$C_{16}H_{13}BrN_2O_2$

C9	0.6727 (4)	0.1184 (4)	1.8255 (4)	0.0588 (9)
N2	0.5704 (3)	0.2062 (3)	1.7754 (3)	0.0503 (7)
C10	0.3208 (6)	−0.0491 (4)	1.7010 (5)	0.0825 (12)
C11	0.1836 (3)	0.3779 (3)	1.4161 (3)	0.0433 (6)
C12	0.2497 (4)	0.4554 (3)	1.2570 (3)	0.0440 (7)
C13	0.1896 (4)	0.4143 (3)	1.1638 (3)	0.0455 (7)
C14	0.0629 (4)	0.2993 (3)	1.2267 (4)	0.0541 (8)
C15	−0.0017 (4)	0.2220 (4)	1.3853 (4)	0.0616 (9)
C16	0.0585 (4)	0.2603 (4)	1.4808 (4)	0.0566 (9)

Table 2. *Selected geometric parameters (Å, °)*

N1—C4	1.379 (3)	N1—C5	1.438 (4)
N1—C3	1.395 (4)		
C4—N1—C3	113.0 (2)	C3—N1—C5	123.9 (2)
C4—N1—C5	123.1 (2)		

The H atoms were located from the $\Delta\rho$ map after anisotropic refinement of non-H atoms. The isotropic displacement parameters for all H atoms were held at 1.5 times the respective values for the parent C atom and their positions were refined using a riding model. The highest residual electron density exists in the proximity of the Br atom.

Data collection: KUMA Diffraction software. Cell refinement: KUMA Diffraction software. Data reduction: *DATARED* (Pèpe, 1979); KUMA Diffraction software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

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(Z)-4-[(S)-2,2-Dimethyl-1,3-dioxolan-4-yl-methylidene]-2-phenyl-1,3-oxazol-5(4H)-one

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Abstract

In the title compound, $C_{15}H_{15}NO_4$, the whole molecule, except for the dioxolane ring, adopts a nearly planar conformation. The dioxolane ring, which has an envelope conformation, is mainly situated on the *si,si* diastereotopic face of the olefinic bond. In the crystals of the title compound, rows of molecules are held together along the *x* direction by C···O intermolecular hydrogen bonds.

Comment

Azalactones unsaturated in position 4 are easily transformed into *N*-acyl-α,β-didehydroamino acid derivatives, which are powerful synthetic tools (Schmidt, Lieberknecht & Wild, 1988) present in many natural peptides, several of which exhibit biological activity (Schmidt, Häusler, Oehler & Poisel, 1979). Moreover, these compounds have proved to be useful intermediates in the synthesis of amino acids (Badsashah, Khan & Kidwai, 1972; Karpeiskaya, Levitina, Godunova & Klavunovskii, 1986), cycloaliphatic amino acids (Cativiela, Mayoral, Avenoza, González & Roy, 1990; Cativiela, Díaz-de-Villegas, Mayoral, Avenoza & Peregrina, 1993; Cativiela, Díaz-de-Villegas, Avenoza & Peregrina, 1993) and cyclopropylamino acids (Arenal, Bernabé, Fernández-Alvarez & Penadés-Ullate, 1985; Bland, Shah, Bortolusi & Stammer, 1988). In particular, (Z)-4-[(S)-2,2-dimethyl-1,3-dioxolan-4-ylmethylidene]-2-phenyl-1,3-oxazol-5(4H)-one, (I), has been successfully used as a substrate in asymmetric Diels–Alder (Buñuel, Cativiela & Díaz-de-Villegas, 1994, 1995; Buñuel, Cativiela, Díaz-de-Villegas & Garcia, 1994) and 1,3-dipolar cycloaddition (Cativiela, Díaz-de-Villegas, Lahoz & Jiménez, 1994; Cativiela, Díaz-de-Villegas & Jiménez, 1995a,b,c) reactions to afford versatile precursors of interesting cyclic amino acids. We report here the crystal-structure analysis of this chiral (Z)-azalactone derived from (R)-glyceraldehyde in order to provide conformational data to assist in the interpretation of the stereochemical course of reactions where the title compound is used as a substrate.

(I)
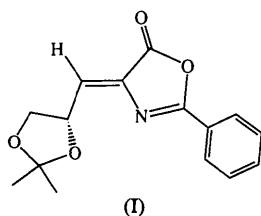
The crystal structures of some achiral 4-arylmethyl-ene-5(4*H*)-oxazolones have been reported previously (Busetti, Mayoral, Cativiela, Díaz-de-Villegas & Ajò, 1989, 1993), but to the best of our knowledge, no structure of a 4-alkylidene-5(4*H*)-oxazolone with a chiral substituent in position 4 has been reported to date.

A perspective view of the title molecule with the numbering scheme used in this analysis is shown in Fig. 1. The X-ray analysis confirms that the C3 atom is *cis* with respect to the N atom [torsion angle N—C1—C2—C3 −1.4 (7)°].
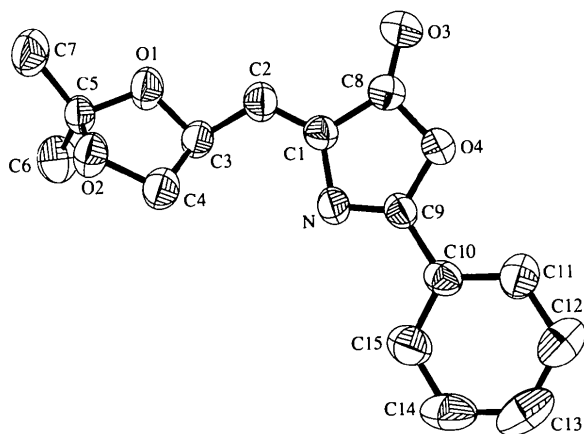

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The displacements of the atoms in the approximately planar oxazolone ring from the least-squares plane vary from 0.012 (3) for O4 to −0.026 (4) Å for C8. The exocyclic C2, O3 and C10 atoms deviate from the plane by 0.081 (4), −0.054 (4) and −0.069 (4) Å, respectively. The phenyl and 5(4*H*)-oxazolone rings are nearly coplanar, with an angle between them of 4.27 (15)°. The almost planar disposition of the whole molecule, except for the dioxolane ring [maximum deviations from the mean plane are −0.055 (4) for the O3 atom and 0.067 (3) Å for the O4 atom], allows electronic conjugation, resulting in a rather short N—C1 bond [1.397 (5) Å] and a rather long N—C9 bond [1.303 (5) Å] compared with those of similar species derived from $C_{\alpha,\alpha}$-disubstituted glycines (Toniolo *et al.*, 1991). The exocyclic bond angles about the carbonyl O3—C8 group of the lactone moiety differ by 11.4°, the larger value being for the O3—C8—C1 angle [133.7 (4)°]. This is in agreement with published data on other oxazolones. An additional result, common to

all oxazolones, is the widening of the N—C9—C10 exocyclic bond angle to greater than 126° [127.1 (4)°].

The 1,3-dioxolane ring adopts a major envelope conformation [puckering parameters (Cremer & Pople, 1975) $Q = 0.330 (3)$ Å and φ −41.7 (6)°], with atom C5 deviating by −0.504 (4) Å from the plane through the other four atoms.

The spatial arrangement of the dioxolane ring relative to the rest of the nearly planar molecule is defined by the torsion angles around the C1—C2 bond; C1—C2—C3—C4, C1—C2—C3—O1 and H2—C2—C3—H3 are 58.4 (5), 175.8 (4) and 126°, respectively. The value of the H2—C2—C3—H3 torsion angle is in excellent agreement with that estimated by applying the Karplus-type equation developed especially for the C_{sp^2}—C_{sp^3} rotamer by Garbish (Garbish, 1964; Vorontsva & Bochkov, 1974; Jankowski, Berlanger, Soler & Zamojski, 1979) ($J_{2,3} = 7.4$ Hz; dihedral angle 137°) and that obtained when *AM*1 semi-empirical calculations were used to evaluate the conformational energy curve derived from rotation about the C2—C3 bond (131°; Buñuel, Cativiela, Díaz-de-Villegas & Garcia, 1994). In this conformation, the H atom at the stereogenic centre occupies a synclinal position in the plane of the neighbouring π system [C1—C2—C3—H3 −52.5 (6)°] and the 1,3-dioxolane ring is mainly situated on the *si,si* diastereotopic face of the olefinic bond.

In the crystals of the title compound, rows of molecules are held together along the *x* direction (Fig. 2) by C⋯O intermolecular hydrogen bonds (Souhassou, Aubry, Boussard & Marraud, 1986); C14⋯O3^i 3.286 (6), H14⋯O3^i 2.286 (6) Å and C14—H14⋯O3^i 165° [symmetry code: (i) 1 + *x*, *y*, *z*].
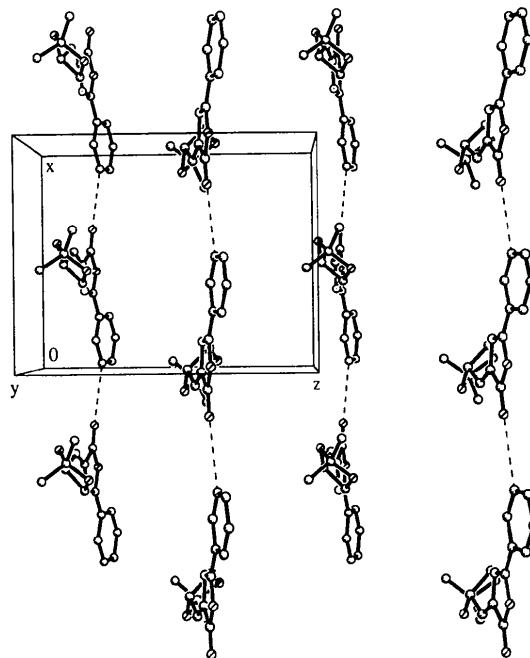

Fig. 2. Packing diagram viewed down the crystallographic *y* axis.

$C_{15}H_{15}NO_4$

Experimental

The title compound was isolated by chromatography from a mixture of both stereoisomers (Z/E 4/1) obtained by a modified Erlenmeyer–Plöchl azalactone synthesis (Combs & Armstrong, 1992) from hippuric acid and 1,2:5,6-di-O-isopropyl-idene-D-mannitol under oxidative conditions. Measurement of the long-range ^{13}C–^{1}H coupling constants between the olefinic proton and the C8 carbonyl atom in the fully coupled ^{13}C NMR (75 MHz) spectra allowed us to assign the configuration of each azalactone isomer (Cativiela, Díaz-de-Villegas, Lahoz & Jiménez, 1994). Crystals were obtained by slow evaporation from a hexane solution.

Crystal data

$C_{15}H_{15}NO_4$	Mo $K\alpha$ radiation
$M_r = 273.28$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 24
$P2_12_12_1$	reflections
$a = 10.1560 (10)$ Å	$\theta = 12.26–12.45°$
$b = 10.751 (2)$ Å	$\mu = 0.093$ mm^{-1}
$c = 13.007 (2)$ Å	$T = 293 (2)$ K
$V = 1420.2 (4)$ Å^3	Prism
$Z = 4$	$0.40 \times 0.32 \times 0.22$ mm
$D_x = 1.278$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Siemens $P4$ diffractometer	$\theta_{max} = 25°$
$\theta/2\theta$ scans	$h = -1 \rightarrow 12$
Absorption correction:	$k = -1 \rightarrow 12$
none	$l = -1 \rightarrow 15$
1930 measured reflections	3 standard reflections
1779 independent reflections	monitored every 97
1314 observed reflections	reflections
$[I > 2\sigma(I)]$	intensity decay: none
$R_{int} = 0.0144$	

Refinement

Refinement on F^2	Extinction correction: none
$R(F) = 0.0483$	Atomic scattering factors
$wR(F^2) = 0.1561$	from *International Tables*
$S = 1.051$	*for Crystallography* (1992,
1779 reflections	Vol. C, Tables 4.2.6.8 and
182 parameters	6.1.1.4)
Only H-atom U's refined	Absolute configuration: the
$w = 1/[\sigma^2(F_o^2) + (0.1006P)^2]$	absolute configuration was
where $P = (F_o^2 + 2F_c^2)/3$	assigned on the basis of
$(\Delta/\sigma)_{max} = 0.023$	the known configuration
$\Delta\rho_{max} = 0.154$ e Å^{-3}	of the mannitol reagent
$\Delta\rho_{min} = -0.164$ e Å^{-3}	

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

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

	x	y	z	U_{eq}
O1	-0.1014 (3)	0.2645 (2)	0.5282 (2)	0.0633 (9)
O2	0.0344 (3)	0.1831 (3)	0.6473 (2)	0.0586 (8)
O3	-0.1900 (3)	0.7260 (3)	0.6292 (3)	0.0750 (10)
O4	0.0231 (2)	0.7859 (2)	0.6376 (2)	0.0521 (7)
N	0.1280 (3)	0.6035 (3)	0.6055 (3)	0.0503 (9)
C1	-0.0075 (4)	0.5822 (4)	0.5997 (3)	0.0484 (10)
C2	-0.0687 (4)	0.4755 (3)	0.5734 (3)	0.0532 (11)
C3	-0.0016 (4)	0.3575 (4)	0.5425 (3)	0.0523 (10)
C4	0.0947 (4)	0.3001 (4)	0.6208 (3)	0.0597 (11)
C5	-0.0481 (4)	0.1481 (3)	0.5634 (3)	0.0493 (10)
C6	0.0311 (5)	0.0867 (5)	0.4782 (4)	0.0773 (14)
C7	-0.1588 (5)	0.0690 (4)	0.6024 (4)	0.0707 (13)
C8	-0.0780 (4)	0.6990 (4)	0.6233 (3)	0.0546 (11)
C9	0.1386 (4)	0.7207 (3)	0.6294 (3)	0.0442 (9)
C10	0.2601 (4)	0.7904 (4)	0.6477 (3)	0.0473 (9)
C11	0.2562 (5)	0.9158 (4)	0.6792 (3)	0.0610 (12)
C12	0.3711 (6)	0.9802 (5)	0.6981 (4)	0.0768 (14)
C13	0.4915 (6)	0.9213 (6)	0.6876 (4)	0.085 (2)
C14	0.4973 (5)	0.7971 (7)	0.6565 (4)	0.082 (2)
C15	0.3818 (4)	0.7334 (5)	0.6374 (4)	0.0693 (13)

Table 2. *Selected geometric parameters (Å, °)*

O1—C3	1.437 (5)	C2—C3	1.495 (6)
O1—C5	1.439 (4)	C3—C4	1.541 (6)
O2—C5	1.427 (5)	C5—C7	1.498 (6)
O2—C4	1.441 (5)	C5—C6	1.520 (6)
O3—C8	1.176 (5)	C9—C10	1.463 (6)
O4—C9	1.371 (4)	C10—C15	1.386 (5)
O4—C8	1.400 (5)	C10—C11	1.409 (6)
N—C9	1.303 (5)	C11—C12	1.379 (7)
N—C1	1.397 (5)	C12—C13	1.384 (8)
C1—C2	1.349 (5)	C13—C14	1.396 (9)
C1—C8	1.478 (6)	C14—C15	1.382 (7)
C3—O1—C5	107.4 (3)	O1—C5—C6	110.1 (3)
C5—O2—C4	107.3 (3)	C7—C5—C6	113.4 (4)
C9—O4—C8	106.0 (3)	O3—C8—O4	122.4 (4)
C9—N—C1	104.6 (3)	O3—C8—C1	133.7 (4)
C2—C1—N	127.4 (4)	O4—C8—C1	103.9 (3)
C2—C1—C8	123.5 (3)	N—C9—O4	116.3 (4)
N—C1—C8	109.1 (3)	N—C9—C10	127.1 (4)
C1—C2—C3	125.4 (4)	O4—C9—C10	116.6 (3)
O1—C3—C2	107.7 (3)	C15—C10—C11	118.5 (4)
O1—C3—C4	104.7 (3)	C15—C10—C9	120.6 (4)
C2—C3—C4	116.8 (4)	C11—C10—C9	120.9 (4)
O2—C4—C3	103.8 (3)	C12—C11—C10	120.5 (5)
O2—C5—O1	103.6 (3)	C11—C12—C13	120.0 (5)
O2—C5—C7	109.4 (3)	C12—C13—C14	120.2 (5)
O1—C5—C7	108.6 (3)	C15—C14—C13	119.4 (5)
O2—C5—C6	111.2 (4)	C14—C15—C10	121.3 (5)

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL93*. Molecular geometry calculations: *PARST* (Nardelli, 1983).

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8,9,10,11-Tetrahydrobenz[*c*]acridine

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Abstract

The molecule of the title compound, $C_{17}H_{15}N$, is planar except for the cyclohexane ring which is in a half-chair conformation.

Comment

Polycyclic aromatic hydrocarbons are useful in carcinogenic studies (Lehr & Jerina, 1983; Kar, Karmakar & Ray, 1989) and are also important for studying the role of 'bay regions' in a molecule towards carcinogenic activity (Kumar, 1985). As part of studies on the synthesis, characterization and bioactivity of polycyclic aromatic hydrocarbon derivatives, the structure of 8,9,10,11-tetrahydrobenz[*c*]acridine, (I), has been determined.

(I)
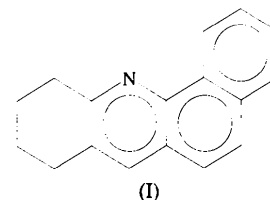
A displacement ellipsoid plot of (I) with the atom-numbering scheme is shown in Fig. 1. The bond lengths and angles observed in this structure are normal, and the cyclohexane ring (C1–C6) is in a half-chair conformation; the asymmetry parameter ΔC_2(C1–C6) is 0.026 (1) (Nardelli, 1983a). The cyclohexane rings of a related structure, 1,2,3,4,6,7-hexahydro-10-chloronaphth-[3,2-*c*]acridine, were found to undergo conformational flexibility with major and minor disorder components (Ray, Halder, Nigam, Sivakumar & Fun, 1995), but in the present structure, only one conformation is observed. The r.m.s. deviation of the C and N atoms, other than the C2, C3, C4 and C5 atoms, from their mean plane is 0.025 (2) Å and the dihedral angle between

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