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(5*R*)-5-[(1*R*)-2,2-Dichloro-1-methylcyclopropyl]-2-methylcyclohex-2-en-1-one

Brahim Boualy,[a] Mohamed Anoir Harrad,[a] Larbi El Firdoussi,[a] Mustapha Ait Ali[a] and Corrado Rizzoli[b]*

[a]Laboratoire de Chimie de Coordination, Université Cadi Ayyad, Faculté des Sciences-Semlalia, BP 2390, 40001 Marrakech, Morocco, and [b]Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universitá degli Studi di Parma, Viale G. P. Usberti 17/A, I-43124 Parma, Italy
Correspondence e-mail: corrado.rizzoli@unipr.it

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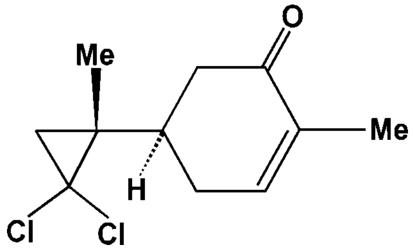
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.046; wR factor = 0.126; data-to-parameter ratio = 12.1.

The title compound, $C_{11}H_{14}Cl_2O$, was synthesized by the reaction of a dichloromethane solution of (*R*)-carvone and potassium *tert*-butanolate in the presence of a catalytic amount of benzyltriethylammonium chloride in chloroform. The cyclohexene ring adopts a half-boat conformation. The cyclopropyl ring is unsymmetrical, the shortest C—C bond being distal to the alkyl-substituted C atom. The crystal packing is stabilized only by van der Waals interactions.

Related literature

For background to and applications of dichlorocyclopropane derivatives, see: Hirota *et al.* (1996); Künzer *et al.* (1996); Ziyat *et al.* (2004); Fedorynski (2003). For the synthesis and structures of optically active dihalogenocylopropanes reported by our group, see: Ziyat *et al.* (2002); Boualy *et al.* (2009); Ziyat *et al.* (2006). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{11}H_{14}Cl_2O$
M_r = 233.12
Monoclinic, $P2_1$
a = 6.5722 (3) Å
b = 8.4802 (4) Å
c = 10.8022 (5) Å
β = 104.435 (4)°
V = 583.04 (5) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 4.73 mm^{-1}
T = 294 K
0.25 × 0.20 × 0.14 mm

Data collection

Siemens AED diffractometer
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.327, T_{max} = 0.519
2295 measured reflections
1576 independent reflections
1554 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
3 standard reflections every 100 reflections
intensity decay: 0.3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.126
S = 1.09
1576 reflections
130 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Absolute structure: Flack (1983), 394 Friedel pairs
Flack parameter: 0.00 (2)

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: GK2382).

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supplementary materials

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(5*R*)-5-[(1*R*)-2,2-Dichloro-1-methylcyclopropyl]-2-methylcyclohex-2-en-1-one

B. Boualy, **M. A. Harrad**, **L. El Firdoussi**, **M. A. Ali** and **C. Rizzoli**

Comment

Dichlorocyclopropanes play an important role in organic synthesis, due to the widespread occurrence of these structures in biologically active compounds (Hirota *et al.*, 1996; Künzer *et al.*, 1996). These compounds have found wide applications as substrates for the synthesis of many class of compounds such as pyrethroides (Ziyat *et al.*, 2004), benzocyclopropenes or cyclopentadiene derivatives (Fedorynski, 2003), which are not easily obtained using other starting materials. As a part of our ongoing research aimed at the synthesis of optically active dihalogenocylopropanes from terpenes (Ziyat *et al.*, 2002; Ziyat *et al.*, 2004; Boualy *et al.*, 2009; Ziyat *et al.*, 2006), the title compound has been prepared and its crystal structure is reported herein.

In the title compound (Fig. 1), the cyclohexene ring adopts a half-boat conformation [puckering parameters for ring C6/C1/C2/C3/C4/C5: Q = 0.478 (4) Å, θ = 126.7 (4)°, φ = -171.0 (6)°; Cremer & Pople, 1975] with atom C6 displaced by 0.645 (3) Å from the mean plane through the C1–C5 atoms. The cyclopropyl ring (C7–C9) is tilted by 57.64 (19)° with respect to this plane. As already observed in related compounds (Ziyat *et al.*, 2002), the geometry of the cyclopropyl ring is unsymmetrical, the distal bond to the alkyl-substituted C7 carbon atom (C8—C9 = 1.477 (6) Å) being significantly shorter than the vicinal bonds (C7—C8 = 1.518 (6) Å; C7—C9 = 1.500 (4) Å). The crystal packing (Fig. 2) is governed only by van der Waals interactions. The shortest intermolecular halogen···halogen separation is $\text{Cl1}\cdots\text{Cl2}^{\text{i}}$ = 3.990 (3) Å (symmetry code: (i) 2 - x, -1/2 + y, 1 - z).

Experimental

Potassium *tert*-butanolate (4.00 g, 19.8 mmol) was added to (*R*)-carvone (1.47 g, 9.8 mmol) and benzyltriethylammonium chloride (0.02 g, 0.1 mmol) in dichloromethane (60 ml). The mixture was stirred for 10 min, then chloroform (0.8 ml, 9.8 mmol) was added dropwise over a period of 30 min. The mixture was stirred for 8 h at 25°C, and then hydrolyzed by addition of water (20 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 ml). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Column chromatography on silica gel (hexane/ethyl acetate, 5:1 *v*/*v*) of the residue gave 1.24 g (5.3 mmol, 54% yield) of the title compound as colourless crystals. Slow evaporation of a chloroform solution of the title compound at 25°C afforded crystals suitable for X-ray crystallographic analysis. *M*.p. 392 K. $[\alpha]^{20}_{D}$ = +7.72° (*c* 1, chloroform). ^{1}H NMR (300 MHz, $CDCl_3$, $\delta_{\text{p.p.m.}}$): 1.18 (*s*, 2H), 1.3 (*s*, 3H), 1.78 (*d*, *J* = 0.9 Hz, 3H), 2.1 (*m*, 1H), 2.3–2.5 (*m*, 4H), 6.77 (*m*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, $\delta_{\text{p.p.m.}}$): 15.6 (CH_3), 16.0 (CH_3), 28.5 (CH_2), 32.5 (CH_2), 40.8 (C^q), 41.4 (CH_2), 41.8 (CH), 65.8 (C^q), 135.5 ($=C^q$), 144.5 ($=$CH), 199 (C$=$O). MS (70 eV) m/*z* (%): 233 [M^+].

Refinement

All H atoms were fixed geometrically and treated as riding, with C–H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl H atoms. The absolute configuration of the molecule was established by the known chirality of the (*R*)-carvone starting material and, in spite of the low Friedel pair coverage (40%), the value of the resulting Flack (1983) parameter was in accordance with this configuration. For the inverted structure, the Flack parameter refined to 0.71 (3), and the values of $R[F^2>2\sigma(F^2)]$ and $wR(F^2)$ increased to 0.0583 and 0.1695, respectively.

Figures

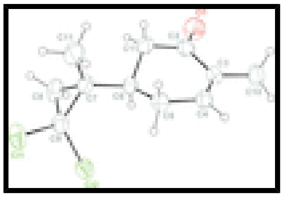

Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 40% probability level.

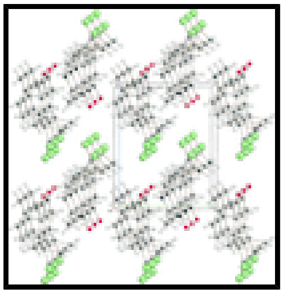

Fig. 2. Crystal packing of the title compound approximately viewed along the *a* axis.

(5*R*)-5-[(1*R*)-2,2-Dichloro-1-methylcyclopropyl]-2-methylcyclohex- 2-en-1-one

Crystal data

$C_{11}H_{14}Cl_2O$

M_r = 233.12

Monoclinic, $P2_1$

Hall symbol: P 2yb

a = 6.5722 (3) Å

b = 8.4802 (4) Å

c = 10.8022 (5) Å

β = 104.435 (4)°

V = 583.04 (5) Å^3

Z = 2

F(000) = 244

D_x = 1.328 Mg m^{-3}

Cu $K\alpha$ radiation, λ = 1.54178 Å

Cell parameters from 48 reflections

θ = 22.5–35.9°

μ = 4.73 mm^{-1}

T = 294 K

Irregular block, colourless

0.25 × 0.20 × 0.14 mm

Data collection

Siemens AED diffractometer

Radiation source: fine-focus sealed tube

1554 reflections with $I > 2\sigma(I)$

R_{int} = 0.057

graphite	$\theta_{\text{max}} = 69.8°$, $\theta_{\text{min}} = 4.2°$
θ/2θ scans	$h = -7 \rightarrow 6$
Absorption correction: part of the refinement model (ΔF) (*DIFABS*; Walker & Stuart, 1983)	$k = -10 \rightarrow 6$
$T_{\text{min}} = 0.327$, $T_{\text{max}} = 0.519$	$l = -12 \rightarrow 13$
2295 measured reflections	3 standard reflections every 100 reflections
1576 independent reflections	intensity decay: 0.3%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.083P)^2 + 0.0912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.43$ e Å^{-3}
1576 reflections	$\Delta\rho_{\text{min}} = -0.30$ e Å^{-3}
130 parameters	Extinction correction: *SHELXL*
1 restraint	Extinction coefficient: 0.014 (3)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 394 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.00 (2)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	1.34023 (13)	0.77757 (15)	0.58246 (8)	0.0824 (4)
Cl2	0.90330 (12)	0.84462 (16)	0.47313 (8)	0.0858 (4)
O1	0.7651 (5)	0.7920 (6)	−0.1253 (3)	0.0987 (12)
C1	1.0031 (5)	0.7536 (6)	0.0774 (3)	0.0693 (10)
H1A	1.0523	0.8597	0.0677	0.083*
H1B	1.1099	0.6805	0.0652	0.083*
C2	0.8020 (5)	0.7244 (5)	−0.0244 (3)	0.0636 (8)
C3	0.6586 (5)	0.6053 (4)	0.0053 (3)	0.0554 (7)
C4	0.7023 (5)	0.5357 (4)	0.1185 (3)	0.0571 (7)
H4	0.6091	0.4590	0.1322	0.069*
C5	0.8894 (4)	0.5702 (4)	0.2264 (3)	0.0548 (7)
H5A	0.9982	0.4927	0.2270	0.066*
H5B	0.8499	0.5627	0.3069	0.066*

C6	0.9740 (4)	0.7342 (4)	0.2127 (3)	0.0496 (6)
H6	0.8668	0.8101	0.2227	0.059*
C7	1.1744 (4)	0.7717 (5)	0.3144 (3)	0.0584 (7)
C8	1.2112 (6)	0.9436 (6)	0.3526 (4)	0.0799 (11)
H8A	1.3547	0.9822	0.3731	0.096*
H8B	1.1062	1.0197	0.3108	0.096*
C9	1.1528 (4)	0.8301 (5)	0.4415 (3)	0.0614 (7)
C10	0.4642 (6)	0.5669 (7)	−0.0993 (4)	0.0791 (11)
H10A	0.3966	0.6630	−0.1344	0.119*
H10B	0.3692	0.5055	−0.0644	0.119*
H10C	0.5037	0.5079	−0.1655	0.119*
C11	1.3618 (5)	0.6704 (8)	0.3127 (4)	0.0909 (15)
H11A	1.3816	0.6673	0.2276	0.136*
H11B	1.3386	0.5654	0.3395	0.136*
H11C	1.4848	0.7138	0.3699	0.136*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0728 (5)	0.0887 (7)	0.0691 (5)	0.0062 (4)	−0.0133 (3)	−0.0101 (5)
Cl2	0.0610 (4)	0.1189 (9)	0.0741 (5)	0.0072 (5)	0.0107 (3)	−0.0351 (6)
O1	0.115 (2)	0.115 (3)	0.0616 (14)	−0.024 (2)	0.0147 (13)	0.028 (2)
C1	0.0660 (16)	0.081 (3)	0.0632 (17)	−0.0162 (17)	0.0201 (13)	0.007 (2)
C2	0.0756 (17)	0.066 (2)	0.0503 (15)	−0.0062 (16)	0.0182 (13)	0.0030 (17)
C3	0.0608 (14)	0.0537 (16)	0.0500 (14)	−0.0017 (14)	0.0104 (11)	−0.0062 (15)
C4	0.0616 (15)	0.0554 (17)	0.0544 (16)	−0.0067 (13)	0.0146 (12)	−0.0029 (15)
C5	0.0571 (14)	0.0535 (17)	0.0515 (15)	0.0014 (12)	0.0091 (11)	0.0047 (14)
C6	0.0467 (12)	0.0490 (16)	0.0512 (14)	0.0010 (10)	0.0087 (10)	−0.0009 (13)
C7	0.0443 (12)	0.0613 (18)	0.0666 (17)	−0.0028 (13)	0.0083 (11)	−0.0043 (17)
C8	0.075 (2)	0.064 (2)	0.090 (3)	−0.0173 (18)	0.0005 (17)	−0.001 (2)
C9	0.0511 (13)	0.0621 (19)	0.0632 (15)	0.0017 (13)	−0.0003 (11)	−0.0075 (17)
C10	0.081 (2)	0.086 (3)	0.0612 (18)	−0.019 (2)	0.0007 (15)	−0.007 (2)
C11	0.0462 (15)	0.124 (4)	0.097 (3)	0.015 (2)	0.0073 (16)	−0.027 (3)

Geometric parameters (Å, °)

Cl1—C9	1.760 (3)	C6—C7	1.523 (4)
Cl2—C9	1.761 (3)	C6—H6	0.9800
O1—C2	1.202 (4)	C7—C9	1.500 (4)
C1—C2	1.514 (4)	C7—C11	1.506 (5)
C1—C6	1.529 (4)	C7—C8	1.518 (6)
C1—H1A	0.9700	C8—C9	1.477 (6)
C1—H1B	0.9700	C8—H8A	0.9700
C2—C3	1.470 (5)	C8—H8B	0.9700
C3—C4	1.323 (4)	C10—H10A	0.9600
C3—C10	1.515 (4)	C10—H10B	0.9600
C4—C5	1.497 (4)	C10—H10C	0.9600
C4—H4	0.9300	C11—H11A	0.9600
C5—C6	1.519 (5)	C11—H11B	0.9600

C5—H5A	0.9700	C11—H11C	0.9600
C5—H5B	0.9700		
C2—C1—C6	112.4 (2)	C11—C7—C8	118.4 (3)
C2—C1—H1A	109.1	C9—C7—C6	117.9 (2)
C6—C1—H1A	109.1	C11—C7—C6	115.8 (3)
C2—C1—H1B	109.1	C8—C7—C6	116.5 (3)
C6—C1—H1B	109.1	C9—C8—C7	60.1 (3)
H1A—C1—H1B	107.8	C9—C8—H8A	117.8
O1—C2—C3	122.0 (3)	C7—C8—H8A	117.8
O1—C2—C1	121.5 (3)	C9—C8—H8B	117.8
C3—C2—C1	116.5 (3)	C7—C8—H8B	117.8
C4—C3—C2	120.3 (3)	H8A—C8—H8B	114.9
C4—C3—C10	122.8 (3)	C8—C9—C7	61.3 (3)
C2—C3—C10	116.9 (3)	C8—C9—Cl1	119.2 (2)
C3—C4—C5	125.4 (3)	C7—C9—Cl1	120.2 (2)
C3—C4—H4	117.3	C8—C9—Cl2	119.1 (3)
C5—C4—H4	117.3	C7—C9—Cl2	120.4 (2)
C4—C5—C6	110.7 (3)	Cl1—C9—Cl2	109.55 (18)
C4—C5—H5A	109.5	C3—C10—H10A	109.5
C6—C5—H5A	109.5	C3—C10—H10B	109.5
C4—C5—H5B	109.5	H10A—C10—H10B	109.5
C6—C5—H5B	109.5	C3—C10—H10C	109.5
H5A—C5—H5B	108.1	H10A—C10—H10C	109.5
C5—C6—C7	113.1 (3)	H10B—C10—H10C	109.5
C5—C6—C1	109.1 (3)	C7—C11—H11A	109.5
C7—C6—C1	112.1 (2)	C7—C11—H11B	109.5
C5—C6—H6	107.4	H11A—C11—H11B	109.5
C7—C6—H6	107.4	C7—C11—H11C	109.5
C1—C6—H6	107.4	H11A—C11—H11C	109.5
C9—C7—C11	117.6 (3)	H11B—C11—H11C	109.5
C9—C7—C8	58.6 (3)		

Fig. 1

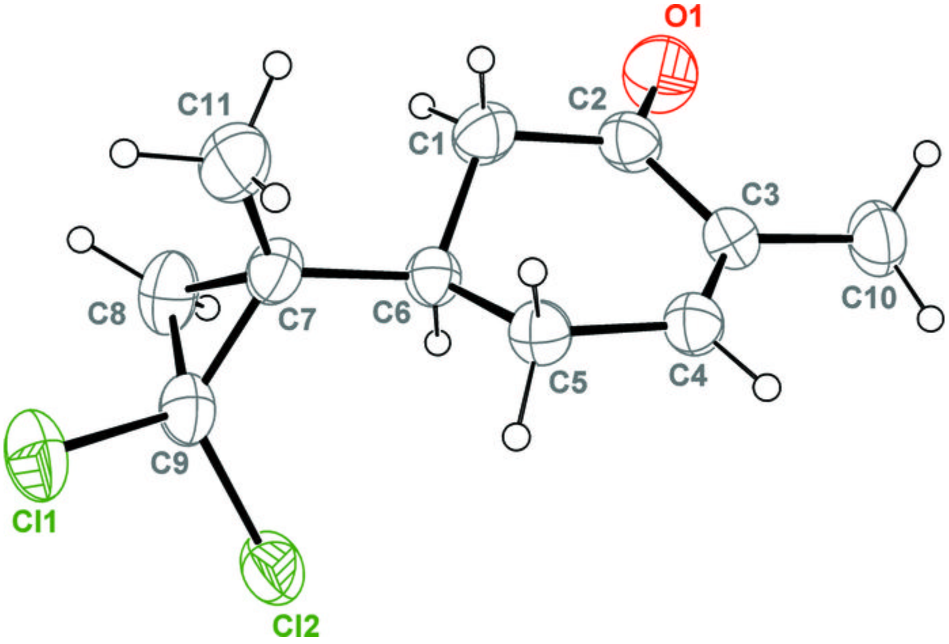

Fig. 2