

rac-2-tert-Butyl-2,4,5,6,6-pentachloro-cyclohex-3-en-1-one

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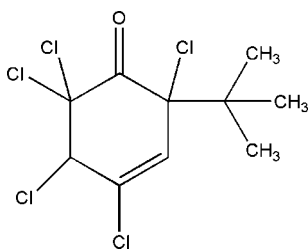
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.082; data-to-parameter ratio = 19.5.

The title compound, $\text{C}_{10}\text{H}_{11}\text{Cl}_5\text{O}$, is a chiral molecule with two stereogenic centres. However, it crystallizes as a racemate. One of enantiomers reveals the relative configuration ($2S^*,5R^*$). The cyclohexene ring adopts a half-chair conformation.

Related literature

For general background to the synthesis of 2-tert-butyl-2,4,5,6,6-pentachlorocyclohex-3-enone and its derivatives, see: Hartshorn *et al.* (1992).

**Experimental***Crystal data*

$\text{C}_{10}\text{H}_{11}\text{Cl}_5\text{O}$
 $M_r = 324.44$
 Monoclinic, $P2_1/n$
 $a = 6.9466$ (7) Å
 $b = 15.7237$ (15) Å
 $c = 12.1785$ (13) Å
 $\beta = 94.903$ (5)°

$V = 1325.3$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.07$ mm⁻¹
 $T = 296$ K
 $0.30 \times 0.30 \times 0.20$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.740$, $T_{\max} = 0.815$

11583 measured reflections
 2880 independent reflections
 2472 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.082$
 $S = 1.00$
 2880 reflections

148 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; 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: KP2308).

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supplementary materials

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***rac*-2-*tert*-Butyl-2,4,5,6,6-pentachlorocyclohex-3-en-1-one**

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Comment

The synthesis of 2-*tert*-butyl-2,4,5,6,6-pentachlorocyclohex-3-enone and derivatives has been studied (Hartshorn *et al.*, 1992). Here we describe recrystallisation and structural characteristics of the target compound. In the title compound, C₁₀H₁₁Cl₅O (I), the cyclohexene ring adopts a half-chair conformation (Fig. 1). The *tert*-butyl group is attached in a pseudo-axial position. Torsion angle between the *tert*-butyl group and the carbonyl group is O1—C1—C1—C7 is 39.5 (3) °. The molecule (I) possess two stereogenic centres at C2 and C5 carbon atoms. The crystal of (I) is racemate and consists of enantiomeric pairs with the relative configuration 2*S**,5*R**. The crystal packing is realised by van der Waals interactions.

Experimental

2,6-di-*tert*-butylphenol (2.30 mol) and ammonium thiocyanate (4.83 mol) in methanol (1200 mL) was stirred with cooling at 273 K. While the temperature was kept in the range from 273 K to 283 K, chlorine gas was slowly bubbled through the mixture for about 1 h, during which the reaction mixture turned to yellow colour. Ammonia was then bubbled through the mixture for about 1.5 h, keeping the reaction mixture in the temperature range from 273 K to 283 K. The reaction was stirred for one more h at 273 K, poured into 2 L of cold distilled water and refrigerated overnight. The aqueous phase was decanted and the solid was taken up in methanol, precipitated by addition of water, filtered and dried. The resulting gummy yellow solid was recrystallised from methanol and dried in vacuum to yield the product as a white powder. The crystals were dissolved in methanol and recrystallised to yield colourless block-shaped crystals of the title compound.

Refinement

The other hydrogen atoms were placed in calculated positions with and refined in the riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Figures

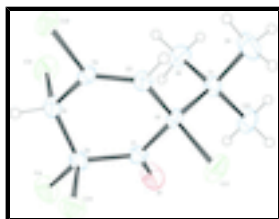


Fig. 1. The molecular structure of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

rac-2-*tert*-Butyl-2,4,5,6,6-pentachlorocyclohex-3-en-1-one

Crystal data

$C_{10}H_{11}Cl_5O$	$F(000) = 656$
$M_r = 324.44$	$D_x = 1.626 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2yn	Cell parameters from 6043 reflections
$a = 6.9466 (7) \text{ \AA}$	$\theta = 2.6\text{--}28.3^\circ$
$b = 15.7237 (15) \text{ \AA}$	$\mu = 1.07 \text{ mm}^{-1}$
$c = 12.1785 (13) \text{ \AA}$	$T = 296 \text{ K}$
$\beta = 94.903 (5)^\circ$	Prism, colourless
$V = 1325.3 (2) \text{ \AA}^3$	$0.30 \times 0.30 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	2880 independent reflections
Radiation source: fine-focus sealed tube graphite	2472 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.024$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 2.1^\circ$
$T_{\text{min}} = 0.740$, $T_{\text{max}} = 0.815$	$h = -8 \rightarrow 8$
11583 measured reflections	$k = -19 \rightarrow 20$
	$l = -13 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.5385P]$
2880 reflections	where $P = (F_o^2 + 2F_c^2)/3$
148 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.71222 (8)	0.85115 (3)	0.19948 (5)	0.05953 (16)
Cl2	1.04573 (7)	0.57732 (3)	0.09467 (4)	0.04698 (13)
Cl3	1.04201 (9)	0.55909 (4)	0.38510 (5)	0.06249 (17)
Cl4	0.60933 (10)	0.59189 (4)	0.43935 (5)	0.0725 (2)
Cl5	0.51257 (7)	0.65020 (4)	0.21735 (5)	0.05830 (16)
O1	0.7230 (3)	0.76496 (11)	0.44023 (14)	0.0731 (5)
C1	0.7672 (3)	0.73432 (11)	0.35685 (15)	0.0392 (4)
C2	0.8874 (2)	0.78139 (10)	0.27498 (13)	0.0332 (3)
C3	0.9594 (2)	0.72330 (10)	0.18964 (13)	0.0322 (3)
H3	1.0140	0.7479	0.1302	0.039*
C4	0.9500 (2)	0.63939 (10)	0.19366 (13)	0.0311 (3)
C5	0.8610 (3)	0.58988 (11)	0.28024 (14)	0.0382 (4)
H5	0.8030	0.5383	0.2464	0.046*
C6	0.7021 (3)	0.64222 (12)	0.32611 (15)	0.0412 (4)
C7	1.0544 (3)	0.83642 (11)	0.33343 (15)	0.0393 (4)
C8	1.1855 (3)	0.77762 (14)	0.40573 (18)	0.0555 (5)
H8A	1.1150	0.7548	0.4635	0.083*
H8B	1.2949	0.8091	0.4374	0.083*
H8C	1.2290	0.7319	0.3618	0.083*
C9	1.1720 (4)	0.87761 (16)	0.2469 (2)	0.0649 (6)
H9A	1.2300	0.8341	0.2054	0.097*
H9B	1.2713	0.9127	0.2830	0.097*
H9C	1.0884	0.9119	0.1981	0.097*
C10	0.9811 (3)	0.90805 (13)	0.40509 (18)	0.0549 (5)
H10A	1.0887	0.9412	0.4357	0.082*
H10B	0.9150	0.8838	0.4637	0.082*
H10C	0.8939	0.9439	0.3606	0.082*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0644 (3)	0.0425 (3)	0.0680 (3)	0.0196 (2)	-0.0158 (3)	-0.0037 (2)
Cl2	0.0602 (3)	0.0397 (2)	0.0426 (3)	0.0075 (2)	0.0136 (2)	-0.01185 (18)
Cl3	0.0763 (4)	0.0583 (3)	0.0519 (3)	0.0143 (3)	-0.0003 (3)	0.0212 (2)
Cl4	0.0883 (5)	0.0718 (4)	0.0632 (4)	-0.0239 (3)	0.0395 (3)	0.0014 (3)
Cl5	0.0372 (2)	0.0698 (4)	0.0671 (3)	-0.0054 (2)	-0.0002 (2)	-0.0178 (3)
O1	0.0907 (12)	0.0659 (10)	0.0698 (11)	-0.0203 (9)	0.0479 (10)	-0.0304 (8)
C1	0.0370 (9)	0.0393 (9)	0.0423 (10)	0.0002 (7)	0.0098 (7)	-0.0097 (7)
C2	0.0370 (9)	0.0268 (8)	0.0353 (9)	0.0040 (6)	0.0009 (7)	-0.0029 (6)

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C3	0.0372 (9)	0.0322 (8)	0.0270 (8)	0.0004 (7)	0.0026 (6)	-0.0002 (6)
C4	0.0335 (8)	0.0311 (8)	0.0286 (8)	0.0034 (6)	0.0025 (6)	-0.0050 (6)
C5	0.0482 (10)	0.0295 (8)	0.0372 (9)	-0.0016 (7)	0.0051 (7)	-0.0005 (7)
C6	0.0421 (10)	0.0421 (10)	0.0409 (10)	-0.0075 (8)	0.0116 (8)	-0.0024 (8)
C7	0.0442 (10)	0.0331 (9)	0.0405 (10)	-0.0044 (7)	0.0024 (8)	-0.0088 (7)
C8	0.0505 (12)	0.0561 (12)	0.0570 (13)	0.0041 (10)	-0.0118 (9)	-0.0138 (10)
C9	0.0754 (16)	0.0562 (13)	0.0650 (14)	-0.0310 (12)	0.0174 (12)	-0.0111 (11)
C10	0.0675 (14)	0.0396 (10)	0.0570 (13)	0.0000 (10)	0.0016 (10)	-0.0186 (9)

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

C11—C2	1.8271 (17)	C5—H5	0.9800
C12—C4	1.7278 (16)	C7—C8	1.524 (3)
C13—C5	1.7808 (19)	C7—C9	1.531 (3)
C14—C6	1.7593 (18)	C7—C10	1.538 (2)
C15—C6	1.790 (2)	C8—H8A	0.9600
O1—C1	1.188 (2)	C8—H8B	0.9600
C1—C2	1.543 (2)	C8—H8C	0.9600
C1—C6	1.553 (2)	C9—H9A	0.9600
C2—C3	1.501 (2)	C9—H9B	0.9600
C2—C7	1.569 (2)	C9—H9C	0.9600
C3—C4	1.322 (2)	C10—H10A	0.9600
C3—H3	0.9300	C10—H10B	0.9600
C4—C5	1.487 (2)	C10—H10C	0.9600
C5—C6	1.521 (3)		
O1—C1—C2	123.48 (16)	C14—C6—C15	108.43 (10)
O1—C1—C6	119.52 (17)	C8—C7—C9	109.08 (18)
C2—C1—C6	117.00 (14)	C8—C7—C10	109.08 (16)
C3—C2—C1	112.72 (13)	C9—C7—C10	107.62 (17)
C3—C2—C7	111.88 (14)	C8—C7—C2	108.04 (14)
C1—C2—C7	113.04 (14)	C9—C7—C2	109.78 (15)
C3—C2—C11	105.30 (11)	C10—C7—C2	113.17 (16)
C1—C2—C11	103.84 (11)	C7—C8—H8A	109.5
C7—C2—C11	109.40 (11)	C7—C8—H8B	109.5
C4—C3—C2	124.13 (15)	H8A—C8—H8B	109.5
C4—C3—H3	117.9	C7—C8—H8C	109.5
C2—C3—H3	117.9	H8A—C8—H8C	109.5
C3—C4—C5	125.00 (15)	H8B—C8—H8C	109.5
C3—C4—C12	120.98 (13)	C7—C9—H9A	109.5
C5—C4—C12	114.03 (12)	C7—C9—H9B	109.5
C4—C5—C6	109.63 (14)	H9A—C9—H9B	109.5
C4—C5—C13	109.88 (12)	C7—C9—H9C	109.5
C6—C5—C13	111.96 (13)	H9A—C9—H9C	109.5
C4—C5—H5	108.4	H9B—C9—H9C	109.5
C6—C5—H5	108.4	C7—C10—H10A	109.5
C13—C5—H5	108.4	C7—C10—H10B	109.5
C5—C6—C1	112.78 (14)	H10A—C10—H10B	109.5
C5—C6—C14	111.74 (13)	C7—C10—H10C	109.5
C1—C6—C14	110.43 (13)	H10A—C10—H10C	109.5

C5—C6—C15	106.09 (12)	H10B—C10—H10C	109.5
C1—C6—C15	107.08 (13)		
O1—C1—C2—C3	167.6 (2)	C13—C5—C6—C14	-51.23 (16)
C6—C1—C2—C3	-12.6 (2)	C4—C5—C6—C15	68.58 (15)
O1—C1—C2—C7	39.5 (3)	C13—C5—C6—C15	-169.21 (9)
C6—C1—C2—C7	-140.75 (16)	O1—C1—C6—C5	-137.5 (2)
O1—C1—C2—C11	-79.0 (2)	C2—C1—C6—C5	42.7 (2)
C6—C1—C2—C11	100.79 (15)	O1—C1—C6—C14	-11.7 (2)
C1—C2—C3—C4	-10.6 (2)	C2—C1—C6—C14	168.56 (13)
C7—C2—C3—C4	118.08 (18)	O1—C1—C6—C15	106.2 (2)
C11—C2—C3—C4	-123.17 (16)	C2—C1—C6—C15	-73.58 (17)
C2—C3—C4—C5	2.4 (3)	C3—C2—C7—C8	-69.95 (19)
C2—C3—C4—C12	-177.26 (12)	C1—C2—C7—C8	58.59 (19)
C3—C4—C5—C6	28.3 (2)	C11—C2—C7—C8	173.76 (13)
C12—C4—C5—C6	-152.03 (13)	C3—C2—C7—C9	48.9 (2)
C3—C4—C5—C13	-95.12 (18)	C1—C2—C7—C9	177.43 (16)
C12—C4—C5—C13	84.53 (13)	C11—C2—C7—C9	-67.40 (18)
C4—C5—C6—C1	-48.3 (2)	C3—C2—C7—C10	169.15 (16)
C13—C5—C6—C1	73.88 (17)	C1—C2—C7—C10	-62.3 (2)
C4—C5—C6—C14	-173.43 (12)	C11—C2—C7—C10	52.87 (18)

Fig. 1

