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## Structure Reports

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2,2'-[2,3,5,6-Tetramethyl-*p*-phenylenebis(methyleneoxy)]dibenzoic acid

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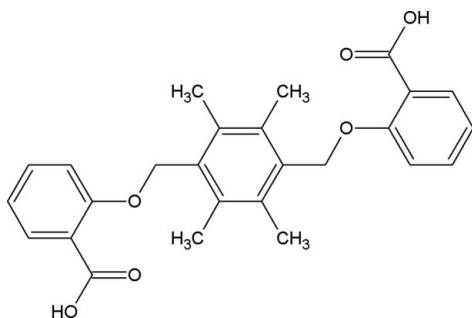
Received 29 January 2010; accepted 24 March 2010

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å; disorder in main residue;  $R$  factor = 0.050;  $wR$  factor = 0.157; data-to-parameter ratio = 14.6.

The asymmetric unit of the title compound,  $\text{C}_{26}\text{H}_{26}\text{O}_6$ , contains only a half-molecule, the other half being generated by an inversion center. The two carboxyphenoxymethyl units occupy the 1,4-positions of the central aromatic ring. The central ring and the six linked C atoms are almost planar, with a maximum deviation of 0.0286 (17) Å, and the plane makes a dihedral angle of 75.50 (6)° with the benzene ring. In the crystal, strong  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the carboxyl groups of adjacent molecules and  $\text{C}-\text{H}\cdots\pi$  interactions link the molecules into zigzag chains along (220) and ( $\bar{1}10$ ); the two types of chain are arranged alternately, forming a three-dimensional framework.

## Related literature

For a structure with a similar central ring, see: Britton (2003). For structures with similar hydrogen-bonded carboxylate groups, see: Bailey & Brown (1967); Glidewell *et al.* (2004).



## Experimental

## Crystal data

$\text{C}_{26}\text{H}_{26}\text{O}_6$   
 $M_r = 434.47$   
 Monoclinic,  $P2_1/c$   
 $a = 9.2841$  (16) Å  
 $b = 8.6936$  (15) Å  
 $c = 14.075$  (2) Å  
 $\beta = 96.902$  (3)°  
 $V = 1127.8$  (3) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.16 \times 0.12 \times 0.06$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.985$ ,  $T_{\max} = 0.994$   
 6437 measured reflections  
 2322 independent reflections  
 1269 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.157$   
 $S = 1.02$   
 2322 reflections  
 159 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.15$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the central C9,C10,C12',C9'C10',C12 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2A-\text{H}2A\cdots\text{O}1^i$	0.82	1.83	2.624 (9)	164
$\text{O}2B-\text{H}2B\cdots\text{O}1^i$	0.82	1.91	2.721 (16)	168
$\text{C}5-\text{H}5\cdots\text{Cg}1^{\text{ii}}$	0.93	2.80	3.356 (5)	120

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINTE-Plus (Bruker, 2007); data reduction: SAINTE-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2194).

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**supplementary materials**

*Acta Cryst.* (2010). E66, o995 [ doi:10.1107/S1600536810011220 ]

## 2,2'-[2,3,5,6-Tetramethyl-*p*-phenylenebis(methyleneoxy)]dibenzoic acid

T. Hu

### Comment

The title compound (I), was designed as a ligand for preparing MOF materials. This paper reports its single crystal structure in the solid state. The asymmetric unit contains only half of the molecule, with the other half generated by an inversion center at (0,1/2,0). (Fig 1.). The two branches of benzenic-carboxylate acid groups of the title compound occupy the 1, 4 positions of the central aromatic ring to form a line. The central ring with its linked six C atoms, similar to the one observed in Britton (2003), is almost planar, with a maxima deviation of  $-0.0286$  ( $17^\circ$ ) for C13 and makes a dihedral angle of  $75.50$  ( $6^\circ$ ) with the benzene ring. Strong C—H $\cdots$  $\pi$  bond was observed in the structure, with a perpendicular distance of  $2.700$  ( $3^\circ$ ) to the C9 C10-C12-C9<sub>i</sub>C10<sub>i</sub>C12<sub>i</sub> ring plane (i:-x, -y, -z). Meanwhile, the structure of the two carboxylate groups linked by the strong H-bond (Table 1) is comparable to that described in Bailey & Brown (1967) and Glidewell *et al.* (2004). Strong hydrogen bondings between the carboxylate groups of the adjacent molecules link the molecules of title compound into zig-zag chains along (220) and (-110) directions, respectively (Fig. 2), and these two chains were arranged alternatively to form a 3D framework (Fig. 3).

### Experimental

1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.2 g, 10.0 mmol), methyl salicylate (3.08 g, 22.0 mmol) and K<sub>2</sub>CO<sub>3</sub> (3.04 g, 22 mmol) were put into 40 ml of acetone and the mixture was heated to reflux for 6 hours. The resulting mixture was filtrated while it was still hot. Lots of white precipitate was formed when the filtrate was cooled down to room temperature. The precipitate was filtrated and was put into 30 ml methanol. NaOH aqueous solution (20 ml, 2 mol/L) was added and the solution was stirred for 8 hours under refluxing. After cooling to room temperature, the pH value of the clear solution was adjusted to 2 by dilute hydrochloric acid. The clear solution was allowed to evaporate slowly under inert atmosphere. Prismatic crystals of the title compound were obtained after 2 days. The crystals were filtered, washed by cold EtOH and dried in air.

### Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H =  $0.930$  Å and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  for aromatic hydrogens, and with C—H =  $0.960$  Å and  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$  for H atoms of the methyl groups, and with C—H =  $0.970$  Å and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  for H atoms of the methylene group, and with O—H =  $0.820$  Å and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$  for the hydroxide H atom, respectively. O2 atom was treated as disordered in two positions of O2a and O2b with the occupation factors of 0.58, and 0.42, respectively.

## Figures

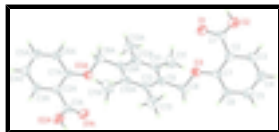


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids. The atoms marked with A are derived from the reference atoms by means of the  $(-x, 1-y, -z)$  symmetry transformation..

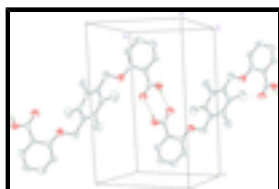


Fig. 2. Zig-zag chain along  $(220)$  direction in the structure. Strong hydrogen bondings are shown as dash lines.

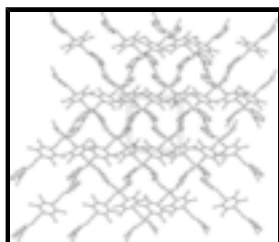


Fig. 3. Packing diagram viewed down the  $c$  axis.

## 2,2'-[2,3,5,6-Tetramethyl-*p*-phenylenebis(methyleneoxy)]dibenzoic acid

### Crystal data

$C_{26}H_{26}O_6$

$M_r = 434.47$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 9.2841$  (16) Å

$b = 8.6936$  (15) Å

$c = 14.075$  (2) Å

$\beta = 96.902$  (3)°

$V = 1127.8$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 460$

$D_x = 1.279$  Mg m<sup>-3</sup>

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

Cell parameters from 1055 reflections

$\theta = 2.8$ – $27.5$ °

$\mu = 0.09$  mm<sup>-1</sup>

$T = 293$  K

Prism, colorless

$0.16 \times 0.12 \times 0.06$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

phi and  $\omega$  scans

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

$T_{\min} = 0.985$ ,  $T_{\max} = 0.994$

6437 measured reflections

2322 independent reflections

1269 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\text{max}} = 27.5$ °,  $\theta_{\text{min}} = 2.2$ °

$h = -10 \rightarrow 12$

$k = -11 \rightarrow 11$

$l = -16 \rightarrow 18$

*Refinement*

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.157$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.1641P]$
2322 reflections	where $P = (F_o^2 + 2F_c^2)/3$
159 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$

*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.

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.4303 (2)	0.0417 (3)	0.12146 (17)	0.0593 (6)	
C2	0.3798 (2)	0.0589 (3)	0.21720 (15)	0.0552 (6)	
C3	0.4391 (3)	-0.0387 (3)	0.29015 (17)	0.0711 (7)	
H3	0.5065	-0.1123	0.2768	0.085*	
C4	0.4006 (3)	-0.0291 (3)	0.38111 (18)	0.0820 (8)	
H4	0.4405	-0.0963	0.4286	0.098*	
C5	0.3027 (3)	0.0805 (3)	0.40112 (17)	0.0775 (8)	
H5	0.2774	0.0885	0.4629	0.093*	
C6	0.2413 (3)	0.1787 (3)	0.33116 (17)	0.0666 (7)	
H6	0.1750	0.2526	0.3459	0.080*	
C7	0.2781 (2)	0.1680 (3)	0.23858 (15)	0.0558 (6)	
C8	0.1090 (3)	0.3686 (3)	0.18341 (18)	0.0764 (8)	
H8A	0.1458	0.4480	0.2283	0.092*	
H8B	0.0318	0.3139	0.2097	0.092*	
C9	0.0536 (3)	0.4386 (3)	0.08832 (18)	0.0666 (7)	
C10	-0.0399 (3)	0.3513 (3)	0.0242 (2)	0.0687 (7)	
C11	-0.0835 (3)	0.1899 (3)	0.0519 (2)	0.1008 (10)	
H11A	-0.1073	0.1293	-0.0048	0.151*	

## supplementary materials

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H11B	-0.1664	0.1959	0.0865	0.151*	
H11C	-0.0043	0.1428	0.0916	0.151*	
C12	0.0955 (2)	0.5869 (3)	0.06413 (19)	0.0687 (7)	
C13	0.2028 (3)	0.6782 (4)	0.1319 (2)	0.1005 (10)	
H13A	0.2806	0.7135	0.0983	0.151*	
H13B	0.2412	0.6137	0.1843	0.151*	
H13C	0.1545	0.7649	0.1560	0.151*	
O1	0.3567 (2)	0.0876 (2)	0.04745 (12)	0.0919 (7)	
O2A	0.5605 (9)	-0.0059 (16)	0.1171 (6)	0.076 (3)	0.59 (4)
H2A	0.5699	-0.0296	0.0618	0.114*	0.59 (4)
O2B	0.524 (3)	-0.059 (4)	0.1191 (11)	0.130 (6)	0.41 (4)
H2B	0.5576	-0.0543	0.0678	0.196*	0.41 (4)
O3	0.22344 (16)	0.26410 (18)	0.16631 (11)	0.0674 (5)	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0584 (15)	0.0585 (15)	0.0617 (15)	0.0095 (12)	0.0096 (12)	-0.0021 (11)
C2	0.0541 (13)	0.0586 (13)	0.0532 (13)	0.0005 (11)	0.0072 (10)	-0.0003 (10)
C3	0.0738 (16)	0.0709 (16)	0.0683 (16)	0.0109 (13)	0.0072 (13)	0.0078 (13)
C4	0.094 (2)	0.092 (2)	0.0604 (16)	0.0041 (17)	0.0079 (14)	0.0189 (14)
C5	0.0815 (18)	0.096 (2)	0.0577 (15)	-0.0132 (16)	0.0189 (14)	0.0057 (15)
C6	0.0649 (15)	0.0753 (17)	0.0631 (15)	-0.0003 (13)	0.0218 (12)	-0.0003 (13)
C7	0.0540 (13)	0.0596 (14)	0.0553 (13)	-0.0030 (11)	0.0122 (10)	0.0025 (11)
C8	0.0746 (16)	0.0790 (18)	0.0793 (17)	0.0215 (14)	0.0239 (14)	-0.0003 (14)
C9	0.0591 (14)	0.0666 (16)	0.0768 (16)	0.0177 (12)	0.0189 (13)	0.0001 (13)
C10	0.0618 (15)	0.0567 (15)	0.0899 (18)	0.0113 (12)	0.0192 (14)	0.0024 (14)
C11	0.100 (2)	0.072 (2)	0.130 (3)	-0.0029 (16)	0.0143 (19)	0.0104 (17)
C12	0.0569 (14)	0.0634 (16)	0.0872 (18)	0.0098 (12)	0.0143 (13)	-0.0102 (14)
C13	0.092 (2)	0.094 (2)	0.112 (2)	-0.0043 (18)	0.0007 (18)	-0.0085 (18)
O1	0.0932 (13)	0.1265 (17)	0.0561 (11)	0.0414 (12)	0.0097 (10)	0.0044 (10)
O2A	0.062 (4)	0.116 (6)	0.052 (3)	0.028 (3)	0.011 (3)	0.003 (3)
O2B	0.160 (11)	0.133 (12)	0.115 (8)	0.077 (9)	0.088 (7)	0.054 (6)
O3	0.0686 (10)	0.0736 (11)	0.0631 (10)	0.0220 (8)	0.0207 (8)	0.0080 (8)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—O2B	1.237 (16)	C8—H8A	0.9700
C1—O1	1.241 (3)	C8—H8B	0.9700
C1—O2A	1.286 (9)	C9—C10	1.399 (3)
C1—C2	1.487 (3)	C9—C12	1.401 (3)
C2—C3	1.393 (3)	C10—C12 <sup>i</sup>	1.395 (3)
C2—C7	1.397 (3)	C10—C11	1.524 (4)
C3—C4	1.372 (3)	C11—H11A	0.9600
C3—H3	0.9300	C11—H11B	0.9600
C4—C5	1.369 (4)	C11—H11C	0.9600
C4—H4	0.9300	C12—C10 <sup>i</sup>	1.395 (3)
C5—C6	1.375 (3)	C12—C13	1.518 (4)

C5—H5	0.9300	C13—H13A	0.9600
C6—C7	1.389 (3)	C13—H13B	0.9600
C6—H6	0.9300	C13—H13C	0.9600
C7—O3	1.366 (3)	O2A—H2A	0.8200
C8—O3	1.440 (3)	O2B—H2B	0.8200
C8—C9	1.503 (3)		
O2B—C1—O1	121.6 (9)	C9—C8—H8B	110.4
O1—C1—O2A	119.3 (5)	H8A—C8—H8B	108.6
O2B—C1—C2	113.3 (7)	C10—C9—C12	120.8 (2)
O1—C1—C2	121.8 (2)	C10—C9—C8	118.3 (2)
O2A—C1—C2	118.4 (4)	C12—C9—C8	120.9 (2)
C3—C2—C7	118.2 (2)	C12 <sup>i</sup> —C10—C9	120.0 (2)
C3—C2—C1	117.9 (2)	C12 <sup>i</sup> —C10—C11	120.1 (2)
C7—C2—C1	124.0 (2)	C9—C10—C11	119.8 (2)
C4—C3—C2	121.8 (2)	C10—C11—H11A	109.5
C4—C3—H3	119.1	C10—C11—H11B	109.5
C2—C3—H3	119.1	H11A—C11—H11B	109.5
C5—C4—C3	119.2 (2)	C10—C11—H11C	109.5
C5—C4—H4	120.4	H11A—C11—H11C	109.5
C3—C4—H4	120.4	H11B—C11—H11C	109.5
C4—C5—C6	120.9 (2)	C10 <sup>i</sup> —C12—C9	119.2 (2)
C4—C5—H5	119.6	C10 <sup>i</sup> —C12—C13	120.2 (3)
C6—C5—H5	119.6	C9—C12—C13	120.6 (3)
C5—C6—C7	120.2 (2)	C12—C13—H13A	109.5
C5—C6—H6	119.9	C12—C13—H13B	109.5
C7—C6—H6	119.9	H13A—C13—H13B	109.5
O3—C7—C6	123.1 (2)	C12—C13—H13C	109.5
O3—C7—C2	117.07 (19)	H13A—C13—H13C	109.5
C6—C7—C2	119.8 (2)	H13B—C13—H13C	109.5
O3—C8—C9	106.66 (18)	C1—O2A—H2A	109.5
O3—C8—H8A	110.4	C1—O2B—H2B	109.5
C9—C8—H8A	110.4	C7—O3—C8	118.47 (17)
O3—C8—H8B	110.4		
O2B—C1—C2—C3	-2(2)	C3—C2—C7—C6	1.4 (3)
O1—C1—C2—C3	158.1 (2)	C1—C2—C7—C6	-177.8 (2)
O2A—C1—C2—C3	-30.0 (8)	O3—C8—C9—C10	78.2 (3)
O2B—C1—C2—C7	178 (2)	O3—C8—C9—C12	-101.3 (2)
O1—C1—C2—C7	-22.7 (4)	C12—C9—C10—C12 <sup>i</sup>	-1.6 (4)
O2A—C1—C2—C7	149.2 (8)	C8—C9—C10—C12 <sup>i</sup>	179.0 (2)
C7—C2—C3—C4	-0.4 (4)	C12—C9—C10—C11	179.7 (2)
C1—C2—C3—C4	178.9 (2)	C8—C9—C10—C11	0.3 (3)
C2—C3—C4—C5	-0.8 (4)	C10—C9—C12—C10 <sup>i</sup>	1.5 (4)
C3—C4—C5—C6	1.0 (4)	C8—C9—C12—C10 <sup>i</sup>	-179.0 (2)
C4—C5—C6—C7	0.0 (4)	C10—C9—C12—C13	-177.0 (2)
C5—C6—C7—O3	-178.6 (2)	C8—C9—C12—C13	2.5 (3)
C5—C6—C7—C2	-1.3 (3)	C6—C7—O3—C8	-8.1 (3)
C3—C2—C7—O3	178.9 (2)	C2—C7—O3—C8	174.5 (2)

## supplementary materials

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C1—C2—C7—O3                      -0.3 (3)                      C9—C8—O3—C7                      -170.4 (2)  
Symmetry codes: (i)  $-x, -y+1, -z$ .

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 is the centroid of the central C9,C10,C12',C9'C10',C12 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2A—H2A $\cdots$ O1 <sup>ii</sup>	0.82	1.83	2.624 (9)	164.
O2B—H2B $\cdots$ O1 <sup>ii</sup>	0.82	1.91	2.721 (16)	168.
C5—H5 $\cdots$ Cg1 <sup>iii</sup>	0.93	2.80	3.356 (5)	120.

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



Fig. 1

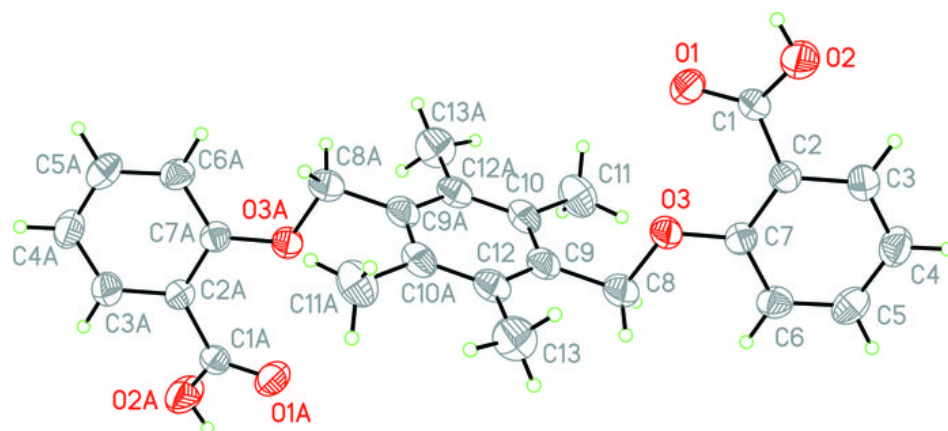


Fig. 2

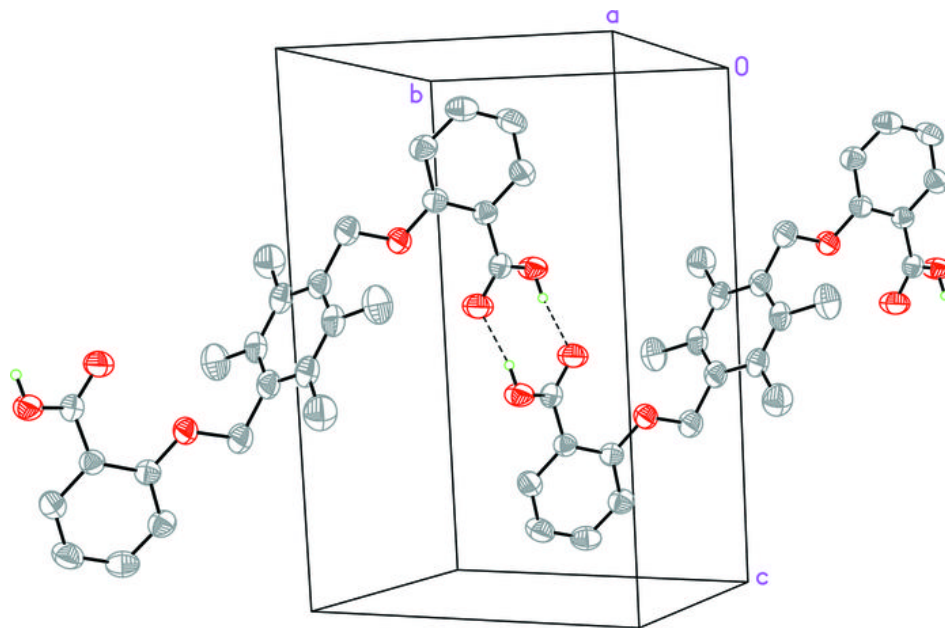


Fig. 3

