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3-(4-Chlorophenyl)-2*H*-benz[*b*][1,4]oxazine

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.132
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{14}H_{10}ClNO$, is a nitrogen derivative closely related to natural 3′,7-epoxy-8,4′-oxyneolignans, which are of interest because of their cytotoxic activity. Centrosymmetric hydrogen bonding occurs between pairs of molecules.

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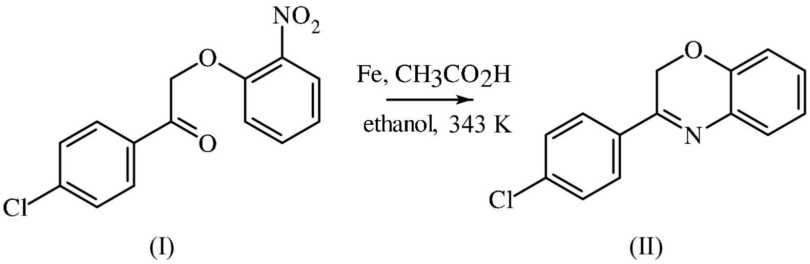
Comment

Neolignans belong to an important group of bioactive natural products widely distributed in terrestrial plants (Gottlieb & Yoshida, 1990). In particular, neolignans with a 3-aryl-1,4-benzodioxane skeleton constitute the frameworks of a small group, named 3′,7-epoxy-8,4′-oxyneolignans, whose members have been isolated from plants of the *Lauraceae*, *Myristicaceae*, and *Phytolaccaceae* families (Paulino Filho, 1985). Their structural elements seem to occur only rarely in lignins (Hwang & Sakakibara, 1981). In connection with some other natural and synthetic work on biologically active neolignan derivatives (Barata *et al.*, 2000), we became interested in the preparation of C-7 nitrogen analogues of 3′,7-epoxy-8,4′-oxyneolignans, such as compound (II), previously obtained in moderate yields (Shridhar *et al.*, 1981; Sabitha & Rao, 1987). Compounds with the 2*H*-benz[*b*][1,4]oxazine system have been synthesized in an attempt to obtain anti-inflammatory, central muscle relaxant, diuretic, antibacterial, anti-amoebic, antitrichomonal and anthelmintic agents (Shridhar *et al.*, 1986).



The title compound, (II), has not shown *in vitro* antibacterial activity against *Escherichia coli* (Oliveira *et al.*, 1994), despite the moderate antibacterial activity (Santos *et al.*, 1994) of the starting compound, (I), which has been evaluated using CO_2 conductimetric determination by flow injection analysis (Jardim *et al.*, 1990). In this paper, the crystal structure of (II) is described. In (II), the chain of atoms C7/N/C10/C9/O/C8 is analogous to a 3′,7-epoxy-8,4′-oxyneolignan, and compound (II) can be considered its nitrogen derivative, according to accepted neolignan nomenclature (Moss, 2000). The present crystal structure will enable conclusions to be drawn about the geometry of this derivative and may contribute to the under-

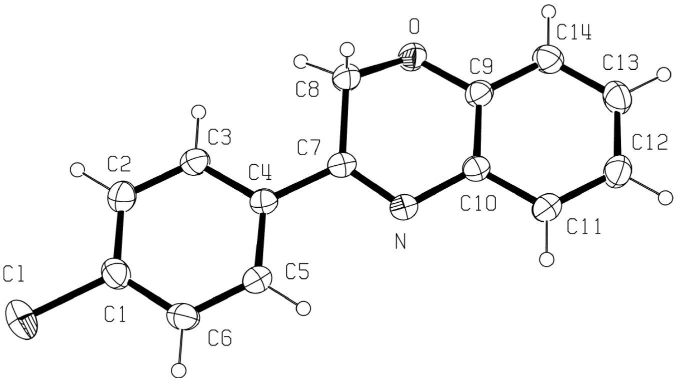


Figure 1
View of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

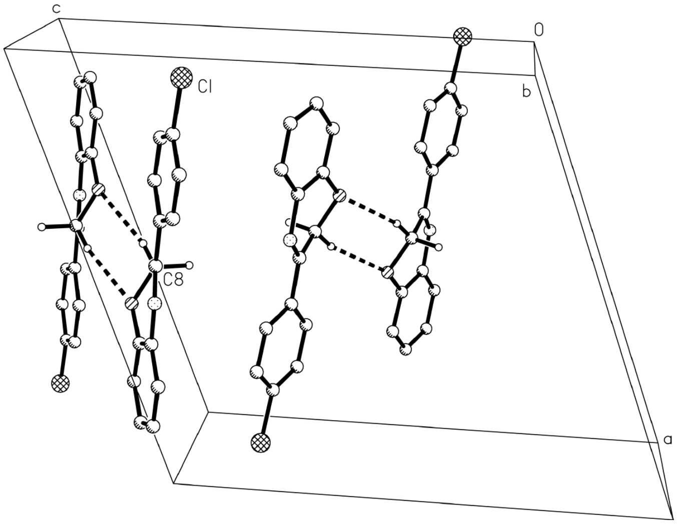


Figure 2
Packing diagram of (II), with intermolecular C—H···O non-classical hydrogen bonds shown as dashed lines. Only the H atoms attached to C8 are shown for clarity.

standing of the biological differences between the above compounds.

Fig. 1 shows a molecule of (II) with the atomic numbering scheme and Table 1 lists selected bond distances and angles. The ring O→C9→ ···→C8 shows a screw-boat conformation, according to the Cremer & Pople (1975) parameters Q = 0.354 (2) Å, θ = 66.2 (3)° and φ = 34.3 (4)°. The aromatic rings are coplanar within 0.03 Å, and the N, O, C7 and C8 atoms are out of this plane by 0.126 (2), −0.069 (2), 0.099 (2) and −0.453 (3) Å, respectively. Steric strain as a result of the C8—H8$A\cdots$O^{i} interaction [symmetry code: (i) $1 - x, 1 - y, 2 - z$] leads to distortions of the C8 environment, as can be seen in Tables 1 and 2. The average bond angle at C8 is 109.4°. A search of the November 2004 release of the Cambridge Structural Database (Allen, 2002) showed a compound similar to (II), *viz*. 3-methyl-2-phenyl-2*H*-benz[1,4]oxazin-2-ol (Santes *et al.*, 1999), with the same 2*H*-benz[*b*][1,4]oxazine ring, but with different substituents. No significant differences were found in the bond distances and angles of the two molecules, except that, in the case of (II), the C7—C8—O angle is 112.6 (2)°, while in the earlier structure, the corresponding angle is 110.6°, consistent with the distortion observed in our case. The molecules of (II) are linked into pairs about crystallographic inversion centres through a non-classical hydrogen-bonded network (Gu *et al.*, 1999); the geometric parameters are reported in Table 2. Repetition of these pairs of molecules by crystal symmetry results in the formation of columns of molecules, as can be seen in a projection along the monoclinic *b* axis (Fig. 2).

Experimental

Compound (II) was obtained in 98% yield from the reduction of 1-(4-chlorophenyl)-2-(2-nitrophenoxy)propan-1-one, (I), using the method described previously by Owsley & Bloomfield (1977). Prismatic crystals (m.p. 433–434 K) were obtained from a solution in EtOH. FT–IR (Perkin–Elmer, KBr, ν, cm^{-1}): 1610 (C$=$N), 1090 and 1220 (C—O), 880 (C—N); ^{1}H NMR (Varian Gemini, 300 MHz, $CDCl_3$/TMS, δ, p.p.m.): 4.98 (*s*, H8), 6.81 (*dd*, J = 1.5 and 7.8 Hz, H14), 6.94 (*ddd*, J = 1.5, 7.5 and 8.4 Hz, H12), 7.06 (*ddd*, J = 2.4, 7.5 and 7.8 Hz, H13), 7.31 (*dd*, J = 2.4 and 8.4 Hz, H11), 7.40 (*dd*, J = 2.4 and 8.4 Hz, H2 and H6), 7.87 (*dd*, J = 2.4 and 8.4 Hz, H3 and H5); ^{13}C NMR (Varian Gemini, 75 MHz, $CDCl_3$/TMS, δ, p.p.m.): 133.8 (C4), 129.0 (C3, C5), 127.7 (C2, C6), 137.0 (C1), 157.3 (C7), 62.6 (C8), 146.2 (C9), 133.6 (C10), 127.8 (C11), 122.4 (C12), 128.8 (C13), 115.6 (C14); EI–MS [Varian MAT-311A, m/z, (relative abundance)]: 253 (100) (M^+), 252 (46) (M^+-1), 182 (8) (M^+-HCN), 137 (53) (ArCN$^+$), 111 (8) (Ar$^+$).

Crystal data

$C_{14}H_{10}ClNO$
M_r = 243.68
Monoclinic, $P2_1/c$
a = 13.861 (3) Å
b = 5.834 (1) Å
c = 14.903 (3) Å
β = 110.65 (3)°
V = 1127.7 (4) Å^3
Z = 4
D_x = 1.435 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 9.8–13.8°
μ = 0.32 mm^{-1}
T = 298 (2) K
Prism, light brown
0.35 × 0.35 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.901, $T_{\max}$ = 0.970
2055 measured reflections
1970 independent reflections
1543 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\max}$ = 25.0°
$h = -16 \rightarrow 0$
$k = -6 \rightarrow 0$
$l = -16 \rightarrow 17$
2 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.132
S = 1.05
1970 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.5604P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.004
$\Delta\rho_{\max}$ = 0.47 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.017 (3)

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Table 1
Selected geometric parameters (Å, °).

Cl—C1	1.738 (2)	N—C10	1.413 (3)
O—C9	1.373 (3)	C7—C8	1.506 (3)
O—C8	1.423 (3)	C8—H8*B*	1.12 (2)
N—C7	1.283 (3)	C8—H8*A*	0.88 (2)
C9—O—C8	114.05 (17)	C7—C8—H8*B*	113.0 (14)
C7—N—C10	117.16 (18)	O—C8—H8*A*	106.6 (18)
O—C8—C7	112.6 (2)	C7—C8—H8*A*	112.1 (18)
O—C8—H8*B*	111.1 (14)	H8*B*—C8—H8*A*	101 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O^{i}	0.88 (2)	2.60 (2)	3.465 (3)	166 (2)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

The H atoms on atom C8 were found in a difference Fourier map and their positions were refined with the restraints $H\cdots H = 1.59$ (4) Å and C—H = 0.97 (4) Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. These restraints ensure a reasonable geometry for the C8 group, since it has one H atom involved in hydrogen bonding. All other H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances of 0.93 Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* in *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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