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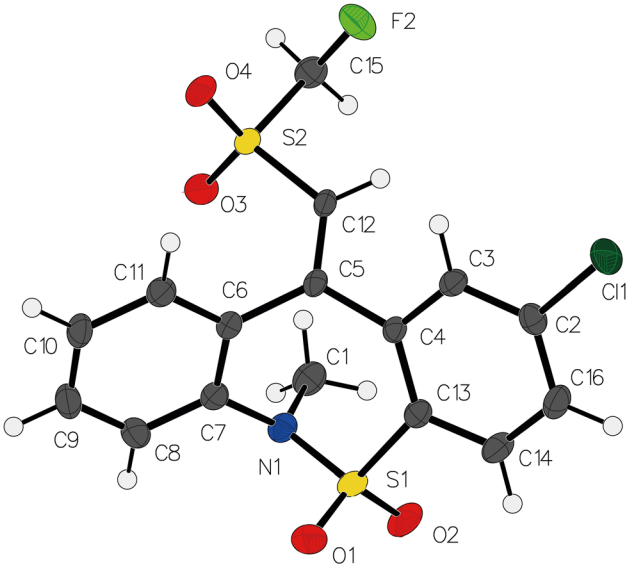
Crystal structure of 2-chloro-11-(((fluoromethyl) sulfonyl)methyl)-6-methyl-6,11-dihydrodibenzo [*c*,*f*][1,2]thiazepine 5,5-dioxide, $C_{16}H_{13}ClFNO_4S_2$



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Abstract

$C_{16}H_{13}ClFNO_4S_2$, monoclinic, $P2_1/c$ (no. 14), a = 8.9984(2) Å, b = 18.0668(6) Å, c = 10.3178(3) Å, β = 95.5070(10)°, V = 1669.65(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0405 $wR_{ref}(F^2)$ = 0.1048, T = 150 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.08 × 0.06 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.51 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE, φ and ω scans
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12889, 3393, 0.057
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2,698
$N(param)_{refined}$:	227
Programs:	Bruker,[1] SHELX,[2, 3] Olex2[4]

1 Source of materials

The reaction components, including 4-bromo–*N*-(2-ethynylphenyl)–N-methylbenzenesulfonamide (3 mmol, 1 eq.), 2,4-difluoro-1-iodobenzene (12 mmol, 4 eq.), di-tert-butyl sulfoxide (12 mmol, 4 eq.), and [Ir(dtbbpy) $(ppy)_2$][PF_6] (3 mol%, photocatalyst), were sequentially introduced into the dried vessel. The reaction setup was sealed with a Teflon-coated septum cap and purged with nitrogen gas (3 min) to establish an inert atmosphere. The heterogeneous mixture was maintained under magnetic stirring at ambient temperature while irradiated with blue light from a 30 W LED array (λ = 350 nm) for 24 h. Upon reaction completion, the process was quenched by sequential addition of ethyl acetate (20 mL × 3). The organic phase was separated using a separatory funnel, washed successively with saturated sodium bicarbonate solution (60 mL) and brine (60 mL), and dried over anhydrous $MgSO_4$. After gravity filtration, the solvent was removed through rotary evaporation. The crude product was purified by flash column chromatography (silica gel, 200–300 mesh, EtOAc/hexane 1:1 v/v). A portion of the isolated compound (0.1 g) was dissolved in EtOAc (10 mL) and allowed to slowly evaporate at room temperature, yielding colorless needle-like crystals of the target molecule.

2 Experimental details

Single-crystal X-ray diffraction data for the title compound were obtained through Mo Kα radiation measurements (λ = 0.7093 Å) collected at 150 K using a Bruker D8 Venture

diffractometer.[1] The initial phase solution was derived using the ShelXT algorithm,[2] followed by progressive iterative modeling and constrained least-squares optimization employing ShelXL[3] within the Olex2 integrated software environment.[4]

3 Comment

The dioxodibenzothiazepines and their derivatives represent a structurally intriguing and biologically significant class of heterocyclic compounds, characterized by a fused bicyclic framework incorporating two benzene rings, a thiazepine ring, and two oxygen atoms in the 5,5-position.[5] These molecules have garnered considerable attention in medicinal chemistry and organic synthesis. The absence of definitive single-crystal structures for many derivatives has limited the understanding of critical structural determinants of biological activity, such as conformational flexibility, hydrogen-bonding networks, and π-π stacking interactions.[6–9]

The molecular structure of the title compound (depicted in the figure) features a fused bicyclic framework comprising carbon, oxygen, sulfur, nitrogen, and fluorine atoms. The core architecture consists of a 6, 11-dihydrodibenzo[*c*,*f*][1,2]thiazepine ring system fused to a thiazepine moiety .[10–13] A fluoromethylsulfonyl group ($–SO_2CH_2F$) at position C12, a chloro substituent at C2, and a methyl group ($–CH_3$) at N1, all strategically positioned to modulate electronic properties and steric interactions. Aromatic carbons are connected *via* conjugated double bonds, while sulfur and nitrogen atoms form heterocyclic rings. The C15–F2 bonds in the fluoromethylsulfonyl moiety exhibit short lengths (1.375 Å), consistent with their high electronegativity, whereas adjacent C15–S2 single bonds display longer distances (1.796 Å). The S–O double bonds (S2–O3 and S2–O4) align with typical values (1.4385 and 1.4380 Å) for thiazepine derivatives.

Steric and electronic effects are further governed by the dihedral angles, which influence planarity and conformational flexibility. The chloro substituent at C2 and fluorinated groups contribute to significant steric hindrance. These structural features collectively determine the molecule's physicochemical properties, including solubility and reactivity.

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