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(S)-4-(2-Chloropropan-2-yl)-1-(2,2,2-trichloroethyl)cyclohexeneBrahim Boualy,^a Mohamed Anoir Harrad,^a Larbi El Firdoussi,^a Mustapha Ait Ali^a and Corrado Rizzoli^{b*}^aEquipe de Chimie de Coordination et Catalyse, Faculté des Sciences-Semlalia, BP 2390, 40001 Marrakech, Morocco, and ^bDipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Viale G. P. Usberti 17/A, I-43124 Parma, Italy

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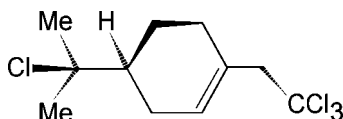
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.040; wR factor = 0.129; data-to-parameter ratio = 18.6.

The title compound, $\text{C}_{11}\text{H}_{16}\text{Cl}_4$, was synthesized by the reaction of (1*S*)- β -pinene with triethylamine in the presence of ZnCl_2 . The cyclohexene ring assumes a half-boat conformation. The crystal packing is governed only by van der Waals interactions. The structure, which has been refined in $P2_1$, presents a striking $P2_1/m$ pseudosymmetry.

Related literature

For background to the synthesis of polyhalogenated compounds, see: Delaude *et al.* (2004); Borguet *et al.* (2007). For the synthesis and structure of natural chlorinated compounds reported by our group, see: Ziyat *et al.* (2002, 2004); Boualy *et al.* (2009). For bond-length data, see: Allen *et al.* (1987). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{16}\text{Cl}_4$
 $M_r = 290.04$
 Monoclinic, $P2_1$
 $a = 10.6558$ (7) Å
 $b = 10.3017$ (6) Å

$c = 6.3119$ (3) Å
 $\beta = 91.251$ (5)°
 $V = 692.71$ (7) Å³
 $Z = 2$
 Cu $K\alpha$ radiation

$\mu = 7.50$ mm⁻¹
 $T = 294$ K

0.21 × 0.09 × 0.07 mm

Data collection

Siemens AED diffractometer
 Absorption correction:
 refined from ΔF (DIFABS);
 Walker & Stuart, 1983)
 $T_{\min} = 0.456$, $T_{\max} = 0.601$
 2764 measured reflections

2528 independent reflections
 2206 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 3 standard reflections every 100 reflections
 intensity decay: 0.02%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.129$
 $S = 1.16$
 2528 reflections
 136 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³
 Absolute structure: Flack (1983);
 1188 Friedel pairs
 Flack parameter: -0.04 (3)

Data collection: AED (Belletti *et al.*, 1993); cell refinement: AED; data reduction: AED; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and SCHAKAL97 (Keller, 1997); software used to prepare material for publication: SHELXL97 and PARST95 (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2395).

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supporting information

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(S)-4-(2-Chloropropan-2-yl)-1-(2,2,2-trichloroethyl)cyclohexene

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S1. Comment

The research on polyhalogenated alkanes, lactams and lactones, which are versatile intermediates in the synthesis of natural products and bioactive molecules, has held the attention of chemists for many years (Delaude *et al.*, 2004). Among others, the Kharasch reaction is an effective method for the formation of these polyhalogenated products. This process consists in the addition of a polyhalogenated alkane to an alkene and requires either a radical initiator or a transition metal catalyst (Borguet *et al.*, 2007). In the course of our ongoing research program aimed at the synthesis of natural chlorinated compounds (Ziyat *et al.*, 2002; Ziyat *et al.*, 2004; Boualy *et al.*, 2009), the title compound has been obtained and its crystal structure is reported herein.

In the molecule of the title compound (Fig. 1) all bond lengths (Allen *et al.*, 1987) and angles are normal. The cyclohexene ring assumes a half-boat conformation, with puckering parameters Q , θ and φ of 0.493 (4) Å, 51.9 (4)° and -142.0 (6)°, respectively (Cremer & Pople, 1975). The crystal structure (Fig. 2) is stabilized only by van der Waals interactions. The shortest intermolecular Cl...Cl separation observed is 3.5306 (11) Å (Cl2...Cl4ⁱ; symmetry code: (i) 1 + x, y, -1 + z). The structure, which has been refined in P2₁, presents a striking P2₁/m pseudosymmetry (See refinement section for details).

S2. Experimental

A mixture of (1*S*)- β -pinene (1 g, 7.34 mmol) and triethylamine (1 ml, 7.11 mmol) in carbon tetrachloride (15 ml) was added to a solution of ZnCl₂ in (1.1 g, 8.09 mmol) in water (15 ml) under stirring at room temperature. On completion of the reaction, the mixture was diluted with 25 ml of water, extracted with carbon tetrachloride (3 × 10 ml) and dried over Na₂SO₄. The title compound was isolated as a white powder by column chromatography on silica gel using *n*-hexane as eluent (yield 90%; m. p. = 48 °C), but colourless single crystals suitable for X-ray analysis were obtained by slow evaporation of a *n*-hexane solution. ¹H NMR (300 MHz, CDCl₃): δ p.p.m. 5.71 (m, 1H), 3.28 (s, 2H), 2.29 (m, 3H), 1.97 (m, 2H), 1.65 (m, 1H), 1.53 (s, 3H), 1.54 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ p.p.m. 131.03 (C_q), 130.53 (CH=C), 99.06 (CCl₃), 73.09 (CCl), 62.02 (CH₂-CCl₃), 45.73 (CH), 30.61 (CH₂), 29.83 (CH₃), 29.76 (CH₃), 28.19 (CH₂), 24.56 (CH₂).

S3. Refinement

The molecule contains one chiral carbon atom at C4. Irrespective of this it is possible to solve the structure in the higher symmetry P2₁/m space group, but this forces the molecule to have a crystallographically imposed mirror symmetry passing through C1 and C4 of the cyclohexene ring, resulting in the C2 (sp²) and C6 (sp³) carbon atoms to be symmetry-related and disordered over two orientations. This disorder is totally absent in the noncentrosymmetric P2₁ space group. Moreover, refining in P2₁/m results in significantly worse R values (R1 = 5.4%, wR2 = 18.2%). All H atoms were

calculated geometrically and refined using a riding model, with C—H = 0.93–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms.

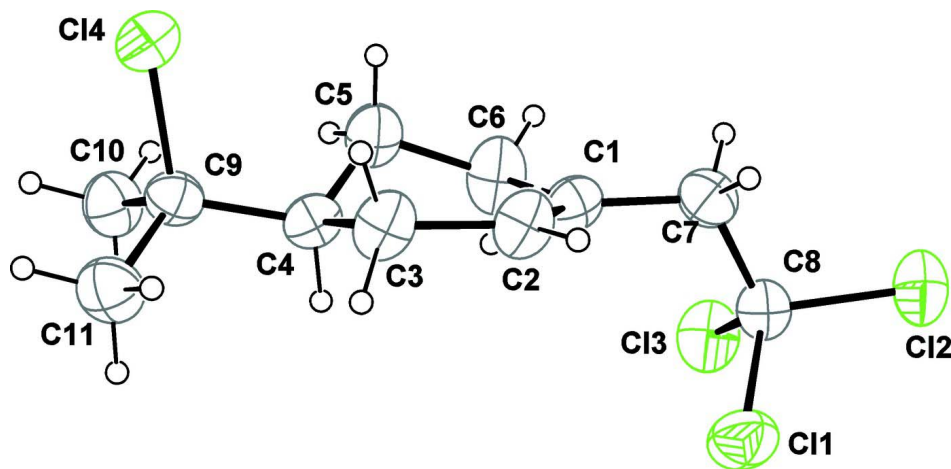


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

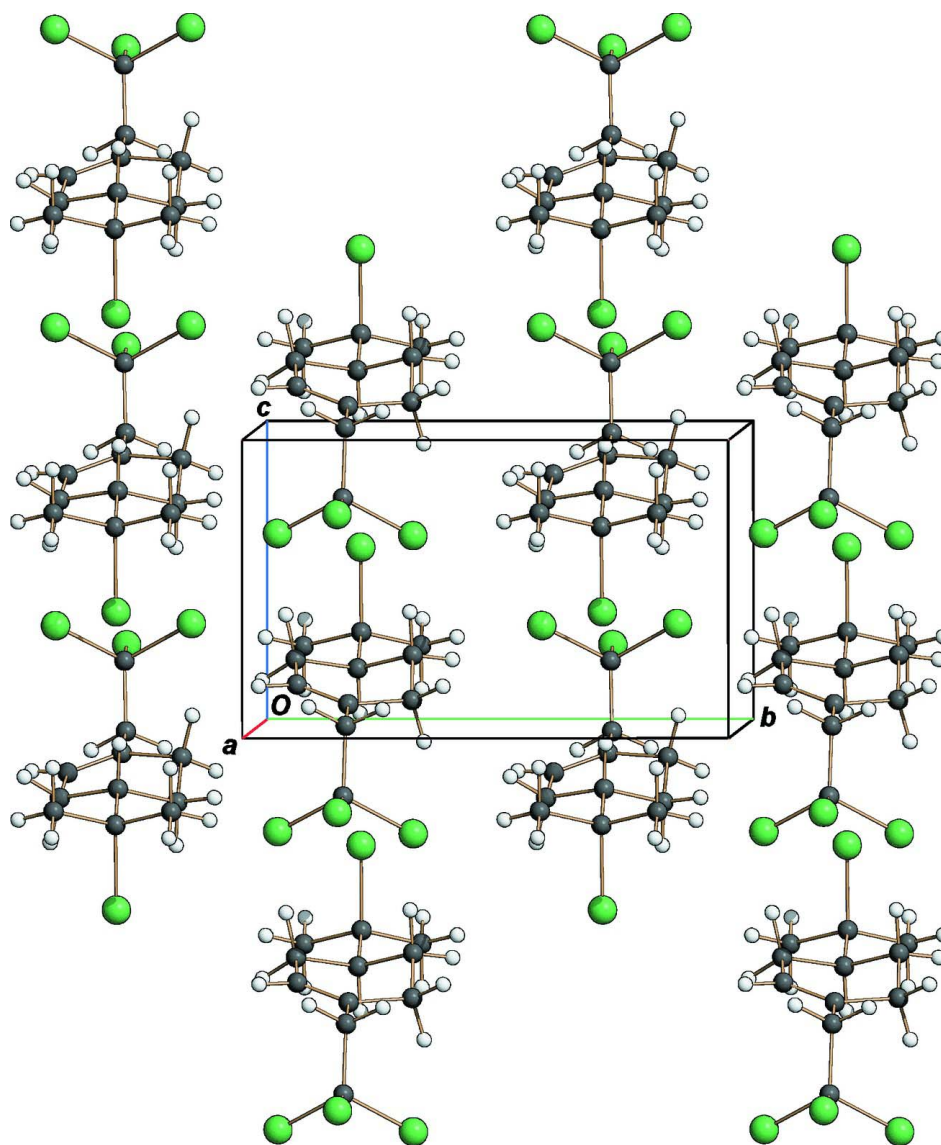


Figure 2

Crystal packing of the title compound approximately viewed along the *a* axis.

(S)-4-(2-Chloropropan-2-yl)-1-(2,2,2-trichloroethyl)cyclohexene

Crystal data

$C_{11}H_{16}Cl_4$

$M_r = 290.04$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_1y$

$a = 10.6558\ (7)\ \text{\AA}$

$b = 10.3017\ (6)\ \text{\AA}$

$c = 6.3119\ (3)\ \text{\AA}$

$\beta = 91.251\ (5)^\circ$

$V = 692.71\ (7)\ \text{\AA}^3$

$Z = 2$

$F(000) = 300$

$D_x = 1.391\ \text{Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54178\ \text{\AA}$

Cell parameters from 48 reflections

$\theta = 19.3\text{--}31.4^\circ$

$\mu = 7.50\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Irregular block, colourless

$0.21 \times 0.09 \times 0.07\ \text{mm}$

Data collection

Siemens AED diffractometer	2528 independent reflections
Radiation source: fine-focus sealed tube	2206 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.038$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 68.0^\circ$, $\theta_{\text{min}} = 4.2^\circ$
Absorption correction: part of the refinement model (ΔF) (DIFABS; Walker & Stuart, 1983)	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.456$, $T_{\text{max}} = 0.601$	$k = -12 \rightarrow 12$
2764 measured reflections	$l = -1 \rightarrow 7$
	3 standard reflections every 100 reflections
	intensity decay: 0.02%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2]$
$wR(F^2) = 0.129$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2528 reflections	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
136 parameters	$\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$
1 restraint	Absolute structure: Flack (1983); 1188 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: -0.04 (3)
Secondary atom site location: difference Fourier map	

Special details

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.92140 (14)	0.06856 (10)	-0.3180 (2)	0.0976 (4)
C12	1.15231 (7)	0.20291 (18)	-0.23878 (15)	0.0990 (3)
C13	0.92735 (12)	0.34740 (9)	-0.3247 (2)	0.0954 (4)
C14	0.46844 (7)	0.21653 (15)	0.60646 (11)	0.0855 (3)
C1	0.8287 (2)	0.2091 (4)	0.1030 (4)	0.0667 (6)
C2	0.7742 (4)	0.1006 (3)	0.1658 (7)	0.0733 (9)
H2	0.8213	0.0247	0.1630	0.088*
C3	0.6416 (4)	0.0915 (3)	0.2416 (7)	0.0762 (11)
H3A	0.6436	0.0713	0.3917	0.091*
H3B	0.5996	0.0205	0.1683	0.091*
C4	0.5658 (2)	0.2149 (4)	0.2064 (4)	0.0630 (5)
H4	0.5460	0.2189	0.0542	0.076*
C5	0.6483 (4)	0.3326 (4)	0.2565 (7)	0.0766 (11)
H5A	0.5994	0.4114	0.2382	0.092*
H5B	0.6776	0.3285	0.4029	0.092*
C6	0.7592 (5)	0.3362 (4)	0.1129 (8)	0.0912 (13)

H6A	0.8167	0.4032	0.1621	0.109*
H6B	0.7302	0.3596	-0.0288	0.109*
C7	0.9642 (2)	0.2108 (5)	0.0397 (4)	0.0721 (6)
H7A	1.0063	0.1370	0.1052	0.086*
H7B	1.0031	0.2887	0.0971	0.086*
C8	0.9870 (2)	0.2066 (5)	-0.1959 (4)	0.0696 (6)
C9	0.4387 (2)	0.2159 (4)	0.3195 (4)	0.0657 (6)
C10	0.3606 (4)	0.3349 (4)	0.2697 (7)	0.0826 (11)
H10A	0.4088	0.4115	0.3014	0.124*
H10B	0.2866	0.3341	0.3539	0.124*
H10C	0.3367	0.3347	0.1222	0.124*
C11	0.3614 (5)	0.0931 (4)	0.2681 (8)	0.0870 (13)
H11A	0.4109	0.0175	0.3001	0.131*
H11B	0.3379	0.0929	0.1204	0.131*
H11C	0.2872	0.0924	0.3518	0.131*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.1090 (9)	0.0869 (6)	0.0972 (9)	-0.0153 (6)	0.0089 (8)	-0.0282 (6)
C12	0.0705 (4)	0.1114 (7)	0.1159 (6)	0.0073 (6)	0.0184 (4)	0.0098 (8)
C13	0.0994 (8)	0.0875 (7)	0.0998 (8)	0.0092 (6)	0.0124 (7)	0.0294 (6)
C14	0.0896 (5)	0.1015 (6)	0.0658 (4)	-0.0017 (7)	0.0100 (3)	-0.0054 (6)
C1	0.0785 (14)	0.0560 (12)	0.0656 (13)	0.011 (2)	0.0025 (11)	-0.002 (2)
C2	0.084 (2)	0.0530 (17)	0.083 (2)	0.0111 (15)	0.0145 (18)	0.0110 (15)
C3	0.090 (3)	0.0472 (18)	0.092 (3)	0.0030 (16)	0.020 (2)	0.0037 (17)
C4	0.0766 (14)	0.0513 (12)	0.0611 (12)	0.0043 (18)	0.0036 (10)	0.0010 (18)
C5	0.079 (2)	0.0523 (17)	0.099 (3)	-0.0007 (16)	0.013 (2)	-0.009 (2)
C6	0.091 (2)	0.0473 (15)	0.136 (4)	0.0015 (16)	0.028 (3)	0.008 (2)
C7	0.0728 (14)	0.0695 (14)	0.0736 (14)	0.000 (2)	-0.0061 (11)	0.007 (2)
C8	0.0673 (13)	0.0629 (13)	0.0787 (15)	0.0014 (19)	0.0050 (11)	0.005 (2)
C9	0.0712 (14)	0.0567 (13)	0.0691 (13)	-0.0005 (18)	-0.0036 (10)	-0.0042 (19)
C10	0.078 (3)	0.071 (2)	0.099 (3)	0.0121 (19)	0.002 (2)	0.001 (2)
C11	0.089 (3)	0.071 (3)	0.100 (4)	-0.007 (2)	-0.001 (3)	-0.008 (2)

Geometric parameters (Å, °)

C11—C8	1.755 (4)	C5—H5A	0.9700
C12—C8	1.789 (3)	C5—H5B	0.9700
C13—C8	1.774 (4)	C6—H6A	0.9700
C14—C9	1.832 (3)	C6—H6B	0.9700
C1—C2	1.324 (5)	C7—C8	1.512 (4)
C1—C6	1.506 (5)	C7—H7A	0.9700
C1—C7	1.507 (4)	C7—H7B	0.9700
C2—C3	1.504 (6)	C9—C10	1.511 (5)
C2—H2	0.9300	C9—C11	1.541 (6)
C3—C4	1.520 (5)	C10—H10A	0.9600
C3—H3A	0.9700	C10—H10B	0.9600

C3—H3B	0.9700	C10—H10C	0.9600
C4—C5	1.526 (5)	C11—H11A	0.9600
C4—C9	1.545 (4)	C11—H11B	0.9600
C4—H4	0.9800	C11—H11C	0.9600
C5—C6	1.505 (6)		
C2—C1—C6	120.1 (3)	C1—C7—C8	115.8 (2)
C2—C1—C7	121.2 (4)	C1—C7—H7A	108.3
C6—C1—C7	118.5 (4)	C8—C7—H7A	108.3
C1—C2—C3	124.7 (3)	C1—C7—H7B	108.3
C1—C2—H2	117.7	C8—C7—H7B	108.3
C3—C2—H2	117.7	H7A—C7—H7B	107.4
C2—C3—C4	113.6 (3)	C7—C8—C11	112.6 (3)
C2—C3—H3A	108.8	C7—C8—C13	111.3 (3)
C4—C3—H3A	108.8	C11—C8—C13	109.02 (15)
C2—C3—H3B	108.8	C7—C8—C12	109.21 (18)
C4—C3—H3B	108.8	C11—C8—C12	107.5 (2)
H3A—C3—H3B	107.7	C13—C8—C12	107.0 (2)
C3—C4—C5	109.4 (2)	C10—C9—C11	109.4 (2)
C3—C4—C9	114.0 (3)	C10—C9—C4	113.2 (3)
C5—C4—C9	113.9 (3)	C11—C9—C4	111.5 (3)
C3—C4—H4	106.3	C10—C9—C14	106.6 (2)
C5—C4—H4	106.3	C11—C9—C14	106.9 (3)
C9—C4—H4	106.3	C4—C9—C14	108.81 (17)
C6—C5—C4	110.5 (3)	C9—C10—H10A	109.5
C6—C5—H5A	109.5	C9—C10—H10B	109.5
C4—C5—H5A	109.5	H10A—C10—H10B	109.5
C6—C5—H5B	109.5	C9—C10—H10C	109.5
C4—C5—H5B	109.5	H10A—C10—H10C	109.5
H5A—C5—H5B	108.1	H10B—C10—H10C	109.5
C5—C6—C1	113.4 (3)	C9—C11—H11A	109.5
C5—C6—H6A	108.9	C9—C11—H11B	109.5
C1—C6—H6A	108.9	H11A—C11—H11B	109.5
C5—C6—H6B	108.9	C9—C11—H11C	109.5
C1—C6—H6B	108.9	H11A—C11—H11C	109.5
H6A—C6—H6B	107.7	H11B—C11—H11C	109.5