



Crystal structure of butane-1,4-diyl bis(furan-2-carboxylate)

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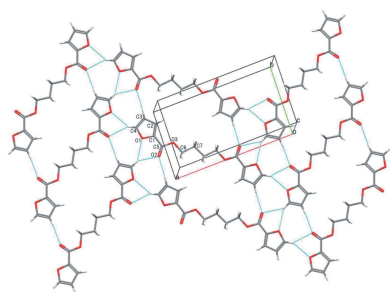
The asymmetric unit of the title compound, C₁₄H₁₄O₆, a monomeric compound of poly(butylene 2,5-furandicarboxylate), consists of one half-molecule, the whole all-*trans* molecule being generated by an inversion centre. In the crystal, the molecules are interconnected *via* C—H···O interactions, forming a molecular sheet parallel to (10 $\bar{2}$). The molecular sheets are further linked by C—H··· π interactions.

1. Chemical context

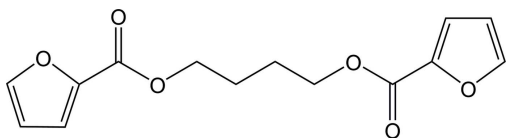
To suppress global warming, materials derived from fossil fuels have been attempted to be replaced with plant-based products. For example, plant-derived furan-2,5-dicarboxylic acid is expected to be substituted for terephthalic acid, raw materials of aromatic polyesters such as poly(ethylene terephthalate) and poly(butylene terephthalate) (abbreviated herein as PBT) (Gandini *et al.*, 2016); therefore, in the future, the substitute for PBT will possibly be poly(butylene 2,5-furandicarboxylate) (PBF), the alternate copolymer of furan-2,5-dicarboxylic acid and butane-1,4-diol.

The ultimate mechanical stiffness of polymers mostly corresponds to the crystalline modulus in the chain-axis direction at 0 K and depends largely on the chain conformation (Kurita *et al.*, 2018). Therefore, it is of significance to determine conformations of polymers in crystal and to relate such structural information to their mechanical properties. PBT is known to exhibit two crystal structures of α and β forms (Yokouchi *et al.*, 1976; Desborough & Hall, 1977). The α form adopts *gauche*⁺ (*g*⁺), *gauche*⁺ (*g*⁺), *trans* (*t*), *gauche*[−] (*g*[−]) and *gauche*[−] (*g*[−]) conformations in the O—CH₂—CH₂—CH₂—O unit (referred hereafter to as the spacer), while the β form has a near all-*trans* spacer. It is known that mechanical stresses induce the α -to- β transformation, which will absorb impact and avoid fracture. Owing to such remarkable structural characteristics, PBT has been used for engineering plastics superior in impact resistance.

Single crystal X-ray structure analysis of butane-1,4-diyl dibenzoate (BT), a model compound of PBT, showed that its spacer lies in a *tggtt* conformation different from that of PBT (Palmer *et al.*, 1985). A powder X-ray diffraction study on PBF (Zhu *et al.*, 2013) has estimated dihedral angles of its spacer to be 180° (*trans*), 66° (*+synclinal*), 99° (*+anticlinal*), 124° (*+anticlinal*) and 148° (*+anticlinal*) and hence quite different from those of PBT and BT. In this study, we have conducted a single-crystal X-ray diffraction experiment on a model



compound of PBF, butane-1,4-diyl bis(furan-2-carboxylate) (BF), to investigate its spacer conformation and intermolecular interactions and compare them with those of PBF, BT and PBT.



2. Structural commentary

The BF spacer of the title compound adopts an all-*trans* conformation (Fig. 1), which is different from those of PBF as well as PBT and BT. The unit cell includes four molecules, each of which is located on an inversion centre, and hence one half-molecule corresponds to the asymmetric unit. The furan O1/C1–C4 ring is planar, while the carboxy O2/C5/O3 plane is slightly twisted from the furan ring, with a dihedral angle of 4.00 (15)°.

3. Supramolecular features

In the crystal, the BF molecules are interconnected by C–H···O interactions (Table 1) to form a molecular sheet parallel to (10 $\bar{2}$) (Fig. 2). The sheets are further linked *via* a C–H··· π interaction (Table 1 and Fig. 3), forming a three-dimensional network. In the BT crystal (Palmer *et al.*, 1985), the benzene rings face to each other to form intermolecular π – π interactions with centroid–centroid distances of 4.169 (2) and 3.910 (2) Å. In addition, the benzene rings act as donors in C–H··· π interactions. As stated above, BF seems to prefer the C–H···O interactions and adopt a spacer conformation so as to fulfill the C–H···O interactions efficiently, whereas BT and PBT (Yokouchi *et al.*, 1976; Desborough & Hall, 1977) tend to adapt a spacer conformation to form π – π interactions.

4. Database survey

A search in the Cambridge Structural Database (Version 5.40, last update February 2019; Groom *et al.*, 2016) for BF itself

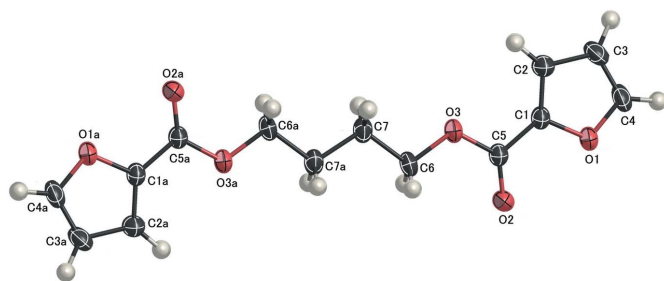


Figure 1

The molecular structure of the title compound, showing the atom-labelling scheme. Atoms with suffix a are generated by the symmetry operation $(-x + \frac{3}{2}, -y + \frac{1}{2}, -z)$. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the O1/C1–C4 ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C3–H3···O2 ⁱ	0.95	2.41	3.3526 (15)	174
C4–H4···O1 ⁱⁱ	0.95	2.60	3.4142 (18)	145
C4–H4···O2 ⁱⁱ	0.95	2.49	3.317 (2)	146
C6–H6B···Cg1 ⁱⁱⁱ	0.99	2.66	3.5869 (16)	156

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{5}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 2, -y + 1, -z$.

gave only one similar compound, PBF (Zhu *et al.*, 2013), mentioned above. Although a search for dimethyl furan-2,5-dicarboxylate (DMF-2,5-DC) gave no hits, 20 compounds related to furan-2,5-dicarboxylic acid (FDCA) were suggested as similar compounds. They are FDCA itself (Martuscelli & Pedone, 1968) and complexes including FDCA. The crystal structure of dimethyl furan-2,4-dicarboxylate (DMF-2,4-DC) was reported (Thiyagarajan *et al.*, 2013). DMF-2,4-DC forms π – π interactions between the furan rings with centroid–centroid distances of 3.6995 (12) and 3.7684 (14) Å, and C–H···O interactions [C···O = 3.333 (2), 3.276 (3) and

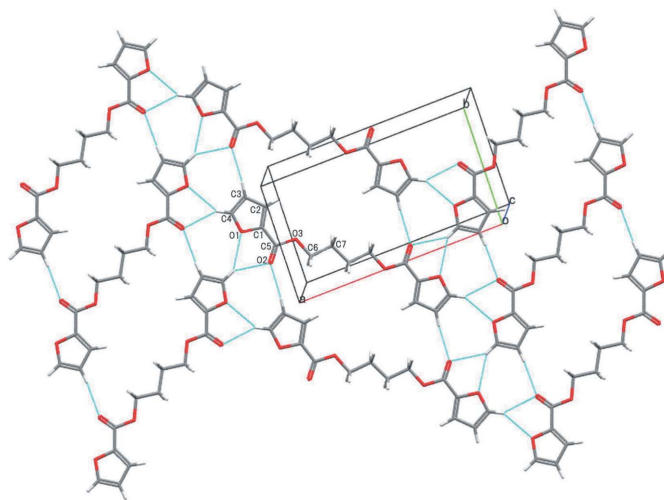


Figure 2

A packing diagram of the title compound, showing the molecular sheet formed by C–H···O interactions (blue lines).

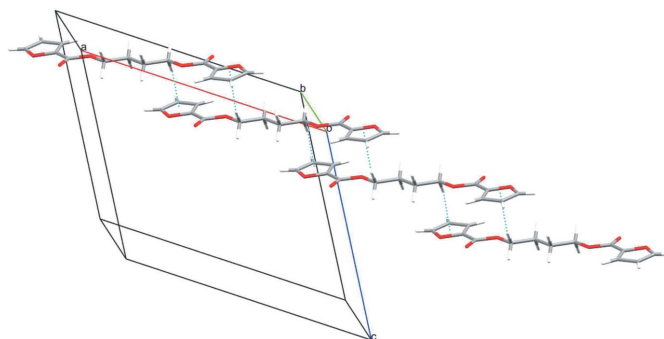


Figure 3

A packing diagram of the title compound, showing the intermolecular C–H··· π interactions (blue dotted lines) between the molecular sheets.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₄ O ₆
<i>M_r</i>	278.25
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.1298 (17), 7.8773 (8), 13.5247 (14)
β (°)	123.6698 (12)
<i>V</i> (Å ³)	1430.2 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.10
Crystal size (mm)	0.40 × 0.20 × 0.20
Data collection	
Diffraction	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T_{min}</i> , <i>T_{max}</i>	0.94, 0.98
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	3968, 1625, 1254
<i>R_{int}</i>	0.038
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.098, 1.03
No. of reflections	1625
No. of parameters	91
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.40, -0.25

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *XSHEL* (Bruker, 2013), *PLATON* (Spek, 2009) and *XCIF* (Bruker, 2013).

3.465 (2) Å]. The dihedral angles between the carboxy group and the furan ring are 1.11–5.86°.

5. Synthesis and crystallization

Furan-2-carbonyl chloride (2.2 ml, 22 mmol) was added dropwise under a nitrogen atmosphere to butane-1,4-diol (0.89 ml, 10 mmol) and pyridine (6.0 ml) put in a three-necked flask dipped in ice–water and stirred at room temperature for 28 h. The reaction mixture was extracted with chloroform (10 ml) and water (10 ml), and the organic layer was washed thrice with aqueous sodium bicarbonate (10%), dried over anhydrous sodium sulfate overnight and filtrated. The filtrate was condensed on a rotary evaporator, and the residue was

dried *in vacuo* and identified by ¹H and ¹³C NMR as BF (yield 73%).

A small amount of BF was dissolved in benzene in a small phial, which was put in a larger phial including a small volume of *n*-hexane. The outer vessel was capped and stood still. After a few weeks, single crystals were found to precipitate at the bottom of the inner phial.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were geometrically positioned with C–H = 0.95 and 0.99 Å for the aromatic and methylene groups, respectively, and were refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Funding information

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *XSHEL* (Bruker, 2013); software used to prepare material for publication: *PLATON* (Spek, 2009) and *XCIF* (Bruker, 2013).

(I)

Crystal data

$C_{14}H_{14}O_6$

$M_r = 278.25$

Monoclinic, $C2/c$

$a = 16.1298$ (17) Å

$b = 7.8773$ (8) Å

$c = 13.5247$ (14) Å

$\beta = 123.6698$ (12)°

$V = 1430.2$ (3) Å³

$Z = 4$

$F(000) = 584$

$D_x = 1.292$ Mg m⁻³

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

Cell parameters from 1288 reflections

$\theta = 3.0$ – 26.3 °

$\mu = 0.10$ mm⁻¹

$T = 173$ K

Prismatic, colourless

$0.40 \times 0.20 \times 0.20$ mm

Data collection

Bruker APEXII CCD area detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.94$, $T_{\max} = 0.98$

3968 measured reflections

1625 independent reflections

1254 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.0$ °

$h = -20$ → 19

$k = -9$ → 10

$l = -17$ → 16

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.098$

$S = 1.03$

1625 reflections

91 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.4241P]$

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

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

$\Delta\rho_{\max} = 0.40$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Special details

Experimental. SADABS (Sheldrick, 1996)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.06223 (8)	0.66487 (14)	0.16074 (10)	0.0256 (3)
C2	1.01643 (9)	0.81730 (15)	0.13072 (12)	0.0327 (3)
H2	0.9468	0.8379	0.0893	0.039*
C3	1.09319 (10)	0.94116 (16)	0.17360 (12)	0.0374 (3)
H3	1.085	1.0609	0.1664	0.045*
C4	1.17928 (10)	0.85557 (16)	0.22604 (12)	0.0362 (3)
H4	1.243	0.907	0.2627	0.043*
C5	1.02744 (8)	0.48957 (14)	0.14292 (10)	0.0246 (3)
C6	0.88565 (9)	0.31465 (14)	0.06770 (11)	0.0287 (3)
H6A	0.9159	0.2497	0.1427	0.034*
H6B	0.8977	0.2524	0.0132	0.034*
C7	0.77555 (9)	0.33626 (15)	0.01192 (12)	0.0318 (3)
H7A	0.7459	0.3994	-0.0637	0.038*
H7B	0.7646	0.4033	0.0656	0.038*
O1	1.16329 (6)	0.68497 (10)	0.21987 (8)	0.0318 (2)
O2	1.08020 (6)	0.36607 (10)	0.17085 (8)	0.0341 (2)
O3	0.92865 (6)	0.48359 (10)	0.09086 (8)	0.0318 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0210 (6)	0.0253 (6)	0.0304 (6)	-0.0036 (4)	0.0142 (5)	-0.0020 (5)
C2	0.0278 (6)	0.0268 (6)	0.0433 (7)	0.0012 (5)	0.0198 (6)	0.0003 (5)
C3	0.0427 (8)	0.0207 (6)	0.0519 (8)	-0.0041 (5)	0.0281 (7)	-0.0042 (5)
C4	0.0341 (7)	0.0272 (7)	0.0473 (8)	-0.0128 (5)	0.0225 (6)	-0.0096 (6)
C5	0.0222 (6)	0.0245 (6)	0.0273 (6)	-0.0033 (4)	0.0139 (5)	-0.0009 (4)
C6	0.0254 (6)	0.0240 (6)	0.0351 (7)	-0.0087 (4)	0.0157 (5)	-0.0029 (5)
C7	0.0247 (6)	0.0305 (7)	0.0362 (7)	-0.0065 (5)	0.0144 (5)	0.0005 (5)
O1	0.0225 (4)	0.0247 (5)	0.0435 (5)	-0.0055 (3)	0.0154 (4)	-0.0040 (4)
O2	0.0270 (5)	0.0219 (5)	0.0486 (6)	-0.0008 (3)	0.0180 (4)	-0.0007 (4)
O3	0.0216 (5)	0.0248 (5)	0.0450 (5)	-0.0056 (3)	0.0160 (4)	-0.0008 (4)

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

C1—C2	1.3490 (16)	C5—O2	1.2070 (14)
C1—O1	1.3698 (14)	C5—O3	1.3390 (14)
C1—C5	1.4594 (15)	C6—O3	1.4524 (13)
C2—C3	1.4230 (17)	C6—C7	1.5054 (17)

C2—H2	0.95	C6—H6A	0.99
C3—C4	1.3394 (18)	C6—H6B	0.99
C3—H3	0.95	C7—C7 ⁱ	1.528 (2)
C4—O1	1.3622 (14)	C7—H7A	0.99
C4—H4	0.95	C7—H7B	0.99
C2—C1—O1	110.40 (10)	O3—C6—C7	107.10 (9)
C2—C1—C5	134.13 (11)	O3—C6—H6A	110.3
O1—C1—C5	115.46 (10)	C7—C6—H6A	110.3
C1—C2—C3	106.27 (11)	O3—C6—H6B	110.3
C1—C2—H2	126.9	C7—C6—H6B	110.3
C3—C2—H2	126.9	H6A—C6—H6B	108.5
C4—C3—C2	106.44 (11)	C6—C7—C7 ⁱ	110.71 (13)
C4—C3—H3	126.8	C6—C7—H7A	109.5
C2—C3—H3	126.8	C7 ⁱ —C7—H7A	109.5
C3—C4—O1	111.02 (11)	C6—C7—H7B	109.5
C3—C4—H4	124.5	C7 ⁱ —C7—H7B	109.5
O1—C4—H4	124.5	H7A—C7—H7B	108.1
O2—C5—O3	124.28 (10)	C4—O1—C1	105.87 (9)
O2—C5—C1	124.83 (10)	C5—O3—C6	115.62 (9)
O3—C5—C1	110.89 (10)		
O1—C1—C2—C3	-0.07 (14)	O1—C1—C5—O3	176.33 (9)
C1—C2—C3—C4	0.03 (15)	C1—C5—O3—C6	179.42 (9)
C2—C3—C4—O1	0.02 (15)	C7—C6—O3—C5	178.85 (10)
C3—C4—O1—C1	-0.06 (14)	O3—C6—C7—C7 ⁱ	-178.14 (12)
C2—C1—O1—C4	0.08 (14)	C5—C1—C2—C3	-179.47 (13)
O1—C1—C5—O2	-3.87 (17)	C5—C1—O1—C4	179.61 (10)
C2—C1—C5—O2	175.50 (14)	O2—C5—O3—C6	-0.38 (17)
C2—C1—C5—O3	-4.3 (2)		

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

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

*Cg*1 is the centroid of the O1/C1—C4 ring.

<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>
C3—H3 \cdots O2 ⁱⁱ	0.95	2.41	3.3526 (15)	174
C4—H4 \cdots O1 ⁱⁱⁱ	0.95	2.60	3.4142 (18)	145
C4—H4 \cdots O2 ⁱⁱⁱ	0.95	2.49	3.317 (2)	146
C6—H6B \cdots <i>Cg</i> 1 ^{iv}	0.99	2.66	3.5869 (16)	156

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