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{2-Methylidene-3-[(phenylsulfanyl)methyl]but-3-en-1-ylsulfanyl}benzene: flip-flop disorder

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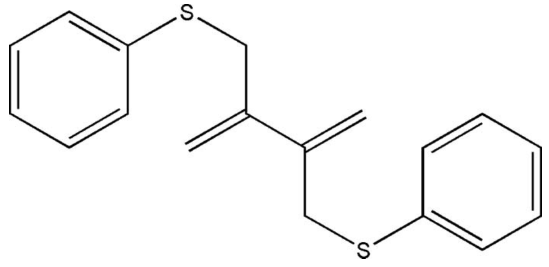
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.039; wR factor = 0.102; data-to-parameter ratio = 11.8.

In the title compound, $C_{18}H_{18}S_2$, the planar divinyl group displays a static flip-flop disorder. The molecule has crystallographically imposed C_2 symmetry. The site occupancies of the major and minor components of the disordered divinyl plane are 0.789 (5) and 0.212 (6), respectively. Co-operative C—H$\cdots\pi$ interactions form molecular dimers. The dimers associate in a one-dimensional chain along the a axis.

Related literature

For related literature, see: Allen *et al.* (1987); Arul Murugan (2005); Whitesell (1989); Yasuda *et al.* (2003).



Experimental

Crystal data

$C_{18}H_{18}S_2$
M_r = 298.44
Orthorhombic, *Pbca*
a = 8.2205 (2) Å
b = 10.1243 (3) Å
c = 18.6848 (7) Å
V = 1555.08 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 295 (2) K
0.20 × 0.15 × 0.10 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min}$ = 0.935, $T_{\max}$ = 0.969
7493 measured reflections
1481 independent reflections
1154 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
S = 1.05
1481 reflections
125 parameters
4 restraints
Only H-atom coordinates refined
$\Delta\rho_{\max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.759 (2)	C8—C9	1.299 (4)
S1—C7	1.806 (3)	C8—C8^{i}	1.467 (5)
C7—C8	1.527 (4)	C8′—C9^{i}	1.387 (4)
C7—C8′	1.593 (5)	C8′—C8′^{i}	1.480 (6)
C1—S1—C7	106.72 (13)	C9—C8—C7	123.6 (3)
C6—C1—S1	125.47 (19)	C8^{i}—C8—C7	114.6 (3)
C2—C1—S1	115.70 (18)	C9^{i}—C8′—C8′^{i}	111.6 (5)
C8—C7—S1	107.37 (19)	C9^{i}—C8′—C7	139.9 (3)
C8′—C7—S1	106.5 (4)	C8′^{i}—C8′—C7	107.7 (4)
C9—C8—C8^{i}	121.8 (4)		
C7—S1—C1—C6	−10.0 (3)	S1—C7—C8′—C9^{i}	74.6 (12)
C1—S1—C7—C8	−162.4 (2)	S1—C7—C8′—C8′^{i}	−93.6 (10)
C1—S1—C7—C8′	−119.4 (2)	C7—C8—C8^{i}—C7^{i}	180.0 (3)
S1—C7—C8—C9	−85.5 (4)	C7—C8′—C8′^{i}—C7^{i}	180.0 (3)
S1—C7—C8—C8^{i}	90.9 (4)		

Symmetry code: (i) $-x+2, -y+1, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H9$B\cdots Cg1^{ii}$	0.89 (3)	2.67 (3)	3.528 (3)	173 (3)

Symmetry code: (ii) $-x+1, -y+1, -z$. $Cg1$ is the centroid of the C1–C6 ring.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2119).

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supplementary materials

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{2-Methylidene-3-[(phenylsulfanyl)methyl]but-3-en-1-ylsulfanyl}benzene: flip-flop disorder

K. Sathiyanarayanan, **A. George Fernand**, **V. Dhanasekaran** and **R. S. Rathore**

Comment

The title compound, ({2-methylidene-3-[(phenylsulfanyl)methyl]but-3-en-1-yl}sulfanyl)benzene, (I), is synthesized as a chiral molecule possessing C_2 symmetry. The introduction of C_2 symmetry in a chiral ligand is a useful strategy of stereochemically restricting the number of diastereomeric transition states (Whitesell, 1989).

Selected bond distances and bond angles are provided in Table 1. Due to the molecular symmetry (C_2), which is retained in the crystal, the asymmetric unit is composed of one-half of the molecule (Z' = 0.5). In the crystal structure, the flip of the central planar divinyl (2,3-dimethyl-1,3-butadiene) group about the C7—C7$^{(i)}$ axis (symmetry code (i): -x+2, -y+1, -z) gives rise to a static configurational disorder. As a result of that, the divinyl plane is disordered over two sites with site occupancies of 0.789 (5) and 0.212 (6). Because of the molecular and crystal symmetry, only the intermediate C-atoms of the divinyl occupies two distinct sites (C8/C8'). The flip-flop disorder of divinyl plane, illustrated in Fig. 1, is similar to classical peptide plane flip and also previously observed in 4-vinyl benzoic acid (Yasuda *et al.*, 2003; Arul Murugan, 2005).

The least-square planes in (I) are defined by thiophenyl (S1/C1—C6) and disordered divinyl groups (atoms: C7/C8/C9,C7$^{(i)}$/C8$^{(i)}$/C9$^{(i)}$; symmetry code (i): -x+2, -y+1, -z) [C7/C8'/C9/C7$^{(i)}$/C8'$^{(i)}$/C9$^{(i)}$]. The data inside the square bracket correspond to the minor component of the disordered divinyl group. The inclination angle between these two planes is 87.5 (1)[87.9 (1)]° and the maximum out of plane deviations are 0.01 (1)Å for atom S1, and, -0.02 (1)[-0.05 (1)]Å, for atom C8[C8'], respectively. Essential torsion angles are given in Table 1.

Crystal packing is purely governed by weak intermolecular forces. The cooperative C9—H9B ··· Cg1$^{(ii)}$ interaction (symmetry code (ii): 1-x, 1-y, -z) form a closed dimers (Table 2). These dimers are linked again by the same C—H ··· π interactions and form a one-dimensional chain along a-axis. Packing view, in Fig. 2, highlight cooperative intermolecular association.

Experimental

2,3 - bis(iodomethyl)buta-1,3-diene (1 mol) was dropwise added to sodium thiophenoxide (2 mol) with cooling . The reaction mixture was stirred overnight at room temperature and poured on crushed ice. The resulting solids were filtered and dissolved in ether. The ether extract was washed with sodium thiosulphate and 10% sodium hydroxide and finally with water. The product was obtained by removal of ether after drying, which was recrystallized from hexane at room temperature (yield, 58%; m.p. 321 K).

Refinement

The bond distances (Allen *et al.*, 1987) of minor component of the disordered divinyl group was restrained to C7—C8' = 1.593 (5); C8'—C8'$^{(i)}$ = 1.480 (6); C8'—C9$^{(i)}$ = 1.387 (4) Å; symmetry code (i): -x+2, -y+1, -z. The same anisotropic displacement parameters were assigned to both the disordered atoms C8 and C8'. The positions of all H atoms were freely refined. The distances with H-atoms are in ranges:- C_{ar}—H = 0.89 (3)-0.94 (3); C_{sp2}—H = 0.86 (4)-0.94 (4); and $C_{methylene}$—H = 0.86 (3) - 1.00 (3)%A with $U_{iso}(H) = 1.2 U_{eq}(C)$.

Figures

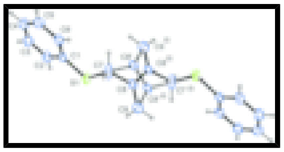

Fig. 1. A Complete view of (I). The planar divinyl group displays a static flip-flop disorder. For clarity, the minor component of the disordered divinyl group are shown with dashed lines. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Symmetry code (i): -x+2, -y+1, -z.

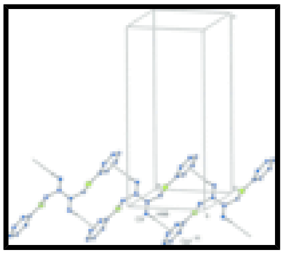

Fig. 2. Projection of the crystal packing down the b-axis showing cooperative C—H···π interactions forming one-dimensional chain of molecular dimers along a-axis. Cg1 is the centroid of (C1—C6) ring. For clarity only the major component of the disorder is shown. Symmetry code (ii): = 1-x, 1-y, -z. Color Key: C blue, H white, S green.

{2-Methylidene-3-[(phenylsulfanyl)methyl]but-3-en-1-ylsulfanyl}benzene

Crystal data

$C_{18}H_{18}S_2$	$D_x = 1.275$ Mg m^{-3}
$M_r = 298.44$	Melting point: 321 K
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2284 reflections
a = 8.2205 (2) Å	θ = 3.3–25.3°
b = 10.1243 (3) Å	μ = 0.33 mm^{-1}
c = 18.6848 (7) Å	*T* = 295 (2) K
V = 1555.08 (8) Å^3	Prism, colourless
Z = 4	0.20 × 0.15 × 0.10 mm
$F_{000} = 632$	

Data collection

Bruker APEXII diffractometer	1481 independent reflections
Radiation source: fine-focus sealed tube	1154 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.031$
T = 295(2) K	$\theta_{max} = 25.8°$
ω and φ scans	$\theta_{min} = 3.3°$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$h = -10 \rightarrow 9$
$T_{min} = 0.935$, $T_{max} = 0.969$	$k = -12 \rightarrow 12$
7493 measured reflections	$l = -22 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	Only H-atom coordinates refined
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.7833P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{max} = 0.004$
$S = 1.05$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
1481 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}
125 parameters	Extinction correction: none
4 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

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.

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 > 2sigma(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	$U_{iso}*/U_{eq}$	Occ. (<1)
S1	0.67527 (7)	0.55095 (6)	0.06937 (4)	0.0543 (3)	
C1	0.5499 (2)	0.4583 (2)	0.12679 (13)	0.0396 (5)	
C2	0.4799 (3)	0.5278 (3)	0.18288 (14)	0.0506 (6)	
H2	0.502 (3)	0.619 (3)	0.1868 (14)	0.061*	
C3	0.3811 (3)	0.4647 (3)	0.23169 (15)	0.0591 (7)	
H3	0.337 (3)	0.514 (3)	0.2689 (16)	0.071*	
C4	0.3508 (3)	0.3319 (3)	0.22554 (15)	0.0595 (7)	
H4	0.281 (4)	0.292 (3)	0.2591 (16)	0.071*	
C5	0.4192 (3)	0.2630 (3)	0.16993 (16)	0.0561 (7)	
H5	0.402 (4)	0.175 (3)	0.1642 (15)	0.067*	
C6	0.5177 (3)	0.3248 (2)	0.12034 (15)	0.0465 (6)	
H6	0.558 (3)	0.280 (3)	0.0834 (15)	0.056*	
C7	0.7789 (3)	0.4342 (3)	0.0123 (2)	0.0632 (8)	
H7A	0.717 (4)	0.407 (3)	−0.0221 (17)	0.076*	
H7B	0.802 (4)	0.358 (3)	0.0441 (16)	0.076*	
C8	0.9245 (3)	0.5055 (3)	−0.02066 (15)	0.0408 (8)	0.789 (5)
C9	0.9157 (4)	0.5764 (4)	−0.07846 (18)	0.0758 (10)	

H9A	0.993 (4)	0.625 (3)	−0.1050 (19)	0.091*	
H9B	0.823 (4)	0.577 (3)	−0.100 (2)	0.091*	
C8'	0.9684 (6)	0.4528 (8)	0.0268 (4)	0.0408 (18)	0.212 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0416 (4)	0.0445 (4)	0.0769 (5)	−0.0037 (3)	0.0195 (3)	−0.0058 (3)
C1	0.0257 (10)	0.0446 (12)	0.0484 (13)	0.0013 (9)	−0.0041 (9)	−0.0025 (10)
C2	0.0424 (13)	0.0500 (14)	0.0594 (16)	0.0016 (11)	−0.0009 (12)	−0.0115 (12)
C3	0.0494 (15)	0.078 (2)	0.0497 (16)	0.0101 (14)	0.0057 (12)	−0.0054 (14)
C4	0.0488 (16)	0.0727 (19)	0.0570 (17)	0.0017 (13)	0.0050 (13)	0.0182 (15)
C5	0.0506 (15)	0.0475 (14)	0.0702 (19)	−0.0015 (12)	−0.0018 (13)	0.0106 (14)
C6	0.0402 (13)	0.0432 (13)	0.0560 (15)	0.0036 (10)	0.0015 (11)	−0.0029 (12)
C7	0.0370 (14)	0.0690 (18)	0.084 (2)	−0.0144 (12)	0.0162 (13)	−0.0314 (16)
C8	0.0322 (14)	0.0499 (16)	0.0401 (18)	0.0041 (12)	−0.0037 (12)	−0.0032 (14)
C9	0.0459 (17)	0.116 (3)	0.066 (2)	0.0061 (17)	−0.0062 (14)	0.0309 (19)
C8'	0.032 (5)	0.0499 (14)	0.0401 (16)	0.0041 (12)	−0.0037 (14)	−0.0032 (18)

Geometric parameters (Å, °)

S1—C1	1.759 (2)	C7—C8	1.527 (4)
S1—C7	1.806 (3)	C7—C8'	1.593 (5)
C1—C6	1.382 (3)	C7—H7A	0.86 (3)
C1—C2	1.387 (3)	C7—H7B	1.00 (3)
C2—C3	1.378 (4)	C8—C8'^{i}	0.984 (5)
C2—H2	0.94 (3)	C8—C8'	1.097 (5)
C3—C4	1.373 (4)	C8—C9	1.299 (4)
C3—H3	0.93 (3)	C8—C8^{i}	1.467 (5)
C4—C5	1.372 (4)	C9—C8'^{i}	1.387 (4)
C4—H4	0.94 (3)	C9—H9A	0.94 (4)
C5—C6	1.381 (4)	C9—H9B	0.86 (4)
C5—H5	0.91 (3)	C8'—C9^{i}	1.387 (4)
C6—H6	0.89 (3)	C8'—C8'^{i}	1.480 (6)
C1—S1—C7	106.72 (13)	C8'—C7—S1	106.5 (4)
C6—C1—C2	118.8 (2)	C8—C7—H7A	108 (2)
C6—C1—S1	125.47 (19)	C8'—C7—H7A	138 (2)
C2—C1—S1	115.70 (18)	S1—C7—H7A	111 (2)
C3—C2—C1	120.6 (2)	C8—C7—H7B	117.4 (18)
C3—C2—H2	120.9 (16)	C8'—C7—H7B	78.7 (18)
C1—C2—H2	118.5 (17)	S1—C7—H7B	104.4 (18)
C4—C3—C2	120.4 (3)	H7A—C7—H7B	108 (3)
C4—C3—H3	121.1 (19)	C9—C8—C8^{i}	121.8 (4)
C2—C3—H3	118.6 (19)	C9—C8—C7	123.6 (3)
C5—C4—C3	119.2 (3)	C8^{i}—C8—C7	114.6 (3)
C5—C4—H4	122.2 (18)	C8—C9—H9A	133 (2)
C3—C4—H4	118.6 (17)	C8'^{i}—C9—H9A	91 (2)

C4—C5—C6	121.2 (3)	C8—C9—H9B	116 (2)
C4—C5—H5	121.6 (19)	C8$'^{\rm i}$—C9—H9B	159 (2)
C6—C5—H5	117.2 (19)	H9A—C9—H9B	111 (3)
C5—C6—C1	119.8 (2)	C9$^{\rm i}$—C8'—C8$'^{\rm i}$	111.6 (5)
C5—C6—H6	120.2 (17)	C9$^{\rm i}$—C8'—C7	139.9 (3)
C1—C6—H6	120.0 (17)	C8$'^{\rm i}$—C8'—C7	107.7 (4)
C8—C7—S1	107.37 (19)		
C7—S1—C1—C6	−10.0 (3)	S1—C1—C6—C5	178.79 (19)
C7—S1—C1—C2	169.71 (19)	C1—S1—C7—C8	−162.4 (2)
C6—C1—C2—C3	0.5 (4)	C1—S1—C7—C8'	−119.4 (2)
S1—C1—C2—C3	−179.2 (2)	S1—C7—C8—C9	−85.5 (4)
C1—C2—C3—C4	0.1 (4)	S1—C7—C8—C8$^{\rm i}$	90.9 (4)
C2—C3—C4—C5	−0.4 (4)	S1—C7—C8'—C9$^{\rm i}$	74.6 (12)
C3—C4—C5—C6	0.1 (4)	S1—C7—C8'—C8$'^{\rm i}$	−93.6 (10)
C4—C5—C6—C1	0.6 (4)	C7—C8—C8$^{\rm i}$—C7$^{\rm i}$	180.0 (3)
C2—C1—C6—C5	−0.9 (4)	C7—C8'—C8$'^{\rm i}$—C7$^{\rm i}$	180.0 (3)

Symmetry codes: (i) $-x+2, -y+1, -z$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9B···Cg1$^{\rm ii}$	0.89 (3)	2.67 (3)	3.528 (3)	173 (3)

Symmetry codes: (ii) $-x+1, -y+1, -z$.

Fig. 1

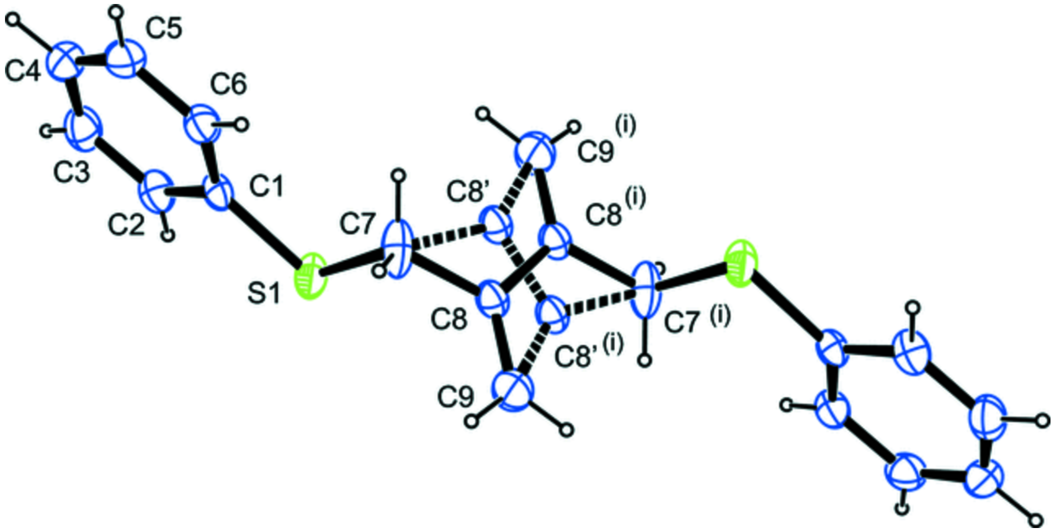

Fig. 2