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Crystal structure of *tert*-butyl (phenylsulfinyl) carbamate, $C_{11}H_{15}NO_3S$

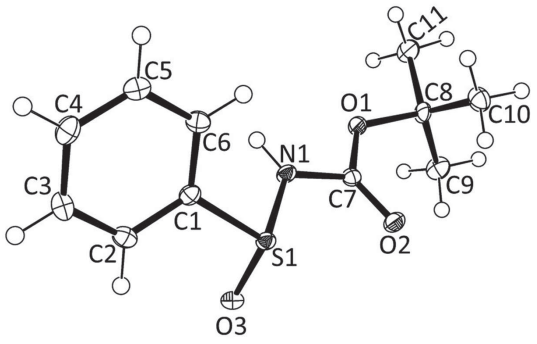

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Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	0.35 × 0.22 × 0.13 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.7 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	51°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6515, 2182, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2165
$N(param)_{refined}$:	147
Programs:	Bruker programs [1, 2], SHELX [3], ORTEP-3 [4]

Abstract

$C_{11}H_{15}NO_3S$, orthorhombic, $Pna2_1$ (no. 33), $a = 9.5337(10)$ Å, $b = 10.7168(11)$ Å, $c = 11.5675(11)$ Å, $V = 1181.9(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0252$, $wR_{ref}(F^2) = 0.0689$, $T = 173$ K.

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

Source of material

The title compound was prepared from benzenesulfinamide according to the literature procedure [5]. In a round bottom flask, benzenesulfinamide 3 (0.40 g, 2.80 mmol) was dissolved in dry THF (12 mL) and cooled to −78 °C. After stirring the mixture for 10 min at −78 °C, *n*-butyl lithium (2.80 mL, 7.10 mmol) was added dropwise over 10 min. The mixture was stirred for 10 more minutes at −78 °C, followed by rapid addition of di-*tert*-butyl dicarbonate (0.742 g, 3.40 mmol), stirring was continued for 10 min at −78°C which gradually raised the temperature to RT and stirred overnight at room temperature. A saturated solution of $NaHCO_3$ was then added and diluted with dichloromethane. The water phase was extracted with dichloromethane, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using dichloromethane as eluent yielded the title compound (0.306 g, 45%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 10.49 (s, 1H), 7.68–7.66 (m, 2H), 7.59–7.56 (m, 3H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm 153.40, 143.49, 131.26, 128.97, 124.93, 81.47, 27.75. The title compound (10 mg) was dissolved in acetonitrile in a vial by sonication for 3 min. The vial was covered with parafilm with a tiny outlet to enable evaporate ion. Crystals suitable for X-ray diffraction formed over the period of 5 days.

Experimental details

The data were scaled and absorption correction performed using SADABS [1]. The structure was solved by direct methods using SHELXS-97 [3]. All hydrogen atoms were placed in idealised positions and refined in riding models with U_{iso} assigned the values to be 1.2 or 1.5 times those of their parent atoms and the constraint distances of CH ranging from 0.95 Å to 1.00 Å.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.9431(2)	0.0504(2)	1.01470(19)	0.0143(5)
C2	0.8834(2)	−0.0146(2)	1.1060(2)	0.0174(5)
H2	0.799584	0.014566	1.141348	0.021*
C3	0.9480(3)	−0.1230(2)	1.1451(2)	0.0204(5)
H3	0.908463	−0.168381	1.207648	0.024*
C4	1.0706(2)	−0.1653(2)	1.0926(2)	0.0208(5)
H4	1.114818	−0.239137	1.119661	0.025*
C5	1.1280(2)	−0.0996(2)	1.0011(2)	0.0188(5)
H5	1.211468	−0.128958	0.965504	0.023*
C6	1.0650(2)	0.0084(2)	0.9609(2)	0.0165(4)
H6	1.104166	0.053032	0.897766	0.020*
C7	0.9550(2)	0.3748(2)	0.86506(19)	0.0132(4)
C8	1.0808(2)	0.5492(2)	0.7767(2)	0.0164(5)
C9	0.9718(2)	0.6497(2)	0.7992(2)	0.0221(5)
H9A	0.980867	0.715584	0.740876	0.033*
H9B	0.877792	0.613103	0.794808	0.033*
H9C	0.986575	0.685250	0.876257	0.033*
C10	1.0704(3)	0.4934(2)	0.6563(2)	0.0219(5)
H10A	1.079151	0.559802	0.598540	0.033*
H10B	1.145864	0.432406	0.645298	0.033*
H10C	0.979451	0.451844	0.647370	0.033*
C11	1.2279(2)	0.5987(2)	0.7986(2)	0.0225(5)
H11A	1.248103	0.666469	0.744200	0.034*
H11B	1.234258	0.630202	0.877920	0.034*
H11C	1.296101	0.531287	0.787675	0.034*
N1	0.97629(18)	0.27716(16)	0.94124(16)	0.0139(4)
H1	1.055026	0.268412	0.980118	0.017*
O1	1.06762(15)	0.44860(15)	0.86515(14)	0.0156(4)
O2	0.84904(14)	0.38734(16)	0.80861(15)	0.0178(4)
O3	0.74651(15)	0.21720(15)	1.04930(13)	0.0161(4)
S1	0.84269(5)	0.17653(4)	0.95484(5)	0.01270(18)

Discussion

Bioisosterism is an advantageous approach in medicinal chemistry, which facilitates the greater selectivity for a determined receptor or enzymatic isoform subtype. It can result in less side effects, decreased toxicity, improved solubility-hydrophobicity and different/better metabolic stability [6, 7]. Sulphur isosters *viz*. sulfines, sulfoximines, sulfonimidamides, sulfonamides, are the compounds of much interest in pharamceutical chemistry [8]. Sulfonamides are found to be an integral part of more than hundred approved drugs or molecules in clinical trials. Sulfonimidamide is an isostere of sulphonamide, which is formed by replacing one of the O-atoms by nitrogen of sulfonamide. The title compound can be considered as a potential pecursor for the preparation of sulfonimidamids [9–12]. However crystal structures of sulfinylcarbamate derivatives are rare.

Crystal structure of the title compound shows that the sulfinyl (S=O) group is perpendicular to the amide bond of the molecule as it is observed in the crystal structures of most of the sulfonylcarbamate derivatives. The major interactions among molecules in the crystal structure of the title compound are established by N—H···O=S hydrogen bonds [d(N···O) = 2.864 Å] formed by sulfinyl and amide groups. From the CSD analysis it was noticed that this type of interactions occured only in a few cases of sulfonyl derivatives, while in most of the cases the major interactions among molecules in the crystals were established through the amide groups. In addition to N—H···O hydrogen bonds, the C—H···O secondary interactions formed by the carbonyl (C=O) and aromatic H-atoms are also involved in connecting adjacent molecules forming hydrogen bonded 1D tape-like arrangment running along [100] and such tapes are connected through various very weak C—H···O and C—H···π interactions.

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