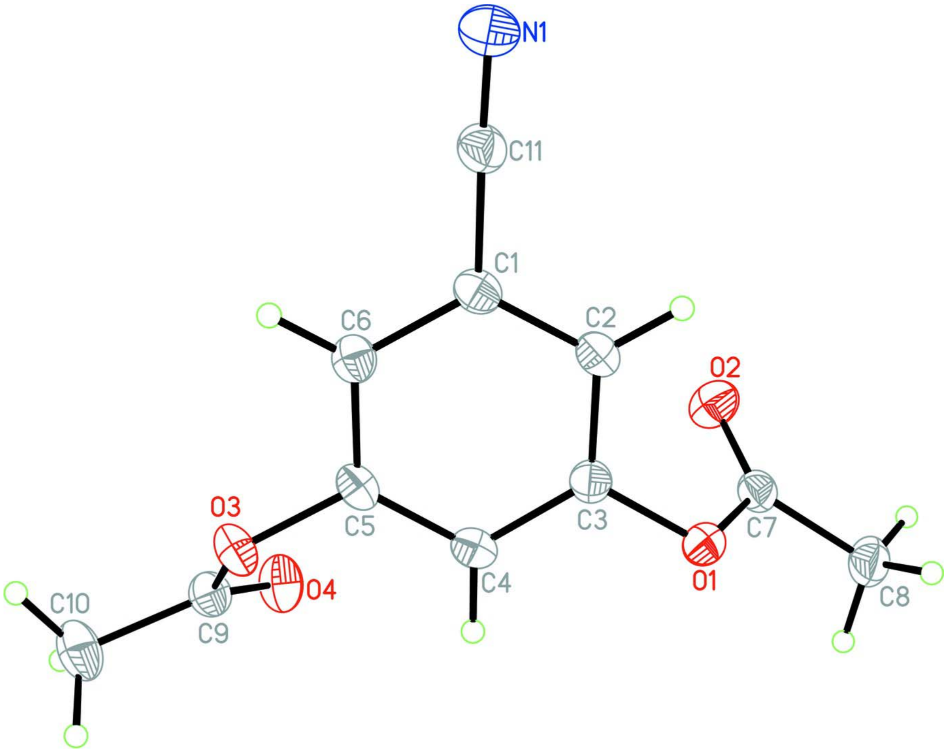

Figure 1

Moleculear structure of the title compound showing the atomic numbering and 50% probability displacement ellipsoids.

5-Cyano-1,3-phenylene diacetate

Crystal data

$C_{11}H_9NO_4$	$F(000) = 456$
$M_r = 219.19$	$D_x = 1.363$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6321 reflections
$a = 6.2293$ (5) Å	$\theta = 2.8$–27.1°
$b = 21.1153$ (17) Å	$\mu = 0.11$ mm^{-1}
$c = 8.5989$ (7) Å	$T = 200$ K
$\beta = 109.171$ (1)°	Block, colourless
$V = 1068.32$ (15) Å^3	0.22 × 0.16 × 0.10 mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	14252 measured reflections
Radiation source: fine-focus sealed tube	2340 independent reflections
Graphite monochromator	2067 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	$\theta_{max} = 27.1°$, $\theta_{min} = 1.9°$
	$h = -7 \rightarrow 7$
	$k = -27 \rightarrow 27$
$T_{min} = 0.977$, $T_{max} = 0.990$	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.092$

$S = 1.01$

2340 reflections

148 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

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.2P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.17$ 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: 0.015 (3)

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 (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.44864 (12)	0.62983 (4)	0.67935 (9)	0.0388 (2)
C1	0.26158 (17)	0.53192 (5)	0.30796 (13)	0.0347 (2)
N1	−0.0537 (2)	0.45024 (6)	0.17554 (15)	0.0578 (3)
O2	0.11962 (15)	0.68031 (4)	0.55736 (11)	0.0484 (2)
C2	0.26753 (17)	0.55886 (5)	0.45661 (13)	0.0345 (2)
H2A	0.1601	0.5470	0.5083	0.041*
O3	0.73998 (13)	0.60722 (4)	0.23031 (10)	0.0397 (2)
C3	0.43337 (17)	0.60332 (5)	0.52755 (13)	0.0331 (2)
O4	0.67580 (16)	0.71218 (4)	0.23128 (11)	0.0493 (2)
C4	0.59239 (17)	0.62130 (5)	0.45604 (13)	0.0349 (2)
H4A	0.7062	0.6517	0.5071	0.042*
C5	0.58096 (17)	0.59369 (5)	0.30774 (13)	0.0339 (2)
C6	0.41844 (18)	0.54912 (5)	0.23152 (14)	0.0355 (2)
H6A	0.4137	0.5307	0.1297	0.043*
C7	0.27412 (18)	0.66893 (5)	0.67974 (13)	0.0361 (2)
C8	0.3085 (2)	0.69393 (6)	0.84782 (15)	0.0490 (3)
H8A	0.1718	0.7167	0.8487	0.073*
H8B	0.4387	0.7229	0.8795	0.073*
H8C	0.3377	0.6587	0.9261	0.073*
C9	0.77434 (19)	0.66931 (5)	0.19634 (14)	0.0374 (3)
C10	0.9438 (2)	0.67242 (6)	0.10879 (19)	0.0531 (3)
H10A	0.9422	0.7149	0.0623	0.080*
H10B	0.9055	0.6410	0.0199	0.080*
H10C	1.0956	0.6634	0.1864	0.080*

C11	0.0867 (2)	0.48624 (5)	0.23206 (15)	0.0410 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0349 (4)	0.0484 (5)	0.0320 (4)	0.0001 (3)	0.0095 (3)	−0.0013 (3)
C1	0.0325 (5)	0.0302 (5)	0.0416 (6)	−0.0003 (4)	0.0125 (4)	0.0017 (4)
N1	0.0610 (7)	0.0529 (6)	0.0611 (7)	−0.0218 (5)	0.0224 (6)	−0.0100 (5)
O2	0.0467 (5)	0.0513 (5)	0.0431 (5)	0.0103 (4)	0.0091 (4)	−0.0065 (4)
C2	0.0307 (5)	0.0358 (5)	0.0392 (6)	0.0002 (4)	0.0142 (4)	0.0042 (4)
O3	0.0395 (4)	0.0349 (4)	0.0539 (5)	−0.0003 (3)	0.0278 (4)	0.0008 (3)
C3	0.0309 (5)	0.0361 (5)	0.0322 (5)	0.0034 (4)	0.0101 (4)	0.0021 (4)
O4	0.0627 (6)	0.0390 (4)	0.0547 (5)	0.0099 (4)	0.0309 (4)	0.0054 (4)
C4	0.0280 (5)	0.0349 (5)	0.0406 (6)	−0.0003 (4)	0.0099 (4)	0.0017 (4)
C5	0.0303 (5)	0.0328 (5)	0.0425 (6)	0.0028 (4)	0.0171 (4)	0.0044 (4)
C6	0.0379 (5)	0.0320 (5)	0.0392 (5)	0.0024 (4)	0.0160 (4)	−0.0002 (4)
C7	0.0380 (5)	0.0363 (5)	0.0370 (6)	−0.0058 (4)	0.0163 (4)	−0.0014 (4)
C8	0.0608 (8)	0.0515 (7)	0.0400 (6)	−0.0111 (6)	0.0238 (6)	−0.0082 (5)
C9	0.0389 (6)	0.0358 (5)	0.0394 (6)	−0.0003 (4)	0.0153 (4)	0.0021 (4)
C10	0.0602 (8)	0.0441 (7)	0.0695 (9)	−0.0025 (6)	0.0411 (7)	0.0047 (6)
C11	0.0437 (6)	0.0377 (6)	0.0443 (6)	−0.0053 (5)	0.0183 (5)	−0.0017 (5)

Geometric parameters (Å, º)

O1—C7	1.3661 (13)	C4—C5	1.3826 (15)
O1—C3	1.3944 (12)	C4—H4A	0.9500
C1—C2	1.3884 (15)	C5—C6	1.3800 (15)
C1—C6	1.3930 (15)	C6—H6A	0.9500
C1—C11	1.4409 (15)	C7—C8	1.4866 (16)
N1—C11	1.1402 (15)	C8—H8A	0.9800
O2—C7	1.1943 (14)	C8—H8B	0.9800
C2—C3	1.3809 (15)	C8—H8C	0.9800
C2—H2A	0.9500	C9—C10	1.4859 (16)
O3—C9	1.3752 (13)	C10—H10A	0.9800
O3—C5	1.3926 (12)	C10—H10B	0.9800
C3—C4	1.3797 (14)	C10—H10C	0.9800
O4—C9	1.1865 (13)		
C7—O1—C3	115.80 (8)	O2—C7—O1	122.08 (10)
C2—C1—C6	121.12 (10)	O2—C7—C8	127.04 (11)
C2—C1—C11	118.61 (9)	O1—C7—C8	110.88 (10)
C6—C1—C11	120.26 (10)	C7—C8—H8A	109.5
C3—C2—C1	118.37 (9)	C7—C8—H8B	109.5
C3—C2—H2A	120.8	H8A—C8—H8B	109.5
C1—C2—H2A	120.8	C7—C8—H8C	109.5
C9—O3—C5	118.81 (8)	H8A—C8—H8C	109.5
C4—C3—C2	122.18 (10)	H8B—C8—H8C	109.5
C4—C3—O1	117.94 (9)	O4—C9—O3	122.96 (10)
C2—C3—O1	119.84 (9)	O4—C9—C10	127.40 (11)
C3—C4—C5	117.91 (10)	O3—C9—C10	109.62 (9)

C3—C4—H4A	121.0	C9—C10—H10A	109.5
C5—C4—H4A	121.0	C9—C10—H10B	109.5
C6—C5—C4	122.22 (9)	H10A—C10—H10B	109.5
C6—C5—O3	116.03 (9)	C9—C10—H10C	109.5
C4—C5—O3	121.68 (9)	H10A—C10—H10C	109.5
C5—C6—C1	118.20 (10)	H10B—C10—H10C	109.5
C5—C6—H6A	120.9	N1—C11—C1	178.16 (13)
C1—C6—H6A	120.9		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*A*···O2^{i}	0.95	2.54	3.3495 (14)	143
C10—H10*A*···O2^{ii}	0.98	2.48	3.3738 (15)	151

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*+1, −*y*+3/2, *z*−1/2.