Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(2*RS*,4*SR*)-7-Bromo-2-*exo*-(2-chlorophenyl)-2,3,4,5-tetrahydro-1,4-epoxynaphtho[1,2-*b*]azepine: sheets built by the π-stacking of hydrogen-bonded chains

Andrés F. Yépes,[a] Alirio Palma,[a] Justo Cobo[b] and Christopher Glidewell[c]*

[a]Laboratorio de Síntesis Orgánica, Escuela de Química, Universidad Industrial de Santander, AA 678 Bucaramanga, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

Received 17 January 2012
Accepted 2 February 2012
Online 23 February 2012

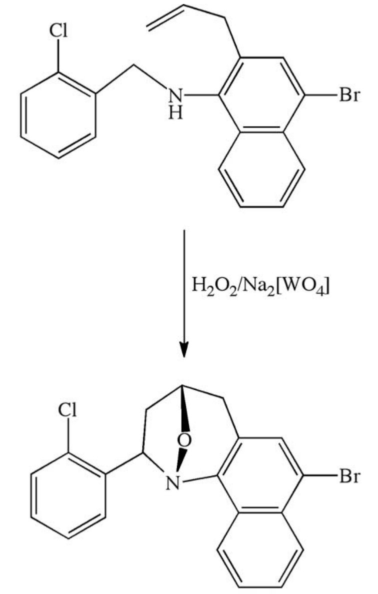
The molecules of the title compound, $C_{20}H_{15}BrClNO$, are linked into chains by a C—H$\cdots\pi$(arene) hydrogen bond, in which the acceptor is the brominated ring of the naphthalene unit, and these chains are linked by an aromatic π–π stacking interaction, again involving the naphthalene unit, into a sheet structure.

Comment

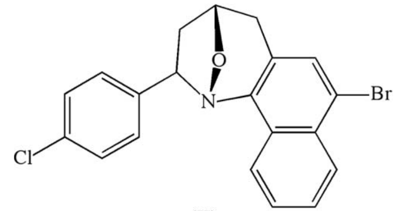
We report here the molecular and supramolecular structure of 7-bromo-2-*exo*-(2-chlorophenyl)-2,3,4,5-tetrahydro-1,4-epoxynaphtho[1,2-*b*]azepine, (I) (Fig. 1), which we compare with the 2-(4-chlorophenyl)- positional isomer, (II) (see Scheme), the structure of which was reported recently (Palma *et al.*, 2009). The synthetic route involves the oxidation of the corresponding 2-allyl-*N*-arylmethyl-1-naphthylamine with an excess of aqueous hydrogen peroxide in the presence of catalytic quantities of sodium tungstate, followed by a thermally induced intramolecular 1,3-dipolar cycloaddition of the intermediate nitrone (*cf.* Acosta *et al.*, 2008).

The molecule of (I) contains two stereogenic centres, at atoms C2 and C4 (Fig. 1), and the reference molecule was selected to have the *R* configuration at C2; on this basis, the configuration at C4 is *S*. Since (I) crystallizes in the centrosymmetric space group $P2_1/c$, the unit cell accommodates equal numbers of the two enantiomers, so that the compound crystallizes as a true racemate with configuration 2*RS*,4*SR*. The isomeric compound (II) also crystallizes as a racemate, with the configuration 2*RS*,4*SR*, but in a different centrosymmetric space group, *viz*. *Pbca*.

The conformations of the fused heterocyclic ring systems in (I) and (II) are very similar, as shown by the values (Table 2) of the ring-puckering parameters (Cremer & Pople, 1975). The five-membered rings are twisted about a line between atom C3 and the mid-point of the N1—O14 bond. The six-membered rings have conformations intermediate between envelope and half-chair forms. For a six-membered ring with equal bond lengths, the idealized values of the ring-puckering parameters are $\theta = 54.7^\circ$ and $\varphi = (60k)^\circ$ for an envelope conformation, and $\theta = 50.8^\circ$ and $\varphi = (60k + 30)^\circ$ for a half-chair form, where k represents an integer in both cases. The specification of the molecular conformation can be completed by the torsion angle N1—C2—C21—C22, defining the orientation of the



(I)



(II)

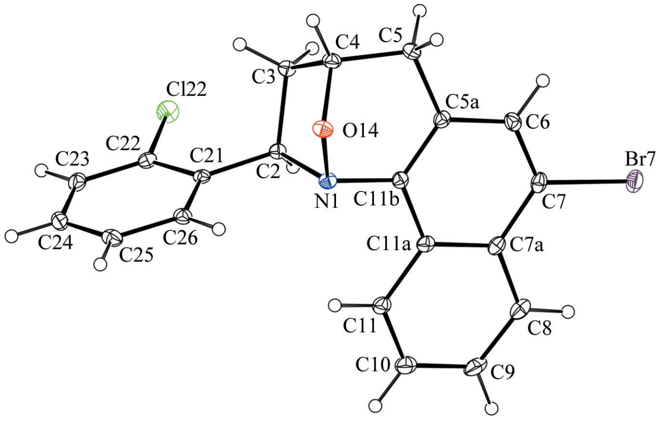


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

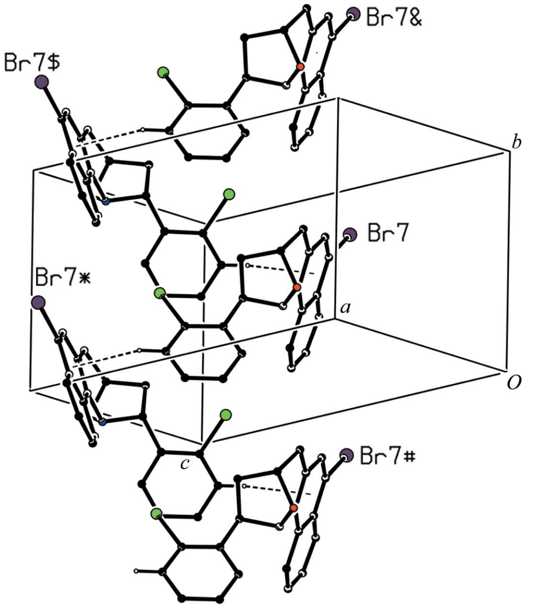


Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain parallel to [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(-x + 1, y - \frac{1}{2}, -z + \frac{3}{2})$, $(x, y - 1, z)$, $(-x + 1, y + \frac{1}{2}, -z + \frac{3}{2})$ and $(x, y + 1, z)$, respectively.

pendant aryl ring relative to the fused ring system; the values of this angle in (I) and (II) are fairly similar, *viz.* −173.87 (19)° in (I) and 172.4 (3)° in (II).

Thus, despite the different crystallization behaviour, as shown by the different space groups, the molecular conformations of (I) and (II) are very similar. However, the supramolecular assembly in these two compounds is significantly different.

The crystal structure of (I) contains no C—H⋯O or C—H⋯N hydrogen bonds, and the supramolecular assembly is determined by a combination of a C—H⋯π(arene) hydrogen bond (Table 1) and an aromatic π–π stacking interaction. The C—H⋯π(arene) hydrogen bond utilizes the brominated ring of the naphthalene unit as the acceptor, and it links molecules related by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ into a chain running parallel to the [010] direction (Fig. 2).

Within the naphthalene unit, the two rings are not quite parallel and the angle between the normals of the two six-membered rings is 2.76 (11)°. In the aromatic π–π stacking interaction (Fig. 3), the distance between the centroid of the brominated ring C5a/C6/C7/C7a/C11a/C11b of the molecule at (x, y, z) and that of the unsubstituted ring C7a/C8/C9/C10/C11/C11a in the molecule at $(-x, -y + 1, -z + 1)$ is 3.816 (2) Å. These rings make a dihedral angle of 2.76 (11)° and the shortest mean perpendicular distance between the ring planes is *ca* 3.46 Å. Thus, the molecules at (x, y, z) and $(-x + 1, y - \frac{1}{2}, -z + \frac{3}{2})$, which form parts of the hydrogen-bonded chain along $(\frac{1}{2}, y, \frac{3}{4})$, form π–π stacking interactions with the molecules at $(-x, -y + 1, -z + 1)$ and $(x + 1, -y + \frac{1}{2}, z + \frac{1}{2})$, respectively, which form parts of the hydrogen-bonded chains along $(-\frac{1}{2}, y, \frac{1}{4})$ and $(\frac{3}{2}, y, \frac{5}{4})$, respectively. Hence, the action of the π–π stacking interaction is to link the hydrogen-bonded chains which run parallel to [010] into a sheet lying parallel to $(10\overline{2})$ (Fig. 4). Both faces of the naphthalene unit are involved in the sheet formation, with one face acting as the hydrogen-bond acceptor and the other participating in the π–π stacking interaction (Fig. 4).

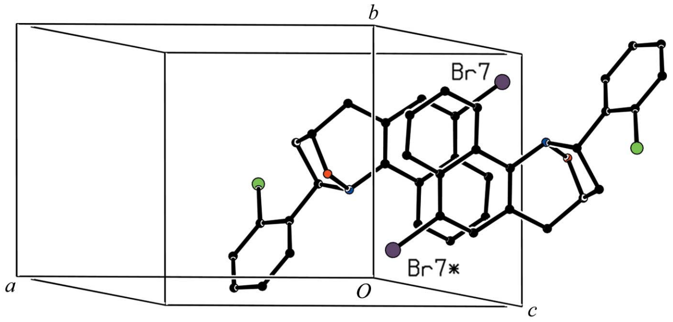


Figure 3
Part of the crystal structure of (I), showing the π–π stacking interaction which links the hydrogen-bonded chains. For the sake of clarity, H atoms have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(-x, -y + 1, -z + 1)$.

By contrast, there are no C—H⋯π hydrogen bonds in the structure of (II). Instead, the assembly in (II) is determined by a combination of a C—H⋯O hydrogen bond and an aromatic π–π stacking interaction involving the pendant 4-chlorophenyl rings of inversion-related pairs of molecules (Palma *et al.*, 2009). The C—H⋯O hydrogen bond links molecules related by a *b*-glide plane in the space group *Pbca* into a chain running parallel to [010], and these chains are linked by the π–π stacking interaction into a sheet lying parallel to (001).

It is of interest to note here that, although the structures of (I) and (II) contain π–π stacking interactions, these involve only the naphthalene unit in (I) and only the pendant phenyl ring in (II).

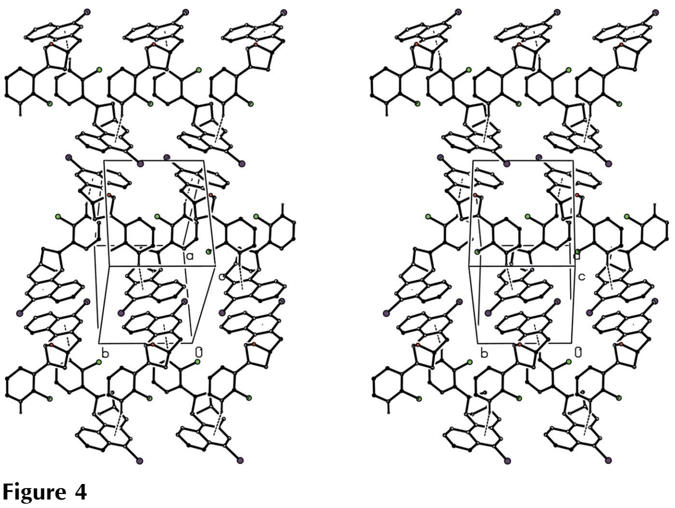


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a sheet parallel to $(10\overline{2})$ formed by the π-stacking of hydrogen-bonded chains. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

o124 Yépes *et al.* • $C_{20}H_{15}BrClNO$ *Acta Cryst.* (2012). C**68**, o123–o125

Experimental

Sodium tungstate dihydrate (5–10 mol%), followed by 30% aqueous hydrogen peroxide solution (30 mmol), were added to a stirred and cooled (ice bath) solution of 2-allyl-4-bromo-*N*-(2-chlorobenzyl)-1-naphthylamine (10 mmol) in acetone–water (30 ml, 10:1 *v*/*v*). The resulting mixture was stirred at 273 K for 2 h and then at ambient temperature for an additional 72 h. The reaction mixture was filtered and then extracted with ethyl acetate, and the organic fraction was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then toluene (30 ml) was added to the solid residue. The resulting solution was heated at 363–373 K for 12 h. The solution was then cooled to ambient temperature and the solvent removed under reduced pressure, before the crude product was purified by silica-gel column chromatography using heptane–ethyl acetate (from 30:1 to 10:1 *v*/*v*) as eluent; evaporation of the eluted solution, at ambient temperature and exposed to air, gave the product, (I), as pale-yellow crystals suitable for single-crystal X-ray diffraction (yield 48%, m.p. 464–465 K). MS (70 eV) *m*/*z* (%): 399 (M^+, ^{35}Cl, ^{79}Br, 1), 365 (100), 348 (6), 322 (2), 335 (4), 257 (3), 231 (1).

Crystal data

$C_{20}H_{15}BrClNO$
$M_r = 400.68$
Monoclinic, $P2_1/c$
$a = 11.5083\ (8)$ Å
$b = 8.1027\ (6)$ Å
$c = 18.3210\ (16)$ Å
$\beta = 110.505\ (5)^\circ$

$V = 1600.2\ (2)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.74$ mm^{-1}
$T = 120$ K
$0.38 \times 0.30 \times 0.10$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.422$, $T_{\max} = 0.771$

22802 measured reflections
3672 independent reflections
2969 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.069$
$S = 1.12$
3672 reflections

217 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.99 (CH_2) or 1.00 Å (aliphatic CH), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Table 1
Hydrogen-bond geometry (Å, °).

Cg represents the centroid of the C5a/C6/C7/C7a/C11a/C11b ring.

D—H···A	D—H	H···A	D···A	D—H···A
C23—H23···$Cg^{\rm i}$	0.95	2.62	3.494 (3)	153

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Table 2
Ring-puckering parameters (Å, °) for (I) and (II).

Puckering parameters for five-membered rings are defined for the atom sequence O14—N1—C2—C3—C4, those for six-membered rings for the atom sequence O14—N1—C11b—C5a—C5—C4 and those for seven-membered rings for the atom sequence N1—C2—C3—C4—C5—C5a—C11b.

Parameter	(I)	(II)†
(*a*) Five-membered rings		
Q_2	0.444 (2)	0.442 (3)
φ_2	12.9 (3)	16.2 (4)
(*b*) Six-membered rings		
Q	0.620 (2)	0.617 (3)
θ	127.21 (18)	128.3 (3)
φ	165.5 (3)	165.1 (4)
(*c*) Seven-membered rings		
Q	1.085 (2)	1.101 (3)
φ_2	16.58 (14)	15.80 (17)
φ_3	300.9 (4)	298.8 (6)

† Data for (II) are taken from Palma *et al.* (2009).

The authors thank the Centro de Instrumentación Científico-Técnica of the Universidad de Jaén and the staff for the data collection. AFY and AP thank COLCIENCIAS for financial support (grant No. 1102-521-28229). JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3167). Services for accessing these data are described at the back of the journal.

References

Acosta, L. M., Bahsas, A., Palma, A., Cobo, J., Low, J. N. & Glidewell, C. (2008). *Acta Cryst.* C**64**, o514–o518.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Palma, A., Bahsas, A., Yépes, A. F., Cobo, J., Hursthouse, M. B. & Glidewell, C. (2009). *Acta Cryst.* C**65**, o140–o145.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Acta Cryst. (2012). C**68**, o123–o125 Yépes *et al.* • $C_{20}H_{15}BrClNO$ **o125**