C2	0.5842 (3)	0.1271 (4)	0.3089 (2)	0.042 (1)
C21	0.4545 (3)	0.1193 (5)	0.2560 (3)	0.041 (1)
C22	0.3854 (3)	0.0582 (5)	0.3210 (3)	0.048 (1)
C23	0.2628 (3)	0.0585 (5)	0.2770 (3)	0.055 (2)
C24	0.2017 (3)	0.1215 (5)	0.1645 (3)	0.054 (2)
N24	0.0795 (3)	0.1208 (7)	0.1189 (4)	0.090 (2)
C25	0.2690 (3)	0.1835 (5)	0.0981 (3)	0.052 (2)
C26	0.3927 (3)	0.1819 (5)	0.1440 (3)	0.046 (2)
N3	0.6414 (3)	0.1681 (4)	0.4214 (2)	0.056 (1)
C4	0.7593 (3)	0.1646 (5)	0.4363 (3)	0.058 (2)
C5	0.7748 (3)	0.1216 (5)	0.3348 (3)	0.048 (1)
N50	0.8830 (3)	0.1151 (5)	0.3106 (3)	0.071 (2)
O501	0.9777 (2)	0.1343 (5)	0.3921 (3)	0.093 (1)
O502	0.8786 (2)	0.0923 (6)	0.2105 (3)	0.116 (2)

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

N1—C11	1.471 (4)	C24—N24	1.363 (4)
N1—C2	1.355 (4)	C24—C25	1.397 (5)
N1—C5	1.380 (3)	C25—C26	1.380 (4)
C2—C21	1.452 (4)	N3—C4	1.347 (5)
C2—N3	1.343 (3)	C4—C5	1.353 (5)
C21—C22	1.398 (5)	C5—N50	1.413 (5)
C21—C26	1.392 (4)	N50—O501	1.228 (3)
C22—C23	1.367 (4)	N50—O502	1.218 (5)
C23—C24	1.397 (4)		
C2—N1—C5	105.3 (2)	C23—C24—N24	121.4 (3)
C11—N1—C5	127.8 (3)	N24—C24—C25	120.2 (3)
C11—N1—C2	126.1 (3)	C24—C25—C26	120.1 (3)
N1—C2—N3	111.5 (3)	C21—C26—C25	122.1 (3)
N1—C2—C21	125.1 (3)	C2—N3—C4	105.7 (3)
C21—C2—N3	123.5 (3)	N3—C4—C5	110.0 (3)
C2—C21—C26	123.0 (3)	N1—C5—C4	107.6 (3)
C2—C21—C22	119.9 (3)	C4—C5—N50	128.2 (3)
C22—C21—C26	116.9 (3)	N1—C5—N50	124.1 (3)
C21—C22—C23	121.9 (3)	C5—N50—O502	119.0 (3)
C22—C23—C24	120.7 (3)	C5—N50—O501	118.1 (3)
C23—C24—C25	118.3 (3)	O501—N50—O502	122.9 (4)

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Methyl DL-3-Benzyl-2,2-dioxo-1,2,3-oxathiazolidine-4-carboxylate – an Intermediate for Amino Acid Synthesis

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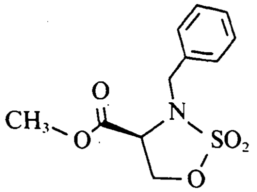
Abstract

The first structural measurements on a cyclic sulfamidate, DL-3-benzyl-2,2-dioxo-1,2,3-oxathiazolidine-4-carboxylate, $C_{11}H_{13}NO_5S$, show that the ring N atom has almost planar bonding geometry (sum of angles at N = 357.8°), in contrast to that found in simple dialkyl sulfonamides and acyclic sulfamate esters. The structure contains a close 1,4 N···O contact [2.764 (3) Å].

Comment

The methyl ester of DL-serine can be converted to the 1,2,3-oxathiazolidine dioxide (1) by three steps: benzylation, cyclization with thionyl chloride, and oxidation with sodium periodate catalysed by ruthenium trichloride. This cyclic sulfamidate reacts with nucleophiles by ring opening at C-5 to produce precursors of new amino acids (Gritsonie, Pilkington & Wallis, 1994; Baldwin, Spivey & Schofield, 1990). We were interested in the bonding geometry at the N atom in (1), and how this might be affected by the sizes of the N-atom substituent and the adjacent carboxylic ester group. By analogy with *N*,*N*-dimethyl sulfonamides in which the N atom is typically *circa* 0.27 Å out of the plane defined by the atoms to which it is bonded (Häkkinen, Ruostesuo & Kivekäs, 1988; Cromer, Ryan, Karthikeyan & Paine, 1990), pyramidal geometry around the N atom was expected. The only *N*,*N*-dialkyl sulfamate esters recorded in the Cambridge Structural Database (1992) also show similar pyramidal bonding geometry at the N atom (Potekhin, Sedov, Struchov, Zyk, Kutateladze, Lapin & Zefirov, 1986; Zefirov, Zyk, Kutateladze, Potekhin & Struchov, 1987).



(1)

The structure of (1), shown in Fig. 1, is the first structure of a 1,2,3-oxathiazolidine ring system to be reported. Quite surprisingly, the bonding geometry at the N atom is close to planar, as the sum of the angles at N(1) is 357.8° and the N atom lies only 0.130 (2) Å out of the plane of the three atoms to which it is bonded. This slightly pyramidal geometry around the N atom moves the benzyl group away from the ester group so that the C(3)—N(1)—C(1)—C(4) torsion angle is −77.3 (3)°. The best planes of the phenyl group and ester group lie at 83.4 (1)° to each other. The endocyclic angle at N(1) is 113.6 (2)°, the largest angle in this ring. It is notable that the N atom is involved in a short 1,4 contact with the carbonyl O atom [2.764 (3) Å]. The strongly electron-attracting SO_2 group presumably lowers the electron density at N, and the approach of the O atom may indeed contribute to the pyramidal geometry at the N atom. [The approach of H atoms has been found to have a similar effect on carbonyl C atoms (Baldwin, Beckwith, Orrell, Prout & Wallis, 1984).]

The conformation of the oxathiazolidine ring is close to an 'envelope'. The 'flap' atom, O(3), lies 0.416 (2) Å out of the plane defined by the ring atoms S(1), N(1) and C(1), on the same side as the ester group, while C(2) lies 0.108 (3) Å out of this plane on the opposite side. The S(1)—N(1)—C(1)—C(2) torsion angle is only −4.2 (3)°. The N(1)—S(1) and O(3)—S(1) distances [1.612 (2) and 1.565 (2) Å, respectively] are close to those found in acyclic sulfamate esters, but the endocyclic angle at S(1) is *circa* 8° smaller. There are no short intermolecular contacts in the crystal packing arrangement of (1).

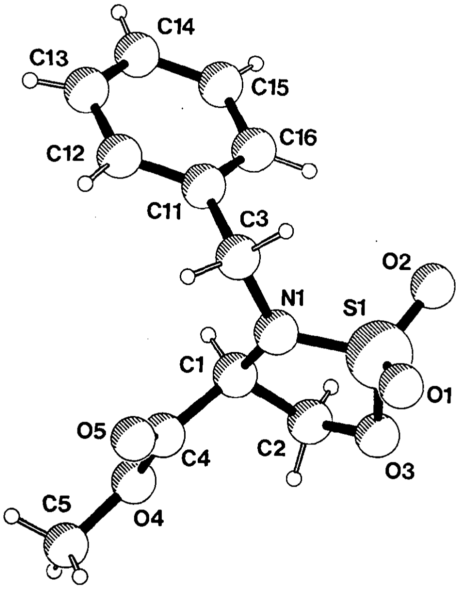


Fig. 1. Molecular structure of (1) with atomic labelling (Spek, 1991).

Experimental

N-Benzyl-DL-serine methyl ester was converted to the corresponding cyclic sulfamidite by reaction with thionyl chloride and pyridine in tetrahydrofuran, and oxidized to (1) with sodium periodate and a catalytic amount of ruthenium trichloride (Gritsonie, Pilkington & Wallis, 1994).

Crystal data

$C_{11}H_{13}NO_5S$
$M_r = 271.29$
Monoclinic
$P2_1/c$
$a = 11.7580\ (90)$ Å
$b = 10.6460\ (40)$ Å
$c = 9.9220\ (20)$ Å
$\beta = 101.68\ (2)°$
$V = 1216.28\ (107)$ Å^3
$Z = 4$
$D_x = 1.4815$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 13$–$15°$
$\mu = 0.266$ mm^{-1}
$T = 293$ K
Block
0.225 × 0.225 × 0.100 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: none
2136 measured reflections
2015 independent reflections
1662 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.02$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
1 standard reflection monitored every 200 reflections intensity variation: 1%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.047$
$S = 1.43$
1662 reflections
215 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{\rm max} = 0.23$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.56$ e Å^{-3}
Atomic scattering factors from Cromer & Mann (1968) (S, O, N, C) and Stewart, Davidson & Simpson (1965) (H)

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

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
S1	0.01100 (6)	−0.08620 (6)	0.25390 (7)	0.0306 (2)
O1	0.0650 (2)	−0.0998 (2)	0.3942 (2)	0.0505 (8)

O2	0.0481 (2)	0.0174 (2)	0.1843 (2)	0.0511 (8)
O3	0.0263 (2)	−0.2122 (2)	0.1783 (2)	0.0399 (7)
O4	−0.2757 (2)	−0.3778 (2)	0.0956 (2)	0.0410 (7)
O5	−0.2667 (2)	−0.2855 (2)	0.2993 (2)	0.0486 (8)
N1	−0.1284 (2)	−0.0956 (2)	0.2309 (2)	0.0346 (8)
C1	−0.1787 (2)	−0.1864 (3)	0.1277 (3)	0.0285 (9)
C2	−0.0756 (3)	−0.2343 (3)	0.0694 (3)	0.0348 (11)
C3	−0.1959 (3)	0.0036 (3)	0.2812 (3)	0.0375 (11)
C4	−0.2436 (2)	−0.2880 (3)	0.1876 (3)	0.0290 (8)
C5	−0.3348 (4)	−0.4851 (4)	0.1389 (5)	0.0598 (17)
C11	−0.2762 (2)	0.0724 (3)	0.1673 (3)	0.0335 (9)
C12	−0.3919 (3)	0.0855 (4)	0.1718 (4)	0.0524 (12)
C13	−0.4664 (4)	0.1513 (5)	0.0716 (5)	0.0705 (17)
C14	−0.4268 (4)	0.2010 (4)	−0.0374 (5)	0.0627 (15)
C15	−0.3120 (4)	0.1886 (3)	−0.0440 (4)	0.0584 (14)
C16	−0.2369 (3)	0.1250 (3)	0.0592 (4)	0.0473 (12)

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

S1—O1	1.416 (2)	C1—C2	1.532 (4)
S1—O2	1.416 (2)	C1—C4	1.513 (3)
S1—O3	1.565 (2)	C3—C11	1.508 (3)
S1—N1	1.612 (2)	C11—C12	1.377 (4)
O3—C2	1.461 (3)	C11—C16	1.370 (4)
O4—C4	1.323 (3)	C12—C13	1.376 (5)
O4—C5	1.447 (4)	C13—C14	1.368 (6)
O5—C4	1.194 (3)	C14—C15	1.371 (6)
N1—C1	1.445 (3)	C15—C16	1.386 (4)
N1—C3	1.468 (4)		
O3—S1—N1	95.2 (1)	O3—C2—C1	105.1 (2)
O2—S1—N1	112.6 (1)	N1—C3—C11	113.2 (2)
O2—S1—O3	110.9 (1)	O5—C4—C1	125.2 (3)
O1—S1—N1	111.9 (1)	O4—C4—C1	110.0 (2)
O1—S1—O3	108.2 (1)	O4—C4—O5	124.8 (3)
O1—S1—O2	116.0 (2)	C3—C11—C16	121.7 (3)
S1—O3—C2	109.6 (2)	C3—C11—C12	119.8 (3)
C4—O4—C5	116.9 (3)	C12—C11—C16	118.4 (3)
S1—N1—C3	120.8 (2)	C11—C12—C13	121.1 (4)
S1—N1—C1	113.6 (2)	C12—C13—C14	120.0 (4)
C1—N1—C3	123.4 (2)	C13—C14—C15	119.8 (4)
N1—C1—C4	111.5 (2)	C14—C15—C16	119.9 (4)
N1—C1—C2	104.4 (2)	C11—C16—C15	120.8 (4)
C2—C1—C4	114.3 (2)		

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1983). Program(s) used to solve structure: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLUTON* (Spek, 1991). Software used to prepare material for publication: *PARST* (Nardelli, 1992).

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3-Phenyl-1-(2,4,6-triphenylphenyl)propane-1,3-dione

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Abstract

The title compound, $C_{33}H_{24}O_2$, consists of well separated $C_{33}H_{24}O_2$ units. The bulky 1,3-diketone occurs in its enol form (as suggested by spectroscopic studies) with the hydroxy group in the neighbourhood of the unsubstituted phenyl ring. C—O bond distances