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N-Allyl-*N*-(2-nitrobenzenesulfonyl)-L-phenylalanine methyl ester

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Key indicators

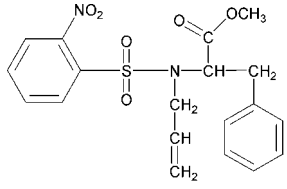
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
R factor = 0.040
wR factor = 0.123
Data-to-parameter ratio = 11.0

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, $C_{19}H_{20}N_2O_6S$, has been determined as part of an ongoing investigation into the preparation of bis-*N*-alkylated amino acids for subsequent alkene cross-metathesis reactions to generate dynamic combinatorial libraries. The overall molecular conformation is stabilized by well defined intramolecular C—H···O interactions.

Comment

The synthesis of a range of *N*-allyl substituted amino acids is desirable for the investigation of the biological applications of these molecules, as cross-metathesis of the allyl moieties permits a combinatorial approach to the generation of libraries for biological screening. In this approach, both protection and activation of the amino acid nitrogen is required in order to facilitate subsequent high-yielding mono-allylation. The 2-nitrobenzenesulfonyl group (oNBS) is introduced prior to allylation and serves a dual role of protection and activation, with the electron-withdrawing effect of the oNBS group greatly increasing the acidity of the amino H atom.



(I)

The title compound, (I), crystallizes in the space group $P2_12_12_1$ with one molecule in the asymmetric unit (Fig. 1). Molecules are separated by normal van der Waals distances. The bond lengths (Table 1) are in accord with conventional values (Allen *et al.*, 1987). The conformational structure and shape of the molecules of (I) appear to be determined by a number of well defined intramolecular C—H···O interactions (Table 2) with, for example, the 2-nitrobenzenesulfonyl group 'spiralling' above the plane of the carboxylate group to bring nitro atom O2 into close proximity to the α carbon C7. It is of interest to note also in this structure, that the geometry about the amino N atom is almost trigonal planar with S1—N2—C10 = 116.7 (2)°, S1—N2—C7 = 120.5 (2)° and C7—N2—C10 = 118.8 (3)° (Σ = 355.9°).

Experimental

Compound (I) was synthesized following published procedures (Reichwein & Liskamp, 2000). Allyl bromide (2.85 ml, 32.93 mmol)

was added to a solution of 2-nitrobenzenesulfonyl-L-phenylalanine methyl ester (6.485 g, 17.8 mmol) and K_2CO_3 (4.98 g, 36.05 mmol) in anhydrous DMF (50 ml) and the mixture stirred at room temperature for 16 h. Water (40 ml) was added and the mixture extracted from ether (3 × 30 ml), the combined extracts washed with brine (3 × 40 ml) and dried over $MgSO_4$ before solvent was removed under reduced pressure. The resultant yellow oil afforded colourless crystals on standing. Yield: 6.51 g (90.4%); m.p. 326–327 K; ^{1}H NMR ($CDCl_3$, 200 MHz, p.p.m.): 7.54–7.85 [*m*, 4H, CH_{arom}(oNBS)], 7.18–7.28 (*m*, 5H, CH_{arom}Phe), 5.70–5.85(*m*, 1H, HC═), 5.07–5.28 (*m*, 2H, ═CH_2), 4.91 (*t*, 1H, J = 7.4 Hz, αCH), 3.85–4.20 (*m*, 2H, βCH_2), 3.55 (*s*, 3H, OCH_3), 3.36 (*dd*, 1H, ^2J = 14 Hz, ^3J = 7.4 Hz, NCH of NCH_2), 3.04 (*dd*, 1H,^2J = 14 Hz, ^3J = 7.4 Hz, NCH of NCH_2).

Crystal data

$C_{19}H_{20}N_2O_6S$
M_r = 404.44
Orthorhombic, $P2_12_12_1$
a = 9.2756 (15) Å
b = 27.430 (4) Å
c = 7.8548 (12) Å
V = 1998.5 (5) Å^3
Z = 4
D_x = 1.344 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 12.6–17.0°
μ = 0.20 mm^{-1}
T = 295 K
Prism, colourless
0.50 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω scans
Absorption correction: none
3271 measured reflections
2796 independent reflections
2049 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.5°
$h = -5 \rightarrow 12$
$k = 0 \rightarrow 35$
$l = -4 \rightarrow 10$
3 standard reflections
every 150 reflections
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.123
S = 1.03
2796 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.3341P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.035
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0066 (16)
Absolute structure: Flack (1983)
Flack parameter = 0.15 (14)

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.425 (3)	O6—C9	1.453 (5)
S1—O4	1.427 (3)	N1—C2	1.478 (5)
S1—N2	1.619 (3)	N2—C7	1.462 (4)
S1—C1	1.778 (3)	N2—C10	1.474 (5)
O1—N1	1.204 (6)	C7—C13	1.528 (5)
O2—N1	1.217 (5)	C10—C11	1.467 (7)
O5—C8	1.194 (5)	C11—C12	1.157 (8)
O6—C8	1.330 (4)	C13—C14	1.521 (5)
O3—S1—O4	119.47 (16)	S1—C1—C2	124.7 (3)
O3—S1—N2	108.23 (15)	S1—C1—C6	117.5 (3)
O3—S1—C1	107.62 (17)	C2—C1—C6	117.8 (3)
O4—S1—N2	106.83 (16)	N1—C2—C1	122.9 (3)
O4—S1—C1	105.74 (15)	N1—C2—C3	115.7 (4)
N2—S1—C1	108.56 (15)	N2—C7—C8	111.5 (3)
C8—O6—C9	116.2 (3)	N2—C7—C13	111.8 (3)
O1—N1—O2	124.9 (4)	C8—C7—C13	111.2 (3)
O1—N1—C2	116.3 (4)	O5—C8—O6	125.2 (3)
O2—N1—C2	118.8 (4)	O5—C8—C7	124.9 (3)
S1—N2—C7	120.5 (2)	O6—C8—C7	109.9 (3)
S1—N2—C10	116.7 (2)	N2—C10—C11	117.0 (4)
C7—N2—C10	118.8 (3)		

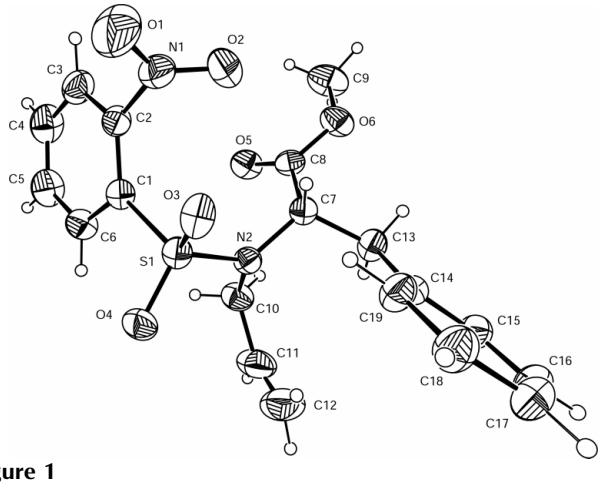


Figure 1
View of the title compound, with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O4	0.95	2.49	2.870 (4)	104
C7—H7···O2	0.95	2.55	3.123 (5)	119
C7—H7···O3	0.95	2.39	2.900 (4)	113
C19—H19···O3	0.95	2.51	3.403 (4)	157
C10—H101···O5	0.96	2.52	2.972 (5)	109
C13—H132···O6	0.96	2.40	2.827 (5)	107

H atoms were constrained as riding atoms, with C—H distances set to 0.95 Å.

Data collection: *MSC/AFC-7 Diffractometer Control Software for Windows* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC-7 Diffractometer Control Software for Windows*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–2001); program(s) used to solve structure: *TEXSAN for Windows*; program(s) used to refine structure: *TEXSAN for Windows* and *SHELXL*97 (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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