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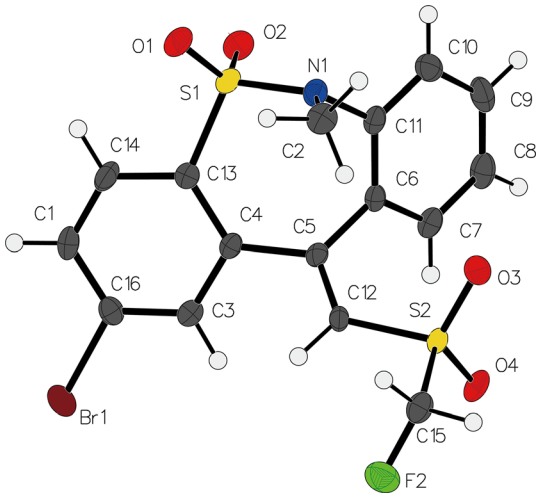
Crystal structure of 2-bromo-11-(((fluoromethyl)sulfonyl)methyl)-6-methyl-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine 5,5-dioxide, $C_{16}H_{13}BrFNO_4S_2$



https://doi.org/10.1515/ncrs-2025-0125
Received March 9, 2025; accepted April 2, 2025;
published online April 24, 2025

Abstract

$C_{16}H_{13}BrFNO_4S_2$, monoclinic, $P2_1/c$ (no. 14), a = 9.1629(2) Å, b = 17.9824(4) Å, c = 10.3488(2) Å, β = 95.501(1)°, V = 1697.33(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0331, $wR_{ref}(F^2)$ = 0.0804, T = 150 K.

CCDC no.: 2440471

The molecular structure is shown in the figure. Table 1 contains the 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:	0.13 × 0.09 × 0.07 mm
Wavelength:	Mo*K*α radiation (0.71073 Å)
μ:	2.70 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}:	19810, 3472, 0.061
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,956
$N(param)_{refined}$:	227
Programs:	Bruker,[1] SHELX,[2,3] Olex2[4]

1 Source of materials

A Pyrex reaction tube (100 mL) was prepared by oven-drying under a nitrogen atmosphere at 120 °C for 4 h to ensure complete removal of moisture. The reagents, 4-bromo-N-(2-ethynylphenyl)-*N*-methylbenzenesulfonamide (3 mmol, 1 equiv.), 2,4-difluoro-1-iodobenzene (12 mmol, 4 equiv.), di-tert-butyl sulfoxide (12 mmol, 4 equiv.), [Ir(dtbbpy)(ppy)$_2$][PF$_6$] (3 mol%, photoredox catalyst), and dichloromethane (15 mL, solvent) were added sequentially. The reaction vessel was sealed with a Teflon-lined cap and purged with nitrogen gas (3 min) to establish an inert atmosphere. The mixture was stirred magnetically at room temperature (25 °C) while exposed to blue light irradiation (λ = 350 nm, 30 W LED array) for 24 h. Upon reaction completion, the mixture was quenched by addition of ethyl acetate (20 mL × 3). The organic layers were separated, washed sequentially with saturated $NaHCO_3$ solution (60 mL) and brine (60 mL), and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified *via* flash column chromatography (silica gel, 200–300 mesh, EtOAc/hexane 1:1). A portion of the purified material (0.1 g) was dissolved in EtOAc (10 mL) and slowly evaporated at ambient temperature to afford colorless crystals of the title compound.

2 Experimental details

The crystal structure of the title compound was determined using Mo-Kα radiation collected at 150 K on a Bruker D8

Venture diffractometer.[1] The initial phase solution was achieved in ShelXT,[2] followed by iterative model building and restrained least-squares refinement using ShelXL[3] within the Olex2 software platform.[4]

3 Comment

Dioxodibenzothiazepines represent a class of fused heterocyclic compounds characterized by their conjugated benzene and thiazepine rings fused through oxygen and sulfur atoms, forming a rigid polycyclic scaffold.[5] These structures are of growing interest due to their unique electronic properties, such as enhanced π-conjugation and redox activity.[6–8] Such compounds serve as versatile platforms in medicinal chemistry (e.g., as calcium channel modulators) and materials science (e.g., organic semiconductors), where subtle structural modifications can drastically alter their biological activity and electronic behavior.

As illustrated in the figure, the compound features a fused dihydrodibenzo[*c*,*f*][1,2]thiazepine core, a benzothiazepine derivative. This fusion forms a bicyclic system comprising a seven-membered thiazepine ring and a six-membered benzene ring, consistent with structurally analogous compounds reported in literature.[9–13] The N1-nitrogen atom of the thiazepine ring is substituted with a methyl group ($-CH_3$), while position 11 hosts a ((fluoromethyl) sulfonyl)methyl fragment introducing both sulfonyl $-SO_2^-$ and $-CH_2F$ groups. The aromatic stability of the benzene rings and thiazepine ring is maintained through an alternating pattern of single and double bonds, with a C=C double bond contributing to planarity and electron delocalization.

In the solid state, the polycyclic framework is stabilized by specific intra-atomic interactions, wherein carbon atoms (C1–C16) form the backbone with C–C bond lengths ranging from 1.50 to 1.55 Å. Sulfur (S1) engages in double bonds (S=O) (1.45 Å) and single bonds (C–S) (1.82 Å). Bromine (Br1) is bonded *via* a weak aryl–C–Br linkage (2.00 Å), and flourine (F2) forms a short C–F bond (1.35 Å), confirming its incorporation within the sulfonyl-fluoromethyl substituent. Collectively, these structural features define the molecule's electronic properties, reactivity profile, and potential applications in biological or material science contexts.

Acknowledgments: This work was financially supported by China National Drug Control Research Center 2021: DR (2021) J011.

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