Table 2. *Bond lengths* (Å), *bond angles* (°) *and some torsion angles* (°) *with e.s.d.'s in parentheses*

O1—C3	1.460 (9)	C2—C3	1.528 (9)
O2—C4	1.438 (10)	C3—C4	1.546 (10)
O3—C9	1.452 (11)	C4—C5	1.556 (13)
C1—C2	1.545 (13)	C5—C6	1.553 (9)
C1—C6	1.572 (10)	C5—C13	1.525 (11)
C1—C11	1.544 (12)	C6—C7	1.494 (13)
C1—C12	1.524 (9)	C7—C8	1.335 (11)
C8—C9	1.490 (13)	C9—C10	1.511 (10)
C11—C1—C12	107.9 (7)	O2—C4—C5	113.7 (8)
C6—C1—C12	109.6 (7)	C4—C5—C13	110.6 (7)
C6—C1—C11	111.0 (7)	C4—C5—C6	111.2 (8)
C2—C1—C12	108.0 (8)	C6—C5—C13	111.8 (7)
C2—C1—C11	111.7 (8)	C1—C6—C5	111.2 (6)
C2—C1—C6	108.7 (7)	C5—C6—C7	110.7 (6)
C1—C2—C3	118.2 (8)	C1—C6—C7	113.6 (6)
O1—C3—C2	109.4 (7)	C6—C7—C8	124.0 (10)
C2—C3—C4	111.8 (7)	C7—C8—C9	127.9 (9)
O1—C3—C4	109.0 (7)	O3—C9—C8	111.6 (7)
O2—C4—C3	108.9 (8)	C8—C9—C10	112.5 (8)
C3—C4—C5	113.5 (6)	O3—C9—C10	108.8 (9)
C2—C1—C6—C7	179.4 (9)	O1—C3—C4—O2	157.4 (7)
C12—C1—C6—C5	−172.5 (8)	C2—C3—C4—C5	46.1 (11)
C11—C1—C6—C5	68.5 (10)	O1—C3—C4—C5	−74.9 (10)
C2—C1—C6—C5	−54.7 (10)	C3—C4—C5—C6	−53.7 (10)
C6—C1—C2—C3	50.2 (11)	O2—C4—C5—C6	71.5 (10)
C11—C1—C2—C3	−72.5 (10)	C3—C4—C5—C13	−178.6 (8)
C11—C1—C6—C7	−57.1 (10)	C4—C5—C6—C1	58.3 (10)
C1—C2—C3—O1	74.6 (10)	C13—C5—C6—C1	−177.5 (8)
C1—C2—C3—C4	−46.2 (11)	C6—C7—C8—C9	179.4 (9)

1.450 (10) Å. The valence angles involving tetrahedral and trigonal C atoms have mean values of 111.1 (7) and 126.0 (10)°, respectively. Molecular packing is determined by hydrogen bonds of the O—H···O type involving the hydroxy O atoms in the equivalent positions $-x$, $y-\frac{1}{2}$, $-z-1$ [O(1)···O(2) 2.846 (1), H(1)···O(2) 1.972 (1) Å, O(1)—H(1)···O(2) 143.3 (6)°], and $x+1$, y, z [O(2)···O(3) 2.860 (1), H(2)···O(3) 1.941 (1) Å, O(2)—H(2)···O(3) 150.5 (5)°]. Other contacts are consistent with van der Waals interactions.

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Structure of (2*S*,5*S*)-2-Hydroxymethyl-5-methoxy-*N*-*o*-nitrobenzoylpyrrolidine

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Abstract. $C_{13}H_{16}N_2O_5$, $M_r = 280.3$, monoclinic, $P2_1$, $a = 10.307$ (3), $b = 9.364$ (3), $c = 7.394$ (2) Å, $\beta =$ 104.65 (2)°, $V = 690.5$ Å^3, $Z = 2$, $D_x = 1.35$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 7.9$ cm^{-1}, $F(000) = 296$, $T = 293$ K, $R = 0.055$ for 1209 observed reflexions. The benzamide group is not planar. The hydroxyl group is engaged in an intramolecular hydrogen bond with the carbonyl of the amido group. A

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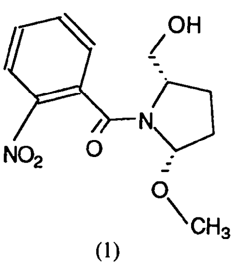
Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic thermal factors* (Å² × 10³) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

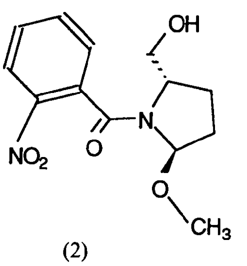
	x	y	z	U_{eq}
N1	2945 (2)	6008 (3)	5333 (3)	40 (1)
C5	3624 (3)	5465 (4)	7179 (4)	47 (2)
C4	5039 (3)	6062 (6)	7457 (5)	66 (4)
C3	5267 (4)	5913 (6)	5496 (6)	72 (4)
C2	3904 (3)	6223 (4)	4155 (4)	53 (3)
C6	3614 (4)	5256 (6)	2453 (5)	70 (4)
O7	2489 (4)	5678 (6)	1031 (4)	98 (4)
O8	3733 (3)	3975 (3)	7175 (4)	73 (3)
C9	2571 (6)	3241 (6)	7175 (9)	94 (6)
C1′	933 (3)	6764 (4)	6305 (4)	38 (2)
C2′	1017 (3)	7838 (1)	7633 (4)	39 (2)
C3′	104 (4)	7951 (4)	8719 (5)	54 (3)
C4′	−898 (3)	6934 (5)	8509 (5)	60 (3)
C5′	−975 (3)	5839 (5)	7282 (6)	57 (3)
C6′	−75 (3)	5755 (4)	6176 (5)	51 (2)
C7′	1771 (3)	6703 (4)	4908 (4)	44 (2)
O8′	1283 (3)	7221 (4)	3360 (3)	73 (3)
N9′	2089 (3)	8895 (4)	7925 (4)	51 (2)
O10′	2809 (3)	8926 (4)	6870 (5)	89 (3)
O11′	2225 (4)	9727 (6)	9196 (7)	118 (5)

correlation has been established between the signs of the circular dichroism bands and the sign of the torsional angle between the *o*-nitrophenyl and the amido group (+90.9°).

Introduction. The diastereomers (2*S*)-2-hydroxymethyl-5-methoxy-*N*-*o*-nitrobenzoylpyrrolidines (1) (5*S*,*cis*) and (2) (5*R*,*trans*) constitute useful intermediates in the synthesis of pyrrolo[1,4]benzodiazepines related to the antitumor antibiotic neothramycins (Andriamialisoa & Langlois, 1986). Their relative configurations were previously assigned by ¹H NMR spectroscopy of the racemic compounds (Langlois, Bourrel & Andriamialisoa, 1986).



(1)



(2)

A circular dichroism study on optically pure compounds (1) and (2) as well as several derivatives showed that the curves of diastereomers *cis* and *trans* were virtually 'enantiomeric' with five Cotton effects alternating in sign between 230 and 340 nm (Snatzke & Langlois, 1986). These results could be explained by the presence of an inherently chiral chromophore: the *o*-nitrobenzamide group deviating from planarity. To correlate the signs of the CD bands with the *o*-nitrobenzamide torsional angle, (1) was submitted to X-ray analysis.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N1—C5	1.459 (4)	C1′—C6′	1.390 (5)
N1—C2	1.487 (4)	C1′—C7′	1.506 (4)
N1—C7′	1.339 (4)	C2′—C3′	1.388 (5)
C5—C4	1.526 (5)	C2′—N9′	1.458 (4)
C5—O8	1.399 (5)	C3′—C4′	1.384 (6)
C4—C3	1.533 (6)	C4′—C5′	1.358 (6)
C3—C2	1.528 (5)	C5′—C6′	1.385 (5)
C2—C6	1.518 (5)	C7′—O8′	1.228 (4)
C6—O7	1.411 (5)	N9′—O10′	1.206 (5)
O8—C9	1.381 (7)	N9′—O11′	1.201 (6)
C1′—C2′	1.393 (4)		

C5—N1—C2	111.2 (2)	C5—N1—C7′	125.4 (3)
C2—N1—C7′	119.5 (3)	N1—C5—C4	102.4 (3)
N1—C5—O8	111.5 (3)	C4—C5—O8	106.9 (3)
C5—C4—C3	102.1 (3)	C4—C3—C2	105.1 (3)
N1—C2—C3	103.4 (3)	N1—C2—C6	112.6 (3)
C3—C2—C6	112.4 (3)	C2—C6—O7	113.8 (4)
C5—O8—C9	115.2 (4)	C2′—C1′—C6′	116.8 (3)
C2′—C1′—C7′	124.5 (3)	C6′—C1′—C7′	118.4 (3)
C1′—C2′—C3′	122.2 (3)	C1′—C2′—N9′	120.3 (2)
C3′—C2′—N9′	117.5 (2)	C2′—C3′—C4′	118.6 (3)
C3′—C4′—C5′	120.7 (4)	C4′—C5′—C6′	120.2 (4)
C1′—C6′—C5′	121.4 (3)	N1—C7′—C1′	119.9 (3)
N1—C7′—O8′	122.9 (3)	C1′—C7′—O8′	117.0 (3)
C2′—N9′—O10′	119.2 (3)	C2′—N9′—O11′	119.4 (3)
O10′—N9′—O11′	121.4 (4)		

C5—N1—C2—C3	−5.7 (3)	N1—C2—C6—O7	74.7 (4)
N1—C2—C3—C4	−19.3 (3)	C5—N1—C7′—C1′	−10.3 (3)
C2—C3—C4—C5	36.2 (4)	N1—C7′—C1′—C2′	90.9 (3)
C3—C4—C5—N1	−38.7 (4)	C1′—C2′—N9′—O10′	8.1 (3)
C4—C5—N1—C2	28.3 (3)	C1′—C2′—N9′—O11′	−172.8 (4)
N1—C5—O8—C9	−76.7 (4)	N1—C7′—O8′—H7	22.3 (24)
N1—C2—C6—O7	74.7 (4)	C2—C6—O7—H7	−24.3 (28)
C2—N1—C7′—O8′	19.2 (3)		

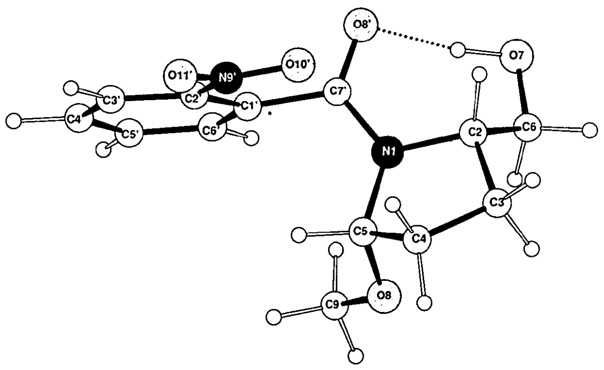


Fig. 1. General view of the molecule.

Experimental. Crystal of dimensions 0.5 × 0.3 × 0.1 mm, Philips PW1100 diffractometer, data collected with ω–2θ scan, graphite-monochromated Cu $K\alpha$ radiation, lattice parameters from 24 reflexions ($6 < \theta < 59°$), monitored reflexions ($\bar{1}\bar{3}1$, $\bar{3}21$, $\bar{2}3\bar{3}$) showed no variation in intensity; 2056 measured reflexions ($-11 < h < 11$, $-10 < k < 10$, $0 < l < 8$, $\theta_{max} = 65°$), 1237 unique ($R_{int} = 0.031$), 1209 observed with $I > 3\sigma(I)$; structure solved by direct methods (Riche, 1973), full-matrix minimization of $\sum w(F_o - |F_c|)^2$ (*SHELX76*; Sheldrick, 1976) where the y coordinate for N1 and N9′ were alternately fixed, $R = 0.055$, $wR = 0.074$, $w = 1/[\sigma^2(F_o) + 0.00047F_o^2]$, $(\Delta\rho)_{max} = 0.2$, $(\Delta\rho)_{min} = -0.3$ e Å^{-3}, $\Delta/\sigma_{max} = 0.04$, $S = 0.91$; H atoms located on difference Fourier maps were given the equivalent isotropic thermal factor of the bonded atom. The H-atom positions were generated geometrically (C—H = 1.08 Å), except for H7 which was refined. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters and equivalent isotropic thermal factors are given in Table 1.* Bond distances, bond angles and selected torsion angles are listed in Table 2. Numbering scheme and absolute configuration are depicted in Fig. 1.

The *o*-nitrobenzamide group is not planar. The aromatic ring is almost perpendicular to the amido group, the dihedral angle between these planes being 94 (1)°. The signs of the CD bands can be ascribed to the sign of the dihedral angle N1—C7′—C1′—C2′ [+90.9 (3)°] which characterizes the chirality of the *o*-nitrobenzamide group. It is anticipated that the sign of the torsion angle N1—C7′—C1′—C2′ would be negative in (2). The amido group (C1′, C7′, N1, O8′) is planar [maximum deviation 0.027 (3) Å], the C2 and C5 atoms deviating from that plane by 0.332 (4) and 0.131 (4) Å, respectively. The sum of the bond angles around the N1 atom is 356.2 (6)°, near the expected value (360°) for sp^2 hybridization. Torsional angles show the five-membered ring in a near-envelope conformation with atom C4 out of the plane of the four others by 0.593 (6) Å [C6 −1.279 (5) and O8 −1.340 (3) Å]. The hydroxyl group is engaged in an intramolecular hydrogen bond with the carbonyl O atom of the amido group [O7···O8′ = 2.772 (4), O7—H = 1.05 (7), H···O8′ = 1.73 (7) Å, ∠O7—H···O8′ = 171 (4)°].

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* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55336 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0277]

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A Substrate for the Asymmetric Nazarov Cyclization

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Abstract. [1*R*-(2-*exo*,3-*exo*)]-3-{[*N*-(3,5-Dimethylphenyl)]benzenesulfonylamino}-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl [2*R*-(2α,3β,5β,6α)]-tetrahydro-2,5,6-trimethyl-4-oxo-2*H*-pyran-3-carboxylate, $C_{33}H_{43}NO_6S$, $M_r = 581.7$, orthorhombic, $P2_12_12_1$, $a = 11.945$ (2), $b = 22.240$ (6), $c = 24.407$ (5) Å, $V = 6483.9$ Å^3, $Z = 8$, $D_x = 1.19$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.3$ cm^{-1}, $F(000) = 2496$, $T = 293$ K, $R = 0.050$ for 1992 observed reflections. The two unique molecules have similar conformations and orientations in the crystal lattice. The N atoms of the tertiary sulfonamides have pyramidal bonding geometries [sum of angles at N: 349 (2) and 347 (2)°] and the N and S aromatic rings lie close to one another with angles of only 24.1 (4) and 28.4 (5)° between their least-squares planes.

Introduction. The Nazarov cyclization reaction is a very useful method of preparing substituted cyclopentenones (Santelli-Rouvier & Santelli, 1983). With a view to modifying this reaction to produce enantiomerically pure products, the racemic ester (1) was prepared [by the reaction of ethyl acetoacetate and

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