Synthesis, crystal structures, and Hirshfeld analysis of three hexahydroquinoline derivatives

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Three hexahydroquinoline derivatives were synthesized and crystallized in an effort to study the structure–activity relationships of these calcium-channel antagonists. The derivatives are ethyl 4-(2-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, C22H27NO4, (I), ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, C22H27NO4, (II), and ethyl 4-(3,4-dihydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate, C21H24NO5, (III). In these hexahydroquinoline derivatives, 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 substituted phenyl group at the pseudo-axial position are retained. Hydrogen bonds are the main contributors to the packing of the molecules in these crystals.

1. Chemical context

4-Aryl-1,4-dihydropyridines (DHPs) that bind the L-type voltage-gated calcium channels (VGCC) have been applied in general medical practice for over three decades (Zamponi, 2016). Many modifications on 1,4-DHP have been performed to obtain active compounds such as calcium-channel agonists or antagonists (Martin et al., 1995; Rose, 1990; Rose & Draeger, 1992; Trippier et al., 2013). One such modification is fusing a cyclohexanone ring to form hexahydroquinoline (HHQ), in which the orientation of the carbonyl group of the ester substituent at the 5-position in the 1,4-DHP ring has been fixed. This class of compounds has been shown to have calcium-channel antagonistic activity (Aygün Cevher et al., 2019), inhibit the multidrug-resistance transporter (MDR) (Shahraki et al., 2017, 2020), as well as possessing anti-inflammatory and stem-cell differentiation properties, and have been implicated in slowing neurodegenerative disorders (Trippier et al., 2013). Recently, specific substitutions of the cyclohexanone ring were found to have distinct selectivity profiles to different calcium channel subtypes (Schaller et al., 2018). Another report also showed that the 4-aryl-hexahydroquinolines, especially the ones containing a methoxy moiety, exhibit good antioxidant property as radical scavengers (Yang et al., 2011). In a continuation of our study on the structure–activity relationship of this class of 4-aryl-hexahydroquinolines (Steiger et al., 2014, 2018, 2020), and to understand stereoelectronic effects, which define selectivity, as well as to explore the scope and limitations of our synthetic methodologies (Steiger et al., 2016), we report herein the
2. Structural commentary

The asymmetric unit of the title compound I contains one independent molecule, which crystallizes in the triclinic \( P \overline{1} \) space group (Fig. 1). Compounds II and III both crystallize in the monoclinic space group \( P2_1/n \). The asymmetric unit of compound II contains two independent molecules, \( A \) and \( B \) (Fig. 2), while compound III has only one independent molecule in the asymmetric unit (Fig. 3). Similar to the other 4-aryl-hexahydroquinoline derivatives that we have reported (Steiger, et al., 2014; 2018; 2020), compounds I, II, and III all share the common structural features such as a flattened boat conformation on the 1,4-DHP ring, envelope conformation of the cyclohexanone ring, and the pseudo-axial position of the 4-aryl group.

The shallow-boat confirmation of the 1,4-DHP ring is one of the factors that leads to higher calcium-channel activity (Linden et al., 2004). The shallowness of the boat conformation in these three compounds are indicated by the marginal displacements of atom N1 and C4 from the mean plane (the base of the boat) defined by the two double bonds (\( \text{C2=}=\text{C3 and C9}=-\text{C10} \)). The distances between N1 and the mean plane formed by \( \text{C2}/\text{C3}/\text{C9}/\text{C10} \) are 0.159 (3), 0.110 (2), 0.110 (3), and 0.181 (2) \( \text{Å} \) for compounds I, IIA, IIB, and III, respectively. The corresponding distances between C4 and the same mean plane are 0.341 (3), 0.295 (3), 0.253 (3), and 0.399 (2) \( \text{Å} \) for compounds I, IIA, IIB, and III, respectively.

The pseudo-axial position of the C4-aryl group to the 1,4-DHP ring is another key factor that is essential for pharmacological activity (Langs et al., 1987). In the title compounds, the substituted phenyl rings are almost orthogonal to the base of the 1,4-DHP ring, with the mean plane normal to normal angles being 89.09 (7), 92.52 (6), 93.52 (6), and 90.59 (5) \( \text{°} \) for compounds I, IIA, IIB, and III, respectively (see Table 1 for calculated parameters). It is noteworthy that the para-methoxy group on the phenyl ring is flexible and can be either anti- or syn- periplanar to the H atom on C4, i.e. pointing either to (IIA) or away from (IIB) the 1,4-DHP ring.
In all three compounds, the cyclohexanone rings adopt the envelope conformation, which can be quantified using Cremer & Pople’s ring-puckering parameters. Ideally, the envelope conformation would have $\psi = 54.7^\circ$ (or $\psi = 125.3^\circ$ in the case of an absolute configuration change) and $\theta = n \times 60^\circ$. The $\theta$ and $\psi$ values of the title compounds are very close to the ideal angles with deviations less than $10^\circ$ and are listed in Table 2.

Although the carbonyl on the ester group is conjugated to the adjacent endocyclic double bond and is co-planar to the 1,4-DHP mean plane, the whole ester group is flexible. The $\text{C}=\text{O}$ bond can be either cis (I, IIA and IIB) or trans (III) to the adjacent double bond, and the extended or curled orientations of the ethyl group are observed in these crystal structures. The disordered ethyl groups in compound I and compound II also indicate the flexibility of the ester group.

### Table 1
Calculated parameters (Å, °) related to the 1,4-DHP ring.

| Compound | 1,4-DHP mean plane (C2/C3/C10/C9) r.m.s.d | N to ring mean plane distance | C to ring mean plane distance | Phenyl ring to 1,4-DHP mean planes normal-to-normal angle | N1—C4—C17—C18 torsion angle |
|----------|----------------------------------------|------------------------------|-----------------------------|---------------------------------------------------|-------------------------------|
| I        | 0.015                                  | 0.159 (3)                    | 0.341 (3)                   | 89.09 (7)                                        | 173.28 (16)                  |
| IIA      | 0.005                                  | 0.110 (2)                    | 0.295 (3)                   | 92.52 (6)                                        | 1.16 (18)                    |
| IIB      | 0.005                                  | 0.110 (3)                    | 0.253 (3)                   | 93.52 (6)                                        | 13.41 (14)                   |
| III      | 0.001                                  | 0.181 (2)                    | 0.399 (2)                   | 90.59 (5)                                        | 18.38 (15)                   |

### Table 2
Parameters (Å, °) related to the envelope conformation on the cyclohexanone ring.

| Compound | Mean plane (C5/C6/C8–C10) r.m.s.d | C7 to mean plane distance | C11—C7—C4—C17 torsion angle | $Q$ | $\theta$ | $\psi$ |
|----------|------------------------------------|---------------------------|-------------------------------|-----|---------|-------|
| I        | 0.025                              | 0.636 (3)                 | 2.53 (18)                     | 0.458 (2) | 60.7 (3) | 117.2 (3) |
| IIA      | 0.015                              | 0.644 (2)                 | 7.96 (14)                     | 0.4616 (18) | 56.1 (2) | 115.7 (3) |
| IIB      | 0.019                              | 0.645 (3)                 | 13.85 (14)                    | 0.4638 (19) | 121.2 (2) | 303.0 (3) |
| III      | 0.028                              | 0.6408 (19)               | 0.8 (1)                       | 0.4623 (15) | 56.53 (19) | 111.1 (2) |

3. Supramolecular features

In compound I, hydrogen bonds between N1—H1 and O1 form a chain perpendicular to the (100) plane. Short contact C23—H23A $\cdots$ O2 links alternate enantiomers to form a pair perpendicular to the (001) plane (Table 3, Fig. 4).

In compound II, hydrogen bonds N1A$\cdots$H1A$\cdots$O1B and N1B$\cdots$H1B$\cdots$O1A link the two independent molecules A and B to form a chain perpendicular to the (010) plane. Close contacts C23B$\cdots$H23B$\cdots$O2A and C23A$\cdots$H23D$\cdots$O2B link the two independent molecules zigzaggedly along the $c$-axis direction (Table 4, Fig. 5).

In compound III, a chain is formed by hydrogen bonds N1—H1 $\cdots$O1i and O4—H4 $\cdots$O2i between alternating...
enantiomers and runs perpendicular to the (101) plane. Hydrogen bond O5—H5···O1′ links the molecules in a chain perpendicular to the (100) plane and cross-links the other chain to form a sheet of molecules parallel to the (010) plane (Table 5, Fig. 6).

4. Hirshfeld surface analysis

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was performed, and the associated two-dimensional fingerprint plots (McKinnon et al., 2007) were generated to quantify the intermolecular interactions using Crystal Explorer 21.5 (Spackman et al., 2021). The Hirshfeld surface of the title compound I is mapped over \( d_{	ext{norm}} \) in a fixed color scale of 0.5596 (red) to 1.4022 (blue) arbitrary units (Fig. 7). The N—H···O hydrogen bond is apparent as red spots on the surface. A \( \pi \)-interaction between the ester ethyl group and the phenyl ring is noticeable. The delineated two-dimensional

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···O1′ | 0.88 (2) | 2.01 (2) | 2.870 (2) | 165 (2) |
| C13—H13B···O2 | 0.96 | 2.13 | 2.846 (3) | 131 |
| C13—H13C···O4′ | 0.96 | 2.59 | 3.300 (3) | 131 |
| C23—H23A···O2’ | 0.96 | 2.57 | 3.492 (3) | 161 |

Symmetry codes: (i) \( x + 1, y, z \); (ii) \( x + 1, y + 1, z + 1 \).

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1A—H1A···O1B | 0.82 (2) | 2.02 (2) | 2.827 (2) | 167 (2) |
| N1B—H1B···O1A’ | 0.87 (2) | 1.95 (2) | 2.8167 (19) | 172 (2) |

Symmetry code: (i) \( x, y − 1, z \).

Table 5
Hydrogen-bond geometry (Å, °) for III.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···O1′ | 0.876 (18) | 1.971 (19) | 2.8378 (15) | 169.8 (16) |
| O4—H4···O2 | 0.87 (2) | 1.82 (2) | 2.6894 (14) | 175 (2) |
| O5—H5···O1’ | 0.85 (2) | 2.33 (2) | 3.0293 (14) | 140 (2) |

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

Figure 6
The packing of title compound III. Intermolecular hydrogen bonds (shown in dashed lines) cross link the molecules to form a sheet parallel to the (010) plane. H atoms not involved in these hydrogen bonds are removed for clarity.

Figure 7
Hirshfeld surface of I mapped over \( d_{	ext{norm}} \). Short and long contacts are indicated as red and blue regions, respectively. Contacts with distances approximately equal to the sum of the van der Waals radii are colored white. A \( \sigma-\pi \) interaction between C15—H15 and phenyl ring is shown as green dashed lines. Hydrogen bond C23—H23A···O2 is shown as red dashed lines.

Figure 8
The two-dimensional fingerprint plots for I delineated into (a) H···H contacts, (b) H···O/O···H contacts, (c) H···C/C···H contacts. Other contact contributions less than 1% are omitted.
fingerprint plots (Fig. 8) show that the contributions to the overall Hirshfeld surface area arise from H–H contacts (65.3%), O–H/O–H–O contacts (17.7%), and C–H/H–C interactions (16.4%).

For compound II, the Hirshfeld surface analysis was performed with two independent molecules, in a fixed color scale of 0.6119 (red) to 1.7055 (blue) arbitrary units. In addition to hydrogen bonds, σ–π interactions are also identifiable between C6A–H6AB and double bond C2A–C3A (Fig. 9). The delineated two-dimensional fingerprint plots shown in Fig. 10 indicate that H···H contacts (65.6%) make the main contribution to the overall Hirshfeld surface area. The O···H/H···O contacts and C···H/H···C interactions contribute 19.4% and 14.0% of the Hirshfeld surface, respectively.

The Hirshfeld surface of the title compound III is mapped over $d_{norm}$ in a fixed color scale of −0.7001 (red) to 3.4800 (blue) arbitrary units (Fig. 11). Besides the obvious short contacts from hydrogen bonds, a short contact of 2.6137 (14) Å between H8A and C20 is also observed, indicated as red and blue regions, respectively. Contacts with distances approximately equal to the sum of the van der Waals radii are colored white. The close contact between H8A and C20 is shown as a dashed line.
cating a σ-π- interaction between C8—H8A and ring C17–C22. The delineated two-dimensional fingerprint plots shown in Fig. 12 indicate that two main contributions to the overall Hirshfeld surface area arise from H···H contacts (61.2%) and O···H/H···O contacts (24.3%). C···H/H···C interactions contribute 13.1% of the Hirshfeld surface.

5. Database survey
A search for 4-phenyl-5-oxo-hexahydroquinoline-3-carboxylate in the Cambridge Structural Database (CSD version 5.43, November 2021 update; Groom et al., 2016) resulted in 53 hits, of which a meta-methoxyl-substituted 4-phenyl-5-oxo-hexahydroquinoline-3-carboxylate (refcode TANVUC; Li, 2017) should be mentioned. Similar to the title compounds I and IIA, the meta-methoxyl group in TANVUC is exo to the 1,4-DHP ring and carbonyl group on the ester is in a cis orientation to the endocyclic double bond. All of the resulting hits display common structural features, such as the flat-boat conformation of the 1,4-DHP ring, the envelope conformation of the fused cyclohexanone ring, and the substituted aryl ring at the pseudo-axial position to the 1,4-DHP ring.

6. Synthesis and crystallization
An oven-dried 100 ml round-bottom flask equipped with a magnetic stir bar was charged with 10 mmol of dimedone, 10 mmol of ethyl acetoacetate and 5 mol % of ytterbium(III) acetate in the Cambridge Structural Database (CSD version 5.43, November 2021 update; Groom et al., 2016) resulted in 53 hits, of which a meta-methoxyl-substituted 4-phenyl-5-oxo-hexahydroquinoline-3-carboxylate (refcode TANVUC; Li, 2017) should be mentioned. Similar to the title compounds I and IIA, the meta-methoxyl group in TANVUC is exo to the 1,4-DHP ring and carbonyl group on the ester is in a cis orientation to the endocyclic double bond. All of the resulting hits display common structural features, such as the flat-boat conformation of the 1,4-DHP ring, the envelope conformation of the fused cyclohexanone ring, and the substituted aryl ring at the pseudo-axial position to the 1,4-DHP ring.

An oven-dried 100 ml round-bottom flask equipped with a magnetic stir bar was charged with 10 mmol of dimedone, 10 mmol of ethyl acetoacetate and 5 mol % of ytterbium(III) trifluoromethanesulfonate. The mixture was then taken up in 30 ml of absolute ethanol, capped and put under an inert atmosphere of argon, after which the solution was allowed to stir at room temperature for 20 min. The appropriate corresponding benzaldehyde (10 mmol) and 10 mmol of ammonium chloride were added, and the mixture was allowed to stir at room temperature for 48 h. Reaction progress was monitored via 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 crystallized from hexane and ethyl acetate (1:4 v/v) as white-to-yellow crystalline solids.

Crystal data, data collection and structure refinement details are summarized in Table 6. Carbon-bound hydrogen atoms on all three compounds were fixed geometrically and treated as riding with C—H = 0.95–0.98 Å and refined with Uiso(H) = 1.2Ueq (CH, CH2) or 1.5Ueq (CH3). Hydrogen atoms attached to nitrogen and oxygen were found in difference-Fourier map and refined freely. Eight reflections (010, 001, 011, 100, 001, 002, and 002) in compound I and eight reflections (040, 020, 123, 723, 076, 031, 112, and 516) in compound III were omitted because of poor agreement between the observed and calculated intensities.

Data of compound I were acquired at room temperature due to the disintegration of the crystals at low temperatures. The sample measured was identified as two crystals, mis-oriented by 0.24° approximately about the [001] reciprocal-space axis. For the purposes of data collection and subsequent structure refinement, the structure was treated using facilities for handling twinning by non-merohedry, namely HKLF5 data entry 78 applied to bond lengths on the atoms of the ester as well.

The crystals of compound II were found to be pseudo-merohedric twins by a 180° rotation about the c axis. Application of the twin operation (−1, 0, 0, 0, −1, 0, 0, 0, 1) yielded a twin component ratio of 0.6938 (8):0.3062 (8). The ester group on molecule B is also disordered. Atomic displacement equivalency restraints and bond-length restraints (Sheldrick, 2015) were applied to the carbon atoms and the single-bond oxygen atom of the disordered ester group.

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Compound III was co-crystallized with hexanes. However, being a mixture of disordered hexane isomers, the refinement around the hexanes did not give satisfactory results. The
Table 6
Experimental details.

|   | I  | II | III |
|---|----|----|-----|
| Crystal data | C$_2$H$_2$NO$_4$ | C$_2$H$_2$NO$_4$ | C$_2$H$_2$NO$_4$ |
| $M_r$ | 369.44 | 369.44 | 371.42 |
| Crystal system, space group | Triclinic, $P\bar{T}$ | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 300 | 120 | 100 |
| $a$, $b$, $c$ (Å) | 7.2941 (2), 9.6773 (3), 14.4302 (4) | 15.3492 (15), 14.0314 (14), 18.3862 (18) | 90, 90, 0834 (17), 90 |
| $\alpha$, $\beta$, $\gamma$ (°) | 82.1997 (17), 88.3216 (16), 75.9397 (16) | 90, 90, 0834 (17), 90 |
| $\nu$ (mm$^{-1}$) | 0.09 | 0.09 | 0.08 |
| Crystal size (mm) | 0.35 × 0.19 × 0.14 | 0.35 × 0.15 × 0.14 | 0.64 × 0.13 × 0.06 |
| Data collection | Refinement | Refinement | Refinement |
| No. of measured, independent and observed $|F| > 2\sigma(|F|)$ reflections | 34490, 34490, 22410 | 66519, 8085, 7121 | 40175, 5517, 4263 |
| $R_{int}$ | 0.067 | 0.055 | 0.046 |
| $\sin \theta/\lambda_{max}$ (Å$^{-1}$) | 0.670 | 0.625 | 0.668 |
| Refinement | | | |
| $R(F^2)$ | 0.055, 0.145, 1.03 | 0.039, 0.093, 1.04 | 0.045, 0.123, 1.04 |
| No. of reflections | 34490 | 8085 | 5517 |
| No. of observations | 285 | 536 | 260 |
| No. of parameters | 39 | 39 | 0 |
| No. of restraints | | | |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å$^{-3}$) | 0.25, −0.17 | 0.33, −0.30 | 0.41, −0.21 |

OLEX2 SMTBX (Rees et al., 2005) solvent-masking procedure was used to calculate and mask the solvent-accessible void. There are 192 electrons found in a volume of 464 Å$^3$ in one void per unit cell. This is consistent with the presence of one C$_2$H$_13$ molecule per asymmetric unit, which accounts for 200 electrons per unit cell.

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Computing details

For all structures, data collection: APEX2 (Bruker, 2012); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL2018/1 (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

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

Crystal data

C_{22}H_{27}NO_{4} \quad Z = 2
M_r = 369.44
Triclinic, \( P \overline{1} \)
\( a = 7.2941 (2) \) Å
\( b = 9.6773 (3) \) Å
\( c = 14.4302 (4) \) Å
\( \alpha = 82.1992 (17) \)°
\( \beta = 88.3216 (16) \)°
\( \gamma = 75.9397 (16) \)°
\( V = 978.92 (5) \) Å³

Data collection

Bruker SMART BREEZE CCD diffractometer
Radiation source: 2 kW sealed X-ray tube
\( \phi \) and \( \omega \) scans
34490 measured reflections
34490 independent reflections

Refinement

Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F > 2\sigma(F)] = 0.055 \)
\( wR(F^2) = 0.145 \)
\( S = 1.03 \)
34490 reflections
285 parameters
39 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
\( w = 1/[\sigma(F_c^2) + (0.0533P)^2 + 0.1957P] \)
where \( P = (F_c^2 + 2F_s^2)/3 \)
\( \Delta_r \rho_{\text{max}} < 0.001 \)
\( \Delta \rho_{\text{max}} = 0.25 \) e Å\(^{-3} \)
\( \Delta \rho_{\text{min}} = -0.17 \) e Å\(^{-3} \)
Special details

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

Refinement. Refined as a 2-component twin. Twin law (-1 0 0 0 1 0 0.0123 -0.407 1) was applied and the structure was refined using HKLF5 data, yielding a ratio of 0.866 (2):0.134 (2) for the two twin components.

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

|        | x          | y          | z          | U(eq) | Occ. (<1) |
|--------|------------|------------|------------|-------|-----------|
| O1     | 0.25132 (18)| 0.32563 (17)| 0.92561 (11)| 0.0527 (4) |
| O2     | 0.6827 (3)  | 0.6344 (2)  | 0.60678 (12)| 0.0767 (6) |
| O4     | 0.2571 (2)  | 0.3067 (2)  | 0.67486 (12)| 0.0678 (5) |
| N1     | 0.8600 (2)  | 0.39276 (19)| 0.87300 (13)| 0.0423 (5) |
| H1     | 0.973 (3)   | 0.384 (2)   | 0.8957 (16) | 0.059 (7)* |
| C2     | 0.8111 (3)  | 0.4770 (2)  | 0.78765 (15)| 0.0392 (5) |
| C3     | 0.6490 (3)  | 0.4763 (2)  | 0.74504 (14)| 0.0367 (5) |
| C4     | 0.5269 (3)  | 0.3751 (2)  | 0.78681 (13)| 0.0353 (5) |
| H4     | 0.393905    | 0.425869    | 0.777076    | 0.042*    |
| C5     | 0.4146 (3)  | 0.3084 (2)  | 0.95350 (14)| 0.0356 (5) |
| C6     | 0.4605 (3)  | 0.2630 (2)  | 1.05554 (14)| 0.0428 (5) |
| H6A    | 0.385700    | 0.195992    | 1.080077    | 0.051*    |
| H6B    | 0.421654    | 0.346858    | 1.087912    | 0.051*    |
| C7     | 0.6677 (3)  | 0.1929 (2)  | 1.07869 (14)| 0.0415 (5) |
| C8     | 0.7858 (3)  | 0.2895 (2)  | 1.02836 (14)| 0.0415 (5) |
| H8A    | 0.772188    | 0.373330    | 1.060330    | 0.050*    |
| H8B    | 0.917788    | 0.238044    | 1.031904    | 0.050*    |
| C9     | 0.7317 (3)  | 0.3380 (2)  | 0.92783 (14)| 0.0343 (5) |
| C10    | 0.5631 (2)  | 0.3384 (2)  | 0.89123 (13)| 0.0332 (5) |
| C11    | 0.7238 (3)  | 0.0433 (2)  | 1.04788 (19)| 0.0628 (7) |
| H11A   | 0.646747    | -0.015615   | 1.079713    | 0.094*    |
| H11B   | 0.854309    | 0.000489    | 1.063006    | 0.094*    |
| H11C   | 0.705584    | 0.051153    | 0.981582    | 0.094*    |
| C12    | 0.7000 (4)  | 0.1791 (3)  | 1.18439 (16)| 0.0682 (8) |
| H12A   | 0.667684    | 0.272852    | 1.204085    | 0.102*    |
| H12B   | 0.830489    | 0.134601    | 1.198617    | 0.102*    |
| H12C   | 0.622130    | 0.121222    | 1.216662    | 0.102*    |
| C13    | 0.9461 (3)  | 0.5694 (3)  | 0.75745 (17)| 0.0561 (6) |
| H13A   | 0.928499    | 0.645503    | 0.795594    | 0.084*    |
| H13B   | 0.922670    | 0.609745    | 0.693126    | 0.084*    |
| H13C   | 1.073547    | 0.512033    | 0.764320    | 0.084*    |
| C14    | 0.5891 (3)  | 0.5687 (2)  | 0.65630 (15)| 0.0449 (5) |
| C17    | 0.5638 (3)  | 0.2400 (2)  | 0.73826 (14)| 0.0390 (5) |
| C18    | 0.4292 (3)  | 0.2107 (2)  | 0.68159 (15)| 0.0457 (5) |
| C19    | 0.4721 (4)  | 0.0891 (3)  | 0.63638 (17)| 0.0579 (7) |
| H19    | 0.382214    | 0.071800    | 0.597968    | 0.069*    |
| C20    | 0.6446 (4)  | -0.0051 (3) | 0.64774 (18)| 0.0659 (7) |
### Atomic displacement parameters (Å²)

|     | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-----|------|------|------|------|------|------|
| O1  | 0.0281 (8) | 0.0690 (11) | 0.0605 (10) | −0.0152 (7) | −0.0053 (7) | 0.0009 (8) |
| O2  | 0.0943 (14) | 0.0879 (14) | 0.0531 (11) | −0.0447 (12) | 0.0001 (10) | 0.0141 (10) |
| O4  | 0.0469 (10) | 0.0883 (13) | 0.0737 (12) | −0.0127 (9) | −0.0184 (8) | −0.0322 (10) |
| N1  | 0.0260 (9) | 0.0524 (12) | 0.0487 (11) | −0.0131 (8) | −0.0046 (8) | 0.0003 (9) |
| C2  | 0.0344 (11) | 0.0393 (12) | 0.0436 (13) | −0.0091 (9) | 0.0055 (9) | −0.0055 (10) |
| C3  | 0.0365 (11) | 0.0347 (11) | 0.0378 (12) | −0.0062 (9) | 0.0022 (9) | −0.0060 (9) |
| C4  | 0.0275 (10) | 0.0407 (12) | 0.0367 (12) | −0.0062 (8) | −0.0040 (8) | −0.0039 (9) |
| C5  | 0.0297 (10) | 0.0340 (11) | 0.0438 (12) | −0.0080 (8) | −0.0012 (9) | −0.0066 (9) |
| C6  | 0.0383 (12) | 0.0474 (13) | 0.0429 (13) | −0.0111 (10) | 0.0027 (10) | −0.0057 (10) |
| C7  | 0.0412 (12) | 0.0423 (12) | 0.0394 (12) | −0.0084 (10) | −0.0043 (9) | −0.0016 (10) |
| C8  | 0.0352 (11) | 0.0449 (13) | 0.0447 (13) | −0.0093 (10) | −0.0094 (9) | −0.0054 (10) |
| C9  | 0.0292 (10) | 0.0357 (11) | 0.0386 (12) | −0.0083 (8) | −0.0011 (9) | −0.0061 (9) |
| C10 | 0.0275 (10) | 0.0351 (11) | 0.0367 (11) | −0.0064 (8) | −0.0034 (8) | −0.0053 (9) |
| C11 | 0.0600 (15) | 0.0419 (14) | 0.0818 (19) | −0.0060 (12) | −0.0071 (14) | −0.0017 (13) |
| C12 | 0.0687 (17) | 0.090 (2) | 0.0428 (15) | −0.0203 (15) | −0.0092 (12) | 0.0054 (14) |
| C13 | 0.0487 (14) | 0.0604 (15) | 0.0646 (16) | −0.0262 (12) | 0.0055 (12) | −0.0040 (13) |
| C14 | 0.0553 (15) | 0.0398 (13) | 0.0385 (13) | −0.0086 (11) | 0.0041 (11) | −0.0074 (10) |
| C17 | 0.0411 (12) | 0.0416 (12) | 0.0352 (12) | −0.0130 (10) | −0.0012 (9) | −0.0027 (10) |
| C18 | 0.0457 (13) | 0.0524 (14) | 0.0432 (13) | −0.0196 (11) | −0.0011 (10) | −0.0066 (11) |
Geometric parameters (Å, º)

|     |          |          |          |          |          |          |
|-----|----------|----------|----------|----------|----------|----------|
| C19 | 0.0748 (18) | 0.0606 (16) | 0.0493 (15) | −0.0332 (15) | −0.0029 (13) | −0.0142 (13) |
| C20 | 0.095 (2) | 0.0472 (15) | 0.0603 (17) | −0.0204 (15) | 0.0043 (15) | −0.0175 (13) |
| C21 | 0.0742 (18) | 0.0518 (16) | 0.0733 (19) | 0.0020 (13) | −0.0064 (15) | −0.0167 (14) |
| C22 | 0.0511 (14) | 0.0502 (14) | 0.0563 (15) | −0.0044 (11) | −0.0088 (11) | −0.0130 (12) |
| C23 | 0.0526 (15) | 0.135 (3) | 0.0679 (19) | −0.0298 (17) | −0.0130 (14) | −0.0334 (18) |
| O3  | 0.052 (2) | 0.048 (5) | 0.042 (2) | −0.010 (2) | −0.0128 (16) | 0.003 (3) |
| C15 | 0.067 (3) | 0.060 (3) | 0.041 (2) | −0.015 (2) | −0.0144 (19) | 0.003 (2) |
| C16 | 0.083 (3) | 0.058 (3) | 0.063 (3) | −0.009 (2) | −0.0144 (19) | 0.006 (2) |
| O3A | 0.062 (5) | 0.057 (9) | 0.044 (5) | 0.004 (6) | −0.010 (4) | 0.008 (6) |
| C15A| 0.077 (9) | 0.057 (10) | 0.038 (7) | −0.005 (8) | −0.009 (6) | 0.012 (7) |
| C16A| 0.104 (19) | 0.10 (2) | 0.074 (16) | −0.016 (18) | −0.034 (14) | 0.016 (18) |

C1—C5 1.233 (2) C13—H13A 0.9600
O2—C14 1.200 (2) C13—H13B 0.9600
O4—C18 1.366 (3) C13—H13C 0.9600
O4—C23 1.420 (3) C14—O3 1.382 (10)
N1—H1 0.88 (2) C14—O3A 1.25 (3)
N1—C2 1.386 (3) C15—H15A 1.399 (3)
N1—C9 1.366 (2) C15—H15B 1.378 (3)
N1—C2 1.350 (3) C15—C16 1.388 (3)
C2—C3 1.502 (3) C2—C3 1.520 (3)
C2—C13 1.502 (3) C2—C13 1.502 (3)
C3—C4 1.532 (3) C3—C4 1.547 (3)
C3—C14 1.471 (3) C3—C14 1.474 (3)
C4—H4 0.9800 C20—C21 1.366 (3)
C4—C10 1.516 (3) C20—H20 0.9300
C4—C17 1.529 (3) C20—H20 0.9300
C5—C6 1.502 (3) C21—C22 1.383 (3)
C5—C10 1.446 (3) C21—H21 0.9600
C6—H6A 0.9700 C21—H21 0.9600
C6—H6B 0.9700 C21—H21 0.9600
C6—H6C 0.9700 C21—H21 0.9600
C7—C8 1.525 (3) O3—C15 1.460 (10)
C7—C11 1.528 (3) C15—H15A 0.9700
C7—C12 1.533 (3) C15—H15B 0.9700
C8—H8A 0.9700 C15—H15B 0.9700
C8—H8B 0.9700 C15—H15B 0.9700
C8—H8C 0.9700 C15—H15B 0.9700
C9—C10 1.351 (2) C15—C16 1.501 (8)
C11—H11A 0.9600 C15—H15C 0.9700
C11—H11B 0.9600 C15—H15C 0.9700
C11—H11C 0.9600 C15—H15D 0.9700
C12—H12A 0.9600 C15—H15D 0.9700
C12—H12B 0.9600 C16A—H16E 0.9600
C12—H12C 0.9600 C16A—H16E 0.9600
C18—O4—C23 118.3 (2) H13A—C13—H13B 109.5
| Bond/Distance/Angle | Value   | Bond/Distance/Angle | Value   |
|---------------------|---------|---------------------|---------|
| C2—N1—H1           | 118.3 (15) | H13A—C13—H13C      | 109.5   |
| C9—N1—H1           | 118.9 (15) | H13B—C13—H13C      | 109.5   |
| C9—N1—C2           | 122.25 (17) | O2—C14—C3         | 126.6 (2) |
| N1—C2—C13          | 112.68 (18) | O2—C14—O3         | 123.1 (5) |
| C3—C2—N1           | 119.51 (18) | O2—C14—O3A        | 116.9 (14) |
| C3—C2—C13          | 127.6 (2) | O3—C14—C3         | 110.0 (5) |
| C2—C3—C4           | 120.45 (17) | O3A—C14—C3       | 115.2 (11) |
| C2—C3—C14          | 120.91 (19) | C18—C17—C4       | 122.77 (19) |
| C14—C3—C4          | 118.61 (18) | C22—C17—C4       | 120.36 (18) |
| C3—C4—H4           | 108.2  | C22—C17—C18       | 116.9 (2) |
| C10—C4—C3          | 109.37 (15) | O4—C18—C17       | 116.32 (19) |
| C10—C4—H4          | 108.2  | O4—C18—C19       | 123.2 (2) |
| C10—C4—C17         | 111.63 (16) | C19—C18—C17     | 120.5 (2) |
| C17—C4—C3          | 111.17 (16) | C18—C19—H19     | 119.7   |
| C17—C4—H4          | 108.2  | C20—C19—C18      | 120.6 (2) |
| O1—C5—C6           | 119.83 (18) | C20—C19—H19     | 119.7   |
| O1—C5—C10          | 121.75 (18) | C19—C20—H20   | 119.9   |
| C10—C5—C6          | 118.34 (16) | C19—C20—C21   | 120.2 (2) |
| C5—C6—H6A          | 108.4  | C21—C20—H21   | 120.3   |
| C5—C6—H6B          | 108.4  | C20—C21—C22   | 119.3 (2) |
| C5—C6—C7           | 115.67 (17) | C20—C21—C22   | 120.3   |
| H6A—C6—H6B         | 107.4  | C22—C21—H21   | 120.3   |
| C7—C6—H6A          | 108.4  | C17—C22—C21   | 122.5 (2) |
| C7—C6—H6B          | 108.4  | C17—C22—H22   | 118.7   |
| C6—C7—C11          | 110.41 (18) | C21—C22—H22   | 118.7   |
| C6—C7—C12          | 109.80 (18) | O4—C23—H23A   | 109.5   |
| C8—C7—C6           | 107.87 (16) | O4—C23—H23B   | 109.5   |
| C8—C7—C11          | 110.68 (19) | O4—C23—H23C   | 109.5   |
| C8—C7—C12          | 109.10 (18) | H23A—C23—H23B | 109.5   |
| C11—C7—C12         | 108.95 (19) | H23A—C23—H23C | 109.5   |
| C7—C8—H8A          | 108.9  | H23B—C23—H23C | 109.5   |
| C7—C8—H8B          | 108.9  | C14—C15—O3     | 118.3 (9) |
| H8A—C8—H8B         | 107.7  | C14—C15—H15A | 109.1   |
| C9—C8—C7           | 113.37 (16) | O3—C15—H15B   | 109.1   |
| C9—C8—H8A          | 108.9  | O3—C15—C16   | 112.5 (9) |
| C9—C8—H8B          | 108.9  | H15A—C15—H15B | 107.8   |
| N1—C9—C8           | 116.06 (17) | C16—C15—H15A | 109.1   |
| C10—C9—N1          | 119.62 (18) | C16—C15—H15B | 109.1   |
| C10—C9—C8          | 124.19 (18) | C15—C16—H16A | 109.5   |
| C5—C10—C4          | 120.18 (16) | C15—C16—H16B | 109.5   |
| C9—C10—C4          | 120.76 (17) | C15—C16—H16C | 109.5   |
| C9—C10—C5          | 119.03 (18) | H16A—C16—H16B | 109.5   |
| C7—C11—H11A        | 109.5  | H16A—C16—H16C | 109.5   |
| C7—C11—H11B        | 109.5  | H16B—C16—H16C | 109.5   |
| C7—C11—H11C        | 109.5  | C14—O3A—C15A  | 111 (2)  |
| H11A—C11—H11B      | 109.5  | O3A—C15A—H15C | 111.3   |
| H11A—C11—H11C      | 109.5  | O3A—C15A—H15D | 111.3   |
| H11B—C11—H11C      | 109.5  | H15C—C15A—H15D | 109.2   |
| C7—C12—H12A   | 109.5 | C16A—C15A—O3A   | 102 (2) |
| C7—C12—H12B   | 109.5 | C16A—C15A—H15C  | 111.3  |
| C7—C12—H12C   | 109.5 | C16A—C15A—H15D  | 111.3  |
| H12A—C12—H12B | 109.5 | C15A—C16A—H16D  | 109.5  |
| H12A—C12—H12C | 109.5 | C15A—C16A—H16E  | 109.5  |
| H12B—C12—H12C | 109.5 | C15A—C16A—H16F  | 109.5  |
| C2—C13—H13A   | 109.5 | H16D—C16A—H16E  | 109.5  |
| C2—C13—H13B   | 109.5 | H16D—C16A—H16F  | 109.5  |
| C2—C13—H13C   | 109.5 | H16E—C16A—H16F  | 109.5  |
| O1—C5—C6—C7   | 158.59 (18) | C6—C5—C10—C4   | 175.97 (18) |
| O1—C5—C10—C9  | −7.4 (3)    | C6—C5—C10—C9   | −6.2 (3)    |
| O1—C5—C10—C10 | 170.39 (19) | C6—C7—C8—C9   | −47.3 (2)    |
| O2—C14—O3—C15 | −6 (2)      | C7—C8—C9—N1     | −163.74 (17) |
| O2—C14—O3A—C15A | 10 (4)   | C7—C8—C9—C10   | 20.4 (3)    |
| O4—C18—C19—C20| −178.1 (2)  | C8—C9—C10—C4   | −173.83 (18) |
| N1—C2—C3—C4   | −4.4 (3)    | C8—C9—C10—C5   | 8.4 (3)     |
| N1—C2—C3—C14  | 177.57 (19) | C9—N1—C2—C3   | −17.4 (3)   |
| N1—C9—C10—C4  | 10.5 (3)    | C9—N1—C2—C3   | 158.14 (19) |
| N1—C9—C10—C5  | −167.32 (18) | C10—C4—C17—C18 | 125.8 (2)   |
| C2—N1—C9—C8   | −161.64 (19) | C10—C4—C17—C22 | −55.3 (2)   |
| C2—N1—C9—C10  | 14.4 (3)    | C10—C5—C6—C7   | −24.7 (3)   |
| C2—C3—C4—C10  | 25.1 (3)    | C11—C7—C8—C9   | 73.6 (2)    |
| C2—C3—C4—C17  | −98.6 (2)   | C12—C7—C8—C9   | −166.52 (19) |
| C2—C3—C14—O2  | 11.7 (3)    | C13—C2—C3—C4   | −179.3 (2)  |
| C2—C3—C14—O3  | −174.2 (9)  | C13—C2—C3—C4   | 2.7 (3)     |
| C2—C3—C14—O3A | −155 (3)    | C14—C3—C4—C10  | −156.85 (17) |
| C3—C4—C10—C5  | 149.48 (17) | C14—C3—C4—C17  | 79.4 (2)    |
| C3—C4—C10—C9  | −28.3 (2)   | C14—O3—C15—C16 | −93.5 (15)  |
| C3—C4—C17—C18 | −111.8 (2)  | C14—O3A—C15A—C16A | 179 (5)   |
| C3—C4—C17—C22 | 67.1 (2)    | C17—C4—C10—C5  | −87.1 (2)   |
| C3—C14—O3—C15 | 179.4 (11)  | C17—C4—C10—C9  | 95.2 (2)    |
| C3—C14—O3A—C15A | 178 (2) | C17—C18—C19—C20 | 1.2 (3) |
| C4—C3—C14—O2  | −166.3 (2)  | C18—C17—C22—C21 | 0.4 (3) |
| C4—C3—C14—O3  | 7.7 (9)     | C18—C19—C20—C21 | −0.2 (4) |
| C4—C3—C14—O3A | 27 (3)      | C19—C20—C21—C22 | −0.7 (4) |
| C4—C17—C18—O4 | −3.0 (3)    | C20—C21—C22—C17 | 0.5 (4) |
| C4—C17—C18—C19| 177.7 (2)   | C22—C17—C18—O4  | 178.08 (19) |
| C5—C6—C7—C8   | 50.3 (2)    | C22—C17—C18—C19 | −1.3 (3) |
| C5—C6—C7—C11  | −70.8 (2)   | C23—O4—C18—C17  | 174.8 (2) |
| C5—C6—C7—C12  | 169.07 (19) | C23—O4—C18—C19  | −5.8 (3) |

**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| N1—H1···O1i | 0.88 (2) | 2.01 (2) | 2.870 (2) | 165 (2) |
| C13—H13B···O2 | 0.96 | 2.13 | 2.846 (3) | 131 |
C13—H13C···O4i 0.96 2.59 3.300 (3) 131
C23—H23A···O2ii 0.96 2.57 3.492 (3) 161

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

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

Crystal data

C22H27NO4

F(000) = 1584
Mr = 369.44

P21/n

a = 15.3492 (15) Å
b = 14.0314 (14) Å
c = 18.3862 (18) Å
β = 90.0834 (17)°

V = 3959.8 (7) Å3
Z = 8

F(000) = 1584
Dx = 1.239 Mg m−3
Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 9980 reflections

θ = 2.3–26.4°
μ = 0.09 mm−1

T = 120 K
Rod, colourless
0.35 × 0.15 × 0.14 mm

Data collection

Bruker APEXII CCD
diffractometer

θmax = 26.4°, θmin = 1.3°

h = −19→19
k = −17→17
l = −22→22

66519 measured reflections
8085 independent reflections
7121 reflections with I > 2σ(I)

Refinement

Refinement on F2

Least-squares matrix: full

R[F2 > 2σ(F2)] = 0.039
wR(F2) = 0.093
S = 1.04

8085 reflections
536 parameters
39 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/[σ2(Fo2) + (0.0433P)2 + 1.0284P]

where P = (Fo2 + 2Fc2)/3

(Δ/σ)max = 0.001
Δρmax = 0.33 e Å−3
Δρmin = −0.30 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.

Refinement. Refined as a 2-component twin. Application of the twin law (-1, 0, 0, -1, 0, 0, 1) yielded a twin domain ratio of 0.6938 (8):0.3062 (8).

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

|    | x    | y    | z    | Ueq  | Occ. (<1) |
|----|------|------|------|------|-----------|
| O1A| 0.45938 (8) | 1.14027 (8) | 0.37758 (7) | 0.0261 (3) |
| O2A| 0.83266 (9) | 0.94867 (10) | 0.38491 (8) | 0.0353 (3) |
| O3A| 0.76656 (8) | 1.07646 (9) | 0.33709 (7) | 0.0239 (3) |
| O4A| 0.58302 (9) | 1.01706 (9) | 0.04318 (7) | 0.0279 (3) |
| N1A| 0.57551 (10) | 0.83505 (11) | 0.40985 (8) | 0.0195 (3) |
| Atom  | x        | y        | z        | U_eq |
|-------|----------|----------|----------|------|
| H1A   | 0.5659 (13) | 0.7789 (15) | 0.4186 (11) | 0.023 (5)* |
| C2A   | 0.66070 (11) | 0.86446 (12) | 0.39877 (9) | 0.0196 (4) |
| C3A   | 0.67643 (11) | 0.95409 (12) | 0.37482 (9) | 0.0186 (4) |
| C4A   | 0.60238 (10) | 1.01965 (12) | 0.35175 (9) | 0.0175 (3) |
| H4A   | 0.616041 | 1.085397 | 0.369398 | 0.021* |
| C5A   | 0.44879 (11) | 1.05602 (12) | 0.39480 (9) | 0.0182 (4) |
| C6A   | 0.36366 (11) | 1.02348 (12) | 0.42708 (10) | 0.0200 (4) |
| H6AA  | 0.315982 | 1.062202 | 0.406008 | 0.024* |
| H6AB  | 0.364850 | 1.035734 | 0.480100 | 0.024* |
| C7A   | 0.34314 (11) | 0.91751 (12) | 0.41443 (9) | 0.0193 (4) |
| C8A   | 0.42224 (11) | 0.85979 (12) | 0.43937 (9) | 0.0186 (3) |
| H8AA  | 0.424860 | 0.860609 | 0.493173 | 0.022* |
| H8AB  | 0.414748 | 0.792748 | 0.423785 | 0.022* |
| C9A   | 0.50663 (11) | 0.89679 (12) | 0.40982 (9) | 0.0170 (3) |
| C10A  | 0.51830 (11) | 0.98787 (12) | 0.38714 (9) | 0.0167 (3) |
| C11A  | 0.32322 (12) | 0.90078 (13) | 0.33413 (10) | 0.0248 (4) |
| H11D  | 0.275190 | 0.942331 | 0.318973 | 0.037* |
| H11E  | 0.306604 | 0.834047 | 0.326715 | 0.037* |
| H11F  | 0.375071 | 0.915231 | 0.305108 | 0.037* |
| C12A  | 0.26398 (12) | 0.88893 (13) | 0.45999 (11) | 0.0266 (4) |
| H12D  | 0.276470 | 0.900163 | 0.511574 | 0.040* |
| H12E  | 0.251289 | 0.821217 | 0.452347 | 0.040* |
| H12F  | 0.213502 | 0.927113 | 0.445243 | 0.040* |
| C13A  | 0.72712 (12) | 0.79058 (13) | 0.41851 (11) | 0.0263 (4) |
| H13D  | 0.752914 | 0.806281 | 0.465804 | 0.039* |
| H13E  | 0.772869 | 0.789171 | 0.381402 | 0.039* |
| H13F  | 0.699027 | 0.727966 | 0.421239 | 0.039* |
| C14A  | 0.76640 (11) | 0.98918 (13) | 0.36709 (9) | 0.0214 (4) |
| C15A  | 0.85044 (12) | 1.11883 (14) | 0.32108 (11) | 0.0289 (4) |
| H15E  | 0.893385 | 1.068708 | 0.308859 | 0.035* |
| H15F  | 0.872177 | 1.154790 | 0.363730 | 0.035* |
| C16A  | 0.83761 (13) | 1.18449 (14) | 0.25765 (12) | 0.0352 (5) |
| H16G  | 0.811091 | 1.149255 | 0.217271 | 0.053* |
| H16H  | 0.894095 | 1.210040 | 0.242322 | 0.053* |
| H16I  | 0.799255 | 1.237092 | 0.271891 | 0.053* |
| C17A  | 0.59364 (10) | 1.02320 (12) | 0.26930 (9) | 0.0177 (4) |
| C18A  | 0.57574 (11) | 0.93988 (12) | 0.23039 (9) | 0.0214 (4) |
| H18A  | 0.565952 | 0.882052 | 0.255969 | 0.026* |
| C19A  | 0.57207 (11) | 0.94030 (13) | 0.15539 (10) | 0.0218 (4) |
| H19A  | 0.560018 | 0.882987 | 0.129776 | 0.026* |
| C20A  | 0.58598 (11) | 1.02449 (13) | 0.11729 (9) | 0.0217 (4) |
| C21A  | 0.60189 (11) | 1.10830 (13) | 0.15485 (10) | 0.0232 (4) |
| H21A  | 0.610207 | 1.166456 | 0.129332 | 0.028* |
| C22A  | 0.60553 (11) | 1.10619 (12) | 0.23063 (10) | 0.0216 (4) |
| H22A  | 0.616536 | 1.163699 | 0.256321 | 0.026* |
| C23A  | 0.58707 (15) | 1.10334 (15) | 0.00256 (11) | 0.0359 (5) |
| H23D  | 0.581901 | 1.088987 | −0.049428 | 0.054* |
| H23E  | 0.642866 | 1.135061 | 0.011879 | 0.054* |
| Atom | x     | y     | z     | U ‖  | U ‖  |
|------|-------|-------|-------|------|------|
|     |       |       |       |      |      |
| H23F | 0.539242 | 1.145358 | 0.017281 | 0.054* |
| O1B  | 0.53248 (9) | 0.63931 (8) | 0.41653 (7) | 0.0275 (3) |
| O2B  | 0.16407 (8) | 0.44710 (11) | 0.34002 (8) | 0.0367 (3) |
| O4B  | 0.45174 (10) | 0.69033 (9) | 0.07234 (7) | 0.0325 (3) |
| N1B  | 0.41867 (10) | 0.33580 (11) | 0.37064 (9) | 0.0232 (3) |
| H1B  | 0.4275 (14) | 0.2749 (16) | 0.3763 (12) | 0.037 (6)* |
| C2B  | 0.33400 (11) | 0.36815 (12) | 0.36142 (10) | 0.0224 (4) |
| C3B  | 0.31849 (11) | 0.46259 (13) | 0.35623 (10) | 0.0226 (4) |
| C4B  | 0.39216 (11) | 0.53471 (12) | 0.35400 (10) | 0.0201 (4) |
| H4B  | 0.375782 | 0.589307 | 0.386149 | 0.024* |
| C5B  | 0.54390 (12) | 0.55231 (12) | 0.41031 (9) | 0.0207 (4) |
| C6B  | 0.62933 (12) | 0.50822 (13) | 0.43392 (10) | 0.0236 (4) |
| H6BA | 0.629257 | 0.502553 | 0.487587 | 0.028* |
| H6BB | 0.677155 | 0.552131 | 0.420484 | 0.028* |
| C7B  | 0.64891 (12) | 0.41011 (13) | 0.40149 (10) | 0.0223 (4) |
| C8B  | 0.56843 (11) | 0.34979 (12) | 0.41231 (10) | 0.0221 (4) |
| H8BA | 0.576211 | 0.287574 | 0.385247 | 0.026* |
| H8BB | 0.562928 | 0.332075 | 0.464561 | 0.026* |
| C9B  | 0.48608 (11) | 0.39520 (12) | 0.38717 (10) | 0.0195 (4) |
| C10B | 0.47532 (11) | 0.49112 (12) | 0.38389 (10) | 0.0190 (4) |
| C11B | 0.67057 (13) | 0.41894 (14) | 0.32069 (10) | 0.0290 (4) |
| H11A | 0.681145 | 0.355422 | 0.300374 | 0.044* |
| H11B | 0.722849 | 0.458254 | 0.314753 | 0.044* |
| H11C | 0.621608 | 0.448806 | 0.295120 | 0.044* |
| C12B | 0.72593 (12) | 0.36470 (15) | 0.44191 (12) | 0.0314 (5) |
| H12A | 0.711607 | 0.358440 | 0.493620 | 0.047* |
| H12B | 0.777587 | 0.405106 | 0.436484 | 0.047* |
| H12C | 0.737796 | 0.301528 | 0.421460 | 0.047* |
| C13B | 0.26813 (12) | 0.28863 (14) | 0.35968 (12) | 0.0323 (5) |
| H13A | 0.297954 | 0.227423 | 0.365980 | 0.048* |
| H13B | 0.237582 | 0.289167 | 0.312845 | 0.048* |
| H13C | 0.226000 | 0.297564 | 0.399095 | 0.048* |
| C14B | 0.22780 (13) | 0.49593 (14) | 0.34891 (12) | 0.0317 (4) |
| C17B | 0.40645 (11) | 0.57381 (12) | 0.27734 (10) | 0.0204 (4) |
| C18B | 0.41311 (12) | 0.51382 (13) | 0.21751 (10) | 0.0235 (4) |
| H18B | 0.407494 | 0.446967 | 0.224204 | 0.028* |
| C19B | 0.42785 (12) | 0.54948 (13) | 0.14796 (10) | 0.0247 (4) |
| H19B | 0.432202 | 0.507346 | 0.107685 | 0.030* |
| C20B | 0.43611 (11) | 0.64698 (13) | 0.13795 (10) | 0.0231 (4) |
| C21B | 0.42916 (11) | 0.70792 (12) | 0.19706 (10) | 0.0231 (4) |
| H21B | 0.434268 | 0.774830 | 0.190398 | 0.028* |
| C22B | 0.41482 (12) | 0.67106 (12) | 0.26552 (10) | 0.0220 (4) |
| H22B | 0.410556 | 0.713382 | 0.305688 | 0.026* |
| C23B | 0.46826 (19) | 0.62980 (17) | 0.01175 (12) | 0.0469 (6) |
| H23A | 0.481787 | 0.668742 | −0.031018 | 0.070* |
| H23B | 0.416580 | 0.590883 | 0.001799 | 0.070* |
| H23C | 0.517779 | 0.588112 | 0.022755 | 0.070* |
| O3B  | 0.2269 (3) | 0.5956 (3) | 0.3723 (4) | 0.0335 (6) | 0.432 (8) |
### Atomic displacement parameters (Å²)

|         | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|---------|-----|-----|-----|-----|-----|-----|
| O1A     | 0.0244 (6) | 0.0130 (6) | 0.0411 (8) | 0.0011 (5) | 0.0035 (6) | 0.0025 (5) |
| O2A     | 0.0192 (7) | 0.0410 (8) | 0.0458 (9) | 0.0025 (6) | −0.0023 (6) | 0.0152 (7) |
| O3A     | 0.0159 (6) | 0.0237 (7) | 0.0323 (7) | −0.0027 (5) | 0.0006 (5) | 0.0033 (5) |
| O4A     | 0.0322 (7) | 0.0335 (7) | 0.0180 (7) | −0.0002 (6) | −0.0006 (5) | 0.0040 (5) |
| N1A     | 0.0205 (7) | 0.0116 (7) | 0.0264 (8) | 0.0011 (6) | −0.0005 (6) | 0.0012 (6) |
| C2A     | 0.0206 (9) | 0.0202 (9) | 0.0180 (9) | 0.0027 (7) | −0.0015 (7) | −0.0033 (7) |
| C3A     | 0.0174 (8) | 0.0211 (9) | 0.0172 (8) | 0.0029 (7) | −0.0001 (7) | −0.0001 (7) |
| C4A     | 0.0176 (8) | 0.0147 (8) | 0.0201 (9) | −0.0010 (6) | −0.0002 (7) | −0.0001 (7) |
| C5A     | 0.0211 (9) | 0.0153 (8) | 0.0182 (8) | −0.0009 (7) | −0.0017 (7) | −0.0008 (7) |
| C6A     | 0.0211 (9) | 0.0169 (9) | 0.0221 (9) | 0.0026 (7) | 0.0024 (7) | −0.0022 (7) |
| C7A     | 0.0186 (8) | 0.0176 (8) | 0.0216 (9) | −0.0006 (7) | 0.0004 (7) | 0.0010 (7) |
| C8A     | 0.0219 (9) | 0.0146 (8) | 0.0194 (9) | −0.0019 (7) | 0.0000 (7) | −0.0005 (6) |
| C9A     | 0.0210 (8) | 0.0145 (8) | 0.0156 (8) | 0.0015 (7) | −0.0021 (7) | −0.0002 (7) |
| C10A    | 0.0181 (8) | 0.0160 (8) | 0.0161 (8) | 0.0009 (7) | −0.0015 (7) | −0.0010 (7) |
| C11A    | 0.0224 (9) | 0.0259 (10) | 0.0260 (10) | 0.0016 (7) | −0.0045 (7) | −0.0046 (8) |
| C12A    | 0.0227 (9) | 0.0234 (10) | 0.0337 (11) | −0.0014 (8) | 0.0040 (8) | 0.0002 (8) |
| C13A    | 0.0242 (9) | 0.0229 (9) | 0.0325 (11) | 0.0054 (7) | −0.0024 (8) | 0.0009 (8) |
| C14A    | 0.0212 (9) | 0.0249 (9) | 0.0189 (9) | 0.0015 (7) | −0.0019 (7) | −0.0001 (7) |
| C15A    | 0.0172 (9) | 0.0315 (10) | 0.0380 (11) | −0.0060 (8) | 0.0015 (8) | −0.0021 (9) |
| C16A    | 0.0258 (10) | 0.0281 (11) | 0.0518 (13) | −0.0037 (8) | 0.0069 (9) | 0.0071 (10) |
| C17A    | 0.0137 (8) | 0.0190 (9) | 0.0204 (9) | 0.0022 (7) | 0.0005 (7) | 0.0008 (7) |
| C18A    | 0.0221 (9) | 0.0171 (9) | 0.0249 (9) | 0.0007 (7) | 0.0005 (7) | 0.0027 (7) |
| C19A    | 0.0215 (9) | 0.0202 (9) | 0.0236 (9) | 0.0013 (7) | −0.0013 (7) | −0.0018 (7) |
| C20A    | 0.0162 (8) | 0.0305 (10) | 0.0183 (9) | −0.0004 (7) | 0.0003 (7) | 0.0035 (7) |
| C21A    | 0.0209 (9) | 0.0232 (9) | 0.0253 (10) | −0.0046 (7) | −0.0007 (7) | 0.0066 (8) |
| C22A    | 0.0210 (9) | 0.0199 (9) | 0.0240 (9) | −0.0032 (7) | −0.0016 (7) | 0.0012 (7) |
| C23A    | 0.0439 (12) | 0.0408 (12) | 0.0230 (10) | −0.0123 (10) | 0.0000 (9) | 0.0099 (9) |
| O1B     | 0.0316 (7) | 0.0147 (6) | 0.0361 (8) | −0.0032 (5) | 0.0028 (6) | −0.0020 (6) |
| O2B     | 0.0181 (7) | 0.0555 (10) | 0.0366 (8) | −0.0001 (7) | −0.0001 (6) | 0.0014 (7) |
### Geometric parameters (Å, °)

| Bond/Angle | Distance | Angle |
|------------|----------|-------|
| O1A—C5A   | 1.235 (2) |       |
| O2A—C14A  | 1.210 (2) |       |
| O3A—C14A  | 1.343 (2) |       |
| O3A—C15A  | 1.449 (2) |       |
| O4A—C20A  | 1.367 (2) |       |
| O4A—C23A  | 1.424 (2) |       |
| N1A—H1A   | 0.82 (2)  |       |
| N1A—C2A   | 1.386 (2) |       |
| N1A—C9A   | 1.367 (2) |       |
| C2A—C3A   | 1.354 (2) |       |
| C2A—C13A  | 1.498 (2) |       |
| C3A—C4A   | 1.522 (2) |       |
| C3A—C14A  | 1.473 (2) |       |
| C4A—H4A   | 1.0000    |       |
| C4A—C10A  | 1.513 (2) |       |
| C4A—C17A  | 1.523 (2) |       |
| C5A—C6A   | 1.507 (2) |       |
C5A—C10A 1.440 (2) C7B—C12B 1.534 (3)
C6A—H6AA 0.9900 C8B—H8BA 0.9900
C6A—H6AB 0.9900 C8B—H8BB 0.9900
C6A—C7A 1.538 (2) C8B—C9B 1.500 (2)
C7A—C8A 1.529 (2) C9B—C10B 1.357 (2)
C7A—C11A 1.526 (2) C11B—H11A 0.9800
C7A—C12A 1.530 (2) C11B—H11B 0.9800
C8A—H8AA 0.9900 C11B—H11C 0.9800
C8A—H8AB 0.9900 C12B—H12A 0.9800
C8A—C9A 1.498 (2) C12B—H12B 0.9800
C9A—C10A 1.356 (2) C12B—H12C 0.9800
C11A—H11D 0.9800 C13B—H13A 0.9800
C11A—H11E 0.9800 C13B—H13B 0.9800
C11A—H11F 0.9800 C13B—H13C 0.9800
C12A—H12D 0.9800 C14B—O3B 1.464 (5)
C12A—H12E 0.9800 C14B—O3C 1.305 (4)
C12A—H12F 0.9800 C17B—C18B 1.389 (3)
C13A—H13D 0.9800 C17B—C22B 1.388 (2)
C13A—H13E 0.9800 C18B—H18B 0.9500
C13A—H13F 0.9800 C18B—C19B 1.392 (3)
C15A—H15E 0.9900 C19B—H19B 0.9500
C15A—H15F 0.9900 C19B—C20B 1.386 (2)
C15A—C16A 1.499 (3) C20B—C21B 1.387 (3)
C16A—H16G 0.9800 C21B—H21B 0.9500
C16A—H16H 0.9800 C21B—C22B 1.379 (3)
C16A—H16I 0.9800 C22B—H22B 0.9500
C17A—C18A 1.398 (2) C23B—H23A 0.9800
C17A—C22A 1.377 (2) C23B—H23B 0.9800
C18A—H18A 0.9500 C23B—H23C 0.9800
C18A—C19A 1.380 (2) O3B—C15B 1.480 (5)
C19A—H19A 0.9500 C15B—H15A 0.9900
C19A—C20A 1.390 (3) C15B—H15B 0.9900
C20A—C21A 1.385 (3) C15B—C16B 1.495 (7)
C21A—H21A 0.9500 C16B—H16A 0.9800
C21A—C22A 1.395 (3) C16B—H16B 0.9800
C22A—H22A 0.9500 C16B—H16C 0.9800
C23A—H23D 0.9800 O3C—C15C 1.461 (4)
C23A—H23E 0.9800 C15C—H15C 0.9900
C23A—H23F 0.9800 C15C—H15D 0.9900
O1B—C5B 1.239 (2) C15C—C16C 1.454 (6)
O2B—C14B 1.205 (2) C16C—H16D 0.9800
O4B—C20B 1.372 (2) C16C—H16E 0.9800
O4B—C23B 1.424 (3) C16C—H16F 0.9800
C14A—O3A—C15A 117.37 (14) C2B—C3B—C14B 118.97 (17)
C20A—O4A—C23A 117.16 (15) C14B—C3B—C4B 119.29 (15)
C2A—N1A—H1A 119.1 (14) C3B—C4B—H4B 107.9
C9A—N1A—H1A 118.1 (14) C3B—C4B—C17B 111.84 (15)
C9A—N1A—C2A  122.74 (15)  C10B—C4B—C17B  110.35 (14)
N1A—C2A—C13A  113.58 (15)  C10B—C4B—H14B  107.9
C3A—C2A—N1A  119.53 (15)  C10B—C4B—C17B  110.91 (14)
C3A—C2A—C13A  126.84 (16)  C17B—C4B—H14B  107.9
C2A—C3A—C4A  121.22 (15)  O1B—C5B—C6B  119.96 (16)
C2A—C3A—C14A  120.62 (15)  O1B—C5B—C10B  120.96 (16)
C14A—C3A—C4A  118.09 (15)  C10B—C5B—C6B  119.02 (15)
C3A—C4A—H4A  108.1  C5B—C6B—H6BA  108.5
C3A—C4A—C17A  111.21 (14)  C5B—C6B—H6BB  108.5
C10A—C4A—C3A  109.82 (13)  C10B—C5B—C7B  115.26 (15)
C10A—C4A—H4A  108.1  H6BA—C6B—H6BB  107.5
C10A—C4A—C17A  111.34 (14)  C7B—C6B—H6BA  108.5
C17A—C4A—H4A  108.1  C7B—C6B—H6BB  108.5
O1A—C5A—C6A  120.38 (15)  C6B—C7B—C12B  109.67 (16)
O1A—C5A—C10A  120.86 (16)  C8B—C7B—C11B  110.52 (15)
C10A—C5A—C6A  118.72 (14)  C8B—C7B—C12B  110.84 (15)
C5A—C6A—H6AA  108.7  C11B—C7B—C6B  114.03 (15)
C5A—C6A—H6AB  108.7  C11B—C7B—C12B  109.64 (15)
C5A—C6A—C7A  114.27 (14)  C11B—C7B—C12B  109.64 (15)
H6AA—C6A—H6AB  107.6  C7B—C8B—H8BA  109.0
C7A—C6A—H6AA  108.7  C7B—C8B—H8BB  109.0
C7A—C6A—H6AB  108.7  C7B—C8B—H8BB  109.0
C8A—C7A—C6A  107.72 (13)  C9B—C8B—H8BA  112.93 (14)
C8A—C7A—C12A  109.13 (14)  C9B—C8B—H8BB  109.0
C11A—C7A—C6A  109.63 (14)  C10B—C9B—C8B  115.97 (15)
C11A—C7A—C8A  111.51 (14)  C10B—C9B—C8B  120.28 (16)
C11A—C7A—C12A  109.35 (14)  C10B—C9B—C8B  123.67 (16)
C12A—C7A—C6A  109.46 (14)  C5B—C10B—C4B  119.68 (15)
C7A—C8A—H8AA  108.9  C9B—C10B—C4B  121.19 (15)
C7A—C8A—H8AB  108.9  C8B—C10B—C4B  109.0
H8AA—C8A—H8AB  107.7  C5B—C10B—C11B  110.5
C9A—C8A—C7A  113.21 (14)  C7B—C11B—H11A  109.5
C9A—C8A—H8AA  108.9  C7B—C11B—H11B  110.5
C9A—C8A—H8AB  108.9  C7B—C11B—H11C  109.5
N1A—C9A—C8A  116.70 (14)  H11A—C11B—H11B  109.5
C10A—C9A—N1A  119.66 (15)  H11A—C11B—H11C  109.5
C10A—C9A—C8A  123.56 (15)  H11B—C11B—H11C  109.5
C5A—C10A—C4A  118.62 (14)  C7B—C12B—H12A  109.5
C9A—C10A—C4A  121.53 (15)  C7B—C12B—H12B  109.5
C9A—C10A—C5A  119.83 (15)  C7B—C12B—H12C  109.5
C7A—C11A—H11D  109.5  C12A—C12B—H12C  109.5
C7A—C11A—H11E  109.5  H12A—C12B—H12C  109.5
C7A—C11A—H11F  109.5  H12B—C12B—H12C  109.5
H11D—C11A—H11E  109.5  C2B—C13B—H13A  109.5
H11D—C11A—H11F  109.5  C2B—C13B—H13B  109.5
H11E—C11A—H11F  109.5  C2B—C13B—H13C  109.5
C7A—C12A—H12D  109.5  H13A—C13B—H13B  109.5
C7A—C12A—H12E  109.5  H13A—C13B—H13C  109.5
| Bond/Angle | Bond/Angle | Bond/Angle |
|-----------|-----------|-----------|
| C7A—C12A—H12F | 109.5 | H13B—C13B—H13C | 109.5 |
| H12D—C12A—H12E | 109.5 | O2B—C14B—C3B | 126.73 (18) |
| H12D—C12A—H12F | 109.5 | O2B—C14B—O3B | 125.1 (2) |
| H12E—C12A—H12F | 109.5 | O2B—C14B—O3C | 117.4 (2) |
| C2A—C13A—H13D | 109.5 | O3B—C14B—C3B | 106.6 (2) |
| C2A—C13A—H13E | 109.5 | O3C—C14B—C3B | 114.9 (2) |
| C2A—C13A—H13F | 109.5 | C18B—C17B—C4B | 121.57 (15) |
| H13D—C13A—H13E | 109.5 | C22B—C17B—C4B | 120.71 (16) |
| H13D—C13A—H13F | 109.5 | C22B—C17B—C18B | 117.71 (17) |
| H13E—C13A—H13F | 109.5 | C17B—C18B—H18B | 119.3 |
| C2A—C14A—C3A | 127.20 (17) | O2B—C14B—C3B | 125.1 (2) |
| C2A—C14A—C3A | 110.28 (14) | O2B—C14B—O3B | 117.4 (2) |
| O3A—C14A—C3A | 110.3 | O3B—C14B—O3C | 114.9 (2) |
| O3A—C15A—H15E | 110.3 | O3C—C14B—C3B | 114.9 (2) |
| O3A—C15A—H15F | 110.3 | C18B—C17B—C4B | 121.57 (15) |
| O3A—C15A—H15E | 107.13 (15) | C22B—C17B—C4B | 120.71 (16) |
| H15E—C15A—H15F | 108.5 | C22B—C17B—C18B | 117.71 (17) |
| C16A—C15A—H15E | 110.3 | C17B—C18B—C19B | 119.46 (17) |
| C16A—C15A—H15F | 110.3 | C17B—C18B—H18B | 119.3 |
| C16A—C15A—H15E | 109.5 | C17B—C18B—C19B | 121.46 (16) |
| C15A—C16A—H16G | 110.3 | C17B—C18B—H18B | 120.1 |
| C15A—C16A—H16H | 109.5 | C17B—C18B—C19B | 119.3 |
| C15A—C16A—H16I | 109.5 | C18B—C19B—H18B | 120.3 |
| C15A—C16A—H16I | 110.3 | C18B—C19B—C18B | 121.79 (17) |
| C16G—C16A—H16I | 109.5 | C20B—C19B—C18B | 120.1 |
| H16G—C16A—H16I | 109.5 | C20B—C19B—H19B | 120.3 |
| H16H—C16A—H16I | 109.5 | C20B—C21B—C20B | 119.77 (16) |
| C18A—C17A—C4A | 119.95 (15) | C20B—C21B—H21B | 120.1 |
| C22A—C17A—C4A | 122.03 (15) | C20B—C21B—H21B | 120.1 |
| C22A—C17A—C18A | 117.99 (16) | C22B—C21B—H21B | 119.1 |
| C17A—C18A—H18A | 119.5 | C17B—C22B—H22B | 121.79 (17) |
| C19A—C18A—C17A | 121.04 (16) | C17B—C22B—H22B | 119.1 |
| C19A—C18A—C17A | 119.5 | C17B—C22B—H22B | 119.1 |
| C18A—C19A—H19A | 120.0 | C17B—C22B—H22B | 119.1 |
| C18A—C19A—C20A | 120.08 (17) | C18B—C15B—H15A | 110.0 |
| C20A—C19A—H19A | 120.0 | O3B—C15B—C15A | 110.0 |
| O4A—C20A—C19A | 115.63 (16) | O3B—C15B—C15A | 110.0 |
| O4A—C20A—C21A | 124.56 (16) | O3B—C15B—H15B | 108.4 (5) |
| C21A—C20A—H19A | 119.81 (16) | O3B—C15B—H15B | 108.4 |
| C20A—C21A—H21A | 120.4 | C15B—C16B—H16A | 108.4 |
| C20A—C21A—C22A | 119.13 (16) | C15B—C16B—H16A | 109.5 |
| C22A—C21A—H21A | 120.4 | C15B—C16B—H16A | 109.5 |
| C17A—C22A—C21A | 121.92 (17) | C15B—C16B—H16A | 109.5 |
| C17A—C22A—H22A | 119.0 | H16A—C16B—H16C | 108.3 |
| C21A—C22A—H22A | 119.0 | H16B—C16B—H16C | 108.3 |
| C21A—C22A—H22A | 119.0 | H16B—C16B—H16C | 109.5 |
| O4A—C23A—H23D | 109.5 | O4B—C23B—H23A | 109.5 |
| O4A—C23A—H23E | 109.5 | O4B—C23B—H23B | 109.5 |
| O4A—C23A—H23F | 109.5 | O4B—C23B—H23C | 109.5 |
| H23D—C23A—H23E | 109.5 | H23A—C23B—H23B | 109.5 |
| H23D—C23A—H23F | 109.5 | H23A—C23B—H23B | 109.5 |

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H23E—C23A—H23F 109.5
C2B—O4B—C23B 117.05 (15)
C2B—N1B—H1B 118.7 (15)
C9B—N1B—H1B 117.1 (15)
C9B—N1B—C2B 122.57 (15)
N1B—C2B—C13B 112.90 (15)
C3B—C2B—N1B 119.68 (16)
C2B—C2B—C13B 127.41 (17)
C2B—C3B—C4B 121.67 (15)
O1A—C5A—C6A—C7A 153.92 (16)
O1A—C5A—C10A—C4A 106.2 (2)
O1A—C5A—C10A—C9A 176.67 (16)
O4A—C20A—C21A—C22A 178.33 (16)
N1A—C2A—C3A—C4A 6.9 (2)
N1A—C2A—C3A—C14A 176.06 (15)
N1A—C9A—C10A—C4A 8.8 (2)
N1A—C9A—C10A—C5A 172.28 (16)
C2A—N1A—C9A—C14A 176.06 (15)
C2A—N1A—C9A—C10A 106.2 (2)
C2A—C3A—C4A—C10A 22.8 (2)
C2A—C3A—C4A—C17A 100.92 (19)
C2A—C3A—C14A—O2A 5.7 (3)
C2A—C3A—C14A—O3A 174.96 (15)
C3A—C4A—C10A—C5A 157.86 (15)
C3A—C4A—C10A—C9A 23.8 (2)
C3A—C4A—C14A—C10A 10.6 (2)
C3A—C4A—C14A—O2A 22.8 (2)
C3A—C4A—C14A—O3A 174.96 (15)
C4A—C3A—C14A—O2A 5.7 (3)
C4A—C3A—C14A—O3A 174.96 (15)
C5A—C6A—C7A—C8A 51.96 (19)
C5A—C6A—C7A—C11A 69.55 (18)
C5A—C6A—C7A—C12A 170.51 (15)
C6A—C5A—C10A—C4A 177.41 (15)
C6A—C5A—C10A—C9A 0.9 (2)
C6A—C7A—C8A—C9A 48.74 (18)
C7A—C8A—C9A—N1A 160.18 (15)
C7A—C8A—C9A—C10A 23.2 (2)
C8A—C9A—C10A—C4A 174.68 (15)
C8A—C9A—C10A—C5A 3.6 (3)
C9A—N1A—C2A—C3A 11.6 (2)
C9A—N1A—C2A—C13A 166.11 (2)
C10A—C4A—C17A—C18A 62.3 (2)
C10A—C4A—C17A—C22A 119.77 (17)
C10A—C5A—C6A—C7A 28.5 (2)
C11A—C7A—C8A—C9A 71.59 (18)
\[C12A-C7A-C8A-C9A -167.50 (14)\]
\[C10B-C4B-C17B-C22B -103.88 (18)\]
\[C13A-C2A-C3A-C14A -1.3 (3)\]
\[C11B-C7B-C8B-C9B -70.53 (19)\]
\[C14A-O3A-C15A-C16A 151.27 (16)\]
\[C14B-O3B-C15B-C16B -91.8 (6)\]
\[C15A-O3A-C14A-O2A 4.7 (3)\]
\[C14B-O3B-C15B-C16B 173.67 (18)\]
\[C17A-C4A-C10A-C5A -78.52 (19)\]
\[C17B-C4B-C10B-C5B 76.8 (2)\]

**Hydrogen-bond geometry (Å, °)**

| D—H···A     | D—H  | H···A   | D···A   | D—H···A |
|-------------|------|--------|--------|---------|
| N1A—H1A···O1B | 0.82 (2) | 2.02 (2) | 2.827 (2) | 167 (2) |
| N1B—H1B···O1A' | 0.87 (2) | 1.95 (2) | 2.8167 (19) | 172 (2) |

Symmetry code: (i) x, y−1, z.

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

**Crystal data**

\[C_{21}H_{25}NO_{5}\]

\[M_r = 371.42\]

Monoclinic, \(P2_1/n\)

\[a = 9.2745 (3) \text{ Å}\]

\[b = 22.1655 (7) \text{ Å}\]

\[c = 11.3475 (4) \text{ Å}\]

\[\beta = 108.2014 (17)°\]

\[V = 2216.03 (13) \text{ Å}^3\]

\[Z = 4\]

\[D_r = 1.113 \text{ Mg m}^{-3}\]

Mo Kα radiation, \(\lambda = 0.71073 \text{ Å}\)

Cell parameters from 9215 reflections

θ = 2.5–28.3°

θ max = 28.4°, θ min = 2.5°

\[h = -12 \rightarrow 12\]

\[k = -29 \rightarrow 29\]

\[l = -15 \rightarrow 15\]

4263 reflections with \(I > 2\sigma(I)\)

\(R_{int} = 0.046\)

θ min = 28.4°, θ min = 2.5°

\(h = -12 \rightarrow 12\)

\(k = -29 \rightarrow 29\)

5517 independent reflections

**Data collection**

Bruker SMART BREEZE CCD diffractometer

2 kW sealed X-ray tube

\(\varphi\) and \(\omega\) scans

40175 measured reflections

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Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.123$

$S = 1.04$

5517 reflections

260 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

$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.7593P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\Delta/\sigma)_{\text{max}} < 0.001$

$\rho_{\text{max}} = 0.41 \text{ e Å}^{-3}$

$\rho_{\text{min}} = -0.21 \text{ e Å}^{-3}$

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.

Refinement. Disordered hexanes molecules were identified in the final stage of refinement. The disorder of the hexanes was dealt with by application of the Olex2/smbx_masks (Rees, et al., 2005), which allows for the mathematical compensation of the electron contribution of disordered solvent contained in the voids to the calculated diffraction intensities.

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

|     | x      | y      | z      | Uiso*/Ueq |
|-----|--------|--------|--------|-----------|
| O1  | 1.16874(11)| 0.16574(4)| 0.51737(9)| 0.0186(2) |
| O2  | 0.97871(12)| 0.34503(5)| 0.68766(9)| 0.0208(2) |
| O4  | 0.45936(11)| 0.14086(5)| 0.41764(10)| 0.0240(2) |
| O5  | 0.49133(12)| 0.12980(5)| 0.65976(10)| 0.0218(2) |
| O3  | 0.87314(12)| 0.41878(4)| 0.55338(9)| 0.0216(2) |
| N1  | 0.78891(13)| 0.29217(5)| 0.26502(10)| 0.0156(2) |
| C5  | 1.08644(15)| 0.18180(6)| 0.41329(12)| 0.0149(3) |
| C8  | 0.89609(15)| 0.21511(6)| 0.16440(12)| 0.0160(3) |
| H8A | 0.958420   | 0.240536  | 0.127373  | 0.019*    |
| H8B | 0.792707   | 0.212750  | 0.104128  | 0.019*    |
| C4  | 0.93969(14)| 0.25570(6)| 0.50871(11)| 0.0139(3) |
| H4A | 1.037134   | 0.257551  | 0.578628  | 0.017*    |
| C6  | 1.10852(15)| 0.15446(6)| 0.29827(12)| 0.0174(3) |
| H6A | 1.148756   | 0.113046  | 0.318085  | 0.021*    |
| H6B | 1.185931   | 0.178302  | 0.275254  | 0.021*    |
| C17 | 0.82560(15)| 0.21896(6)| 0.55115(12)| 0.0149(3) |
| C18 | 0.69686(15)| 0.19536(6)| 0.46308(12)| 0.0160(3) |
| H18 | 0.684531   | 0.200209  | 0.377301  | 0.019*    |
| C22 | 0.84222(16)| 0.21058(6)| 0.67665(12)| 0.0177(3) |
| H22 | 0.930164   | 0.225397  | 0.737945  | 0.021*    |
| C20 | 0.60235(15)| 0.15836(6)| 0.62458(13)| 0.0173(3) |
| C9  | 0.88732(14)| 0.24475(6)| 0.28105(12)| 0.0145(3) |
| C2  | 0.79999(15)| 0.33426(6)| 0.35723(12)| 0.0155(3) |
| C19 | 0.58740(15)| 0.16513(6)| 0.49897(12)| 0.0169(3) |
| C3  | 0.88223(15)| 0.31999(6)| 0.47602(12)| 0.0149(3) |
### Atomic displacement parameters (Å²)

|     | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| O1  | 0.0193 (5) | 0.0216 (5) | 0.0118 (5) | 0.0028 (4) | 0.0004 (4) | 0.0001 (4) |
| O2  | 0.0256 (5) | 0.0223 (5) | 0.0116 (5) | 0.0036 (4) | 0.0016 (4) | −0.0014 (4) |
| O4  | 0.0182 (5) | 0.0382 (6) | 0.0143 (5) | −0.0089 (4) | 0.0033 (4) | −0.0007 (5) |
| O5  | 0.0209 (5) | 0.0285 (6) | 0.0175 (5) | −0.0020 (4) | 0.0084 (4) | 0.0032 (4)  |
| O3  | 0.0317 (6) | 0.0170 (5) | 0.0131 (5) | 0.0018 (4)  | 0.0024 (4) | −0.0023 (4) |
| N1  | 0.0169 (5) | 0.0181 (6) | 0.0089 (5) | 0.0018 (4)  | 0.0000 (4) | 0.0000 (4)  |
| C5  | 0.0150 (6) | 0.0160 (6) | 0.0128 (6) | −0.0027 (5) | 0.0031 (5) | −0.0007 (5) |
| C8  | 0.0165 (6) | 0.0198 (7) | 0.0101 (6) | 0.0003 (5)  | 0.0018 (5) | −0.0002 (5) |
| C4  | 0.0132 (6) | 0.0173 (6) | 0.0090 (6) | 0.0014 (5)  | 0.0002 (5) | −0.0004 (5) |
| C6  | 0.0154 (6) | 0.0216 (7) | 0.0135 (6) | 0.0037 (5)  | 0.0020 (5) | −0.0017 (5) |
| C17 | 0.0159 (6) | 0.0148 (6) | 0.0135 (6) | 0.0027 (5)  | 0.0041 (5) | 0.0010 (5)  |
| C18 | 0.0167 (6) | 0.0199 (7) | 0.0109 (6) | 0.0018 (5)  | 0.0035 (5) | 0.0014 (5)  |
| C22 | 0.0197 (6) | 0.0192 (7) | 0.0123 (6) | 0.0011 (5)  | 0.0021 (5) | −0.0009 (5) |
| C20 | 0.0187 (6) | 0.0179 (7) | 0.0163 (7) | 0.0025 (5)  | 0.0068 (5) | 0.0024 (5)  |
| C9  | 0.0134 (6) | 0.0161 (6) | 0.0136 (6) | −0.0030 (5) | 0.0034 (5) | −0.0010 (5) |
| C2  | 0.0152 (6) | 0.0170 (7) | 0.0141 (6) | −0.0008 (5) | 0.0042 (5) | 0.0003 (5)  |
| C19 | 0.0154 (6) | 0.0192 (7) | 0.0142 (6) | 0.0016 (5)  | 0.0021 (5) | 0.0002 (5)  |
### Geometric parameters (Å, °)

| Bond/Angle | Length/Distance | Angle |
|------------|----------------|-------|
| O1—C5      | 1.2413 (16)    |       |
| O2—C14     | 1.2240 (16)    |       |
| O4—C19     | 1.3662 (16)    |       |
| O4—H4      | 0.87 (2)       |       |
| O5—O5      | 1.3701 (17)    |       |
| O5—H5      | 0.85 (2)       |       |
| O3—C14     | 1.4578 (17)    |       |
| N1—C9      | 1.3666 (17)    |       |
| N1—C2      | 1.3814 (17)    |       |
| N1—C1      | 0.876 (18)     |       |
| C5—C6      | 1.5099 (18)    |       |
| C8—H8A     | 0.9900         |       |
| C8—H8B     | 0.9900         |       |
| C8—C9      | 1.5026 (18)    |       |
| C8—C7      | 1.5317 (19)    |       |
| C4—H4A     | 1.0000         |       |
| C4—C17     | 1.5275 (18)    |       |
| C4—C3      | 1.5260 (19)    |       |
| C4—C10     | 1.5153 (18)    |       |
| C6—H6A     | 0.9900         |       |
| C6—H6B     | 0.9900         |       |
| C6—C7      | 1.5336 (18)    |       |
| C17—C18    | 1.3973 (18)    |       |
| C17—C22    | 1.3961 (18)    |       |
| C18—H18    | 0.9500         |       |
| C19—O4—H4  | 108.5 (14)     |       |
| C20—O5—H5  | 109.9 (15)     |       |
| C14—O3—C15 | 116.21 (11)    |       |
| C9—N1—C2   | 122.01 (11)    |       |
| C9—N1—H1   | 117.7 (12)     |       |
| C2—N1—H1   | 116.6 (12)     |       |
| O1—C5—C6   | 119.89 (12)    |       |

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sup-19
| Bond/Distance                  | Value 1 | Value 2 | Value 3 |
|-------------------------------|---------|---------|---------|
| O1—C5—C10                    | 122.08  | (12)    |         |
| C10—C5—C6                    | 118.01  | (11)    |         |
| H8A—C8—H8B                   | 107.7   |         |         |
| C9—C8—H8A                    | 108.9   |         |         |
| C9—C8—H8B                    | 108.9   |         |         |
| C9—C8—C7                     | 113.23  | (11)    |         |
| C7—C8—H8A                    | 108.9   |         |         |
| C7—C8—H8B                    | 108.9   |         |         |
| C17—C4—H4A                   | 108.4   |         |         |
| C3—C4—H4A                    | 108.4   |         |         |
| C3—C4—C17                    | 110.54  | (11)    |         |
| C10—C4—C4—C17                | 112.27  | (11)    |         |
| C10—C4—C3                    | 108.83  | (11)    |         |
| C5—C6—H6A                    | 108.6   |         |         |
| C5—C6—H6B                    | 108.6   |         |         |
| C5—C6—C7                     | 114.61  | (11)    |         |
| H6A—C6—H6B                   | 107.6   |         |         |
| C7—C6—H6A                    | 108.6   |         |         |
| C7—C6—H6B                    | 108.6   |         |         |
| C18—C17—C4                   | 119.69  | (11)    |         |
| C22—C17—C4                   | 121.73  | (12)    |         |
| C22—C17—C18                  | 118.51  | (12)    |         |
| C17—C18—H18                  | 119.5   |         |         |
| C19—C18—C17                  | 120.91  | (12)    |         |
| C19—C18—H18                  | 119.5   |         |         |
| C17—C22—H22                  | 119.8   |         |         |
| C21—C22—C22                  | 120.41  | (12)    |         |
| O5—C20—C19                   | 120.20  | (12)    |         |
| O5—C20—C21                   | 120.70  | (12)    |         |
| C21—C20—C19                  | 119.10  | (13)    |         |
| N1—C9—C8                     | 115.90  | (11)    |         |
| C10—C9—N1                    | 119.90  | (12)    |         |
| C10—C9—C8                    | 124.20  | (12)    |         |
| N1—C2—C13                    | 112.97  | (11)    |         |
| C3—C2—N1                     | 118.61  | (12)    |         |
| C3—C2—C13                    | 128.42  | (13)    |         |
| O4—C19—C18                   | 123.80  | (12)    |         |
| O4—C19—C20                   | 115.81  | (12)    |         |
| C18—C19—C20                  | 120.38  | (12)    |         |
| O1—C5—C6—C7                  | 150.87  | (13)    | 0.8     |
| O1—C5—C10—C4                 | −4.0    | (2)     | −17.94  |
| O1—C5—C10—C9                 | 178.22  | (13)    | 161.87  |
| O5—C20—C19—O4                | −1.13   | (19)    | −47.01  |
| O5—C20—C19—C18               | 178.15  | (13)    | −165.35 |
| O5—C20—C21—C22               | −178.88 | (13)    | 73.93   |
N1—C9—C10—C5  \ -173.59 (12) 
N1—C9—C10—C4  \ 8.57 (19) 
N1—C2—C3—C4  \ -9.26 (19) 
N1—C2—C3—C14  \ 174.56 (12) 
C5—C6—C7—C8  \ 53.26 (15) 
C5—C6—C7—C12  \ 171.44 (12) 
C5—C6—C7—C11  \ -67.84 (15) 
C8—C9—C10—C5  \ 5.3 (2) 
C8—C9—C10—C4  \ -172.52 (12) 
C4—C17—C18—C19  \ -176.06 (12) 
C17—C4—C3—C14  \ 84.38 (13) 
C17—C4—C3—C10  \ -86.21 (14) 
C17—C4—C3—C2  \ 91.60 (15) 
C17—C18—C19—O4  \ -179.79 (13) 
C17—C18—C19—C20  \ 1.0 (2) 
C17—C22—C21—C20  \ 0.5 (2) 
C18—C17—C22—C21  \ -1.6 (2) 

Hydrogen-bond geometry (\AA, °)

| D—H  | H···A  | D···A  | D—H···A   |
|------|-------|-------|-----------|
| N1—H1···O1i | 0.876 (18) | 1.971 (19) | 2.8378 (15) | 169.8 (16) |
| O4—H4···O2i | 0.87 (2) | 1.82 (2) | 2.6894 (14) | 175 (2) |
| O5—H5···O1ii | 0.85 (2) | 2.33 (2) | 3.0293 (14) | 140 (2) |

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