Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

A chain of π-stacked molecules in 4-(2-chlorophenyl)pyrrolo[1,2-*a*]-quinoxaline and a hydrogen-bonded sheet in (4*RS*)-4-(1,3-1,3-benzodioxol-6-yl)-4,5-dihydropyrrolo[1,2-*a*]-quinoxaline

Juan C. Castillo,[a] Rodrigo Abonía,[a] Justo Cobo[b] and Christopher Glidewell[c]*

[a]Departamento de Química, Universidad de Valle, AA 25360 Cali, 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

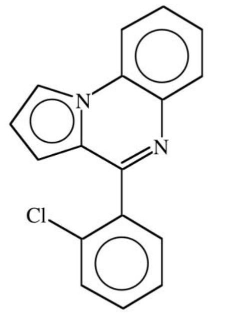
Received 21 March 2013
Accepted 3 April 2013

In the molecule of 4-(2-chlorophenyl)pyrrolo[1,2-*a*]quinoxaline, $C_{17}H_{11}ClN_2$, (I), the bond lengths are consistent with electron delocalization in the two outer rings of the fused tricyclic system, with a localized double bond in the central ring. The molecules of (I) are linked into chains by a π–π stacking interaction. In (4*RS*)-4-(1,3-benzodioxol-6-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline, $C_{18}H_{14}N_2O_2$, (II), the central ring of the fused tricyclic system adopts a conformation intermediate between screw-boat and half-chair forms. A combination of N—H$\cdots$O and C—H$\cdots\pi$(arene) hydrogen bonds links the molecules of (II) into a sheet. Comparisons are made with related compounds.

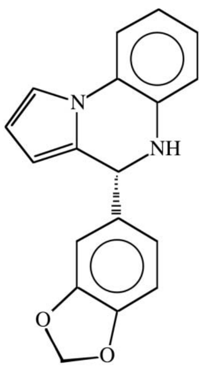
Comment

Pyrrolo[1,2-*a*]quinoxalines and their 4,5-dihydro derivatives exhibit interesting pharmacological properties (Maeba *et al.*, 1990; Lancelot *et al.*, 1994; Grande *et al.*, 2007). Some compounds containing this system have shown activity as potent IkappaB kinase (IKK) inhibitors (Beaulieu *et al.*, 2007), as potent and selective serotonin-1B agonists (Neale *et al.*, 1987), and as antileishmanial agents (Guillon *et al.*, 2007), and have also shown antiproliferative activity against human leukaemia and breast cancer (Desplat *et al.*, 2010). Here, we report the molecular and supramolecular structures of the title compounds, 4-(2-chlorophenyl)pyrrolo[1,2-*a*]quinoxaline, (I) (Fig. 1), and (4*RS*)-4-(1,3-benzodioxol-6-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline, (II) (Fig. 2), as representative examples of these classes of compound, prepared as part of our current programme related to the synthesis of novel quinoxaline derivatives of biological interest (Abonía *et al.*, 2001; Castillo *et al.*, 2010).

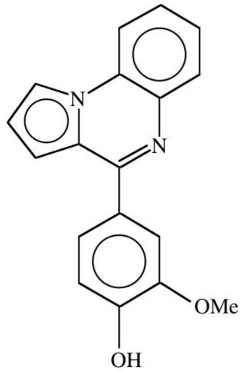
Compound (I) contains a formally aromatic six-membered heterocyclic ring, while (II) contains a reduced 4,5-dihydro-ring in the corresponding position. We also compare the structures of (I) and (II) with those of their analogues, (III) (Castillo *et al.*, 2010) and (IV) (Castillo *et al.*, 2013) (see Scheme). Compounds (I) and (III) contain the same fused ring system but differ in the substituents carried by the pendent aryl ring; (II) and (IV) both contain the same reduced ring system, but (II) contains a benzodioxolyl substituent where (IV) contains a dimethoxyphenyl substituent.



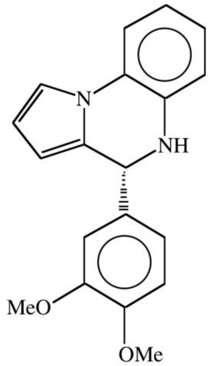
(I)



(II)



(III)



(IV)

The crystallization characteristics of (I)–(IV), despite their rather similar constitutions, are all different. Thus, (I), (II) and (IV) all crystallize with $Z' = 1$, but in three different space groups ($P2_1/c$, $C2/c$ and $Pbca$, respectively), while (III) crystallizes with $Z' = 2$. Despite the absence in (III) of any crystallographic symmetry in addition to that of the space group $P2_1/c$, where it crystallizes as a pseudo-merohedral twin emulating a metrically orthorhombic cell, the two independent molecules are nonetheless related by an approximate, but noncrystallographic, pseudo-screw axis parallel to the [100] direction of the monoclinic unit cell (Castillo *et al.*, 2010). The molecules of (II) contain a stereogenic centre at atom C4 and the reference molecule was selected as one having the *R* configuration at C4. Likewise, there is a stereogenic centre at atom C4 in (IV), but this compound exhibits configurational disorder, with a given molecular site occupied by a fraction 0.692 (5) of one enantiomer and 0.308 (5) of the other (Castillo *et al.*, 2013).

doi:10.1107/S0108270113009098

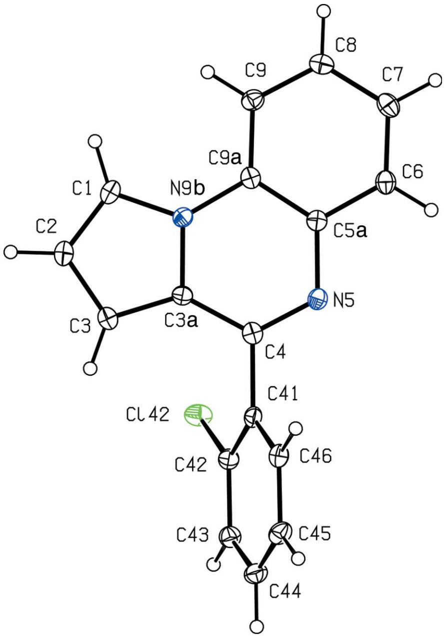


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The bond lengths in (I) and (II) (Tables 1 and 2) show some interesting contrasts, consequent upon the difference in the oxidation level of their respective six-membered heterocyclic rings. In (I), the C—C distances in the five-membered ring span a range of less than 0.03 Å, despite the fact that the C1—C2 and C3—C3a bonds are formally double, while C2—C3 is formally a single bond. These distances thus indicate some degree of electron delocalization in this ring. By contrast, in (II) the C—C distances in the pyrrole ring show a much clearer distinction between single and double bonds. At the same time, the bond lengths for the fused carbocyclic ring of (I), but not for that of (II), indicate some slight bond fixation in the C6—C7 and C8—C9 bonds, while in the central fused ring of (I) there is a clearly localized double bond at C4—N5. The overall pattern of the distances in (I) indicates the presence of 6π circuits in the two outer rings of the fused system and a localized double bond in the central ring, analogous to the electronic structure of phenanthrene (Glidewell & Lloyd, 1984, 1986). This pattern of distances in (I) is fairly similar to that found for (III) (Castillo *et al.*, 2010).

In (II), the dioxolane ring is essentially planar, with a maximum deviation from the mean plane of the five ring atoms of only 0.034 (2) Å for atom O43. For the central ring of the fused tricyclic system, the ring-puckering parameters (Cremer & Pople, 1975) for the atom sequence N5–C4–C3a–N9b–C9a–C5a are Q = 0.345 (2) Å, θ = 118.2 (3)° and φ = 216.4 (3)°, indicative of a conformation intermediate between screw-boat and half-chair forms, for which the idealized values of θ are 112.5 and 129.2°, respectively, with both forms having an idealized value for φ of $(60k + 30)°$, where k represents an integer. For the major and minor disorder forms of (IV) (Castillo *et al.*, 2013), the ring-puckering angles for the atom sequences corresponding to that of (II) are, respectively, θ = 121 (2) and 62 (4)°, and φ = 212 (2) and 29 (4)°, showing the close conformational similarity between (II) and the major form of (IV). These parameters also confirm the enantiomeric nature of the two disorder components of (IV), since a change of absolute configuration transforms θ into $(180 - \theta)$ and φ into $(180 + \varphi)$. Consequent upon the puckering of the central fused ring of (II), the dihedral angle between the planes of the two outer rings of the fused tricyclic system is 10.0 (2)°, whereas the corresponding dihedral angle in (I) is only 1.3 (2)°. In (I), the dihedral angle between the pendent aryl ring and the adjacent heterocyclic ring is 67.2 (2)°, and in (II) the corresponding angle is 87.1 (2)°.

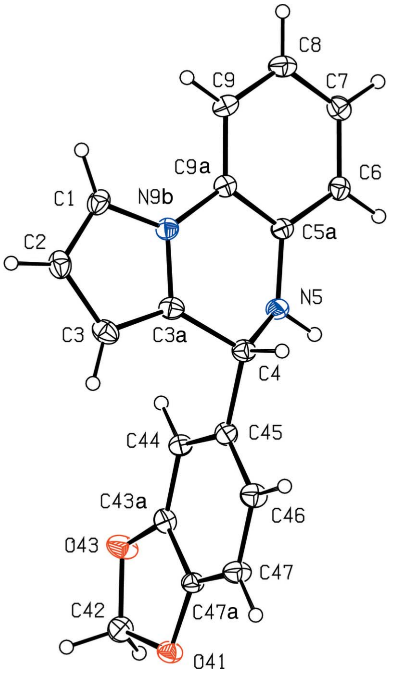


Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

The supramolecular assembly in the crystal structure of (I) is very simple, as there are no hydrogen bonds of any type present. The principal direction-specific intermolecular interaction is a π–π stacking interaction between the five-membered ring of the molecule at (x, y, z) and the fused aryl ring of the molecule at $(x, -y + \frac{3}{2}, z - \frac{1}{2})$. The planes of these two rings make a dihedral angle of less than 1°, with a ring-centroid separation of 3.690 (2) Å. The shortest interplanar spacing is *ca* 3.45 Å, with a ring-centroid offset of *ca* 1.32 Å, and the shortest of the individual atom–atom distances associated with this contact is C1$\cdots$C9a^{i} of 3.282 (3) Å [symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$]. By this means, molecules related by the c-glide plane at $y = \frac{3}{4}$ are linked into a chain running parallel to the [001] direction (Fig. 3). The only other direction-specific interaction between molecules is a Cl$\cdots$Cl contact of 3.213 (2) Å involving the molecules at (x, y, z) and $(-x + 1, -y + 1, -z + 2)$. While this distance is certainly less than the van der Waals sum (Bondi, 1964), the expected partial negative charges on the two atoms involved, together with their rather low polarizability, makes it unclear whether this contact is attractive or repulsive.

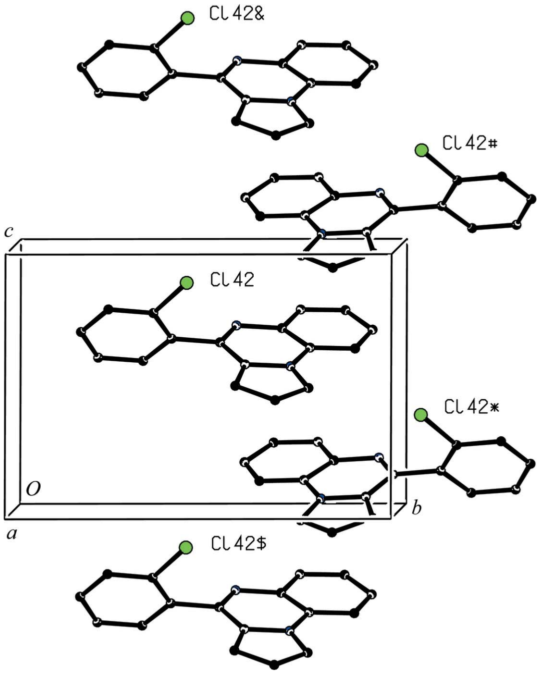


Figure 3
Part of the crystal structure of (I), showing the formation of a chain of π-stacked molecules along [001]. For the sake of clarity, all H atoms have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(x, -y + \frac{3}{2}, z - \frac{1}{2})$, $(x, -y + \frac{3}{2}, z + \frac{1}{2})$, $(x, y, z - 1)$ and $(x, y, z + 1)$, respectively.

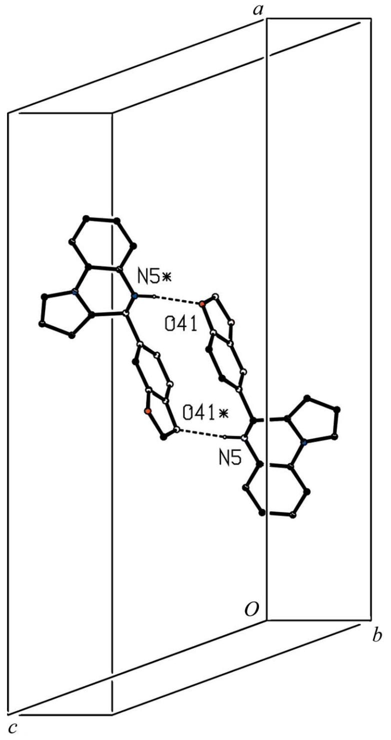


Figure 4
Part of the crystal structure of (II), showing the formation of a centrosymmetric hydrogen-bonded dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + 1, -y + 1, -z + 1)$.

The supramolecular assembly in (II) takes the form of a sheet built from a combination of N—H$\cdots$O and C—H$\cdots\pi$(arene) hydrogen bonds (Table 3). Inversion-related pairs of molecules are linked by paired N—H$\cdots$O hydrogen bonds to form a cyclic centrosymmetric dimer characterized by an $R^2_2(16)$ motif (Bernstein *et al.*, 1995) and centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 4). This dimeric unit can conveniently be regarded as the key building block for the sheet formation. Within the reference dimer, the C1 atoms at (x, y, z) and $(-x + 1, -y + 1, -z + 1)$ act as hydrogen-bond donors to, respectively, the C5a/C6–C8/C9/C9a fused aryl rings in the molecules at $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$ and $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$, which themselves form parts of the cyclic dimers centred at (0, 1, 0) and (1, 0, 1). Similarly, the fused aryl rings at (x, y, z) and $(-x + 1, -y + 1, -z + 1)$ accept hydrogen bonds from the C1 atoms in the molecules at, respectively, $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ and $(x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2})$, which form parts of the cyclic dimers centred at (0, 0, 0) and (1, 1, 1). In this manner, a single C—H$\cdots\pi$(arene) hydrogen bond links the cyclic $R^2_2(16)$ dimers into a sheet lying parallel to $(10\overline{1})$ (Fig. 5).

A number of other C—H$\cdots\pi$ contacts can be identified in the structure of (II) (Table 3), all of which lie within the reference sheet described above, so that, even if they were regarded as structurally significant, they could not affect the dimensionality of the supramolecular aggregation but would merely increase its complexity. The contact involving atom C42 has a C—H$\cdots$(ring centroid) angle of only 123° and the corresponding interaction energy is thus likely to be very small (Wood *et al.*, 2009). The two contacts from atoms C8 and C46 both involve the pyrrole ring where, as noted above, there is a considerable degree of bond fixation, so that the delocalized aromatic character of this ring is likely to be rather modest.

It is of interest briefly to compare the supramolecular assemblies in (I) and (II) with those in, respectively, (III) and

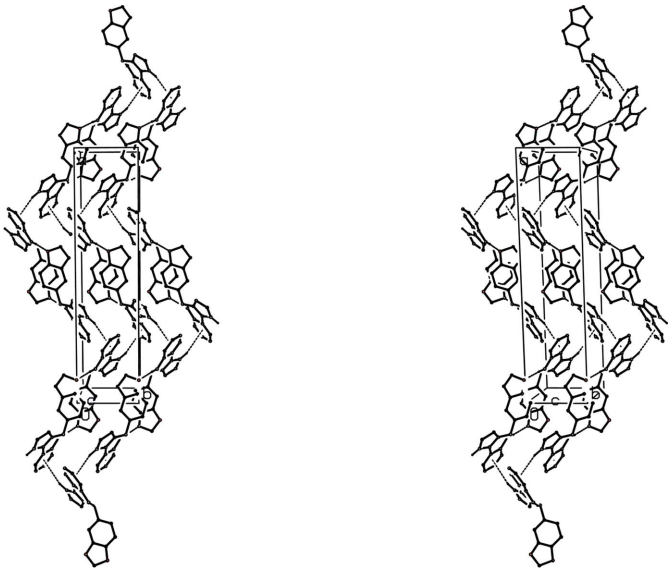


Figure 5
A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded sheet lying parallel to $(10\overline{1})$. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

(IV) (Castillo *et al.*, 2010, 2013). The presence of both hydroxy and methoxy substituents in the molecules of (III) naturally leads to a more complex mode of supramolecular assembly for (III) than was found for (I). In (III), where $Z' = 2$, a combination of two independent O—H···N hydrogen bonds and four independent C—H···O hydrogen bonds gives rise to a complex sheet structure. By contrast with the structure of (I), there are no π–π stacking interactions in the structure of (III). For both the major and minor disorder components of (IV), molecules are linked by pairs of N—H···O hydrogen bonds to form cyclic centrosymmetric $R_2^2(14)$ dimers, somewhat similar to the dimer formed in (II), but reinforced in (IV) by a π–π interaction within the dimer involving the pendent phenyl rings. By contrast, there are no π–π stacking interactions in the structure of (II).

Experimental

For the synthesis of (I), a mixture of 1-(2-aminophenyl)pyrrole (0.63 mmol), 2-chlorobenzaldehyde (0.63 mmol) and palladium/charcoal (10%, 0.63 mmol) was dissolved in acetonitrile (2 ml). The solution was stirred at ambient temperature for 48 h until the starting materials were no longer detected by thin-layer chromatography. The palladium/charcoal was then removed by filtration, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using a chloroform–hexane mixture (3:1 *v*/*v*) as eluent. Colourless crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in air, from a solution in ethanol (yield 91%, m.p. 453 K). MS (70 eV) *m*/*z* (%): 280/278 (34/100) [M^+], 254/252 (8/25), 121 (41); analysis found: C 73.3, H 3.9, N 10.1%; $C_{17}H_{11}ClN_2$ requires: C 73.3, H 4.0, N 10.1%. For the synthesis of (II), a mixture of 1-(2-aminophenyl)pyrrole (0.63 mmol) and piperonal (0.63 mmol) was dissolved in a mixture of acetonitrile and water (2:1 *v*/*v*, 1.5 ml). The mixture was left at ambient temperature without stirring for 6 d; the resulting solid product was collected by filtration and washed with hexane. Yellow crystals of (II) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in air, from a solution in ethanol (yield 86%, m.p. 434 K). MS (70 eV) *m*/*z* (%): 290 (42) [M^+], 229 (7), 169 (100), 157 (9), 115 (8); analysis found: C 74.3, H 4.9, N 9.4%; $C_{18}H_{14}N_2O_2$ requires: C 74.5, H 4.9, N 9.7%.

Compound (I)

Crystal data

$C_{17}H_{11}ClN_2$
$M_r = 278.73$
Monoclinic, $P2_1/c$
$a = 13.5649$ (13) Å
$b = 11.8142$ (11) Å
$c = 8.1678$ (12) Å
$\beta = 99.281$ (10)°

$V = 1291.8$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.29$ mm^{-1}
$T = 120$ K
$0.42 \times 0.25 \times 0.22$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.890$, $T_{\max} = 0.940$

18171 measured reflections
2984 independent reflections
2187 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C2	1.375 (3)	C7—C8	1.399 (3)
C2—C3	1.402 (3)	C8—C9	1.386 (3)
C3—C3a	1.391 (3)	C9—C9a	1.389 (3)
C3a—C4	1.422 (3)	C9a—N9b	1.401 (2)
C4—N5	1.313 (2)	N9b—C1	1.368 (2)
N5—C5a	1.402 (2)	C3a—N9b	1.397 (2)
C5a—C6	1.405 (3)	C5a—C9a	1.410 (3)
C6—C7	1.379 (3)		
C3a—C4—C41—C42	68.1 (2)	N5—C4—C41—C42	−113.1 (2)

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.116$
$S = 1.06$
2984 reflections

181 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Compound (II)

Crystal data

$C_{18}H_{14}N_2O_2$
$M_r = 290.31$
Monoclinic, $C2/c$
$a = 26.590$ (3) Å
$b = 6.2890$ (9) Å
$c = 17.2655$ (19) Å
$\beta = 104.017$ (11)°

$V = 2801.3$ (6) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 120$ K
$0.45 \times 0.24 \times 0.16$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.960$, $T_{\max} = 0.986$

23085 measured reflections
3225 independent reflections
2350 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.114$
$S = 1.08$
3225 reflections

199 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

All H atoms were located in difference maps. C-bound H atoms were then treated as riding in geometrically idealized positions, with C—H = 0.95 (aromatic and pyrrole), 0.99 (CH_2) or 1.00 Å (aliphatic), and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). The N-bound H atom in (II) was permitted to ride at the position found in a difference map, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(N), giving N—H = 0.88 Å.

Table 2
Selected geometric parameters (Å, °) for (II).

C1—C2	1.367 (3)	C7—C8	1.386 (3)
C2—C3	1.420 (3)	C8—C9	1.392 (3)
C3—C3a	1.373 (2)	C9—C9a	1.384 (2)
C3a—C4	1.505 (2)	C9a—N9b	1.418 (2)
C4—N5	1.457 (2)	N9b—C1	1.381 (2)
N5—C5a	1.384 (2)	C3a—N9b	1.381 (2)
C5a—C6	1.396 (2)	C5a—C9a	1.403 (2)
C6—C7	1.385 (2)		
C3a—C4—C45—C44	65.8 (2)	N5—C4—C45—C44	−53.4 (2)
C3a—C4—C45—C46	−113.83 (19)	N5—C4—C45—C46	126.93 (17)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

*Cg*1 represents the centroid of the C5a/C6–C9/C9a ring and *Cg*2 represents the centroid of the C1–C3/C3a/N9b ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···O41^{i}	0.88	2.18	3.052 (2)	173
C1—H1···*Cg*1^{ii}	0.95	2.95	3.878 (2)	165
C8—H8···*Cg*2^{ii}	0.95	2.70	3.568 (2)	152
C42—H42*A*···*Cg*1^{iii}	0.99	2.99	3.628 (2)	123
C46—H46···*Cg*2^{iv}	0.95	2.90	3.845 (2)	173

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $x, y-1, z$.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I); *SIR2004* (Burla *et al.*, 2005) for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The authors thank the Centro de Instrumentación Científico-Técnica of the Universidad de Jaén and the staff for the data collection. JCC and RA thank COLCIENCIAS and Universidad del Valle for financial support. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: YF3029). Services for accessing these data are described at the back of the journal.

References

Abonía, R., Insuasty, B., Quiroga, J., Kolshorn, H. & Meier, H. (2001). *J. Heterocycl. Chem.* **38**, 671–674.

Beaulieu, F., Ouellet, C., Ruediger, E., Belema, M., Qiu, Y., Yang, X., Banville, J., Burke, J., Gregor, K., MacMaster, J., Martel, A., McIntyre, K., Pattoli, M., Zusi, F. & Vyas, D. (2007). *Bioorg. Med. Chem. Lett.* **17**, 1233–1237.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

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.

Castillo, J. C., Abonía, R., Cobo, J. & Glidewell, C. (2010). *Acta Cryst.* C**66**, o385–o388.

Castillo, J. C., Abonía, R., Cobo, J. & Glidewell, C. (2013). Private communication (deposition number 927877). CCDC, Union Road, Cambridge, England.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Desplat, V., Moreau, S., Gay, A., Fabre, S. B., Thiolat, D., Massip, S., Macky, G., Godde, F., Mossalayi, D., Jarry, C. & Guillon, J. (2010). *J. Enzyme Inhib. Med. Chem.* **25**, 204–215.

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.

Glidewell, C. & Lloyd, D. (1984). *Tetrahedron*, **40**, 4455–4472.

Glidewell, C. & Lloyd, D. (1986). *J. Chem. Educ.* **63**, 306–309.

Grande, F., Aiello, F., De Grazia, O., Brizzi, A., Garofalo, A. & Neamati, N. (2007). *Bioorg. Med. Chem.* **15**, 288–294.

Guillon, J., Forfar, I., Desplat, V., Fabre, S. B., Thiolat, D., Massip, S., Carrie, H., Mossalayi, D. & Jarry, C. (2007). *J. Enzyme Inhib. Med. Chem.* **22**, 541–549.

Lancelot, J.-C., Prunier, H., Robba, M., Delagrange, P., Renard, P. & Adam, G. (1994). Eur. Patent Appl. EP 623620.

Maeba, I., Kitaori, K., Itaya, Y. & Ito, C. (1990). *J. Chem. Soc. Perkin Trans. 1*, pp. 67–72.

Neale, R., Fallon, S., Boyar, W., Wasley, J., Martin, L., Stone, G., Glaeser, B., Sinton, C. & Williams, M. (1987). *Eur. J. Pharmacol.* **136**, 1–9.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

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.

Wood, P. A., Allen, F. H. & Pidcock, E. (2009). *CrystEngComm*, **11**, 1563–1571.

supplementary materials

Acta Cryst. (2013). C**69**, 544-548   [doi:10.1107/S0108270113009098]

A chain of *π*-stacked molecules in 4-(2-chlorophenyl)pyrrolo[1,2-*a*]quinoxaline and a hydrogen-bonded sheet in (4*RS*)-4-(1,3-1,3-benzodioxol-6-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline

Juan C. Castillo, Rodrigo Abonía, Justo Cobo and Christopher Glidewell

(I) 4-(2-Chlorophenyl)pyrrolo[1,2-*a*]quinoxaline

Crystal data

$C_{17}H_{11}ClN_2$
$M_r = 278.73$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.5649$ (13) Å
$b = 11.8142$ (11) Å
$c = 8.1678$ (12) Å
$\beta = 99.281$ (10)°
$V = 1291.8$ (3) Å^3
$Z = 4$
$F(000) = 576$
$D_x = 1.433$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2984 reflections
$\theta = 3.0$–27.5°
$\mu = 0.28$ mm^{-1}
$T = 120$ K
Block, colourless
0.42 × 0.25 × 0.22 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Radiation source: Bruker Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.890$, $T_{max} = 0.940$
18171 measured reflections
2984 independent reflections
2187 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -17 \rightarrow 17$
$k = -14 \rightarrow 15$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.116$
$S = 1.06$
2984 reflections
181 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.6625P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.34705 (14)	0.75957 (17)	0.4570 (2)	0.0252 (4)
H1	0.3527	0.8382	0.4357	0.030*
C2	0.40865 (14)	0.67575 (17)	0.4147 (2)	0.0270 (4)
H2	0.4642	0.6868	0.3591	0.032*
C3	0.37595 (14)	0.57131 (17)	0.4673 (2)	0.0247 (4)
H3	0.4048	0.4993	0.4538	0.030*
C3a	0.29317 (13)	0.59319 (16)	0.5431 (2)	0.0210 (4)
C4	0.22842 (13)	0.52535 (16)	0.6229 (2)	0.0216 (4)
N5	0.15083 (11)	0.56487 (13)	0.68203 (19)	0.0219 (3)
C5a	0.13447 (13)	0.68197 (16)	0.6709 (2)	0.0213 (4)
C6	0.05335 (14)	0.72742 (17)	0.7364 (2)	0.0251 (4)
H6	0.0103	0.6782	0.7840	0.030*
C7	0.03527 (15)	0.84232 (18)	0.7328 (2)	0.0277 (4)
H7	−0.0197	0.8718	0.7780	0.033*
C8	0.09805 (15)	0.91530 (17)	0.6624 (2)	0.0276 (4)
H8	0.0854	0.9944	0.6601	0.033*
C9	0.17847 (15)	0.87330 (16)	0.5960 (2)	0.0256 (4)
H9	0.2208	0.9231	0.5480	0.031*
C9a	0.19646 (13)	0.75749 (16)	0.6006 (2)	0.0210 (4)
N9b	0.27628 (11)	0.70985 (13)	0.53517 (18)	0.0209 (3)
C41	0.24779 (14)	0.40080 (16)	0.6382 (2)	0.0217 (4)
C42	0.33173 (14)	0.35660 (16)	0.7397 (2)	0.0230 (4)
Cl42	0.41717 (4)	0.44616 (4)	0.85870 (6)	0.03018 (16)
C43	0.34865 (15)	0.24091 (16)	0.7547 (2)	0.0262 (4)
H43	0.4060	0.2126	0.8251	0.031*
C44	0.28068 (15)	0.16737 (17)	0.6655 (2)	0.0287 (4)
H44	0.2917	0.0880	0.6741	0.034*
C45	0.19673 (15)	0.20885 (17)	0.5637 (2)	0.0275 (4)
H45	0.1502	0.1580	0.5033	0.033*
C46	0.18072 (14)	0.32427 (17)	0.5504 (2)	0.0247 (4)
H46	0.1231	0.3520	0.4802	0.030*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0244 (10)	0.0283 (10)	0.0233 (9)	−0.0063 (8)	0.0048 (8)	0.0025 (8)
C2	0.0226 (10)	0.0330 (11)	0.0262 (10)	−0.0027 (8)	0.0068 (8)	0.0011 (8)
C3	0.0215 (9)	0.0282 (11)	0.0249 (9)	0.0015 (8)	0.0048 (8)	−0.0016 (8)
C3a	0.0219 (9)	0.0202 (9)	0.0204 (9)	0.0003 (7)	0.0019 (7)	−0.0010 (7)
C4	0.0191 (9)	0.0266 (10)	0.0177 (9)	−0.0005 (8)	−0.0006 (7)	−0.0018 (7)
N5	0.0196 (8)	0.0240 (8)	0.0217 (8)	−0.0024 (6)	0.0023 (6)	−0.0002 (6)
C5a	0.0202 (9)	0.0241 (10)	0.0187 (9)	0.0003 (8)	0.0003 (7)	0.0008 (7)
C6	0.0207 (9)	0.0308 (11)	0.0237 (10)	−0.0011 (8)	0.0029 (8)	−0.0004 (8)
C7	0.0243 (10)	0.0338 (11)	0.0244 (10)	0.0054 (9)	0.0019 (8)	−0.0026 (8)
C8	0.0313 (11)	0.0229 (10)	0.0281 (10)	0.0034 (8)	0.0030 (8)	−0.0014 (8)
C9	0.0289 (10)	0.0235 (10)	0.0241 (10)	−0.0021 (8)	0.0034 (8)	−0.0006 (8)
C9a	0.0191 (9)	0.0253 (10)	0.0181 (9)	−0.0002 (7)	0.0009 (7)	−0.0019 (7)

N9b	0.0212 (8)	0.0206 (8)	0.0206 (7)	−0.0012 (6)	0.0027 (6)	0.0003 (6)
C41	0.0217 (9)	0.0236 (9)	0.0210 (9)	−0.0022 (8)	0.0073 (7)	0.0006 (7)
C42	0.0242 (9)	0.0225 (9)	0.0225 (9)	−0.0022 (8)	0.0044 (7)	−0.0032 (7)
Cl42	0.0299 (3)	0.0247 (3)	0.0324 (3)	−0.0005 (2)	−0.00563 (19)	−0.0037 (2)
C43	0.0283 (10)	0.0253 (10)	0.0255 (10)	0.0009 (8)	0.0057 (8)	0.0002 (8)
C44	0.0365 (11)	0.0211 (10)	0.0299 (10)	−0.0019 (9)	0.0093 (9)	−0.0003 (8)
C45	0.0322 (11)	0.0244 (10)	0.0260 (10)	−0.0086 (8)	0.0046 (8)	−0.0044 (8)
C46	0.0218 (9)	0.0290 (10)	0.0234 (9)	−0.0029 (8)	0.0044 (7)	0.0000 (8)

Geometric parameters (Å, º)

C1—C2	1.375 (3)	C9—H9	0.9500
C1—H1	0.9500	C9a—N9b	1.401 (2)
C2—C3	1.402 (3)	N9b—C1	1.368 (2)
C2—H2	0.9500	C3a—N9b	1.397 (2)
C3—C3a	1.391 (3)	C5a—C9a	1.410 (3)
C3—H3	0.9500	C4—C41	1.497 (3)
C3a—C4	1.422 (3)	C41—C46	1.396 (3)
C4—N5	1.313 (2)	C41—C42	1.397 (3)
N5—C5a	1.402 (2)	C42—C43	1.388 (3)
C5a—C6	1.405 (3)	C42—Cl42	1.7448 (19)
C6—C7	1.379 (3)	C43—C44	1.385 (3)
C6—H6	0.9500	C43—H43	0.9500
C7—C8	1.399 (3)	C44—C45	1.386 (3)
C7—H7	0.9500	C44—H44	0.9500
C8—C9	1.386 (3)	C45—C46	1.382 (3)
C8—H8	0.9500	C45—H45	0.9500
C9—C9a	1.389 (3)	C46—H46	0.9500
N9b—C1—C2	107.96 (17)	C8—C9—C9a	119.21 (18)
N9b—C1—H1	126.0	C8—C9—H9	120.4
C2—C1—H1	126.0	C9a—C9—H9	120.4
C1—C2—C3	108.77 (17)	C9—C9a—N9b	121.92 (17)
C1—C2—H2	125.6	C9—C9a—C5a	121.36 (17)
C3—C2—H2	125.6	N9b—C9a—C5a	116.73 (16)
C3a—C3—C2	106.91 (17)	C1—N9b—C3a	108.85 (15)
C3a—C3—H3	126.5	C1—N9b—C9a	130.49 (16)
C2—C3—H3	126.5	C3a—N9b—C9a	120.65 (15)
C3—C3a—N9b	107.51 (16)	C46—C41—C42	117.65 (17)
C3—C3a—C4	134.56 (18)	C46—C41—C4	120.19 (17)
N9b—C3a—C4	117.93 (16)	C42—C41—C4	122.16 (16)
N5—C4—C3a	124.00 (17)	C43—C42—C41	121.85 (17)
N5—C4—C41	117.36 (16)	C43—C42—Cl42	117.54 (15)
C3a—C4—C41	118.63 (16)	C41—C42—Cl42	120.57 (14)
C4—N5—C5a	117.08 (16)	C44—C43—C42	118.98 (19)
N5—C5a—C6	118.55 (17)	C44—C43—H43	120.5
N5—C5a—C9a	123.51 (17)	C42—C43—H43	120.5
C6—C5a—C9a	117.92 (17)	C43—C44—C45	120.41 (18)
C7—C6—C5a	121.02 (18)	C43—C44—H44	119.8
C7—C6—H6	119.5	C45—C44—H44	119.8

C5a—C6—H6	119.5	C46—C45—C44	119.96 (18)
C6—C7—C8	119.85 (19)	C46—C45—H45	120.0
C6—C7—H7	120.1	C44—C45—H45	120.0
C8—C7—H7	120.1	C45—C46—C41	121.14 (18)
C9—C8—C7	120.65 (19)	C45—C46—H46	119.4
C9—C8—H8	119.7	C41—C46—H46	119.4
C7—C8—H8	119.7		

N9b—C1—C2—C3	0.0 (2)	C2—C1—N9b—C9a	−179.42 (17)
C1—C2—C3—C3a	−0.2 (2)	C3—C3a—N9b—C1	−0.2 (2)
C2—C3—C3a—N9b	0.2 (2)	C4—C3a—N9b—C1	178.91 (16)
C2—C3—C3a—C4	−178.7 (2)	C3—C3a—N9b—C9a	179.37 (15)
C3—C3a—C4—N5	−177.53 (19)	C4—C3a—N9b—C9a	−1.5 (2)
N9b—C3a—C4—N5	3.6 (3)	C9—C9a—N9b—C1	−1.2 (3)
C3—C3a—C4—C41	1.1 (3)	C5a—C9a—N9b—C1	178.48 (18)
N9b—C3a—C4—C41	−177.72 (15)	C9—C9a—N9b—C3a	179.32 (17)
C3a—C4—N5—C5a	−2.8 (3)	C5a—C9a—N9b—C3a	−1.0 (2)
C41—C4—N5—C5a	178.51 (15)	N5—C4—C41—C46	66.5 (2)
C4—N5—C5a—C6	−178.58 (16)	C3a—C4—C41—C46	−112.3 (2)
C4—N5—C5a—C9a	0.0 (3)	C3a—C4—C41—C42	68.1 (2)
N5—C5a—C6—C7	178.30 (17)	N5—C4—C41—C42	−113.1 (2)
C9a—C5a—C6—C7	−0.3 (3)	C46—C41—C42—C43	−0.3 (3)
C5a—C6—C7—C8	0.3 (3)	C4—C41—C42—C43	179.27 (17)
C6—C7—C8—C9	0.0 (3)	C46—C41—C42—Cl42	−177.96 (13)
C7—C8—C9—C9a	−0.2 (3)	C4—C41—C42—Cl42	1.6 (2)
C8—C9—C9a—N9b	179.79 (17)	C41—C42—C43—C44	0.5 (3)
C8—C9—C9a—C5a	0.2 (3)	Cl42—C42—C43—C44	178.18 (14)
N5—C5a—C9a—C9	−178.45 (17)	C42—C43—C44—C45	−0.4 (3)
C6—C5a—C9a—C9	0.1 (3)	C43—C44—C45—C46	0.3 (3)
N5—C5a—C9a—N9b	1.9 (3)	C44—C45—C46—C41	−0.1 (3)
C6—C5a—C9a—N9b	−179.53 (16)	C42—C41—C46—C45	0.1 (3)
C2—C1—N9b—C3a	0.1 (2)	C4—C41—C46—C45	−179.45 (17)

(II) (*RS*)-4-(1,3-Benzodioxol-6-yl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline

Crystal data

$C_{18}H_{14}N_2O_2$
M_r = 290.31
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 26.590 (3) Å
b = 6.2890 (9) Å
c = 17.2655 (19) Å
β = 104.017 (11)°
V = 2801.3 (6) Å^3
Z = 8

F(000) = 1216
D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3225 reflections
θ = 2.6–27.5°
μ = 0.09 mm^{-1}
T = 120 K
Block, yellow
0.45 × 0.24 × 0.16 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer

Radiation source: Bruker Nonius FR591 rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm^{-1}

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.960$, $T_{\max} = 0.986$

23085 measured reflections

3225 independent reflections

2350 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 27.5°$, $\theta_{\min} = 2.6°$

$h = -34 \rightarrow 34$

$k = -8 \rightarrow 7$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.114$

$S = 1.08$

3225 reflections

199 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 3.2029P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.32$ e Å^{-3}

$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.33788 (7)	1.1611 (3)	0.20621 (10)	0.0301 (4)
H1	0.3143	1.2745	0.1888	0.036*
C2	0.37700 (7)	1.0999 (3)	0.17223 (11)	0.0326 (4)
H2	0.3853	1.1632	0.1270	0.039*
C3	0.40297 (7)	0.9250 (3)	0.21654 (10)	0.0324 (4)
H3	0.4318	0.8505	0.2066	0.039*
C3a	0.37859 (6)	0.8837 (3)	0.27650 (10)	0.0275 (4)
C4	0.38528 (6)	0.7100 (3)	0.33813 (10)	0.0269 (4)
H4	0.3637	0.5846	0.3148	0.032*
N5	0.36709 (5)	0.7916 (2)	0.40552 (8)	0.0265 (3)
H5	0.3752	0.7109	0.4484	0.032*
C5a	0.32160 (6)	0.9076 (3)	0.39337 (10)	0.0231 (4)
C6	0.29136 (6)	0.9131 (3)	0.44910 (10)	0.0255 (4)
H6	0.3006	0.8271	0.4956	0.031*
C7	0.24801 (7)	1.0424 (3)	0.43741 (10)	0.0293 (4)
H7	0.2281	1.0455	0.4762	0.035*
C8	0.23350 (7)	1.1672 (3)	0.36950 (11)	0.0332 (4)
H8	0.2037	1.2554	0.3616	0.040*
C9	0.26298 (7)	1.1623 (3)	0.31302 (10)	0.0297 (4)
H9	0.2531	1.2467	0.2662	0.036*
C9a	0.30662 (6)	1.0348 (3)	0.32491 (10)	0.0235 (4)
N9b	0.33884 (5)	1.0288 (2)	0.27039 (8)	0.0246 (3)
O41	0.59642 (4)	0.5001 (2)	0.45054 (7)	0.0287 (3)
C42	0.61376 (7)	0.7065 (3)	0.48326 (11)	0.0334 (4)
H42A	0.6322	0.6926	0.5402	0.040*
H42B	0.6379	0.7691	0.4540	0.040*

O43	0.56956 (5)	0.8395 (2)	0.47560 (8)	0.0386 (3)
C43a	0.52790 (6)	0.7248 (3)	0.43325 (10)	0.0269 (4)
C44	0.47709 (6)	0.7900 (3)	0.40861 (10)	0.0281 (4)
H44	0.4666	0.9287	0.4198	0.034*
C45	0.44164 (6)	0.6418 (3)	0.36624 (10)	0.0269 (4)
C46	0.45736 (7)	0.4415 (3)	0.35024 (11)	0.0317 (4)
H46	0.4325	0.3438	0.3214	0.038*
C47	0.50945 (7)	0.3788 (3)	0.37585 (11)	0.0327 (4)
H47	0.5205	0.2409	0.3647	0.039*
C47a	0.54357 (6)	0.5245 (3)	0.41741 (10)	0.0244 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0308 (9)	0.0288 (10)	0.0271 (9)	−0.0022 (8)	0.0002 (7)	0.0066 (8)
C2	0.0302 (9)	0.0386 (11)	0.0275 (9)	−0.0077 (8)	0.0039 (7)	0.0040 (8)
C3	0.0257 (9)	0.0447 (12)	0.0263 (9)	0.0008 (8)	0.0057 (7)	−0.0009 (8)
C3a	0.0250 (8)	0.0323 (10)	0.0231 (8)	0.0022 (7)	0.0020 (7)	−0.0011 (7)
C4	0.0241 (8)	0.0280 (10)	0.0273 (9)	0.0003 (7)	0.0038 (7)	−0.0007 (7)
N5	0.0241 (7)	0.0306 (8)	0.0246 (7)	0.0050 (6)	0.0053 (6)	0.0063 (6)
C5a	0.0202 (8)	0.0210 (9)	0.0255 (8)	−0.0016 (7)	0.0007 (6)	−0.0023 (7)
C6	0.0257 (8)	0.0251 (9)	0.0248 (8)	−0.0035 (7)	0.0041 (7)	−0.0008 (7)
C7	0.0287 (9)	0.0298 (10)	0.0306 (9)	−0.0021 (8)	0.0097 (7)	−0.0049 (8)
C8	0.0298 (9)	0.0299 (10)	0.0392 (10)	0.0070 (8)	0.0070 (8)	−0.0033 (8)
C9	0.0310 (9)	0.0267 (10)	0.0289 (9)	0.0061 (8)	0.0027 (7)	0.0025 (8)
C9a	0.0231 (8)	0.0235 (9)	0.0220 (8)	−0.0019 (7)	0.0018 (6)	−0.0031 (7)
N9b	0.0238 (7)	0.0269 (8)	0.0214 (7)	0.0007 (6)	0.0021 (5)	0.0017 (6)
O41	0.0215 (6)	0.0298 (7)	0.0329 (6)	0.0005 (5)	0.0028 (5)	−0.0024 (5)
C42	0.0278 (9)	0.0323 (11)	0.0360 (10)	−0.0047 (8)	−0.0005 (7)	0.0005 (8)
O43	0.0252 (6)	0.0343 (8)	0.0547 (8)	−0.0017 (6)	0.0065 (6)	−0.0162 (7)
C43a	0.0271 (8)	0.0286 (10)	0.0254 (8)	−0.0036 (7)	0.0070 (7)	−0.0028 (7)
C44	0.0284 (9)	0.0234 (9)	0.0340 (9)	0.0036 (7)	0.0107 (7)	−0.0001 (7)
C45	0.0252 (8)	0.0305 (10)	0.0243 (8)	−0.0004 (7)	0.0048 (7)	0.0023 (7)
C46	0.0279 (9)	0.0315 (10)	0.0338 (10)	−0.0007 (8)	0.0036 (7)	−0.0054 (8)
C47	0.0282 (9)	0.0293 (10)	0.0385 (10)	0.0042 (8)	0.0042 (8)	−0.0058 (8)
C47a	0.0216 (8)	0.0267 (9)	0.0243 (8)	0.0031 (7)	0.0042 (6)	0.0028 (7)

Geometric parameters (Å, º)

C1—C2	1.367 (3)	C9a—N9b	1.418 (2)
C1—H1	0.9500	N9b—C1	1.381 (2)
C2—C3	1.420 (3)	C3a—N9b	1.381 (2)
C2—H2	0.9500	C5a—C9a	1.403 (2)
C3—C3a	1.373 (2)	C4—C45	1.521 (2)
C3—H3	0.9500	O41—C47a	1.3917 (19)
C3a—C4	1.505 (2)	O41—C42	1.446 (2)
C4—N5	1.457 (2)	C42—O43	1.423 (2)
C4—H4	1.0000	C42—H42A	0.9900
N5—C5a	1.384 (2)	C42—H42B	0.9900
N5—H5	0.8801	O43—C43a	1.375 (2)

C5a—C6	1.396 (2)	C43a—C47a	1.375 (3)
C6—C7	1.385 (2)	C43a—C44	1.377 (2)
C6—H6	0.9500	C44—C45	1.399 (2)
C7—C8	1.386 (3)	C44—H44	0.9500
C7—H7	0.9500	C45—C46	1.377 (3)
C8—C9	1.392 (3)	C46—C47	1.404 (2)
C8—H8	0.9500	C46—H46	0.9500
C9—C9a	1.384 (2)	C47—C47a	1.364 (2)
C9—H9	0.9500	C47—H47	0.9500

C2—C1—N9b	107.85 (16)	C9a—C9—H9	119.9
C2—C1—H1	126.1	C8—C9—H9	119.9
N9b—C1—H1	126.1	C9—C9a—C5a	120.79 (16)
C1—C2—C3	107.96 (16)	C9—C9a—N9b	122.44 (15)
C1—C2—H2	126.0	C5a—C9a—N9b	116.76 (14)
C3—C2—H2	126.0	C1—N9b—C3a	108.94 (15)
C3a—C3—C2	107.21 (16)	C1—N9b—C9a	128.30 (15)
C3a—C3—H3	126.4	C3a—N9b—C9a	122.74 (14)
C2—C3—H3	126.4	C47a—O41—C42	104.85 (13)
C3—C3a—N9b	108.04 (15)	O43—C42—O41	108.29 (13)
C3—C3a—C4	132.36 (16)	O43—C42—H42A	110.0
N9b—C3a—C4	119.41 (15)	O41—C42—H42A	110.0
N5—C4—C3a	107.66 (14)	O43—C42—H42B	110.0
N5—C4—C45	109.66 (13)	O41—C42—H42B	110.0
C3a—C4—C45	111.65 (14)	H42A—C42—H42B	108.4
N5—C4—H4	109.3	C43a—O43—C42	106.37 (14)
C3a—C4—H4	109.3	O43—C43a—C47a	110.04 (15)
C45—C4—H4	109.3	O43—C43a—C44	127.75 (17)
C5a—N5—C4	120.77 (13)	C47a—C43a—C44	122.21 (16)
C5a—N5—H5	117.3	C43a—C44—C45	116.73 (16)
C4—N5—H5	114.0	C43a—C44—H44	121.6
N5—C5a—C6	122.45 (15)	C45—C44—H44	121.6
N5—C5a—C9a	119.18 (15)	C46—C45—C44	121.03 (16)
C6—C5a—C9a	118.26 (15)	C46—C45—C4	121.18 (16)
C7—C6—C5a	120.81 (16)	C44—C45—C4	117.79 (16)
C7—C6—H6	119.6	C45—C46—C47	121.19 (17)
C5a—C6—H6	119.6	C45—C46—H46	119.4
C6—C7—C8	120.48 (17)	C47—C46—H46	119.4
C6—C7—H7	119.8	C47a—C47—C46	117.17 (17)
C8—C7—H7	119.8	C47a—C47—H47	121.4
C7—C8—C9	119.44 (17)	C46—C47—H47	121.4
C7—C8—H8	120.3	C47—C47a—C43a	121.66 (16)
C9—C8—H8	120.3	C47—C47a—O41	128.22 (16)
C9a—C9—C8	120.21 (16)	C43a—C47a—O41	110.11 (15)

N9b—C1—C2—C3	−0.1 (2)	C4—C3a—N9b—C9a	6.3 (2)
C1—C2—C3—C3a	0.3 (2)	C9—C9a—N9b—C1	10.1 (3)
C2—C3—C3a—N9b	−0.4 (2)	C5a—C9a—N9b—C1	−168.62 (16)
C2—C3—C3a—C4	174.46 (18)	C9—C9a—N9b—C3a	−171.77 (16)

C3—C3a—C4—N5	155.30 (18)	C5a—C9a—N9b—C3a	9.5 (2)
N9b—C3a—C4—N5	−30.3 (2)	C47a—O41—C42—O43	5.94 (18)
C3—C3a—C4—C45	34.9 (3)	O41—C42—O43—C43a	−5.37 (19)
N9b—C3a—C4—C45	−150.72 (15)	C42—O43—C43a—C47a	2.70 (19)
C3a—C4—N5—C5a	43.5 (2)	C42—O43—C43a—C44	−177.50 (18)
C45—C4—N5—C5a	165.13 (15)	O43—C43a—C44—C45	−179.76 (16)
C4—N5—C5a—C6	152.41 (16)	C47a—C43a—C44—C45	0.0 (3)
C4—N5—C5a—C9a	−31.5 (2)	C43a—C44—C45—C46	−0.2 (3)
N5—C5a—C6—C7	175.53 (16)	C43a—C44—C45—C4	−179.83 (15)
C9a—C5a—C6—C7	−0.6 (2)	C3a—C4—C45—C44	65.8 (2)
C5a—C6—C7—C8	0.7 (3)	C3a—C4—C45—C46	−113.83 (19)
C6—C7—C8—C9	−0.2 (3)	N5—C4—C45—C44	−53.4 (2)
C7—C8—C9—C9a	−0.4 (3)	N5—C4—C45—C46	126.93 (17)
C8—C9—C9a—C5a	0.5 (3)	C44—C45—C46—C47	0.0 (3)
C8—C9—C9a—N9b	−178.08 (16)	C4—C45—C46—C47	179.67 (16)
N5—C5a—C9a—C9	−176.30 (15)	C45—C46—C47—C47a	0.3 (3)
C6—C5a—C9a—C9	0.0 (2)	C46—C47—C47a—C43a	−0.4 (3)
N5—C5a—C9a—N9b	2.4 (2)	C46—C47—C47a—O41	178.36 (16)
C6—C5a—C9a—N9b	178.68 (14)	O43—C43a—C47a—C47	−179.89 (16)
C2—C1—N9b—C3a	−0.20 (19)	C44—C43a—C47a—C47	0.3 (3)
C2—C1—N9b—C9a	178.18 (16)	O43—C43a—C47a—O41	1.11 (19)
C3—C3a—N9b—C1	0.38 (19)	C44—C43a—C47a—O41	−178.70 (15)
C4—C3a—N9b—C1	−175.26 (14)	C42—O41—C47a—C47	176.75 (18)
C3—C3a—N9b—C9a	−178.11 (15)	C42—O41—C47a—C43a	−4.34 (18)

Hydrogen-bond geometry (Å, º)

Cg1 represents the centroid of the C5a/C6–C9/C9a ring and Cg2 represents the centroid of the C1–C3/C3a/N9b ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···O41^{i}	0.88	2.18	3.052 (2)	173
C1—H1···*Cg*1^{ii}	0.95	2.95	3.878 (2)	165
C8—H8···*Cg*2^{ii}	0.95	2.70	3.568 (2)	152
C42—H42*A*···*Cg*1^{iii}	0.99	2.99	3.628 (2)	123
C46—H46···*Cg*2^{iv}	0.95	2.90	3.845 (2)	173

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) −*x*+1, −*y*+2, −*z*+1; (iv) *x*, *y*−1, *z*.