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N-(2-Nitrobenzenesulfonyl)-L-alanine methyl ester

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
R factor = 0.036
wR factor = 0.105
Data-to-parameter ratio = 9.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $C_{10}H_{12}N_2O_6S$, has been determined as part of an ongoing investigation into the preparation of substituted amino acids suitable for the generation of combinatorial libraries. The molecular conformation is stabilized by intra- and intermolecular N—H···O and C—H···O hydrogen-bonding interactions.

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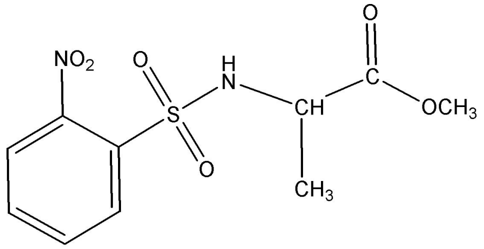
Comment

In a previous paper, we reported the structure of *N*-(2-nitrobenzenesulfonyl)glycine methyl ester (Bornaghi *et al.*, 2005). This work is part of our ongoing investigation into the development of *N*-substituted amino acids as building blocks for dynamic combinatorial chemistry (Lehn & Eliseev, 2001) and subsequent biological screening. Our synthetic approach utilizes concomitant protection and activation of the amino acid nitrogen with the 2-nitrobenzene sulfonyl (oNBS) group. The oNBS group is introduced with the premise that the electron-withdrawing nature of this group will increase the acidity of the NH proton, ensuring the amide becomes susceptible for further high-yielding *N*-substituted products.



(I)

In this paper, we report the structure of the L-alanine methyl ester compound, oNBS–Ala–OMe, (I), which crystallizes in space group $P2_1$ with one discrete molecule in the asymmetric unit (Fig. 1). The bond lengths and angles for (I) (Table 1) are in accord with data for structures of related oNBS protected amino acid compounds (Bornaghi *et al.*, 2005; Iacapino *et al.*, 1999; Hammarström *et al.*, 2000; Giraldés *et al.*, 2001). In the structure, the S—N bond lies approximately perpendicular to the plane of the benzene ring, with a torsion angle N1—S1—C1—C2 of 80.3 (3)°. The methyl ester group is planar and folds back over the plane of the benzene ring such that atom O5 is situated directly above atom C1, with C1···O5 = 3.212 (5) Å. The NO_2 group is rotated out of the plane of the benzene ring, with a torsion angle O1—N2—C2—C1 of −43.3 (6)°. The nitro atom O2 forms weak intramolecular N—H···O hydrogen bonds with the H atom on N1 (Table 2). N1 is also involved in intermolecular N—H···O hydrogen bonding to the sulfonyl atom O4 to form a polymeric chain along the *c*

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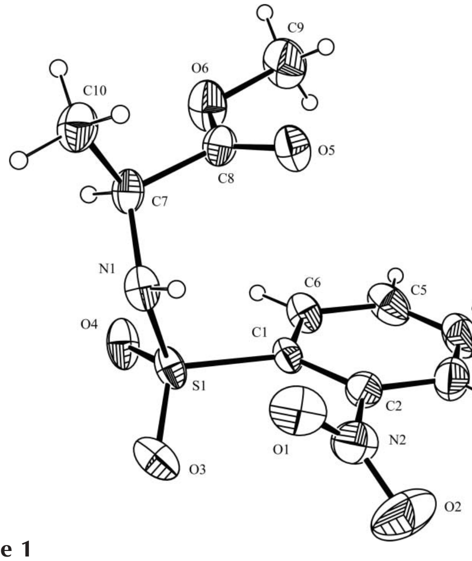

Figure 1
View of the title compound with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms are included with arbitrary radii.

axis (Table 2 and Fig. 2). The crystal structure is stabilized also by a number of intra- and intermolecular C—H$\cdots$O hydrogen-bond interactions (Table 2).

Experimental

Triethylamine (5.06 g, 0.05 mol) was added dropwise to a solution of L-alanine methyl ester hydrochloride (2 g, 0.014 mol) and 2-nitrobenzene sulfonyl chloride (3.5 g, 0.016 mol) in anhydrous dichloromethane (DCM, 50 ml). The reaction mixture was stirred at room temperature for 18 h, diluted with DCM (50 ml) and then washed with 2 *M* HCl (2 × 100 ml), 1 *M* $NaHCO_3$ (1 × 100 ml), saturated brine (1 × 100 ml) and dried over $MgSO_4$. The volatiles were removed under reduced pressure to give a yellow residue. The title compound was obtained in 70.8% yield following recrystallization from a mixture of ethyl acetate and hexane (m.p. 359 K). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.48 (*d*, 3H, *J* = 6.6 Hz, CH_3), 3.52 (*s*, 3H, OCH_3), 4.25 (*m*, 1H, αCH), 5.92 (*br. s*, 1H, NH), 7.76 (*m*, 1H, ArH), 7.92 (*m*, 1H, ArH), 8.07 (*m*, 1H, ArH). MS (LRMSES): *m*/*z* 289 $[M + H]^+$, 311 $[M + Na]^+$.

Crystal data

$C_{10}H_{12}N_2O_6S$
$M_r = 288.29$
Monoclinic, $P2_1$
$a = 8.845$ (3) Å
$b = 13.335$ (5) Å
$c = 5.5203$ (10) Å
$\beta = 95.10$ (2)°
$V = 648.5$ (3) Å^3
$Z = 2$
$D_x = 1.476$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.8$–17.0°
$\mu = 0.27$ mm^{-1}
$T = 295$ K
Prism, colorless
0.40 × 0.20 × 0.15 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
1708 measured reflections
1608 independent reflections
1252 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -6 \rightarrow 17$
$l = -7 \rightarrow 7$
3 standard reflections every 150 reflections intensity decay: 1.8%

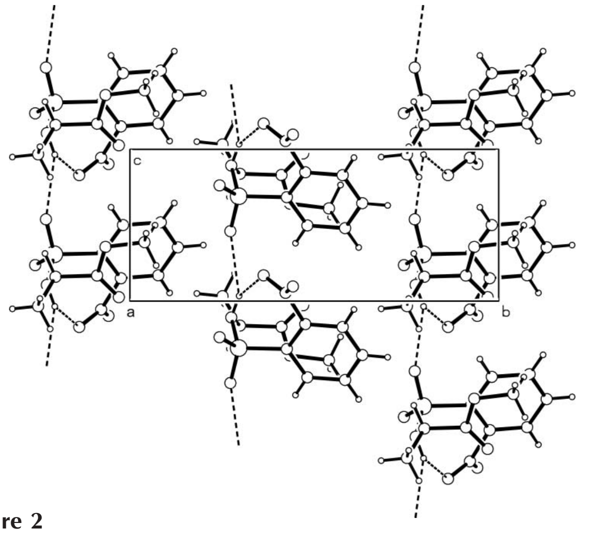

Figure 2
View of the crystal packing projected on to the *bc* plane. Hydrogen bonding is shown as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.106$
$S = 1.02$
1608 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.041 (7)
Absolute structure: Flack (1983)
Flack parameter = 0.24 (12)

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.426 (3)	O5—C8	1.191 (5)
S1—O4	1.433 (3)	O6—C8	1.322 (5)
S1—N1	1.613 (3)	O6—C9	1.455 (6)
S1—C1	1.776 (3)	N1—C7	1.468 (5)
O1—N2	1.212 (5)	N2—C2	1.485 (5)
O2—N2	1.200 (5)		
O3—S1—O4	119.29 (18)	O2—N2—C2	117.2 (4)
O3—S1—N1	108.52 (17)	S1—C1—C2	125.3 (3)
O3—S1—C1	108.05 (17)	S1—C1—C6	117.1 (3)
O4—S1—N1	105.97 (18)	N2—C2—C3	116.6 (4)
O4—S1—C1	105.97 (15)	N2—C2—C1	121.3 (3)
N1—S1—C1	108.66 (15)	N1—C7—C10	109.8 (3)
C8—O6—C9	116.2 (4)	N1—C7—C8	112.2 (3)
S1—N1—C7	120.02 (19)	O6—C8—C7	110.3 (3)
O1—N2—O2	124.6 (4)	O5—C8—O6	125.0 (4)
O1—N2—C2	118.3 (3)	O5—C8—C7	124.7 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1	0.86	2.39	2.999 (5)	128
N1—H1$\cdots$O4$^{\rm i}$	0.86	2.37	3.125 (3)	147
C3—H3$\cdots$O3$^{\rm ii}$	0.95	2.44	3.276 (6)	146
C6—H6$\cdots$O4	0.95	2.40	2.820 (5)	107
C6—H6$\cdots$O5$^{\rm iii}$	0.95	2.53	3.339 (5)	144
C7—H7$\cdots$O4	0.95	2.49	2.863 (4)	103
C9—H9$B\cdots$O5	0.95	2.29	2.668 (7)	103

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, \frac{1}{2} + y, -z$; (iii) $x, y, 1 + z$.

C—H H atoms were constrained as riding atoms, with C—H = 0.93–0.96 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The N—H H atom was located in a difference map and constrained as a riding atom with N—H = 0.86 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N). The absolute configuration, determined with low precision from anomalous scattering effects, is in accord with the known configuration of the starting material.

Data collection and cell refinement: *MSC/AFC-7 Diffractometer Control Software for Windows* (Molecular Structure Corporation, 1999); data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *TEXSAN for Windows*; program(s) used to refine structure: *TEXSAN for Windows* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON* (Spek, 2003).

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