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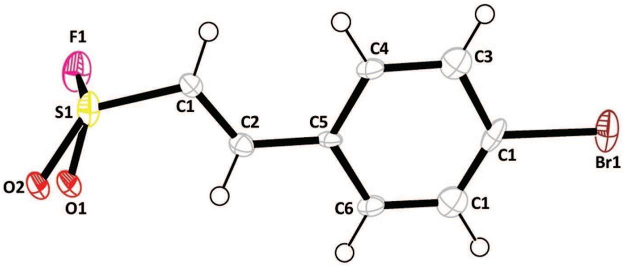
Crystal structure of (*E*)-2-(4-bromophenyl) ethenesulfonyl fluoride ($C_8H_6BrFO_2S$)



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Abstract

$C_8H_6BrFO_2S$, monoclinic, $P2_1/m$ (no. 11), $a = 4.7846(2)$ Å, $b = 9.6099(4)$ Å, $c = 10.3260(4)$ Å, $\beta = 103.137(1)°$, $V = 462.36(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0193$, $wR_{ref}(F^2) = 0.0502$, $T = 100(2)$ K.

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Source of materials

A tube was charged with a solution of ethenesulfonyl fluoride (1.47 mmol, 49.8 mL) in 2.0 mL of dry THF was added $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2$ (0.99 mmol), LiOAc (0.59 mmol) under inert atmosphere. Thereafter 4-bromo boronic acid (0.49 mmol) dissolved in dry THF (2.0 mL) was added to the reaction mixture drop wise via a syringe over ~30 min. The reaction mixture was stirred at room temperature for 3–5 h and the reaction progress was monitored using TLC. Upon completion, the reaction mixture was filtered through a plug of Celite. The filtrate was concentrated under vacuum and purified through silica gel 60 mesh column chromatography using 2–4% ethyl acetate in hexane as eluent to obtain the pure (*E*)-2-(4-bromophenyl)ethenesulfonyl fluoride. 15 mg of the title compound was dissolved in 1 mL of distilled ethyl acetate and kept in a 5 mL vial covered with aluminium foil for the slow evaporation of the solvent at ambient condition. Single crystals suitable for X-ray diffraction were

Table 1: Data collection and handling.

Crystal:	Rod, colorless
Size:	0.21 × 0.18 × 0.14 mm
Wavelength:	Mo *Kα* radiation ($\lambda = 0.71073$ Å)
μ:	4.648 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, Φ and *ω-scans*
$2\theta_{max}$, completeness:	27.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6634, 1090, 0.0349
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1012
$N(param)_{refined}$:	104
Programs:	Bruker programs [1, 2], SHELX [3], OLEX2 [4], ORTEP-3 [5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	−0.42176(6)	0.7331(4)	0.54163(3)	0.0317(5)
S1	0.47358(11)	0.750000	−0.10167(5)	0.02368(15)
F1	0.2201(4)	0.7292(9)	−0.22788(17)	0.0326(17)
O1	0.6577(8)	0.8750(4)	−0.1193(4)	0.0239(7)
O2	0.5720(9)	0.8748(4)	−0.0945(4)	0.0268(8)
C1	0.2959(6)	0.6968(3)	0.0209(3)	0.0179(5)
H1	0.253999	0.601698	0.032759	0.021
C2	0.2235(6)	0.7954(3)	0.0957(3)	0.0171(6)
H2	0.278273	0.887670	0.079591	0.021
C3	−0.159(2)	0.6289(9)	0.3433(10)	0.0266(6)
H3	−0.210634	0.539859	0.370115	0.032
C4	−0.0033(7)	0.6468(5)	0.2428(4)	0.0188(7)
H4	0.055192	0.566597	0.202126	0.023
C5	0.0665(6)	0.7771(2)	0.2016(3)	0.0138(9)
C6	−0.0164(7)	0.8951(5)	0.2600(4)	0.0188(7)
H6	0.026229	0.985187	0.231774	0.023
C7	−0.161(2)	0.8797(9)	0.3591(11)	0.0266(6)
H7	−0.214248	0.960618	0.400403	0.032
C8	−0.2303(5)	0.7539(14)	0.4005(2)	0.0226(6)

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obtained after three days upon complete evaporation of the solvent.

Experimental details

Crystal data, data collection and structure refinement details are summarized in Table 1. Data reduction and cell refinement were performed using the program SAINT-Plus [1, 2]. All hydrogen atoms were placed in idealised positions and refined in riding models with the U_{iso} values set to 1.2 or 1.5 times of those of their parent atoms and the constraint distances of C—H ranging from 0.95 Å to 1.00 Å.

Comment

The use of ethene sulfonyl fluoride (ESF) remained obscure until Krutak et al. published the synthesis of ESF in large scale [6]. Ethene sulfonyl fluoride is now an extremely useful synthetic intermediate in organic chemistry and this is mainly due to the two electrophilic sites encountered in this material. Furthermore, ESF has been coupled to a number of different substituted boronic acids via oxidative Heck protocols [7, 8]. More interestingly is the two chemo-selective electrophilic sites which are being preserved during the Heck coupling. This offers substituted ESF many applications such as the use in synthetic chemistry and medicinal chemistry as Michael acceptor for N, O, S and C nucleophiles [9, 10]. And also as sulfur(VI) fluoride exchange which offer connective chemistry with a wide variety of applications in material science, chemical synthesis and drug discovery [11]. The β-vinyl functionality is known as a Michael acceptor. It allows the reactivity upon itself without altering the sulfonyl fluoride (SF) head. Thereafter another nucleophile can be applied in the presence of a strong base such as DBU, NaH, etc., however SF can be activated via silyl ethers thus making it feasible under moderate bases such as trimethylamine [10].

The crystal structure analysis of the title compound reveals that the molecule is disordered over two positions. The title compound is planar with O and F atoms are attached to S-atom out of plane. The disordered ethene group is parallel to the bromophenyl ring. The torsion angle of C5—C2—C1—S1 is 178.1(2)° which shows the planarity of the disordered ethene moiety with respect to bromophenyl ring. The torsion angle of F1—S1—C1—C2 is −106.6(4)° which shows that the F-atom is almost perpendicular to the disordered bromophenyl-ethene moiety. Molecular packing analysis shows that the intermolecular contacts among the title molecules in the crystal structure is established through halogen-halogen interactions formed between F and Br atoms with the F1···Br1 distance of 3.23 Å and C6—Br1···F1 angle of 177.28°. In three-dimensional structural arrangement, the molecules are closely packed as stair-steps through the F···Br interactions as well as weak C—H···O hydrogen bonds formed between sulfonyl and ethene moieties. Also, there is a possibility of parallel-displaced π···π interactions between the aromatic rings of the adjacent layers which can be viewed along *b*-axis. The crystal structure of (*E*)-2-(4-chlorophenyl)ethenesulfonyl chloride, the chloride analogue of the title compound, was obtained from Cambridge Structural Database (CSD) analysis [Ref. code: IYEPIN] [12]. The molecular packing in both crystal structures were compared. This reveals that the pattern of the intermolecular interactions and the three-dimensional molecular packing of the title compound are similar to that of its chloride analogue.

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