N-allyl-N-(2-nitrobenzenesulfonyl)-L-leucine methyl ester

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N-Allyl-N-(2-nitrobenzenesulfonyl)-L-leucine methyl ester

The structure of the title compound, C_{16}H_{22}N_{2}O_{6}S, has been determined as part of an ongoing investigation into the preparation of N-alkylated amino acid precursors for alkene cross-metathesis reactions for the generation of dynamic combinatorial libraries. The overall molecular conformation is stabilized by intramolecular C–H⋯O interactions.

Comment

As part of our interest in the development of dynamic combinatorial libraries (Cousins et al., 1999; Ramstrom & Lehn, 2000; Bunyapaiboonsri et al., 2001; Lehn & Eliseev, 2001), we have synthesized a range of N-allyl-substituted amino acids as precursors for cross-metathesis of amino acids using Grubbs catalysts (Fürstner, 2000; Connon & Blechert, 2003). In this approach, the 2-nitrobenzenesulfonyl group (oNBS) is introduced prior to allylation in order to, firstly, protect the nitrogen, and secondly, increase the acidity of the NH proton such that the amide becomes more susceptible to allylation. We have previously reported the structure of N-allyl-N-(2-nitrobenzenesulfonyl)-L-phenylalanine methyl ester (Poulsen et al., 2003). In the present communication, we report the structure of the related compound N-allyl-N-(2-nitrobenzenesulfonyl)-L-leucine methyl ester, (I).

The molecules of (I) are separated by normal van der Waals distances, with bond lengths in accord with conventional values (Allen et al., 1987) (Table 1). The conformational structure of (I) (Fig. 1) is very similar to that of the phenylalanine analog, with the shape determined by a number of intramolecular C–H⋯O interactions (Table 2) and the ‘spiralling’ of the 2-nitrobenzenesulfonyl group above the plane of the carboxylate group to bring nitro atom O2 into close proximity to α atom C7.

Experimental

Similar to the L-phenylalanine analog, (I) was prepared in accord with published procedures (Reichwein & Liskamp, 2000). To a solution of 2-nitrobenzenesulfonyl-L-leucine methyl ester (9.09 g, 27.5 mmol) were added K_{2}CO_{3} (7.6 g, 55 mmol) and allyl bromide (3.65 ml, 42 mmol) in anhydrous DMF (120 ml). The reaction mixture was stirred at room temperature for 18 h. Water (200 ml) was added

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean σ(C–C) = 0.007 Å

R factor = 0.040

wR factor = 0.120

Data-to-parameter ratio = 10.4

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

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and the mixture was extracted with diethyl ether (3 × 150 ml). The combined extracts were washed with brine (2 × 200 ml) and dried over MgSO₄. The solvent was removed under reduced pressure to give an oily yellow residue. Crystals of (I) suitable for X-ray diffraction studies were obtained by crystallization from a mixture of hexane and ethyl acetate (yield 7.6 g, 83%; m.p. 342 K). ¹H NMR (CDCl₃, 200 MHz, p.p.m.): 0.92 (d, 3H, J = 6.1 Hz, CH₃), 1.65–1.80 (m, 3H, γ-CH and β-CH₂), 3.55 (s, 3H, OCH₃), 3.80–3.92 (m, 1H, NCH of NCH₂), 4.11–4.22 (m, 1H, NCH of NCH₂), 4.69–4.77 (m, 1H, α-CH), 5.11–5.26 (m, 2H, = CH₂), 5.87–6.07 (m, 1H, =CH), 7.57–7.72 (m, 3H, ArH), 8.02–8.10 (m, 1H, ArH). ¹³C NMR (CDCl₃, 50 MHz, p.p.m.): 21.4 and 22.9 (CH₃), 24.4 (CH₃), 59.2 (OCH₃), 117.8 (=CH₂), 124.2, 131.4, 131.6, 133.2, 133.7, 135.6 and 148.3 (CH from Ar and = CH), 172.0 (CO). MS (LRMSES): m/z 371.1 [M + H]⁺, 393.1 [M + Na]⁺.

Crystal data

C₁₆H₂₂N₂O₆S, Mr = 370.43
Monoclinic, C2
a = 15.7515 (15) Å
b = 8.2452 (17) Å
c = 15.673 (2) Å
β = 110.153 (9)°
V = 1910.9 (5) Å³
Z = 4

Data collection

Rigaku AFC-7R diffractometer
θ = h = 8 → 20
ω–2θ scans
Absorption correction: none
2590 measured reflections
2353 independent reflections
2334 reflections with I > 2σ(I)
Rint = 0.025

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.040
w = 1/[σ²(F²) + 0.0061P²]
where P² = (F² + 2F₀²)/3
(Δσ/σ)max = 0.009
Δρmax = 0.16 e Å⁻³
Δρmin = 0.21 e Å⁻³

H atoms were constrained as riding atoms, with C–H distances set at 0.95 Å. Ueq(H) values were set at 1.2Ueq of the parent atom.

Data collection: MSC/AFC-7 Diffractometer Control for Windows (Molecular Structure Corporation, 1999); cell refinement: MSC/AFC-7 Diffractometer Control 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 SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2002) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: TEXSAN for Windows and PLATON.

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References


