

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1415). Services for accessing these data are described at the back of the journal.

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## Two novel optically active penam derivatives

ALEKSANDAR DANILOVSKI, MLADEN VINKOVIĆ AND JURE J. HERAK

PLIVA Inc. – Research Institute, Prilaz baruna Filipovića 25, HR-10000 Zagreb, Croatia. E-mail: sasa@zagreb.zoak.pmf.hr

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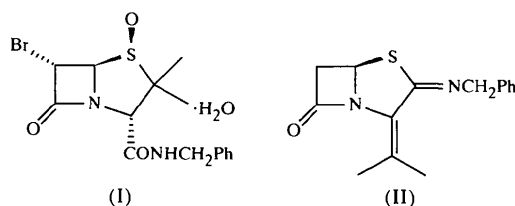
### Abstract

The X-ray structure analyses of the two optically active penam derivatives, (2*S*,4*S*,5*R*,6*S*)-2-benzylcarbonyl-6-bromo-3,3-dimethyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one 4-oxide hydrate, C<sub>15</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>3</sub>S·H<sub>2</sub>O, (I), and (5*R*)-3-benzylimino-2-isopropylidene-4-thia-1-aza-

bicyclo[3.2.0]heptan-7-one, C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>OS, (II), have been determined in order to ascertain their absolute configurations. Both compounds adopt the open-book conformation for the fused β-lactam and thiazolidine rings. The β-lactam ring is in a distorted planar conformation, while the thiazolidine ring is in an envelope conformation. The pyramidalization effect of the N1 atom in both compounds has been characterized by a displacement of the N atom from the plane of its substituents: the N atom is displaced 0.344 (5) and 0.350 (5) Å in molecules A and B of compound (I) and 0.410 (5) Å in compound (II).

### Comment

As a continuation of our previous studies (Herak *et al.*, 1994, 1995; Herak, 1996) of penicillanic acid amide (penam), two novel optically active penam derivatives, (2*S*,4*S*,5*R*,6*S*)-2-benzylcarbonyl-6-bromo-3,3-dimethyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one 4-oxide hydrate, (I), and (5*R*)-3-benzylimino-2-isopropylidene-4-thia-1-azabicyclo-[3.2.0]heptan-7-one, (II), have been synthesized (Herak & Vinković, 1996) and structurally characterized. Their main importance arises from their subsequent transformation into chiral 4-substituted-2-azetidinone or into other non-classical bicyclic β-lactams.



The present study has been undertaken in order to confirm the absolute configurations of both penam compounds, as well as to elucidate their conformational properties. The atomic numbering scheme and the displacement ellipsoids for both compounds are depicted in Figs. 1 and 2. The crystal structure determination of compound (I), which crystallizes in the form of the monohydrate, revealed the presence of two independent molecules per asymmetric unit. These two molecules differ primarily in the conformation of the benzyl group [the N23—C24—C25—C30 torsion angles are  $-50.4$  (12) and  $72.3$  (10)° in molecules A and B, respectively].

According to the spectroscopic data, the configuration at atom S4 in compound (I) is indecisive. The absolute configurations of all four chiral centres in (I) (Fig. 1) have been verified by the estimated Flack parameter (Flack, 1983) of  $-0.014$  (12). From this, it follows that S4 has the *S* configuration, with H2 in the *syn*-axial position. It was assumed that the right D-enantiomer of

compound (II) is the one with no configuration change at the C5 atom (Fig. 2); the estimated Flack parameter of 0.07 (19) proved this assumption.

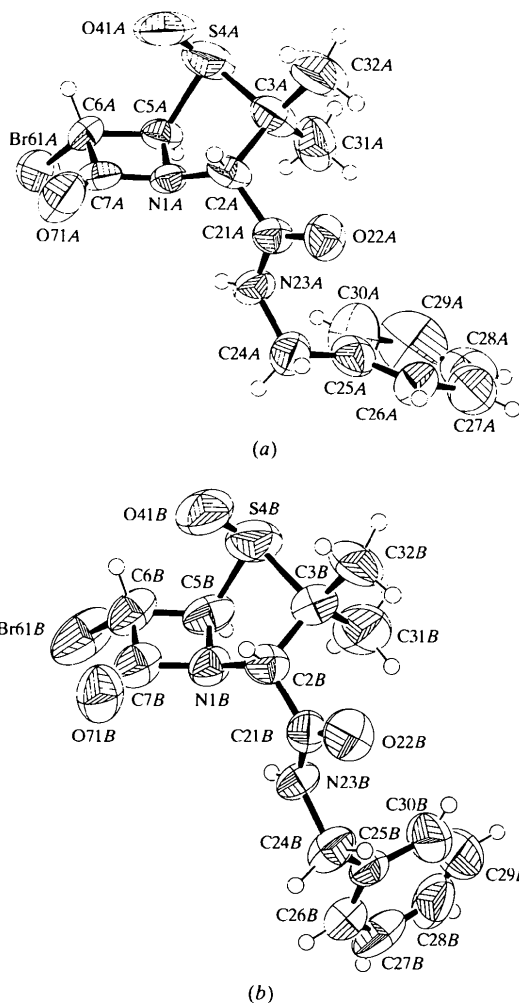


Fig. 1. Views of (a) molecule A and (b) molecule B of compound (I) with the atomic numbering scheme. Non-H atoms are drawn at the 50% probability level, while H atoms are shown as spheres of an arbitrary radius. The water molecule has been omitted.

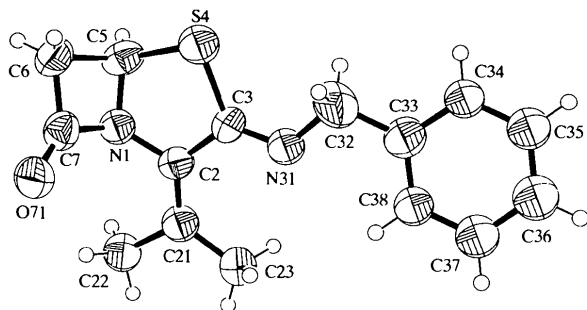


Fig. 2. View of compound (II) with the atomic numbering scheme. Non-H atoms are drawn at the 50% probability level, while H atoms are shown as spheres of an arbitrary radius.

Both compounds have an open-book conformation for the fused  $\beta$ -lactam and thiazolidine rings (penam system). The four-membered  $\beta$ -lactam ring has adopted a distorted planar conformation (the substituents plane is defined through atoms C2, C5 and C7). The coplanarity of the N1 atom with its three substituents is an important consideration that is related to the chemical reactivity and biological activity of  $\beta$ -lactam compounds. This coplanarity can be expressed as the perpendicular distance of the N1 atom from its substituents plane (Sweet, 1972; Page, 1987). The perpendicular distances of the N1 atom from the plane of its substituents are 0.344 (5) and 0.350 (5) Å in molecules A and B of (I), respectively, and 0.410 (5) Å in (II).

The five-membered thiazolidine ring has adopted an envelope conformation. In compound (I), the S4 atom is displaced by 0.883 (2) and 0.878 (3) Å out of the plane defined through the four remaining atoms, N1, C2, C3 and C5, in molecules A and B, respectively. Because of the two exocyclic double bonds attached to the C2—C3 bond in compound (II), and the subsequent hybridization change of the C2 and C3 atoms from  $Csp^3$  in (I) to  $Csp^2$  in (II), it is the C5 atom in (II), rather than S4, which is out of the plane of the remaining atoms (N1, C2, C3 and S4) by 0.327 (6) Å. The aperture of the open-book conformation can be defined as the angle between the plane of the  $\beta$ -lactam and thiazolidine rings. It is larger in compound (I) [129.8 (3) and 129.2 (4)° in molecules A and B, respectively] than in compound (II) [122.0 (2)°].

Each molecule in compound (I) is linked by two C(4) (notation according to graph-set analysis; Bernstein *et al.*, 1995) intermolecular O22A...H23B—N23B and O22B...H23A—N23A hydrogen bonds to each of the molecules on either side of it [ $d(O22...N23) = 2.921$  (7) and 2.827 (7) Å, in molecules A and B, respectively]. In addition to these C(4) intermolecular hydrogen bonds, S(5) intramolecular N1...H23—N23 hydrogen bonds are also detected [ $d(N1...N23) = 2.708$  (8) and 2.813 (8) Å, in molecules A and B, respectively]. Together these form a tricentred bifurcated hydrogen bond.

## Experimental

The syntheses of both title compounds have been reported previously by Herak & Vinković (1996). Colourless crystals of (I) and (II) used in this structure determination were obtained by slow evaporation of diethyl ether solution at room temperature.

### Compound (I)

#### Crystal data

$C_{15}H_{17}BrN_2O_3S \cdot H_2O$   
 $M_r = 403.29$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å

Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>  
*a* = 9.798 (3) Å  
*b* = 18.752 (4) Å  
*c* = 19.246 (2) Å  
*V* = 3536.1 (14) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.515 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

#### Data collection

Philips PW1100 diffractometer upgraded by Stoe & Cie  
 $\omega$  scans  
 Absorption correction: semi-empirical via  $\psi$  scans (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.098, *T<sub>max</sub>* = 0.658  
 10 411 measured reflections  
 5710 independent reflections (plus 3678 Friedel-related reflections)

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.069  
*wR*(*F*<sup>2</sup>) = 0.118  
*S* = 1.239  
 9386 reflections  
 415 parameters  
 Only coordinates of H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.0338P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = -0.001

Cell parameters from 20 reflections  
 $\theta = 2.0\text{--}14.5^\circ$   
 $\mu = 2.463 \text{ mm}^{-1}$   
*T* = 293 K  
 Prism  
 0.42 × 0.33 × 0.17 mm  
 Colourless

2812 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.042  
 $\theta_{\text{max}} = 30^\circ$   
*h* = -10 → 10  
*k* = -26 → 26  
*l* = -27 → 27  
 3 standard reflections frequency: 90 min  
 intensity decay: 6.4%

$\Delta\rho_{\text{max}} = 0.411 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.383 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: 5249  
 Friedel pairs used in refinement (Flack, 1983)  
 Flack parameter = -0.014 (12)

Table 1. Selected geometric parameters (Å, °) for (I)

N1A—C7A	1.364 (9)	N1B—C7B	1.390 (13)
N23A—C21A	1.317 (8)	N23B—C21B	1.298 (9)
N23A—C24A	1.474 (9)	N23B—C24B	1.451 (9)
C2A—C21A	1.487 (10)	C2B—C21B	1.502 (10)
C2A—C3A	1.571 (10)	C2B—C3B	1.526 (12)
C5A—S4A—C3A	87.9 (3)	C5B—S4B—C3B	88.7 (4)
C7A—N1A—C2A	129.8 (6)	C7B—N1B—C5B	94.8 (7)
C7A—N1A—C5A	93.4 (5)	C7B—N1B—C2B	128.7 (7)
C2A—N1A—C5A	118.7 (5)	C5B—N1B—C2B	118.4 (6)
N1A—C5A—C6A	88.7 (5)	N1B—C5B—C6B	87.9 (6)
N1A—C5A—S4A	103.2 (4)	N1B—C5B—S4B	102.7 (5)
C6A—C5A—S4A	117.1 (5)	C6B—C5B—S4B	114.7 (6)
C2A—C3A—S4A	104.3 (5)	C32B—C3B—S4B	107.1 (6)
C5A—C6A—C7A	85.2 (5)	C5B—C6B—C7B	87.4 (7)
N1A—C7A—C6A	92.4 (6)	N1B—C7B—C6B	90.0 (9)
C3A—S4A—C5A—N1A	38.4 (5)		
C3A—S4A—C5A—C6A	133.7 (6)		
C7A—N1A—C2A—C3A	-127.8 (7)		
C5A—N1A—C2A—C3A	-4.7 (9)		
N1A—C2A—C3A—S4A	33.2 (7)		
C5A—S4A—C3A—C2A	-42.3 (5)		
C21A—N23A—C24A—C25A	-83.9 (9)		
N23A—C24A—C25A—C30A	-50.4 (12)		
C3B—S4B—C5B—N1B	37.4 (6)		
C3B—S4B—C5B—C6B	131.0 (7)		
C7B—N1B—C2B—C3B	-128.6 (9)		

C5B—N1B—C2B—C3B	-4.9 (9)
N1B—C2B—C3B—S4B	32.6 (7)
C5B—S4B—C3B—C32B	-163.1 (9)
C21B—N23B—C24B—C25B	-127.6 (8)
N23B—C24B—C25B—C30B	72.3 (10)

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

D—H...A	D—H	H...A	D...A	D—H...A
N23A—H23A...N1A	0.860 (8)	2.312 (8)	2.708 (8)	108.3 (6)
N23B—H23B...N1B	0.859 (8)	2.437 (8)	2.813 (8)	107.1 (6)
N23B—H23B...O22A	0.859 (8)	2.070 (7)	2.921 (7)	170.5 (7)
N23A—H23A...O22B	0.860 (8)	2.028 (7)	2.827 (7)	154.2 (7)

Symmetry code: (i) -*x*,  $\frac{1}{2}$  + *y*,  $\frac{1}{2}$  - *z*.

#### Compound (II)

##### Crystal data

C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>OS  
*M<sub>r</sub>* = 272.36  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 5.295 (6) Å  
*b* = 11.559 (8) Å  
*c* = 11.698 (11) Å  
 $\beta = 90.64 (8)^\circ$   
*V* = 715.9 (12) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.263 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

##### Mo *K*α radiation

$\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 19 reflections  
 $\theta = 20\text{--}30^\circ$   
 $\mu = 0.220 \text{ mm}^{-1}$   
*T* = 293 K  
 Prism  
 0.53 × 0.45 × 0.15 mm  
 Colourless

##### Data collection

Philips PW1100 diffractometer upgraded by Stoe & Cie  
 $2\theta/\omega$  scans  
 Absorption correction: none  
 3265 measured reflections  
 1633 independent reflections  
 886 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.109  
 $\theta_{\text{max}} = 27^\circ$   
*h* = -6 → 6  
*k* = 0 → 14  
*l* = -14 → 14  
 3 standard reflections frequency: 60 min  
 intensity decay: 2.7%

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.061  
*wR*(*F*<sup>2</sup>) = 0.115  
*S* = 1.164  
 1630 reflections  
 188 parameters  
 Only coordinates of H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.0338P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\text{max}} = 0.256 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.304 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: retention of *R* configuration at atom C5 assumed (Flack, 1983)  
 Flack parameter = 0.07 (19)

Table 3. Selected geometric parameters (Å, °) for (II)

N1—C7	1.409 (8)	N31—C32	1.457 (7)
N31—C3	1.257 (6)	C3—C2	1.484 (7)
C3—S4—C5	92.5 (3)	N1—C5—C6	89.1 (4)
C7—N1—C2	125.8 (4)	N1—C5—S4	105.9 (4)
C7—N1—C5	92.5 (5)	C6—C5—S4	117.4 (5)
C2—N1—C5	116.8 (4)	C7—C6—C5	84.4 (4)
C2—C3—S4	110.8 (4)	N1—C7—C6	92.7 (4)

C5—S4—C3—C2	−8.2 (4)	C3—S4—C5—N1	17.0 (4)
C7—N1—C2—C3	−96.9 (6)	C3—S4—C5—C6	114.4 (4)
C5—N1—C2—C3	18.1 (6)	N31—C32—C33—C38	−18.7 (7)
S4—C3—C2—N1	−3.5 (5)		

Despite the fairly large size of crystal (II), it showed weak diffraction power, *i.e.* only 4.2% of observed reflections satisfied the  $I > 2\sigma(I)$  criterion in the  $25 < \theta < 27^\circ$  resolution shell. Therefore, the reflection to parameter ratio is rather small. The data were corrected for Lorentz and polarization effects and an absorption correction (North *et al.*, 1968) was applied to the data of crystal (I). Both structures were solved by direct methods and refined by full-matrix least-squares calculations based on  $F^2$ , with anisotropic displacement parameters for all non-H atoms. The amide-H atoms in (I) were located in difference Fourier maps and all other H atoms in (I), as well as all those in (II), were placed in geometrical positions.

For both compounds, data collection: *STADIA* (Stoe & Cie, 1996a); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1996b); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *PLATON93* (Spek, 1993a) and *PLUTON93* (Spek, 1993b); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1291). Services for accessing these data are described at the back of the journal.

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## Acefluoranthylene†

MARTIN LUTZ,<sup>a</sup> ANTHONY L. SPEK,<sup>a</sup> MARTIN SAROBE<sup>b</sup>  
AND LEONARDUS W. JENNESKENS<sup>b</sup>

<sup>a</sup>*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands, and*  
<sup>b</sup>*Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands. E-mail: m.lutz@chem.uu.nl*

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## Abstract

The title compound, C<sub>18</sub>H<sub>10</sub>, expresses a curvature in the solid state about the planar central pentagon and shows distinct bond length alternations. The single bonds in the fused cyclopenteno ring are the longest bonds in the molecule, in the range 1.487(2)–1.491(2) Å. The shortest bond, at 1.354(2) Å, is a double bond between the two adjacent hexagons.

## Comment

Polycyclic aromatic hydrocarbons are of great interest as components of the smoke produced during incomplete combustion of fossil fuels and tobacco. They are of particular interest because of the high toxicity of many representatives of this class of compounds (Jacob, 1996). In recent times, polycyclic aromatic compounds have also attracted interest as key planar intermediates in the formation of fullerenes.

Acefluoranthylene, (I), was prepared in the context of our investigations into the generation of polycyclic aromatic compounds using flash vacuum thermolysis (FVT; Sarobe *et al.*, 1995; Jenneskens *et al.*, 1996). Fig. 1 shows a molecular plot of the title compound with the atom-numbering scheme. The molecule is curved in the solid state. The maximum deviation from planarity is with atoms C17 and C18, which deviate by 0.347(5) and 0.305(5) Å, respectively, from the least-squares plane defined by the central five-membered ring. A rigid-body motion analysis (Schomaker & Trueblood, 1968) leads to  $R = \Sigma(|U_{\text{obs}} - U_{\text{calc}}|)/\Sigma|U_{\text{obs}}| = 0.065$ . This low  $R$  value is a strong indication that the whole molecule behaves as a rigid body (Dunitz, 1979), which is to be expected for a polycyclic aromatic system. A comparison of the anisotropic vibration parameters in the covalent bond direction of atom pairs (Hirshfeld, 1976) shows only a variation of less than  $2\sigma$  and confirms the consistency of the model.

† Cyclopenta[cd]fluoranthene.