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Crystal structure of (*E*)-2-(4-cyanophenyl)ethenesulfonyl fluoride, C₉H₆FNO₂S

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.31 × 0.24 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.34 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX2, φ and ω
$\theta_{\max}$, completeness:	28.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18629, 4527, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4232
$N(\text{param})_{\text{refined}}$:	253
Programs:	COSMO [1], Olex2 [2], Bruker [3], SHELX [4, 5]

<https://doi.org/10.1515/ncrs-2018-0449>

Received October 24, 2018; accepted January 8, 2019; available online February 1, 2019

Abstract

C₉H₆FNO₂S, triclinic, $P\bar{1}$ (no. 2), $a = 7.2786(2)$ Å, $b = 8.1014(3)$ Å, $c = 16.1084(5)$ Å, $\alpha = 76.320(1)^\circ$, $\beta = 87.918(1)^\circ$, $\gamma = 80.784(1)^\circ$, $V = 911.00(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0298$, $wR_{\text{ref}}(F^2) = 0.0857$, $T = 100(2)$ K.

CCDC no.: 1889568

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The β -(hetero)arylethenesulfonyl fluoride compound, C₉H₆FNO₂S, was obtained according to the literature procedure [1]. A 10 mL single-neck round-bottom flask was charged with 4-cyanophenylboronic acid (1.4 mmol, 200 mg, 1 equiv), ESF (previously prepared according to Sharpless et al. [6]

(8.4 mmol, 696 μ L, 6 equiv), DDQ (2.1 mmol, 477 mg, 1.5 equiv), Pd(OAc)₂ (5 mol%, 16 mg) and AcOH (7.2 mL). The reaction mixture was stirred at 80 °C for 12 h until completion as judged by TLC analysis. Purification of the crude mixture by silica gel column chromatography (EtOAc/Hexane 30%) afforded the product (201 mg, 70% yield) as a white solid, $R_f = 0.62$ (EtOAc/Hexane 30%). Crystals were grown from ethanol at room temperature. ¹H NMR (CDCl₃, 400 MHz): δ 7.81 (1H, d, $J = 17.8$ Hz), 7.78 (2H, d, $J = 8.4$ Hz), 7.67 (2H, d, $J = 8.4$ Hz), 6.98 (1H, dd, $J = 17.8, 2.4$ Hz) ppm.

Experimental details

Hydrogen atom positions were calculated geometrically and refined using the riding model 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

β -Arylethenesulfonyl fluorides represent a class of novel sulfur-containing functional compounds that have extended the fundamental concepts of modern organic synthesis. To this end, the development of innovative and more efficient synthetic protocols for the reaction of aryl- or heteroaryl-boronic acids and ethenesulfonyl fluoride (ESF) affording the product have been reported [7, 8]. Due to the privileged vinyl and S-F functionalities these products present, additional molecular modifications hold great potential in drug design, organocatalysis, and functional materials [7, 9, 10]. Hence, following our research on β -arylethenesulfonyl fluorides as

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
S1	0.45429(4)	0.55598(4)	0.31284(2)	0.01671(8)
S2	0.04500(4)	0.24418(4)	−0.15216(2)	0.01987(9)
F1	0.34950(12)	0.73037(11)	0.25969(6)	0.02877(19)
F2	−0.09838(12)	0.40971(11)	−0.15050(6)	0.02838(19)
O1	0.54466(13)	0.59674(13)	0.37998(6)	0.0225(2)
O2	0.56019(16)	0.47944(15)	0.25187(8)	0.0335(3)
O3	−0.04002(14)	0.10502(13)	−0.10576(6)	0.0241(2)
O4	0.09356(15)	0.25777(16)	−0.23918(6)	0.0322(3)
N1	−0.45673(16)	−0.03294(15)	0.61782(7)	0.0221(2)
N2	1.00339(17)	0.22857(17)	0.22434(8)	0.0270(3)
C1	0.27142(16)	0.44685(15)	0.34930(8)	0.0165(2)
H1	0.197778	0.413804	0.310352	0.020*
C2	0.23442(16)	0.40933(15)	0.43273(8)	0.0149(2)
H2	0.309386	0.446371	0.469674	0.018*
C3	0.08490(16)	0.31428(15)	0.47085(7)	0.0139(2)
C4	0.09304(16)	0.23666(15)	0.55839(8)	0.0159(2)
H4	0.193509	0.247195	0.591823	0.019*
C5	−0.04496(17)	0.14458(16)	0.59636(8)	0.0167(2)
H5	−0.038825	0.090699	0.655581	0.020*
C6	−0.19311(16)	0.13167(15)	0.54683(8)	0.0150(2)
C7	−0.20378(17)	0.21015(16)	0.45960(8)	0.0171(2)
H7	−0.305129	0.200749	0.426363	0.021*
C8	−0.06516(17)	0.30168(16)	0.42215(8)	0.0165(2)
H8	−0.072016	0.356252	0.363017	0.020*
C9	−0.33929(17)	0.03881(16)	0.58644(8)	0.0174(2)
C10	0.22819(18)	0.27936(17)	−0.09676(8)	0.0202(2)
H10	0.301480	0.364544	−0.122940	0.024*
C11	0.26705(17)	0.18755(16)	−0.01752(8)	0.0182(2)
H11	0.186313	0.108481	0.007925	0.022*
C12	0.42516(17)	0.19948(16)	0.03333(8)	0.0174(2)
C13	0.57327(18)	0.28237(18)	−0.00331(8)	0.0208(2)
H13	0.572750	0.333437	−0.062826	0.025*
C14	0.72029(18)	0.29013(17)	0.04689(8)	0.0207(2)
H14	0.820671	0.346478	0.021940	0.025*
C15	0.72088(18)	0.21501(17)	0.13428(8)	0.0188(2)
C16	0.57451(19)	0.13221(18)	0.17185(8)	0.0223(3)
H16	0.574995	0.082016	0.231463	0.027*
C17	0.42809(18)	0.12416(18)	0.12095(8)	0.0212(3)
H17	0.328478	0.066721	0.145931	0.025*
C18	0.87720(19)	0.22208(18)	0.18540(8)	0.0215(3)

versatile building blocks [11], we report herein the structure characterization of (*E*)-2-(4-cyanophenyl)ethenesulfonyl fluoride by spectroscopic and X-ray single crystal crystallography techniques.

In the crystal structure of the title compound there are two molecules in the asymmetric unit. The analysis of the geometry reveals that the ethene moieties are being slightly deviated from the plan of cyanophenyl groups. This is revealed by the torsion angles around the

cyanophenylethene moieties whose values are C4–C3–C2–C1 160.57(12)° and C17–C12–C11–C10 166.56(13)°, respectively, for both symmetrically independent molecules. Furthermore, the molecular packing analysis shows that no significant intermolecular interactions are there. However, the adjacent symmetrically equivalent molecules are interconnected through cyclic homo-synthon with the graph set of R²₂(10) constituted by very weak C–H···O hydrogen bonds formed between the ethenesulfonyl moieties of the molecules with hydrogen bond values of (i) D···A = 3.456(2) Å, D–H···A = 149.43(14)° and (ii) D···A = 3.329(2) Å and D–H···A = 163.88(12)°. The two sets of hydrogen bond values represent the two types of cyclic dimers formed among the symmetrically equivalent molecules.

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