organic compounds

(S)-4-(4-Mercaptophenyl)-2,2,4-trimethylchroman

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Crystallization of the title compound, $C_{18}H_{20}OS$, from cyclohexane gives the unsolvated crystal structure. Linear strands of molecules are formed by S—H⋯O hydrogen bonds, with edge-to-face π–π interactions connecting neighboring strands.

Related literature

For related literature, see: Brienne & Jacques (1975); Esterhuysen *et al.* (2005); Finocchearo & Failla (1996); Hardy *et al.* (1977); Jacobs *et al.* (2006); Lloyd & Bredenkamp (2005); Lloyd *et al.* (2005).
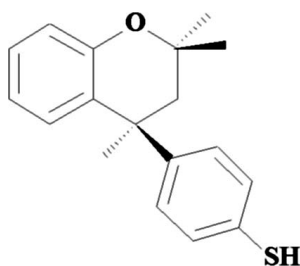
Experimental

Crystal data

$C_{18}H_{20}OS$
$M_r = 284.40$
Orthorhombic, $P2_12_12_1$
$a = 10.4001$ (17) Å
$b = 10.5186$ (17) Å
$c = 13.415$ (2) Å

$V = 1467.5$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.21$ mm^{-1}
$T = 100$ (2) K
$0.34 \times 0.22 \times 0.09$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: none
9049 measured reflections

3229 independent reflections
2993 reflections with $I > 2\sigma(I)$
$R_{int} = 0.085$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.083$
$wR(F^2) = 0.202$
$S = 1.13$
3229 reflections
185 parameters
H-atom parameters constrained

$\Delta\rho_{max} = 0.95$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}
Absolute structure: Flack (1983), 1373 Friedel pairs
Flack parameter: 0.08 (16)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
S20—H20⋯O1^i	1.20	2.30	3.488 (4)	171

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001; Atwood & Barbour, 2003); software used to prepare material for publication: *X-SEED*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2464).

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supplementary materials

(*S*)-4-(4-Mercaptophenyl)-2,2,4-trimethylchroman

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Comment

In conjunction with our investigation on the formation of clathrates (Esterhuysen *et al.*, 2005; Lloyd & Bredenkamp, 2005; Lloyd *et al.*, 2005) we have synthesized an enantiomerically pure form of 4-*p*-mercaptophenyl-2,2,4-trimethylchroman, (I), the thiol derivative of Dianin's compound.

It is well known that a racemic mixture of (I) packs in such a way that six thiol molecules are linked to each other by a network of S—H···S hydrogen bonds such that the S atoms form a near-planar hexagon (Hardy *et al.*, 1977). Thus three molecules having identical chirality point upwards and three molecules of opposing chirality point downwards (Finocchearo & Failla, 1996).

Herein we report the crystal structure which reveals that the packing of the chirally pure compound (Fig 1) is very different from that of its racemate. The packing can be described as sheets of hydrogen–bonded molecules forming infinite chains, parallel to the *b* axis (Fig 2). Two adjacent chains are held together by edge-to-face π-π interactions forming double strands (C—H to centroid distance of 3.897 Å) (Fig 3). This packing is very similar to the close packed (*S*)-Dianin's structure (Lloyd & Bredenkamp, 2005).

Experimental

Dianin's compound was synthesized according to the literature method (Brienne & Jacques, 1975) and the chirally pure (S)-enantiomer was sequentially converted to the thiol derivative (Hardy *et al.*, 1977). Single crystals suitable for X-ray analysis were then obtained by slow evaporation of a solution of (S)-4-*p*-mercaptophenyl-2,2,4-trimethylchroman in cyclohexane.

Refinement

All H atoms were positioned geometrically and constrained to ride on their parent atoms; U_{iso}(H) values were set at 1.2 times U_{eq}(C, S) for CH$_2$, aromatic C and S—H groups and 1.5 times U_{eq}(C) for CH$_3$ groups.
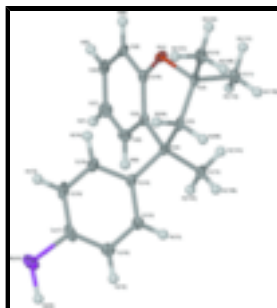
Figures

Fig. 1. The molecular structure of (I), showing atom labels and 50% probability displacement ellipsoids for non-H atoms.
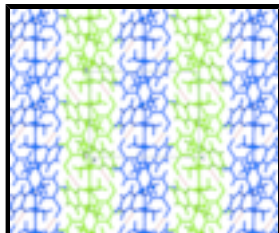
Fig. 2. Infinite chains of hydrogen-bonded molecules extend along [010], with two neighboring chains forming edge-to-face π-π interactions to assemble a double strand. Each colour here represents one of these double strands.
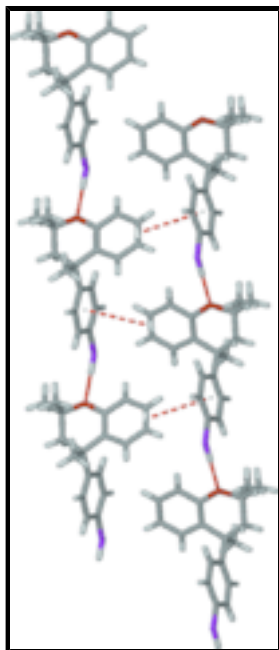
Fig. 3. The intermolecular hydrogen bonding and the π-π interactions are shown as red dashed lines.

(*S*)-4-(4-Mercaptophenyl)-2,2,4-trimethylchroman

Crystal data

$C_{18}H_{20}OS$	$F_{000} = 608$
$M_r = 284.40$	$D_x = 1.287$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 3826 reflections
$a = 10.4001\ (17)$ Å	$\theta = 2.5–28.0°$
$b = 10.5186\ (17)$ Å	$\mu = 0.21$ mm^{-1}
$c = 13.415\ (2)$ Å	$T = 100\ (2)$ K
$V = 1467.5\ (4)$ Å^3	Rectangular block, colourless
$Z = 4$	$0.34 \times 0.22 \times 0.09$ mm

Data collection

Bruker APEX CCD area-detector diffractometer	2993 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.085$
Monochromator: graphite	$\theta_{max} = 27.1°$

$T = 100(2)$ K	$\theta_{min} = 2.5°$
ω scans	$h = -13 \rightarrow 12$
Absorption correction: none	$k = -13 \rightarrow 11$
9049 measured reflections	$l = -15 \rightarrow 17$
3229 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.1287P)^2 + 1.5786P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.202$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.13$	$\Delta\rho_{max} = 0.95$ e Å^{-3}
3229 reflections	$\Delta\rho_{min} = -0.82$ e Å^{-3}
185 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1373 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.08 (16)

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$^2 > 2$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}
O1	0.2990 (2)	0.3661 (2)	0.40764 (19)	0.0204 (6)
C2	0.3537 (3)	0.4103 (4)	0.5025 (2)	0.0189 (7)
C3	0.3591 (3)	0.5545 (3)	0.5013 (2)	0.0176 (7)
H3A	0.4214	0.5810	0.4495	0.021*
H3B	0.3931	0.5836	0.5663	0.021*
C4	0.2305 (3)	0.6243 (3)	0.4816 (2)	0.0161 (7)
C5	0.1486 (3)	0.5440 (3)	0.4105 (3)	0.0153 (7)
C6	0.0307 (3)	0.5912 (4)	0.3745 (3)	0.0196 (7)
H6	0.0023	0.6726	0.3959	0.023*
C7	−0.0447 (3)	0.5230 (4)	0.3091 (3)	0.0224 (8)
H7	−0.1244	0.5565	0.2867	0.027*
C8	−0.0031 (3)	0.4045 (4)	0.2762 (3)	0.0217 (7)

H8	−0.0535	0.3576	0.2300	0.026*
C9	0.1109 (4)	0.3555 (4)	0.3105 (2)	0.0201 (7)
H9	0.1387	0.2742	0.2883	0.024*
C10	0.1862 (3)	0.4240 (3)	0.3777 (3)	0.0166 (7)
C11	0.2756 (4)	0.3518 (4)	0.5873 (3)	0.0241 (8)
H11A	0.1852	0.3769	0.5806	0.036*
H11B	0.3090	0.3821	0.6513	0.036*
H11C	0.2823	0.2590	0.5844	0.036*
C12	0.4894 (4)	0.3556 (4)	0.5036 (3)	0.0266 (8)
H12A	0.4851	0.2627	0.4994	0.040*
H12B	0.5326	0.3802	0.5656	0.040*
H12C	0.5378	0.3888	0.4466	0.040*
C13	0.1558 (4)	0.6458 (4)	0.5788 (3)	0.0203 (7)
H13A	0.0789	0.6968	0.5650	0.030*
H13B	0.2106	0.6908	0.6266	0.030*
H13C	0.1302	0.5636	0.6068	0.030*
C14	0.2636 (3)	0.7516 (3)	0.4314 (3)	0.0159 (7)
C15	0.2511 (3)	0.8686 (3)	0.4769 (3)	0.0193 (7)
H15	0.2137	0.8732	0.5414	0.023*
C16	0.2916 (4)	0.9798 (4)	0.4310 (3)	0.0224 (8)
H16	0.2834	1.0591	0.4643	0.027*
C17	0.3444 (4)	0.9742 (4)	0.3354 (3)	0.0234 (8)
C18	0.3545 (3)	0.8584 (4)	0.2882 (3)	0.0230 (8)
H18	0.3893	0.8540	0.2228	0.028*
C19	0.3149 (3)	0.7495 (4)	0.3348 (3)	0.0205 (7)
H19	0.3224	0.6706	0.3008	0.025*
S20	0.40742 (10)	1.10569 (9)	0.27025 (8)	0.0319 (3)
H20	0.3792	1.2019	0.3131	0.038*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0182 (12)	0.0245 (13)	0.0185 (12)	0.0082 (10)	−0.0025 (10)	−0.0046 (11)
C2	0.0143 (15)	0.0305 (19)	0.0118 (15)	0.0046 (14)	0.0008 (12)	0.0034 (14)
C3	0.0148 (15)	0.0269 (17)	0.0111 (15)	−0.0027 (14)	−0.0027 (12)	0.0023 (14)
C4	0.0123 (14)	0.0224 (17)	0.0137 (15)	−0.0011 (12)	0.0007 (12)	−0.0026 (13)
C5	0.0106 (14)	0.0225 (17)	0.0128 (15)	−0.0009 (13)	0.0024 (12)	0.0014 (13)
C6	0.0128 (15)	0.0200 (17)	0.0259 (18)	0.0005 (14)	−0.0014 (13)	−0.0010 (15)
C7	0.0117 (16)	0.0288 (19)	0.0267 (19)	−0.0021 (13)	−0.0040 (13)	0.0023 (16)
C8	0.0204 (17)	0.0285 (18)	0.0161 (16)	−0.0090 (14)	−0.0020 (13)	0.0013 (16)
C9	0.0247 (18)	0.0228 (16)	0.0127 (14)	−0.0004 (14)	0.0017 (13)	−0.0038 (13)
C10	0.0132 (15)	0.0222 (17)	0.0144 (15)	−0.0013 (12)	−0.0005 (12)	0.0030 (13)
C11	0.0245 (18)	0.0270 (19)	0.0207 (17)	−0.0022 (15)	0.0034 (15)	0.0056 (16)
C12	0.0231 (19)	0.036 (2)	0.0204 (17)	0.0066 (16)	−0.0012 (15)	0.0038 (17)
C13	0.0199 (17)	0.0269 (18)	0.0141 (16)	−0.0018 (14)	0.0068 (13)	−0.0004 (14)
C14	0.0107 (14)	0.0230 (17)	0.0141 (16)	−0.0015 (13)	−0.0024 (12)	0.0001 (13)
C15	0.0145 (16)	0.0232 (17)	0.0202 (17)	−0.0020 (13)	0.0041 (13)	0.0022 (14)
C16	0.0165 (17)	0.0230 (18)	0.028 (2)	−0.0019 (13)	0.0006 (14)	−0.0009 (15)

C17	0.0111 (16)	0.0297 (19)	0.029 (2)	−0.0073 (14)	−0.0075 (14)	0.0137 (16)
C18	0.0147 (15)	0.039 (2)	0.0154 (16)	−0.0090 (15)	−0.0049 (13)	0.0029 (15)
C19	0.0164 (16)	0.0294 (19)	0.0158 (17)	0.0014 (14)	−0.0032 (13)	−0.0010 (15)
S20	0.0311 (6)	0.0228 (5)	0.0419 (6)	−0.0045 (4)	−0.0043 (5)	0.0083 (4)

Geometric parameters (Å, °)

O1—C10	1.381 (4)	C11—H11A	0.9800
O1—C2	1.469 (4)	C11—H11B	0.9800
C2—C3	1.518 (5)	C11—H11C	0.9800
C2—C12	1.524 (5)	C12—H12A	0.9800
C2—C11	1.528 (5)	C12—H12B	0.9800
C3—C4	1.549 (5)	C12—H12C	0.9800
C3—H3A	0.9900	C13—H13A	0.9800
C3—H3B	0.9900	C13—H13B	0.9800
C4—C13	1.533 (4)	C13—H13C	0.9800
C4—C5	1.533 (4)	C14—C15	1.381 (5)
C4—C14	1.538 (5)	C14—C19	1.402 (5)
C5—C10	1.393 (5)	C15—C16	1.387 (5)
C5—C6	1.409 (5)	C15—H15	0.9500
C6—C7	1.378 (5)	C16—C17	1.397 (6)
C6—H6	0.9500	C16—H16	0.9500
C7—C8	1.391 (6)	C17—C18	1.377 (6)
C7—H7	0.9500	C17—S20	1.762 (4)
C8—C9	1.372 (5)	C18—C19	1.368 (5)
C8—H8	0.9500	C18—H18	0.9500
C9—C10	1.395 (5)	C19—H19	0.9500
C9—H9	0.9500	S20—H20	1.2000
C10—O1—C2	116.2 (3)	C2—C11—H11A	109.5
O1—C2—C3	108.7 (3)	C2—C11—H11B	109.5
O1—C2—C12	104.4 (3)	H11A—C11—H11B	109.5
C3—C2—C12	110.1 (3)	C2—C11—H11C	109.5
O1—C2—C11	108.2 (3)	H11A—C11—H11C	109.5
C3—C2—C11	115.4 (3)	H11B—C11—H11C	109.5
C12—C2—C11	109.5 (3)	C2—C12—H12A	109.5
C2—C3—C4	116.3 (3)	C2—C12—H12B	109.5
C2—C3—H3A	108.2	H12A—C12—H12B	109.5
C4—C3—H3A	108.2	C2—C12—H12C	109.5
C2—C3—H3B	108.2	H12A—C12—H12C	109.5
C4—C3—H3B	108.2	H12B—C12—H12C	109.5
H3A—C3—H3B	107.4	C4—C13—H13A	109.5
C13—C4—C5	109.2 (3)	C4—C13—H13B	109.5
C13—C4—C14	111.0 (3)	H13A—C13—H13B	109.5
C5—C4—C14	109.3 (3)	C4—C13—H13C	109.5
C13—C4—C3	111.3 (3)	H13A—C13—H13C	109.5
C5—C4—C3	108.9 (3)	H13B—C13—H13C	109.5
C14—C4—C3	107.1 (3)	C15—C14—C19	117.3 (3)
C10—C5—C6	117.1 (3)	C15—C14—C4	124.2 (3)
C10—C5—C4	122.7 (3)	C19—C14—C4	118.5 (3)

C6—C5—C4	120.2 (3)	C14—C15—C16	121.8 (3)
C7—C6—C5	122.0 (3)	C14—C15—H15	119.1
C7—C6—H6	119.0	C16—C15—H15	119.1
C5—C6—H6	119.0	C15—C16—C17	119.5 (4)
C6—C7—C8	119.4 (3)	C15—C16—H16	120.3
C6—C7—H7	120.3	C17—C16—H16	120.3
C8—C7—H7	120.3	C18—C17—C16	119.3 (3)
C9—C8—C7	120.0 (3)	C18—C17—S20	116.0 (3)
C9—C8—H8	120.0	C16—C17—S20	124.7 (3)
C7—C8—H8	120.0	C19—C18—C17	120.5 (3)
C8—C9—C10	120.5 (3)	C19—C18—H18	119.7
C8—C9—H9	119.7	C17—C18—H18	119.7
C10—C9—H9	119.7	C18—C19—C14	121.6 (4)
O1—C10—C5	123.1 (3)	C18—C19—H19	119.2
O1—C10—C9	116.0 (3)	C14—C19—H19	119.2
C5—C10—C9	121.0 (3)	C17—S20—H20	109.5
C10—O1—C2—C3	−49.3 (4)	C6—C5—C10—O1	−179.6 (3)
C10—O1—C2—C12	−166.8 (3)	C4—C5—C10—O1	1.2 (5)
C10—O1—C2—C11	76.7 (4)	C6—C5—C10—C9	1.2 (5)
O1—C2—C3—C4	56.0 (4)	C4—C5—C10—C9	−178.0 (3)
C12—C2—C3—C4	169.8 (3)	C8—C9—C10—O1	180.0 (3)
C11—C2—C3—C4	−65.7 (4)	C8—C9—C10—C5	−0.8 (5)
C2—C3—C4—C13	87.2 (4)	C13—C4—C14—C15	12.1 (4)
C2—C3—C4—C5	−33.3 (4)	C5—C4—C14—C15	132.6 (3)
C2—C3—C4—C14	−151.4 (3)	C3—C4—C14—C15	−109.5 (4)
C13—C4—C5—C10	−117.5 (4)	C13—C4—C14—C19	−170.8 (3)
C14—C4—C5—C10	120.9 (3)	C5—C4—C14—C19	−50.2 (4)
C3—C4—C5—C10	4.2 (4)	C3—C4—C14—C19	67.6 (4)
C13—C4—C5—C6	63.3 (4)	C19—C14—C15—C16	−2.2 (5)
C14—C4—C5—C6	−58.3 (4)	C4—C14—C15—C16	175.0 (3)
C3—C4—C5—C6	−175.0 (3)	C14—C15—C16—C17	1.1 (6)
C10—C5—C6—C7	−0.4 (5)	C15—C16—C17—C18	0.4 (5)
C4—C5—C6—C7	178.9 (3)	C15—C16—C17—S20	−176.6 (3)
C5—C6—C7—C8	−0.9 (6)	C16—C17—C18—C19	−0.9 (5)
C6—C7—C8—C9	1.4 (6)	S20—C17—C18—C19	176.4 (3)
C7—C8—C9—C10	−0.5 (5)	C17—C18—C19—C14	−0.2 (5)
C2—O1—C10—C5	22.9 (5)	C15—C14—C19—C18	1.8 (5)
C2—O1—C10—C9	−157.9 (3)	C4—C14—C19—C18	−175.6 (3)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
S20—H20···O1[i]	1.20	2.30	3.488 (4)	171

Symmetry codes: (i) *x*, *y*+1, *z*.

Fig. 1

Fig. 2

Fig. 3