

1,2-Difluorophenyl 4-vinylphenyl sulfone

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Key indicators

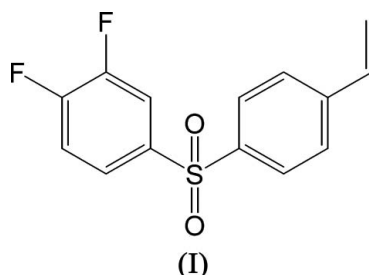
Single-crystal X-ray study
 $T = 103$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.046
 wR factor = 0.119
Data-to-parameter ratio = 14.5

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

The title compound, $\text{C}_{14}\text{H}_{10}\text{F}_2\text{O}_2\text{S}$, has a distorted tetrahedral geometry around the S atom. There are intermolecular hydrogen bonds between aryl H atoms and both F and O atoms.

Comment

One approach to preparing polymers with high dielectric constants is to attach freely rotating polar groups to a carbon polymer backbone (Zhu *et al.*, 1994; Cardoso *et al.*, 1997). The title monomer, (I), is one product of a reaction between a 3,4-difluorophenyl Grignard reagent and styrene sulfonyl fluoride. It is one of a small number of styrene sulfones that has been structurally characterized to date (Galdecka & Galdecka, 1999; Uddin *et al.*, 2004; Polborn & Severin, 2000).



The S atom of (I) has a distorted tetrahedral geometry. The C—S—C angle of $105.51(8)^\circ$ and the O—S—O angle of $119.87(10)^\circ$ are in the correct range for unstrained diaryl sulfones (Jeyakanthan *et al.*, 1998). The difluorophenyl groups pack opposite to each other around a center of inversion and the sulfone dipoles are aligned in rows, with each row alternating in opposite directions around a center of inversion (Fig. 2).

The hydrogen-bonding geometry in (I) is normal (Table 2), and similar hydrogen bonding between aryl H atoms and sulfone O atoms is observed in most diaryl sulfone compounds (Glidewell *et al.*, 2001).

Experimental

Styrene sulfonyl chloride (3.5 ml, 22.4 mmol) (Prib & Gritsai, 1968) was combined with dry acetonitrile (MeCN) (20 ml) and a less than stoichiometric amount of dry KF (0.53 g, 9.1 mmol) in an H-tube under N_2 . The mixture was stirred for 5 d and then filtered, affording a solution containing $\text{C}_2\text{H}_3\text{C}_6\text{H}_4\text{SO}_2\text{F}$ [^{19}F NMR: 66 p.p.m. ($\text{CFCl}_3 = 0$)]. The MeCN was removed from the solution under a vacuum, affording 2.84 g of a sulfonyl fluoride–chloride mixture. Dry tetrahydrofuran (THF) (10 ml) was added and the solution was cooled to 195 K. With a syringe, 3,4-difluorophenylmagnesium bromide (30 ml,

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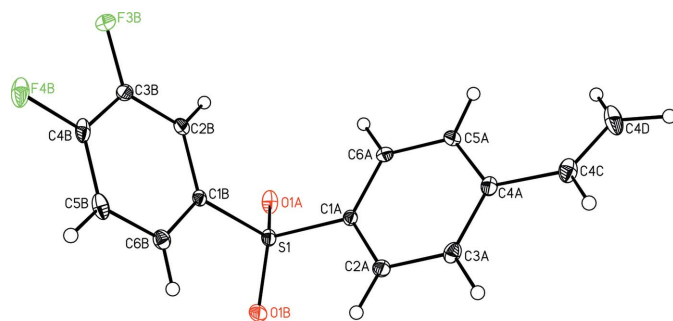


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are represented by circles of arbitrary size.

0.5 M solution in THF; Aldrich) was added over a period of 30 min, and the mixture was allowed to warm up over 18 h with stirring. Saturated NH_4Cl solution was added, the THF was removed under a vacuum, and the resulting mixture was extracted three times with CH_2Cl_2 (100 ml) to remove the product from insoluble salts and polymer. The extract was subjected to rotary evaporation and crystals of (I) slowly formed in the liquid in low yield. Recrystallization from CHCl_3 afforded 0.20 g of (I). Spectroscopic analysis: ^1H NMR (CDCl_3 , δ , p.p.m.): 5.36 (*d*, *trans*-CH, $J = 11.1$ Hz), 5.79 (*d*, *cis*-CH, $J = 17.7$ Hz), 6.64 (*q*, CH), 7.21 (*m*, 1H), 7.45 (*d*, 2H *ortho*, $J = 8.4$ Hz), 7.65 (*m*, 2H, *ortho* on $\text{C}_6\text{H}_3\text{F}_2$), 7.80 (*d*, 2H *meta*, $J = 7.8$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ , p.p.m.): 118.2 (CH_2), 135.0 ($=\text{CH}$), 142.8 (C-1), 128.0 (2 C, *ortho*), 127.0 (2 C, *meta*), 139.4 (C-4), 138.6 (*m*, C-1), 117.4 [C-2, *d* of d , $^2J(\text{C}-\text{F}) = 19.6$ Hz, $^3J(\text{C}-\text{F}) = 1.7$ Hz], 150.2 [C-3, *d* of d , $^1J(\text{C}-\text{F}) = 255.1$ Hz, $^2J(\text{C}-\text{F}) = 13.4$ Hz], 153.4 [C-4, *d* of d , $^1J(\text{C}-\text{F}) = 258.0$ Hz, $^2J(\text{C}-\text{F}) = 12.6$ Hz], 118.4 [C-5, *d*, $^2J(\text{C}-\text{F}) = 18.5$ Hz], 124.7 (C-6, *m*); ^{19}F NMR: -129 (*m*), -133.6 (*m*); IR (neat, KBr plate, ν , cm^{-1}): 3118, 3084, 3060 (*m*, C—H), 2170 (*w*, C=C).

Crystal data

$\text{C}_{14}\text{H}_{10}\text{F}_2\text{O}_2\text{S}$
 $M_r = 280.28$
 Monoclinic, $P2_1/c$
 $a = 12.255$ (4) Å
 $b = 7.819$ (3) Å
 $c = 14.148$ (5) Å
 $\beta = 114.912$ (6)°
 $V = 1229.6$ (7) Å³
 $Z = 4$

$D_x = 1.514$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6947 reflections
 $\theta = 5.8$ – 29.4 °
 $\mu = 0.28$ mm⁻¹
 $T = 103$ (2) K
 Chunk, colorless
 $0.45 \times 0.22 \times 0.22$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 2001)
 $T_{\min} = 0.919$, $T_{\max} = 0.952$
 10361 measured reflections

2929 independent reflections
 2424 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$
 $\theta_{\text{max}} = 27.9$ °
 $h = -16 \rightarrow 15$
 $k = -9 \rightarrow 10$
 $l = -18 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.119$
 $S = 1.04$
 2929 reflections
 202 parameters
 Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.8623P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

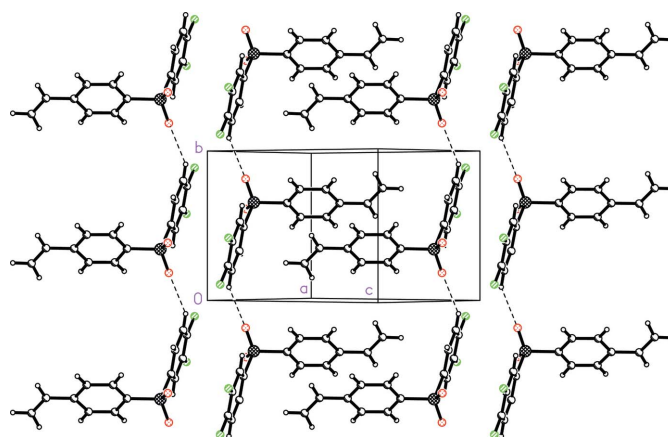


Figure 2

A packing diagram for (I), showing the antiparallel alignment of the sulfone dipoles. Hydrogen bonds are shown as dashed lines.

Table 1

Selected geometric parameters (Å, °).

S1—O1A	1.4310 (16)	C4A—C4C	1.469 (3)
S1—O1B	1.4361 (16)	C4C—C4D	1.299 (4)
S1—C1A	1.7529 (19)	C3B—F3B	1.339 (2)
S1—C1B	1.7564 (19)	C4B—F4B	1.339 (2)
O1A—S1—O1B	119.87 (10)	C3A—C4A—C4C	119.13 (19)
O1A—S1—C1A	107.29 (9)	C5A—C4A—C4C	122.20 (19)
O1B—S1—C1A	108.63 (9)	C4D—C4C—C4A	126.2 (2)
O1A—S1—C1B	107.16 (9)	C5A—C6A—C1A	119.35 (18)
O1B—S1—C1B	107.52 (9)	C5A—C6A—H6AA	120.1 (15)
C1A—S1—C1B	105.50 (8)	C3B—C2B—C1B	118.01 (19)
C1A—C2A—C3A	118.70 (19)	C1B—C2B—H2BA	122.2 (15)
C1A—C2A—H2AA	121.5 (15)	C5B—C6B—C1B	119.7 (2)
C3A—C2A—H2AA	119.8 (15)	C1B—C6B—H6BA	121.4 (16)
C3A—C4A—C5A	118.67 (18)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3A—H3AA \cdots O1A ⁱ	0.96 (2)	2.56 (3)	3.516 (3)	175 (2)
C5A—H5AA \cdots O1B ⁱⁱ	0.95 (2)	2.49 (2)	3.300 (3)	143.5 (19)
C6A—H6AA \cdots F3B ⁱⁱⁱ	0.92 (2)	2.50 (2)	3.401 (2)	168 (2)
C5B—H5BA \cdots O1A ^{iv}	0.94 (3)	2.36 (3)	3.197 (3)	149 (2)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, y - 1, z$.

The ten H atoms were initially located in a difference Fourier map. Their positions, however, were not idealized; instead, their positional parameters were refined while constraining their displacement parameters to be $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

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