Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

C—H···O and C—H···π(arene) interactions in (2*S*,4*S*,5*R*)-(–)-2-(4-propoxyphenyl)-3,4-dimethyl-5-phenyl-1,3-oxazolidine

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.079
Data-to-parameter ratio = 10.1

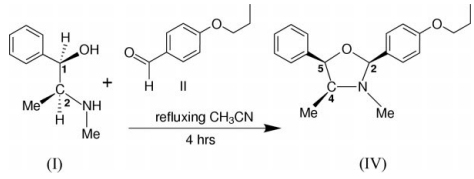
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 14 November 2003
Accepted 15 December 2003
Online 17 January 2004

The title compound, $C_{20}H_{25}NO_2$, a condensation product of l-ephedrine and 4-propoxyaldehyde, is of interest in studies on weak interactions. It crystallizes with C—H···O and C—H···π(arene) intermolecular interactions as a one-dimensional chain [C···O = 3.3745 (19) Å, C—H···O = 139°; C—H···*Cg*1 = 3.6987 (16) Å, C—H···*Cg*1 = 161°, where *Cg*1 is the centroid of the symmetry-related 4-propoxy-substituted aromatic ring].

Comment

The general principles underlying recognition processes are reasonably well understood, and interactions involving guest–host systems can usually be rationalized in terms of preferred combinations of hydrogen-bond donors and acceptors (Etter *et al.*, 1990; Bernstein *et al.*, 1995). Such studies, and especially those related to the structure and reactivity of biological molecules, are central to understanding drug behaviour in medicinal chemistry. Amino acid derivatives constitute the most notable class of chiral systems, with studies in asymmetric synthesis, catalysis and medicinal chemistry. The chiral aminoalcohol (1*R*,2*S*)-(−)-ephedrine, (I), has previously been reacted with aromatic aldehydes, *e.g.* bromobenzaldehyde (Just *et al.*, 1983), and heteroaromatic systems, *e.g.* pyrrole (III*a*) (Gallagher & Fitzsimons, 1999).



The title compound, (IV), a derivative of (1*R*,2*S*)-(−)-ephedrine, (I), and *para*-propoxybenzaldehyde, (II), is of current interest as a model compound for studies of weak interactions in systems lacking strong hydrogen-bond donors and acceptors, as well as for alkoxyaromatic derivatives which are frequently used in liquid crystal applications (Bruce, 1993; Cromhout & Hutton, 2000). The reactions of (I) with heteroaromatic aldehydes and related structural studies have been reported (Just *et al.*, 1983; Bourne *et al.*, 1997), as have pyrrole (III*a*) (Gallagher & Fitzsimons, 1999), imidazole (III*b*) (Gallagher *et al.*, 1998) and thiazole (III*c*) relatives (Fitzsimons & Gallagher, 1999).

Two views of (IV) are depicted with the atomic numbering scheme in Figs 1 and 2. Bond lengths and angles are unexceptional and in accord with anticipated values (Allen, 2002). The absolute configuration is based on and deduced from that of (I), in combination with NMR data. The oxazolidine ring

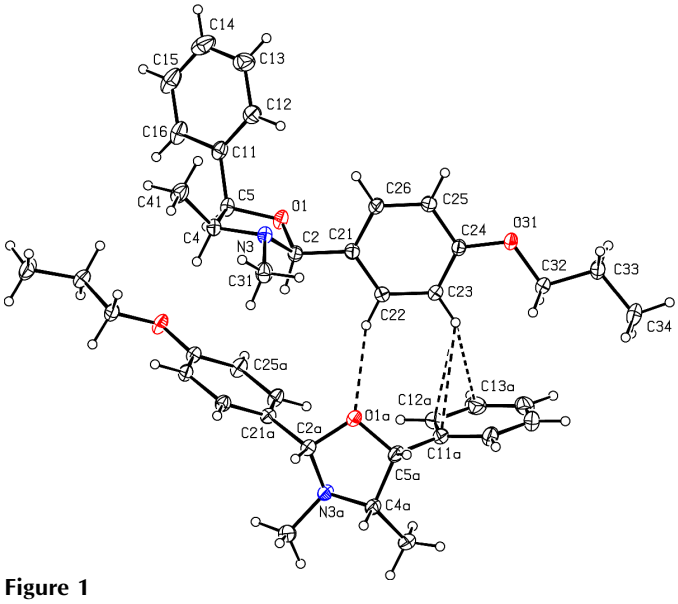


Figure 1
A view of (IV) with the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed lines indicate the C—H···O and C—H···π(arene) interactions. Atoms with suffix '*a*' are at the symmetry-related site $(1-x, \frac{1}{2}+y, -z)$.

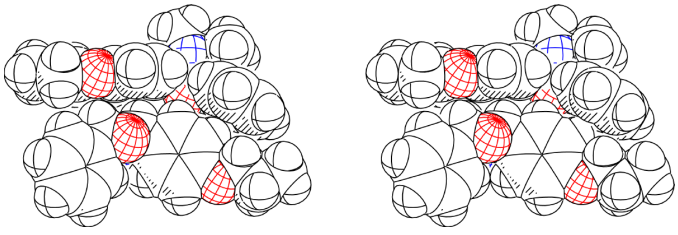


Figure 2
A stereoview of the interactions between molecules, with atoms drawn as their van der Waals spheres.

adopts an envelope conformation, with atom N3 0.602 (2) Å from the O1/C2/C4/C5 plane. This conformation compares favourably with that for (III*a*), in which N3 deviates by 0.609 (6) and 0.623 (6) Å in two independent molecules, (III*b*) [0.566 (3)–0.615 (3) Å (Z' = 4)] and (III*c*) [0.623 (2) Å], suggesting that the nature of the aromatic ring has little effect on the envelope conformation of the five-membered C_3NO central ring, this being a favourable energy conformation for these systems. The distortion in the central five-membered C_3NO ring can also be analysed by the internal torsion angles: in the propoxyphenyl system (IV) the range is from 11.71 (15)° for C2—O1—C5—C4 to 44.92 (14)° for O1—C2—N3—C4, so that a description of N3 being out of the plane of the other four atoms is obvious and the C_3O four-atom plane is defined as C2/O1/C5/C4. The C_6H_5 ring is at an angle of 79.23 (5)° to this C2/O1/C5/C4 plane, which is oriented at 79.14 (5)° to the 1,4-disubstituted C_6H_4 ring. The propoxy OC_3 chain is also co-planar with the C_6H_4 ring, with a dihedral angle of 6.7 (2)°.

There are two intermolecular interactions of note, involving C—H···O and C—H···π(arene). These are relatively long and involve a symmetry-related molecule at the position $(1-x, \frac{1}{2}+y, -z)$. They generate a one-dimensional chain along the *a*-axis direction, as depicted (as dashed lines) in Fig. 1; the C23—H23···π(C21—C26)^{i} interaction is shown with the three closest C—H···C(arene) interactions. A stereoview with the atoms drawn as their van der Waals spheres (Fig. 2) reveals the two primary hydrogen-bonding interactions and several contacts between the two molecules as they stack along the 2_1 axis.

A search for 4-propoxy aromatic derivatives (as $CH_3—CH_2—CH_2—O—C_6H_2$) in the Cambridge Structural Database (CSD; Version 5.24, July 2003; Allen, 2002) reveals a total of 19 derivatives (with coordinates available and with $R < 0.10$). Analysis of the geometry of the propoxy moiety in (IV) reveals the common distortion at the O31—C24—C23/25 angle (Table 1) with O31—C24—C23 = 124.58 (13)°, O31—C24—C25 = 115.60 (13)° and C24—O31—C32—C33 = −179.33 (13)°. The structure CIBCOF {1-(1,3-dioxaindan-5-yl)-2-[(4-phenyl-1,3-oxazolidin-2-on-3-yl)carbonyl]-2-(3-propoxybenzoyl)ethene} is representative of the CSD entries and contains a similar propoxy deformation, with O—C—C angles of 114.2/124.9° and a C—O—C—C angle of 20.3° (Pridgen *et al.*, 1999). Examination of the structure with *PLATON* (Spek, 2003) showed that there are no solvent-accessible voids in the crystal structure.

Experimental

The title compound was prepared by refluxing 4-propoxybenzaldehyde (1.58 g, 0.01 mmol) and (1*R*,2*S*)-(−)-ephedrine (1.65 g, 0.01 mmol) in 20 ml of acetonitrile for 4 h. On cooling, the product was filtered and recrystallized from ethanol, yield 2.84 g (88%), m.p. 343–345 K. IR (KBr): ν 1615, 1512, 1455, 1391, 1243 cm^{-1}; ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0.80 (*d*, 3 H, CCH_3), 1.09 (*t*, 3 H, CH_3), 1.85 (*m*, 2H, $—CH_2—$), 2.18 (*s*, 3H, NCH_3), 2.97 (*m*, 1H, MeCH), 3.97 (*t*, 2H, $—CH_2$), 4.67 [*s*, 1H, OC(N)H], 5.15 (*d*, 1H, PhCH), 6.97 (*d*, 2H, aromatic CH—C_6H_4), 7.30, 7.36 (*m*, 1H, 2H, C_6H_5), 7.46 (*d*, 2H, C_6H_5), 7.59 (*d*, 2H, aromatic CH—C_6H_4).

Crystal data

$C_{20}H_{25}NO_2$	D_x = 1.177 Mg m^{-3}
M_r = 311.41	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 14364 reflections
a = 9.2962 (2) Å	θ = 2.6–27.5°
b = 8.2755 (2) Å	μ = 0.08 mm^{-1}
c = 11.4267 (3) Å	T = 150 (2) K
β = 91.0830 (11)°	Block, colourless
V = 878.91 (4) Å^3	0.36 × 0.30 × 0.20 mm
Z = 2	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.036
φ and ω scans with κ offsets	θ_{max} = 27.5°
Absorption correction: none	$h = -12 \rightarrow 12$
8081 measured reflections	$k = -9 \rightarrow 10$
2136 independent reflections	$l = -13 \rightarrow 14$
1988 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.0616P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	
$wR(F^2)$ = 0.079	
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
2136 reflections	$\Delta\rho_{max}$ = 0.14 e Å^{-3}
212 parameters	$\Delta\rho_{min}$ = −0.11 e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.068 (15)

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.4305 (18)	C24—O31	1.3731 (17)
O1—C5	1.4373 (17)	O31—C32	1.4386 (17)
C2—N3	1.4635 (18)	C32—C33	1.507 (2)
N3—C4	1.4676 (18)	C33—C34	1.514 (2)
C4—C5	1.552 (2)		
C2—O1—C5	107.60 (11)	O31—C24—C25	115.60 (13)
O1—C2—N3	103.03 (11)	C23—C24—C25	119.82 (13)
C2—N3—C4	102.71 (11)	C24—O31—C32	117.55 (12)
N3—C4—C5	102.30 (11)	O31—C32—C33	107.64 (13)
O1—C5—C4	104.80 (12)	C32—C33—C34	112.06 (15)
O31—C24—C23	124.58 (13)		
C5—O1—C2—N3	−35.09 (14)	N3—C4—C5—O1	15.80 (15)
O1—C2—N3—C4	44.92 (14)	C4—C5—C11—C12	71.67 (18)
C2—N3—C4—C5	−36.61 (14)	O1—C2—C21—C26	62.48 (17)
C2—O1—C5—C4	11.71 (15)	C24—O31—C32—C33	−179.93 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22···O1^{i}	0.95	2.60	3.3745 (19)	139
C23—H23···*Cg*1^{i}	0.95	2.79	3.6987 (16)	161

Symmetry code: (i) $1-x, \frac{1}{2}+y, -z$. *Cg*1 is the centroid of the symmetry-related 4-propoxy-substituted aromatic ring.

H atoms were treated as riding atoms, with C—H = 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. In the absence of significant anomalous scattering, the Flack (1983) parameter, with a value of −0.1 (8), was inconclusive (Flack & Bernardinelli, 2000); the Friedel equivalents were merged prior to the final least-squares refinement cycles. The absolute configuration was deduced from that of the starting material and NMR data.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

AJL thanks the University of Toronto for funding a diffractometer and computer systems. JFG thanks the School of Chemical Sciences, Dublin City University, for funds for undergraduate research.

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