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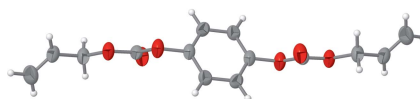
Structural data: full structural data are available from iucrdata.iucr.org

1,4-Phenylene diallyl bis(carbonate)

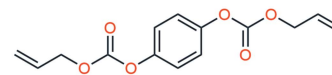
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The title molecule, C₁₄H₁₄O₆, is based on a benzene core di-substituted by allyl carbonate groups in the *para* positions. The molecule is placed on an inversion centre, and the substituents are twisted with respect to the central benzene ring plane. The crystal structure does not include significant intermolecular interactions other than weak C—H···O contacts between CH groups in the benzene ring and carbonate O atoms.

3D view



Chemical scheme



Structure description

Allylic compounds are common reagents in organic chemistry for obtaining new allyl derivatives and polymeric materials (*e.g.* Nair *et al.*, 2010). Within this class of compounds, functional allyl aromatic carbonates (Flores Ahuactzin *et al.*, 2009) are also suitable building blocks to produce diallyl carbonate compounds (López *et al.*, 1997), as well as reactive homopolycarbonates or copolymers, obtained by free radical polymerization. Concerning diallyl carbonates, they can be used as cross-linking agents (Nair *et al.*, 2010; López & Burillo, 1991), and they can also be polymerized to homopolymers or copolymers, such as poly[allyl(*p*-allylcarbonate)benzoate] (López-V *et al.*, 2011) or poly[1-benzoate-2,3-diallylcarbonate glycerol] (López *et al.*, 1997).

The reaction between allyl chloroformate (ACF) and a diol affords mono allyl carbonate and diallyl carbonate derivatives. The reaction of ACF with hydroquinone gives allyl-4-hydroxyphenyl carbonate (Flores *et al.*, 2009) and 1,4-phenylene diallyl bis(carbonate). Herein, we report the structure of the latter. The title compound represents the first instance of a 1,4-phenylene bis(carbonate) derivative to be characterized by X-ray diffraction.



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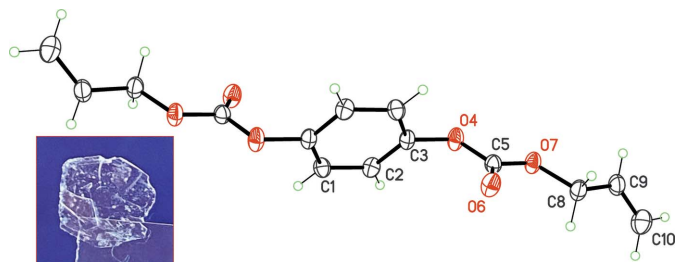


Figure 1

Molecular structure of the title compound. Non-H atoms are drawn at the 30% probability level. Non-labelled atoms are generated by the symmetry operation $1 - x, 1 - y, -z$. The inset is the raw material as obtained from the synthesis. The edges of the hexagonal flake have dimensions of *ca* 5 mm.

The molecule lies on an inversion centre in space group $P2_1/n$, with the symmetry element coinciding with the centre of the benzene ring (Fig. 1). This ring is disubstituted in the *para* positions by allyl carbonate groups, which are not coplanar with the ring: the dihedral angle between the mean plane of the benzene and the plane of the carbonate group O4/C5/O6/O7 is $68.69(4)^\circ$, and the dihedral angle between the carbonate group and the allyl group C8/C9/C10 is $51.1(2)^\circ$. This twisted conformation was previously observed for the four reported X-ray structures bearing a benzene ring substituted by an allyl carbonate group (Flores Ahuactzin *et al.*, 2009; Herrera-González *et al.*, 2009; Li *et al.*, 2019; Schmid *et al.*, 2019). This conformation does not promote strong intermolecular contacts in the crystal structure, as hydrogen bonds or π - π interactions. The benzene H atoms are, however, engaged in C—H \cdots O contacts with neighbouring molecules. The C1—H1 group makes an almost linear contact with the carbonate O atom O7 (Table 1, entry 1; Fig. 2), while C2—H2 interacts with the carbonyl O atom O6, forming centrosymmetric $R_2^2(14)$ ring motifs in the crystal (Table 1, entry 2; Fig. 3).

Synthesis and crystallization

To a three-neck round-bottom flask connected to an addition funnel, hydroquinone (2.28 g, 20.7 mmol) was added and

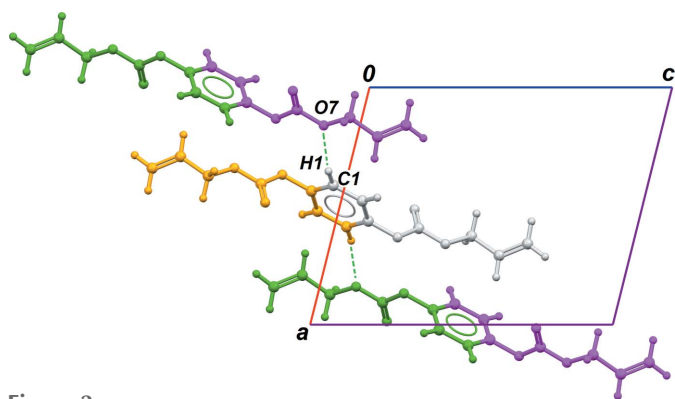


Figure 2

Part of the crystal structure based on C1—H1 \cdots O7 interactions (Table 1, entry 1). The asymmetric unit is coloured in grey, while orange, green and magenta moieties are generated by inversion, 2_1 axis and n glide plane, respectively.

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots O7 ⁱ	0.93	2.59	3.5100 (16)	169
C2—H2 \cdots O6 ⁱⁱ	0.93	2.57	3.4555 (16)	160

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

dissolved in 20 ml of THF under an argon atmosphere. After continuous agitation, a homogeneous phase was observed in the reaction flask, and NaHCO_3 (0.86 g, 10.3 mmol), previously dissolved in 5 ml of distilled water, was added. Then, the reaction flask was placed in an ice bath and allyl chloroformate (1.09 ml, 10.3 mmol) was slowly added dropwise, maintaining the agitation. After complete addition, the reaction was left for 5–10 minutes at 273 K, and then at room temperature for 2 h. After completion of the reaction, the products were extracted in a separation funnel using CH_2Cl_2 , and dried over anhydrous Na_2SO_4 . The reaction mixture was filtered and concentrated. The resulting concentrated solution was precipitated into hexane. The precipitate was collected, washed with hexane, and dried *in vacuo* (yield: 1.152 g, 20%). Transparent prismatic single crystals were recovered from this material for X-ray study (see Fig. 1, inset). ^1H NMR (500 MHz, CDCl_3), δ (p.p.m.): 4.75 (*d*, $J = 5.0$ Hz, 4H), 5.34 (*d*, $J = 10.0$ Hz, 2H), 5.44 (*dd*, $J = 17.5, 1.5$ Hz, 2H), 5.90 (*m*, 2H), 7.21 (*s*, 4H); ^{13}C NMR (125 MHz, CDCl_3), δ (p.p.m.): 69.3 ($-\text{CH}_2-$), 119.7 ($=\text{CH}_2$), 122.0 (benzene), 131.1 ($=\text{CH}$), 148.6 (benzene), 154.3 (C=O); FTIR (ATR, ν , cm^{-1}): 3082 ($\text{C}_{sp^2}-\text{H}$), 2960 ($\text{C}_{sp^3}-\text{H}$), 1757 (C=O), 1649 (C=C, allyl), 1602 (C=C, aromatic), 770 (aromatic ring), 730 ($\text{C}_{sp^3}-\text{H}$).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

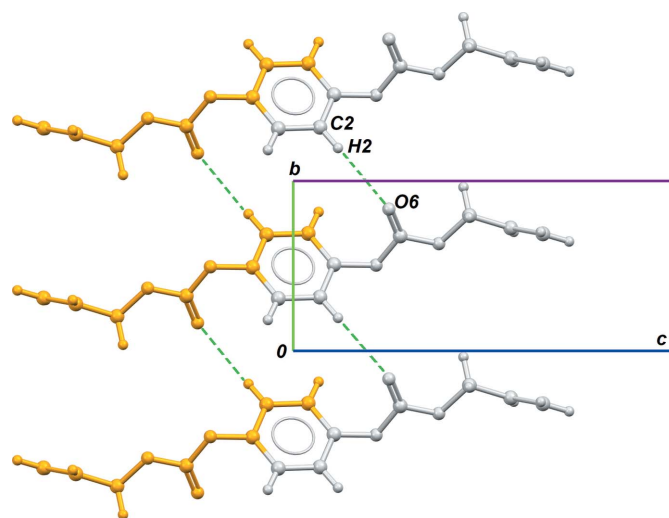


Figure 3

Part of the crystal structure based on C2—H2 \cdots O6 interactions (Table 1, entry 2). Grey fragments are generated from the asymmetric unit by lattice translations, and orange fragments are generated by inversion.

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>P</i> 2 ₁ / <i>n</i>
Temperature (K)	253
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2808 (13), 5.4764 (6), 12.7396 (15)
β (°)	104.070 (9)
<i>V</i> (Å ³)	695.74 (14)
<i>Z</i>	2
Radiation type	Ag <i>K</i> α , λ = 0.56083 Å
μ (mm ⁻¹)	0.06
Crystal size (mm)	0.60 × 0.50 × 0.50
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (<i>X-AREA</i> ; Stoe & Cie, 2018)
<i>T</i> _{min} , <i>T</i> _{max}	0.536, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	16744, 1620, 1305
<i>R</i> _{int}	0.029
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.653
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.102, 1.04
No. of reflections	1620
No. of parameters	98
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.18, -0.15

Computer programs: *X-AREA* (Stoe & Cie, 2018), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020) and *pubCIF* (Westrip, 2010).

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full crystallographic data

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1,4-Phenylene diallyl bis(carbonate)

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1,4-Phenylene diallyl bis(carbonate)

Crystal data

$C_{14}H_{14}O_6$

$M_r = 278.25$

Monoclinic, $P2_1/n$

$a = 10.2808$ (13) Å

$b = 5.4764$ (6) Å

$c = 12.7396$ (15) Å

$\beta = 104.070$ (9)°

$V = 695.74$ (14) Å³

$Z = 2$

$F(000) = 292$

$D_x = 1.328$ Mg m⁻³

Ag $K\alpha$ radiation, $\lambda = 0.56083$ Å

Cell parameters from 19549 reflections

$\theta = 2.3$ – 31.6 °

$\mu = 0.06$ mm⁻¹

$T = 253$ K

Prism, colourless

$0.60 \times 0.50 \times 0.50$ mm

Data collection

Stoe Stadivari

diffractometer

Radiation source: Sealed X-ray tube, Axo Astix-f Microfocus source

Graded multilayer mirror monochromator

Detector resolution: 5.81 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(X-AREA; Stoe & Cie, 2018)

$T_{\min} = 0.536$, $T_{\max} = 1.000$

16744 measured reflections

1620 independent reflections

1305 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 21.5$ °, $\theta_{\min} = 2.3$ °

$h = -13 \rightarrow 13$

$k = -7 \rightarrow 7$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.102$

$S = 1.04$

1620 reflections

98 parameters

0 restraints

0 constraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.1879P]$

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

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

$\Delta\rho_{\max} = 0.18$ e Å⁻³

$\Delta\rho_{\min} = -0.15$ e Å⁻³

Extinction correction: SHELXL-2018/3
(Sheldrick 2015b),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.023 (6)

Special details

Refinement. Allyl H atoms (H10*a* and H10*b*) were refined with free coordinates, and other H atoms were placed on calculated positions. All H atoms were refined with isotropic displacements, calculated as $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}(\text{carrier C atom})$.

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	0.41290 (13)	0.3086 (2)	−0.03895 (10)	0.0404 (3)
H1	0.354051	0.182011	−0.066169	0.049*
C2	0.47808 (13)	0.3163 (2)	0.06961 (10)	0.0401 (3)
H2	0.464542	0.194551	0.116732	0.048*
C3	0.56326 (12)	0.5078 (2)	0.10622 (9)	0.0365 (3)
O4	0.63189 (9)	0.50484 (17)	0.21618 (7)	0.0450 (3)
C5	0.59396 (12)	0.6762 (2)	0.27902 (9)	0.0366 (3)
O6	0.51476 (10)	0.83464 (18)	0.24966 (7)	0.0498 (3)
O7	0.66007 (9)	0.63120 (18)	0.37984 (6)	0.0440 (3)
C8	0.62690 (13)	0.7968 (3)	0.45975 (10)	0.0444 (3)
H8A	0.532199	0.785459	0.457866	0.053*
H8B	0.646954	0.964013	0.444160	0.053*
C9	0.70837 (14)	0.7236 (3)	0.56723 (10)	0.0476 (3)
H9	0.799945	0.700847	0.575414	0.057*
C10	0.6593 (2)	0.6888 (3)	0.65149 (13)	0.0630 (4)
H10A	0.7141 (18)	0.644 (4)	0.7198 (16)	0.076*
H10B	0.5653 (19)	0.700 (4)	0.6461 (14)	0.076*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0448 (6)	0.0346 (6)	0.0399 (7)	−0.0038 (5)	0.0063 (5)	−0.0041 (5)
C2	0.0516 (7)	0.0331 (6)	0.0356 (6)	0.0008 (5)	0.0109 (5)	0.0029 (5)
C3	0.0409 (6)	0.0367 (6)	0.0290 (6)	0.0076 (5)	0.0031 (4)	−0.0027 (5)
O4	0.0532 (5)	0.0449 (5)	0.0309 (4)	0.0150 (4)	−0.0012 (4)	−0.0038 (4)
C5	0.0368 (6)	0.0387 (6)	0.0320 (6)	0.0025 (5)	0.0040 (4)	0.0004 (5)
O6	0.0567 (6)	0.0520 (6)	0.0366 (5)	0.0203 (4)	0.0035 (4)	0.0010 (4)
O7	0.0472 (5)	0.0508 (5)	0.0291 (4)	0.0135 (4)	0.0000 (3)	−0.0038 (4)
C8	0.0470 (7)	0.0497 (7)	0.0343 (6)	0.0064 (6)	0.0057 (5)	−0.0070 (5)
C9	0.0469 (7)	0.0544 (8)	0.0371 (7)	0.0016 (6)	0.0019 (5)	−0.0077 (6)
C10	0.0770 (11)	0.0669 (10)	0.0434 (8)	0.0006 (9)	0.0112 (7)	0.0051 (7)

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

C1—C3 ⁱ	1.3811 (17)	O7—C8	1.4640 (15)
C1—C2	1.3830 (17)	C8—C9	1.4763 (17)
C1—H1	0.9300	C8—H8A	0.9700
C2—C3	1.3733 (18)	C8—H8B	0.9700
C2—H2	0.9300	C9—C10	1.306 (2)
C3—O4	1.4071 (14)	C9—H9	0.9300

O4—C5	1.3513 (14)	C10—H10A	0.947 (19)
C5—O6	1.1863 (14)	C10—H10B	0.954 (18)
C5—O7	1.3221 (14)		
C3 ⁱ —C1—C2	118.84 (11)	C5—O7—C8	114.10 (9)
C3 ⁱ —C1—H1	120.6	O7—C8—C9	107.53 (10)
C2—C1—H1	120.6	O7—C8—H8A	110.2
C3—C2—C1	118.48 (11)	C9—C8—H8A	110.2
C3—C2—H2	120.8	O7—C8—H8B	110.2
C1—C2—H2	120.8	C9—C8—H8B	110.2
C2—C3—C1 ⁱ	122.68 (11)	H8A—C8—H8B	108.5
C2—C3—O4	116.95 (11)	C10—C9—C8	123.81 (14)
C1 ⁱ —C3—O4	120.30 (11)	C10—C9—H9	118.1
C5—O4—C3	115.77 (9)	C8—C9—H9	118.1
O6—C5—O7	126.45 (11)	C9—C10—H10A	122.1 (12)
O6—C5—O4	126.58 (11)	C9—C10—H10B	121.3 (11)
O7—C5—O4	106.96 (9)	H10A—C10—H10B	116.6 (16)
C3 ⁱ —C1—C2—C3	0.5 (2)	C3—O4—C5—O7	174.50 (10)
C1—C2—C3—C1 ⁱ	-0.5 (2)	O6—C5—O7—C8	0.88 (19)
C1—C2—C3—O4	-177.58 (11)	O4—C5—O7—C8	-177.99 (10)
C2—C3—O4—C5	-110.62 (12)	C5—O7—C8—C9	-179.91 (11)
C1 ⁱ —C3—O4—C5	72.25 (15)	O7—C8—C9—C10	-130.59 (16)
C3—O4—C5—O6	-4.37 (19)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots O7 ⁱⁱ	0.93	2.59	3.5100 (16)	169
C2—H2 \cdots O6 ⁱⁱⁱ	0.93	2.57	3.4555 (16)	160

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