

The plane through the three extra atoms (NCN) that complete the seven-membered ring forms an angle of 70° with the axis of the biphenyl part. The N atoms are sp^3 hybridized in spite of being next to a benzene ring. Often N atoms next to double bonds or aromatic systems are sp^2 hybridized in the same plane as the π system, but here the lone pair is instead engaged in hydrogen bonding. Fig. 2 shows how all N and O atoms take part in the double hydrogen bonds that link the molecules into chains along *c*. The hydrogen bonds are in the range 2.83–2.95 Å, and are probably not quite linear because that would not give the best angles at O and N.

The bond lengths are all in the expected range, especially when thermal motion is taken into account. An analysis of the thermal motion in terms of a rigid body for each molecule (Schomaker & Trueblood, 1968) shows a not too good agreement but the corrections brought the lengths of the outer bonds in the benzene rings up to 1.39–1.40 Å.

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Methyl Benzylpenicillate: A Penicillin Rearrangement Product

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Abstract. $C_{17}H_{20}N_2O_4S$, monoclinic, $P2_1$, $a = 12.435$ (3), $b = 6.211$ (1), $c = 12.834$ (3) Å, $\beta = 118.31$ (2)°, $Z = 2$, $D_o = 1.32$, $D_c = 1.326$ g cm⁻³. An envelope thiazolidine ring is fused to a planar NCNCC ring. The ring junction at C(5) is *trans* to the carboxy-methyl side chain.

Introduction. Crystals suitable for X-ray diffraction were obtained by recrystallization from benzene. Precession photographs (Mo $K\alpha$ radiation) provided initial cell dimensions, and the space group $P2_1$ was indicated by systematic absences ($0k0$ for odd k) and the optical activity of the compound.

A well-formed plate crystal ($\sim 0.6 \times 0.6 \times 0.2$ mm) was mounted in a Lindemann-glass tube on a Hilger & Watts Y290 four-circle diffractometer with a few degrees from the φ axis. Cell parameters and the orientation matrix were refined by a least-squares procedure from 12 reflexions ($2\theta > 40^\circ$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, Zr filter, room temperature).

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Intensities were collected for all independent reflexions with $2\theta \leq 55^\circ$ (θ - 2θ step scan: 2 s count at each of 50 steps of 0.02° in θ , 25 s background count at each end). Calibrated attenuators were inserted into the beam for very intense reflexions. Three periodically monitored standard reflexions showed no significant variation. Absorption corrections were not applied ($\mu = 2.10$ cm⁻¹).

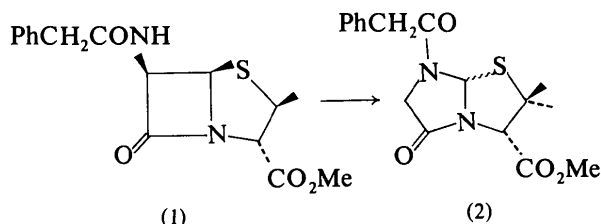
All 2037 independent reflexions with measured $I > 0$ were used for structure solution and refinement.

Attempts to solve the structure by direct methods failed: it was subsequently found that several atoms had y coordinates very close to that of the S atom (totalling about 25% of the scattering power). x and z coordinates for the S atom were obtained from a Patterson synthesis; y was fixed at 0 to define the cell origin. Other non-hydrogen atoms were located by Fourier syntheses. Refinement of coordinates and anisotropic thermal parameters was by full-matrix least-squares methods, to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F)$ based on counting statistics]. H atoms (clearly revealed in a difference synthesis after refinement of the other atoms had converged) were placed in geometrically calculated

positions ($C-H = 0.95 \text{ \AA}$; Churchill, 1973) for the final cycles, with group isotropic thermal parameters.

The final values of R and $R_w [= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}]$ were 5.18% and 4.81%. The number of parameters refined was 224. An analysis of variance showed no trends with $\sin \theta$, $|F_o|$ or indices. A final difference synthesis contained no significant features. Scattering factors for uncharged atoms were those of Cromer & Waber (1974) with anomalous scattering corrections (Cromer & Ibers, 1974). Atomic coordinates are given in Table 1.*

Discussion. The conversion of methyl benzylpenicillinate (1) into methyl benzylpenicillinate (2)



was one of the first encountered penicillin rearrangements (Peck & Folkers, 1949). It is accomplished by refluxing in benzene or toluene containing a trace of iodine. Various mechanisms have been proposed

* Lists of structure factors, thermal parameters and hydrogen atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33768 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) for non-hydrogen atoms

	x	y	z
S(1)	1505 (1)	0	4871 (1)
C(2)	2112 (3)	-1954 (6)	6093 (3)
C(21)	1718 (4)	-4241 (7)	5636 (5)
C(22)	1646 (4)	-1349 (9)	6969 (4)
C(3)	3523 (3)	-1768 (6)	6605 (3)
C(31)	4083 (3)	68 (8)	7481 (3)
O(32)	4296 (3)	1813 (6)	7260 (3)
O(33)	4281 (3)	-545 (5)	8547 (2)
C(34)	4656 (7)	1191 (11)	9431 (4)
N(4)	3721 (2)	-1459 (4)	5594 (2)
C(5)	2904 (2)	57 (6)	4729 (2)
N(6)	2798 (2)	-739 (4)	3624 (2)
C(7)	3434 (2)	-2783 (5)	3773 (3)
C(8)	3997 (2)	-3180 (5)	5080 (3)
O(81)	4568 (2)	-4749 (5)	5608 (2)
C(61)	2365 (3)	584 (5)	2677 (3)
O(62)	1938 (2)	2345 (4)	2703 (2)
C(63)	2461 (3)	-263 (7)	1617 (3)
C(64)	1849 (3)	1119 (6)	531 (3)
C(65)	820 (3)	410 (7)	-462 (3)
C(66)	275 (3)	1680 (9)	-1471 (3)
C(67)	744 (4)	3659 (9)	-1491 (4)
C(68)	1757 (4)	4392 (8)	-503 (4)
C(69)	2310 (3)	3134 (7)	497 (3)

(Johnson, Woodward & Robinson, 1949; Jansen & Robinson, 1967; Sharma & Stoodley, 1978). The stereochemistry of the ring junction of the product is an important piece of evidence, but has never been conclusively demonstrated. The crystal structure determination was undertaken to resolve this. The absolute configuration was deduced from that known for the starting material. The H atoms attached to the ring C atoms (3) and (5) (standard chemical numbering system) are found to be mutually *trans* (Fig. 1). Bond lengths and angles are given in Fig. 2.

The thiazolidine ring [S(1)–C(5)] has an envelope conformation, with a 'flap' angle of 141.7° between the plane of C(2), C(3), N(4) and the least-squares plane fitted to N(4), C(5), S(1), C(2) (r.m.s. deviation of the four atoms from the plane = 0.01 \AA). The other five-membered ring [N(4)–C(8)] is almost planar, showing a slight puckering [deviations from least-squares plane: N(4) 0.034 , C(5) -0.033 , N(6) 0.021 , C(7) -0.002 , C(8) -0.020 \AA]. The angle between the two least-squares planes is 120.5° .

Rotational conformation about bonds is either constrained by ring geometry, or assumed to be

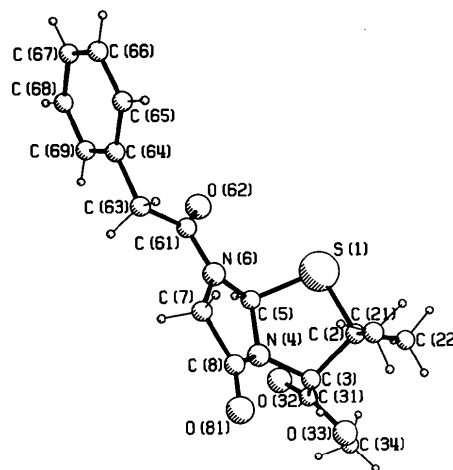


Fig. 1. Perspective view showing the atom-labelling scheme.

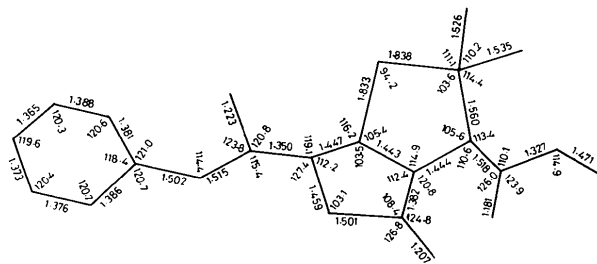


Fig. 2. Bond lengths and angles not involving H atoms. The molecule is distorted (and rotated) from the view of Fig. 1 for clarity. E.s.d.'s in bond lengths are $0.003-0.007 \text{ \AA}$; in angles $0.2-0.4^\circ$. Not shown in the figure: S(1)–C(2)–C(22) 108.6° , C(21)–C(2)–C(3) 108.8° .

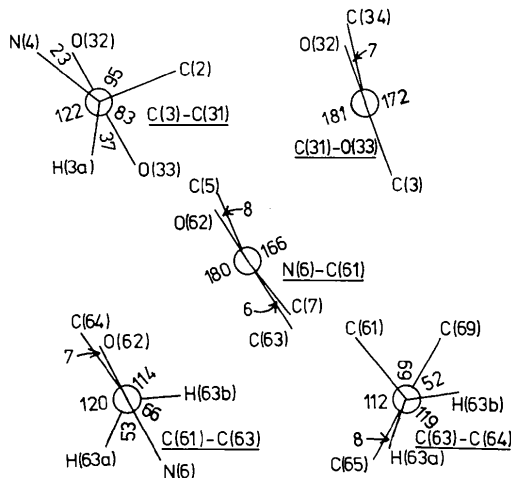


Fig. 3. Torsion angles ($^{\circ}$) for the side chains.

staggered for the placing of the H atoms, except for the side chains attached to C(3) and N(6). Torsion angles for these are shown in Fig. 3; they result from electronic (conjugation) and steric effects.

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(±)-2-*exo*- and *endo*-Methylamino-1,2,3,4-tetrahydro-1,4-ethanonaphthalene Hydrochlorides

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Abstract. $C_{13}H_{18}ClN$ (*exo*), $M_r = 223.75$, monoclinic, $P2_1/n$, $Z = 4$, $a = 10.703(2)$, $b = 7.503(2)$, $c = 15.251(2)$ Å, $\beta = 97.78(2)^{\circ}$, $D_o = 1.23$, $D_c = 1.23$ g cm^{-3} , $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu(Mo K\alpha) = 2.856$ cm^{-1} , $R = 0.037$ for 2142 observed reflections after anisotropic refinement of all non-hydrogen atoms and positional-parameter refinement of H atoms. $C_{13}H_{18}ClN$ (*endo*), $M_r = 223.75$, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.955(4)$, $b = 14.702(5)$, $c = 10.215(3)$ Å, $\beta = 93.28(2)^{\circ}$, $D_o = 1.25$, $D_c = 1.25$ g cm^{-3} , $\lambda(Mo K\alpha) =$

0.7107 Å, $\mu(Mo K\alpha) = 2.905$ cm^{-1} , $R = 0.078$ for 1175 observed reflections after anisotropic refinement of all non-hydrogen atoms.

Introduction. Single crystals of the title compounds were obtained as colorless prisms upon recrystallization from ethanol. Both compounds showed monoclinic symmetry and systematic absences consistent with the space group $P2_1/n$. Intensity data were collected using crystals $0.25 \times 0.30 \times 0.40$ mm in size (*exo*) and $0.25 \times 0.25 \times 0.35$ mm in size (*endo*), an Enraf-Nonius CAD-4 diffractometer, a graphite monochromator, Mo $K\alpha$ radiation, and the $\theta-2\theta$ scanning technique. Intensities were measured for 3908 indepen-

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