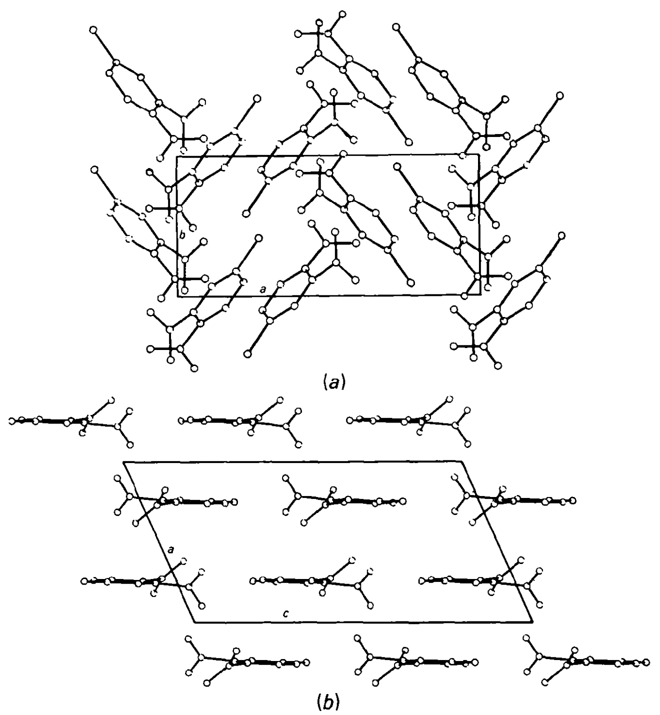

Fig. 2. Packing of molecules in (a) γ-4-chloro-1,2-dinitrobenzene and (b) β-4-chloro-1,2-dinitrobenzene.

The polymorphs appear to contain alternative and quite different modes of packing of almost identical molecules. Similar intermolecular interactions are involved in the two structures giving rise to closely similar unit-cell volumes.

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Acta Cryst. (1985). C**41**, 1512–1514

Benzyl (±)-1α-Hydroxy-7β-phenoxyacetamido-1-carbacephalosporanate*

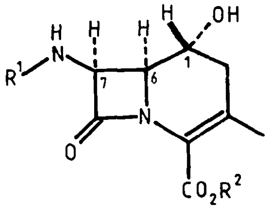
By George A. Sim

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

(*Received* 3 *June* 1985; *accepted* 28 *June* 1985)

Abstract. $C_{24}H_{24}N_2O_6$, $M_r = 436{\cdot}47$, monoclinic, $I2/c$, $a = 20{\cdot}900\,(3)$, $b = 10{\cdot}340\,(2)$, $c = 24{\cdot}226\,(5)$ Å, $\beta = 120{\cdot}82\,(2)°$, $V = 4496\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}29$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 1840$, $T = 293$ K, $R = 0{\cdot}045$ for 2466 reflections. The β-lactam N atom is displaced by 0·20 (1) Å from the plane of the three atoms to which it is bonded; despite this, the compound lacks antibiotic activity. The N—C and C—O bond lengths show that there is less $p\pi$ overlap in the β-lactam than in the side-chain amide. There are two intermolecular hydrogen bonds.

Introduction. 1-Carbacephem derivatives have high levels of antibacterial activity (Doyle *et al.*, 1980). The 1α-hydroxy-1-carbacephem system (1) was prepared in the hope that it would display enhanced activity by analogy with cephen *R*-sulfoxides (de Koning, Marx, Poot, Smid & Vermeij, 1977) but, in the event, proved to be inactive (Bremner, Colvin, Gallacher & MacLeod, 1983). An X-ray study of the title compound [(1): $R^1 = PhOCH_2CO$ and $R^2 = PhCH_2$] was undertaken to confirm the structure and relative stereochemistry and to obtain geometrical details of the β-lactam system.



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[*] Benzyl (±)-5α-hydroxy-3-methyl-8-oxo-7β-phenoxyacetamido-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylate.

0108-2701/85/101512-03$01.50

Experimental. Colourless crystal, dimensions 0·40 × 0·20 × 0·15 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Mo $K\alpha$ radiation. Cell dimensions from setting angles of 24 independent reflections. 5025 intensities surveyed in the range θ 2–27°; 276 equivalent reflections merged to give 138 with R_{int} 0·022; 2466 independent reflections with $I > 2{\cdot}5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined with a version of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) adapted for the Glasgow University ICL 2976 computer by Dr C. J. Gilmore. Subsequent calculations used the *SHELX* (Sheldrick, 1976) and *GX* (Mallinson & Muir, 1985) systems of programs. H atoms located in difference Fourier synthesis. Least-squares calculations on F with anisotropic thermal parameters for C, N and O atoms and isotropic for H atoms converged at R 0·045, wR 0·048, S 1·83, $\Delta/\sigma \le 0{\cdot}04$, $w = 1/\sigma^2(|F_o|)$. Full-matrix least-squares program currently implemented in the *GX* system on the SEL 32/27 computer permits a maximum of 350 variables; two groups of ten H atoms, H(1)–H(13) and H(20)–H(32), were alternately held fixed during successive final least-squares calculations. Final $\Delta\rho$ max. 0·22, min. $-0{\cdot}24$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn with *ORTEP* (Johnson, 1965) illustrates the molecular geometry and confirms Colvin's assignment of relative stereochemistry, with the substituents at C(1) and C(7) in a *trans* arrangement.

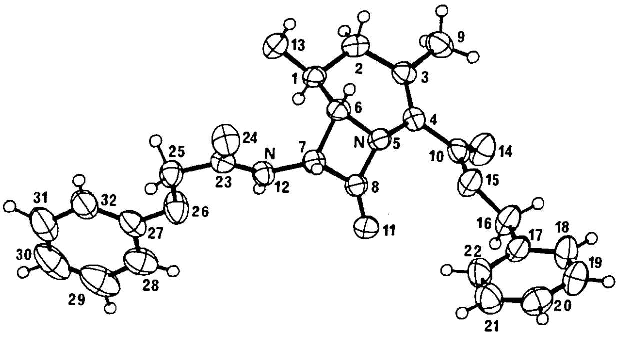

Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C, N and O atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0·1 Å.

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

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
C(1)	0·36821 (14)	0·10980 (25)	0·28251 (11)	0·045
C(2)	0·36681 (15)	−0·03559 (25)	0·27187 (12)	0·052
C(3)	0·38847 (14)	−0·08213 (24)	0·22461 (12)	0·045
C(4)	0·39393 (14)	0·00072 (24)	0·18466 (12)	0·043
N(5)	0·37334 (11)	0·13203 (19)	0·18511 (9)	0·042
C(6)	0·33469 (13)	0·17701 (24)	0·21793 (11)	0·041
C(7)	0·36035 (13)	0·31579 (24)	0·21325 (11)	0·042
C(8)	0·40510 (15)	0·24836 (25)	0·18745 (11)	0·042
C(9)	0·39960 (17)	−0·22588 (27)	0·22417 (14)	0·061
C(10)	0·41793 (15)	−0·03175 (26)	0·13863 (12)	0·045
O(11)	0·45115 (10)	0·28101 (18)	0·17432 (9)	0·059
N(12)	0·40388 (11)	0·39104 (20)	0·27080 (9)	0·043
O(13)	0·33201 (10)	0·14512 (19)	0·31629 (8)	0·060
O(14)	0·45880 (12)	−0·11949 (20)	0·14481 (9)	0·067
O(15)	0·39002 (11)	0·05052 (18)	0·08902 (8)	0·058
C(16)	0·4200 (2)	0·0372 (4)	0·0468 (2)	0·070
C(17)	0·37798 (16)	0·12903 (27)	−0·00787 (12)	0·055
C(18)	0·3424 (2)	0·0856 (3)	−0·0702 (2)	0·070
C(19)	0·30308 (19)	0·16970 (37)	−0·12073 (15)	0·072
C(20)	0·29946 (19)	0·29705 (37)	−0·10933 (16)	0·069
C(21)	0·3348 (2)	0·3425 (4)	−0·0476 (2)	0·077
C(22)	0·3749 (2)	0·2591 (3)	0·0030 (2)	0·070
C(23)	0·37297 (14)	0·46887 (24)	0·29376 (12)	0·044
O(24)	0·30500 (10)	0·48295 (20)	0·26783 (9)	0·062
C(25)	0·42338 (15)	0·53920 (31)	0·35569 (14)	0·052
O(26)	0·49747 (10)	0·53210 (20)	0·36942 (9)	0·064
C(27)	0·55221 (16)	0·59235 (26)	0·42418 (13)	0·053
C(28)	0·62130 (18)	0·59491 (34)	0·42960 (18)	0·070
C(29)	0·6801 (2)	0·6536 (4)	0·4823 (2)	0·089
C(30)	0·6709 (3)	0·7050 (4)	0·5293 (2)	0·090
C(31)	0·6026 (3)	0·7022 (3)	0·5246 (2)	0·082
C(32)	0·5420 (2)	0·6450 (3)	0·4711 (2)	0·067

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(1)–C(2)	1·523 (4)	C(1)–C(6)	1·516 (4)
C(1)–O(13)	1·418 (3)	C(2)–C(3)	1·509 (4)
C(3)–C(4)	1·340 (4)	C(3)–C(9)	1·505 (4)
C(4)–N(5)	1·426 (4)	C(4)–C(10)	1·477 (4)
N(5)–C(6)	1·469 (4)	N(5)–C(8)	1·361 (4)
C(6)–C(7)	1·556 (4)	C(7)–C(8)	1·533 (4)
C(7)–N(12)	1·441 (4)	C(8)–O(11)	1·206 (4)
C(10)–O(14)	1·202 (4)	C(10)–O(15)	1·338 (4)
N(12)–C(23)	1·320 (4)	O(15)–C(16)	1·454 (4)
C(16)–C(17)	1·496 (5)	C(17)–C(18)	1·373 (5)
C(17)–C(22)	1·378 (5)	C(18)–C(19)	1·379 (5)
C(19)–C(20)	1·355 (6)	C(20)–C(21)	1·368 (5)
C(21)–C(22)	1·377 (5)	C(23)–O(24)	1·233 (4)
C(23)–C(25)	1·507 (4)	C(25)–O(26)	1·409 (4)
O(26)–C(27)	1·379 (4)	C(27)–C(28)	1·382 (5)
C(27)–C(32)	1·371 (5)	C(28)–C(29)	1·379 (6)
C(29)–C(30)	1·355 (7)	C(30)–C(31)	1·373 (7)
C(31)–C(32)	1·397 (6)		

C(2)–C(1)–C(6)	108·6 (2)	C(2)–C(1)–O(13)	112·5 (3)
C(6)–C(1)–O(13)	112·1 (2)	C(1)–C(2)–C(3)	117·1 (3)
C(2)–C(3)–C(4)	120·9 (3)	C(2)–C(3)–C(9)	115·3 (3)
C(4)–C(3)–C(9)	123·7 (3)	C(3)–C(4)–N(5)	117·7 (3)
C(3)–C(4)–C(10)	126·0 (3)	N(5)–C(4)–C(10)	116·3 (3)
C(4)–N(5)–C(6)	123·9 (2)	C(4)–N(5)–C(8)	134·4 (3)
C(6)–N(5)–C(8)	95·1 (2)	C(1)–C(6)–N(5)	108·8 (2)
C(1)–C(6)–C(7)	120·2 (2)	N(5)–C(6)–C(7)	87·0 (2)
C(6)–C(7)–C(8)	85·1 (2)	C(6)–C(7)–N(12)	119·8 (2)
C(8)–C(7)–N(12)	115·2 (2)	N(5)–C(8)–C(7)	91·9 (2)
N(5)–C(8)–O(11)	132·4 (3)	C(7)–C(8)–O(11)	135·7 (3)
C(4)–C(10)–O(14)	124·9 (3)	C(4)–C(10)–O(15)	111·9 (3)
O(14)–C(10)–O(15)	123·2 (3)	C(7)–N(12)–C(23)	122·3 (3)
C(10)–O(15)–C(16)	115·1 (3)	O(15)–C(16)–C(17)	107·1 (3)
C(16)–C(17)–C(18)	120·5 (3)	C(16)–C(17)–C(22)	120·9 (3)
C(18)–C(17)–C(22)	118·6 (3)	C(17)–C(18)–C(19)	120·7 (4)
C(18)–C(19)–C(20)	120·2 (4)	C(19)–C(20)–C(21)	120·1 (4)
C(20)–C(21)–C(22)	120·0 (4)	C(17)–C(22)–C(21)	120·5 (3)
N(12)–C(23)–O(24)	122·8 (3)	N(12)–C(23)–C(25)	118·1 (3)
O(24)–C(23)–C(25)	119·1 (3)	C(23)–C(25)–O(26)	109·5 (3)
C(25)–O(26)–C(27)	118·2 (3)	O(26)–C(27)–C(28)	114·3 (3)
O(26)–C(27)–C(32)	124·9 (3)	C(28)–C(27)–C(32)	120·8 (3)
C(27)–C(28)–C(29)	119·2 (4)	C(28)–C(29)–C(30)	120·5 (4)
C(29)–C(30)–C(31)	120·7 (5)	C(30)–C(31)–C(32)	119·7 (4)
C(27)–C(32)–C(31)	119·0 (4)		

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* Coordinates and bond lengths involving H atoms, together with lists of structure factors, anisotropic thermal parameters and torsion angles, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42343 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The nitrogen atom of the β-lactam, N(5), is displaced by 0·204 (2) Å from the plane of C(4), C(6) and C(8), similar to displacements in the cephalosporins (Sweet & Dahl, 1970). The out-of-plane distortions of an amide group can be partitioned among out-of-plane bending at the nitrogen (χ_N) and the carbonyl carbon (χ_C) and twisting around the N—CO bond (τ) (Winkler & Dunitz, 1971). The appropriate parameters here are χ_N −29·5, χ_C 0·6 and τ 186·9° [*i.e.* a twist of 6·9°], conforming to earlier observations that out-of-plane bending in strained amides is greater at nitrogen than at the carbonyl carbon (Winkler & Dunitz, 1971; Buchanan, Kitson, Mallinson, Sim, White & Cox, 1983). The torsion angles within the non-planar four-membered ring are 6·6 (2)–7·6 (2), mean 7·2°.

The nitrogen atom has pyramidal geometry in several biologically active β-lactams (Sweet & Dahl, 1970). The present results show that pyramidal geometry can also be associated with the absence of antibiotic activity. A recent review has reported that pyramidal geometry at the β-lactam nitrogen is not necessary for antibiotic activity (Page, 1984).

The N—CO bond in the β-lactam, 1·361 (4) Å, is rather longer than N(12)—C(23) in the side-chain amide, 1·320 (4) Å, and, conversely, the β-lactam C(8)—O(11) distance of 1·206 (4) Å is shorter than the C(23)—O(24) distance of 1·233 (4) Å. These results indicate less $p\pi$ overlap in the β-lactam than in the normal side-chain amide.

There are two hydrogen-bonded intermolecular contacts in the crystal: O(13)H···O(24) ($\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$) 2·85 (1) Å and O(11)···HN(12) ($1-x, y, \frac{1}{2}-z$) 2·85 (1) Å.

I am grateful to Dr E. W. Colvin for excellent crystals of the title compound.

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Acta Cryst. (1985). C**41**, 1514–1516

Structure of an *N*-Sulphinylaniline Cycloadduct

BY ZBIGNIEW DAUTER,* PETER HANSON, COLIN D. REYNOLDS,† WILLIAM A. STOCKBURN AND THOMAS W. STONE

Department of Chemistry, University of York, York YO1 5DD, England

(*Received* 25 *January* 1985; *accepted* 2 *July* 1985)

Abstract. (8a*RS*,9*RS*,10a*SR*)-10-Phenyl-1,2,3,4,5,6,7,8,8a,10a-decahydro-10*H*-9-thia-10-azaphenanthrene 9-oxide, $C_{18}H_{23}NOS$, $M_r = 301·45$, monoclinic, $P2_1$, $a = 5·661\ (2)$, $b = 18·071\ (5)$, $c = 8·178\ (4)$ Å, $\beta = 103·74\ (3)°$, $V = 812·67$ Å^3, $Z = 2$, $D_x = 1·23$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 1·64$ mm^{-1}, $F(000) = 324$, $T = 290\ (1)$ K, $R = 0·062$ for 1112 observed reflections. In the title compound the S—O bond is *trans* to the two C—H bonds of the ring junctions. The heterocyclic ring adopts a conformation such that S and N are displaced by −0·65 (1) and 0·18 (1) Å from the mean plane of the other four atoms. The S—O, S—N and S—C bond lengths are 1·475 (5), 1·680 (6) and 1·779 (8) Å, respectively.

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* Permanent address: Department of Biochemistry, Technical University of Gdansk, Gdansk, Poland.

† Permanent address: Biophysics Laboratory, Department of Physics, Liverpool Polytechnic, Liverpool L3 3AF, England.

0108-2701/85/101514-03$01.50