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N-(2-Nitrophenylsulfonyl)glycine methyl ester

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.050
wR factor = 0.206
Data-to-parameter ratio = 12.5

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, $C_9H_{10}N_2O_6S$, has been determined as part of an ongoing investigation into the preparation of *N*-allyl-substituted amino acids suitable for alkene cross-metathesis reactions in the generation of combinatorial libraries. The conformational structure is determined by intra- and intermolecular N—H···O and C—H···O hydrogen-bonding interactions.

Comment

Nitrobenzenesulfonyl (NBS) groups are used in amine chemistry as both protecting and activating groups for subsequent chemistry at the N atom (Kan & Fukuyama, 2004). As part of our ongoing investigations into the synthesis of *N*-allyl substituted amino acids as building blocks for dynamic combinatorial chemistry and subsequent biological screening (Bornaghi *et al.*, 2004; Poulsen *et al.*, 2003), we reacted *ortho*-nitrobenzenesulfonyl chloride (*o*NBSCl) with α-amino acid methyl ester hydrochlorides in the presence of base to give compounds of the type *o*NBS-*Y*-OMe (*Y* = amino acid). While many of these compounds can be isolated only as oils or non-crystalline solids, a small number yield crystals suitable for X-ray diffraction studies. In the present paper, we report the structure of the glycine methyl ester compound, *o*NBS-Gly-OMe, (I), which precipitates as well formed crystals in space group $P2_1/c$ with one discrete molecule in the asymmetric unit (Fig. 1). The bond lengths and angles in (I) (Table 1) are in accord with data for structures of related *o*NBS-protected amino acid compounds (Iacopino *et al.*, 1999; Hammarström *et al.*, 2000; Giraldés *et al.*, 2001). The NO_2 group is rotated out of the plane of the benzene ring with an O1—N2—C2—C1 torsion angle of 43.1 (5)°. For comparison, the corresponding angle in the parent glycine compound, *o*NBS-Gly-OH, is 31.7 (3)° (Iacopino *et al.*, 1999). The S atom lies slightly out of

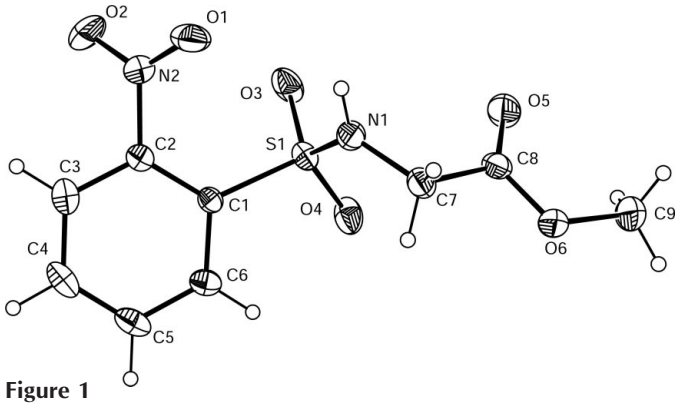
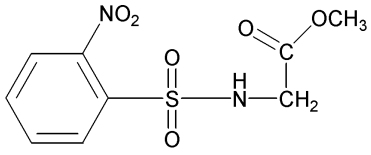


Figure 1
View of the title compound, with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

the plane of the benzene ring [0.189 (1) Å] while the S1—N1 bond is almost perpendicular to the benzene plane, with an N1—S1—C1—C2 torsion angle of 85.9 (3)°. The glycine–methyl ester fragment [N1—C7—C8(–O5)—O6—C9] is planar and extends as a 'tail' away from the *o*NBS group. The H atom on the N atom forms a weak N—H···O hydrogen bond with nitro atom O1, with an N1···O1 distance of 3.040 (5) Å (Table 2).



(I)

In the crystal structure, the molecules are disposed about crystallographic glide planes such that the nitrophenyl groups stack in parallel polymeric arrays along the *c* axis (Fig. 2). The distance between the centroids of the adjacent benzene rings is 3.71 Å, indicative of π–π interactions. These columns are linked in a zigzag fashion along the *b* axis through C—H···O(nitro) interactions. The amino acid ester tails extend in the direction of the *a* axis and link through extensive C—H···O interactions between the methylene (C7) and methyl (C9) H atoms and the carbonyl (O5), ester (O6) and sulfonyl (O3 and O4) O atoms. A feature of the intermolecular bonding in this section of the structure is the formation of an $R_2^2(10)$ ring motif (Bernstein *et al.*,1995) through N1—H1···O3^{i} and C7—H7*A*···O5^{i} hydrogen bonds [symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; Table 2].

Experimental

Compound (I) was prepared in accordance with literature procedures (Albanese *et al.*, 2000; Falkiewicz *et al.*, 2001). Triethylamine (14 g, 0.138 mol) was added dropwise to a solution of glycine methyl ester hydrochloride (5 g, 0.040 mol) and 2-nitrobenzene sulfonyl chloride (9.7 g, 0.044 mol) in anhydrous dichloromethane (DCM, 200 ml). The reaction mixture was stirred at room temperature for 72 h, after which DCM (100 ml) was added. The solution was washed with 2*M* HCl (2 × 300 ml), 1*M* $NaHCO_3$ (1 × 300 ml) and saturated aqueous NaCl solution (1 × 300 ml), and dried over $MgSO_4$. The volatiles were removed under reduced pressure to give a pale-yellow solid residue (yield 7.51 g). This residue was further recrystallized from a 2:3 mixture of ethyl acetate and hexane. *M*.p. 380 K. ^{1}H NMR ($CDCl_3$, 200 MHz, p.p.m.): δ 3.63 (*s*, 3H, OCH_3), 4.04 (*d*, 1H, J = 5.8 Hz, αCH), 6.08 (*br*, *s*, 1H, NH), 7.78 (*m*, 2H, ArH), 7.97 (*m*, 1H, ArH), 8.13 (*m*, 1H, ArH). MS (LRMSES): *m*/*z* 275 [M + H]$^+$, 297 [M + Na]$^+$.

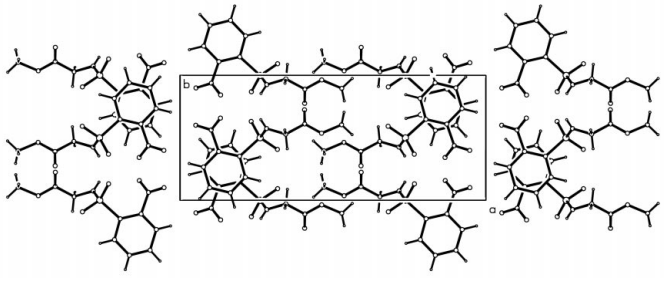


Figure 2
View of the crystal packing projected on to the *ab* plane.

Crystal data

$C_9H_{10}N_2O_6S$	D_x = 1.579 Mg m^{-3}
M_r = 274.26	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
a = 19.805 (3) Å	θ = 12.6–15.8°
b = 7.988 (2) Å	μ = 0.30 mm^{-1}
c = 7.369 (2) Å	T = 295 K
β = 98.18 (2)°	Prism, colorless
V = 1153.9 (5) Å^3	0.50 × 0.30 × 0.30 mm
Z = 4	

Data collection

Rigaku AFC-7*R* diffractometer	θ_{max} = 25.0°
ω–2θ scans	$h = -11 \rightarrow 23$
Absorption correction: none	$k = 0 \rightarrow 9$
2280 measured reflections	$l = -8 \rightarrow 8$
2037 independent reflections	3 standard reflections
1621 reflections with $I > 2\sigma(I)$	every 150 reflections
R_{int} = 0.035	intensity decay: 0.3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1367P)^2 + 0.8688P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.050	
$wR(F^2)$ = 0.206	
S = 1.09	$(\Delta/\sigma)_{max} < 0.001$
2037 reflections	$\Delta\rho_{max}$ = 0.40 e Å^{-3}
163 parameters	$\Delta\rho_{min}$ = −0.56 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.432 (3)	O5—C8	1.193 (5)
S1—O4	1.422 (3)	O6—C8	1.322 (5)
S1—N1	1.601 (3)	O6—C9	1.449 (5)
S1—C1	1.791 (3)	N1—C7	1.435 (5)
O1—N2	1.216 (5)	N2—C2	1.465 (5)
O2—N2	1.212 (5)		
O3—S1—O4	120.06 (18)	O2—N2—C2	117.8 (3)
O3—S1—N1	109.64 (17)	S1—C1—C6	116.6 (3)
O3—S1—C1	105.83 (17)	S1—C1—C2	125.2 (3)
O4—S1—N1	107.18 (17)	N2—C2—C1	122.1 (3)
O4—S1—C1	105.93 (17)	N2—C2—C3	116.3 (3)
N1—S1—C1	107.58 (15)	N1—C7—C8	113.7 (3)
C8—O6—C9	117.2 (3)	O6—C8—C7	108.9 (3)
S1—N1—C7	122.4 (3)	O5—C8—O6	125.6 (4)
O1—N2—O2	124.4 (4)	O5—C8—C7	125.5 (4)
O1—N2—C2	117.8 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.84	2.57	3.040 (5)	116
N1—H1···O3^{i}	0.84	2.13	2.941 (4)	160
C6—H6···O4	0.95	2.42	2.824 (5)	105
C7—H7*A*···O5^{i}	0.96	2.53	3.257 (5)	133

Symmetry code: (i) $x, -y + \frac{3}{2}, +z + \frac{1}{2}$.

H atoms attached to C atoms were constrained as riding atoms, with C—H set to 0.95 Å. U_{iso}(H) values were set to 1.2U_{eq} of the parent atom. The amide H atom was located in a difference Fourier

synthesis and constrained as a riding atom with N—H set at 0.85 Å.

Data collection: *MSC/AFC7 Diffractometer Control Software for Windows* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC7 Diffractometer Control Software for Windows*; 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: *PLATON* (Spek, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON*.

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References

Albanese, D., Landini, D., Lupi, V. & Penso, M. (2000). *Eur. J. Org. Chem.* pp. 1443–1449.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 155–1573.

Bornaghi, L. F., Poulsen, S -A. & Healy, P. C. (2004). *Acta Cryst.* E**60**, o383–o385.

Falkiewicz, B., Kołodziejczyk, A. S., Liberek, B. & Wiśnieski, K. (2001). *Tetrahedron*, **57**, 7909–7917.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Giraldés, J., McLaughlin, M. L. & Fronczek, F. R. (2001). *Acta Cryst.* E**57**, o48–o49.

Hammarström, L. G. J., Zhang, T., Giraldés, J., McLaughlin, M. L., Billodeaux, D. R. & Fronczek, F. R. (2000). *Acta Cryst.* C**56**, 1484–1486.

Iacopino, D., Menabue, L. & Salidini, M. (1999). *Aust. J. Chem.* **52**, 741–748.

Kan, T. & Fukuyama, T. (2004). *Chem. Commun.* pp. 353–359.

Molecular Structure Corporation (1999). *MSC/AFC7 Diffractometer Control Software for Windows*. Version 1.02. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Molecular Structure Corporation. (2001). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Poulsen, S.-A, Noack, C. L. & Healy, P. C. (2003). *Acta Cryst.* E**59**, o967–o968.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2001). *PLATON for Windows*. Version 121201. University of Utrecht, The Netherlands.