Acta Crystallographica Section C
Structural Chemistry
ISSN 2053-2296

The effect of bromine scanning around the phenyl group of 4-phenylquinolone derivatives

Scott A. Steiger,[a] Anthony J. Monacelli,[b] Chun Li,[b] Janet L. Hunting[b] and Nicholas R. Natale[a]*

[a]Department of Biomedical and Pharmaceutical Sciences, University of Montana, 32 Campus Drive, Missoula, MT 59812, USA, and [b]Department of Chemistry, Ithaca College, 953 Danby Road, Ithaca, NY 14850, USA
Correspondence e-mail: nicholas.natale@mso.umt.edu

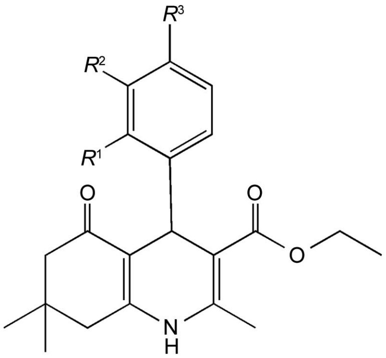
Received 25 April 2014
Accepted 4 July 2014

Three quinolone compounds were synthesized and crystallized in an effort to study the structure–activity relationship of these calcium-channel antagonists. In all three quinolones, *viz.* ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (I), ethyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (II), and ethyl 4-(2-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (III), all $C_{21}H_{24}BrNO_3$, common structural features such as a flat boat conformation of the 1,4-dihydropyridine (1,4-DHP) ring, an envelope conformation of the fused cyclohexanone ring and a bromophenyl ring at the pseudo-axial position and orthogonal to the 1,4-DHP ring are retained. However, due to the different packing interactions in each compound, halogen bonds are observed in (I) and (III). Compound (III) crystallizes with two molecules in the asymmetric unit. All of the prepared derivatives satisfy the basic structural requirements to possess moderate activity as calcium-channel antagonists.

Keywords: crystal structure; structure–activity relationships; calcium-channel antagonists; quinolone compounds; halogen bonding; 1,4-dihydropyridine rings; hydrogen bonding; bromine scanning.

1. Introduction

The 1,4-dihydropyridine (1,4-DHP) heterocycle comprises a large family of medicinally important compounds. The substructure has garnered the most attention as a class of calcium-channel antagonists working as slow calcium-channel blockers, which have been used in the treatment of angina pectoris and hypertension (Wishart *et al.*, 2006). The examination of Hantzsch 1,4-dihydropyridine ester derivatives has produced more active and longer-acting agents than the prototypical nifedipine molecule (Triggle, 2003). Many other derivatives have been synthesized to yield compounds active as calcium-channel agonists or antagonists (Martin-Leon *et al.*, 1995; Rose, 1990; Rose & Draeger, 1992). A fused cyclohexanone ring is one of the modifications to 1,4-DHP compounds and this class has been shown to have moderate calcium-channel antagonistic activity, as well as modest anti-inflammatory and stem-cell differentiation properties, and has been implicated in slowing neurodegenerative disorders (Tippier *et al.*, 2014). Thus, further understanding of the structure–activity relationship of 1,4-DHP compounds and their derivatives will allow for the determination of off-target activity and the reduction of side effects. It has been proven that the flattened boat conformation of the 1,4-DHP ring is one factor that leads to higher calcium-channel activity (Linden *et al.*, 2014). Atoms N1 and C4 of the 1,4-DHP ring can be marginally displaced from the mean plane of the boat (Linden *et al.*, 2002). An aryl group in the 4-position of the 1,4-DHP ring is essential for optimal activity (Shaldam *et al.*, 2014). One study showed that an aryl ring with halogen or other electron-withdrawing groups exhibits higher receptor-binding activity (Takahashi *et al.*, 2008). On the 1,4-DHP ring, ester groups are usually substituted at the 3- and 5-positions. It has been suggested that at least one *cis*-ester is required for the calcium-channel antagonistic effect and hydrogen bonding to the receptor (Fossheim, 1986). In an effort to find more active calcium-channel antagonists in the 1,4-DHP genre, we have synthesized a series of 1,4-DHP fused-ring derivatives, *i.e.* hexahydroquinolones. In this paper, we report three structures which have bromine substituted at the *para*-, *meta*- and *ortho*-positions on the phenyl ring attached to the 1,4-DHP ring, *viz.* compounds (I)–(III).



(I) $R^1 = R^2 = H, R^3 = Br$
(II) $R^1 = H, R^2 = Br, R^3 = H$
(III) $R^1 = Br, R^2 = R^3 = H$

2. Experimental

2.1. Synthesis and crystallization

An oven-dried 100 ml round-bottomed flask was charged with dimedone (0.757 g), ethyl acetoacetate (0.703 g), ytterbium(III) trifluoromethanesulfonate (0.170 g) and a magnetic stirrer bar. The mixture was then taken up in absolute ethanol (13.5 ml), capped, placed under an inert atmosphere of argon and stirred at room temperature for 20 min. Homologues of

doi:10.1107/S2053229614015617

Table 1
Experimental details.

For all structures: $C_{21}H_{24}BrNO_3$, M_r = 418.32, Z = 8. Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker SMART BREEZE CCD area-detector diffractometer. Absorption was corrected for by multi-scan methods (*SADABS*; Bruker, 2008). H atoms were treated by a mixture of independent and constrained refinement.

	(I)	(II)	(III)
Crystal data			
Crystal system, space group	Orthorhombic, *Pbcn*	Orthorhombic, *Pbcn*	Monoclinic, $P2_1/c$
a, b, c (Å)	18.0371 (4), 15.4309 (3), 14.2604 (3)	17.0813 (5), 15.4877 (5), 14.2544 (5)	14.5012 (18), 18.299 (2), 15.1952 (19)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 107.5262 (15), 90
V (Å^3)	3969.08 (14)	3771.0 (2)	3844.9 (8)
μ (mm^{-1})	2.09	2.20	2.16
Crystal size (mm)	0.26 × 0.18 × 0.13	0.40 × 0.21 × 0.19	0.34 × 0.16 × 0.08
Data collection			
$T_{\min}$, $T_{\max}$	0.909, 1.000	0.839, 1.000	0.866, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35271, 4558, 3391	55070, 5055, 4278	45465, 8935, 6859
$R_{\rm int}$	0.038	0.032	0.065
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.650	0.684	0.653
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.101, 1.04	0.032, 0.084, 1.03	0.036, 0.081, 1.02
No. of reflections	4558	5055	8935
No. of parameters	243	243	485
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.49, −1.21	1.31, −0.38	1.46, −0.47

Computer programs: *APEX2* (Bruker, 2008), *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

bromobenzaldehyde (1.0 g, 5.405 mmol) and a quantity of ammonium acetate (0.419 g) were added to the stirred solution, and stirring was continued at room temperature for a further 48 h. The progress of the reaction was monitored *via* thin-layer chromatography (TLC). Once the reaction was complete, excess solvent was removed *via* rotary evaporation. The solution was then purified *via* silica-column chromatography. The products were recrystallized from hexane and ethyl acetate (1:4 *v*/*v*) as white to light-yellow crystalline solids [for (I): yield 1.91 g, 4.57 mmol, 84.00%; for (II): yield 1.86 g, 4.45 mmol, 82.30%; for (III): yield 1.45 g, 3.466 mmol, 63.76%]. Analytical samples of the products were again recrystallized from a minimum of warm hexane and ethyl acetate (1:4 *v*/*v*), to which hexane was added dropwise to a faint opalescence, and slow evaporation produced diffraction-quality crystals as white to light-yellow crystalline solids.

2.2. Characterization information

Melting points were determined in open capillary tubes with a Mel-Temp melting point apparatus (200 W) and are uncorrected. Structures were confirmed with ^{1}H and ^{13}C NMR, and mass spectroscopy. ^{1}H NMR spectra were obtained in chloroform-d_1 using a Bruker AMX 400 MHz spectrometer. Chemical shifts are reported as p.p.m. relative to tetramethylsilane (TMS). LC–MS (liquid chromatography–mass spectrometry) data were obtained using a Waters LCT Premier XE series spectrometer.

Compound (I). ^{1}H NMR (CDCl$_3$): δ 7.31 (*d*, J = 8.28 Hz, 2H), 7.20 (*d*, J = 8.28 Hz, 2H), 6.01 (*bs*, 1H), 5.02 (*s*, 1H), 4.05 (*q*, J = 7.03 Hz, 2H), 2.38 (*s*, 3H), 2.21 (*s*, 2H), 2.17 (*s*, 2H), 1.20 (*t*, J = 7.15 Hz, 3H), 1.08 (*s*, 3H), 0.93 (*s*, 6H); ^{13}C NMR (CDCl$_3$): δ 195.42, 167.19, 148.01, 146.07, 143.60, 130.96, 129.89, 119.82, 111.90, 105.72, 59.94, 50.69, 41.14, 36.33, 32.75, 29.44, 27.15, 19.49, 14.23. HRMS calculated for $C_{21}H_{24}BrNO_3$: 418.1018; found: 418.1024. MS, m/z = 418 ([M + 1] 100), 419 ([M + 2] 10), 420 ([M + 3] 100). M.p. 527–528 K. TLC [SiO$_2$, hexane–EtOAc (3:2 *v*/*v*)]: R_F = 0.19.

Compound (II). ^{1}H NMR (CDCl$_3$): δ 7.41 (*s*, 1H), 7.26 (*d*, J = 7.53 Hz, 1H), 7.22 (*d*, J = 8.53 Hz, 1H), 7.07 (*t*, J = 7.78 Hz, 1H), 6.09 (*bs*, 1H), 5.03 (*s*, 1H), 4.07 (*m*, J = 7.15 Hz, 2H), 2.38 (*s*, 3H), 2.31 (*s*, 2H), 2.22 (*s*, 2H), 1.21 (*t*, J = 7.15 Hz, 3H), 1.09 (*s*, 3H), 0.96 (*s*, 6H); ^{13}C NMR (CDCl$_3$): δ 195.39, 167.15, 149.30, 148.24, 143.79, 131.09, 129.17, 126.97, 122.10, 111.71, 105.60, 59.96, 50.69, 41.12, 36.64, 32.78, 29.40, 27.22, 19.51, 14.21. HRMS calculated for $C_{21}H_{24}BrNO_3$: 418.1018; found: 418.0979. MS, m/z = 418 ([M + 1] 100), 419 ([M + 2] 90). M.p. 508–509 K. TLC [SiO$_2$, hexane–EtOAc (3:2 *v*/*v*)]: R_F = 0.12.

Compound (III). ^{1}H NMR (CDCl$_3$): δ 7.44 (*dd*, J = 7.91 Hz, 1H), 7.37 (*dd*, J = 7.78 Hz, 1H), 7.16 (*tt*, J = 7.53 Hz, 1H), 6.94 (*tt*, J = 7.91 Hz, 1H), 5.92 (*bs*, 1H), 5.37 (*s*, 1H), 4.08 (*m*, J = 7.15 Hz, 2H), 2.32 (*s*, 3H), 2.30 (*s*, 2H), 2.19 (*s*, 2H), 1.18 (*t*, J = 7.03 Hz, 3H), 1.08 (*s*, 3H), 0.96 (*s*, 6H); ^{13}C NMR (CDCl$_3$): δ 195.30, 167.44, 148.04, 145.88, 143.22, 133.08, 132.03, 127.49, 126.97, 123.38, 111.74, 105.86, 59.84, 50.69, 41.29, 37.98, 32.58, 29.28, 27.38, 19.49, 14.36. HRMS calculated for $C_{21}H_{24}BrNO_3$: 418.1018; found: 418.1037. MS: m/z = 417 ([M] 100), 418 ([M + 1] 100), 419 ([M + 2] 30). M.p. 473–477 K. TLC [SiO$_2$, hexane–EtOAc (3:2 *v*/*v*)]: R_F = 0.23.

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The methyl H atoms were constrained to an ideal geometry, with C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C), and were allowed to rotate freely about their C—C bonds. The remaining C-bound H atoms were placed in calculated positions, with C—H = 0.95–1.00 Å, and

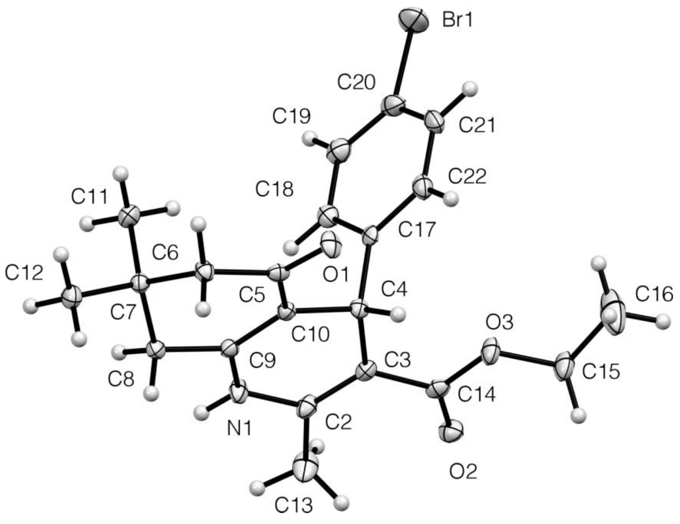


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

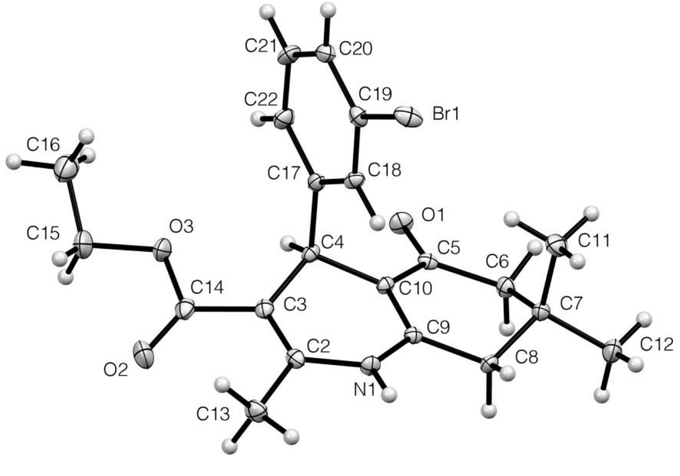


Figure 2
The asymmetric unit of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

refined as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The positions of the amine H atoms were determined from difference Fourier maps and refined freely along with their isotropic displacement parameters. Two low-angle reflections of (I) and four of (III) were omitted from the refinement because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop.

3. Results and discussion

Both ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (I) (Fig. 1), and ethyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (II) (Fig. 2), crystallize in the orthorhombic space group *Pbcn* with one molecule in the asymmetric unit. The asymmetric unit of ethyl 4-(2-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, (III) (Fig. 3), is composed of two symmetry-independent molecules, (III*A*) and (III*B*), which crystallize in the monoclinic space group $P2_1/c$. All three compounds have very similar structural conformations, which accommodate the requirements for calcium-channel antagonists.

In all three structures, the 1,4-DHP ring is characterized by a shallow or flattened boat conformation, which is one of the factors that leads to higher calcium-channel activity. The boat conformation can be quantified by ring-puckering parameters (Cremer & Pople, 1975). An ideal boat would have $\theta = 90°$ and $\varphi = n \times 60°$. Calculated using *PLATON* (Spek, 2009), the puckering parameters in (I) are $Q = 0.196$ (2) Å, $\theta = 106.5$ (6)° and $\varphi = 5.2$ (8)° for the atom sequence N1–C2–C3–C4–C10–C9. The corresponding parameters for (II) are $Q = 0.3014$ (17) Å, $\theta = 107.1$ (3)° and $\varphi = 0.9$ (3)°, while for (III), two sets were obtained as $Q_A = 0.162$ (3) Å, $\theta_A = 67.3$ (10)° and $\varphi_A = 197.5$ (10)°, and $Q_B = 0.279$ (3) Å, $\theta_B = 106.9$ (6)° and $\varphi_B = 3.9$ (6)° for molecules *A* and *B*, respectively. The shallowness of the boat conformation is indicated by the marginal displacements of atoms N1 and C4 from the mean plane (the base of the boat) defined by the two double bonds (C2═C3 and C10═C9). The deviation of atom N1 from the base of the

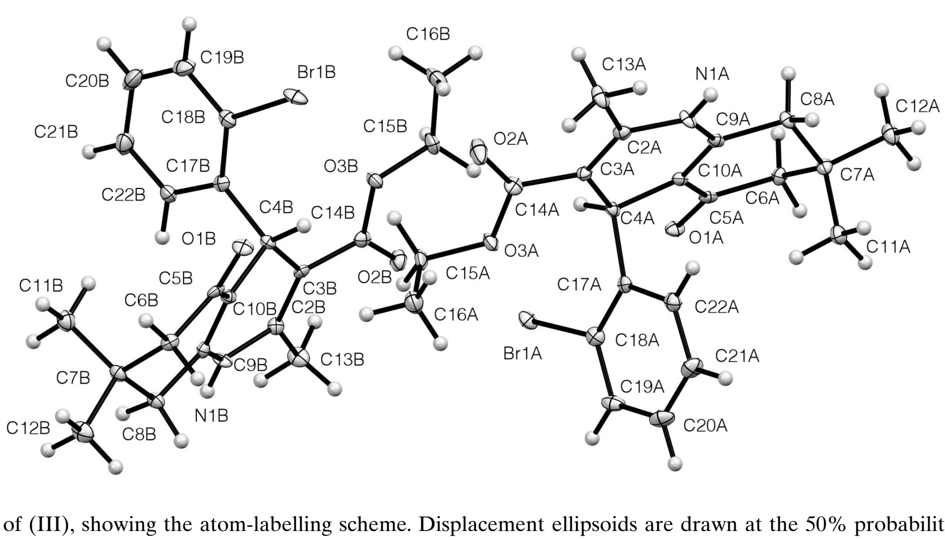


Figure 3
The asymmetric unit of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

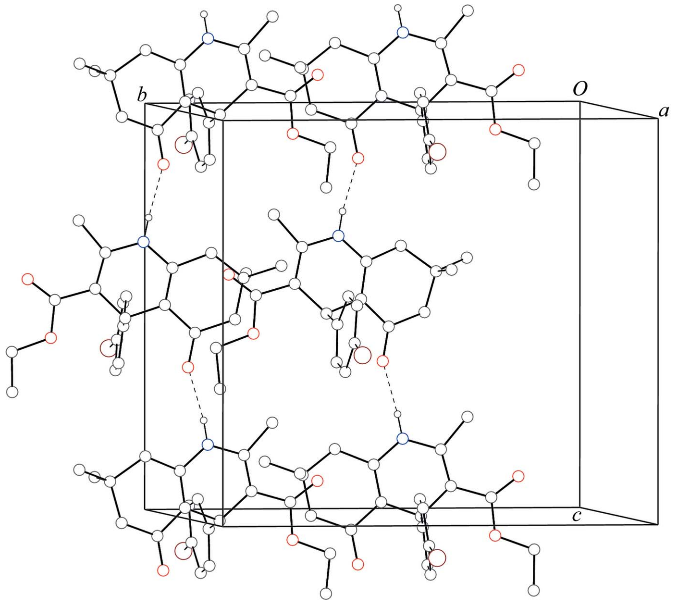


Figure 4
Part of the crystal structure of (I), showing the formation of chains of molecules running along the *c* axis. Hydrogen bonds are indicated by dashed lines. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.89 (3)	1.94 (3)	2.812 (2)	168 (3)

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

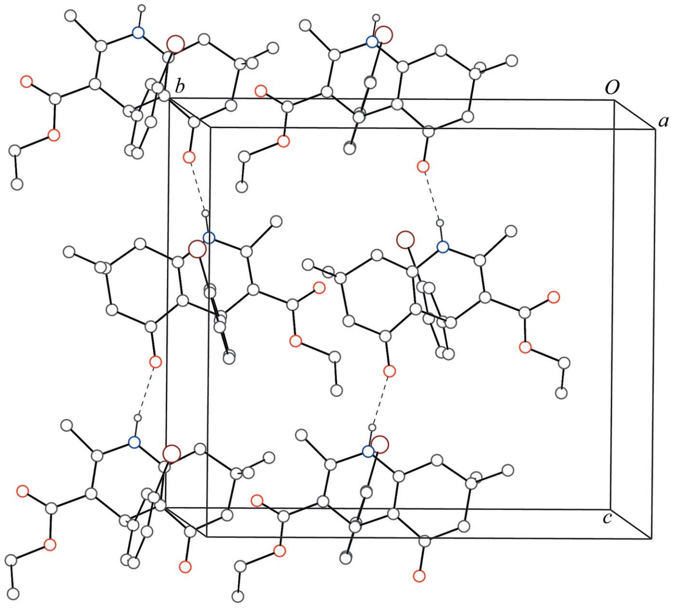


Figure 5
Part of the crystal structure of (II), showing the formation of chains of molecules running along the *c* axis. Hydrogen bonds are indicated by dashed lines. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86 (2)	2.05 (2)	2.8896 (19)	166 (2)

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

boat is generally smaller, between 0.00 and 0.19 Å, while the deviation of atom C4 is most frequently found around 0.3 Å (Linden *et al.*, 2004, 2005). These are also observed in the title compounds: the deviations of atom N1 are 0.095 (3), 0.142 (2), 0.047 (3) and 0.134 (3) Å for (I), (II), (III*A*) and (III*B*), respectively; and the deviations of atom C4 are 0.235 (4), 0.365 (2), 0.207 (4) and 0.336 (4) Å for (I), (II), (III*A*) and (III*B*), respectively. The sum of the absolute values of the internal ring torsion angles is also considered a quantitative measure of the 'flatness' of the 1,4-DHP ring (Rowan & Holt, 1995). A flattened or unpuckered ring shows a sum of 0 and 240° for an ideal boat conformation of the ring (Triggle *et al.*, 1989). Here, this sum is 67.7 (9)° for (I), 104.3 (5)° for (II), 55.8 (9)° for (III*A*) and 96.5 (8)° for (III*B*), indicating flattened boat conformations, compared with a sum of 72° for nifedipine, the known standard for 1,4-DHPs.

The relationship between the 1,4-DHP pyridine ring and the aryl group attached at the C4 position is another key factor in the 1,4-DHP structure–activity relationship. It has been reported that the pseudo-axial position of the aryl ring is essential for pharmacological activity (Langs *et al.*, 1987). In the title compounds, the bromophenyl rings are almost orthogonal to the base of the 1,4-DHP ring defined by atoms C2, C3, C10 and C9, with dihedral angles between the mean planes (plane C2/C3/C10/C9 to plane C17–C22) of 86.32 (8), 88.46 (5), 99.37 (8) and 89.36 (9)° for (I), (II), (III*A*) and (III*B*), respectively. Another quantitative descriptive factor is the pseudo-torsion angle between the N1···C4 axis and the bond in the phenyl group directly above the 1,4-DHP ring [C17—C18 in compounds (I) and (II), and C17—C22 in compound (III)]. The N1···C4—C17—C18 pseudo-torsion angles are −6.75 (19) and 7.14 (17)° for (I) and (II), respectively. The corresponding pseudo-torsion angles in (III) show an even more orthogonal configuration, as the values are −2.0 (3) and −3.3 (3)° for (III*A*) and (III*B*), respectively. The *ortho*-bromo group is placed in a synperiplanar orientation with respect to the C4—H bond. Such an orientation has been observed in other *ortho*-substituted phenyl rings in 4-aryl-1,4-DHP compounds (Linden *et al.*, 2004). It is worth noting that, although *meta*-NO_2 substitution has been reported to be synperiplanar to the H atom on C4 (Morales *et al.*, 1996), the *meta*-Br in (II) is in an antiperiplanar position. As in other reported *ortho*-substituted structures, compound (III) has the Br pointing away from the 1,4-DHP ring.

Due to the electron delocalization of the conjugate system, each ester group is coplanar with the mean plane of the 1,4-DHP ring and at a *cis* orientation to the adjacent endocyclic double bond. The planarity extends out through the ester chains in (I) and (II). However, in (III), because of the

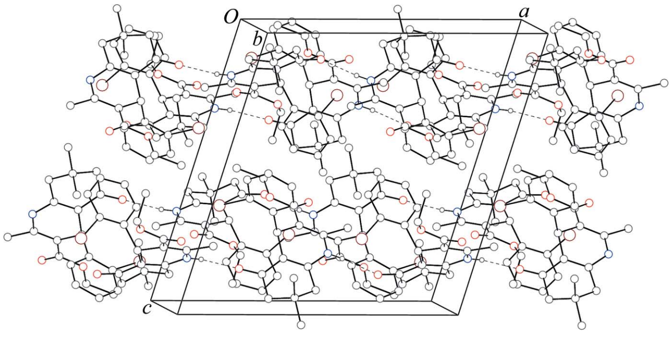


Figure 6
Part of the crystal structure of (III), showing the formation of chains of molecules running along the *a* axis. Hydrogen bonds are indicated by dashed lines. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

different packing pattern, the end methyl group in (III*A*) is curled up in the direction of the aryl group. As a result, it pushes the aryl group slightly away from the orthogonal position, thus making the dihedral angle between the 1,4-DHP ring and the aryl ring the most strongly deviating from 90°: 99.37 (8)° in (III*A*) *versus* 89.36 (9)° in (III*B*).

Again, Cremer & Pople's ring puckering parameters can be used to quantify the conformations of the fused cyclohexanone rings. In all three compounds, the cyclohexanone rings adopt the envelope conformation, which ideally would have θ = 54.7° (or θ = 125.3° in the case of an absolute configuration change) and $\varphi = n \times 60°$. For (I), the puckering parameters are Q = 0.447 (3) Å, θ = 57.4 (4)° and φ = 178.6 (4)° for the atom sequence C5–C10. For the same atom sequence in (II), (III*A*) and (III*B*), the corresponding puckering parameters are Q = 0.4595 (18) Å, θ = 59.4 (2)° and φ = 122.0 (3)° for (II), Q = 0.462 (3) Å, θ = 122.5 (4)° and φ = 2.9 (4)° for (III*A*), and Q = 0.477 (3) Å, θ = 59.4 (4)° and φ = 183.4 (4)° for (III*B*). All these parameters are very close to those of the ideal envelope conformation. Because of the almost perfect envelope conformation, atom C7 stands out from the plane formed by the rest of the atoms in the ring and lies on the same side of the ring plane as the C4-aryl ring. It is also interesting that the axial methyl group on C7 is almost synperiplanar to the bond that connects atom C4 to the aryl ring. The relationship can be shown by the C11—C7···C4—C17 pseudo-torsion angle, which is 13.86 (17)° for (I), 4.51 (13)° for (II), −16.2 (2)° for (III*A*) and 5.5 (2)° for (III*B*).

One feature which has not been reported previously for this type of structure is intermolecular halogen bonding between Br and the ester carbonyl O atom. A halogen bond is defined as a short C—X···O—Y interaction, where the X···O distance is less than or equal to the sums of the respective van der Waals radii (3.37 Å for Br···O), with the C—X···O angle $\simeq$ 165° and the X···O—Y angle $\simeq$ 120° (Auffinger *et al.*, 2004). Although (II) has an X···O distance of 3.4837 (14) Å, which is only slightly longer than the sum of the van der Waals radii, the angles of 166.17 (13)° for Br1···O2—C14^{ii} and 77.24 (6)° for C19—Br1···O2^{ii} are out of the range for halogen bonds. Also in (III), the distance of Br1*B*···O2*A* at 4.048 (2) Å is out of halogen bond range. However, the Br···O distance is 3.1976 (18) Å in (I), with C20—Br1···O2^{iii} = 152.24 (9)° and Br1···O2^{iii}—C14^{iii} = 111.06 (15)°, while in (III), Br1*A*···O2*B* = 3.1764 (18) Å and the angles are Br1*A*···O2*B*—C14*B* = 106.79 (16)° and C18*A*—Br1*A*···O2*B* = 160.65 (8)° [symmetry codes: (ii) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, z; (iii) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$]. These values are within the range for halogen bonds. Halogen bonding has been known for decades and has been found in biological systems, where the halogen acts as a Lewis acid and the interacting atom can be any electron-donating entity. For example, in addition to the backbone carbonyl O atom as the most prominent Lewis base involved in halogen bonds, hydroxy and carboxyl substituents in the side-chain groups can also form halogen bonds in protein-binding sites (Wilcken *et al.*, 2013). The possibility of halogen bonding from Br in these three compounds needs to be considered during the study of their structure–activity relationships.

Table 4
Hydrogen-bond geometry (Å, °) for (III).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*B*—H1*B*···O1*A*^{i}	0.80 (3)	2.02 (3)	2.818 (3)	174 (3)
N1*A*—H1*A*···O1*B*^{ii}	0.83 (3)	2.07 (3)	2.884 (3)	165 (2)

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

In all three compounds, hydrogen bonds are formed between the N—H group of one molecule and the carbonyl O atom in the cyclohexanone ring of another molecule (Tables 2, 3 and 4). These hydrogen bonds link the molecules into extended chains running along the *c* axis in both (I) and (II), but along the *a* axis in (III) (Figs. 4, 5 and 6). In compound (I), the largest difference hole of −1.21 e Å^{-3}, which is 0.68 Å from atom Br1, may indicate a slight disorder of the Br atom.

In conclusion, the structures reported here demonstrate that the usually observed conformational features have been conserved in cyclohexanone-fused 1,4-DHP derivatives. As a promising base structure for calcium-channel antagonists, different substitutions and more structural modifications are being carried out in our group; progress will be reported in due course.

SS, CL and NRN thank the National Institutes of Health for grants NINDS P20RR015583 Center for Structural and Functional Neuroscience (CSFN) and P20RR017670 Center for Environmental Health Sciences (CEHS). NRN also thanks the University of Montana Grant Program (NN).

Supporting information for this paper is available from the IUCr electronic archives (Reference: SF3233).

References

Auffinger, P., Hays, F. A., Westhof, E. & Ho, P. S. (2004). *Proc. Natl Acad. Sci. USA*, **101**, 16789–16794.

Bruker (2008). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

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

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Fossheim, R. (1986). *J. Med. Chem.* **29**, 305–307.
Langs, D. A., Strong, P. D. & Triggle, D. J. (1987). *Acta Cryst.* C**43**, 707–711.
Linden, A., Şafak, C. & Aydın, F. (2004). *Acta Cryst.* C**60**, o711–o713.
Linden, A., Şafak, C. & Kismetlı, E. (2002). *Acta Cryst.* C**58**, o436–o438.
Linden, A., Safak, C. & Simsek, R. (1998). *Acta Cryst.* C**54**, 879–882.
Linden, A., Şimşek, R., Gündüz, M. & Şafak, C. (2005). *Acta Cryst.* C**61**, o731–o734.
Martin-Leon, N., Quinteiro, M., Seoane, C., Soto, J., Mora, A., Suarez, M., Ochoa, E., Morales, A. & Bosque, J. (1995). *J. Heterocycl. Chem.* **32**, 235–238.
Morales, A. D., García-Granda, S., Navarro, M. S., Diviú, A. M. & Pérez-Barquero, R. E. (1996). *Acta Cryst.* C**52**, 2356–2359.
Rose, U. (1990). *Arch. Pharm.* **323**, 281–286.
Rose, U. & Draeger, M. (1992). *J. Med. Chem.* **35**, 2238–2243.
Rowan, K. R. & Holt, E. M. (1995). *Acta Cryst.* C**51**, 2554–2559.
Shaldam, M., Elhamamsy, M., Esmat, Eman. & El-Morselhy, T. (2014). *ISRN Med. Chem.* pp. 1–14.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Takahashi, D., Oyunzul, L., Onoue, S., Ito, Y., Uchida, S., Simsek, R., Gunduz, M. G., Safak, C. & Yamada, S. (2008). *Biol. Pharm. Bull.* **31**, 473–479.
Tippier, P., Labby, K., Hawker, D., Mataka, J. & Silverman, R. (2014). *J. Med. Chem.* **56**, 3121–3147.
Wilcken, R., Zimmermann, M. O., Lange, A., Joerger, A. C. & Boeckler, F. M. (2013). *J. Med. Chem.* **56**, 1363–1388.
Wishart, D. S., Knox, C., Guo, A. C., Shrivastava, S., Hassanali, M., Stothard, P., Chang, Z. & Woolsey, J. (2006). *Nucleic Acids Res.* **34**, 668–672.
Triggle, D. J. (2003). *Cell. Mol. Neurobiol.* **23**, 293–303.
Triggle, D. J., Langs, D. & Janis, R. (1989). *Med. Res. Rev.* **9**, 123–180.

supporting information

Acta Cryst. (2014). C**70**, 790-795 [doi:10.1107/S2053229614015617]

The effect of bromine scanning around the phenyl group of 4-phenylquinolone derivatives

Scott A. Steiger, Anthony J. Monacelli, Chun Li, Janet L. Hunting and Nicholas R. Natale

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

(I) Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

Crystal data

$C_{21}H_{24}BrNO_3$
$M_r = 418.32$
Orthorhombic, *Pbcn*
$a = 18.0371$ (4) Å
$b = 15.4309$ (3) Å
$c = 14.2604$ (3) Å
$V = 3969.08$ (14) Å^3
$Z = 8$
$F(000) = 1728$
$D_x = 1.400$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9956 reflections
$\theta = 2.3$–27.5°
$\mu = 2.09$ mm^{-1}
$T = 100$ K
Prism, light yellow
0.26 × 0.18 × 0.13 mm

Data collection

Bruker SMART BREEZE CCD area-detector diffractometer
Radiation source: 2 kW sealed X-ray tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.909$, $T_{max} = 1.000$
35271 measured reflections
4558 independent reflections
3391 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.9°$
$h = -19 \rightarrow 23$
$k = -20 \rightarrow 19$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.101$
$S = 1.04$
4558 reflections
243 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 5.4149P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.49$ e Å^{-3}
$\Delta\rho_{min} = -1.21$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Br1	0.01835 (2)	0.08589 (2)	0.60206 (2)	0.03911 (12)
O1	0.39646 (10)	−0.02836 (11)	0.63323 (11)	0.0200 (4)
O2	0.35587 (10)	0.33300 (11)	0.41638 (12)	0.0213 (4)
O3	0.34556 (10)	0.27791 (11)	0.56159 (11)	0.0213 (4)
N1	0.39491 (12)	0.07392 (13)	0.32412 (14)	0.0190 (5)
H1	0.4013 (16)	0.0634 (19)	0.264 (2)	0.027 (8)*
C2	0.38319 (14)	0.15957 (16)	0.35057 (16)	0.0178 (5)
C3	0.36618 (13)	0.17953 (15)	0.44025 (16)	0.0148 (5)
C4	0.35425 (13)	0.10862 (15)	0.51345 (15)	0.0137 (5)
H4	0.3808	0.1260	0.5721	0.016*
C5	0.40247 (13)	−0.04303 (16)	0.54818 (16)	0.0145 (5)
C6	0.43032 (14)	−0.13027 (15)	0.51443 (16)	0.0158 (5)
H6A	0.4101	−0.1757	0.5562	0.019*
H6B	0.4850	−0.1314	0.5207	0.019*
C7	0.41033 (14)	−0.15326 (16)	0.41315 (15)	0.0149 (5)
C8	0.42990 (14)	−0.07570 (15)	0.35066 (16)	0.0158 (5)
H8A	0.4845	−0.0721	0.3445	0.019*
H8B	0.4090	−0.0854	0.2873	0.019*
C9	0.40135 (13)	0.00865 (15)	0.38786 (15)	0.0140 (5)
C10	0.38685 (13)	0.02328 (15)	0.47985 (15)	0.0132 (5)
C11	0.32747 (14)	−0.17399 (17)	0.40568 (17)	0.0203 (5)
H11A	0.2985	−0.1230	0.4240	0.030*
H11B	0.3154	−0.2225	0.4474	0.030*
H11C	0.3154	−0.1898	0.3409	0.030*
C12	0.45589 (15)	−0.23200 (16)	0.38188 (17)	0.0210 (5)
H12A	0.4444	−0.2455	0.3163	0.031*
H12B	0.4435	−0.2819	0.4214	0.031*
H12C	0.5088	−0.2189	0.3879	0.031*
C13	0.39310 (19)	0.22252 (18)	0.27089 (17)	0.0323 (7)
H13A	0.4131	0.1919	0.2163	0.048*
H13B	0.4275	0.2684	0.2898	0.048*
H13C	0.3451	0.2482	0.2547	0.048*
C14	0.35600 (13)	0.27062 (16)	0.46787 (17)	0.0166 (5)
C15	0.33581 (17)	0.36583 (17)	0.59609 (18)	0.0254 (6)
H15A	0.2975	0.3962	0.5588	0.030*
H15B	0.3829	0.3984	0.5907	0.030*
C16	0.3126 (3)	0.3606 (2)	0.6959 (2)	0.0582 (12)
H16A	0.2656	0.3291	0.7004	0.087*
H16B	0.3062	0.4193	0.7210	0.087*

H16C	0.3507	0.3301	0.7321	0.087*
C17	0.27210 (13)	0.09825 (14)	0.53660 (16)	0.0149 (5)
C18	0.22092 (14)	0.08222 (16)	0.46580 (17)	0.0182 (5)
H18	0.2378	0.0755	0.4031	0.022*
C19	0.14545 (15)	0.07577 (16)	0.48494 (19)	0.0226 (6)
H19	0.1109	0.0648	0.4361	0.027*
C20	0.12180 (15)	0.08566 (17)	0.5767 (2)	0.0247 (6)
C21	0.17150 (15)	0.09807 (17)	0.64941 (19)	0.0243 (6)
H21	0.1546	0.1021	0.7123	0.029*
C22	0.24660 (15)	0.10459 (16)	0.62882 (17)	0.0204 (5)
H22	0.2811	0.1135	0.6782	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02137 (16)	0.03688 (19)	0.0591 (2)	−0.00082 (14)	0.01586 (14)	−0.01140 (15)
O1	0.0306 (10)	0.0199 (10)	0.0094 (7)	0.0029 (8)	−0.0012 (7)	0.0007 (7)
O2	0.0221 (10)	0.0143 (9)	0.0274 (9)	0.0020 (8)	0.0039 (7)	0.0039 (8)
O3	0.0328 (11)	0.0115 (9)	0.0194 (8)	0.0013 (8)	−0.0009 (8)	−0.0020 (7)
N1	0.0314 (12)	0.0157 (11)	0.0098 (9)	−0.0012 (9)	0.0002 (8)	−0.0005 (8)
C2	0.0234 (13)	0.0134 (12)	0.0166 (11)	−0.0016 (10)	−0.0033 (10)	0.0016 (10)
C3	0.0143 (12)	0.0123 (12)	0.0179 (11)	−0.0008 (10)	−0.0022 (9)	0.0003 (9)
C4	0.0171 (12)	0.0128 (12)	0.0113 (10)	0.0000 (10)	−0.0005 (9)	0.0009 (9)
C5	0.0114 (11)	0.0165 (12)	0.0156 (11)	−0.0018 (10)	−0.0006 (9)	0.0013 (10)
C6	0.0187 (12)	0.0137 (12)	0.0150 (11)	0.0020 (10)	0.0013 (9)	0.0004 (9)
C7	0.0177 (12)	0.0135 (12)	0.0134 (11)	−0.0004 (10)	0.0006 (9)	−0.0006 (9)
C8	0.0193 (12)	0.0147 (13)	0.0135 (11)	−0.0018 (10)	0.0026 (9)	−0.0012 (9)
C9	0.0142 (11)	0.0135 (12)	0.0143 (11)	−0.0022 (10)	−0.0005 (9)	−0.0002 (9)
C10	0.0132 (11)	0.0117 (12)	0.0146 (11)	−0.0001 (9)	0.0009 (9)	0.0000 (9)
C11	0.0204 (13)	0.0188 (13)	0.0217 (12)	−0.0041 (11)	0.0006 (10)	−0.0036 (11)
C12	0.0258 (13)	0.0152 (13)	0.0219 (12)	0.0009 (11)	0.0045 (10)	−0.0026 (10)
C13	0.062 (2)	0.0193 (15)	0.0159 (12)	−0.0038 (14)	0.0004 (13)	0.0046 (11)
C14	0.0108 (11)	0.0176 (13)	0.0214 (12)	−0.0017 (10)	−0.0014 (9)	0.0011 (10)
C15	0.0377 (16)	0.0134 (13)	0.0250 (13)	0.0011 (12)	0.0002 (12)	−0.0038 (11)
C16	0.117 (4)	0.0214 (17)	0.0365 (18)	0.014 (2)	0.020 (2)	−0.0008 (15)
C17	0.0198 (12)	0.0070 (11)	0.0178 (11)	0.0016 (10)	0.0031 (9)	−0.0003 (9)
C18	0.0209 (13)	0.0155 (12)	0.0183 (11)	0.0025 (11)	0.0014 (10)	0.0018 (10)
C19	0.0197 (13)	0.0170 (13)	0.0310 (14)	0.0018 (11)	−0.0007 (11)	0.0003 (11)
C20	0.0180 (13)	0.0157 (13)	0.0403 (15)	0.0010 (11)	0.0094 (11)	−0.0013 (12)
C21	0.0300 (15)	0.0180 (14)	0.0248 (13)	0.0016 (11)	0.0127 (11)	−0.0039 (11)
C22	0.0265 (14)	0.0163 (13)	0.0185 (11)	0.0021 (11)	0.0025 (10)	−0.0024 (10)

Geometric parameters (Å, º)

Br1—C20	1.901 (3)	C9—C10	1.357 (3)
O1—C5	1.239 (3)	C11—H11A	0.9800
O2—C14	1.211 (3)	C11—H11B	0.9800
O3—C14	1.354 (3)	C11—H11C	0.9800

O3—C15	1.454 (3)	C12—H12A	0.9800
N1—H1	0.89 (3)	C12—H12B	0.9800
N1—C2	1.391 (3)	C12—H12C	0.9800
N1—C9	1.362 (3)	C13—H13A	0.9800
C2—C3	1.351 (3)	C13—H13B	0.9800
C2—C13	1.505 (3)	C13—H13C	0.9800
C3—C4	1.528 (3)	C15—H15A	0.9900
C3—C14	1.471 (3)	C15—H15B	0.9900
C4—H4	1.0000	C15—C16	1.485 (4)
C4—C10	1.520 (3)	C16—H16A	0.9800
C4—C17	1.526 (3)	C16—H16B	0.9800
C5—C6	1.515 (3)	C16—H16C	0.9800
C5—C10	1.441 (3)	C17—C18	1.390 (3)
C6—H6A	0.9900	C17—C22	1.397 (3)
C6—H6B	0.9900	C18—H18	0.9500
C6—C7	1.530 (3)	C18—C19	1.392 (4)
C7—C8	1.533 (3)	C19—H19	0.9500
C7—C11	1.532 (3)	C19—C20	1.385 (4)
C7—C12	1.533 (3)	C20—C21	1.384 (4)
C8—H8A	0.9900	C21—H21	0.9500
C8—H8B	0.9900	C21—C22	1.390 (4)
C8—C9	1.497 (3)	C22—H22	0.9500

C14—O3—C15	115.35 (19)	H11A—C11—H11C	109.5
C2—N1—H1	117.3 (19)	H11B—C11—H11C	109.5
C9—N1—H1	120.2 (19)	C7—C12—H12A	109.5
C9—N1—C2	122.3 (2)	C7—C12—H12B	109.5
N1—C2—C13	113.0 (2)	C7—C12—H12C	109.5
C3—C2—N1	120.5 (2)	H12A—C12—H12B	109.5
C3—C2—C13	126.5 (2)	H12A—C12—H12C	109.5
C2—C3—C4	121.0 (2)	H12B—C12—H12C	109.5
C2—C3—C14	120.0 (2)	C2—C13—H13A	109.5
C14—C3—C4	118.9 (2)	C2—C13—H13B	109.5
C3—C4—H4	108.1	C2—C13—H13C	109.5
C10—C4—C3	110.53 (18)	H13A—C13—H13B	109.5
C10—C4—H4	108.1	H13A—C13—H13C	109.5
C10—C4—C17	110.66 (19)	H13B—C13—H13C	109.5
C17—C4—C3	111.08 (19)	O2—C14—O3	122.2 (2)
C17—C4—H4	108.1	O2—C14—C3	126.7 (2)
O1—C5—C6	120.2 (2)	O3—C14—C3	111.2 (2)
O1—C5—C10	121.0 (2)	O3—C15—H15A	110.1
C10—C5—C6	118.74 (19)	O3—C15—H15B	110.1
C5—C6—H6A	108.4	O3—C15—C16	107.9 (2)
C5—C6—H6B	108.4	H15A—C15—H15B	108.4
C5—C6—C7	115.32 (19)	C16—C15—H15A	110.1
H6A—C6—H6B	107.5	C16—C15—H15B	110.1
C7—C6—H6A	108.4	C15—C16—H16A	109.5
C7—C6—H6B	108.4	C15—C16—H16B	109.5

C6—C7—C8	108.26 (19)	C15—C16—H16C	109.5
C6—C7—C11	110.12 (19)	H16A—C16—H16B	109.5
C6—C7—C12	109.4 (2)	H16A—C16—H16C	109.5
C11—C7—C8	110.3 (2)	H16B—C16—H16C	109.5
C11—C7—C12	109.7 (2)	C18—C17—C4	120.4 (2)
C12—C7—C8	109.03 (19)	C18—C17—C22	118.5 (2)
C7—C8—H8A	108.9	C22—C17—C4	121.1 (2)
C7—C8—H8B	108.9	C17—C18—H18	119.3
H8A—C8—H8B	107.8	C17—C18—C19	121.3 (2)
C9—C8—C7	113.18 (19)	C19—C18—H18	119.3
C9—C8—H8A	108.9	C18—C19—H19	120.7
C9—C8—H8B	108.9	C20—C19—C18	118.6 (2)
N1—C9—C8	115.85 (19)	C20—C19—H19	120.7
C10—C9—N1	120.4 (2)	C19—C20—Br1	118.8 (2)
C10—C9—C8	123.6 (2)	C21—C20—Br1	119.6 (2)
C5—C10—C4	118.5 (2)	C21—C20—C19	121.6 (2)
C9—C10—C4	121.6 (2)	C20—C21—H21	120.5
C9—C10—C5	119.9 (2)	C20—C21—C22	118.9 (2)
C7—C11—H11A	109.5	C22—C21—H21	120.5
C7—C11—H11B	109.5	C17—C22—H22	119.5
C7—C11—H11C	109.5	C21—C22—C17	121.0 (2)
H11A—C11—H11B	109.5	C21—C22—H22	119.5

Br1—C20—C21—C22	−174.96 (19)	C7—C8—C9—N1	−159.3 (2)
O1—C5—C6—C7	159.3 (2)	C7—C8—C9—C10	24.9 (3)
O1—C5—C10—C4	−7.0 (3)	C8—C9—C10—C4	−176.9 (2)
O1—C5—C10—C9	173.0 (2)	C8—C9—C10—C5	3.2 (4)
N1—C2—C3—C4	−4.1 (4)	C9—N1—C2—C3	−10.4 (4)
N1—C2—C3—C14	178.3 (2)	C9—N1—C2—C13	168.4 (2)
N1—C9—C10—C4	7.5 (4)	C10—C4—C17—C18	−67.8 (3)
N1—C9—C10—C5	−172.4 (2)	C10—C4—C17—C22	112.2 (2)
C2—N1—C9—C8	−167.3 (2)	C10—C5—C6—C7	−23.8 (3)
C2—N1—C9—C10	8.7 (4)	C11—C7—C8—C9	72.0 (2)
C2—C3—C4—C10	17.6 (3)	C12—C7—C8—C9	−167.4 (2)
C2—C3—C4—C17	−105.7 (3)	C13—C2—C3—C4	177.2 (3)
C2—C3—C14—O2	5.8 (4)	C13—C2—C3—C14	−0.4 (4)
C2—C3—C14—O3	−174.8 (2)	C14—O3—C15—C16	170.6 (3)
C3—C4—C10—C5	160.6 (2)	C14—C3—C4—C10	−164.8 (2)
C3—C4—C10—C9	−19.4 (3)	C14—C3—C4—C17	72.0 (3)
C3—C4—C17—C18	55.4 (3)	C15—O3—C14—O2	−1.3 (3)
C3—C4—C17—C22	−124.6 (2)	C15—O3—C14—C3	179.3 (2)
C4—C3—C14—O2	−171.8 (2)	C17—C4—C10—C5	−75.9 (3)
C4—C3—C14—O3	7.6 (3)	C17—C4—C10—C9	104.1 (2)
C4—C17—C18—C19	−177.6 (2)	C17—C18—C19—C20	0.0 (4)
C4—C17—C22—C21	177.8 (2)	C18—C17—C22—C21	−2.2 (4)
C5—C6—C7—C8	48.7 (3)	C18—C19—C20—Br1	175.19 (19)
C5—C6—C7—C11	−72.0 (3)	C18—C19—C20—C21	−2.7 (4)
C5—C6—C7—C12	167.4 (2)	C19—C20—C21—C22	2.9 (4)

C6—C5—C10—C4	176.1 (2)	C20—C21—C22—C17	−0.4 (4)
C6—C5—C10—C9	−3.9 (3)	C22—C17—C18—C19	2.4 (4)
C6—C7—C8—C9	−48.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.89 (3)	1.94 (3)	2.812 (2)	168 (3)

Symmetry code: (i) $x, -y, z-1/2$.

(II) Ethyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

Crystal data

$C_{21}H_{24}BrNO_3$
$M_r = 418.32$
Orthorhombic, *Pbcn*
$a = 17.0813$ (5) Å
$b = 15.4877$ (5) Å
$c = 14.2544$ (5) Å
$V = 3771.0$ (2) Å^3
$Z = 8$
$F(000) = 1728$
$D_x = 1.474$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9015 reflections
$\theta = 2.3–29.1°$
$\mu = 2.20$ mm^{-1}
$T = 100$ K
Prism, light yellow
0.40 × 0.21 × 0.19 mm

Data collection

Bruker SMART BREEZE CCD area-detector diffractometer
Radiation source: 2 kW sealed X-ray tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.839$, $T_{max} = 1.000$
55070 measured reflections
5055 independent reflections
4278 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 29.1°$, $\theta_{min} = 1.8°$
$h = -23 \rightarrow 23$
$k = -21 \rightarrow 21$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.084$
$S = 1.03$
5055 reflections
243 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 3.6244P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.31$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.92434 (2)	0.52663 (2)	0.66172 (2)	0.01998 (7)

O1	0.61002 (8)	0.46449 (8)	0.36349 (9)	0.0170 (3)
O2	0.60547 (9)	0.83120 (9)	0.54611 (11)	0.0273 (3)
O3	0.66301 (8)	0.77388 (8)	0.41978 (10)	0.0235 (3)
N1	0.61112 (9)	0.58166 (9)	0.66708 (10)	0.0132 (3)
C2	0.61780 (9)	0.66563 (11)	0.63433 (12)	0.0132 (3)
C3	0.63546 (9)	0.67997 (11)	0.54285 (12)	0.0132 (3)
C4	0.65961 (9)	0.60546 (10)	0.47927 (11)	0.0117 (3)
H4	0.6397	0.6174	0.4146	0.014*
C10	0.62185 (9)	0.52300 (10)	0.51443 (11)	0.0105 (3)
C9	0.60504 (9)	0.51293 (10)	0.60705 (11)	0.0105 (3)
C8	0.57528 (9)	0.43036 (11)	0.64894 (11)	0.0126 (3)
H8A	0.5176	0.4335	0.6542	0.015*
H8B	0.5968	0.4240	0.7130	0.015*
C7	0.59747 (10)	0.35080 (10)	0.59090 (12)	0.0129 (3)
C6	0.57615 (10)	0.36838 (11)	0.48787 (12)	0.0143 (3)
H6A	0.5981	0.3214	0.4489	0.017*
H6B	0.5185	0.3662	0.4816	0.017*
C5	0.60455 (9)	0.45362 (11)	0.44924 (11)	0.0112 (3)
C11	0.68524 (11)	0.33164 (12)	0.59932 (14)	0.0208 (4)
H11A	0.6988	0.3228	0.6654	0.031*
H11B	0.7152	0.3804	0.5743	0.031*
H11C	0.6978	0.2794	0.5636	0.031*
C12	0.55061 (12)	0.27318 (12)	0.62687 (14)	0.0217 (4)
H12A	0.4946	0.2868	0.6252	0.033*
H12B	0.5663	0.2602	0.6915	0.033*
H12C	0.5610	0.2230	0.5869	0.033*
C13	0.60140 (11)	0.73340 (12)	0.70714 (13)	0.0193 (4)
H13A	0.5964	0.7060	0.7688	0.029*
H13B	0.5525	0.7633	0.6916	0.029*
H13C	0.6446	0.7751	0.7085	0.029*
C14	0.63211 (10)	0.76888 (11)	0.50625 (13)	0.0172 (3)
C15	0.66536 (13)	0.86167 (13)	0.38140 (16)	0.0281 (4)
H15A	0.6813	0.9033	0.4305	0.034*
H15B	0.6131	0.8785	0.3577	0.034*
C16	0.72312 (12)	0.86129 (14)	0.30382 (16)	0.0285 (4)
H16A	0.7739	0.8415	0.3275	0.043*
H16B	0.7285	0.9198	0.2785	0.043*
H16C	0.7052	0.8223	0.2541	0.043*
C17	0.74878 (10)	0.59554 (10)	0.47466 (11)	0.0124 (3)
C18	0.78958 (9)	0.56824 (11)	0.55396 (11)	0.0130 (3)
H18	0.7620	0.5547	0.6099	0.016*
C19	0.87044 (10)	0.56085 (11)	0.55114 (12)	0.0137 (3)
C20	0.91306 (10)	0.57960 (11)	0.47084 (13)	0.0161 (3)
H20	0.9685	0.5752	0.4702	0.019*
C21	0.87189 (11)	0.60498 (12)	0.39144 (13)	0.0199 (4)
H21	0.8996	0.6168	0.3351	0.024*
C22	0.79094 (10)	0.61342 (12)	0.39305 (12)	0.0177 (3)
H22	0.7640	0.6315	0.3381	0.021*

H1	0.6037 (14)	0.5739 (15)	0.7262 (18)	0.021 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01611 (10)	0.02866 (11)	0.01518 (10)	0.00677 (7)	−0.00292 (6)	−0.00298 (7)
O1	0.0224 (6)	0.0199 (6)	0.0087 (5)	0.0009 (5)	−0.0005 (5)	−0.0006 (5)
O2	0.0349 (8)	0.0137 (6)	0.0332 (8)	0.0049 (6)	0.0042 (6)	0.0020 (6)
O3	0.0262 (7)	0.0184 (6)	0.0259 (7)	0.0052 (5)	0.0088 (6)	0.0111 (5)
N1	0.0179 (7)	0.0137 (7)	0.0079 (6)	−0.0008 (5)	0.0009 (5)	−0.0009 (5)
C2	0.0113 (7)	0.0122 (7)	0.0162 (8)	0.0000 (6)	−0.0011 (6)	−0.0025 (6)
C3	0.0111 (7)	0.0124 (7)	0.0161 (8)	−0.0007 (6)	−0.0011 (6)	0.0009 (6)
C4	0.0122 (7)	0.0129 (7)	0.0101 (7)	−0.0011 (6)	−0.0003 (6)	0.0027 (6)
C10	0.0108 (7)	0.0119 (7)	0.0088 (7)	0.0000 (5)	−0.0003 (5)	0.0012 (6)
C9	0.0098 (7)	0.0116 (7)	0.0101 (7)	0.0006 (5)	−0.0004 (5)	0.0001 (6)
C8	0.0140 (7)	0.0132 (8)	0.0105 (7)	0.0001 (6)	0.0022 (6)	0.0021 (6)
C7	0.0144 (7)	0.0116 (7)	0.0126 (8)	0.0008 (6)	0.0014 (6)	0.0010 (6)
C6	0.0167 (8)	0.0127 (7)	0.0135 (8)	−0.0009 (6)	−0.0002 (6)	−0.0017 (6)
C5	0.0095 (7)	0.0143 (7)	0.0097 (7)	0.0024 (6)	−0.0013 (6)	−0.0011 (6)
C11	0.0193 (8)	0.0209 (9)	0.0223 (9)	0.0069 (7)	0.0020 (7)	0.0047 (7)
C12	0.0283 (9)	0.0139 (8)	0.0228 (9)	−0.0023 (7)	0.0063 (8)	0.0020 (7)
C13	0.0218 (9)	0.0165 (8)	0.0196 (9)	0.0005 (7)	0.0027 (7)	−0.0065 (7)
C14	0.0120 (7)	0.0159 (8)	0.0235 (9)	−0.0019 (6)	−0.0006 (7)	0.0047 (7)
C15	0.0332 (11)	0.0183 (9)	0.0327 (11)	0.0053 (8)	0.0059 (9)	0.0103 (8)
C16	0.0278 (10)	0.0272 (10)	0.0306 (11)	−0.0017 (8)	0.0012 (9)	0.0088 (9)
C17	0.0149 (7)	0.0104 (7)	0.0120 (7)	−0.0011 (6)	0.0025 (6)	−0.0008 (6)
C18	0.0132 (7)	0.0151 (8)	0.0106 (7)	−0.0014 (6)	0.0023 (6)	−0.0019 (6)
C19	0.0155 (7)	0.0119 (7)	0.0137 (8)	0.0003 (6)	−0.0016 (6)	−0.0033 (6)
C20	0.0139 (8)	0.0141 (8)	0.0203 (9)	0.0006 (6)	0.0040 (6)	−0.0014 (6)
C21	0.0213 (9)	0.0221 (9)	0.0164 (8)	0.0002 (7)	0.0084 (7)	0.0043 (7)
C22	0.0195 (8)	0.0200 (8)	0.0134 (8)	0.0012 (7)	0.0033 (6)	0.0051 (6)

Geometric parameters (Å, º)

Br1—C19	1.9009 (17)	C6—C5	1.510 (2)
O1—C5	1.237 (2)	C11—H11A	0.9800
O2—C14	1.209 (2)	C11—H11B	0.9800
O3—C14	1.343 (2)	C11—H11C	0.9800
O3—C15	1.466 (2)	C12—H12A	0.9800
N1—C2	1.386 (2)	C12—H12B	0.9800
N1—C9	1.370 (2)	C12—H12C	0.9800
N1—H1	0.86 (2)	C13—H13A	0.9800
C2—C3	1.357 (2)	C13—H13B	0.9800
C2—C13	1.502 (2)	C13—H13C	0.9800
C3—C4	1.524 (2)	C15—H15A	0.9900
C3—C14	1.474 (2)	C15—H15B	0.9900
C4—H4	1.0000	C15—C16	1.482 (3)
C4—C10	1.516 (2)	C16—H16A	0.9800

C4—C17	1.532 (2)	C16—H16B	0.9800
C10—C9	1.360 (2)	C16—H16C	0.9800
C10—C5	1.451 (2)	C17—C18	1.394 (2)
C9—C8	1.500 (2)	C17—C22	1.396 (2)
C8—H8A	0.9900	C18—H18	0.9500
C8—H8B	0.9900	C18—C19	1.386 (2)
C8—C7	1.532 (2)	C19—C20	1.387 (2)
C7—C6	1.537 (2)	C20—H20	0.9500
C7—C11	1.533 (2)	C20—C21	1.389 (3)
C7—C12	1.533 (2)	C21—H21	0.9500
C6—H6A	0.9900	C21—C22	1.389 (3)
C6—H6B	0.9900	C22—H22	0.9500

C14—O3—C15	113.99 (15)	H11A—C11—H11C	109.5
C2—N1—H1	118.2 (16)	H11B—C11—H11C	109.5
C9—N1—C2	121.67 (14)	C7—C12—H12A	109.5
C9—N1—H1	119.5 (16)	C7—C12—H12B	109.5
N1—C2—C13	114.04 (15)	C7—C12—H12C	109.5
C3—C2—N1	119.69 (15)	H12A—C12—H12B	109.5
C3—C2—C13	126.23 (16)	H12A—C12—H12C	109.5
C2—C3—C4	120.52 (15)	H12B—C12—H12C	109.5
C2—C3—C14	118.99 (16)	C2—C13—H13A	109.5
C14—C3—C4	120.49 (15)	C2—C13—H13B	109.5
C3—C4—H4	108.4	C2—C13—H13C	109.5
C3—C4—C17	111.75 (13)	H13A—C13—H13B	109.5
C10—C4—C3	109.02 (13)	H13A—C13—H13C	109.5
C10—C4—H4	108.4	H13B—C13—H13C	109.5
C10—C4—C17	110.65 (13)	O2—C14—O3	122.23 (16)
C17—C4—H4	108.4	O2—C14—C3	126.45 (17)
C9—C10—C4	120.49 (14)	O3—C14—C3	111.32 (15)
C9—C10—C5	119.58 (14)	O3—C15—H15A	110.3
C5—C10—C4	119.92 (14)	O3—C15—H15B	110.3
N1—C9—C8	116.08 (14)	O3—C15—C16	107.04 (16)
C10—C9—N1	120.08 (15)	H15A—C15—H15B	108.6
C10—C9—C8	123.76 (15)	C16—C15—H15A	110.3
C9—C8—H8A	109.0	C16—C15—H15B	110.3
C9—C8—H8B	109.0	C15—C16—H16A	109.5
C9—C8—C7	112.76 (13)	C15—C16—H16B	109.5
H8A—C8—H8B	107.8	C15—C16—H16C	109.5
C7—C8—H8A	109.0	H16A—C16—H16B	109.5
C7—C8—H8B	109.0	H16A—C16—H16C	109.5
C8—C7—C6	108.35 (13)	H16B—C16—H16C	109.5
C8—C7—C11	110.82 (14)	C18—C17—C4	119.53 (14)
C8—C7—C12	108.72 (14)	C18—C17—C22	118.56 (15)
C11—C7—C6	109.92 (14)	C22—C17—C4	121.91 (15)
C12—C7—C6	109.56 (14)	C17—C18—H18	120.0
C12—C7—C11	109.43 (14)	C19—C18—C17	119.98 (15)
C7—C6—H6A	108.5	C19—C18—H18	120.0

C7—C6—H6B	108.5	C18—C19—Br1	118.78 (13)
H6A—C6—H6B	107.5	C18—C19—C20	121.97 (16)
C5—C6—C7	115.28 (14)	C20—C19—Br1	119.24 (13)
C5—C6—H6A	108.5	C19—C20—H20	121.1
C5—C6—H6B	108.5	C19—C20—C21	117.76 (16)
O1—C5—C10	121.10 (15)	C21—C20—H20	121.1
O1—C5—C6	120.22 (15)	C20—C21—H21	119.4
C10—C5—C6	118.63 (14)	C22—C21—C20	121.13 (16)
C7—C11—H11A	109.5	C22—C21—H21	119.4
C7—C11—H11B	109.5	C17—C22—H22	119.7
C7—C11—H11C	109.5	C21—C22—C17	120.58 (17)
H11A—C11—H11B	109.5	C21—C22—H22	119.7

Br1—C19—C20—C21	−179.58 (13)	C9—C10—C5—C6	−6.4 (2)
N1—C2—C3—C4	−8.9 (2)	C9—C8—C7—C6	−49.12 (18)
N1—C2—C3—C14	171.99 (15)	C9—C8—C7—C11	71.56 (18)
N1—C9—C8—C7	−159.09 (14)	C9—C8—C7—C12	−168.13 (14)
C2—N1—C9—C10	13.9 (2)	C8—C7—C6—C5	49.17 (18)
C2—N1—C9—C8	−162.93 (14)	C7—C6—C5—O1	160.14 (15)
C2—C3—C4—C10	28.5 (2)	C7—C6—C5—C10	−22.5 (2)
C2—C3—C4—C17	−94.13 (18)	C5—C10—C9—N1	−171.17 (14)
C2—C3—C14—O2	−10.1 (3)	C5—C10—C9—C8	5.4 (2)
C2—C3—C14—O3	170.08 (15)	C11—C7—C6—C5	−72.07 (18)
C3—C4—C10—C9	−28.9 (2)	C12—C7—C6—C5	167.65 (14)
C3—C4—C10—C5	152.04 (14)	C13—C2—C3—C4	173.19 (16)
C3—C4—C17—C18	68.23 (19)	C13—C2—C3—C14	−5.9 (3)
C3—C4—C17—C22	−111.52 (18)	C14—O3—C15—C16	161.23 (17)
C4—C3—C14—O2	170.86 (17)	C14—C3—C4—C10	−152.46 (14)
C4—C3—C14—O3	−9.0 (2)	C14—C3—C4—C17	84.92 (18)
C4—C10—C9—N1	9.8 (2)	C15—O3—C14—O2	3.3 (3)
C4—C10—C9—C8	−173.61 (14)	C15—O3—C14—C3	−176.83 (15)
C4—C10—C5—O1	−10.0 (2)	C17—C4—C10—C9	94.34 (18)
C4—C10—C5—C6	172.64 (14)	C17—C4—C10—C5	−84.68 (17)
C4—C17—C18—C19	−178.60 (15)	C17—C18—C19—Br1	178.21 (12)
C4—C17—C22—C21	179.09 (16)	C17—C18—C19—C20	−0.3 (3)
C10—C4—C17—C18	−53.5 (2)	C18—C17—C22—C21	−0.7 (3)
C10—C4—C17—C22	126.79 (17)	C18—C19—C20—C21	−1.1 (3)
C10—C9—C8—C7	24.2 (2)	C19—C20—C21—C22	1.6 (3)
C9—N1—C2—C3	−14.3 (2)	C20—C21—C22—C17	−0.7 (3)
C9—N1—C2—C13	163.81 (15)	C22—C17—C18—C19	1.1 (2)
C9—C10—C5—O1	170.98 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86 (2)	2.05 (2)	2.8896 (19)	166 (2)

Symmetry code: (i) *x*, −*y*+1, *z*+1/2.

(III) Ethyl 4-(2-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

Crystal data

$C_{21}H_{24}BrNO_3$	$F(000) = 1728$
$M_r = 418.32$	$D_x = 1.445$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 14.5012$ (18) Å	Cell parameters from 9934 reflections
$b = 18.299$ (2) Å	$\theta = 2.2$–27.7°
$c = 15.1952$ (19) Å	$\mu = 2.16$ mm^{-1}
$\beta = 107.5262$ (15)°	$T = 100$ K
$V = 3844.9$ (8) Å^3	Prism, translucent yellow
$Z = 8$	0.34 × 0.16 × 0.08 mm

Data collection

Bruker SMART BREEZE CCD area-detector diffractometer	8935 independent reflections
Radiation source: 2 kW sealed X-ray tube	6859 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.065$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$\theta_{max} = 27.7°$, $\theta_{min} = 1.5°$
$T_{min} = 0.866$, $T_{max} = 1.000$	$h = -18 \rightarrow 18$
45465 measured reflections	$k = -23 \rightarrow 23$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 2.2792P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
8935 reflections	$\Delta\rho_{max} = 1.46$ e Å^{-3}
485 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
0 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
Br1A	0.39565 (2)	0.30789 (2)	0.25454 (2)	0.01430 (7)
O1A	0.28043 (11)	0.45760 (9)	0.12019 (11)	0.0122 (4)
O2A	0.04711 (13)	0.20468 (10)	0.24987 (15)	0.0262 (5)
O3A	0.20232 (12)	0.23877 (9)	0.29061 (12)	0.0148 (4)
N1A	−0.01715 (15)	0.42917 (11)	0.17929 (14)	0.0110 (4)
C2A	0.00080 (17)	0.35786 (13)	0.21030 (16)	0.0117 (5)
C3A	0.08940 (16)	0.32797 (13)	0.22333 (16)	0.0100 (5)
C4A	0.17328 (16)	0.37166 (13)	0.20857 (16)	0.0096 (5)
H4A	0.2055	0.3416	0.1714	0.012*

C10A	0.13654 (16)	0.44210 (13)	0.15653 (16)	0.0094 (5)
C9A	0.04751 (17)	0.46991 (13)	0.15143 (16)	0.0099 (5)
C8A	0.01507 (17)	0.54547 (13)	0.11637 (17)	0.0113 (5)
H8AA	−0.0255	0.5659	0.1524	0.014*
H8AB	−0.0254	0.5422	0.0511	0.014*
C7A	0.10023 (17)	0.59772 (13)	0.12310 (17)	0.0114 (5)
C6A	0.17181 (17)	0.55891 (13)	0.08212 (16)	0.0111 (5)
H6AA	0.1422	0.5549	0.0145	0.013*
H6AB	0.2305	0.5895	0.0934	0.013*
C5A	0.20149 (17)	0.48342 (13)	0.12076 (16)	0.0104 (5)
C11A	0.15088 (18)	0.61815 (14)	0.22402 (17)	0.0160 (5)
H11A	0.1035	0.6387	0.2515	0.024*
H11B	0.2014	0.6544	0.2267	0.024*
H11C	0.1801	0.5744	0.2584	0.024*
C12A	0.06180 (18)	0.66689 (14)	0.06839 (18)	0.0168 (6)
H12A	0.0299	0.6541	0.0037	0.025*
H12B	0.1156	0.7003	0.0720	0.025*
H12C	0.0152	0.6907	0.0942	0.025*
C13A	−0.08558 (18)	0.32166 (14)	0.22696 (19)	0.0171 (6)
H13A	−0.1282	0.3590	0.2398	0.026*
H13B	−0.0639	0.2885	0.2799	0.026*
H13C	−0.1209	0.2938	0.1720	0.026*
C14A	0.10710 (17)	0.25154 (14)	0.25480 (17)	0.0133 (5)
C15A	0.23069 (18)	0.16497 (13)	0.32241 (18)	0.0155 (5)
H15A	0.2953	0.1544	0.3160	0.019*
H15B	0.1841	0.1298	0.2833	0.019*
C16A	0.2338 (2)	0.15485 (15)	0.42185 (18)	0.0205 (6)
H16A	0.1693	0.1633	0.4279	0.031*
H16B	0.2796	0.1898	0.4607	0.031*
H16C	0.2547	0.1049	0.4415	0.031*
C17A	0.24881 (17)	0.39335 (13)	0.29969 (16)	0.0099 (5)
C18A	0.34612 (17)	0.37375 (14)	0.32615 (16)	0.0129 (5)
C19A	0.41183 (18)	0.40080 (14)	0.40664 (17)	0.0155 (5)
H19A	0.4777	0.3862	0.4236	0.019*
C20A	0.38027 (19)	0.44895 (15)	0.46146 (17)	0.0181 (6)
H20A	0.4250	0.4683	0.5156	0.022*
C21A	0.28354 (19)	0.46919 (14)	0.43783 (17)	0.0167 (6)
H21A	0.2619	0.5022	0.4757	0.020*
C22A	0.21920 (18)	0.44091 (13)	0.35874 (17)	0.0142 (5)
H22A	0.1529	0.4540	0.3437	0.017*
Br1B	0.08223 (2)	0.00989 (2)	0.13780 (2)	0.01685 (7)
O1B	0.21907 (11)	−0.03473 (9)	0.35984 (12)	0.0139 (4)
O2B	0.41353 (12)	0.16979 (9)	0.13408 (12)	0.0158 (4)
O3B	0.26479 (11)	0.12336 (9)	0.11364 (11)	0.0130 (4)
N1B	0.51999 (15)	−0.01424 (12)	0.30637 (14)	0.0116 (4)
C2B	0.48978 (17)	0.04219 (13)	0.24329 (16)	0.0104 (5)
C3B	0.39436 (17)	0.05815 (13)	0.21022 (16)	0.0094 (5)
C4B	0.31871 (16)	0.01002 (13)	0.23282 (16)	0.0090 (5)

H4B	0.2658	0.0421	0.2405	0.011*
C10B	0.36467 (16)	−0.02951 (13)	0.32331 (16)	0.0090 (5)
C9B	0.46114 (17)	−0.04440 (13)	0.35161 (16)	0.0096 (5)
C8B	0.50953 (17)	−0.09235 (13)	0.43263 (16)	0.0114 (5)
H8BA	0.5407	−0.0612	0.4867	0.014*
H8BB	0.5607	−0.1214	0.4182	0.014*
C7B	0.43782 (17)	−0.14455 (13)	0.45732 (16)	0.0117 (5)
C6B	0.35073 (17)	−0.09960 (13)	0.46295 (16)	0.0109 (5)
H6BA	0.3012	−0.1333	0.4724	0.013*
H6BB	0.3715	−0.0673	0.5176	0.013*
C5B	0.30492 (17)	−0.05315 (13)	0.37865 (16)	0.0110 (5)
C12B	0.48777 (19)	−0.17893 (15)	0.55204 (18)	0.0182 (6)
H12D	0.5411	−0.2101	0.5476	0.027*
H12E	0.4409	−0.2084	0.5715	0.027*
H12F	0.5131	−0.1402	0.5974	0.027*
C11B	0.40569 (19)	−0.20507 (14)	0.38480 (18)	0.0165 (6)
H11D	0.3742	−0.1832	0.3243	0.025*
H11E	0.3601	−0.2376	0.4017	0.025*
H11F	0.4623	−0.2332	0.3820	0.025*
C13B	0.57203 (17)	0.07931 (14)	0.22026 (18)	0.0155 (5)
H13D	0.5937	0.1214	0.2611	0.023*
H13E	0.5504	0.0959	0.1559	0.023*
H13F	0.6257	0.0448	0.2287	0.023*
C14B	0.36205 (17)	0.12248 (13)	0.15021 (16)	0.0112 (5)
C15B	0.22766 (18)	0.18339 (14)	0.05020 (18)	0.0164 (6)
H15C	0.2565	0.1822	−0.0011	0.020*
H15D	0.2440	0.2307	0.0827	0.020*
C16B	0.11964 (19)	0.17455 (16)	0.0134 (2)	0.0240 (6)
H16D	0.0924	0.2141	−0.0301	0.036*
H16E	0.0918	0.1763	0.0647	0.036*
H16F	0.1043	0.1274	−0.0183	0.036*
C17B	0.27431 (17)	−0.04582 (13)	0.15652 (16)	0.0107 (5)
C18B	0.17577 (17)	−0.05192 (14)	0.10999 (17)	0.0128 (5)
C19B	0.13963 (19)	−0.10322 (15)	0.04075 (18)	0.0196 (6)
H19B	0.0721	−0.1060	0.0103	0.023*
C20B	0.2024 (2)	−0.15016 (15)	0.01647 (19)	0.0233 (6)
H20B	0.1784	−0.1847	−0.0317	0.028*
C21B	0.3010 (2)	−0.14683 (15)	0.06268 (18)	0.0200 (6)
H21B	0.3444	−0.1797	0.0471	0.024*
C22B	0.33544 (18)	−0.09546 (13)	0.13130 (17)	0.0136 (5)
H22B	0.4029	−0.0937	0.1625	0.016*
H1B	0.576 (2)	−0.0236 (14)	0.3237 (18)	0.011 (7)*
H1A	−0.0714 (19)	0.4467 (14)	0.1738 (17)	0.006 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1A	0.01041 (12)	0.01685 (13)	0.01641 (13)	0.00394 (10)	0.00521 (10)	0.00192 (10)

O1A	0.0075 (8)	0.0155 (9)	0.0138 (9)	−0.0009 (7)	0.0033 (7)	−0.0011 (7)
O2A	0.0129 (10)	0.0128 (10)	0.0512 (14)	−0.0007 (8)	0.0070 (9)	0.0065 (9)
O3A	0.0091 (8)	0.0111 (9)	0.0223 (10)	0.0021 (7)	0.0019 (7)	0.0042 (7)
N1A	0.0059 (10)	0.0129 (11)	0.0156 (11)	0.0031 (9)	0.0054 (8)	0.0037 (9)
C2A	0.0118 (12)	0.0130 (13)	0.0102 (12)	−0.0011 (10)	0.0031 (10)	0.0002 (10)
C3A	0.0080 (11)	0.0102 (12)	0.0113 (12)	−0.0009 (9)	0.0021 (9)	−0.0012 (9)
C4A	0.0079 (11)	0.0107 (12)	0.0100 (11)	0.0023 (9)	0.0024 (9)	−0.0006 (10)
C10A	0.0079 (11)	0.0115 (12)	0.0080 (11)	0.0007 (9)	0.0012 (9)	−0.0011 (9)
C9A	0.0096 (11)	0.0125 (12)	0.0068 (11)	0.0006 (10)	0.0013 (9)	−0.0010 (9)
C8A	0.0088 (12)	0.0124 (13)	0.0134 (12)	0.0021 (10)	0.0044 (10)	0.0008 (10)
C7A	0.0093 (12)	0.0105 (12)	0.0147 (13)	−0.0007 (10)	0.0041 (10)	0.0012 (10)
C6A	0.0125 (12)	0.0100 (12)	0.0118 (12)	−0.0008 (10)	0.0049 (10)	0.0004 (10)
C5A	0.0083 (11)	0.0148 (13)	0.0067 (11)	−0.0008 (10)	0.0004 (9)	−0.0027 (10)
C11A	0.0143 (13)	0.0136 (13)	0.0193 (14)	0.0028 (11)	0.0040 (11)	−0.0018 (11)
C12A	0.0154 (13)	0.0129 (13)	0.0230 (14)	0.0012 (11)	0.0069 (11)	0.0046 (11)
C13A	0.0121 (13)	0.0152 (14)	0.0261 (15)	0.0030 (10)	0.0092 (11)	0.0059 (11)
C14A	0.0087 (12)	0.0153 (13)	0.0173 (13)	0.0011 (10)	0.0063 (10)	−0.0013 (11)
C15A	0.0124 (12)	0.0077 (12)	0.0257 (15)	0.0040 (10)	0.0044 (11)	0.0003 (11)
C16A	0.0233 (15)	0.0165 (14)	0.0209 (15)	0.0048 (12)	0.0052 (12)	0.0017 (11)
C17A	0.0123 (12)	0.0083 (12)	0.0094 (12)	−0.0016 (10)	0.0036 (9)	0.0037 (9)
C18A	0.0135 (12)	0.0143 (13)	0.0123 (12)	−0.0007 (10)	0.0062 (10)	0.0023 (10)
C19A	0.0103 (12)	0.0217 (14)	0.0133 (13)	−0.0039 (11)	0.0017 (10)	0.0050 (11)
C20A	0.0200 (14)	0.0240 (15)	0.0092 (12)	−0.0067 (12)	0.0028 (11)	0.0015 (11)
C21A	0.0222 (14)	0.0181 (14)	0.0111 (13)	−0.0026 (11)	0.0069 (11)	−0.0020 (11)
C22A	0.0152 (13)	0.0125 (13)	0.0145 (13)	−0.0009 (10)	0.0038 (10)	0.0037 (10)
Br1B	0.00708 (12)	0.02538 (15)	0.01687 (13)	0.00182 (10)	0.00179 (9)	0.00505 (11)
O1B	0.0066 (8)	0.0185 (10)	0.0172 (9)	−0.0003 (7)	0.0046 (7)	0.0005 (8)
O2B	0.0155 (9)	0.0108 (9)	0.0220 (10)	−0.0021 (7)	0.0071 (8)	0.0020 (7)
O3B	0.0105 (8)	0.0124 (9)	0.0145 (9)	0.0021 (7)	0.0014 (7)	0.0051 (7)
N1B	0.0045 (10)	0.0172 (12)	0.0133 (11)	0.0020 (9)	0.0031 (8)	0.0025 (9)
C2B	0.0103 (12)	0.0105 (12)	0.0115 (12)	0.0000 (10)	0.0049 (10)	0.0003 (10)
C3B	0.0104 (12)	0.0095 (12)	0.0074 (11)	−0.0011 (9)	0.0010 (9)	−0.0026 (9)
C4B	0.0072 (11)	0.0101 (12)	0.0092 (11)	0.0012 (9)	0.0018 (9)	0.0009 (9)
C10B	0.0077 (11)	0.0101 (12)	0.0092 (11)	0.0006 (9)	0.0023 (9)	−0.0001 (9)
C9B	0.0116 (12)	0.0084 (12)	0.0095 (12)	−0.0002 (10)	0.0040 (9)	−0.0016 (9)
C8B	0.0100 (12)	0.0125 (13)	0.0117 (12)	0.0011 (10)	0.0034 (10)	0.0030 (10)
C7B	0.0124 (12)	0.0122 (13)	0.0106 (12)	0.0005 (10)	0.0036 (10)	0.0027 (10)
C6B	0.0109 (12)	0.0125 (13)	0.0101 (12)	−0.0016 (10)	0.0043 (10)	−0.0009 (10)
C5B	0.0102 (12)	0.0117 (13)	0.0104 (12)	−0.0034 (10)	0.0022 (9)	−0.0062 (10)
C12B	0.0170 (13)	0.0199 (15)	0.0177 (14)	−0.0014 (11)	0.0052 (11)	0.0069 (11)
C11B	0.0175 (13)	0.0140 (14)	0.0183 (14)	0.0002 (11)	0.0057 (11)	0.0022 (11)
C13B	0.0111 (12)	0.0193 (14)	0.0177 (13)	−0.0011 (11)	0.0070 (10)	0.0042 (11)
C14B	0.0109 (12)	0.0128 (13)	0.0105 (12)	0.0011 (10)	0.0041 (9)	−0.0031 (10)
C15B	0.0195 (14)	0.0107 (13)	0.0177 (13)	0.0029 (11)	0.0035 (11)	0.0055 (11)
C16B	0.0187 (14)	0.0223 (15)	0.0276 (16)	0.0073 (12)	0.0016 (12)	0.0115 (12)
C17B	0.0122 (12)	0.0105 (12)	0.0095 (12)	−0.0029 (10)	0.0033 (10)	0.0031 (10)
C18B	0.0104 (12)	0.0137 (13)	0.0145 (13)	0.0002 (10)	0.0041 (10)	0.0044 (10)
C19B	0.0163 (14)	0.0196 (15)	0.0190 (14)	−0.0071 (11)	−0.0005 (11)	0.0015 (11)

C20B	0.0330 (16)	0.0161 (14)	0.0178 (14)	−0.0082 (12)	0.0032 (12)	−0.0046 (11)
C21B	0.0263 (15)	0.0146 (14)	0.0191 (14)	0.0030 (12)	0.0069 (12)	−0.0027 (11)
C22B	0.0133 (12)	0.0121 (13)	0.0137 (13)	0.0017 (10)	0.0013 (10)	0.0026 (10)

Geometric parameters (Å, º)

Br1A—C18A	1.904 (2)	Br1B—C18B	1.909 (2)
O1A—C5A	1.241 (3)	O1B—C5B	1.237 (3)
O2A—C14A	1.208 (3)	O2B—C14B	1.215 (3)
O3A—C14A	1.343 (3)	O3B—C14B	1.351 (3)
O3A—C15A	1.451 (3)	O3B—C15B	1.454 (3)
N1A—C2A	1.385 (3)	N1B—C2B	1.387 (3)
N1A—C9A	1.361 (3)	N1B—C9B	1.363 (3)
N1A—H1A	0.83 (3)	N1B—H1B	0.80 (3)
C2A—C3A	1.355 (3)	C2B—C3B	1.354 (3)
C2A—C13A	1.504 (3)	C2B—C13B	1.503 (3)
C3A—C4A	1.528 (3)	C3B—C4B	1.524 (3)
C3A—C14A	1.475 (3)	C3B—C14B	1.476 (3)
C4A—H4A	1.0000	C4B—H4B	1.0000
C4A—C10A	1.522 (3)	C4B—C10B	1.519 (3)
C4A—C17A	1.537 (3)	C4B—C17B	1.534 (3)
C10A—C9A	1.368 (3)	C10B—C9B	1.362 (3)
C10A—C5A	1.436 (3)	C10B—C5B	1.443 (3)
C9A—C8A	1.505 (3)	C9B—C8B	1.503 (3)
C8A—H8AA	0.9900	C8B—H8BA	0.9900
C8A—H8AB	0.9900	C8B—H8BB	0.9900
C8A—C7A	1.541 (3)	C8B—C7B	1.539 (3)
C7A—C6A	1.536 (3)	C7B—C6B	1.531 (3)
C7A—C11A	1.534 (3)	C7B—C12B	1.538 (3)
C7A—C12A	1.525 (3)	C7B—C11B	1.532 (3)
C6A—H6AA	0.9900	C6B—H6BA	0.9900
C6A—H6AB	0.9900	C6B—H6BB	0.9900
C6A—C5A	1.512 (3)	C6B—C5B	1.514 (3)
C11A—H11A	0.9800	C12B—H12D	0.9800
C11A—H11B	0.9800	C12B—H12E	0.9800
C11A—H11C	0.9800	C12B—H12F	0.9800
C12A—H12A	0.9800	C11B—H11D	0.9800
C12A—H12B	0.9800	C11B—H11E	0.9800
C12A—H12C	0.9800	C11B—H11F	0.9800
C13A—H13A	0.9800	C13B—H13D	0.9800
C13A—H13B	0.9800	C13B—H13E	0.9800
C13A—H13C	0.9800	C13B—H13F	0.9800
C15A—H15A	0.9900	C15B—H15C	0.9900
C15A—H15B	0.9900	C15B—H15D	0.9900
C15A—C16A	1.509 (4)	C15B—C16B	1.505 (4)
C16A—H16A	0.9800	C16B—H16D	0.9800
C16A—H16B	0.9800	C16B—H16E	0.9800
C16A—H16C	0.9800	C16B—H16F	0.9800

C17A—C18A	1.393 (3)	C17B—C18B	1.395 (3)
C17A—C22A	1.407 (3)	C17B—C22B	1.401 (3)
C18A—C19A	1.395 (3)	C18B—C19B	1.390 (4)
C19A—H19A	0.9500	C19B—H19B	0.9500
C19A—C20A	1.382 (4)	C19B—C20B	1.381 (4)
C20A—H20A	0.9500	C20B—H20B	0.9500
C20A—C21A	1.389 (4)	C20B—C21B	1.391 (4)
C21A—H21A	0.9500	C21B—H21B	0.9500
C21A—C22A	1.381 (3)	C21B—C22B	1.381 (4)
C22A—H22A	0.9500	C22B—H22B	0.9500

C14A—O3A—C15A	116.77 (19)	C14B—O3B—C15B	114.45 (19)
C2A—N1A—H1A	118.2 (17)	C2B—N1B—H1B	117.8 (19)
C9A—N1A—C2A	123.0 (2)	C9B—N1B—C2B	122.3 (2)
C9A—N1A—H1A	118.6 (17)	C9B—N1B—H1B	118.8 (19)
N1A—C2A—C13A	113.0 (2)	N1B—C2B—C13B	112.9 (2)
C3A—C2A—N1A	120.2 (2)	C3B—C2B—N1B	119.5 (2)
C3A—C2A—C13A	126.8 (2)	C3B—C2B—C13B	127.6 (2)
C2A—C3A—C4A	121.9 (2)	C2B—C3B—C4B	121.1 (2)
C2A—C3A—C14A	119.7 (2)	C2B—C3B—C14B	120.0 (2)
C14A—C3A—C4A	118.4 (2)	C14B—C3B—C4B	118.9 (2)
C3A—C4A—H4A	108.9	C3B—C4B—H4B	108.5
C3A—C4A—C17A	112.70 (19)	C3B—C4B—C17B	112.42 (19)
C10A—C4A—C3A	110.48 (19)	C10B—C4B—C3B	109.25 (19)
C10A—C4A—H4A	108.9	C10B—C4B—H4B	108.5
C10A—C4A—C17A	107.00 (19)	C10B—C4B—C17B	109.69 (19)
C17A—C4A—H4A	108.9	C17B—C4B—H4B	108.5
C9A—C10A—C4A	121.4 (2)	C9B—C10B—C4B	120.7 (2)
C9A—C10A—C5A	119.9 (2)	C9B—C10B—C5B	119.7 (2)
C5A—C10A—C4A	118.4 (2)	C5B—C10B—C4B	119.6 (2)
N1A—C9A—C10A	120.4 (2)	N1B—C9B—C8B	116.2 (2)
N1A—C9A—C8A	116.2 (2)	C10B—C9B—N1B	120.0 (2)
C10A—C9A—C8A	123.4 (2)	C10B—C9B—C8B	123.9 (2)
C9A—C8A—H8AA	109.0	C9B—C8B—H8BA	109.1
C9A—C8A—H8AB	109.0	C9B—C8B—H8BB	109.1
C9A—C8A—C7A	112.81 (19)	C9B—C8B—C7B	112.27 (19)
H8AA—C8A—H8AB	107.8	H8BA—C8B—H8BB	107.9
C7A—C8A—H8AA	109.0	C7B—C8B—H8BA	109.1
C7A—C8A—H8AB	109.0	C7B—C8B—H8BB	109.1
C6A—C7A—C8A	108.19 (19)	C6B—C7B—C8B	108.03 (19)
C11A—C7A—C8A	110.5 (2)	C6B—C7B—C12B	109.36 (19)
C11A—C7A—C6A	109.8 (2)	C6B—C7B—C11B	110.6 (2)
C12A—C7A—C8A	108.96 (19)	C12B—C7B—C8B	108.64 (19)
C12A—C7A—C6A	110.1 (2)	C11B—C7B—C8B	110.8 (2)
C12A—C7A—C11A	109.2 (2)	C11B—C7B—C12B	109.4 (2)
C7A—C6A—H6AA	108.7	C7B—C6B—H6BA	108.7
C7A—C6A—H6AB	108.7	C7B—C6B—H6BB	108.7
H6AA—C6A—H6AB	107.6	H6BA—C6B—H6BB	107.6

C5A—C6A—C7A	114.4 (2)	C5B—C6B—C7B	114.42 (19)
C5A—C6A—H6AA	108.7	C5B—C6B—H6BA	108.7
C5A—C6A—H6AB	108.7	C5B—C6B—H6BB	108.7
O1A—C5A—C10A	120.9 (2)	O1B—C5B—C10B	121.5 (2)
O1A—C5A—C6A	120.0 (2)	O1B—C5B—C6B	120.2 (2)
C10A—C5A—C6A	119.1 (2)	C10B—C5B—C6B	118.3 (2)
C7A—C11A—H11A	109.5	C7B—C12B—H12D	109.5
C7A—C11A—H11B	109.5	C7B—C12B—H12E	109.5
C7A—C11A—H11C	109.5	C7B—C12B—H12F	109.5
H11A—C11A—H11B	109.5	H12D—C12B—H12E	109.5
H11A—C11A—H11C	109.5	H12D—C12B—H12F	109.5
H11B—C11A—H11C	109.5	H12E—C12B—H12F	109.5
C7A—C12A—H12A	109.5	C7B—C11B—H11D	109.5
C7A—C12A—H12B	109.5	C7B—C11B—H11E	109.5
C7A—C12A—H12C	109.5	C7B—C11B—H11F	109.5
H12A—C12A—H12B	109.5	H11D—C11B—H11E	109.5
H12A—C12A—H12C	109.5	H11D—C11B—H11F	109.5
H12B—C12A—H12C	109.5	H11E—C11B—H11F	109.5
C2A—C13A—H13A	109.5	C2B—C13B—H13D	109.5
C2A—C13A—H13B	109.5	C2B—C13B—H13E	109.5
C2A—C13A—H13C	109.5	C2B—C13B—H13F	109.5
H13A—C13A—H13B	109.5	H13D—C13B—H13E	109.5
H13A—C13A—H13C	109.5	H13D—C13B—H13F	109.5
H13B—C13A—H13C	109.5	H13E—C13B—H13F	109.5
O2A—C14A—O3A	122.3 (2)	O2B—C14B—O3B	122.5 (2)
O2A—C14A—C3A	127.0 (2)	O2B—C14B—C3B	126.3 (2)
O3A—C14A—C3A	110.7 (2)	O3B—C14B—C3B	111.2 (2)
O3A—C15A—H15A	109.3	O3B—C15B—H15C	110.2
O3A—C15A—H15B	109.3	O3B—C15B—H15D	110.2
O3A—C15A—C16A	111.6 (2)	O3B—C15B—C16B	107.5 (2)
H15A—C15A—H15B	108.0	H15C—C15B—H15D	108.5
C16A—C15A—H15A	109.3	C16B—C15B—H15C	110.2
C16A—C15A—H15B	109.3	C16B—C15B—H15D	110.2
C15A—C16A—H16A	109.5	C15B—C16B—H16D	109.5
C15A—C16A—H16B	109.5	C15B—C16B—H16E	109.5
C15A—C16A—H16C	109.5	C15B—C16B—H16F	109.5
H16A—C16A—H16B	109.5	H16D—C16B—H16E	109.5
H16A—C16A—H16C	109.5	H16D—C16B—H16F	109.5
H16B—C16A—H16C	109.5	H16E—C16B—H16F	109.5
C18A—C17A—C4A	125.4 (2)	C18B—C17B—C4B	124.7 (2)
C18A—C17A—C22A	116.9 (2)	C18B—C17B—C22B	116.4 (2)
C22A—C17A—C4A	117.6 (2)	C22B—C17B—C4B	118.9 (2)
C17A—C18A—Br1A	121.46 (18)	C17B—C18B—Br1B	121.88 (19)
C17A—C18A—C19A	121.8 (2)	C19B—C18B—Br1B	115.91 (19)
C19A—C18A—Br1A	116.74 (18)	C19B—C18B—C17B	122.2 (2)
C18A—C19A—H19A	120.3	C18B—C19B—H19B	120.2
C20A—C19A—C18A	119.5 (2)	C20B—C19B—C18B	119.6 (2)
C20A—C19A—H19A	120.3	C20B—C19B—H19B	120.2

C19A—C20A—H20A	119.8	C19B—C20B—H20B	120.1
C19A—C20A—C21A	120.4 (2)	C19B—C20B—C21B	119.9 (2)
C21A—C20A—H20A	119.8	C21B—C20B—H20B	120.1
C20A—C21A—H21A	120.3	C20B—C21B—H21B	120.2
C22A—C21A—C20A	119.3 (2)	C22B—C21B—C20B	119.6 (2)
C22A—C21A—H21A	120.3	C22B—C21B—H21B	120.2
C17A—C22A—H22A	119.0	C17B—C22B—H22B	118.9
C21A—C22A—C17A	122.1 (2)	C21B—C22B—C17B	122.2 (2)
C21A—C22A—H22A	119.0	C21B—C22B—H22B	118.9

Br1A—C18A—C19A—C20A	179.88 (19)	Br1B—C18B—C19B—C20B	−179.9 (2)
N1A—C2A—C3A—C4A	2.6 (4)	N1B—C2B—C3B—C4B	−6.8 (3)
N1A—C2A—C3A—C14A	−178.9 (2)	N1B—C2B—C3B—C14B	174.0 (2)
N1A—C9A—C8A—C7A	157.0 (2)	N1B—C9B—C8B—C7B	−159.6 (2)
C2A—N1A—C9A—C10A	−2.6 (4)	C2B—N1B—C9B—C10B	12.6 (4)
C2A—N1A—C9A—C8A	177.8 (2)	C2B—N1B—C9B—C8B	−166.5 (2)
C2A—C3A—C4A—C10A	−14.1 (3)	C2B—C3B—C4B—C10B	25.5 (3)
C2A—C3A—C4A—C17A	105.6 (3)	C2B—C3B—C4B—C17B	−96.5 (3)
C2A—C3A—C14A—O2A	19.8 (4)	C2B—C3B—C14B—O2B	−9.1 (4)
C2A—C3A—C14A—O3A	−160.9 (2)	C2B—C3B—C14B—O3B	171.1 (2)
C3A—C4A—C10A—C9A	18.3 (3)	C3B—C4B—C10B—C9B	−27.2 (3)
C3A—C4A—C10A—C5A	−168.2 (2)	C3B—C4B—C10B—C5B	154.4 (2)
C3A—C4A—C17A—C18A	120.5 (2)	C3B—C4B—C17B—C18B	−122.8 (2)
C3A—C4A—C17A—C22A	−64.0 (3)	C3B—C4B—C17B—C22B	58.0 (3)
C4A—C3A—C14A—O2A	−161.7 (2)	C4B—C3B—C14B—O2B	171.8 (2)
C4A—C3A—C14A—O3A	17.7 (3)	C4B—C3B—C14B—O3B	−8.1 (3)
C4A—C10A—C9A—N1A	−11.2 (3)	C4B—C10B—C9B—N1B	10.1 (3)
C4A—C10A—C9A—C8A	168.4 (2)	C4B—C10B—C9B—C8B	−170.9 (2)
C4A—C10A—C5A—O1A	10.3 (3)	C4B—C10B—C5B—O1B	−8.5 (3)
C4A—C10A—C5A—C6A	−170.6 (2)	C4B—C10B—C5B—C6B	173.4 (2)
C4A—C17A—C18A—Br1A	−6.1 (3)	C4B—C17B—C18B—Br1B	−0.6 (3)
C4A—C17A—C18A—C19A	174.5 (2)	C4B—C17B—C18B—C19B	179.4 (2)
C4A—C17A—C22A—C21A	−173.7 (2)	C4B—C17B—C22B—C21B	−179.4 (2)
C10A—C4A—C17A—C18A	−117.9 (2)	C10B—C4B—C17B—C18B	115.4 (2)
C10A—C4A—C17A—C22A	57.6 (3)	C10B—C4B—C17B—C22B	−63.7 (3)
C10A—C9A—C8A—C7A	−22.6 (3)	C10B—C9B—C8B—C7B	21.4 (3)
C9A—N1A—C2A—C3A	7.0 (4)	C9B—N1B—C2B—C3B	−14.3 (4)
C9A—N1A—C2A—C13A	−173.5 (2)	C9B—N1B—C2B—C13B	165.5 (2)
C9A—C10A—C5A—O1A	−176.1 (2)	C9B—C10B—C5B—O1B	173.1 (2)
C9A—C10A—C5A—C6A	3.0 (3)	C9B—C10B—C5B—C6B	−5.0 (3)
C9A—C8A—C7A—C6A	48.6 (3)	C9B—C8B—C7B—C6B	−49.2 (3)
C9A—C8A—C7A—C11A	−71.7 (3)	C9B—C8B—C7B—C12B	−167.8 (2)
C9A—C8A—C7A—C12A	168.2 (2)	C9B—C8B—C7B—C11B	72.0 (3)
C8A—C7A—C6A—C5A	−51.3 (3)	C8B—C7B—C6B—C5B	52.6 (3)
C7A—C6A—C5A—O1A	−154.2 (2)	C7B—C6B—C5B—O1B	155.3 (2)
C7A—C6A—C5A—C10A	26.7 (3)	C7B—C6B—C5B—C10B	−26.5 (3)
C5A—C10A—C9A—N1A	175.5 (2)	C5B—C10B—C9B—N1B	−171.5 (2)
C5A—C10A—C9A—C8A	−4.9 (4)	C5B—C10B—C9B—C8B	7.5 (4)

C11A—C7A—C6A—C5A	69.5 (3)	C12B—C7B—C6B—C5B	170.7 (2)
C12A—C7A—C6A—C5A	−170.2 (2)	C11B—C7B—C6B—C5B	−68.8 (3)
C13A—C2A—C3A—C4A	−176.8 (2)	C13B—C2B—C3B—C4B	173.5 (2)
C13A—C2A—C3A—C14A	1.7 (4)	C13B—C2B—C3B—C14B	−5.7 (4)
C14A—O3A—C15A—C16A	−88.5 (3)	C14B—O3B—C15B—C16B	177.9 (2)
C14A—C3A—C4A—C10A	167.4 (2)	C14B—C3B—C4B—C10B	−155.3 (2)
C14A—C3A—C4A—C17A	−73.0 (3)	C14B—C3B—C4B—C17B	82.7 (3)
C15A—O3A—C14A—O2A	0.9 (3)	C15B—O3B—C14B—O2B	2.9 (3)
C15A—O3A—C14A—C3A	−178.5 (2)	C15B—O3B—C14B—C3B	−177.29 (19)
C17A—C4A—C10A—C9A	−104.7 (2)	C17B—C4B—C10B—C9B	96.4 (3)
C17A—C4A—C10A—C5A	68.8 (3)	C17B—C4B—C10B—C5B	−82.0 (3)
C17A—C18A—C19A—C20A	−0.7 (4)	C17B—C18B—C19B—C20B	0.1 (4)
C18A—C17A—C22A—C21A	2.2 (4)	C18B—C17B—C22B—C21B	1.4 (4)
C18A—C19A—C20A—C21A	1.3 (4)	C18B—C19B—C20B—C21B	1.3 (4)
C19A—C20A—C21A—C22A	−0.2 (4)	C19B—C20B—C21B—C22B	−1.3 (4)
C20A—C21A—C22A—C17A	−1.6 (4)	C20B—C21B—C22B—C17B	−0.1 (4)
C22A—C17A—C18A—Br1A	178.40 (17)	C22B—C17B—C18B—Br1B	178.55 (17)
C22A—C17A—C18A—C19A	−1.0 (3)	C22B—C17B—C18B—C19B	−1.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*B*—H1*B*···O1*A*^{i}	0.80 (3)	2.02 (3)	2.818 (3)	174 (3)
N1*A*—H1*A*···O1*B*^{ii}	0.83 (3)	2.07 (3)	2.884 (3)	165 (2)

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