Table 2. *Selected geometric parameters* (Å, °)

Starred atoms are related to the corresponding unstarred atoms by rotation about a twofold axis.

C(1)—C(2)	1.384 (2)	C(7)—C(8)	1.399 (3)
C(1)—C(10)	1.431 (2)	C(8)—C(9)	1.369 (3)
C(1)—C(11)	1.494 (2)	C(9)—C(10)	1.418 (2)
C(2)—C(3)	1.433 (2)	C(35)—C(36)	1.380 (2)
C(2)—C(17)	1.494 (2)	C(35)—C(39)	1.429 (2)
C(3)—C(4)	1.387 (2)	C(35)—C(46)	1.500 (2)
C(3)—C(23)	1.494 (2)	C(36)—C(36)*	1.442 (3)
C(4)—C(5)	1.428 (2)	C(36)—C(40)	1.492 (2)
C(4)—C(29)	1.496 (2)	C(37)—C(37)*	1.415 (3)
C(5)—C(6)	1.423 (2)	C(37)—C(38)	1.371 (2)
C(5)—C(10)	1.426 (2)	C(38)—C(39)	1.416 (2)
C(6)—C(7)	1.365 (3)	C(39)—C(39)*	1.431 (3)
C(2)—C(1)—C(10)	120.0 (2)	C(7)—C(8)—C(9)	120.8 (2)
C(2)—C(1)—C(11)	119.8 (1)	C(8)—C(9)—C(10)	120.5 (2)
C(10)—C(1)—C(11)	120.2 (1)	C(1)—C(10)—C(5)	119.5 (1)
C(1)—C(2)—C(3)	120.4 (1)	C(1)—C(10)—C(9)	121.7 (2)
C(1)—C(2)—C(17)	120.8 (1)	C(5)—C(10)—C(9)	118.8 (2)
C(3)—C(2)—C(17)	118.8 (1)	C(36)—C(35)—C(39)	120.7 (1)
C(2)—C(3)—C(4)	120.5 (1)	C(36)—C(35)—C(46)	121.9 (1)
C(2)—C(3)—C(23)	119.5 (1)	C(39)—C(35)—C(46)	117.4 (1)
C(4)—C(3)—C(23)	120.0 (1)	C(35)—C(36)—C(36)*	120.07 (9)
C(3)—C(4)—C(5)	119.8 (2)	C(35)—C(36)—C(40)	119.9 (1)
C(3)—C(4)—C(29)	120.1 (1)	C(36)*—C(36)—C(40)	120.02 (8)
C(5)—C(4)—C(29)	120.0 (1)	C(37)*—C(37)—C(38)	119.6 (1)
C(4)—C(5)—C(6)	121.7 (2)	C(37)—C(38)—C(39)	122.2 (2)
C(4)—C(5)—C(10)	119.7 (1)	C(35)—C(39)—C(38)	122.6 (1)
C(6)—C(5)—C(10)	118.6 (2)	C(35)—C(39)—C(39)*	119.19 (8)
C(5)—C(6)—C(7)	120.8 (2)	C(38)—C(39)—C(39)*	118.2 (1)
C(6)—C(7)—C(8)	120.4 (2)		

C(2)—C(1)—C(11)—C(16)	64.9 (2)
C(3)—C(2)—C(17)—C(22)	67.2 (2)
C(4)—C(3)—C(23)—C(28)	65.7 (2)
C(5)—C(4)—C(29)—C(34)	73.9 (2)
C(36)—C(35)—C(46)—C(51)	−76.0 (2)
C(36)*—C(36)—C(40)—C(45)	−62.7 (2)

The rather high value of R_{int} is probably a consequence of the very large fluctuations in the laboratory temperature during data collection. ψ scan results indicated that absorption was negligible. Data collection and cell determination: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction and structure refinement: *TEXSAN* (Molecular Structure Corporation, 1985). Structure solution: *SHELXS*86 (Sheldrick, 1985). H atoms were placed in calculated positions and were not refined. A precautionary check for higher symmetry was conducted using the program *MISSYM* (Le Page, 1987) and none was found. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzyl 2-[*N*-Benzyl-*N*-(*p*-toluenesulfonyl)-amino]-2-phenylacetate and its α-Amino Acid

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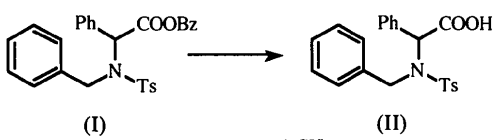
Abstract

The structures of benzyl 2-[*N*-benzyl-*N*-(*p*-toluenesulfonyl)amino]-2-phenylacetate, $C_{29}H_{27}NO_4S$, (I), and 2-[*N*-benzyl-*N*-(*p*-toluenesulfonyl)amino]-2-phenylacetic acid, $C_{22}H_{21}NO_4S$, (II), have been

determined. The geometries of both compounds are similar. The N atoms and the carboxylic C atoms are sp^2 hybridized. The N—C(8)—C(9)—O(3) torsion angle in compound (I) [−18.4 (5)°] and the N—C(8)—C(15)—O(4) torsion angle in compound (II) [9.6 (4)°] characterize a synperiplanar conformation for the N atom and the O atom of the C=O group in both compounds studied.

Comment

In the course of our studies aimed at the synthesis of isoquinoline alkaloids, we have prepared the intermediates benzyl 2-[*N*-benzyl-*N*-(*p*-toluenesulfonyl)-amino]-2-phenylacetate, (I), and its corresponding α-amino acid, 2-[*N*-benzyl-*N*-(*p*-toluenesulfonyl)-amino]-2-phenylacetic acid, (II). There is increasing interest in α-amino acids and their derivatives from biological, biochemical, chemical and medical points of view (Williams, 1989). Consequently, the crystallographic study of compounds (I) and (II) was undertaken.



(I) (II)

Ts = $-SO_2C_6H_4CH_3$
Bz = $-CH_2C_6H_5$
Ph = $-C_6H_5$

The ester (I) was prepared by an alkylation reaction of *N*-tosyl-protected 2-phenylglycine with benzyl bromide under standard conditions. The subsequent debenzylation (H_2/Pt) of (I) gave, quantitatively, the α-amino acid (II). Compounds (I) and (II) were crystallized from methanol and ethanol, respectively, and fully characterized by means of spectroscopic data (NMR, IR and MS). *SCHAKAL* diagrams (Keller, 1988) of the molecules with atom-numbering schemes are shown in Figs. 1 and 2, and views of the unit-cell packing are given in Figs. 3 and 4.

The X-ray crystallographic analyses of (I) and (II) showed the similarity between the structures. The carboxylic C atom is sp^2 hybridized; the sum of the bond angles around this atom is 359.95° in (I) and 359.96° in (II). The sum of the bond angles around the N atom is 358.7 and 356.6° in (I) and (II), respectively. Moreover, the N atoms lie 0.100 (3) Å in (I) and 0.164 (2) Å in (II) out of the planes defined by the three adjacent atoms for each compound. This behaviour suggests that the N atom in each compound is sp^2 hybridized in order to allow the remaining filled *p* orbital to interact more effectively in *d*–*p* π bonding with the S atom (Cook, Glick, Rigau & Johnson, 1971). From the data above, we are able to propose partial sp^3 character for the N atoms, retained by slight but significant pyramidalization. In addition, the S—N bond lengths [1.616 (3) in (I) and 1.631 (2) Å in (II)] show considerable double-bond character, which is consistent with sp^2 character for the N atoms (Singh, Tiwari & Singh, 1985).

Both molecules show a synperiplanar conformation between the N atom and the O atom of the C=O group, with torsion angles N—C(8)—C(9)—O(3) −18.4 (5) in (I) and N—C(8)—C(15)—O(4) 9.6 (4)° in (II), thus allowing the tosyl group to be

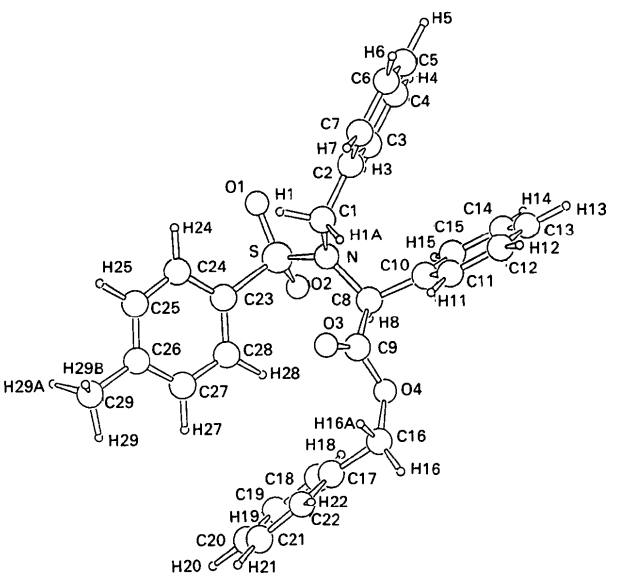


Fig. 1. A view of the ester (I) showing the atomic labelling scheme.

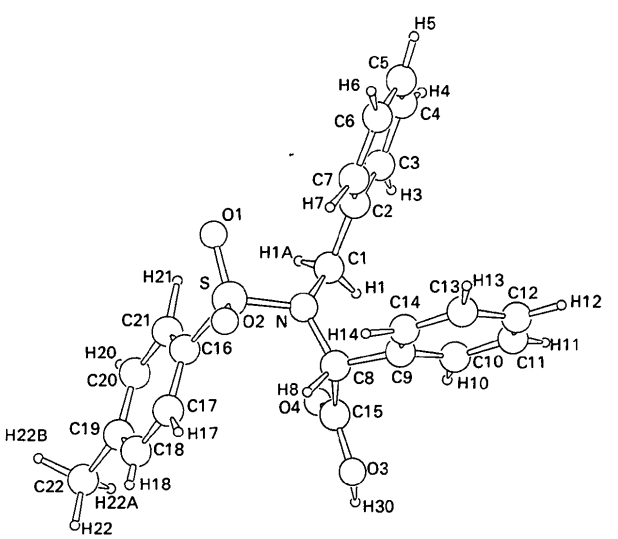


Fig. 2. A view of the α-amino acid (II) showing the atomic labelling scheme.

eclipsed only by the H(8) atom [S—N—C(8)—H(8) torsion angles: 20.8 (4) in (I) and −11 (2)° in (II)]. The benzyl group attached to the N atom shows synclinal conformation with the remaining groups at C(8) as shown by the torsion angles C(1)—N—C(8)—C(10) −55.1 (4)° and C(1)—N—C(8)—C(9) 72.0 (4)° for (I), and C(1)—N—C(8)—C(9) 65.2 (3)° and C(1)—N—C(8)—C(15) −62.9 (3)° for (II). The phenyl ring in (II) attached to C(1) is coplanar with C(1), N and C(2) [N—C(1)—C(2)—C(3) and N—C(1)—C(2)—C(7) being 178.8 (3) and −2.7 (4)°, respectively].

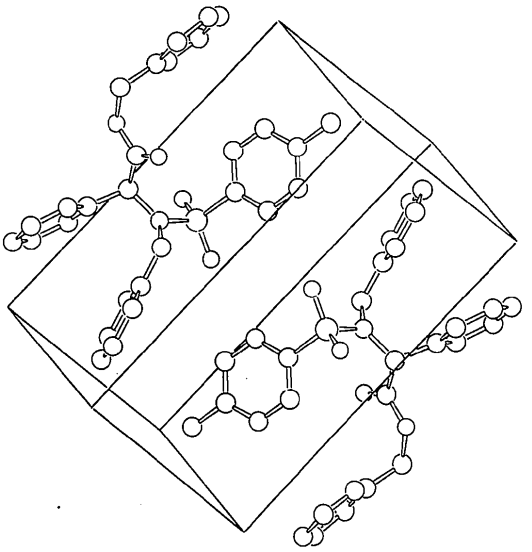


Fig. 3. Crystal packing of the ester (I).

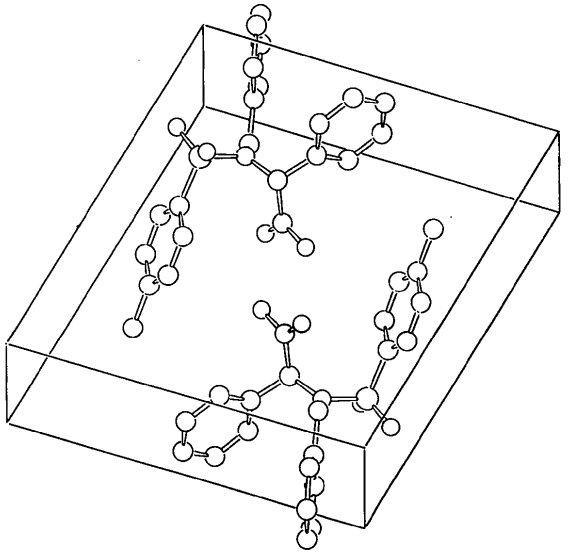


Fig. 4. Crystal packing of the α-amino acid (II).

Experimental

Compound (I)

Crystal data

$C_{29}H_{27}NO_4S$
$M_r = 485.6$
Triclinic
$P\bar{1}$
$a = 13.875$ (4) Å
$b = 11.701$ (3) Å
$c = 8.289$ (2) Å
$\alpha = 73.85$ (2)°
$\beta = 83.60$ (2)°
$\gamma = 76.86$ (3)°
$V = 1257.1$ (9) Å^3
$Z = 2$
$D_x = 1.280$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–14°
$\mu = 0.166$ mm^{-1}
$T = 298$ K
Prismatic
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Philips PW-1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2938 measured reflections
2938 independent reflections
2504 observed reflections [$I \geq 2.5\sigma(I)$]
$\theta_{max} = 30°$
$h = -21 \rightarrow 21$
$k = -18 \rightarrow 18$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity variation: < 1.0%

Refinement

Refinement on F
$R = 0.061$
$wR = 0.057$
$S = 1.32$
2504 reflections
317 parameters
Only coordinates of H atoms refined
$w = 1/(\sigma^2|F_o| + 0.015|F_o|^2)$
$(\Delta/\sigma)_{max} = 0.04$
$\Delta\rho_{max} = 0.7$ e Å^{-3}
$\Delta\rho_{min} = -0.7$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
S	0.51119 (6)	−0.24481 (8)	0.23374 (10)	3.44 (4)
N	0.5680 (2)	−0.2851 (2)	0.0710 (3)	3.23 (11)
O(1)	0.5624 (2)	−0.3210 (3)	0.3780 (3)	4.83 (12)
O(2)	0.4991 (2)	−0.1153 (2)	0.1945 (3)	4.70 (13)
O(3)	0.4415 (2)	−0.3011 (3)	−0.1675 (4)	5.41 (13)
O(4)	0.4533 (2)	−0.1127 (2)	−0.3166 (3)	4.35 (12)
C(1)	0.6106 (2)	−0.4163 (3)	0.0863 (4)	3.80 (14)
C(2)	0.7183 (2)	−0.4559 (3)	0.1199 (4)	3.55 (13)
C(3)	0.7711 (3)	−0.3838 (4)	0.1729 (5)	4.64 (17)
C(4)	0.8714 (3)	−0.4248 (4)	0.2006 (6)	5.60 (20)
C(5)	0.9202 (3)	−0.5361 (5)	0.1777 (6)	6.11 (22)
C(6)	0.8709 (4)	−0.6067 (5)	0.1275 (7)	6.80 (25)
C(7)	0.7688 (3)	−0.5655 (4)	0.0966 (6)	5.51 (20)
C(8)	0.5598 (2)	−0.1986 (3)	−0.0993 (4)	2.96 (12)
C(9)	0.4789 (2)	−0.2134 (3)	−0.1974 (4)	3.30 (13)
C(10)	0.6589 (2)	−0.2056 (3)	−0.1962 (4)	3.36 (13)

C(11)	0.6876 (3)	−0.2745 (4)	−0.3106 (5)	4.54 (17)
C(12)	0.7818 (3)	−0.2819 (4)	−0.3883 (5)	5.56 (21)
C(13)	0.8474 (3)	−0.2184 (5)	−0.3573 (6)	5.63 (21)
C(14)	0.8183 (3)	−0.1482 (5)	−0.2481 (6)	5.94 (22)
C(15)	0.7242 (3)	−0.1390 (4)	−0.1687 (5)	4.42 (16)
C(16)	0.3750 (3)	−0.1046 (4)	−0.4255 (5)	4.88 (18)
C(17)	0.2744 (2)	−0.0647 (4)	−0.3482 (4)	4.20 (16)
C(18)	0.2576 (3)	0.0235 (4)	−0.2565 (5)	5.01 (18)
C(19)	0.1649 (4)	0.0642 (5)	−0.1933 (6)	6.63 (26)
C(20)	0.0867 (4)	0.0214 (5)	−0.2224 (6)	6.75 (25)
C(21)	0.0994 (3)	−0.0625 (5)	−0.3156 (8)	7.38 (28)
C(22)	0.1952 (3)	−0.1071 (4)	−0.3752 (6)	5.80 (21)
C(23)	0.3915 (2)	−0.2778 (3)	0.2563 (4)	3.37 (14)
C(24)	0.3710 (3)	−0.3792 (3)	0.3783 (4)	4.46 (16)
C(25)	0.2763 (3)	−0.4011 (4)	0.3966 (5)	4.90 (18)
C(26)	0.2010 (3)	−0.3242 (4)	0.2992 (5)	4.69 (18)
C(27)	0.2229 (3)	−0.2241 (4)	0.1802 (5)	4.76 (17)
C(28)	0.3178 (2)	−0.1996 (3)	0.1562 (4)	4.09 (15)
C(29)	0.0987 (3)	−0.3527 (5)	0.3220 (7)	7.05 (26)

Table 2. *Selected geometric parameters* (Å, °) *for* (I)

N—S	1.616 (3)	C(12)—C(11)	1.386 (5)
O(1)—S	1.428 (3)	C(13)—C(12)	1.383 (7)
O(2)—S	1.433 (3)	C(14)—C(13)	1.356 (7)
C(23)—S	1.768 (3)	C(15)—C(14)	1.390 (5)
C(1)—N	1.489 (4)	C(17)—C(16)	1.500 (5)
C(8)—N	1.489 (4)	C(18)—C(17)	1.408 (6)
C(9)—O(3)	1.206 (4)	C(22)—C(17)	1.366 (5)
C(9)—O(4)	1.316 (4)	C(19)—C(18)	1.367 (6)
C(16)—O(4)	1.459 (4)	C(20)—C(19)	1.363 (8)
C(2)—C(1)	1.494 (4)	C(21)—C(20)	1.380 (8)
C(3)—C(2)	1.414 (5)	C(22)—C(21)	1.401 (7)
C(7)—C(2)	1.368 (5)	C(24)—C(23)	1.390 (5)
C(4)—C(3)	1.387 (5)	C(28)—C(23)	1.383 (4)
C(5)—C(4)	1.378 (6)	C(25)—C(24)	1.379 (5)
C(6)—C(5)	1.355 (7)	C(26)—C(25)	1.382 (5)
C(7)—C(6)	1.416 (6)	C(27)—C(26)	1.374 (5)
C(9)—C(8)	1.523 (4)	C(29)—C(26)	1.511 (5)
C(10)—C(8)	1.511 (4)	C(28)—C(27)	1.393 (5)
C(11)—C(10)	1.379 (5)	C(15)—C(10)	1.395 (4)
O(1)—S—N	107.5 (1)	C(15)—C(10)—C(8)	118.3 (3)
O(2)—S—N	106.3 (1)	C(15)—C(10)—C(11)	118.6 (3)
O(2)—S—O(1)	120.7 (2)	C(12)—C(11)—C(10)	120.0 (4)
C(23)—S—N	108.0 (1)	C(13)—C(12)—C(11)	121.3 (4)
C(23)—S—O(1)	106.6 (1)	C(14)—C(13)—C(12)	118.8 (4)
C(23)—S—O(2)	107.3 (2)	C(15)—C(14)—C(13)	121.1 (4)
C(1)—N—S	118.9 (2)	C(14)—C(15)—C(10)	120.2 (4)
C(8)—N—S	120.7 (2)	C(17)—C(16)—O(4)	111.4 (3)
C(8)—N—C(1)	119.1 (3)	C(18)—C(17)—C(16)	121.0 (3)
C(16)—O(4)—C(9)	118.8 (3)	C(22)—C(17)—C(16)	120.4 (4)
C(2)—C(1)—N	115.3 (3)	C(22)—C(17)—C(18)	118.4 (4)
C(3)—C(2)—C(1)	122.7 (3)	C(19)—C(18)—C(17)	120.9 (4)
C(7)—C(2)—C(1)	119.1 (3)	C(20)—C(19)—C(18)	119.8 (5)
C(7)—C(2)—C(3)	118.2 (3)	C(21)—C(20)—C(19)	121.0 (4)
C(4)—C(3)—C(2)	120.1 (4)	C(22)—C(21)—C(20)	118.9 (5)
C(5)—C(4)—C(3)	120.4 (4)	C(21)—C(22)—C(17)	120.8 (5)
C(6)—C(5)—C(4)	120.4 (4)	C(24)—C(23)—S	120.0 (2)
C(7)—C(6)—C(5)	119.9 (4)	C(28)—C(23)—S	119.5 (3)
C(6)—C(7)—C(2)	121.0 (4)	C(28)—C(23)—C(24)	120.5 (3)
C(9)—C(8)—N	112.6 (2)	C(25)—C(24)—C(23)	118.9 (3)
C(10)—C(8)—N	111.1 (2)	C(26)—C(25)—C(24)	122.0 (3)
C(10)—C(8)—C(9)	112.4 (3)	C(27)—C(26)—C(25)	118.1 (3)
O(4)—C(9)—O(3)	125.2 (3)	C(29)—C(26)—C(25)	120.2 (4)
C(8)—C(9)—O(3)	125.9 (3)	C(29)—C(26)—C(27)	121.8 (4)
C(8)—C(9)—O(4)	108.9 (3)	C(28)—C(27)—C(26)	121.8 (3)
C(11)—C(10)—C(8)	123.1 (3)	C(27)—C(28)—C(23)	118.8 (3)

Compound (II)

Crystal data

$C_{22}H_{21}NO_4S$
$M_r = 395.48$
Triclinic
$P\bar{1}$
$a = 13.801\ (3)$ Å
$b = 12.307\ (3)$ Å
$c = 6.417\ (2)$ Å
$\alpha = 76.74\ (2)°$
$\beta = 82.18\ (2)°$
$\gamma = 72.84\ (3)°$
$V = 1010.9\ (8)$ Å^3
$Z = 2$
$D_x = 1.299$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8–16°$
$\mu = 0.189$ mm^{-1}
$T = 298$ K
Prismatic
0.2 × 0.15 × 0.1 mm
Colourless

Data collection

Philips PW-1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4132 measured reflections
4132 independent reflections
2507 observed reflections [$I \geq 2.5\sigma(I)$]
$\theta_{max} = 30°$
$h = -21 \rightarrow 21$
$k = -18 \rightarrow 18$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity variation: < 1.0%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.053$
$S = 1.17$
2507 reflections
305 parameters
Only coordinates of H atoms refined
$w = 1/(\sigma^2|F_o| + 0.004|F_o|^2)$
$(\Delta/\sigma)_{max} = 0.06$
$\Delta\rho_{max} = 0.4$ e Å^{-3}
$\Delta\rho_{min} = -0.5$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.68320 (5)	0.16616 (5)	0.14888 (10)	4.22 (3)
N	0.7285 (1)	0.2676 (2)	0.1880 (3)	3.54 (7)
O(1)	0.7568 (2)	0.0598 (2)	0.2175 (4)	6.56 (11)
O(2)	0.6544 (2)	0.1998 (2)	−0.0692 (3)	6.46 (12)
O(3)	0.5387 (2)	0.5411 (2)	0.2104 (3)	5.18 (8)
O(4)	0.6007 (1)	0.3938 (2)	0.4747 (3)	4.66 (7)
C(1)	0.7991 (2)	0.2394 (3)	0.3613 (4)	4.21 (10)
C(2)	0.9095 (2)	0.1920 (2)	0.2980 (4)	3.63 (9)
C(3)	0.9781 (2)	0.1665 (3)	0.4509 (4)	5.22 (13)
C(4)	1.0821 (2)	0.1167 (4)	0.4073 (6)	6.79 (18)
C(5)	1.1173 (2)	0.0970 (3)	0.2068 (6)	6.13 (14)
C(6)	1.0525 (2)	0.1211 (3)	0.0554 (5)	6.49 (16)
C(7)	0.9479 (2)	0.1692 (3)	0.0976 (5)	5.95 (14)
C(8)	0.6738 (2)	0.3883 (2)	0.1092 (3)	3.38 (8)
C(9)	0.7472 (2)	0.4583 (2)	−0.0016 (4)	3.95 (9)
C(10)	0.7802 (2)	0.5276 (3)	0.0990 (5)	5.65 (14)
C(11)	0.8542 (3)	0.5814 (4)	−0.0064 (8)	7.91 (23)
C(12)	0.8926 (3)	0.5683 (4)	−0.2113 (7)	7.84 (20)
C(13)	0.8608 (3)	0.4975 (4)	−0.3095 (6)	7.41 (19)
C(14)	0.7875 (2)	0.4438 (3)	−0.2052 (4)	5.44 (13)
C(15)	0.6014 (2)	0.4416 (2)	0.2854 (4)	3.62 (9)
C(16)	0.5728 (2)	0.1679 (2)	0.3202 (4)	4.12 (10)
C(17)	0.4779 (3)	0.2301 (3)	0.2432 (7)	6.56 (17)
C(18)	0.3930 (3)	0.2357 (4)	0.3817 (10)	8.63 (24)
C(19)	0.3968 (3)	0.1820 (3)	0.5925 (8)	7.51 (21)
C(20)	0.4916 (4)	0.1195 (4)	0.6662 (6)	7.91 (23)
C(21)	0.5793 (3)	0.1118 (3)	0.5323 (5)	6.07 (16)
C(22)	0.3029 (4)	0.1878 (4)	0.7458 (10)	11.62 (34)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

N—S	1.631 (2)	C(9)—C(8)	1.520 (3)
O(1)—S	1.418 (2)	C(15)—C(8)	1.534 (3)
O(2)—S	1.441 (2)	C(10)—C(9)	1.384 (4)
C(16)—S	1.751 (3)	C(14)—C(9)	1.378 (3)
C(1)—N	1.492 (3)	C(11)—C(10)	1.395 (5)
C(8)—N	1.459 (3)	C(12)—C(11)	1.376 (6)
C(15)—O(3)	1.303 (3)	C(13)—C(12)	1.378 (6)
C(15)—O(4)	1.222 (3)	C(14)—C(13)	1.384 (5)
C(2)—C(1)	1.498 (3)	C(17)—C(16)	1.399 (4)
C(3)—C(2)	1.376 (3)	C(21)—C(16)	1.379 (4)
C(7)—C(2)	1.380 (3)	C(18)—C(17)	1.366 (5)
C(4)—C(3)	1.401 (4)	C(19)—C(18)	1.364 (7)
C(5)—C(4)	1.361 (5)	C(20)—C(19)	1.391 (6)
C(6)—C(5)	1.334 (5)	C(22)—C(19)	1.511 (5)
C(7)—C(6)	1.403 (4)	C(21)—C(20)	1.378 (5)
O(1)—S—N	105.9 (1)	C(10)—C(9)—C(8)	122.9 (2)
O(2)—S—N	106.4 (1)	C(14)—C(9)—C(8)	117.4 (2)
O(2)—S—O(1)	120.5 (1)	C(14)—C(9)—C(10)	119.5 (2)
C(16)—S—N	107.3 (1)	C(11)—C(10)—C(9)	119.6 (3)
C(16)—S—O(1)	107.9 (1)	C(12)—C(11)—C(10)	120.4 (4)
C(16)—S—O(2)	108.1 (1)	C(13)—C(12)—C(11)	119.8 (3)
C(1)—N—S	118.9 (2)	C(14)—C(13)—C(12)	119.9 (3)
C(8)—N—S	118.2 (1)	C(13)—C(14)—C(9)	120.7 (3)
C(8)—N—C(1)	119.5 (2)	O(4)—C(15)—O(3)	123.8 (2)
C(2)—C(1)—N	115.8 (2)	C(8)—C(15)—O(3)	112.7 (2)
C(3)—C(2)—C(1)	118.1 (2)	C(8)—C(15)—O(4)	123.4 (2)
C(7)—C(2)—C(1)	124.8 (2)	C(17)—C(16)—S	119.7 (2)
C(7)—C(2)—C(3)	117.1 (2)	C(21)—C(16)—S	120.4 (2)
C(4)—C(3)—C(2)	121.5 (3)	C(21)—C(16)—C(17)	119.9 (3)
C(5)—C(4)—C(3)	119.6 (3)	C(18)—C(17)—C(16)	119.0 (4)
C(6)—C(5)—C(4)	120.0 (3)	C(19)—C(18)—C(17)	122.6 (4)
C(7)—C(6)—C(5)	121.1 (3)	C(20)—C(19)—C(18)	117.7 (3)
C(6)—C(7)—C(2)	120.6 (3)	C(22)—C(19)—C(18)	122.7 (5)
C(9)—C(8)—N	110.8 (2)	C(22)—C(19)—C(20)	119.6 (5)
C(15)—C(8)—N	111.9 (2)	C(21)—C(20)—C(19)	121.7 (4)
C(15)—C(8)—C(9)	113.8 (2)	C(20)—C(21)—C(16)	119.1 (4)

All H-atom positions in (I) were calculated and refined with an overall isotropic temperature factor using a riding model [U_{iso} = 0.108 (4) Å^2]. The positions of four H atoms in (II) were calculated and the remainder were located from a difference synthesis. All were refined with an overall isotropic temperature factor, using a riding model for calculated H atoms [U_{iso} = 0.106 (3) Å^2]. Program used to solve structures: *SHELXS86* (Sheldrich, 1990). Program used to refine structures: *SHELX76* (Sheldrich, 1976). Molecular graphics: *SCHAKAL* (Keller, 1988). Most calculations were performed using *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Class of Substituted 1,2,4-Triazolo-1,3,4-thiadiazepines

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Abstract

A series of 3-aryloxymethyl-(5-nitro-2-furyl)-6-phenyl-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazepine compounds have been synthesized recently by a new route. Reported here are the structures of two such compounds with *para*-substituted aryloxymethyl groups: one has a chloro group, 3-(4-chlorophenyloxymethyl)-8-(5-nitro-2-furyl)-6-phenyl-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazepine, $C_{22}H_{14}ClN_5O_4S$, TD1, and the other a methyl group, 3-(*p*-tolyloxymethyl)-8-(5-nitro-2-furyl)-6-phenyl-1,2,4-triazolo-[3,4-*b*][1,3,4]thiadiazepine, $C_{23}H_{17}N_5O_4S$, TD7. The nitrofuryl and phenyl groups on the thiadiazepine ring are each found to adopt a similar conformation in the two structures, whereas the aryloxymethyl substituents on the triazole rings are conformationally different from each other. Each thiadiazepine ring adopts a boat conformation with the S atom at the apex. The interplanar angle between the

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