

rac-(2*aS*,2*a*¹*R*,3*aR*,3*a*¹*S*,5*aS*,6*aR*)-2*a*-Allyl-2,4-dichloro-2*a*,2*a*¹,3*a*¹,5*a*,6,6*a*-hexahydro-3*aH*-3-oxadicyclopenta[*cd,gh*]pentalen-3*a*-ol

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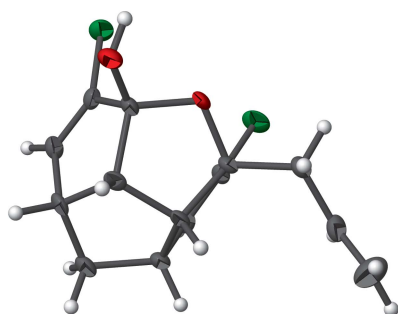
Keywords: crystal structure; triquinane; hemiketal; indium-catalysed; transannular cyclization.

CCDC reference: 2114309

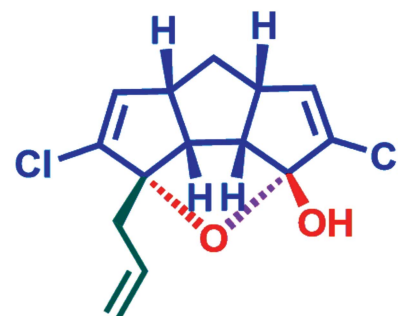
Structural data: full structural data are available from iucrdata.iucr.org

The title racemic triquinane, C₁₄H₁₄Cl₂O₂, is composed of four five-membered rings, one of which is a tetrahydrofuran ring to which an allyl group on one side and a hydroxyl group on the other side are attached. The core of the triquinane unit has a *cis-syn-cis* configuration. In the crystal, the molecules are linked by pairwise O—H...O hydrogen bonds, generating inversion dimers featuring R₂²(8) loops.

3D view



Chemical scheme



Structure description

Compounds with three fused five-membered rings, known as triquinanes, have gained considerable importance because this core is found in several biologically active compounds (Qiu *et al.*, 2018; Kotha *et al.*, 2020). Therefore, convenient methods to prepare and functionalize triquinanes and the study of their stereochemistry are useful exercises (Mehta & Rao, 1985). Our group has prepared triquinanes from cage compounds in a simplified manner using microwave irradiation (Kotha *et al.*, 2019). Thereafter, we attempted to functionalize the triquinanes and observed a transannular attack at the keto centre (O1—C1—O2) leading to the formation of the title compound, **1**.

Compound **1** has three carbocyclic rings (C1/C2/C3/C4/C5, C4/C5/C6/C7/C8 and C6/C7/C9/C10/C11) and a tetrahydrofuran ring (O1/C1/C5/C6/C11). The allyl group is unsymmetrically substituted at C11 and the hydroxy group is attached to C1 (Fig. 1*a*). There are six stereogenic centres in **1**: in the arbitrarily chosen asymmetric molecule, the configurations are C1 *R*, C4 *R*, C5 *S*, C6 *R*, C7 *S* and C11 *S* but crystal symmetry generates a racemic mixture.

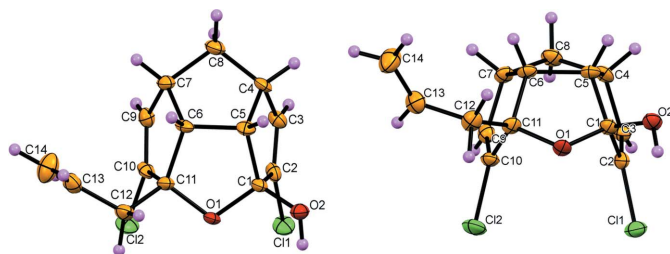


Figure 1
The molecular structure of **1** (a) viewed from above and (b) viewed from the front. Displacement ellipsoids are drawn at the 50% probability level.

The triquinane ring system consists of a *cis-syn-cis* configuration, *i.e.*, the hydrogen atoms at the ring junction are all above the plane and the first and the third rings are below the plane (Fig. 1b). The chlorine atoms are attached to the unsaturated bonds C2–C3 and C9–C10 in *anti*-manner with respect to the H atoms of the ring junction. The middle cyclopentyl ring adopts an envelope conformation and the side rings are almost planar.

In the crystal, the molecules are linked by O–H···O hydrogen bonds, generating inversion dimers featuring $R_2^2(8)$ loops (Table 1, Fig. 2) but no intramolecular hydrogen bonds are present.

Synthesis and crystallization

The synthesis scheme is shown in Fig. 3. Indium ingots (51 mg, 2.7 eq) were cut into small pieces and transferred to a two-

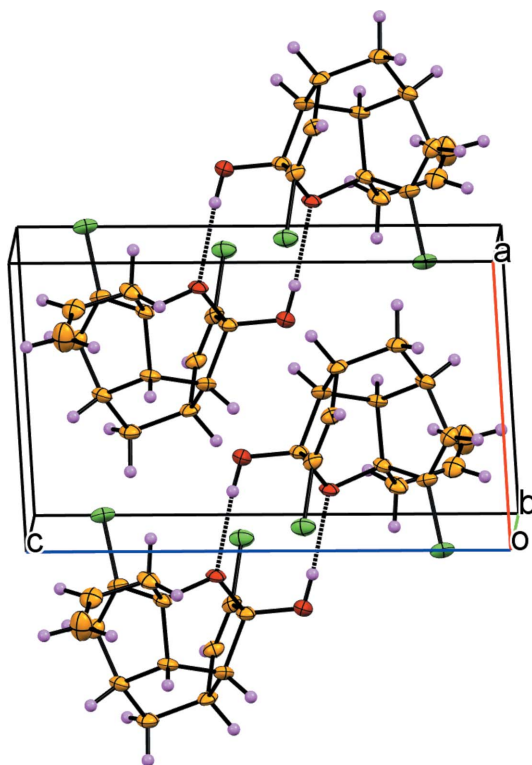


Figure 2
The crystal packing of **1**, viewed along the *b*-axis direction. The hydrogen bonding is shown using dotted lines.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2–H2···O1 ⁱ	0.84	2.06	2.893 (3)	173

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₄ Cl ₂ O ₂
<i>M_r</i>	285.15
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2687 (10), 8.3648 (11), 11.7460 (18)
α , β , γ (°)	80.448 (4), 83.441 (4), 65.285 (4)
<i>V</i> (Å ³)	638.96 (16)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.50
Crystal size (mm)	0.32 × 0.29 × 0.09
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.655, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	19764, 2241, 1662
<i>R_{int}</i>	0.106
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.048, 0.107, 1.09
No. of reflections	2241
No. of parameters	164
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.27, -0.33

Computer programs: APEX2 and SAINT (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

neck round-bottomed flask. Tetrahydrofuran (3 ml) was transferred to the flask under nitrogen at room temperature. Allyl iodide (0.5 ml) was added to this solution *via* a syringe. After one h, the starting material **2** (40 mg) and trimethylchlorosilane (3 drops) was added to the reaction mixture. On completion of the reaction (TLC monitoring) after 1 h, water was added to the reaction mixture. The aqueous layer was extracted with diethyl ether (Lee *et al.* 2001). The compound was purified with column chromatography and silica gel (100–200 mesh) was used. Ethyl acetate:petroleum ether (8% of ethyl acetate in total in 100 ml of solution) was used an eluent.

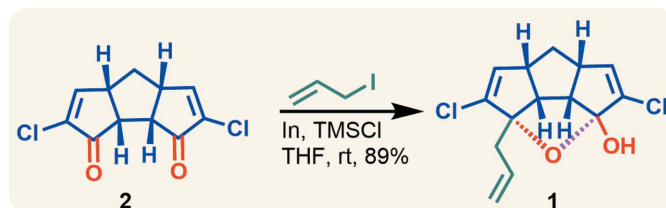


Figure 3
Synthesis scheme for **1**.

After that, the crystals suitable for X-ray crystallographic analysis were grown in air in a glass vial using ethyl acetate as solvent (Fig. 3).

Characterization: colourless crystalline solid; m.p. 120–122°C; ^1H NMR (500 MHz, CDCl_3): δ = 5.73–5.62 (*m*, 3H), 5.20–5.14 (*m*, 2H), 3.39–3.30 (*m*, 2H), 3.23–3.20 (*m*, 1H), 3.02–2.98 (*m*, 1H), 2.63 (*dd*, J = 13.8, 7.0 Hz, 1H), 2.55 (*dd*, J = 13.8, 7.0 Hz, 1H), 1.95–1.87 (*m*, 1H), 1.78 (*d*, J = 13.9 Hz, 1H) p.p.m.; ^{13}C NMR (125 MHz, CDCl_3): δ = 134.1, 133.2, 133.1, 133.0, 132.5, 119.1, 115.5, 97.7, 58.8, 54.8, 47.7, 46.4, 40.4, 35.2 p.p.m.; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{NaO}_2$ [$M + \text{Na}$] $^+$: 307.0262; found: 307.0263.

Refinement

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

Acknowledgements

We thank Darshan S. Mhatre for his help in collecting the X-ray data and with the structure refinement.

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full crystallographic data

IUCrData (2021). 6, x211260 [https://doi.org/10.1107/S2414314621012608]

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rac-(2*aS*,2*a*¹*R*,3*aR*,3*a*¹*S*,5*aS*,6*aR*)-2*a*-Allyl-2,4-dichloro-2*a*,2*a*¹,3*a*¹,5*a*,6,6*a*-hexahydro-3*aH*-3-oxadicyclopenta[*cd,gh*]pentalen-3*a*-ol

Crystal data

C₁₄H₁₄Cl₂O₂

M_r = 285.15

Triclinic, *P* $\bar{1}$

a = 7.2687 (10) Å

b = 8.3648 (11) Å

c = 11.7460 (18) Å

α = 80.448 (4)°

β = 83.441 (4)°

γ = 65.285 (4)°

V = 638.96 (16) Å³

Z = 2

F(000) = 296

D_x = 1.482 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 3239 reflections

θ = 2.7–25.0°

μ = 0.50 mm⁻¹

T = 150 K

Plate, clear light colourless

0.32 × 0.29 × 0.09 mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

T_{min} = 0.655, *T_{max}* = 0.746

19764 measured reflections

2241 independent reflections

1662 reflections with *I* > 2 σ (*I*)

R_{int} = 0.106

θ_{\max} = 25.0°, θ_{\min} = 2.7°

h = -8→8

k = -9→9

l = -13→13

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.048

wR(*F*²) = 0.107

S = 1.09

2241 reflections

164 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[$\sigma^2(F_o^2) + (0.0235P)^2 + 1.1376P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

$\Delta\rho_{\max}$ = 0.27 e Å⁻³

$\Delta\rho_{\min}$ = -0.33 e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.06076 (13)	0.17026 (12)	0.42861 (8)	0.0269 (3)
C12	-0.06759 (13)	0.53279 (13)	0.15245 (8)	0.0328 (3)
O1	0.1461 (3)	0.5253 (3)	0.37821 (19)	0.0191 (5)
O2	0.2783 (3)	0.3694 (3)	0.55085 (19)	0.0221 (6)
H2	0.157708	0.391949	0.574798	0.033*
C1	0.2966 (5)	0.3622 (4)	0.4322 (3)	0.0185 (8)
C11	0.2225 (5)	0.5758 (4)	0.2653 (3)	0.0192 (8)
C3	0.4551 (5)	0.0894 (4)	0.3551 (3)	0.0209 (8)
H3	0.474728	-0.022512	0.335419	0.025*
C10	0.1821 (5)	0.4890 (4)	0.1739 (3)	0.0194 (8)
C6	0.4571 (5)	0.4848 (4)	0.2673 (3)	0.0179 (7)
H6	0.518199	0.572267	0.266037	0.021*
C2	0.2846 (5)	0.1995 (4)	0.4009 (3)	0.0198 (8)
C9	0.3446 (5)	0.3828 (4)	0.1197 (3)	0.0211 (8)
H9	0.342144	0.317963	0.061141	0.025*
C4	0.6154 (5)	0.1623 (4)	0.3377 (3)	0.0203 (8)
H4	0.732882	0.086130	0.386498	0.024*
C7	0.5363 (5)	0.3772 (4)	0.1626 (3)	0.0206 (8)
H7	0.604311	0.435233	0.101481	0.025*
C8	0.6874 (5)	0.1927 (5)	0.2120 (3)	0.0240 (8)
H8A	0.688215	0.100747	0.168389	0.029*
H8B	0.826068	0.188696	0.207430	0.029*
C5	0.5042 (5)	0.3485 (4)	0.3779 (3)	0.0195 (8)
H5	0.584893	0.371253	0.431830	0.023*
C13	0.1802 (5)	0.8510 (5)	0.1251 (3)	0.0270 (9)
H13	0.152010	0.810452	0.061014	0.032*
C12	0.1281 (5)	0.7775 (4)	0.2438 (3)	0.0253 (8)
H12A	-0.021149	0.820022	0.254500	0.030*
H12B	0.174476	0.823785	0.301924	0.030*
C14	0.2611 (6)	0.9658 (5)	0.1035 (4)	0.0399 (11)
H14A	0.291514	1.009520	0.165285	0.048*
H14B	0.289666	1.006095	0.025767	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0202 (5)	0.0279 (5)	0.0360 (6)	-0.0142 (4)	-0.0005 (4)	-0.0023 (4)
C12	0.0145 (5)	0.0479 (6)	0.0353 (6)	-0.0122 (4)	-0.0051 (4)	-0.0026 (5)
O1	0.0093 (12)	0.0173 (12)	0.0240 (14)	0.0000 (10)	0.0021 (10)	-0.0013 (10)
O2	0.0154 (13)	0.0278 (14)	0.0207 (14)	-0.0065 (11)	0.0014 (10)	-0.0045 (11)
C1	0.0109 (17)	0.0171 (18)	0.023 (2)	-0.0020 (14)	0.0003 (14)	-0.0012 (15)
C11	0.0128 (18)	0.0183 (18)	0.022 (2)	-0.0031 (15)	0.0037 (14)	-0.0039 (15)
C3	0.0184 (19)	0.0157 (18)	0.027 (2)	-0.0049 (15)	-0.0040 (15)	-0.0026 (15)
C10	0.0112 (18)	0.0185 (18)	0.028 (2)	-0.0057 (15)	-0.0039 (15)	0.0008 (15)
C6	0.0095 (17)	0.0166 (18)	0.026 (2)	-0.0038 (14)	0.0024 (14)	-0.0049 (15)

C2	0.0189 (19)	0.0156 (18)	0.024 (2)	-0.0074 (16)	-0.0053 (15)	0.0039 (15)
C9	0.023 (2)	0.0166 (18)	0.022 (2)	-0.0073 (16)	-0.0035 (16)	-0.0008 (15)
C4	0.0108 (18)	0.0173 (18)	0.026 (2)	0.0015 (15)	-0.0040 (14)	-0.0026 (15)
C7	0.0134 (18)	0.0202 (18)	0.025 (2)	-0.0049 (15)	0.0038 (14)	-0.0021 (15)
C8	0.0125 (18)	0.024 (2)	0.030 (2)	-0.0022 (16)	-0.0001 (15)	-0.0045 (16)
C5	0.0116 (17)	0.0228 (19)	0.025 (2)	-0.0075 (15)	-0.0002 (14)	-0.0042 (15)
C13	0.026 (2)	0.0174 (19)	0.032 (2)	-0.0030 (16)	-0.0035 (16)	-0.0018 (16)
C12	0.019 (2)	0.0178 (19)	0.031 (2)	-0.0016 (16)	0.0050 (16)	-0.0032 (16)
C14	0.056 (3)	0.043 (3)	0.032 (2)	-0.033 (2)	-0.002 (2)	-0.0005 (19)

Geometric parameters (Å, °)

C11—C2	1.731 (3)	C3—C4	1.506 (5)
C12—C10	1.734 (3)	C10—C9	1.315 (5)
O1—C1	1.444 (4)	C6—C7	1.557 (5)
O1—C11	1.445 (4)	C6—C5	1.545 (5)
O2—C1	1.394 (4)	C9—C7	1.515 (5)
C1—C2	1.506 (5)	C4—C8	1.526 (5)
C1—C5	1.536 (4)	C4—C5	1.552 (5)
C11—C10	1.508 (5)	C7—C8	1.534 (5)
C11—C6	1.550 (4)	C13—C12	1.501 (5)
C11—C12	1.520 (5)	C13—C14	1.300 (5)
C3—C2	1.316 (5)		
C1—O1—C11	110.0 (2)	C5—C6—C11	105.6 (3)
O1—C1—C2	112.9 (3)	C5—C6—C7	106.9 (3)
O1—C1—C5	107.0 (3)	C1—C2—C11	119.8 (2)
O2—C1—O1	107.8 (3)	C3—C2—C11	126.3 (3)
O2—C1—C2	113.5 (3)	C3—C2—C1	113.9 (3)
O2—C1—C5	113.0 (3)	C10—C9—C7	111.3 (3)
C2—C1—C5	102.5 (3)	C3—C4—C8	114.6 (3)
O1—C11—C10	111.4 (3)	C3—C4—C5	103.4 (3)
O1—C11—C6	106.4 (2)	C8—C4—C5	106.3 (3)
O1—C11—C12	106.8 (3)	C9—C7—C6	103.2 (3)
C10—C11—C6	101.7 (3)	C9—C7—C8	115.4 (3)
C10—C11—C12	113.9 (3)	C8—C7—C6	105.4 (3)
C12—C11—C6	116.5 (3)	C4—C8—C7	105.9 (3)
C2—C3—C4	111.8 (3)	C1—C5—C6	105.2 (3)
C11—C10—C12	118.3 (2)	C1—C5—C4	107.3 (3)
C9—C10—C12	126.5 (3)	C6—C5—C4	106.6 (3)
C9—C10—C11	115.1 (3)	C14—C13—C12	125.0 (4)
C11—C6—C7	107.5 (3)	C13—C12—C11	113.3 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
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O2—H2···O1 ⁱ	0.84	2.06	2.893 (3)	173
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