differences in dihedral angles. These results indicate that isomers (3*a*) and (3*b*) are formed by a stereospecific transannular attack by N(1) on the incipient carbonium ion from leuconolam (1*a*) followed by a non-stereospecific anti-Markownikoff HCl addition at the β face of the molecule. The bond configuration about the quaternary carbon atom at the junction of four adjoining rings (two five-membered and two six-membered) manifests the effects of ring strain; the valence angles at C(21) range from 100·7 to 121·9° as compared with 101·3 to 115·0° in leuconolam before ring closure.

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References

GOH, S. H., WEI, C. & MOHD. ALI, A. R. (1984). *Tetrahedron Lett.* **25**, 3483–3484.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SCHILLING, J. W. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 201–204. Copenhagen: Munksgaard.

SHELDRICK, G. M. (1982). *Computational Crystallography*, edited by D. SAYRE, pp. 506–514. New York: Oxford Univ. Press.

WEI, C., MOHD. ALI, A. R., GOH, S. H., SINN, E. & BUTCHER, R. J. (1986). *Acta Cryst.* C**42**, 349–351.

Acta Cryst. (1986). C**42**, 1556–1558

Structure of (4*R*)-4-Benzyl-3-dichloroacetyl-1,3-oxazolidine*

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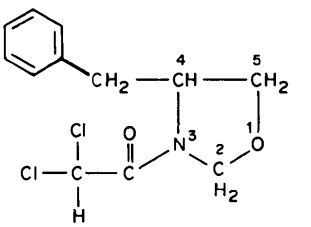
Abstract. $C_{12}H_{13}Cl_2NO_2$, $M_r = 274·1$, orthorhombic, $P2_12_12_1$, $a = 6·235$ (1), $b = 8·219$ (1), $c = 25·636$ (2) Å, $V = 1313·7$ Å^3, $Z = 4$, D_m(flotation in KI solution) = 1·40, $D_x = 1·39$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 4·84$ mm^{-1}, $F(000) = 568·0$, $T = 293$ K, $R = 0·047$ for 979 observed reflections. The absolute configuration determined confirms the title compound to be $R(+)$. The 1,3-oxazolidine ring adopts an envelope conformation with C(9) as flap. The bond lengths and angles of the oxazolidine ring are normal. The molecule has an extended conformation. The molecules are held together by van der Waals interactions.

Introduction. The title compound was prepared in connection with a scheme to synthesize biologically active aminoalcohols. This involves the conversion of phenylalanine to its methyl ester followed by reduction to phenylalaninol (Seki, Koga, Matsuo, Ohki, Matsuo & Yamada, 1965). This by interaction with formaline gave the title compound (Kumar, Natu & Gogte, 1985, unpublished). The aim of the present investigation is to establish the absolute configuration unequivocally.



Experimental. Crystal approx. 0·3 × 0·37 × 0·7 mm, Nonius CAD-4F-11M diffractometer; graphite-monochromated Mo $K\alpha$ radiation; $\omega/2\theta$ scan mode, scan speed 1° min^{-1}; $\theta < 23·5°$, h 0 to 7, k 0 to 9, l 0 to 28. 1179 reflections collected, 979 judged significant ($|F_o| > 3\sigma|F_o|$). Lattice parameters from 25 reflections ($20 < 2\theta < 40°$), three standard reflections (0,2,10, 1,2,13 and 307) every 1000 s, 3% variation in intensity. No correction for absorption. Structure solved by direct methods, program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2).$$

	x	y	z	B_{eq}(Å^2)
Cl(1)	7084 (3)	5909 (2)	−6927 (2)	4·44
Cl(2)	2946 (3)	4302 (2)	−6907 (1)	4·86
N	6663 (8)	4535 (6)	−8119 (2)	2·85
O(1)	9650 (7)	3427 (6)	−8477 (2)	4·07
O(2)	3513 (7)	5745 (5)	−7936 (2)	3·32
C(1)	5097 (10)	4486 (7)	−9563 (2)	3·18
C(2)	3799 (12)	5776 (9)	−9694 (3)	4·39
C(3)	3708 (15)	6311 (12)	−10207 (4)	6·61
C(4)	4854 (15)	5530 (13)	−10587 (3)	6·56
C(5)	6149 (16)	4264 (11)	−10461 (3)	5·99
C(6)	6253 (13)	3725 (9)	−9944 (3)	4·62
C(7)	5223 (10)	3930 (7)	−8999 (2)	3·25
C(8)	6700 (10)	5021 (7)	−8671 (2)	2·77
C(9)	9073 (11)	4779 (8)	−8787 (3)	3·85
C(10)	8719 (10)	3714 (7)	−7984 (2)	3·60
C(11)	5101 (10)	4960 (6)	−7803 (2)	2·66
C(12)	5416 (10)	4433 (7)	−7234 (2)	3·04

least-squares refinement (*LALS*; Gantzel, Sparks & Trueblood, 1961) of scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from difference map) converged to $R = 0{\cdot}047$ and $wR = 0{\cdot}042$; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = (6{\cdot}0 + 1{\cdot}0|F_o| + 0{\cdot}012|F_o|^2)^{-1}$. Max. $(\Delta/\sigma) = 0{\cdot}1$. Final $\Delta\rho$ excursions $< |0{\cdot}2|$ e Å^{-3}. No corrections for secondary extinction. Absolute configuration was determined using the chlorine atoms as anomolous scatterers ($f' = 0{\cdot}132$, $f'' = 0{\cdot}159$ for Mo $K\alpha$) followed by Hamilton's (1965) significance test. Two sets of refinements with the form factor of chlorine corrected for the real part f' and f'' either positive or negative were carried out. The final R factors were 0·050 and 0·047 respectively, $\sum w\Delta F^2$ for the negative f'' refinement was lower. On applying Hamilton's significance test it was found that the lowering in R value is significant at 0·005. This configuration of the structure corresponds to (+)-(4*R*)-4-benzyl-3-dichloroacetyl-1,3-oxazolidine. Absolute configuration checked by optical rotation and NMR using chiral lanthanide shift reagents. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. The atomic parameters with their e.s.d.'s and equivalent isotropic thermal parameters are given in Table 1. Bond lengths and bond angles involving non-H atoms are given in Table 2. Fig. 1 gives a perspective view of the molecule along with the numbering of atoms.

The bond lengths and angles of the oxazolidine ring are normal and agree with those reported (Bellan, Rossi, Chezeau, Roques, Germain & Declercq, 1978). The oxazolidine ring has an envelope conformation (Table 3) with C(9) as flap. The two Cl atoms are staggered with respect to the C(11)–N bond [N–C(11)–C(12)–Cl(1) = 83·0 (5), N–C(11)–C(12)–Cl(2) = −156·5 (4)°]. The phenyl ring is rotated away from the oxazolidine ring [C(1)–C(7)–C(8)–C(9) = −73·1 (6)°] and thus the molecule has an extended conformation as seen in chloramphenicol (Acharya, Sake Gowda & Post, 1979). Molecules are held together by van der Waals interactions.

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Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cl(1)–C(12)	1·782 (7)	C(1)–C(6)	1·367 (9)
Cl(2)–C(12)	1·758 (7)	C(1)–C(7)	1·518 (8)
N–C(8)	1·470 (7)	C(2)–C(3)	1·386 (12)
N–C(10)	1·490 (8)	C(3)–C(4)	1·369 (13)
N–C(11)	1·313 (8)	C(4)–C(5)	1·356 (14)
O(1)–C(9)	1·412 (8)	C(5)–C(6)	1·398 (10)
O(1)–C(10)	1·411 (7)	C(7)–C(8)	1·536 (8)
O(2)–C(11)	1·230 (7)	C(8)–C(9)	1·523 (9)
C(1)–C(2)	1·377 (10)	C(11)–C(12)	1·534 (8)

C(8)–N–C(10)	109·5 (4)	C(1)–C(6)–C(5)	120·6 (7)
C(8)–N–C(11)	122·1 (5)	C(1)–C(7)–C(8)	112·1 (5)
C(10)–N–C(11)	128·0 (5)	N–C(8)–C(7)	111·0 (5)
C(9)–O(1)–C(10)	105·6 (5)	N–C(8)–C(9)	99·7 (5)
C(2)–C(1)–C(6)	119·1 (6)	C(7)–C(8)–C(9)	113·5 (5)
C(2)–C(1)–C(7)	119·7 (6)	O(1)–C(9)–C(8)	103·9 (5)
C(6)–C(1)–C(7)	121·1 (6)	N–C(10)–O(1)	102·8 (5)
C(1)–C(2)–C(3)	120·1 (7)	N–C(11)–O(2)	124·4 (5)
C(2)–C(3)–C(4)	120·3 (9)	N–C(11)–C(12)	114·6 (5)
C(3)–C(4)–C(5)	120·0 (9)	O(2)–C(11)–C(12)	121·0 (5)
C(4)–C(5)–C(6)	119·8 (8)		

Table 3. *Some important torsional angles* (°) *with their e.s.d.'s in parentheses*

N–C(8)–C(9)–O(1)	3·42 (6)	C(10)–N–C(8)–C(9)	−12·8 (6)
C(8)–C(9)–O(1)–C(10)	−45·0 (6)	N–C(11)–C(12)–Cl(1)	83·0 (5)
C(9)–O(1)–C(10)–N	35·4 (6)	N–C(11)–C(12)–Cl(2)	−156·5 (4)
O(1)–C(10)–N–C(8)	−12·7 (6)	C(1)–C(7)–C(8)–C(9)	−73·1 (6)

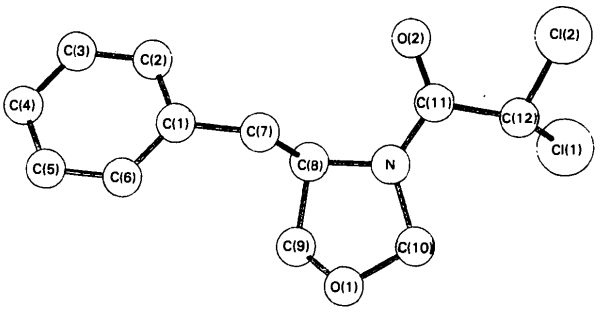

Fig. 1. A perspective view of the molecule showing the numbering scheme.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43080 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

ACHARYA, K. R., SAKE GOWDA, D. S. & POST, M. (1979). *Acta Cryst.* B35, 1360–1363.

BELLAN, J., ROSSI, J. C., CHEZEAU, N., ROQUES, R., GERMAIN, G. & DECLERCQ, J.-P. (1978). *Acta Cryst.* B34, 1648–1652.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *LALS*. A program for the full-matrix least-squares refinement of positional and thermal parameters and scale factors. Univ. of California.

HAMILTON, W. C. (1965). *Acta Cryst.* 18, 502–510.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

SEKI, H., KOGA, K., MATSUO, H., OHKI, S., MATSUO, I. & YAMADA, S. (1965). *Chem. Pharm. Bull.* 13, 995.

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The Structures of 9-*cis*-Retinal and 19,19,19-Trifluoro-9-*cis*-retinal

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Abstract. 9-*cis*-Retinal (I): $C_{20}H_{28}O$, $M_r = 284{\cdot}4$, triclinic, $P\bar{1}$, $a = 5{\cdot}722$ (1), $b = 7{\cdot}279$ (2), $c = 23{\cdot}252$ (9) Å, $\alpha = 89{\cdot}70$ (3), $\beta = 92{\cdot}64$ (3), $\gamma = 108{\cdot}60$ (2)°, $V = 916{\cdot}9$ (5) Å^3, $Z = 2$, $D_x = 1{\cdot}030$ Mg m^{-3}, $F(000) = 312$, $T = 298$ K, μ_o(Cu $K\alpha$) $= 0{\cdot}44$ mm^{-1}. 19,19,19-Trifluoro-9-*cis*-retinal (II): $C_{20}H_{25}F_3O$, $M_r = 338{\cdot}4$, triclinic, $P\bar{1}$, $a = 5{\cdot}745$ (2), $b = 7{\cdot}239$ (5), $c = 23{\cdot}893$ (11) Å, $\alpha = 90{\cdot}56$ (5), $\beta = 93{\cdot}98$ (3), $\gamma = 106{\cdot}93$ (4)°, $V = 947{\cdot}9$ (9) Å^3, $Z = 2$, $D_x = 1{\cdot}186$ Mg m^{-3}, $F(000) = 360$, $T = 296$ K, μ_o(Mo $K\alpha$) $= 0{\cdot}09$ mm^{-1}. The crystal structures have been determined using counter methods and Cu $K\alpha$ radiation ($\lambda_{K\bar{\alpha}} = 1{\cdot}5418$ Å) for (I) and Mo $K\alpha$ radiation ($\lambda_{K\bar{\alpha}} = 0{\cdot}71069$ Å) for (II). The structures have been refined by full-matrix least-squares procedures using 2230 (2σ) and 1545 (2σ) unique and significant reflections to the final R values of 0·055 and 0·067 respectively. The structures of (I) and (II) are nearly isostructural. The structural data of 9-*cis*-retinal are consistent with those reported for NMR studies of (I) in solution.

Introduction. The 9-*cis* isomer of retinal has played an important role in the study of the binding-site specificity of the visual pigment rhodopsin. For example, more than 30 years ago, it was shown to form a pigment analogue when incubated with the apoprotein opsin (Hubbard & Wald, 1952/3; Wald, Brown, Hubbard & Oroshnik, 1955). More recent studies have shown that 9-*cis*-retinal is unique among the other non-naturally occurring retinal isomers, most of which have only been recently synthesized (Crouch, Purvin, Nakanishi & Ebrey, 1975; DeGrip, Liu, Ramamurthy & Asato, 1976; Kini, Matsumoto & Liu, 1979, 1980; Asato, Kini, Denny & Liu, 1983), in that its rate of combination with bovine opsin is an order or two greater in magnitude than the others, second only to the naturally occurring and structurally similar 11-*cis* isomer (Liu, Matsumoto, Kini, Asato, Denny, Kropf & DeGrip, 1984). Furthermore, both low-temperature steady-state spectroscopic studies (Yoshizawa & Wald, 1963) and room-temperature fast kinetic studies (Busch, Applebury, Lamola & Rentzepis, 1972) have shown that bathorhodopsin, the primary photoproduct of rhodopsin, can interconvert nearly equally well between rhodopsin and 9-*cis*-rhodopsin. This unique dynamic property plays an integral part in the recently formulated HT-*n* ('hula twist' at center *n*) model for the primary process of vision (Liu & Asato, 1985). In spite of the obvious biological importance of 9-*cis*-retinal, its crystal structure remained undetermined.

We wish to report the crystal structure of 9-*cis*-retinal and thereby add to the collection of structures of other retinal isomers, which include: all-*trans* (Hamanaka, Mitsui, Ashida & Kakudo, 1972), 11-*cis* (Gilardi, Karle & Karle, 1972; Drikos, Rüppel, Dietrich & Sperling, 1981), 13-*cis* (Simmons, Liu, Denny & Seff, 1981), and methyl-7,9-di*cis*-retinoate

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