



Crystal structure of 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione

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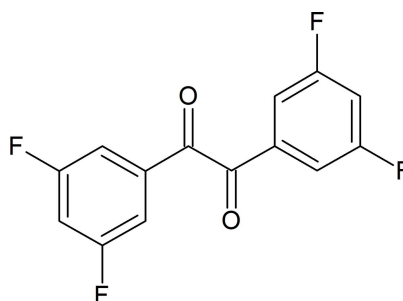
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The title compound, C₁₄H₆F₄O₂, crystallizes with half of a molecule per asymmetric unit and exhibits bond lengths and angles typical of α -diketones. A network of C—H...F contacts and π – π stacking interactions is observed within the structure.

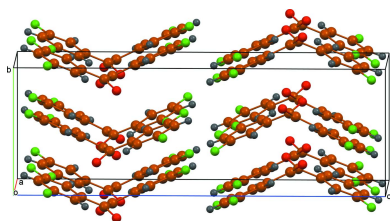
1. Chemical context

Aryl diketones are a class of dicarbonyl compounds with a wide variety of uses in organic synthesis. The title α -diketone, 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione, is used as a precursor in the production of hexabenzocoronenes (Jones *et al.*, 2012). More recently, 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione has been used in the synthesis of various polymers that have been studied for photovoltaics (Cai *et al.*, 2019) and for gas chromatography (GC) stationary phases (Liu *et al.*, 2019). Although the synthetic chemistry is known in the literature, to the best of our knowledge, structural data have not yet been published for the title compound. Herein we report the crystal structure of 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione, isolated as a minor impurity in the synthesis of the related 1,4-diarylketone, 1-(3,5-difluorophenyl)pentane-1,4-dione.



2. Structural commentary

The title compound (Fig. 1) crystallized in the orthorhombic space group *Pbcn*. Benzil (1,2-diphenylethane-1,2-dione) and similar α,α -diketones crystallize in trigonal or monoclinic space groups, respectively (Charpe *et al.*, 2020; El Moncef *et al.*, 2010; Fun *et al.*, 2008). The title compound crystallizes with one half-molecule per asymmetric unit ($Z' = 0.5$), and exhibits the expected bond lengths and angles for α -diketone sp^2 hybridized atoms. Interestingly, the C5—C6—C7—O1 torsion angle [7.55 (19)°] of the title compound is larger compared to



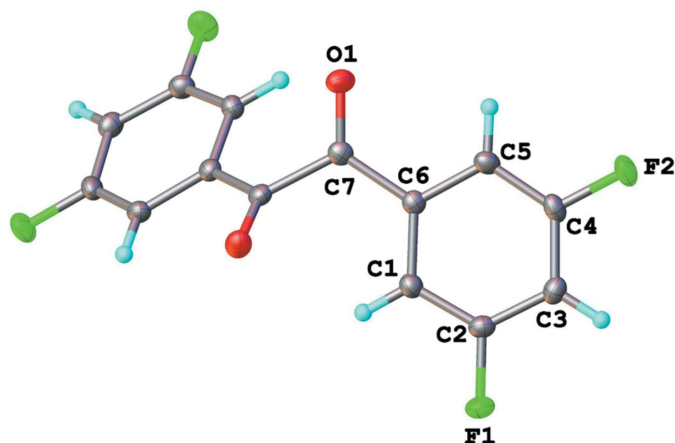


Figure 1
The molecular structure of 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione. Displacement ellipsoids are shown at the 50% probability level.

the same torsion angle in bis(4-fluorophenyl)ethane-1,2-dione [5.69 (18)°; Fun *et al.*, 2008] and benzil [3.80 (18)°; Charpe *et al.*, 2020], but smaller compared to 1,2-bis(3-methoxyphenyl)

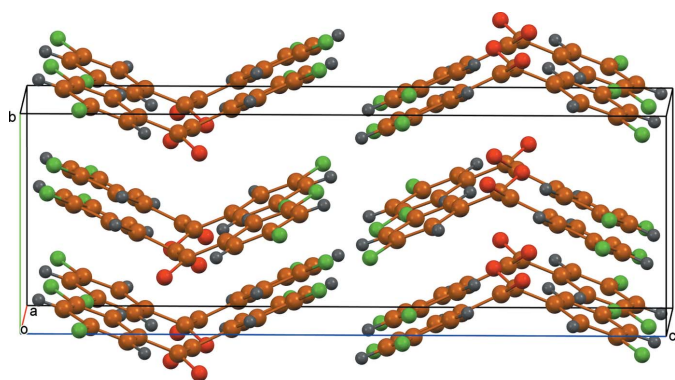


Figure 2
A packing view of 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione.

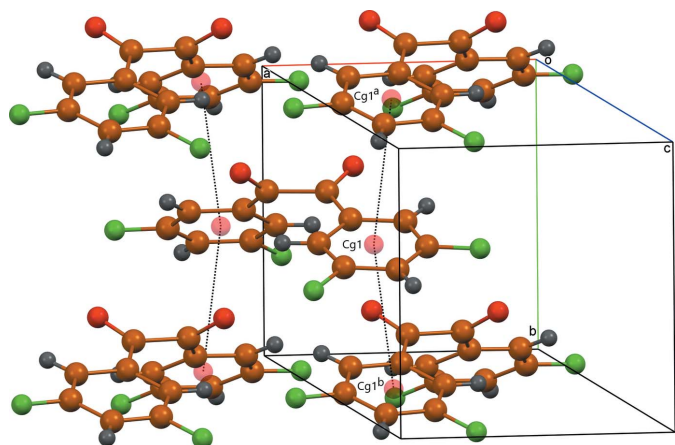


Figure 3
View of π - π stacking interactions in the title structure. Short inter-centroid separations are shown by dashed lines. Cg1 is the centroid of the C1-C6 ring. Symmetry codes: (a) $\frac{3}{2} - x, -\frac{1}{2} + y, z$; (b) $\frac{3}{2} - x, \frac{1}{2} + y, z$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1-H1 \cdots F2 ⁱ	0.93	2.48	3.2281 (16)	137
C3-H3 \cdots F1 ⁱⁱ	0.93	2.46	3.3211 (15)	154
C5-H5 \cdots O1 ⁱⁱⁱ	0.93	2.65	3.517 (2)	156

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

yl)ethane-1,2-dione [7.94 (15)°; Goossens *et al.*, 2005]. The dihedral angle between the two rings is 49.50 (6)° with a C6-C7-C7'-C6' torsion angle of 125.92 (5)°.

3. Supramolecular features

A view of crystal packing of the title compound is presented in Fig. 2. The molecules pack in a stacking pattern maximizing slipped π - π stacking interactions between planes of the difluoroaryl rings with an intercentroid separation of 3.7317 (8) Å, thus forming layers parallel to the bc plane (Fig. 3). Similar π - π stacking interactions with comparable intercentroid separations were observed in bis(4-fluorophenyl)ethane-1,2-dione [3.6416 (9) Å; Fun *et al.*, 2008] and benzil [3.7566 (17) Å; Charpe *et al.*, 2020]. As a result of the packing arrangement of bis(3-methoxyphenyl)ethane-1,2-dione, no π - π stacking interactions were observed (Goossens *et al.*, 2005). The title compound packs in a way that allows close contacts between the fluorine atoms and hydrogen atoms of adjacent molecules, leading to a network of C-H \cdots F interactions (Table 1, Fig. 4) as well as fluorine interactions between neighboring molecules [F1 \cdots F2(1 + x, y, z) = 2.9372 (16) Å, F1 \cdots F1(2 - x, 1 - y, 1 - z) = 2.8614 (16) Å]. A network of C-H \cdots O interactions is also observed between the carbonyl oxygen and H5. This interaction is significantly weaker for 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione in comparison to benzil (O \cdots H = 2.42 Å) and bis(4-fluorophenyl)ethane-1,2-dione (O \cdots H = 2.40 Å). As a result, the π - π stacking and C-H \cdots F interactions play a vital role in how the compound packs within the crystal structure.

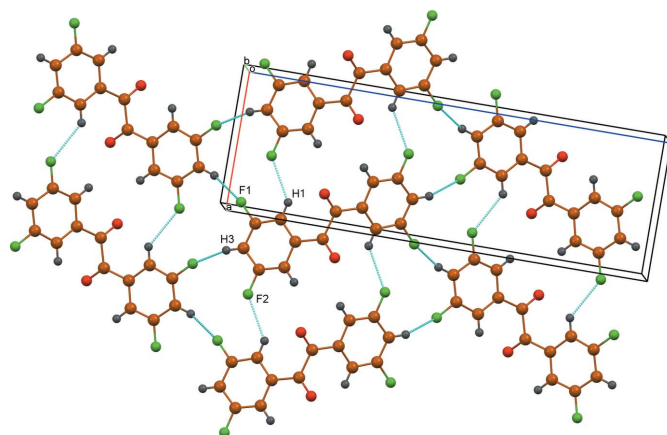


Figure 4
View of intermolecular C-H \cdots F interactions in the title structure (for details see Table 1).

4. Database survey

A search of the Cambridge Structural Database (CSD, version of December 2019; Groom *et al.*, 2016) for aryl substituted α -diketones yielded 178 results. The bond lengths and angles in the title molecule are consistent with α,α -diketones reported in the literature. The most closely related compound was compared to the title compound in the preceding sections.

5. Synthesis and crystallization

Colorless crystals of the title compound suitable for single-crystal X-ray diffraction study were obtained by slow evaporation of a dichloromethane solution of the residue left after isolation of 1-(3,5-difluorophenyl)pentane-1,4-dione.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically (C–H = 0.93 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Funding information

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₆ F ₄ O ₂
<i>M_r</i>	282.19
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0588 (2), 7.4008 (2), 21.5265 (4)
<i>V</i> (Å ³)	1124.56 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.16
Crystal size (mm)	0.30 × 0.14 × 0.10
Data collection	
Diffractometer	XtaLAB Synergy, Single source at offset/far, HyPix3000
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)
<i>T</i> _{min} , <i>T</i> _{max}	0.679, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13347, 1202, 1014
<i>R</i> _{int}	0.034
(sin θ/λ) _{max} (Å ⁻¹)	0.641
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.085, 1.03
No. of reflections	1202
No. of parameters	91
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.21, -0.24

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Crystal structure of 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2020); cell refinement: *CrysAlis PRO* (Rigaku OD, 2020); data reduction: *CrysAlis PRO* (Rigaku OD, 2020); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

1,2-Bis(3,5-difluorophenyl)ethane-1,2-dione

Crystal data

$C_{14}H_6F_4O_2$

$M_r = 282.19$

Orthorhombic, *Pbcn*

$a = 7.0588$ (2) Å

$b = 7.4008$ (2) Å

$c = 21.5265$ (4) Å

$V = 1124.56$ (5) Å³

$Z = 4$

$F(000) = 568$

$D_x = 1.667$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7273 reflections

$\theta = 1.9$ – 27.0°

$\mu = 0.16$ mm⁻¹

$T = 100$ K

Block, colourless

$0.30 \times 0.14 \times 0.10$ mm

Data collection

XtaLAB Synergy, Single source at offset/far,
HyPix3000

diffractometer

Radiation source: micro-focus sealed X-ray
tube, PhotonJet (Mo) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: gaussian
(CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.679$, $T_{\max} = 1.000$

13347 measured reflections

1202 independent reflections

1014 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 27.1^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -8 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -27 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.085$

$S = 1.03$

1202 reflections

91 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.4818P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.21$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ e Å⁻³

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	1.04484 (11)	0.64342 (12)	0.45793 (3)	0.0274 (2)
F2	0.41188 (11)	0.52722 (13)	0.40758 (4)	0.0298 (2)
O1	0.78193 (13)	0.28658 (13)	0.22568 (4)	0.0236 (3)
C1	0.97690 (19)	0.50922 (17)	0.36170 (6)	0.0183 (3)
H1	1.1050	0.5083	0.3516	0.022*
C2	0.91452 (19)	0.57731 (18)	0.41774 (6)	0.0196 (3)
C3	0.72718 (19)	0.58412 (18)	0.43505 (6)	0.0200 (3)
H3	0.6896	0.6293	0.4734	0.024*
C4	0.59783 (19)	0.51991 (19)	0.39216 (6)	0.0200 (3)
C5	0.64773 (18)	0.44830 (18)	0.33558 (6)	0.0190 (3)
H5	0.5563	0.4056	0.3081	0.023*
C6	0.84090 (18)	0.44170 (17)	0.32055 (6)	0.0167 (3)
C7	0.89509 (18)	0.36177 (17)	0.25965 (6)	0.0174 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0235 (5)	0.0368 (5)	0.0218 (4)	−0.0053 (4)	−0.0033 (3)	−0.0094 (3)
F2	0.0151 (4)	0.0487 (6)	0.0254 (5)	0.0037 (4)	0.0047 (3)	−0.0003 (4)
O1	0.0235 (5)	0.0298 (6)	0.0176 (5)	−0.0056 (4)	−0.0014 (4)	−0.0014 (4)
C1	0.0160 (6)	0.0201 (7)	0.0188 (7)	−0.0005 (5)	0.0007 (5)	0.0009 (5)
C2	0.0203 (7)	0.0210 (7)	0.0174 (6)	−0.0013 (5)	−0.0030 (5)	−0.0009 (5)
C3	0.0232 (7)	0.0200 (7)	0.0168 (6)	0.0026 (6)	0.0025 (5)	−0.0003 (5)
C4	0.0142 (7)	0.0240 (7)	0.0220 (7)	0.0024 (5)	0.0028 (5)	0.0046 (5)
C5	0.0170 (6)	0.0230 (7)	0.0168 (6)	−0.0012 (5)	−0.0023 (5)	0.0029 (5)
C6	0.0169 (7)	0.0168 (7)	0.0162 (6)	0.0000 (5)	0.0005 (5)	0.0024 (5)
C7	0.0184 (7)	0.0178 (6)	0.0161 (6)	−0.0001 (5)	−0.0011 (5)	0.0036 (5)

Geometric parameters (\AA , $^\circ$)

F1—C2	1.3543 (15)	C3—H3	0.9300
F2—C4	1.3550 (15)	C3—C4	1.3827 (19)
O1—C7	1.2176 (16)	C4—C5	1.3741 (19)
C1—H1	0.9300	C5—H5	0.9300
C1—C2	1.3796 (18)	C5—C6	1.4023 (18)
C1—C6	1.3985 (18)	C6—C7	1.4882 (17)
C2—C3	1.3748 (19)	C7—C7 ⁱ	1.538 (3)
C2—C1—H1	121.1	C5—C4—C3	123.72 (13)

C2—C1—C6	117.73 (12)	C4—C5—H5	121.1
C6—C1—H1	121.1	C4—C5—C6	117.85 (12)
F1—C2—C1	118.28 (11)	C6—C5—H5	121.1
F1—C2—C3	117.84 (11)	C1—C6—C5	120.59 (12)
C3—C2—C1	123.87 (13)	C1—C6—C7	121.56 (12)
C2—C3—H3	121.9	C5—C6—C7	117.84 (11)
C2—C3—C4	116.21 (12)	O1—C7—C6	122.83 (12)
C4—C3—H3	121.9	O1—C7—C7 ⁱ	117.99 (12)
F2—C4—C3	117.54 (12)	C6—C7—C7 ⁱ	119.05 (12)
F2—C4—C5	118.74 (12)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots F2 ⁱⁱ	0.93	2.48	3.2281 (16)	137
C3—H3 \cdots F1 ⁱⁱⁱ	0.93	2.46	3.3211 (15)	154
C5—H5 \cdots O1 ^{iv}	0.93	2.65	3.517 (2)	156

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

Selected bond distances (\AA) and angles ($^\circ$) for 1,2-bis(3,5-difluorophenyl)ethane-1,2-dione.

C1—C2	1.3796 (18)
C1—C6	1.3985 (18)
C2—C3	1.3748 (19)
C3—C4	1.3827 (19)
C4—C5	1.3741 (19)
C5—C6	1.4023 (18)
C6—C7	1.4882 (17)
C7—C7'	1.538 (3)
C7—O1	1.2176 (16)
F1—C2	1.3543 (15)
F2—C4	1.3550 (15)
C1—C6—C5	120.59 (12)
C1—C6—C7	121.56 (12)
C2—C1—C6	117.73 (12)
C2—C3—C4	116.21 (12)
C3—C2—C1	123.87 (13)
C4—C5—C6	117.85 (12)
C5—C4—C3	123.72 (13)
C5—C6—C7	117.84 (11)
C6—C7—C7'	119.05 (12)
O1—C7—C6	122.83 (12)
O1—C7—C7'	117.99 (12)
F1—C2—C1	118.28 (11)
F1—C2—C3	117.84 (11)

F2-C4-C3	117.54 (12)
F2-C4-C5	118.74 (12)
