Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(2*R*,4*R*)-(4-Iodo-5,5-dimethyl-2-hexylsulfonyl)benzene

Guido J. Reiß[a]* and Marek Masnyk[b]

[a]Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße, D-40225 Düsseldorf, Germany, and [b]Institute of Organic Chemitry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

Correspondence e-mail:
reissg@uni-duesseldorf.de

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.035
wR factor = 0.066
Data-to-parameter ratio = 15.4

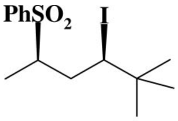
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 24 August 2001
Accepted 13 September 2001
Online 29 September 2001

Structure refinement of X-ray diffraction data in the polar space group $P2_1$ and the assignment of the absolute structure identified the crystal of the title compound, $C_{14}H_{21}IO_2S$, under investigation as the 2*R*,4*R* isomer. The packing is dominated by hydrophobic layers in the $a0c$ and $a\frac{1}{2}c$ planes and hydrophilic stacks along [100].

Comment

As we have reported (Reiß & Masnyk, 2001), (1-iodoethanesulfonyl)benzene reacts with 3,3-dimethylbut-1-ene under standard conditions (Jankowski *et al.*, 1995; Masnyk, 1991) to yield a chromatographically separable mixture of the *RS*,*SR* and the *RR*,*SS* diastereomers of (4-iodo-5,5-dimethyl-2-hexylsulfonyl)benzene. In this context, the crystal structure determination of the title compound, (3*b*), was undertaken to relate the molecular structure to the ^{1}H and ^{13}C NMR data. This should allow us to predict the stereochemistry of analogous compounds from NMR data.



(3*b*)

Crystallization of the title compound from hexane yielded needle-shaped colourless crystals. The compound crystallizes in the polar space group $P2_1$. The crystal is composed of molecules having a 2*R*,4*R*-configuration at both chiral atoms C3 and C5 (Fig. 1).

All bond lengths, bond angles and torsion angles are as expected, including a significant distortion from tetrahedral geometry at the S atom caused by the S═O double bonds (Table 1). Deviations of the ideal bond angles also occur at atoms C3 and C4 since the bulky substituents *tert*-butyl and

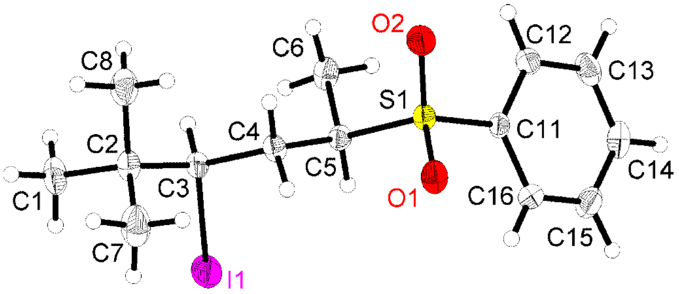


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn with an arbitrary radius.

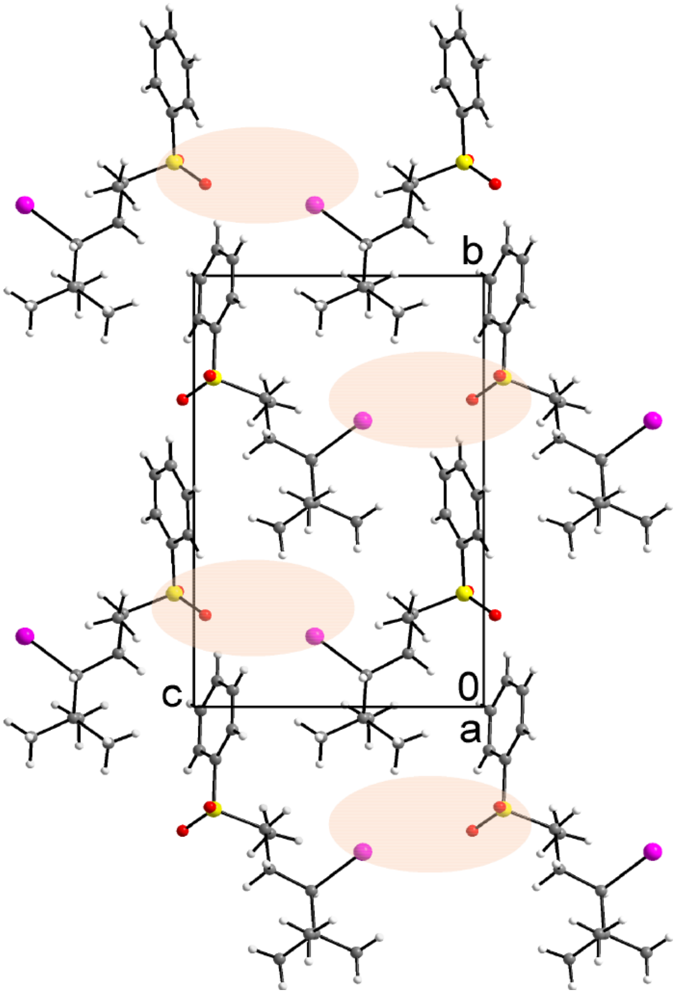


Figure 2
The packing of the title compound viewed down [100].

iodine cause a stretching of the aliphatic section of the molecule. A reason for the formation of enantiopure crystals from a racemic solution of the title compound may be that the molecules do have an excellent fit within the *bc* plane (Fig. 2). This arrangement shows separated hydrophobic regions in the *a*0*c* and $a\frac{1}{2}c$ planes as well as hydrophilic regions perpendicular to the *bc* plane (shaded ellipses).

Experimental

A mixture of (1-iodoethanesulfonyl)benzene (600 mg), 3,3-dimethylbut-1-ene (1.0 ml), benzene (1.5 ml) and benzoyl peroxide (40 mg) was heated for 6 h at 373 K in a sealed tube. The reaction mixture was then chromatographed on silica gel (hexane–ethyl acetate 93:7) yielding 280 mg of the *anti* isomer (2*S*4*R* and 2*R*4*S*) and 350 mg of the *syn* isomer (2*R*4*R* and 2*S*4*S*) (m.p. = 369–371 K). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (*s*, 9H), 1.25 (*d*, *J* = 6.8 Hz, 3H), 1.76 (*ddd*, *J* = 14.5, 11.2, 2.1 Hz, 1H), 2.35 (*ddd*, *J* = 14.5, 12.3, 2.6 Hz, 1H), 3.43 (*dqd*, *J* = 11.2, 6.8, 2.6 Hz, 1H), 3.88 (*dd*, *J* = 12.3, 2.1 Hz, 1H), 7.57–7.61 (*m*, 2H), 7.68 (*tt*, *J* = 7.4, 1.2 Hz, 1H), 7.89–7.92 (*m*, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.63, 28.49, 34.44, 35.90, 51.85, 61.00, 128.83, 129.17, 133.77, 137.29.

Crystal data

$C_{14}H_{21}IO_2S$
$M_r = 380.27$
Monoclinic, $P2_1$
$a = 6.1329$ (8) Å
$b = 14.3524$ (13) Å
$c = 9.4381$ (10) Å
$\beta = 103.919$ (9)°
$V = 806.36$ (15) Å^3
$Z = 2$
$D_x = 1.566$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 7.0$–12.5°
$\mu = 2.11$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
1.00 × 0.50 × 0.30 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: numerical (Stoe & Cie, 1996)
$T_{min} = 0.459$, $T_{max} = 0.623$
3964 measured reflections
3189 independent reflections
2659 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 32.5$°
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 21$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.066$
$S = 1.07$
3189 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.6P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0178 (10)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (2)

Table 1
Selected geometric parameters (Å, °).

I1—C3	2.191 (4)	C2—C7	1.518 (6)
S1—O2	1.428 (3)	C2—C3	1.551 (5)
S1—O1	1.440 (3)	C3—C4	1.521 (5)
S1—C11	1.771 (4)	C4—C5	1.531 (5)
S1—C5	1.807 (3)	C5—C6	1.522 (5)
C2—C8	1.525 (7)		
O2—S1—O1	119.43 (19)	C11—S1—C5	104.03 (17)
O2—S1—C11	108.65 (17)	C4—C3—C2	115.5 (3)
O1—S1—C11	107.54 (18)	C4—C3—I1	108.7 (2)
O2—S1—C5	108.44 (18)	C2—C3—I1	111.9 (2)
O1—S1—C5	107.69 (17)	C3—C4—C5	114.6 (3)
C1—C2—C3—C4	175.4 (4)	C3—C4—C5—S1	179.4 (3)
C2—C3—C4—C5	−172.7 (3)	C11—S1—C5—C4	168.3 (2)

The needle-shaped crystal was mounted using a glass capillary aligned along the φ axis. This special orientation leads to maximum and minimum transmission factors – used for absorption correction – which are different from the theoretical values calulated from the crystal dimensions and the linear absorption coefficient. Atomic coordinates for all H atoms belonging to the CH_2 and the CH groups were included in the final stages of refinement, using a riding model. H atoms belonging to methyl groups were included in the refinement riding on their attached C atom and allowed to rotate about the C—C bond with one common U_{iso} value refined for each group. The absolute configuration assignment has been checked following some generally accepted guidelines (Flack & Bernardinelli, 2000). A comparable refinement of the inverted structure yielded a Flack parameter – calculated by a 'hole in one' method [x = 0.36 (2)] – indicating the wrong absolute structure assignment and significant higher *R* values ($wR2$ = 0.0731 and $R1$ = 0.0377).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

References

Brandenburg, K. (1998). *DIAMOND*. Version 2.0. Bonn, Germany.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Bernardinelli, C. (2000). *J. Appl. Cryst.* **33**, 1143–1148, and references therein.

Jankowski, P., Masnyk, M. & Wicha, J. (1995). *Synlett*, pp. 866–868.

Masnyk, M. (1991). *Tetrahedron Lett.* **32**, 3259–3262.

Reiß, G. J. & Masnyk, M. (2001). *Acta Cryst.* E**57**, o959–o960.

Siemens (1996). *XSCANS*. Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 (Release 97–2 for DOS/WIN95/NT) and *SHELXL*97. University of Göttingen, Germany.

Stoe & Cie (1996). *X-RED*. Revision 1.07. Stoe & Cie GmbH, Darmstadt, Germany.