Table 2. *Inter-plane angles*

The angles refer to the angle between the normals of the respective planes. The Se–P–C plane includes the lead carbon atom of the corresponding phenyl ring.

Plane	σ(plane)	Atoms in plane	Angle to Se–P–C	Angle to hub*
Phenyl 1	0·006 Å	C(1), C(2), C(3), C(4), C(5), C(6)	50·8 (5)°	44·1 (9)°
Phenyl 2	0·008	C(7), C(8), C(9), C(10), C(11), C(12)	54·4 (5)	42·5 (9)
Phenyl 3	0·005	C(13), C(14), C(15), C(16), C(17), C(18)	9·8 (5)	79·6 (9)
Phenyl 1′	0·008	C(1′), C(2′), C(3′), C(4′), C(5′), C(6′)	50·9 (5)	41·7 (9)
Phenyl 2′	0·006	C(7′), C(8′), C(9′), C(10′), C(11′), C(12′)	56·4 (5)	41·6 (9)
Phenyl 3′	0·007	C(13′), C(14′), C(15′), C(16′), C(17′), C(18′)	12·5 (5)	78·4 (9)

* The hub is the plane formed by the three lead atoms: C(1), C(7) and C(13).

The average P=Se distance of 2·106 (1) Å falls within the range of values observed for similar compounds; for example, tri-*m*-tolylphosphine selenide 2·109 (5) Å (Cameron, Howlett & Miller, 1978) and others listed in Table 5 of Gałdecki, Głowka, Michalski, Okruszek & Stec (1977). The average P–C distance is somewhat longer than that observed in TPPS although the average values of both the *X*–P–C and C–P–C angles [in TPPS 113·1 (6) and 105·7 (16)° respectively] are affected by the conformation and bulk of the *R* group rather than by the electronic effect of the atom bonded to P.

The conformation of TPPSe is the same as that observed in the sulfide structure. The conformational angles listed in Table 2 indicate that one phenyl ring lies almost parallel to the P=Se bond. This conformation seems to facilitate efficient packing of the molecules while producing some variation in the individual C–P–C bond angles as noted in Fig. 1.

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Methyl 6α-Ethoxyformamido-6β-phenoxyacetamidopenicillanate

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Abstract. $C_{20}H_{25}N_3O_7S$, $M_r = 451{\cdot}5$, tetragonal, $P4_1$, $a = b = 11{\cdot}943$ (1), $c = 16{\cdot}597$ (1) Å, $U = 2367{\cdot}3$ Å^3, $Z = 4$, $D_m = 1{\cdot}25$, $D_c = 1{\cdot}27$ Mg m^{-3}, $F(000) = 952$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo $K\alpha$) = 0·183 mm^{-1}. The analysis confirms that the reaction of methyl 6α-phenoxyacetamidopenicillanate (I) with *N*-chloro-*N*-sodiourethane in acetonitrile at room temperature proceeds with retention of the stereochemistry at C(6), yielding as major product (80–90%) methyl 6α-ethoxyformamido-6β-phenoxyacetamidopenicillanate (II). The absolute stereochemistry of (II), although not determined from the present analysis, is inferred from the known absolute stereochemistry at C(3) of the starting material (I).

Introduction. Exposure of a small crystal to graphite-monochromated Mo radiation on a Hilger & Watts Y290 diffractometer yielded 1975 independent reflexions [$I \geq 2\sigma_I$, $\sigma_I = (I + B_1 + B_2)^{1/2}$] (measured by the θ,ω-scan technique in the range 2θ = 0–54°). The

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intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by a combination of direct and Fourier methods with programs incorporated in XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Refinement of positional and thermal parameters by least-squares calculations converged to $R = 0{\cdot}037$ and $R' = \sum w\Delta^2/\sum w|F_o|^2 = 0{\cdot}003$, the data having been weighted according to $w = (0{\cdot}0673 + 0{\cdot}0514|F| + 0{\cdot}0029|F|^2)^{-1}$. During the refinement it became apparent that C(71), the terminal atom of the ethoxyformamido chain, was disordered. However, it did not prove possible to resolve alternative sites for this atom, which was therefore included in the refinement as a fixed contributor at a position derived from a difference synthesis. H atoms, for the most part located from difference syntheses, but otherwise placed in calculated positions, were also included as fixed contributors.

Final fractional coordinates are listed in Table 1; Table 2 gives details of the molecular geometry.* The e.s.d.'s derive from the least-squares calculations and should be regarded as minimum values. A view of one molecule, defining the atomic numbering, is shown in Fig. 1.

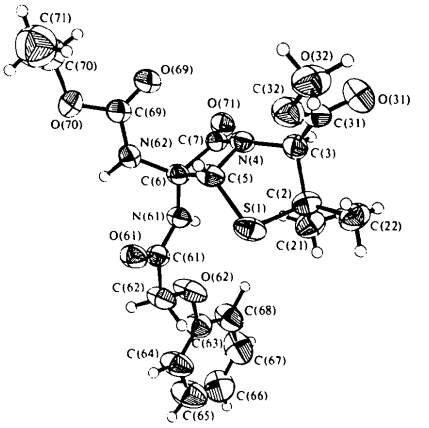


Fig. 1. A view of one molecule showing the atomic numbering. H atoms are numbered as the atoms to which they are bonded.

* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34172 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10⁴) *for non-hydrogen atoms*

	x	y	z
S(1)	2698 (1)	1761 (1)	4681 (1)
C(2)	3055 (3)	846 (3)	5548 (2)
C(3)	2333 (3)	1299 (3)	6266 (2)
N(4)	2208 (2)	2488 (2)	6123 (2)
C(5)	2121 (3)	2867 (3)	5288 (2)
C(6)	2820 (2)	3938 (3)	5543 (2)
C(7)	2841 (2)	3367 (2)	6387 (2)
C(21)	4293 (3)	975 (4)	5748 (3)
C(2)	2777 (4)	−360 (3)	5323 (3)
C(31)	1234 (3)	692 (3)	6357 (3)
O(31)	1115 (3)	−76 (3)	6818 (2)
O(32)	448 (2)	1061 (2)	5872 (2)
C(32)	−614 (4)	456 (4)	5900 (4)
O(71)	3281 (2)	3576 (2)	7020 (1)
N(61)	3923 (2)	3988 (2)	5192 (2)
C(61)	4033 (3)	4148 (3)	4391 (2)
O(61)	3241 (2)	4332 (2)	3950 (2)
C(62)	5186 (3)	4140 (4)	4040 (2)
O(62)	5977 (2)	3839 (3)	4619 (2)
C(63)	7068 (3)	3719 (4)	4376 (3)
C(64)	7459 (4)	4032 (5)	3629 (3)
C(65)	8581 (4)	3846 (6)	3460 (4)
C(66)	9293 (4)	3392 (5)	3995 (5)
C(67)	8893 (4)	3124 (5)	4756 (4)
C(68)	7795 (4)	3281 (5)	4943 (3)
N(62)	2310 (2)	5029 (3)	5483 (2)
C(69)	1349 (4)	5273 (4)	5866 (3)
O(69)	860 (3)	4661 (3)	6318 (3)
O(70)	1007 (3)	6301 (3)	5662 (3)
C(70)	−12 (8)	6733 (7)	6056 (7)
C(71)	−950	6513	5620

Discussion. In the search for improved β-lactam antibiotics, importance has been attached to the introduction of 6α-substituents into the penam nucleus (Mukerjee & Singh, 1975; Stoodley, 1975). Investigations (Campbell & Johnson, 1975; Bremner, Campbell & Johnson, 1976) of the reactions of several 6β-substituted methyl penicillanates with various sodium *N*-chloroalkoxyformamidates revealed products which were clearly the corresponding 6,6-disubstituted penicillanate esters. However, the detailed stereochemistry at C(6) proved to be ambiguous, since plausible mechanistic routes to these products allowed for the possibility of inversion of the original C(6) stereochemistry. Moreover, since these reactions permit facile preparations of 6,6-disubstituted penams, which may then be converted to 6-spiropenicillanates and 7,7-disubstituted cephems, classes of compounds which are both of current interest, it proved desirable to resolve the stereochemical ambiguity. We therefore undertook the analysis of the compound resulting from the reaction of methyl 6β-phenoxyacetamidopenicillanate (I) with *N*-chloro-*N*-sodiourethane, and have shown it to be methyl 6α-ethoxyformamido-6β-phenoxyacetamidopenicillanate (II), thus demonstrating that in this case the original C(6) stereochemistry of (I) has survived the substitution reaction, attack by the alkoxyformamidium entities taking place at the less-hindered α-face of the penicillanate nucleus. By analogy, this conclusion may be extended to other examples which have thus far been prepared (Bremner, Campbell & Johnson, 1977).

Table 2. *Interatomic distances and angles*

(*a*) Bond distances (Å)

S(1)–C(2)	1·856 (4)	N(61)–C(61)	1·350 (4)
S(1)–C(5)	1·800 (4)	C(61)–O(61)	1·215 (4)
C(2)–C(3)	1·568 (5)	C(61)–C(62)	1·495 (5)
C(2)–C(21)	1·524 (5)	C(62)–O(62)	1·394 (5)
C(2)–C(22)	1·525 (6)	O(62)–C(63)	1·372 (5)
C(3)–N(4)	1·447 (4)	C(63)–C(64)	1·376 (7)
C(3)–C(31)	1·508 (5)	C(64)–C(65)	1·387 (7)
N(4)–C(5)	1·461 (4)	C(65)–C(66)	1·343 (9)
N(4)–C(7)	1·365 (4)	C(66)–C(67)	1·389 (10)
C(5)–C(6)	1·585 (5)	C(67)–C(68)	1·360 (6)
C(6)–C(7)	1·558 (5)	C(68)–C(63)	1·383 (6)
C(6)–N(61)	1·442 (4)	N(62)–C(69)	1·343 (6)
C(6)–N(62)	1·441 (4)	C(69)–O(69)	1·210 (6)
C(7)–O(71)	1·202 (4)	C(69)–O(70)	1·338 (6)
C(31)–O(31)	1·203 (5)	O(70)–C(70)	1·474 (11)
C(31)–O(32)	1·312 (5)	[C(70)–C(71)	1·359]
O(32)–C(32)	1·461 (6)		

(*b*) Interbond angles (°)

C(2)–S(1)–C(5)	94·9 (2)	C(6)–N(61)–C(61)	119·6 (3)
S(1)–C(2)–C(3)	105·1 (2)	N(61)–C(61)–O(61)	122·8 (3)
S(1)–C(2)–C(21)	109·5 (3)	N(61)–C(61)–C(62)	118·2 (3)
S(1)–C(2)–C(22)	108·5 (3)	O(61)–C(61)–C(62)	118·9 (3)
C(3)–C(2)–C(21)	109·4 (3)	C(61)–C(62)–O(62)	110·9 (3)
C(3)–C(2)–C(22)	113·1 (3)	C(62)–O(62)–C(63)	117·9 (3)
C(21)–C(2)–C(22)	111·1 (3)	O(62)–C(63)–C(64)	124·0 (4)
C(2)–C(3)–C(4)	105·7 (3)	O(62)–C(63)–C(68)	115·8 (4)
C(2)–C(3)–C(31)	112·9 (3)	C(64)–C(63)–C(68)	120·2 (4)
N(4)–C(3)–C(31)	113·5 (3)	C(63)–C(64)–C(65)	117·8 (5)
C(3)–N(4)–C(5)	117·8 (3)	C(64)–C(65)–C(66)	122·9 (6)
C(3)–N(4)–C(7)	130·1 (3)	C(65)–C(66)–C(67)	118·5 (5)
C(5)–N(4)–C(7)	96·1 (3)	C(66)–C(67)–C(68)	120·5 (5)
N(4)–C(5)–S(1)	106·1 (2)	C(67)–C(68)–C(63)	120·1 (5)
N(4)–C(5)–C(6)	87·7 (2)	C(6)–N(62)–C(69)	121·6 (3)
S(1)–C(5)–C(6)	122·8 (2)	N(62)–C(69)–O(69)	125·4 (4)
C(5)–C(6)–C(7)	84·0 (2)	N(62)–C(69)–O(70)	110·0 (4)
C(5)–C(6)–N(61)	114·0 (3)	O(69)–C(69)–O(70)	124·6 (4)
C(5)–C(6)–N(62)	119·3 (3)	C(69)–O(70)–C(70)	117·5 (5)
C(7)–C(6)–N(61)	111·5 (2)	[O(70)–C(70)–C(71)	112·1]
C(7)–C(6)–N(62)	117·7 (3)	C(3)–C(31)–O(31)	122·3 (4)
N(61)–C(6)–N(62)	108·7 (3)	C(3)–C(31)–O(32)	113·6 (3)
C(6)–C(7)–O(71)	134·6 (3)	O(31)–C(31)–O(32)	124·2 (4)
N(4)–C(7)–O(71)	133·1 (3)	C(31)–O(32)–C(32)	115·8 (3)
C(6)–C(7)–N(4)	92·3 (2)		

(*c*) Selected torsion angles (°)

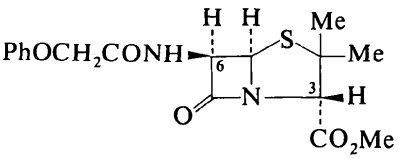
C(5)–S(1)–C(2)–C(3)	18·4 (3)
S(1)–C(2)–C(3)–N(4)	−30·8 (3)
C(2)–C(3)–N(4)–C(5)	34·5 (4)
C(3)–N(4)–C(5)–S(1)	−20·3 (3)
N(4)–C(5)–S(1)–C(2)	−0·8 (2)
C(3)–N(4)–C(5)–C(6)	−143·8 (3)
C(7)–N(4)–C(5)–C(6)	−1·7 (3)
N(4)–C(5)–C(6)–C(7)	1·5 (2)
C(5)–C(6)–C(7)–N(4)	−1·6 (2)
C(6)–C(7)–N(4)–C(5)	1·8 (3)
C(7)–N(4)–C(5)–S(1)	121·8 (2)
C(3)–N(4)–C(7)–O(71)	−40·6 (6)
C(6)–N(62)–C(69)–O(69)	4·4 (7)
C(6)–N(61)–C(61)–O(61)	5·3 (5)

Table 2 (*cont.*)

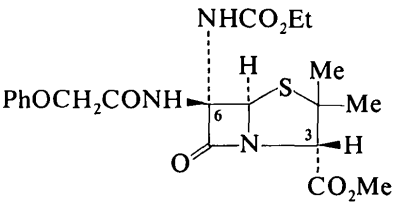
(*d*) Intermolecular contacts <3·50 Å between non-hydrogen atoms

O(31)···C(32^{I})*	3·29 (1)	O(71)···O(61^{II})	3·03 (1)
O(69)···C(22^{I})	3·41 (1)	O(71)···N(62^{II})	2·99 (1)
C(7)···O(61^{II})	3·38 (1)	N(61)···O(61^{II})	3·08 (1)
C(21)···O(61^{II})	3·37 (1)	O(62)···O(61^{II})	3·14 (1)
O(71)···N(61^{II})	3·47 (1)	C(22)···O(69^{III})	3·41 (1)
O(71)···C(61^{II})	3·12 (1)		

* Roman numerals as superscripts refer to the following equivalent positions, which should be applied to the coordinates of the second atom: (I) $y, -x, \frac{1}{4}+z$; (II) $y, 1-x, \frac{1}{4}+z$; (III) $-y, x, -\frac{1}{4}+z$.



(I)



(II)

The molecular geometry of (II) presents few features of novel interest. The five-membered ring adopts an envelope conformation defined by the torsion angles in Table 2, in which C(3) is the out-of-plane atom. The β-lactam system is characterized by an almost planar four-membered ring, which contains a pyramidal N atom [N(4); sum of interbond angles 344·0°]. However, although two examples of unfused β-lactam systems both possess planar rings *and* planar ring-N atoms (Kartha & Ambady, 1973; Colens, Declercq, Germain, Putzeys & Van Meerssche, 1974), an examination of other penicillanate and cephem derivatives reveals both planar and puckered β-lactam rings, and also planar and pyramidal N atoms, these two features occurring together in all combinations with no obvious systematic trend (Vijayan, Anderson & Hodgkin, 1973; Cox, McClure & Sim, 1974; Kobelt & Paulus, 1974*a*,*b*; Paulus, 1974*a*,*b*; Cameron, Cameron, Campbell & Johnson, 1976). One feature of the β-lactam geometry which does appear consistently, particularly in highly substituted examples, is extension of the C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) endocyclic bonds. Thus C(5)–C(6) and C(6)–C(7) of (II) have lengths of 1·585 (5) and 1·558 (5) Å respectively.

The variety and nature of the substituents in (II) would be expected to provide ample opportunity for intermolecular association other than simply by van der Waals attractions. An examination of intermolecular separations (Table 2) reveals that the molecules

associate *via* a complex network of N—H···O hydrogen bonds and dipolar attractions, utilizing most of the available amide and carbonyl functional groups.

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Structure of Demethylsterigmatocystin

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Abstract. $C_{17}H_{10}O_6$, $M_r = 310{\cdot}3$, monoclinic, $C2$, $a = 16{\cdot}359\ (3)$, $b = 7{\cdot}099\ (1)$, $c = 12{\cdot}150\ (1)$ Å, $\beta = 107{\cdot}71\ (1)°$, $D_x = 1{\cdot}53$ Mg m^{-3} for $Z = 4$. The structure was refined by the block-diagonal least-squares method to $R = 0{\cdot}068$ for 962 non-zero reflections. The xanthone skeleton is slightly twisted to take a propeller-like form.

Introduction. The title compound was isolated from *Aspergillus versicolor* (Vuillemin) Tiraboschi, and was shown to be a demethyl derivative of sterigmatocystin (Elsworthy, Holker, McKeown, Robinson & Mulheirn, 1970). The present X-ray analysis was undertaken to reveal the conformation of the dihydrofuro[2,3-*b*]furan moiety which is a common structural unit in toxic metabolites of the genus *Aspergillus*.

Pale yellow needle-shaped crystals elongated along the *b* axis were obtained from acetone solution. The systematic absences uniquely characterized the space group as $C2$, since the compound has optical activity. The unit-cell constants were obtained by least-squares refinement of the setting angles measured on a four-circle diffractometer. The intensities were measured on a Rigaku computer-controlled four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation from a crystal cut to approximate dimensions of $0{\cdot}1 \times 0{\cdot}3 \times 0{\cdot}1$ mm. The θ–2θ scan technique was employed with a scan speed of 4° min^{-1} in 2θ. The scan range for θ was calculated as $1{\cdot}0° + 0{\cdot}15° \tan\theta$. The backgrounds were counted for 10 s at both sides of the scan range. The intensities of 1081 reflections were measured within the range $2\theta \leq 120°$; 962 of these were non-zero, and corrected for Lorentz and polarization factors only. The structure was solved by interpretation of the Patterson function, and refined by block-diagonal least-squares calculations (Ashida, 1973) with anisotropic temperature factors for heavy atoms and fixed isotropic temperature factors (4·0 Å^2)

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