

Fig. 1. X-ray structure of (4*R*)-3-[(2'*R*,3'*R*)-2'-bromo-3'-(phenylbutanoyl)]-4-(phenylmethyl)-2-oxazolidinone.

Lantos, 1986). However, X-ray structures of the intermediate bromide obtained from the electrophilic bromination methodology (Evans *et al.*, 1990) have not been reported to date. In our synthesis (Dharanipragada *et al.*, 1989) of optically pure isomers of β -methylphenylalanine, the stereochemistry at the β -carbon is preset by the choice of starting material, *i.e.* (+)- or (-)-3-phenylbutyric acid, the absolute configuration of which is known (Weidler & Bergson, 1964). Hence, determination of stereochemistry at the α -carbon will support models for asymmetric induction (Evans *et al.*, 1987, 1990). In the present case, since a D-chiral auxiliary was used, one would expect to obtain an *R* configuration at all of the three chiral centers in (3). The X-ray structure supported this expectation (Fig. 1), and the optical rotation, $[\alpha]_D^{23} = -38^\circ$ (c 1.1 g dm⁻³, CHCl₃) (Dharanipragada, VanHulle, Bannister, Bear, Kennedy & Hruby, 1992), was also consistent with this stereochemistry. Interestingly, in the solid state, the carbonyls in (3) are aligned opposite to each other presumably to overcome the dipole-dipole interactions and/or van der Waals repulsions. In the enolate (2), however, one would expect them to be parallel to each other due to cyclization by boron. The torsional angle C₂₁—C₂—C₃—Br is 65.4 (3)°. If the inversion

of configuration during displacement of bromide by azide *via* an S_N2 reaction (Dharanipragada *et al.*, 1989) is taken into account, the resulting amino acid (4) would have $\chi_1 = -65^\circ$, suggesting a *gauche*(-) conformation. The absolute configuration found here is completely consistent with the proposed asymmetric induction.

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Structure of *N*-Benzyl-3-benzylidene-4-methyl-4-nitro-5-phenyl-2-pyrrolidinone

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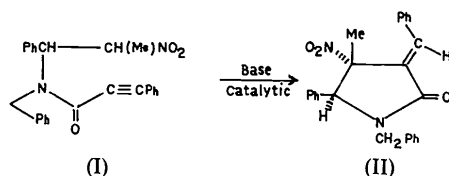
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Abstract. C₂₅H₂₂N₂O₃, $M_r = 398.47$, orthorhombic, $Pbn2_1$, $a = 9.385$ (4), $b = 12.314$ (4), $c = 18.573$ (6) Å, $V = 2146.42$ Å³, $Z = 4$, $D_m = 1.237$, $D_x =$

1.233 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.47$ cm⁻¹, $F(000) = 840$, $T = 298$ K, final $R = 0.039$ for 1518 observed reflections. Results of X-ray analysis reveal

that the methyl group and the phenyl ring attached respectively to the chiral centres at C(4) and C(5) are *cis* with respect to each other. The phenyl ring attached to the olefinic C atom is also in a *cis* orientation with respect to the 4-methyl group.

Introduction. α -Methylene- γ -lactams have cytotoxic activity comparable to the related γ -lactones, but they are much less toxic than the latter group (Belaud, Roussakis, Latournoux, Alami & Villieras, 1985). This special feature would probably make them suitable for therapeutic use in cancer treatment. An efficient stereoselective route to α -methylene- γ -lactams through carbanion addition to acetylenes has recently been described by Patra, Maiti, Chatterjee & Chakravarty (1991). But the stereochemistry of the title compound, obtained through cyclization of the amide (I), could not be settled by the usual spectroscopic analyses. The present X-ray investigation was therefore necessary for an unambiguous establishment of the stereochemistry of the two asymmetric centres as well as that of the *exo*-olefinic bond in the molecule (II).



Experimental. Colourless prismatic specimen, 0.42 \times 0.40 \times 0.64 mm; Nicolet R3m/V diffractometer, graphite-monochromated Mo $K\alpha$ radiation; 35 reflections ($10 < 2\theta < 30^\circ$) used for measuring lattice parameters. Data collected by ω - 2θ scan ($2 \leq 2\theta \leq 50^\circ$), h 0 to 12, k 0 to 15, l 0 to 23. 1915 unique reflections measured (no merging), 1518 reflections with $I > 3\sigma(I)$ considered observed. No significant variation in intensity of three standard reflections measured after every 100 reflections. No decay correction, no absorption correction. Density determined by flotation method in aqueous potassium iodide solution. Structure solved by MULTAN88 (Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988). Full-matrix least-squares refinement on F by SHELX76 (Sheldrick, 1976). Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and 270 parameters for the non-H atoms refined with anisotropic thermal parameters; H atoms with a fixed common $U = 0.08 \text{ \AA}^2$ placed at calculated positions, riding on the C atoms to which they are respectively attached. Weights, $w = 1.00/[\sigma_c^2(F) + 0.005069F^2]$ where σ_c is based on counting statistics only. Final $R = 0.039$, $wR = 0.061$, $S = 1.00$ (maximum $\Delta/\sigma = 0.063$); maximum and minimum peaks

Table 1. Atomic coordinates ($\times 10^4$) of non-hydrogen atoms and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(2)	8105 (3)	384 (2)	7965*	41
C(3)	8091 (3)	-188 (2)	8663 (3)	40
C(4)	7218 (3)	-1216 (2)	8584 (3)	44
C(5)	6473 (3)	-1063 (2)	7842 (3)	42
C(6)	6900 (5)	231 (3)	6789 (3)	59
C(7)	7194 (5)	-589 (3)	6206 (3)	59
C(8)	8366 (6)	-1255 (5)	6223 (4)	82
C(9)	8652 (7)	-1980 (6)	5662 (4)	106
C(10)	7741 (10)	-2033 (6)	5098 (4)	107
C(11)	6581 (8)	-1376 (6)	5062 (4)	105
C(12)	6289 (6)	-658 (5)	5628 (3)	85
C(13)	4873 (3)	-871 (2)	7907 (3)	42
C(14)	3960 (3)	-1741 (3)	7804 (3)	55
C(15)	2510 (4)	-1614 (3)	7909 (4)	74
C(16)	1971 (4)	-627 (4)	8121 (4)	72
C(17)	2875 (4)	238 (3)	8219 (3)	63
C(18)	4333 (4)	117 (2)	8112 (3)	53
C(19)	6250 (4)	-1521 (3)	9202 (3)	58
C(20)	8683 (4)	258 (3)	9245 (3)	51
C(21)	8684 (4)	-143 (3)	9999 (3)	54
C(22)	7884 (6)	411 (4)	10498 (3)	76
C(23)	7832 (8)	49 (6)	11205 (3)	102
C(24)	8622 (8)	-839 (5)	11411 (4)	84
C(25)	9448 (8)	-1364 (4)	10918 (4)	96
C(26)	9479 (6)	-1018 (3)	10209 (3)	75
N(1)	7213 (3)	-149 (2)	7516 (3)	45
N(2)	8344 (3)	-2139 (2)	8488 (3)	51
O(1)	8789 (2)	1210 (2)	7823 (3)	54
O(2)	8506 (3)	-2788 (2)	8972 (3)	74
O(3)	9023 (3)	-2152 (2)	7929 (3)	72

* Fixed to define the origin.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

N(1)—C(2)	1.352 (5)	C(2)—O(1)	1.231 (4)
C(2)—C(3)	1.476 (5)	C(3)—C(20)	1.334 (5)
C(3)—C(4)	1.514 (4)	C(20)—C(21)	1.485 (6)
C(4)—C(5)	1.557 (5)	C(4)—C(19)	1.511 (5)
C(5)—N(1)	1.454 (4)	C(4)—N(2)	1.563 (4)
N(1)—C(6)	1.459 (5)	N(2)—O(2)	1.213 (4)
C(6)—C(7)	1.507 (6)	N(2)—O(3)	1.217 (5)
		C(5)—C(13)	1.525 (4)
C(5)—N(1)—C(2)	114.6 (3)	C(3)—C(4)—C(5)	103.1 (3)
C(5)—N(1)—C(6)	122.5 (3)	C(3)—C(4)—C(19)	117.4 (3)
C(2)—N(1)—C(6)	122.6 (3)	C(3)—C(4)—N(2)	104.6 (2)
N(1)—C(2)—C(3)	107.7 (3)	C(4)—N(2)—O(2)	118.7 (3)
N(1)—C(2)—O(1)	126.3 (3)	C(4)—N(2)—O(3)	117.4 (3)
C(3)—C(2)—O(1)	126.0 (3)	O(2)—N(2)—O(3)	123.9 (3)
C(2)—C(3)—C(4)	108.6 (3)	C(4)—C(5)—N(1)	104.3 (2)
C(2)—C(3)—C(20)	120.7 (3)	C(4)—C(5)—C(13)	113.0 (3)
C(4)—C(3)—C(20)	130.4 (3)	C(13)—C(5)—N(1)	112.6 (2)
C(3)—C(20)—C(21)	128.9 (3)		

in the final difference map 0.14 and -0.15 e \AA^{-3} , respectively. All calculations carried out on a VAX 3400 computer.

Discussion. The refined positional parameters are given in Table 1 and selected bond distances and angles are presented in Table 2.* From a statistical

* Lists of observed and calculated structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54889 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0036]

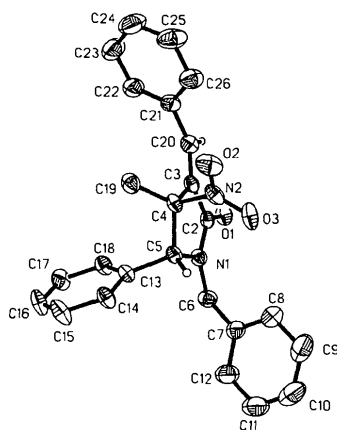


Fig. 1. ORTEPII plot (Johnson, 1976) of the molecule showing the atom-numbering scheme.

study of crystallographic data for 42 pyrrolidinone moieties, Georges, Norberg, Everard & Durant (1989) obtained the following values and statistical standard deviations (enclosed in parentheses) for the bond distances (Å) in the five-membered ring: N(1)—C(2) 1.354 (32), C(2)—C(3) 1.503 (27), C(3)—C(4) 1.510 (53), C(4)—C(5) 1.522 (34), C(5)—N(1) 1.419 (44) Å. Values obtained in the present case compare well with these values.

The ORTEPII plot (Johnson, 1976) of the molecule (Fig. 1) shows that the methyl C atom C(19) and the phenyl ring attached respectively to the two

asymmetric centres C(4) and C(5), have the *cis* stereochemistry. Furthermore, the phenyl ring attached to the olefinic C atom C(20) is in *cis* orientation with respect to the methyl group attached to C(4).

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Structure of 6-Benzyl-5-(3,4-dimethoxybenzyl)-3-methyl-5,6,7,8-tetrahydro-3*H*-oxazolo[5,4-*g*]isoquinolin-2-one

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Abstract. C₂₇H₂₈N₂O₄, *M_r* = 444.5, monoclinic, *P*2₁/*n*, *a* = 7.961 (5), *b* = 11.863 (6), *c* = 24.873 (8) Å, β = 92.29 (1)°, *V* = 2347.16 Å³, *Z* = 4, *D_x* = 1.26 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.49 cm⁻¹,

F(000) = 944.0, *T* = 293 K, *R* = 0.041 for 2854 observed reflections with *I* ≥ 3σ(*I*). The title compound, obtained as a racemate, can be considered as a structural analogue of trimetoquinol, a therapeutic agent which displays various effects in relation to its configuration. It seems then important to specify the

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