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Di-*tert*-butyl cyclohex-2-ene-1,4-diyl dicarbonate

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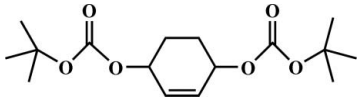
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.005 Å; R factor = 0.068; wR factor = 0.191; data-to-parameter ratio = 14.1.

In the title molecule, $C_{16}H_{26}O_6$, the central cyclohexene ring is in a half-chair conformation. The carbonyl groups are in a *trans* arrangement with respect to each other and the dihedral angle between the mean planes of the carbonate groups is 10.8 (2)°.

Related literature

For synthetic applications of the title compound, see: Ali, Ghafouri *et al.* (2008). For a related structures, see: Ali, Begum *et al.* (2008); Rademeyer *et al.* (2003).



Experimental

Crystal data

$C_{16}H_{26}O_6$
M_r = 314.37
Monoclinic, $P2_1/c$
a = 12.6548 (11) Å
b = 5.8862 (6) Å
c = 23.126 (2) Å
β = 103.147 (5)°
V = 1677.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 150 K
0.10 × 0.09 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing 1995)
T_{min} = 0.865, T_{max} = 1.00
9313 measured reflections
2893 independent reflections
1407 reflections with $I > 2\sigma(I)$
R_{int} = 0.101

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.191
S = 1.00
2893 reflections
205 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); 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: EZ2186).

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supporting information

Acta Cryst. (2009). E**65**, o2690 [https://doi.org/10.1107/S1600536809040343]

Di-*tert*-butyl cyclohex-2-ene-1,4-diyl dicarbonate

Syed Nawazish Ali, Mitchell A. Winnik, Sabira Begum and Alan J. Lough

S1. Comment

The title compound (I), is a new synthetic precursor of *trans*-cyclohex-2-ene-1,4-diol which has been synthesized for plasticizing purposes in order to break the crystallinity of a number of polyformals, and polycarbonates (Ali, Ghafouri *et al.*, 2008). The molecular structure of (I) is shown in Fig. 1. Unlike the crystal structure of *trans*-Cyclohex-2-ene-1,4-diyl bis(4-nitrophenyl) dicarbonate (Ali, Begum *et al.*, 2008) the central cyclohexene ring is completely ordered.

S2. Experimental

A reaction mixture containing *trans*-cyclohex-2-ene-1,4-diol (0.59 g, 5.18 mmol), di-*tert*-butyldicarbonate (2.26 g, 10.36 mmol) and *N*,*N*-dimethylaminopyridine (DMAP) (0.80 g, 6.57 mmol) was stirred in dry dichloromethane (80 ml) at room temperature in a 250 ml round-bottom flask (see Fig. 2). After 4 h, it was transferred to a separatory funnel (250 ml) and washed with CH_3COOH (30 ml *x* 3, 0.1 *M*) to remove the excess of DMAP. The lower organic phase was removed and the aqueous phase was washed with dichloromethane (30 ml *x* 2). All the dichloromethane solutions were combined, washed with deionized water (30 ml *x* 3), and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporator. The resulting oily product was dried in vacuum oven at room temperature to obtain di-*tert*-butyl-cyclo-hex-2-ene-1,4-diyl dicarbonate (I, 1.14 g, 69.5%). The product was then recrystallized from a mixture of $CHCl_3$: MeOH (1:1) to afford needle-shaped crystals by slow evaporation of the solvent at room temperature. In addition to the X-ray structure determination, the structure was also confirmed by comparing the ^1H and ^{13}C NMR data with a related t-Boc protected compound (Rademeyer *et al.*, 2003). ^1H NMR ($CDCl_3$, p.p.m., relative to TMS, 400 MHz): 5.98 (2*H*, br.s, CH=CH), 5.16 (2*H*, m, CH—O), 2.08 (2*H*, m, CH_2—CH_2), 1.80 (2*H*, m, CH_2—CH_2), 1.48 (18*H*, s, CH_3); ^{13}C NMR ($CDCl_3$, p.p.m., relative to TMS, 100 MHz): 168.4 (C=O), 129.1 (CH=CH), 71.4 (2*H*, CH—O), 66.3 ($C(CH_3)_3O$), 25.2 (CH_2), 28.0 (CH_3)

S3. Refinement

Hydrogen atoms were placed in calculated positions with C—H distances ranging from 0.95 to 1.00 Å and included in the refinement in a riding-model approximation with U_{iso}(H) = 1.2U_{eq}(C) or U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

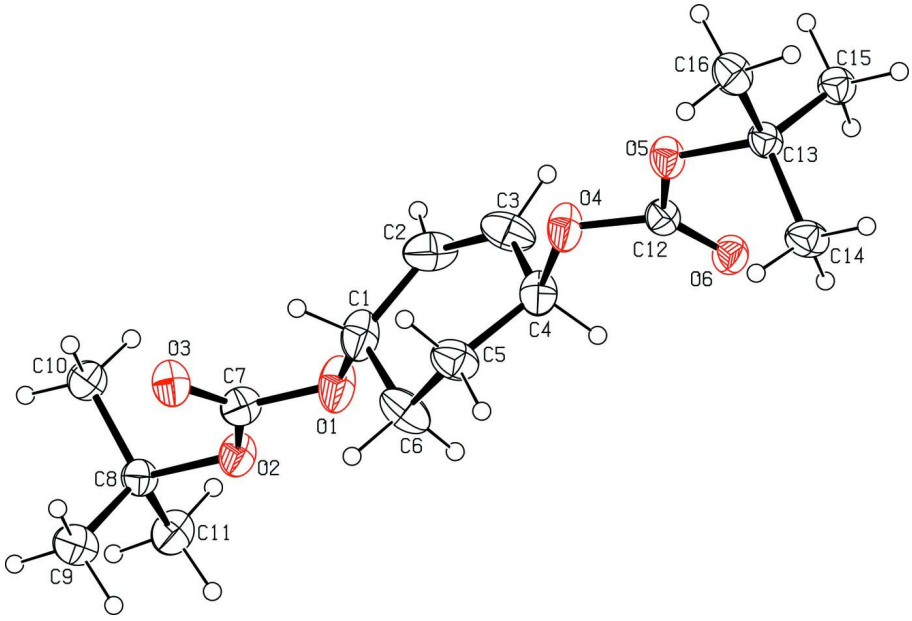

Figure 1

The molecular structure of the title compound showing 30% probability ellipsoids.

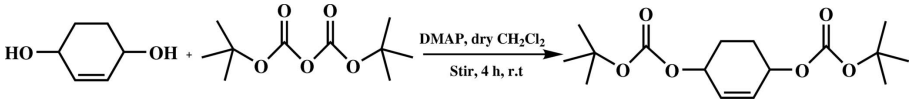

Figure 2

Preparation of the title compound.

Di-*tert*-butyl cyclohex-2-ene-1,4-diyl dicarbonate

Crystal data

$C_{16}H_{26}O_6$
$M_r = 314.37$
Monoclinic, $P2_1/c$
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$b = 5.8862\ (6)$ Å
$c = 23.126\ (2)$ Å
$\beta = 103.147\ (5)°$
$V = 1677.5\ (3)$ Å^3
$Z = 4$
$F(000) = 680$
$D_x = 1.245$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9313 reflections
$\theta = 2.7–25.0°$
$\mu = 0.09$ mm^{-1}
$T = 150$ K
Plate, colourless
0.10 × 0.09 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing 1995)
$T_{min} = 0.865$, $T_{max} = 1.00$
9313 measured reflections
2893 independent reflections
1407 reflections with $I > 2\sigma(I)$
$R_{int} = 0.101$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.7°$
$h = -15\rightarrow15$
$k = -6\rightarrow6$
$l = -27\rightarrow27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.191$
$S = 1.00$
2893 reflections
205 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
$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-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_{iso}*/U_{eq}
O1	0.3871 (2)	−0.2647 (5)	0.54229 (13)	0.0663 (10)
O2	0.28611 (18)	−0.5049 (4)	0.48553 (11)	0.0489 (7)
O3	0.2107 (2)	−0.2869 (4)	0.54593 (11)	0.0503 (7)
O4	0.62164 (19)	0.3112 (4)	0.70717 (12)	0.0558 (8)
O5	0.72570 (17)	0.5487 (4)	0.76245 (10)	0.0448 (7)
O6	0.80169 (19)	0.2813 (4)	0.71320 (11)	0.0460 (7)
C1	0.4089 (3)	−0.0972 (7)	0.59017 (18)	0.0585 (12)
H1A	0.3386	−0.0373	0.5968	0.070*
C2	0.4714 (4)	0.0915 (7)	0.57122 (18)	0.0634 (13)
H2A	0.4502	0.1443	0.5314	0.076*
C3	0.5543 (4)	0.1881 (6)	0.60687 (19)	0.0620 (12)
H3A	0.5873	0.3142	0.5924	0.074*
C4	0.5991 (3)	0.1123 (6)	0.66812 (17)	0.0494 (11)
H4A	0.6678	0.0259	0.6699	0.059*
C5	0.5203 (3)	−0.0339 (7)	0.69112 (17)	0.0589 (12)
H5A	0.5584	−0.1110	0.7280	0.071*
H5B	0.4624	0.0625	0.7007	0.071*
C6	0.4707 (4)	−0.2079 (7)	0.64578 (17)	0.0627 (12)
H6A	0.5287	−0.3047	0.6365	0.075*
H6B	0.4213	−0.3065	0.6622	0.075*
C7	0.2865 (3)	−0.3486 (6)	0.52697 (16)	0.0449 (10)
C8	0.1825 (3)	−0.6087 (6)	0.45306 (15)	0.0405 (9)
C9	0.1263 (3)	−0.7330 (6)	0.49534 (16)	0.0555 (12)
H9A	0.1044	−0.6234	0.5223	0.083*
H9B	0.1764	−0.8441	0.5185	0.083*

H9C	0.0620	−0.8117	0.4725	0.083*
C10	0.1114 (3)	−0.4266 (6)	0.41818 (16)	0.0475 (10)
H10A	0.0908	−0.3174	0.4457	0.071*
H10B	0.0459	−0.4964	0.3938	0.071*
H10C	0.1513	−0.3480	0.3924	0.071*
C11	0.2218 (3)	−0.7736 (6)	0.41206 (17)	0.0551 (12)
H11A	0.2735	−0.8804	0.4357	0.083*
H11B	0.2575	−0.6891	0.3853	0.083*
H11C	0.1598	−0.8577	0.3886	0.083*
C12	0.7258 (3)	0.3718 (6)	0.72638 (15)	0.0387 (9)
C13	0.8304 (3)	0.6424 (6)	0.79714 (15)	0.0389 (9)
C14	0.8905 (3)	0.4608 (6)	0.83795 (16)	0.0506 (11)
H14A	0.9138	0.3407	0.8142	0.076*
H14B	0.8425	0.3961	0.8614	0.076*
H14C	0.9543	0.5278	0.8646	0.076*
C15	0.8964 (3)	0.7397 (6)	0.75658 (16)	0.0441 (10)
H15A	0.8539	0.8562	0.7312	0.066*
H15B	0.9155	0.6184	0.7318	0.066*
H15C	0.9628	0.8081	0.7804	0.066*
C16	0.7894 (3)	0.8280 (6)	0.83263 (16)	0.0498 (10)
H16A	0.7443	0.9354	0.8053	0.075*
H16B	0.8513	0.9086	0.8572	0.075*
H16C	0.7461	0.7591	0.8582	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0400 (15)	0.080 (2)	0.074 (2)	−0.0034 (15)	0.0022 (14)	−0.0451 (17)
O2	0.0407 (14)	0.0519 (16)	0.0495 (16)	−0.0001 (12)	0.0006 (12)	−0.0191 (13)
O3	0.0462 (15)	0.0593 (18)	0.0468 (18)	−0.0065 (13)	0.0135 (14)	−0.0159 (13)
O4	0.0369 (14)	0.0573 (17)	0.071 (2)	−0.0031 (13)	0.0078 (13)	−0.0341 (15)
O5	0.0377 (14)	0.0478 (15)	0.0467 (16)	−0.0061 (12)	0.0049 (12)	−0.0142 (13)
O6	0.0397 (14)	0.0440 (15)	0.0536 (18)	0.0009 (12)	0.0090 (13)	−0.0072 (13)
C1	0.043 (2)	0.067 (3)	0.060 (3)	−0.002 (2)	0.000 (2)	−0.034 (2)
C2	0.090 (3)	0.047 (3)	0.043 (3)	0.003 (2)	−0.005 (2)	−0.002 (2)
C3	0.098 (3)	0.039 (2)	0.054 (3)	−0.014 (2)	0.027 (3)	−0.012 (2)
C4	0.043 (2)	0.052 (2)	0.053 (3)	−0.0016 (19)	0.0120 (19)	−0.022 (2)
C5	0.073 (3)	0.052 (2)	0.048 (3)	−0.011 (2)	0.006 (2)	0.003 (2)
C6	0.086 (3)	0.057 (3)	0.048 (3)	−0.028 (2)	0.022 (2)	−0.009 (2)
C7	0.050 (2)	0.045 (2)	0.035 (2)	0.001 (2)	0.000 (2)	−0.0070 (19)
C8	0.041 (2)	0.041 (2)	0.035 (2)	−0.0049 (17)	−0.0024 (17)	−0.0031 (17)
C9	0.065 (3)	0.052 (3)	0.045 (3)	−0.007 (2)	0.003 (2)	0.001 (2)
C10	0.048 (2)	0.051 (2)	0.040 (2)	−0.0012 (19)	0.0032 (18)	0.0025 (19)
C11	0.055 (2)	0.057 (3)	0.048 (3)	0.003 (2)	0.001 (2)	−0.015 (2)
C12	0.039 (2)	0.042 (2)	0.034 (2)	−0.0034 (19)	0.0052 (18)	0.0001 (18)
C13	0.038 (2)	0.039 (2)	0.035 (2)	−0.0065 (17)	0.0003 (17)	−0.0009 (17)
C14	0.060 (2)	0.044 (2)	0.043 (2)	−0.006 (2)	0.0008 (19)	0.0045 (19)
C15	0.045 (2)	0.042 (2)	0.043 (2)	−0.0025 (18)	0.0069 (18)	−0.0016 (18)

C16	0.052 (2)	0.051 (2)	0.043 (2)	−0.010 (2)	0.0044 (19)	−0.0085 (19)

Geometric parameters (Å, º)

O1—C7	1.337 (4)	C8—C10	1.510 (4)
O1—C1	1.461 (4)	C8—C11	1.518 (5)
O2—C7	1.328 (4)	C8—C9	1.521 (5)
O2—C8	1.486 (4)	C9—H9A	0.9800
O3—C7	1.197 (4)	C9—H9B	0.9800
O4—C12	1.340 (4)	C9—H9C	0.9800
O4—C4	1.466 (4)	C10—H10A	0.9800
O5—C12	1.334 (4)	C10—H10B	0.9800
O5—C13	1.490 (4)	C10—H10C	0.9800
O6—C12	1.197 (4)	C11—H11A	0.9800
C1—C2	1.486 (6)	C11—H11B	0.9800
C1—C6	1.494 (5)	C11—H11C	0.9800
C1—H1A	1.0000	C13—C15	1.504 (5)
C2—C3	1.307 (5)	C13—C14	1.512 (4)
C2—H2A	0.9500	C13—C16	1.527 (5)
C3—C4	1.470 (5)	C14—H14A	0.9800
C3—H3A	0.9500	C14—H14B	0.9800
C4—C5	1.503 (5)	C14—H14C	0.9800
C4—H4A	1.0000	C15—H15A	0.9800
C5—C6	1.497 (5)	C15—H15B	0.9800
C5—H5A	0.9900	C15—H15C	0.9800
C5—H5B	0.9900	C16—H16A	0.9800
C6—H6A	0.9900	C16—H16B	0.9800
C6—H6B	0.9900	C16—H16C	0.9800
C7—O1—C1	117.0 (3)	C8—C9—H9B	109.5
C7—O2—C8	120.5 (3)	H9A—C9—H9B	109.5
C12—O4—C4	117.1 (3)	C8—C9—H9C	109.5
C12—O5—C13	119.9 (3)	H9A—C9—H9C	109.5
O1—C1—C2	107.6 (3)	H9B—C9—H9C	109.5
O1—C1—C6	109.2 (3)	C8—C10—H10A	109.5
C2—C1—C6	111.7 (3)	C8—C10—H10B	109.5
O1—C1—H1A	109.4	H10A—C10—H10B	109.5
C2—C1—H1A	109.4	C8—C10—H10C	109.5
C6—C1—H1A	109.4	H10A—C10—H10C	109.5
C3—C2—C1	122.9 (4)	H10B—C10—H10C	109.5
C3—C2—H2A	118.5	C8—C11—H11A	109.5
C1—C2—H2A	118.5	C8—C11—H11B	109.5
C2—C3—C4	123.6 (4)	H11A—C11—H11B	109.5
C2—C3—H3A	118.2	C8—C11—H11C	109.5
C4—C3—H3A	118.2	H11A—C11—H11C	109.5
O4—C4—C3	109.2 (3)	H11B—C11—H11C	109.5
O4—C4—C5	106.9 (3)	O6—C12—O5	128.4 (3)
C3—C4—C5	111.9 (3)	O6—C12—O4	125.7 (3)

O4—C4—H4A	109.6	O5—C12—O4	106.0 (3)
C3—C4—H4A	109.6	O5—C13—C15	110.9 (3)
C5—C4—H4A	109.6	O5—C13—C14	109.5 (3)
C6—C5—C4	110.5 (3)	C15—C13—C14	112.8 (3)
C6—C5—H5A	109.6	O5—C13—C16	100.6 (3)
C4—C5—H5A	109.6	C15—C13—C16	111.6 (3)
C6—C5—H5B	109.6	C14—C13—C16	110.8 (3)
C4—C5—H5B	109.6	C13—C14—H14A	109.5
H5A—C5—H5B	108.1	C13—C14—H14B	109.5
C1—C6—C5	111.0 (3)	H14A—C14—H14B	109.5
C1—C6—H6A	109.4	C13—C14—H14C	109.5
C5—C6—H6A	109.4	H14A—C14—H14C	109.5
C1—C6—H6B	109.4	H14B—C14—H14C	109.5
C5—C6—H6B	109.4	C13—C15—H15A	109.5
H6A—C6—H6B	108.0	C13—C15—H15B	109.5
O3—C7—O2	127.1 (3)	H15A—C15—H15B	109.5
O3—C7—O1	125.8 (3)	C13—C15—H15C	109.5
O2—C7—O1	107.1 (3)	H15A—C15—H15C	109.5
O2—C8—C10	109.2 (3)	H15B—C15—H15C	109.5
O2—C8—C11	101.6 (3)	C13—C16—H16A	109.5
C10—C8—C11	111.1 (3)	C13—C16—H16B	109.5
O2—C8—C9	111.1 (3)	H16A—C16—H16B	109.5
C10—C8—C9	112.1 (3)	C13—C16—H16C	109.5
C11—C8—C9	111.2 (3)	H16A—C16—H16C	109.5
C8—C9—H9A	109.5	H16B—C16—H16C	109.5