

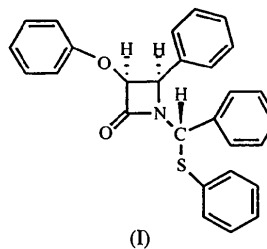
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angle of 120.6 (3)° with respect to one another, while the benzyl and thiophenyl rings attached to the N atom of the β -lactam ring are at an angle of 4.3 (2)° with respect to one another. The central β -lactam ring is bent, with a mean torsion-angle value of 4.3 (2)°.

Comment

β -Lactams with a substituent at the N atom which is easily removable under mild conditions find wide applicability in the synthesis of bicyclic β -lactam antibiotics and non- β -lactam molecules (Lukacs & Ohno, 1990). To achieve this goal, various moieties have been used as the nitrogen protective groups (George, 1993). In our on-going research on β -lactams, we have synthesized several β -lactams with various substituents on the N atom (Srirajan, Deshmukh, Puranik & Bhawal, 1996; Jayaraman, Puranik & Bhawal, 1996). We now report a novel protective group for the N atom of the β -lactam ring of the title compound, (I).



The deprotection of the novel protective group of (I) under mild conditions affords an *N*-unsubstituted β -lactam, which is an important synthon for various biologically active molecules. The X-ray structure determination was undertaken in order to establish unambiguously the stereochemistry at the C2 and C3 atoms of the β -lactam ring and at the C10 chiral centre.

The molecular structure of the title compound consists of a four-membered cyclic amide, with a *cis* disposition of phenoxy and phenyl groups at C2 and C3, and a thiophenylbenzyl group at the N atom of the β -lactam ring. The relative configurations at C2, C3 and C10 were established as *S*, *R* and *R*, respectively. The H atoms at C2 and C3 are *cis* with respect to one another [H2—C2—C3—H3 7.2 (3)°]. The geometry of the four-membered ring is similar to that reported for *cis* β -lactams (Jayaraman, Puranik & Bhawal, 1996; Jayaraman, Srirajan, Deshmukh & Bhawal, 1996; Chiaroni *et al.*, 1995). The β -lactam ring is bent with an average torsion-angle value of 4.3 (2)°, which is consistent with that observed in related structures (Spek, van der Steen, Johann, Jastrzebski & Kotten, 1994; van der Steen, Kleijn, Spek & Kotten, 1990). The internal angles of the four-membered ring vary from 85.6 (3) to 95.7 (3)°.

Acta Cryst. (1997). **C53**, 358–360

Novel Protective Group in β -Lactam Chemistry: 3-Phenoxy-4-phenyl-*N*-[α -(phenylthio)benzyl]azetid-2-one

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(Received 1 May 1996; accepted 25 September 1996)

Abstract

3-Phenoxy-4-phenyl-1-[phenyl(phenylthio)methyl]azetid-2-one, C₂₈H₂₃NO₂S, with a novel protective group, was prepared from thiophenol. The single-crystal analysis of the compound reveals the H atoms at C2 and C3 of the β -lactam ring to be in a *cis* configuration. The relative configuration at the C2, C3 and C10 chiral centres are established as *S*, *R* and *R*, respectively. The phenoxy and phenyl substituents at C2 and C3 are at an

The phenoxy and phenyl substituents at C2 and C3 are at an angle of $120.6(3)^\circ$, while the benzyl and thio-phenyl rings attached to the N atom of the β -lactam ring via C10 are inclined at an angle of $14.3(2)^\circ$. This shows that the two groups (benzyl and thiophenyl) are almost coplanar. The trend of relatively long C—N and short C=O amide bonds when compared with a normal amide bond, which is reported to be a common feature for monocyclic β -lactams (Davis & Storr, 1984), is not observed here. The average bond length and angle of the four phenyl rings are found to be $1.378(7) \text{ \AA}$ and $120.4(4)^\circ$, respectively. The molecules are related in a zipped fashion and show normal van der Waals contacts.

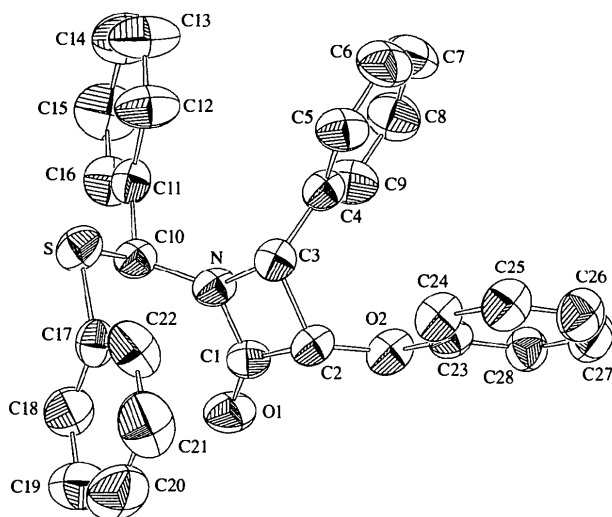


Fig. 1. An ORTEP (Johnson, 1971) drawing of the title compound with the crystallographic numbering of atoms. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Thiophenol (1 mmol) was added dropwise at 273 K to NH_3 (25 ml) and stirred for 30 min. A solution of benzaldehyde (1.2 mmol) in dichloromethane was then added dropwise and the mixture stirred for an additional 28 h at room temperature. The resulting solution was poured into distilled water (20 ml) and extracted with dichloromethane. The usual work-up procedure afforded the imine as a pale yellow solid. The imine on Staudinger reaction (Staudinger, 1907) with phenoxyacetyl chloride in the presence of excess triethylamine at 273 K gave the title β -lactam in 42% yield. The crude product was purified by column chromatography followed by crystallization from an acetone-petroleum ether system (m.p. 488 K).

Crystal data

$\text{C}_{28}\text{H}_{23}\text{NO}_2\text{S}$
 $M_r = 437.53$

Mo $K\alpha$ radiation
 $\lambda = 0.7093 \text{ \AA}$

Monoclinic

$P2_1/c$

$a = 11.813(2) \text{ \AA}$

$b = 6.410(2) \text{ \AA}$

$c = 30.552(4) \text{ \AA}$

$\beta = 91.58(1)^\circ$

$V = 2312.6(9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.257 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Enraf-Nonius CAD-4

diffractometer

$\omega/2\theta$ scans

Absorption correction: none

3339 measured reflections

3339 independent reflections

2358 reflections with

$I > 2\sigma(I)$

Refinement

Refinement on F^2

$R(F) = 0.0677$

$wR(F^2) = 0.2597$

$S = 1.127$

3339 reflections

290 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.1711P)^2 + 0.9959P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.006$

Cell parameters from 25 reflections

$\mu = 0.165 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$1.20 \times 0.32 \times 0.20 \text{ mm}$

Colourless

$\theta_{\text{max}} = 23.44^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 7$

$l = 0 \rightarrow 34$

3 standard reflections

frequency: 60 min

intensity decay: $<4\%$

$\Delta\rho_{\text{max}} = 0.334 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.325 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0001 (17)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Geometric parameters (\AA , $^\circ$)

S—C17	1.775 (4)	C11—C16	1.377 (6)
S—C10	1.848 (4)	C11—C12	1.398 (6)
N—C1	1.368 (5)	C12—C13	1.368 (7)
N—C10	1.429 (5)	C13—C14	1.368 (8)
N—C3	1.490 (5)	C14—C15	1.375 (8)
O1—C1	1.214 (5)	C15—C16	1.359 (7)
O2—C23	1.387 (5)	C17—C18	1.378 (7)
O2—C2	1.398 (5)	C17—C22	1.381 (7)
C1—C2	1.526 (6)	C18—C19	1.374 (8)
C2—C3	1.583 (5)	C19—C20	1.382 (10)
C3—C4	1.495 (6)	C20—C21	1.368 (10)
C4—C9	1.376 (6)	C21—C22	1.399 (8)
C4—C5	1.395 (6)	C23—C28	1.364 (6)
C5—C6	1.355 (7)	C23—C24	1.404 (6)
C6—C7	1.381 (8)	C24—C25	1.409 (6)
C7—C8	1.376 (8)	C25—C26	1.336 (7)
C8—C9	1.371 (7)	C26—C27	1.398 (7)
C10—C11	1.505 (6)	C27—C28	1.376 (7)
C17—S—C10	100.1 (2)	C16—C11—C12	117.5 (4)
C1—N—C10	130.7 (3)	C16—C11—C10	119.9 (4)
C1—N—C3	95.7 (3)	C12—C11—C10	122.6 (4)
C10—N—C3	131.4 (3)	C13—C12—C11	120.2 (4)
C23—O2—C2	117.4 (3)	C12—C13—C14	121.4 (5)
O1—C1—N	130.9 (4)	C13—C14—C15	118.4 (5)
O1—C1—C2	136.8 (4)	C16—C15—C14	120.9 (4)
N—C1—C2	92.3 (3)	C15—C16—C11	121.5 (4)
O2—C2—C1	114.0 (3)	C18—C17—C22	119.5 (4)
O2—C2—C3	118.8 (3)	C18—C17—S	121.6 (3)
C1—C2—C3	86.0 (3)	C22—C17—S	118.9 (4)
N—C3—C4	115.4 (3)	C19—C18—C17	121.0 (5)
N—C3—C2	85.6 (3)	C18—C19—C20	119.7 (6)
C4—C3—C2	117.4 (3)	C21—C20—C19	120.0 (5)
C9—C4—C5	117.7 (4)	C20—C21—C22	120.4 (5)

C9—C4—C3	122.7 (3)	C17—C22—C21	119.4 (5)
C5—C4—C3	119.7 (4)	C28—C23—O2	116.8 (3)
C6—C5—C4	120.9 (4)	C28—C23—C24	121.1 (4)
C5—C6—C7	120.8 (4)	O2—C23—C24	122.1 (4)
C8—C7—C6	119.3 (4)	C23—C24—C25	116.6 (4)
C9—C8—C7	119.6 (5)	C26—C25—C24	122.5 (4)
C8—C9—C4	121.8 (4)	C25—C26—C27	119.6 (4)
N—C10—C11	115.1 (3)	C28—C27—C26	119.7 (4)
N—C10—S	110.2 (3)	C23—C28—C27	120.4 (4)
C11—C10—S	109.0 (3)		

All the crystals obtained were needle shaped and long. Crystals were fragile and so were not cut into smaller crystals.

The structure was solved by direct methods (*MULTAN80*; Main *et al.*, 1980) using *NRCVAX* (PC version) (Gabe, Le Page, Charland, Lee & White, 1989). H atoms, which were geometrically fixed and confirmed from difference Fourier maps, were used in the structure-factor calculations, but were not refined.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *NRCVAX*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *SHELXL93*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: PA1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 360–362

2-[1-(Thiosemicarbazono)ethyl]pyridinium Chloride

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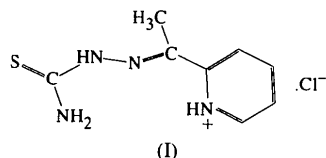
(Received 16 September 1996; accepted 11 November 1996)

Abstract

Dimeric units of the almost planar title compound, C₈H₁₁N₄S⁺.Cl⁻, are formed by N—H...Cl hydrogen bonds between the Cl⁻ anion and the H atom of the protonated pyridinium N atom, and the H atom of the terminal NH₂ group of one thiosemicarbazone molecule and the second NH₂ H atom of a second molecule. The dimeric units are stacked in layers. The C—S bond length is 1.681 (3) Å and considerable double-bond character can be detected for the C—N bonds.

Comment

As part of our systematic studies on the coordination chemistry of indium(III) with tridentate ligands, we prepared the title compound, (I), which has been shown to form complexes with a variety of metal ions (Kovala-Demertzi, Domopoulou, Demertzis, Raptopoulou & Tertzis, 1994; Castineiras, West, Gebremedhin & Romack, 1994; West, Gebremedhin, Butcher & Jasinski, 1995). Complexes with thiosemicarbazone ligands are known to have considerable biological activity and are under discussion for medical purposes.



The title compound, (I), crystallizes as a chloride salt from ethanol solution. The N atom of the pyridine ring is protonated and the Cl⁻ anion is associated *via* hydrogen bonds to the H(1) and H(12B) atoms (Table 2). Another hydrogen bridge between the Cl⁻ anion and the H(12A) atom at (−*x*, 1 − *y*, 2 − *z*) causes a slight association of every two molecules into dimeric units (Fig. 1). The title compound is almost planar [with a maximum deviation from the least-squares plane including all non-H atoms of 0.173 (1) Å and an r.m.s. deviation of 0.085 Å].

The C(11)—S(13) distance of 1.681 (3) Å is intermediate between typical C—S single- and double-bond lengths. This agrees well with the C(11)—N(10) and