Acta Crystallographica Section E
**Structure Reports
Online**

ISSN 1600-5368

2-(2-Bromo-4-chloroanilino)-2-phenylethanol

Eric T. Mack, Matthew J. Brown, Jeanette A. Krause,* Deborah L. Lieberman and Allan R. Pinhas

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, USA

Correspondence e-mail: jeanette.krause@uc.edu

Received 15 July 2005
Accepted 28 July 2005
Online 6 August 2005

Key indicators

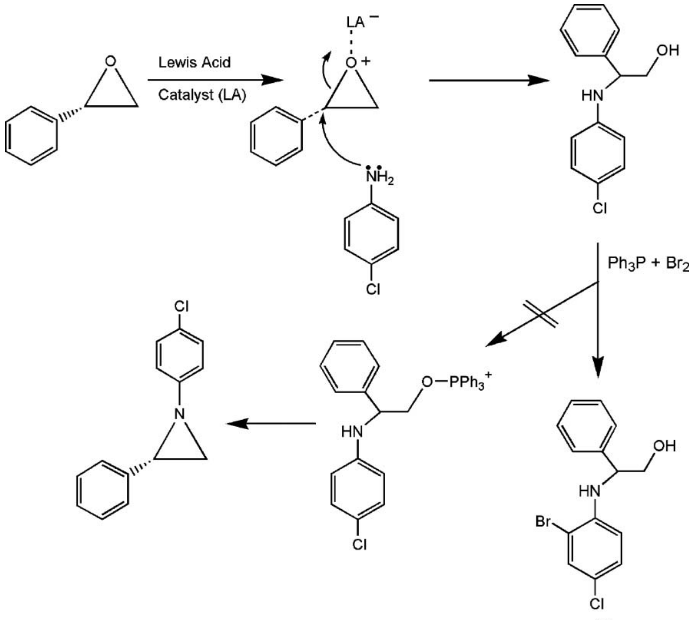
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.023
wR factor = 0.061
Data-to-parameter ratio = 14.7

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

The title complex, $C_{14}H_{13}BrClNO$, adopts a helical motif built up from intermolecular O—H···O interactions with a repeat distance of 8.4 Å. Further assembly of the helices forms a parallel square grid array reminiscent of apolar peptide extended packing motifs.

Comment

In an effort to give our undergraduate laboratory exercises a more research-focused environment, students were instructed to investigate synthetic routes to aziridines. As indicated in the scheme, reacting 2-phenyloxirane with *p*-chloroaniline was thought to be a convenient route to accomplish this goal. What was discovered was that the amine reacted with the oxirane to form 2-(4-chloroanilino)-2-phenylethanol. Upon subsequent addition of the PPh_3/Br_2 solution, however, bromination took place, resulting in the title complex, (I), rather than causing ring closure to form the aziridine.



(I)

β-Amino acids and *β*-aminoalcohols play a role in both synthetic organic and medicinal chemistry (Cole, 1994; Seebach *et al.*, 1996; Goodman & Gilman, 1985). Just as 2-(4-nitroanilino)-2-phenylethanol (Chinnakali *et al.*, 1998), (I) is a *β*-aminoalcohol derivative. Structural features of (I) (Fig. 1) include planar, nearly perpendicular, benzene rings [dihedral angle = 83.98 (5)° *versus* 90.0 (5)° for the nitroanilino analog]. Other metrical details are as expected and agree with literature values (Allen *et al.*, 1987).

doi:10.1107/S1600536805024244

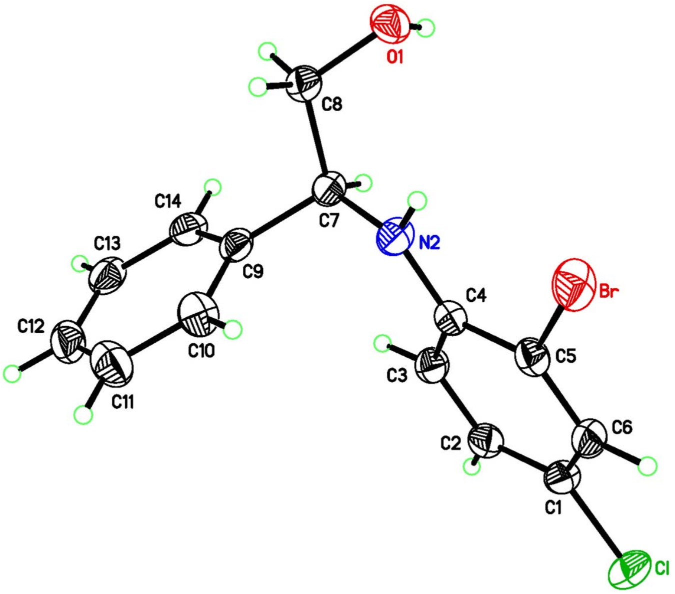


Figure 1
The structure of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids.

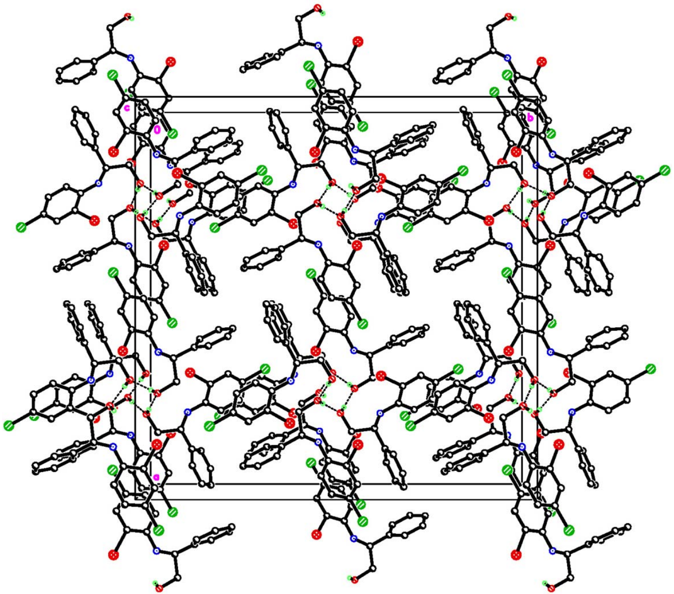


Figure 3
The parallel square grid array (*ab* plane). Only OH H atoms are shown. Hydrogen bonds are shown as dashed lines.

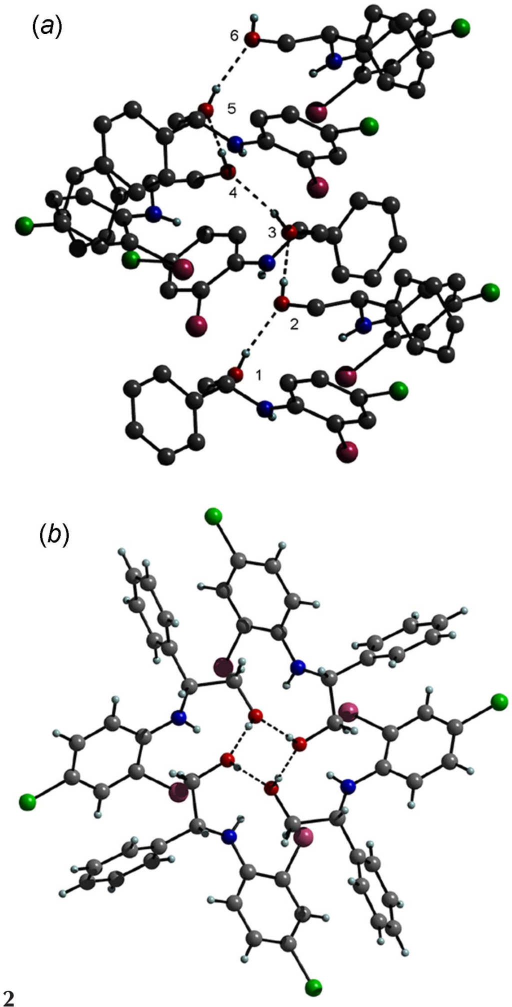


Figure 2
(*a*) The helical packing motif of (I) generated by intermolecular O—H$\cdots$O interactions (dashed lines) (the *c* axis runs vertically and the *a* axis runs horizontally). Only OH and NH H atoms are shown. (*b*) The square helicoid, viewed down the helix.

Of interest is the secondary structure of (I), which packs in a helical motif (Fig. 2). The square helicoid (Fig. 2*b*) is generated by crystallographic fourfold symmetry. The helix is built up from intermolecular O—H$\cdots$O interactions [O1$\cdots$O1^{i} = 2.756 (1) Å, H1$\cdots$O1^{i} = 2.003 (3) Å, O1—H1 = 0.77 (3) Å and O1—H1$\cdots$O1^{i} = 170 (3)°; symmetry code: $\frac{1}{4} - y, x - \frac{1}{4}, z - \frac{1}{4}$]. In Fig. 2*a*, one can see that the helix repeat is such that molecules 1 and 5 are stacked with a repeat distance of 8.4031 (4) Å (the unit cell *b*-axis length). Further assembly of the helices forms a parallel square grid array (Fig. 3), a secondary motif commonly found for apolar peptides (Karle, 1992). The channels formed in this array are devoid of solvent due to the benzene rings pointing inward, creating only a small cavity for potential solvent molecules (vertical/horizontal dimension between the benzene H atoms is approximately 3 Å, while the diagonal dimension is approximately 5 Å). The secondary structure of 2-(4-nitroanilino)-2-phenylethanol differs in that it packs as cylindrical channels about a threefold axis arising from O—H$\cdots$O trimers [O$\cdots$O = 2.710 (5) Å, H$\cdots$O = 1.85 (4) Å and O—H$\cdots$O = 164 (3)°; Chinnakali *et al.*, 1998]. Other compounds containing the —NH—CH(Ph)—CH$_2$—OH fragment show a diverse assortment of secondary structures which include pleated sheets {*e.g.* (*S*)-(+)-2-[(1,1-dimethylethoxy)carbonyl]amino-2-phenylethanol; Sperandio *et al.*, 1998}, zigzag columns {*e.g.* *N*-[(*R*)-2′-hydroxy-1′-phenylethyl]-(*S*)-1-aminio-1,2,3,4-tetrahydro naphthalene; Stalker *et al.*, 2002}, columns of co-crystallized pairs {*e.g.* (3*S*)-*N*-[(1*R*)-1-phenyl-2-hydroxyethyl]-3-phenyl-5-hexynamide triphenylphosphine oxide; Baek *et al.*, 1989}, bilayers or ladders {*e.g.* methyl (2*R*)-(−)-2-chloro-3-[2′-hydroxy-1′(*R*)-phenyl-ethylammonio]propionate chloride; Gnecco *et al.*, 2000} and honeycomb nets {*e.g.* *N*-[(*R*)-α-(hydroxymethyl)-benzyl]-(1*R*,2*S*)-*cis*-2-methylcyclobutane carboxamide; Alexander *et al.*, 2000}.

Experimental

2-Phenyloxirane (1.48 g, 0.04 mol) and *p*-chloroaniline (5.11 g, 0.04 mol) were stirred at room temperature over a period of 24 h in the presence of a Lewis acid, in this case lithium perchlorate (0.53 g, 0.006 mol), to form 2-(4-chloroanilino)-2-phenylethanol (Hancock & Pinhas, 2004). Compound (I) was isolated upon subsequent bromination of the aminoalcohol (4.85 g, 0.02 mol) using a pre-prepared solution of triphenylphosphine (5.26 g, 0.02 mol) and bromine (3.20 g, 0.02 mol) in acetonitrile (12 ml) and slow addition of cooled triethylamine (6.01 g, 0.02 mol). The mixture was allowed to stir at room temperature for 24 h. Suitable crystals of (I) were harvested by slow evaporation of a chloroform solution.

Crystal data

$C_{14}H_{13}BrClNO$
$M_r = 326.61$
Tetragonal, $I4_1/a$
$a = 25.5382$ (8) Å
$c = 8.4031$ (4) Å
$V = 5480.5$ (4) Å^3
$Z = 16$
$D_x = 1.583$ Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 8222 reflections
$\theta = 3.5–67.9°$
$\mu = 5.78$ mm^{-1}
$T = 150$ (2) K
Plate, colorless
0.16 × 0.13 × 0.04 mm

Data collection

Bruker SMART 6000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.458$, $T_{\max} = 0.802$
22328 measured reflections

2492 independent reflections
2405 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 67.9°$
$h = -29 \rightarrow 30$
$k = -30 \rightarrow 30$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.061$
$S = 1.10$
2492 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 4.3217P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

H atoms on N and O atoms were located directly and their positions were refined [O1—H1 = 0.77 (3) Å and N2—H2 = 0.79 (2) Å]. H atoms on C atoms were either located directly or included in calculated positions and subsequently refined using a riding model (C—H = 1.00, 0.99 and 0.95 Å for CH, CH_2 and aromatic H atoms, respectively). H-atom displacement parameters were defined as $U_{\rm iso}(H) = 1.5U_{\rm eq}(O)$ or $1.2U_{\rm eq}(N,C)$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

Funding for the diffractometer through NSF-MRI grant CHE-0215950 is gratefully acknowledged.

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