organic papers

4-Bromo-*β*-(2-oxoquinolin-4-yloxy)cinnamonitrile: a three-dimensional framework structure built from N—H⋯O and C—H⋯O hydrogen bonds, and bromo–carbonyl and aromatic *π*–*π* stacking interactions

Silvia Cruz,[a] José M. de la Torre,[b] Justo Cobo,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Departamento de Química, Universidad de Nariño, Ciudad Universitaria, Torobajo, AA 1175, Pasto, Colombia, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

In the title compound, $C_{18}H_{11}BrN_2O_2$, the molecules are linked into sheets by a combination of one N—H⋯O and two C—H⋯O hydrogen bonds, and the sheets are linked by an aromatic *π*–*π* stacking interaction.

Comment

The title compound, (I), has been prepared from 2,4-dihydroxyquinoline and 4-bromo-*β*-chlorocinnamonitrile as a potential intermediate for the synthesis of fused quinoline derivatives.

(I)
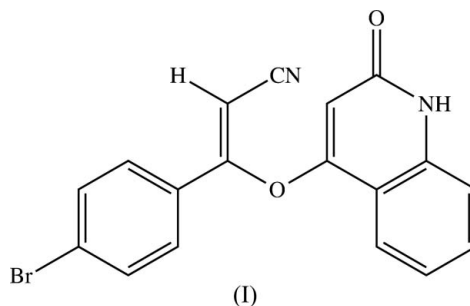
The molecules of compound (I) show a significant deviation from planarity, as shown by the key torsion angles (Table 1). The biggest deviation from planarity is associated with the rotation of the two effectively planar components of the molecule about the O4—C17 bond, which is probably driven by the repulsive interaction between the cyano substituent and the H atom bonded to C3 (Fig. 1). Consistent with this, the bond angle at O4 is abnormally large.
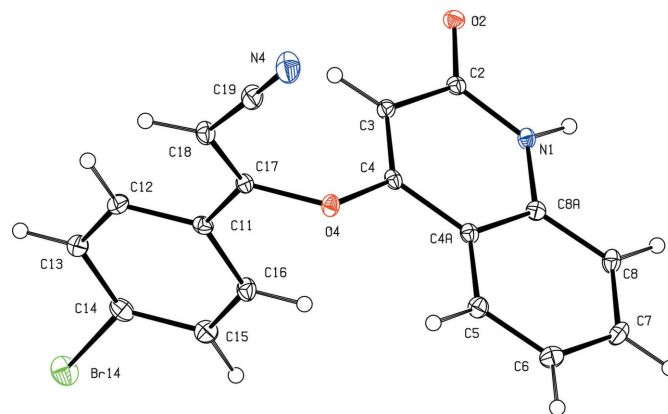
Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
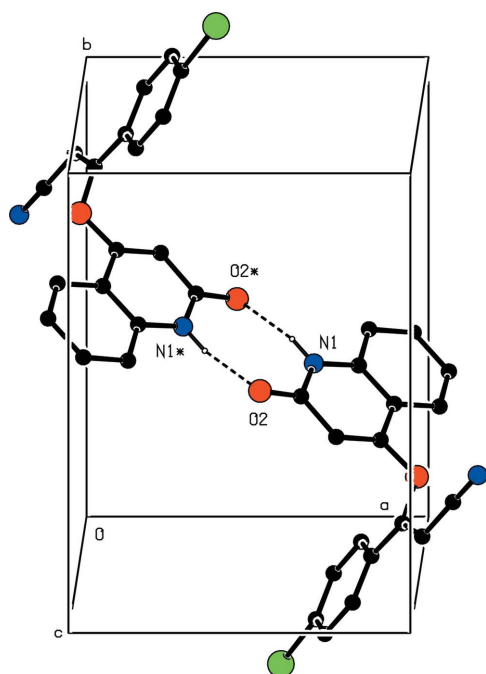
Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $R_2^2(8)$ dimer. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.
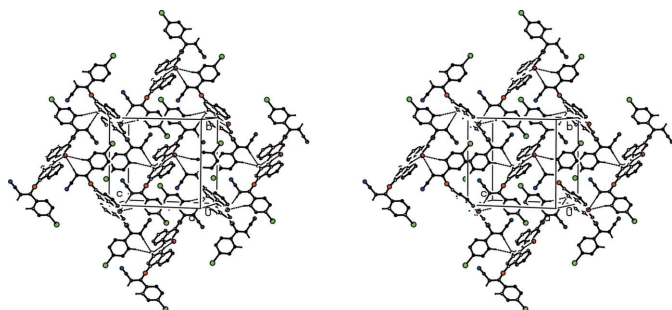

Figure 3
A stereoscopic view of part of the crystal structure of (I), showing the formation of a hydrogen-bonded $(10\bar{1})$ sheet. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

While the C—C distances within the brominated aryl ring span only a rather narrow range [1.383 (3) − 1.400 (3) Å with mean value 1.389 Å], the distances in the other carbocyclic ring show evidence of some bond fixation, with bonds C5—C6 and C7—C8 significantly shorter than the remainder.

The molecules of compound (I) are linked by paired N—H···O hydrogen bonds (Table 2) into centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) dimers, and the reference molecule was selected so that it forms part of a dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). Atoms C12 and C18 in the molecule at (x, y, z) both act as hydrogen bond donors to atom O2 in the molecule at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, in an $R_2^1(7)$ motif. Propagation by the space group of these interactions then links the dimer centred at $(1/2, 1/2, 1/2)$ as donor to those centred at $(1, 0, 1)$ and $(0, 1, 0)$, and as acceptor from those centred at $(0, 0, 0)$ and $(1, 1, 1)$,
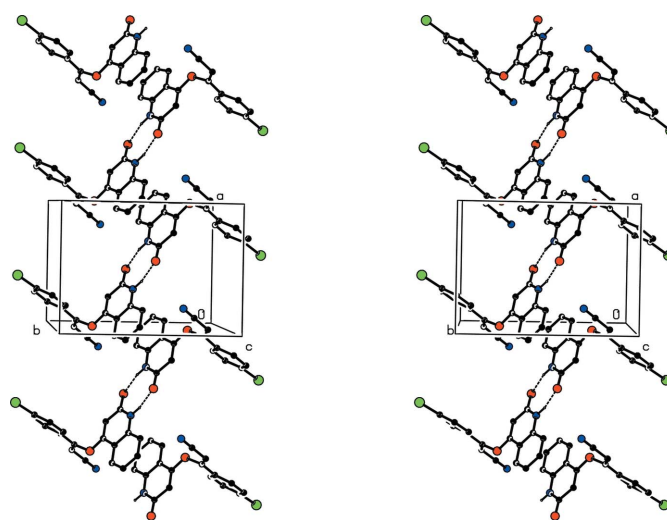

Figure 4
A stereoscopic view of part of the crystal structure of (I), showing the formation of a π-stacked chain of hydrogen-bonded dimers along [100], linking the $(10\bar{1})$ sheets. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted.

thereby forming a $(10\bar{1})$ sheet built from $R_2^1(7)$, $R_2^2(8)$ and $R_6^6(36)$ rings (Fig. 3).

The rings C4A/C5–C8/C8A in the molecules at (x, y, z) and $(2 - x, 1 - y, 1 - z)$ form parts of the $R_2^2(8)$ dimers centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$, respectively. These rings are strictly parallel with an interplanar spacing of 3.439 (2) Å: the corresponding ring-centroid separation is 3.799 (2) and the ring offset is 1.614 (2) Å. The effect of this interaction is to link the sheets along the [100] direction (Fig. 4), so forming a continuous three-dimensional structure.

The Br atom at (x, y, z) makes a short contact with the amide atom O2 in the molecule at $(1 - x, -y, 1 - z)$, with Br···O^{iii} = 3.078 (2) Å and C—Br···O^{iii} = 164.3 (2)° [symmetry code: (iii) $1 - x, -y, 1 - z$] and this weakly attractive bromo–carbonyl interaction links the hydrogen-bonded dimers into a chain of edge-fused $R_2^2(8)$ and $R_2^2(22)$ rings (Bernstein *et al.*, 1995; Starbuck *et al.*, 1999) along [010], further reinforcing the framework (Fig. 5).

Experimental

A solution containing 4-bromo-β-chlorocinnamonitrile (1 mmol), 2,4-dihydroxyquinoline (1 mmol) and triethylamine (0.5 ml) in anhydrous ethanol (10 ml) was heated under reflux for 10 h. The resulting solid product was collected by filtration, washed with ethanol and recrystallized from ethanol to give pale-yellow crystals suitable for single-crystal X-ray diffraction (m.p. 582 K, yield 60%).

Crystal data

$C_{18}H_{11}BrN_2O_2$	$Z = 4$
$M_r = 367.20$	$D_x = 1.607$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.9860$ (2) Å	$\mu = 2.72$ mm^{-1}
$b = 12.4111$ (3) Å	$T = 120$ (2) K
$c = 13.6138$ (3) Å	Block, pale yellow
$\beta = 92.006$ (2)°	$0.70 \times 0.50 \times 0.30$ mm
$V = 1517.36$ (6) Å^3	

Data collection

Bruker–Nonius KappaCCD diffractometer	17684 measured reflections
φ and ω scans	3463 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2907 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.034$
$T_{min} = 0.224$, $T_{max} = 0.441$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 1.024P]$
$wR(F^2) = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} = 0.001$
3463 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.68$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C4A—C5	1.404 (3)	C7—C8	1.375 (3)
C5—C6	1.372 (3)	C8—C8A	1.404 (3)
C6—C7	1.403 (3)	C8A—C4A	1.400 (3)
C4—O4—C17	119.34 (15)		
C3—C4—O4—C17	26.0 (3)	C4—O4—C17—C11	68.3 (2)
C4—O4—C17—C18	−118.0 (2)	O4—C17—C11—C12	−176.79 (18)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O2^i	0.88	1.96	2.814 (2)	164
C12—H12⋯O2^{ii}	0.95	2.52	3.435 (2)	163
C18—H18⋯O2^{ii}	0.95	2.44	3.389 (3)	178

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

All H atoms were located in difference maps and then treated as riding atoms with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SIR2004 (Burla et al., 2005); program(s) used to refine structure: OSCAIL (McArdle, 2003) and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).
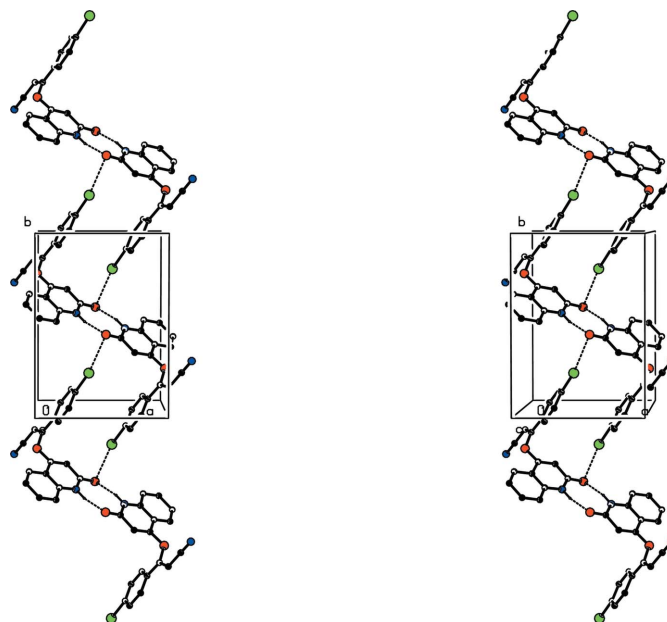
Figure 5
A stereoscopic view of part of the crystal structure of (I), showing the formation of a [010] chain of edge-fused rings formed by hydrogen-bonded dimers linked by the Br⋯O contact. Dashed lines indicate hydrogen bonds and Br⋯O contacts. For the sake of clarity, H atoms bonded to C atoms have been omitted.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. 34, 1555–1573.
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.
Ferguson, G. (1999). PRPKAPPA. University of Guelph, Canada.
Hooft, R. W. W. (1999). COLLECT. Nonius BV, Delft, The Netherlands.
McArdle, P. (2003). OSCAIL for Windows. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
Sheldrick, G. M. (2003). SADABS. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). J. Appl. Cryst. 36, 7–13.
Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). New J. Chem. 23, 969–972.