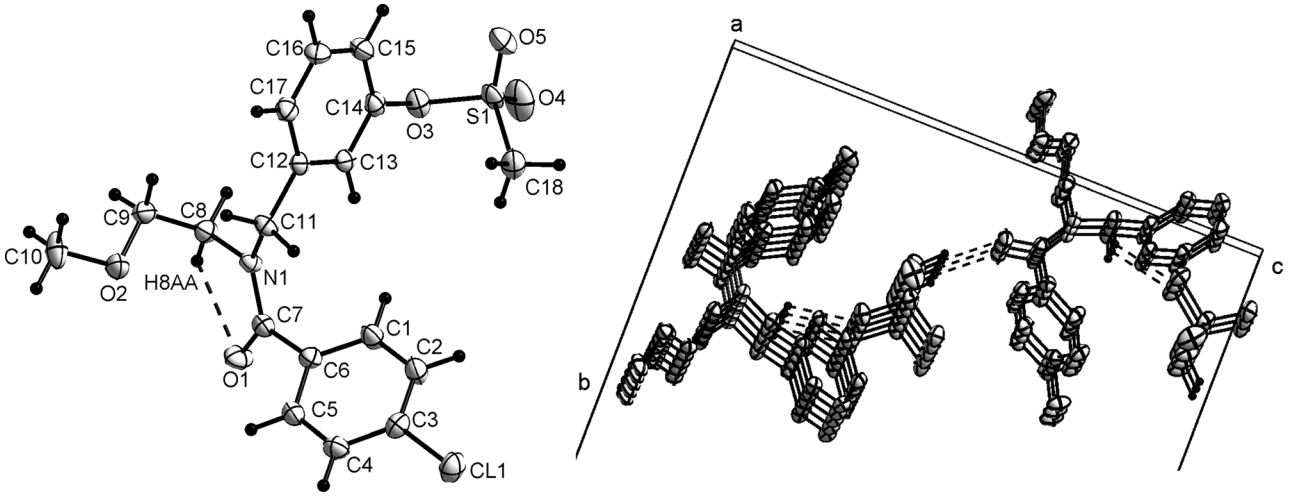
Yong Li, Yundeng Wu* and Jingjing Wang

The crystal structure of 3-((4-chloro-*N*-(2-methoxyethyl)benzamido)methyl)phenyl methanesulfonate, $C_{18}H_{20}ClNO_5S$



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Abstract

$C_{18}H_{20}ClNO_5S$, monoclinic, $P2_1/n$ (no. 14), a = 5.671(4) Å, b = 18.225(13) Å, c = 17.99(2) Å, β = 90.18(4)°, V = 1859(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0316, $wR_{ref}(F^2)$ = 0.0813, T = 170 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.07 × 0.05 × 0.03 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.35 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.7°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20,055, 4235, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3660
$N(param)_{refined}$:	266
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4], PLATON [5–8], publCIF [9]

Source of materials

In a representative experiment, approximately 0.2 g (0.5 mmol) 3-((4-chloro-*N*-(2-methoxyethyl)benzamido)methyl) phenyl methanesulfonate was dissolved in a few drops of DMSO in a vial. Several drops of Toluene were added into another vial. Both vials were sitting in a clear beaker sealed with tape for easy viewing and access. Over time the equilibrium of the vapor will exist between the two solvents. During this equilibration process colourless block crystals of the title compound were obtained within about a week.

***Corresponding author: Yundeng Wu**, Technique Center, Jinling Pharmaceutical Company Limited, Nanjing, 210046, Jiangsu Province, People's Republic of China, E-mail: wuyundeng99@163.com. https://orcid.org/0000-0002-8717-1958
Yong Li, School of Chemical Engineering, Ningbo Polytechnic, No. 388, Lushan East Road, Ningbo Economic and Technological Development Zone, Beilun District, Ningbo City, 315806, Zhejiang Province, People's Republic of China, E-mail: 25660315@qq.com
Jingjing Wang, Department of Student Affairs, Ningbo Polytechnic, No. 388, Lushan East Road, Ningbo Economic and Technological Development Zone, Beilun District, Ningbo City, 315806, Zhejiang Province, People's Republic of China, E-mail: 1282485761@qq.com

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.35118 (7)	0.12364 (2)	0.25983 (2)	0.03702 (11)
S1	0.97888 (6)	0.32987 (2)	0.44830 (2)	0.02858 (10)
O1	0.36829 (19)	0.34174 (6)	0.06810 (5)	0.0332 (2)
O3	0.95976 (16)	0.38376 (6)	0.37859 (5)	0.0299 (2)
O4	1.19442 (19)	0.29120 (8)	0.43589 (7)	0.0510 (3)
O5	0.9487 (3)	0.37172 (7)	0.51376 (6)	0.0523 (3)
N1	0.36655 (19)	0.41534 (6)	0.16903 (6)	0.0224 (2)
C1	0.1824 (2)	0.26609 (8)	0.23332 (8)	0.0306 (3)
H1	0.318678	0.280532	0.260464	0.037*
C2	0.0367 (3)	0.21118 (8)	0.26164 (8)	0.0319 (3)
H2	0.075480	0.187726	0.307241	0.038*
C3	−0.1641 (2)	0.19108 (7)	0.22309 (8)	0.0265 (3)
C4	−0.2200 (3)	0.22358 (8)	0.15634 (8)	0.0302 (3)
H4	−0.358215	0.209648	0.129916	0.036*
C5	−0.0701 (3)	0.27734 (8)	0.12818 (8)	0.0287 (3)
H5	−0.106330	0.299300	0.081621	0.034*
C6	0.1313 (2)	0.29976 (7)	0.16635 (7)	0.0238 (3)
C7	0.2962 (2)	0.35439 (7)	0.13072 (7)	0.0239 (3)
C8	0.5344 (2)	0.46649 (8)	0.13390 (7)	0.0255 (3)
H8AA[a]	0.598621	0.443573	0.088351	0.031*
H8AB[a]	0.667708	0.475388	0.168433	0.031*
H8BC[b]	0.660571	0.437583	0.109737	0.031*
H8BD[b]	0.608970	0.496693	0.173237	0.031*
C11	0.2481 (2)	0.44299 (8)	0.23523 (7)	0.0243 (3)
H11A	0.131340	0.406251	0.252101	0.029*
H11B	0.161535	0.488434	0.222311	0.029*
C12	0.4169 (2)	0.45905 (7)	0.29784 (7)	0.0219 (3)
C13	0.6115 (2)	0.41351 (7)	0.31124 (7)	0.0224 (3)
H13	0.641527	0.372231	0.280426	0.027*
C14	0.7578 (2)	0.42985 (7)	0.36984 (7)	0.0245 (3)
C15	0.7211 (3)	0.49028 (8)	0.41532 (8)	0.0320 (3)
H15	0.827353	0.501108	0.454764	0.038*
C16	0.5257 (3)	0.53477 (8)	0.40207 (8)	0.0335 (3)
H16	0.496516	0.575858	0.433205	0.040*
C17	0.3747 (3)	0.51941 (7)	0.34402 (7)	0.0274 (3)
H17	0.241554	0.549882	0.335291	0.033*
C18	0.7423 (3)	0.26952 (9)	0.43723 (9)	0.0347 (3)
H18A	0.593786	0.296802	0.440734	0.052*
H18B	0.747924	0.232080	0.476299	0.052*
H18C	0.752231	0.245816	0.388432	0.052*
O2[a]	0.2271 (4)	0.52557 (12)	0.06773 (13)	0.0329 (7)
C9[a]	0.4224 (6)	0.53887 (18)	0.1139 (2)	0.0300 (8)
H9A[a]	0.371518	0.564663	0.159522	0.036*
H9B[a]	0.537841	0.570294	0.087701	0.036*
C10[a]	0.1265 (18)	0.5942 (5)	0.0447 (6)	0.0389 (16)
H10A[a]	−0.003707	0.585027	0.009971	0.058*
H10B[a]	0.247446	0.623863	0.020087	0.058*
H10C[a]	0.067186	0.620555	0.088282	0.058*
O2A[b]	0.2539 (5)	0.56418 (14)	0.11011 (14)	0.0428 (9)
C9A[b]	0.4238 (6)	0.51791 (18)	0.0758 (2)	0.0288 (8)
H9AA[b]	0.548334	0.548255	0.052594	0.035*
H9AB[b]	0.347165	0.488522	0.036191	0.035*
C10A[b]	0.128 (2)	0.6092 (7)	0.0576 (7)	0.061 (3)
H10D[b]	0.239979	0.641397	0.031836	0.091*
H10E[b]	0.011703	0.639047	0.083862	0.091*
H10F[b]	0.048256	0.577794	0.021193	0.091*

[a]Occupancy: 0.505 (4), [b]Occupancy: 0.495 (4).

Experimental details

A suitable crystal was selected and placed on a 'Bruker APEX-II CCD' diffractometer. Using Olex2 [4], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

Secondary CH2, including C8(H8AA,H8AB), C8(H8BC, H8BD), C11(H11A,H11B), C9(H9A,H9B), C9A(H9AA,H9AB), were refined with riding coordinates. Aromatic/amide H, including C1(H1), C2(H2), C4(H4), C5(H5), C13(H13), C15(H15), C16(H16), C17(H17), were refined with riding coordinates. Methyls, including C18(H18A,H18B,H18C), C10(H10A,H10B, H10C), C10A(H10D,H10E,H10F), were refined as idealised rotating group. U_{iso} values of hydrogen atoms were set to 1.2U_{eq} of the parent atoms for all C(H) groups, C(H,H) groups, C(H,H,H,H) groups and at 1.5U_{eq} for all C(H,H,H) groups.

Statistical disorder is noted in the terminal 2-methoxyethyl groups. For this disorder, distances and U_{iso}/U_{aniso} restraints and constraints were imposed on relative atoms. The C8, C9, O2, C10 and C8A, C9A, O2A, C10A are disordered almost equally over two sites with occupancies 0.505:0.495.

These papers [10–12] also give the results of this classic terminal 2-methoxyethyl disorder.

Comment

The N-substituted sulfonyloxybenzylamines are believed to have ability to improve the overall appearance of skin, including reversing skin wrinkles, by stimulating collagen production with cosmetic compositions comprising effective amounts [13–15].

To the best of our knowledge, this is the first article to report the structure containing the bioactive group of N-substituted sulfonyloxybenzylamine. The structure of another building block, 4-chlorobenzamide, has been reported by literature [16–18] as their main moiety.

The N-substituted sulfonyloxybenzylamines are also part of our continuing interest in synthesis, characterisation and understanding of hydrogen bonding schemes of related compounds [19, 20].

The asymmetric unit of the title structure contains one 3-((4-chloro-N-(2-methoxyethyl)benzamido)methyl)phenyl methanesulfonate molecule (*cf*. left part of the figure, only one component of each of the disordered 2-methoxyethyl groups is shown for clarity purpose). The bond lengths and angles within these moieties are in the expected ranges.

In the amide moiety, nitrogen (N1) and carbonyl groups (C7=O1) form $p–\pi$ conjugation. As a result of conjugation, not only the bond length in the amide moiety tend to be equal, but also the four atoms connected to N1 and C7 are all on the same plane (R.M.S-Error = 0.000 Å for the contributing atoms O1, N1, C6, C7, C8). The conjugation of coplanar structures is also reported by literature [21–23]. This plane encloses an angle of 54.27° with the plane of the 4-chlorophenyl group (C1–C6), and 84.95° with another plane of the phenyl group (C12–C17). There are no classical hydrogen bonds found for the title compound, but five non classical hydrogen bonds. Two of them are intramolecular and the other three are intermolecular hydrogen bonds. In one component of the disordered 2-methoxyethyl groups, O1 participates in intramolecular hydrogen bonds (C8–H8AA···O1, D···A = 2.730(3) Å; *cf*. left part of the figure) to form a five-membered ring (C8–H8AA–O1–C7–N1). In another component of disordered 2-methoxyethyl groups, there is another intramolecular hydrogen bond (C11–H11B···O2A, D···A = 3.154(4) Å; this disordered 2-methoxyethyl group is not shown in the figure for clarity purpose). O3 of sulfonyloxybenzylamine is involved in nonclassic intermolecular hydrogen bond (C11–H11A···O3′; ′ = $-1+x, y, z$, D···A = 3.243(4) Å). The right part of the figure (some hydrogen atoms are omitted for clarity) shows this hydrogen-bonded chains running along *a* axis.

O4 of sulfonyloxybenzylamine is involved in another non-classical intermolecular hydrogen bonds (C18–H18A···O4′, ′ = $-1+x, y, z$, D···A = 3.132(3) Å) running along *a* axis (*cf*. right part of the figure).

The O1 of the amide group is not only involved in intramolecular hydrogen bond but also intermolecular hydrogen bonds (C18–H18B…O1‴; ‴ = $^1/_2+x, ^1/_2-y, ^1/_2+z$, D···A = 3.187(4) Å). This hydrogen-bonded chain running along *c* axis is shown in unit cell (*cf*. right part of the figure).

In total, the three intermolecular hydrogen bonding interactions construct a network parallel to the *ac* plane (*cf*. right part of the figure).

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