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An enantiomerically pure potential toxaphene congener: (1*R*,2*S*,3*S*,4*R*,7*S*)-2-*endo*,3-*exo*,5,5-tetrachloro-7-(chloromethyl)-1,7-bis(dichloromethyl)bicyclo[2.2.1]heptane

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A new enantiomerically pure potential toxaphene congener ($C_{10}H_9Cl_9$) has been isolated from a reaction mixture obtained by the free radical chlorination of (1*S*)-2-*endo*-chlorobornane and its absolute configuration determined. It crystallizes in the monoclinic space group *C*2 with two molecules in the asymmetric unit. This is the first report of the preparation of a single enantiomer of a synthetic polychloroterpene on a multi-milligram scale.

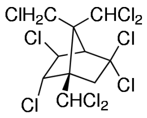
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.065
Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Toxaphene is an insecticidal mixture, produced by the controlled photochlorination of camphene (Saleh, 1991). In the USSR, a similar insecticide was produced by chlorination of α-pinene with azobisisobutyronitrile as initiator (Nikiforov, 2002). Natural camphene occurs in different essential oils in the (+)-form as well as the (−)-form (Windholz *et al.*, 1976). Production of artificial camphene starts from natural α-pinene, which is also chiral. All noted types of camphene are used for toxaphene synthesis by different manufacturers. Some congeners in selected samples of technical Toxaphene were shown to have small deviations from a racemic distribution (Buser & Müller, 1994). Nevertheless, there is no information about any enantiomerically pure congeners of toxaphene. In the present work, we partially modeled the procedure of toxaphene production in the USSR. The initial reaction was ionic addition of hydrogen chloride to (1*S*)-α-pinene resulting in a mixture of (1*S*)-2-*endo*-chlorobornane and 'chlorofenchane' in a *ca* 10:1 ratio. Further exhaustive photochlorination (with a medium-pressure mercury arc lamp) led to a complex mixture of highly chlorinated terpenes, which were separated on a silica-gel column (i.d. 4.7 cm; height 103 cm; eluant: *n*-hexane). The last fraction contained the title compound, (I).



(I)

The title compound crystallizes in the monoclinic non-centrosymmetric space group *C*2 with two molecules in the asymmetric unit. The two independent molecules with the atomic numbering scheme are shown in Figs. 1 and 2. As can also been seen from Figs. 1 and 2, the two molecules have a very similar conformation. The bond lengths and angles are in accordance with the results of Frenzen *et al.* (1994) and are also within the normal range of such bonds (Allen *et al.*, 1987).

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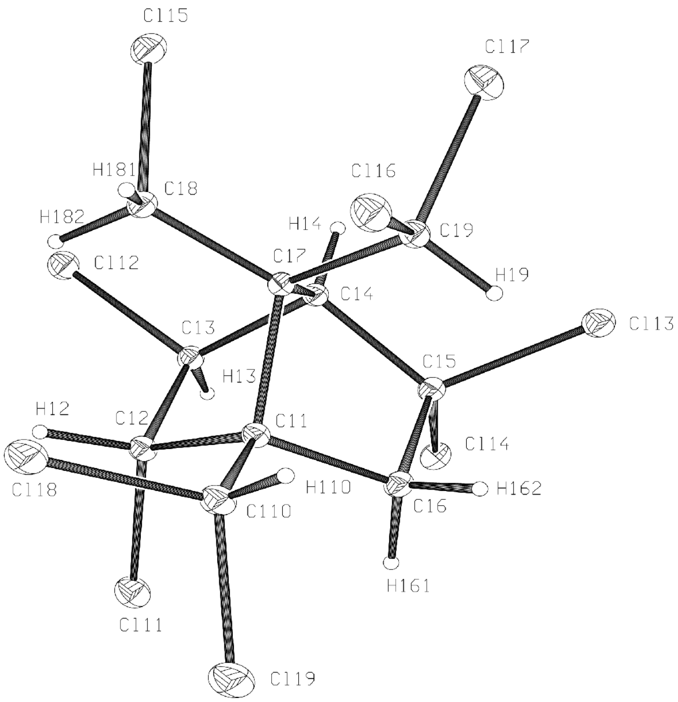

Figure 1
A view of molecule 1 of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 10% probability level.

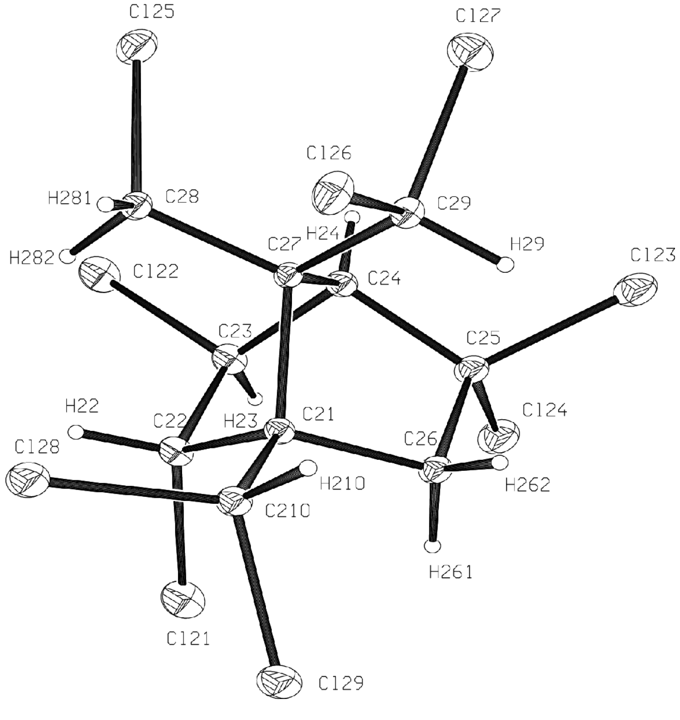

Figure 2
A view of molecule 2 of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 10% probability level.

The mean C—Cl bond lengths are 1.785 (3) and 1.786 (3) Å in molecules 1 and 2, respectively. Interesting features are the small bond angles C14—C17—C11 and C24—C27—C21, with values of 92.1 (2) and 91.7(2 ° and the long bond lengths C11—C17 = 1.605 (3) Å and C21—C27 = 1.602 (3) Å. These may be explained by steric effects from adjacent Cl atoms. Table 1 lists some short (<3.45 Å) intermolecular Cl···Cl contacts involved in the packing of the molecules in the crystal structure and Table 2 lists several C—H···Cl interactions (<2.85 Å) (Bondi, 1964; Nyburg, 1979; Taylor & Kennard, 1982).

Experimental

During silica-gel column separation of the prepared toxaphene-like mixture, one of the fractions was evaporated to dryness. The residue was dissolved in *n*-hexane and cooled overnight in a freezer. A crop of druses was collected and recrystallized from a minimum amount of *n*-hexane by slow evaporation of the solvent in a refrigerator. The purified substance was also characterized by ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (*d, J* = 2.4 Hz, 1H), 6.34 (*bs*, 1H), 5.32 (*d, J* = 3.9 Hz, 1H), 5.17 (*dd*, J_1 = 3.9, J_2 = 2.6 Hz, 1H), 4.89 (*bd*, *J* = 13.5 Hz, 1H), 4.28 (*dd*, J_1 = 13.5, J_2 = 2.4 Hz, 1H), 3.73 (*bd*, *J* = 16.8 Hz, 1H), 3.61 (*s*, 1H), 3.09 (*bd*, *J* = 16.8 Hz, 1H).

Crystal data

$C_{10}H_9Cl_9$
$M_r = 448.22$
Monoclinic, *C*2
$a = 14.891$ (3) Å
$b = 13.416$ (3) Å
$c = 15.936$ (3) Å
$\beta = 91.781$ (16)°
$V = 3182.1$ (11) Å^3
$Z = 8$
$D_x = 1.871$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 14$–18°
$\mu = 1.56$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (*ABSCALC* in *OSCAIL*; McArdle & Daly, 1999; North *et al.*, 1968)
$T_{min} = 0.508$, $T_{max} = 0.651$
7713 measured reflections
6925 independent reflections
6151 reflections with $I > 2\sigma(I)$
$R_{int} = 0.009$
$\theta_{max} = 27.0°$
$h = -18 \rightarrow 18$
$k = -17 \rightarrow 17$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.065$
$S = 1.05$
6925 reflections
415 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 1.5524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: (Flack, 1983)
Flack parameter = −0.03 (5)

Table 1
Selected geometric parameters (Å, °).

Cl14···Cl27	3.376 (1)	Cl15···Cl19^{iii}	3.349 (1)
Cl13···Cl13^{i}	3.446 (1)	Cl21···Cl25^{iv}	3.238 (1)
Cl15···Cl26^{ii}	3.279 (1)		
C15—Cl14···Cl27	93.5 (1)	C18—Cl15···Cl19^{iii}	160.1 (1)
C15—Cl13···Cl13^{i}	137.3 (1)	C22—Cl21···Cl25^{iv}	166.8 (1)
C18—Cl15···Cl26^{ii}	76.4 (1)		

Symmetry codes: (i) $2-x, y, 2-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iv) $\frac{5}{2}-x, \frac{1}{2}+y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···Cl12	1.04 (4)	2.73 (3)	2.787 (3)	82 (2)
C12—H12···Cl18	1.04 (4)	2.72 (3)	3.179 (3)	107 (2)
C13—H13···Cl14	0.83 (4)	2.52 (3)	2.981 (3)	116 (2)
C13—H13···Cl11	0.83 (4)	2.60 (2)	2.735 (3)	90 (2)
C16—H161···Cl14	0.95 (4)	2.64 (3)	2.768 (3)	87 (2)
C16—H161···Cl11	0.95 (4)	2.68 (3)	3.108 (3)	108 (2)
C16—H161···Cl19	0.95 (4)	2.90 (3)	3.084 (3)	92 (2)
C16—H162···Cl13	0.97 (3)	2.67 (3)	2.787 (3)	87 (2)
C18—H181···Cl16	0.93 (3)	2.52 (3)	3.052 (3)	117 (2)
C18—H181···Cl18	0.93 (3)	2.86 (3)	3.203 (3)	104 (2)
C18—H182···Cl12	0.97 (3)	2.59 (3)	3.158 (3)	117 (2)
C18—H182···C12	0.97 (3)	2.53 (3)	2.910 (4)	103 (2)
C19—H19···Cl13	0.94 (3)	2.53 (3)	3.081 (3)	118 (2)
C19—H19···C16	0.94 (3)	2.53 (3)	2.948 (4)	107 (2)
C22—H22···Cl22	0.99 (4)	2.69 (3)	2.791 (3)	85 (2)
C22—H22···Cl28	0.99 (4)	2.72 (3)	3.147 (3)	107 (2)
C23—H23···Cl21	0.91 (4)	2.60 (3)	2.733 (3)	88 (2)
C23—H23···Cl24	0.91 (4)	2.50 (4)	2.972 (4)	112 (3)
C24—H24···Cl22	0.82 (3)	2.82 (3)	2.808 (3)	80 (2)
C26—H262···Cl23	1.01 (3)	2.71 (3)	2.766 (3)	82 (2)
C26—H261···Cl21	0.90 (3)	2.65 (3)	3.129 (3)	114 (2)
C26—H261···Cl29	0.90 (3)	2.84 (3)	3.024 (3)	93 (2)
C26—H261···Cl24	0.90 (3)	2.62 (3)	2.763 (3)	89 (2)
C28—H282···Cl22	0.94 (3)	2.62 (3)	3.182 (3)	119 (2)
C28—H282···C22	0.94 (3)	2.43 (4)	2.884 (4)	110 (2)
C28—H281···Cl28	0.86 (3)	2.85 (3)	3.273 (3)	112 (2)
C28—H281···Cl26	0.86 (3)	2.54 (3)	3.017 (3)	116 (2)
C29—H29···Cl23	0.99 (4)	2.48 (4)	3.086 (3)	119 (3)
C29—H29···C26	0.99 (4)	2.56 (3)	2.952 (4)	103 (2)
C110—H110···Cl16	0.86 (3)	2.65 (3)	3.268 (3)	129 (3)
C210—H210···Cl26	1.02 (3)	2.59 (3)	3.257 (3)	123 (2)
C19—H19···Cl26^{i}	0.94 (3)	2.89 (3)	3.512 (3)	125 (2)
C18—H182···Cl26^{ii}	0.97 (3)	2.81 (3)	3.343 (3)	115 (2)

Symmetry codes: (i) $2 - x, y, 2 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

All H atoms were found in a difference map and were refined independently.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CELDIM* in *CAD*-4-*PC Software*; data reduction: *XCAD* (McArdle & Higgins, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *OSCAIL* (Version 9; McArdle, 1993).

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