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# Ethyl 4-oxo-8-trifluoromethyl-1,4-dihydroquinoline-3-carboxylate

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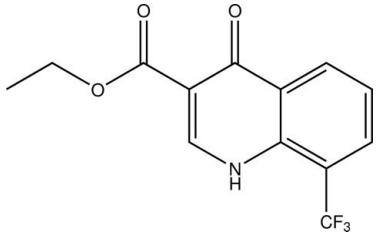
Key indicators: single-crystal X-ray study; $T$ = 200 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.040; $wR$ factor = 0.116; data-to-parameter ratio = 16.1.

The asymmetric unit of the title compound, $C_{13}H_{10}F_3NO_3$, contains two independent molecules with similar conformations. In the crystal, N—H···O hydrogen bonds link alternating independent molecules into chains in [$\bar{1}$10]. In the chain, the quinoline planes of the independent molecules are almost perpendicular to each other, forming a dihedral angle of 89.8 (1)°. $\pi$–$\pi$ interactions between the aromatic rings of quinoline bicycles related by inversion centres [for two independent centrosymmetric dimers, the shortest centroid–centroid distances are 3.495 (1) and 3.603 (1) Å] link the hydrogen-bonded chains into layers parallel to (110). Weak C—H···F and C—H···O interactions further consolidate the crystal packing.

## Related literature

For background information about the pharmacological properties of quinoline derivatives, see: Holla *et al.* (2006); Bekhit *et al.* (2004); Kaur *et al.* (2010); Isloor *et al.* (2009); Vijesh *et al.* (2011). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995). For the synthesis of the title compound, see: Thomas *et al.* (2011).




## Experimental

### Crystal data

$C_{13}H_{10}F_3NO_3$
$M_r$ = 285.22
Triclinic, $P\bar{1}$
$a$ = 9.8248 (3) Å
$b$ = 11.0222 (3) Å
$c$ = 12.3450 (4) Å
$\alpha$ = 72.934 (1)°
$\beta$ = 74.167 (1)°
$\gamma$ = 74.059 (1)°
$V$ = 1201.67 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.14 mm$^{-1}$
$T$ = 200 K
0.53 × 0.38 × 0.32 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.928, $T_{max}$ = 0.956
21419 measured reflections
5963 independent reflections
5051 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.116
$S$ = 1.04
5963 reflections
371 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.39 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O21$^{i}$ | 0.892 (19) | 1.875 (19) | 2.6588 (13) | 145.5 (16) |
| N2—H2···O11$^{ii}$ | 0.851 (18) | 2.011 (17) | 2.7178 (13) | 139.9 (16) |
| N2—H2···O12$^{ii}$ | 0.851 (18) | 2.487 (17) | 3.0380 (15) | 123.2 (14) |
| C212—H21*B*···F22$^{iii}$ | 0.99 | 2.46 | 3.0909 (18) | 121 |
| C204—H204···O13$^{iv}$ | 0.95 | 2.60 | 3.4691 (18) | 153 |

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x+1, y, z$; (iv) $-x, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5354).

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# supporting information

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## Ethyl 4-oxo-8-trifluoromethyl-1,4-dihydroquinoline-3-carboxylate

**B. Garudachari, Arun M. Islor, M. N. Satyanarayan, Thomas Gerber, Eric Hosten and Richard Betz**

### S1. Comment

Quinoline derivatives constitute an important class of compounds that are widely found in plants. A number of synthetic analogues have been developed over the years. Some of them exhibit remarkable effects such as antimicrobial, anti-inflammatory and antimalarial (Holla *et al.*, 2006; Bekhit *et al.*, 2004; Kaur *et al.*, 2010). This follows a broader trend that shows nitrogen-containing heterocycles to be among pharmaceutically active and interesting compounds (Isloor *et al.*, 2009; Vijesh *et al.*, 2011) which justifies our continuing efforts in designing novel heterocyclic molecules of biological importance and study their respective molecular and crystal structure.

The title compound is a derivative of 1,4-dihydroquinoline and does not adopt its aromatic tautomeric form as a quinoline derivative. There are two independent molecules in the asymmetric unit (Fig. 1).

In the crystal, classical N—H···O hydrogen bonds (Table 1) link the alternating independent molecules into chains in [-110] (Fig. 2). In the chain, the quinoline planes of independent molecules are almost perpendicular to each other forming a dihedral angle of 89.8 (1)°. The *π*–*π* interactions between the aromatic rings of the quinoline bicycles related by inversion centres [for two independent centrosymmetric dimers the shortest intercentroid distances are 3.495 (1) and 3.603 (1) Å, respectively] link hydrogen-bonded chains into layers parallel to the (110) plane. Weak intermolecular C–H···F contacts are observed next to intermolecular C–H···O contacts (Table 1). In every case, the range of these contacts falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. While the C–H···O contacts stem from one of the hydrogen atoms on the phenyl moiety bearing the trifluoromethyl substituent and apply the ethereal oxygen atom as acceptor, the classical hydrogen bonds invariably have double bonded oxygen atoms as acceptors. These hydrogen bonds intermittently connect the two different molecules present in the asymmetric unit into chains along [-110] and show bifurcation between the two double bonded oxygen atoms in one case. In total, these contacts connect the molecules to planes parallel to *ab*. In terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the descriptor for the classical hydrogen bonds is *DDD* on the unary level (taking into account the bifurcation). The descriptor for the C–H···O contacts is *D* while a $C^{1}_{1}(11)$ descriptor is found for the C–H···F contacts on the same level.

### S2. Experimental

Diethyl({[3-(trifluoromethyl)phenyl]amino}methylene)malonate (10.0 g, 0.030 mol) and Dowtherm (100 ml) were heated to 250 °C for 5 h. The reaction mixture was then cooled to 25 °C and stirred in *n*-hexane (150 ml) for 10 min. The solid product obtained was filtered, dried and recrystallized from ethanol, yield: 8.0 g (93.0%) (Thomas *et al.*, 2011).

### S3. Refinement

C-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic and vinylic carbon atoms and C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with $U$(H) set to 1.2$U_{eq}$(C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the *SHELX* program suite (Sheldrick, 2008)), with $U$(H) set to 1.5$U_{eq}$(C). Both nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

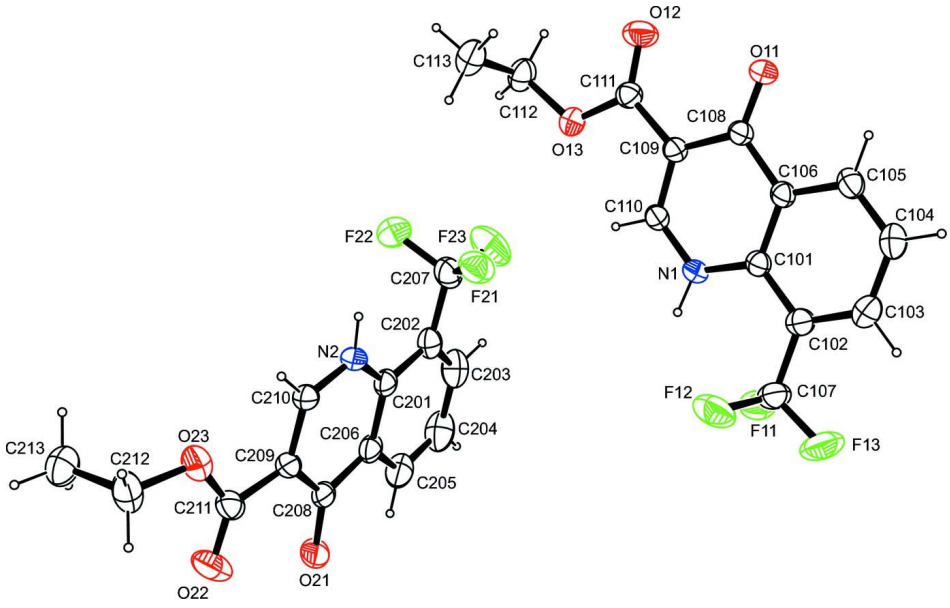


**Figure 1**

Two independent molecules of the title compound, with atom labels and anisotropic displacement ellipsoids drawn at the 50% probability level.

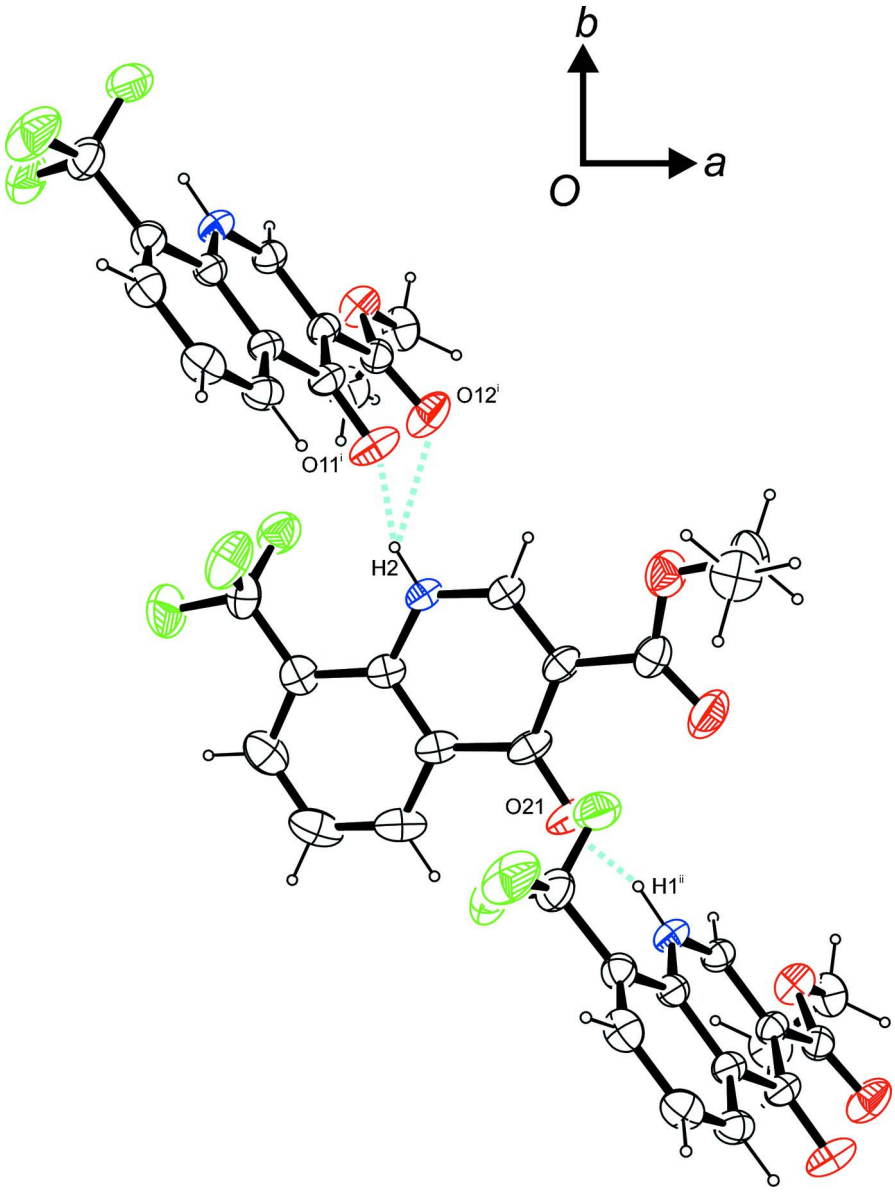


**Figure 2**

A portion of the crystal packing viewed down the *c* axis. Dashed lines denote classical N–H···O hydrogen bonds. Symmetry codes: (i) -*x*, -*y* + 1, -*z* + 1; (ii) -*x* + 1, -*y*, -*z* + 1.

### Ethyl 4-oxo-8-trifluoromethyl-1,4-dihydroquinoline-3-carboxylate

*Crystal data*

$C_{13}H_{10}F_3NO_3$
$M_r$ = 285.22
Triclinic, $P\overline{1}$
Hall symbol: -P 1
*a* = 9.8248 (3) Å
*b* = 11.0222 (3) Å
*c* = 12.3450 (4) Å
*α* = 72.934 (1)°
*β* = 74.167 (1)°
*γ* = 74.059 (1)°
*V* = 1201.67 (6) Å$^3$
*Z* = 4
*F*(000) = 584
$D_x$ = 1.577 Mg m$^{-3}$
Melting point = 570–568 K
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9882 reflections
*θ* = 2.5–28.3°

$\mu$ = 0.14 mm$^{-1}$
$T$ = 200 K

Platelet, colourless
0.53 × 0.38 × 0.32 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.928, $T_{max}$ = 0.956

21419 measured reflections
5963 independent reflections
5051 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016
$\theta_{max}$ = 28.3°, $\theta_{min}$ = 1.8°
$h$ = −13→13
$k$ = −14→14
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.116
$S$ = 1.04
5963 reflections
371 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.3846P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| F11 | 0.33975 (9) | 0.25175 (8) | 0.03791 (8) | 0.0439 (2) |
| F12 | 0.44442 (10) | 0.35929 (10) | 0.09612 (10) | 0.0568 (3) |
| F13 | 0.47655 (10) | 0.37218 (10) | −0.08575 (9) | 0.0631 (3) |
| F21 | 0.16132 (9) | 0.25934 (8) | 0.55061 (8) | 0.0470 (2) |
| F22 | 0.05981 (10) | 0.16771 (11) | 0.71858 (8) | 0.0581 (3) |
| F23 | 0.01521 (11) | 0.13966 (11) | 0.56807 (11) | 0.0657 (3) |
| O11 | −0.20937 (11) | 0.70312 (9) | 0.17938 (8) | 0.0405 (2) |
| O12 | −0.33287 (11) | 0.58234 (11) | 0.40381 (10) | 0.0474 (3) |
| O13 | −0.19356 (10) | 0.39636 (9) | 0.48120 (8) | 0.0360 (2) |
| O21 | 0.71392 (13) | −0.18698 (10) | 0.68194 (9) | 0.0488 (3) |
| O22 | 0.83982 (11) | −0.07326 (11) | 0.79574 (11) | 0.0533 (3) |
| O23 | 0.69974 (11) | 0.11050 (11) | 0.84210 (9) | 0.0445 (2) |
| N1 | 0.12165 (11) | 0.38724 (9) | 0.19918 (9) | 0.0270 (2) |
| H1 | 0.190 (2) | 0.3151 (18) | 0.2098 (16) | 0.046 (5)* |
| N2 | 0.38130 (11) | 0.12577 (10) | 0.69417 (9) | 0.0276 (2) |
| H2 | 0.3130 (19) | 0.1915 (17) | 0.7026 (15) | 0.039 (4)* |
| C101 | 0.13071 (12) | 0.48491 (11) | 0.09948 (10) | 0.0248 (2) |
| C102 | 0.25053 (13) | 0.47904 (12) | 0.00530 (11) | 0.0291 (2) |
| C103 | 0.25240 (14) | 0.57880 (13) | −0.09286 (11) | 0.0341 (3) |
| H103 | 0.3331 | 0.5743 | −0.1560 | 0.041* |
| C104 | 0.13755 (15) | 0.68645 (13) | −0.10101 (11) | 0.0345 (3) |
| H104 | 0.1399 | 0.7543 | −0.1695 | 0.041* |

| | | | | |
|---|---|---|---|---|
| C105 | 0.02133 (14) | 0.69401 (11) | −0.00978 (11) | 0.0307 (2) |
| H105 | −0.0566 | 0.7675 | −0.0154 | 0.037* |
| C106 | 0.01622 (12) | 0.59419 (11) | 0.09183 (10) | 0.0251 (2) |
| C107 | 0.37692 (14) | 0.36615 (14) | 0.01239 (12) | 0.0372 (3) |
| C108 | −0.11013 (12) | 0.60598 (11) | 0.18858 (10) | 0.0269 (2) |
| C109 | −0.10586 (12) | 0.49925 (11) | 0.28998 (10) | 0.0255 (2) |
| C110 | 0.00998 (12) | 0.39563 (11) | 0.28906 (10) | 0.0261 (2) |
| H110 | 0.0107 | 0.3260 | 0.3562 | 0.031* |
| C111 | −0.22344 (12) | 0.50028 (11) | 0.39440 (10) | 0.0281 (2) |
| C112 | −0.29520 (15) | 0.38902 (15) | 0.59208 (11) | 0.0383 (3) |
| H11A | −0.2959 | 0.2970 | 0.6318 | 0.046* |
| H11B | −0.3939 | 0.4329 | 0.5794 | 0.046* |
| C113 | −0.25346 (18) | 0.45247 (16) | 0.66662 (13) | 0.0459 (3) |
| H11C | −0.1546 | 0.4106 | 0.6770 | 0.069* |
| H11D | −0.3202 | 0.4435 | 0.7423 | 0.069* |
| H11E | −0.2583 | 0.5448 | 0.6292 | 0.069* |
| C201 | 0.36760 (13) | 0.02791 (11) | 0.65228 (10) | 0.0278 (2) |
| C202 | 0.24340 (14) | 0.03303 (13) | 0.61281 (11) | 0.0333 (3) |
| C203 | 0.23449 (18) | −0.07003 (15) | 0.57567 (13) | 0.0445 (3) |
| H203 | 0.1504 | −0.0669 | 0.5502 | 0.053* |
| C204 | 0.3472 (2) | −0.17898 (15) | 0.57496 (14) | 0.0498 (4) |
| H204 | 0.3396 | −0.2497 | 0.5494 | 0.060* |
| C205 | 0.46903 (18) | −0.18417 (13) | 0.61103 (12) | 0.0423 (3) |
| H205 | 0.5461 | −0.2582 | 0.6093 | 0.051* |
| C206 | 0.48144 (14) | −0.08153 (11) | 0.65054 (10) | 0.0309 (3) |
| C207 | 0.12056 (14) | 0.14904 (15) | 0.61157 (12) | 0.0390 (3) |
| C208 | 0.61343 (14) | −0.09151 (12) | 0.69029 (10) | 0.0322 (3) |
| C209 | 0.61215 (13) | 0.01330 (12) | 0.73845 (10) | 0.0295 (2) |
| C210 | 0.49545 (13) | 0.11609 (11) | 0.73754 (10) | 0.0277 (2) |
| H210 | 0.4959 | 0.1844 | 0.7697 | 0.033* |
| C211 | 0.73085 (13) | 0.00904 (13) | 0.79296 (11) | 0.0341 (3) |
| C212 | 0.79490 (17) | 0.11036 (17) | 0.91340 (13) | 0.0465 (4) |
| H21A | 0.8003 | 0.2007 | 0.9067 | 0.056* |
| H21B | 0.8936 | 0.0623 | 0.8857 | 0.056* |
| C213 | 0.74080 (19) | 0.04817 (17) | 1.03738 (13) | 0.0484 (4) |
| H21C | 0.6426 | 0.0950 | 1.0643 | 0.073* |
| H21D | 0.8048 | 0.0511 | 1.0846 | 0.073* |
| H21E | 0.7395 | −0.0424 | 1.0444 | 0.073* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| F11 | 0.0417 (4) | 0.0334 (4) | 0.0518 (5) | −0.0007 (3) | −0.0053 (4) | −0.0137 (4) |
| F12 | 0.0366 (4) | 0.0627 (6) | 0.0764 (7) | 0.0050 (4) | −0.0282 (5) | −0.0237 (5) |
| F13 | 0.0424 (5) | 0.0589 (6) | 0.0598 (6) | 0.0010 (4) | 0.0196 (4) | −0.0110 (5) |
| F21 | 0.0428 (5) | 0.0386 (4) | 0.0502 (5) | −0.0027 (3) | −0.0098 (4) | −0.0021 (4) |
| F22 | 0.0385 (5) | 0.0789 (7) | 0.0411 (5) | 0.0022 (4) | 0.0011 (4) | −0.0130 (5) |
| F23 | 0.0512 (6) | 0.0676 (7) | 0.0894 (8) | −0.0103 (5) | −0.0422 (6) | −0.0120 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O11 | 0.0428 (5) | 0.0338 (5) | 0.0311 (5) | 0.0145 (4) | −0.0083 (4) | −0.0078 (4) |
| O12 | 0.0306 (5) | 0.0467 (6) | 0.0462 (6) | 0.0050 (4) | 0.0015 (4) | −0.0042 (5) |
| O13 | 0.0353 (5) | 0.0409 (5) | 0.0252 (4) | −0.0031 (4) | −0.0036 (3) | −0.0049 (4) |
| O21 | 0.0574 (6) | 0.0394 (5) | 0.0384 (5) | 0.0243 (5) | −0.0201 (5) | −0.0154 (4) |
| O22 | 0.0336 (5) | 0.0522 (6) | 0.0669 (8) | 0.0066 (5) | −0.0198 (5) | −0.0091 (5) |
| O23 | 0.0421 (5) | 0.0527 (6) | 0.0424 (6) | −0.0029 (4) | −0.0195 (4) | −0.0136 (5) |
| N1 | 0.0258 (5) | 0.0247 (5) | 0.0271 (5) | 0.0029 (4) | −0.0081 (4) | −0.0061 (4) |
| N2 | 0.0264 (5) | 0.0251 (5) | 0.0278 (5) | 0.0028 (4) | −0.0066 (4) | −0.0078 (4) |
| C101 | 0.0260 (5) | 0.0251 (5) | 0.0254 (5) | −0.0036 (4) | −0.0083 (4) | −0.0082 (4) |
| C102 | 0.0270 (5) | 0.0310 (6) | 0.0305 (6) | −0.0051 (4) | −0.0058 (4) | −0.0101 (5) |
| C103 | 0.0346 (6) | 0.0402 (7) | 0.0286 (6) | −0.0128 (5) | −0.0019 (5) | −0.0094 (5) |
| C104 | 0.0448 (7) | 0.0322 (6) | 0.0274 (6) | −0.0126 (5) | −0.0099 (5) | −0.0020 (5) |
| C105 | 0.0381 (6) | 0.0250 (5) | 0.0299 (6) | −0.0034 (4) | −0.0130 (5) | −0.0055 (4) |
| C106 | 0.0283 (5) | 0.0241 (5) | 0.0243 (5) | −0.0021 (4) | −0.0094 (4) | −0.0076 (4) |
| C107 | 0.0269 (6) | 0.0407 (7) | 0.0392 (7) | −0.0036 (5) | −0.0005 (5) | −0.0118 (6) |
| C108 | 0.0285 (5) | 0.0263 (5) | 0.0258 (5) | 0.0023 (4) | −0.0099 (4) | −0.0094 (4) |
| C109 | 0.0253 (5) | 0.0264 (5) | 0.0251 (5) | −0.0016 (4) | −0.0079 (4) | −0.0079 (4) |
| C110 | 0.0274 (5) | 0.0252 (5) | 0.0248 (5) | −0.0017 (4) | −0.0090 (4) | −0.0050 (4) |
| C111 | 0.0260 (5) | 0.0299 (5) | 0.0291 (6) | −0.0049 (4) | −0.0063 (4) | −0.0086 (4) |
| C112 | 0.0366 (7) | 0.0491 (8) | 0.0279 (6) | −0.0163 (6) | −0.0004 (5) | −0.0061 (5) |
| C113 | 0.0509 (8) | 0.0551 (9) | 0.0326 (7) | −0.0138 (7) | −0.0049 (6) | −0.0128 (6) |
| C201 | 0.0341 (6) | 0.0260 (5) | 0.0197 (5) | −0.0044 (4) | −0.0050 (4) | −0.0026 (4) |
| C202 | 0.0383 (6) | 0.0350 (6) | 0.0250 (6) | −0.0102 (5) | −0.0082 (5) | −0.0010 (5) |
| C203 | 0.0595 (9) | 0.0459 (8) | 0.0352 (7) | −0.0221 (7) | −0.0159 (6) | −0.0045 (6) |
| C204 | 0.0807 (12) | 0.0363 (7) | 0.0400 (8) | −0.0201 (7) | −0.0168 (8) | −0.0093 (6) |
| C205 | 0.0650 (9) | 0.0265 (6) | 0.0319 (6) | −0.0031 (6) | −0.0107 (6) | −0.0074 (5) |
| C206 | 0.0424 (7) | 0.0249 (5) | 0.0202 (5) | −0.0009 (5) | −0.0062 (5) | −0.0038 (4) |
| C207 | 0.0313 (6) | 0.0496 (8) | 0.0348 (7) | −0.0095 (6) | −0.0103 (5) | −0.0042 (6) |
| C208 | 0.0381 (6) | 0.0282 (6) | 0.0200 (5) | 0.0072 (5) | −0.0064 (4) | −0.0032 (4) |
| C209 | 0.0283 (5) | 0.0296 (6) | 0.0233 (5) | 0.0018 (4) | −0.0053 (4) | −0.0029 (4) |
| C210 | 0.0279 (5) | 0.0269 (5) | 0.0247 (5) | −0.0012 (4) | −0.0046 (4) | −0.0057 (4) |
| C211 | 0.0295 (6) | 0.0372 (6) | 0.0282 (6) | −0.0037 (5) | −0.0066 (5) | 0.0010 (5) |
| C212 | 0.0445 (8) | 0.0630 (9) | 0.0355 (7) | −0.0223 (7) | −0.0154 (6) | −0.0003 (6) |
| C213 | 0.0564 (9) | 0.0523 (9) | 0.0335 (7) | −0.0136 (7) | −0.0072 (6) | −0.0055 (6) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| F11—C107 | 1.3341 (16) | C108—C109 | 1.4457 (16) |
| F12—C107 | 1.3470 (17) | C109—C110 | 1.3735 (15) |
| F13—C107 | 1.3310 (16) | C109—C111 | 1.4782 (16) |
| F21—C207 | 1.3307 (17) | C110—H110 | 0.9500 |
| F22—C207 | 1.3437 (17) | C112—C113 | 1.498 (2) |
| F23—C207 | 1.3285 (16) | C112—H11A | 0.9900 |
| O11—C108 | 1.2351 (14) | C112—H11B | 0.9900 |
| O12—C111 | 1.2029 (15) | C113—H11C | 0.9800 |
| O13—C111 | 1.3464 (15) | C113—H11D | 0.9800 |
| O13—C112 | 1.4529 (15) | C113—H11E | 0.9800 |
| O21—C208 | 1.2370 (15) | C201—C206 | 1.4027 (16) |

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|---|---|---|---|
| O22—C211 | 1.1994 (16) | C201—C202 | 1.4141 (17) |
| O23—C211 | 1.3495 (18) | C202—C203 | 1.375 (2) |
| O23—C212 | 1.4479 (17) | C202—C207 | 1.4976 (19) |
| N1—C110 | 1.3355 (15) | C203—C204 | 1.393 (2) |
| N1—C101 | 1.3773 (15) | C203—H203 | 0.9500 |
| N1—H1 | 0.892 (19) | C204—C205 | 1.368 (2) |
| N2—C210 | 1.3358 (15) | C204—H204 | 0.9500 |
| N2—C201 | 1.3763 (15) | C205—C206 | 1.4017 (18) |
| N2—H2 | 0.851 (18) | C205—H205 | 0.9500 |
| C101—C106 | 1.4043 (15) | C206—C208 | 1.4737 (18) |
| C101—C102 | 1.4132 (16) | C208—C209 | 1.4420 (18) |
| C102—C103 | 1.3765 (18) | C209—C210 | 1.3727 (15) |
| C102—C107 | 1.4981 (17) | C209—C211 | 1.4815 (17) |
| C103—C104 | 1.3956 (19) | C210—H210 | 0.9500 |
| C103—H103 | 0.9500 | C212—C213 | 1.495 (2) |
| C104—C105 | 1.3712 (18) | C212—H21A | 0.9900 |
| C104—H104 | 0.9500 | C212—H21B | 0.9900 |
| C105—C106 | 1.4044 (16) | C213—H21C | 0.9800 |
| C105—H105 | 0.9500 | C213—H21D | 0.9800 |
| C106—C108 | 1.4757 (16) | C213—H21E | 0.9800 |

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|---|---|---|---|
| C111—O13—C112 | 117.59 (10) | H11C—C113—H11D | 109.5 |
| C211—O23—C212 | 117.55 (12) | C112—C113—H11E | 109.5 |
| C110—N1—C101 | 121.95 (10) | H11C—C113—H11E | 109.5 |
| C110—N1—H1 | 114.9 (12) | H11D—C113—H11E | 109.5 |
| C101—N1—H1 | 123.2 (12) | N2—C201—C206 | 118.05 (11) |
| C210—N2—C201 | 121.93 (10) | N2—C201—C202 | 122.66 (11) |
| C210—N2—H2 | 115.4 (11) | C206—C201—C202 | 119.28 (11) |
| C201—N2—H2 | 122.2 (11) | C203—C202—C201 | 119.74 (13) |
| N1—C101—C106 | 118.41 (10) | C203—C202—C207 | 119.36 (13) |
| N1—C101—C102 | 122.48 (10) | C201—C202—C207 | 120.90 (11) |
| C106—C101—C102 | 119.12 (10) | C202—C203—C204 | 120.80 (14) |
| C103—C102—C101 | 119.82 (11) | C202—C203—H203 | 119.6 |
| C103—C102—C107 | 119.71 (11) | C204—C203—H203 | 119.6 |
| C101—C102—C107 | 120.46 (11) | C205—C204—C203 | 120.02 (13) |
| C102—C103—C104 | 121.00 (12) | C205—C204—H204 | 120.0 |
| C102—C103—H103 | 119.5 | C203—C204—H204 | 120.0 |
| C104—C103—H103 | 119.5 | C204—C205—C206 | 120.81 (13) |
| C105—C104—C103 | 119.78 (11) | C204—C205—H205 | 119.6 |
| C105—C104—H104 | 120.1 | C206—C205—H205 | 119.6 |
| C103—C104—H104 | 120.1 | C205—C206—C201 | 119.33 (13) |
| C104—C105—C106 | 120.70 (11) | C205—C206—C208 | 119.22 (12) |
| C104—C105—H105 | 119.7 | C201—C206—C208 | 121.44 (11) |
| C106—C105—H105 | 119.7 | F23—C207—F21 | 106.70 (11) |
| C101—C106—C105 | 119.58 (11) | F23—C207—F22 | 106.69 (12) |
| C101—C106—C108 | 121.19 (10) | F21—C207—F22 | 105.13 (12) |
| C105—C106—C108 | 119.22 (10) | F23—C207—C202 | 112.96 (13) |
| F13—C107—F11 | 106.66 (11) | F21—C207—C202 | 113.00 (11) |

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| F13—C107—F12 | 106.61 (11) | F22—C207—C202 | 111.81 (11) |
| F11—C107—F12 | 105.45 (12) | O21—C208—C209 | 125.29 (13) |
| F13—C107—C102 | 112.78 (12) | O21—C208—C206 | 119.16 (12) |
| F11—C107—C102 | 113.23 (10) | C209—C208—C206 | 115.54 (10) |
| F12—C107—C102 | 111.58 (11) | C210—C209—C208 | 118.91 (11) |
| O11—C108—C109 | 124.72 (11) | C210—C209—C211 | 119.79 (11) |
| O11—C108—C106 | 119.80 (11) | C208—C209—C211 | 121.25 (11) |
| C109—C108—C106 | 115.48 (10) | N2—C210—C209 | 123.90 (11) |
| C110—C109—C108 | 119.21 (10) | N2—C210—H210 | 118.0 |
| C110—C109—C111 | 119.66 (10) | C209—C210—H210 | 118.0 |
| C108—C109—C111 | 121.13 (10) | O22—C211—O23 | 123.44 (13) |
| N1—C110—C109 | 123.71 (10) | O22—C211—C209 | 125.73 (13) |
| N1—C110—H110 | 118.1 | O23—C211—C209 | 110.82 (10) |
| C109—C110—H110 | 118.1 | O23—C212—C213 | 110.57 (12) |
| O12—C111—O13 | 122.73 (11) | O23—C212—H21A | 109.5 |
| O12—C111—C109 | 125.78 (11) | C213—C212—H21A | 109.5 |
| O13—C111—C109 | 111.49 (10) | O23—C212—H21B | 109.5 |
| O13—C112—C113 | 110.26 (11) | C213—C212—H21B | 109.5 |
| O13—C112—H11A | 109.6 | H21A—C212—H21B | 108.1 |
| C113—C112—H11A | 109.6 | C212—C213—H21C | 109.5 |
| O13—C112—H11B | 109.6 | C212—C213—H21D | 109.5 |
| C113—C112—H11B | 109.6 | H21C—C213—H21D | 109.5 |
| H11A—C112—H11B | 108.1 | C212—C213—H21E | 109.5 |
| C112—C113—H11C | 109.5 | H21C—C213—H21E | 109.5 |
| C112—C113—H11D | 109.5 | H21D—C213—H21E | 109.5 |

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|---|---|---|---|
| C110—N1—C101—C106 | −2.05 (16) | C210—N2—C201—C206 | −3.23 (17) |
| C110—N1—C101—C102 | 177.88 (10) | C210—N2—C201—C202 | 175.92 (11) |
| N1—C101—C102—C103 | 178.98 (11) | N2—C201—C202—C203 | −177.79 (12) |
| C106—C101—C102—C103 | −1.09 (17) | C206—C201—C202—C203 | 1.35 (18) |
| N1—C101—C102—C107 | −2.20 (17) | N2—C201—C202—C207 | 1.81 (18) |
| C106—C101—C102—C107 | 177.73 (11) | C206—C201—C202—C207 | −179.05 (11) |
| C101—C102—C103—C104 | 0.15 (18) | C201—C202—C203—C204 | −0.8 (2) |
| C107—C102—C103—C104 | −178.67 (12) | C207—C202—C203—C204 | 179.55 (13) |
| C102—C103—C104—C105 | 0.53 (19) | C202—C203—C204—C205 | −0.3 (2) |
| C103—C104—C105—C106 | −0.26 (19) | C203—C204—C205—C206 | 0.9 (2) |
| N1—C101—C106—C105 | −178.71 (10) | C204—C205—C206—C201 | −0.4 (2) |
| C102—C101—C106—C105 | 1.35 (16) | C204—C205—C206—C208 | 179.11 (13) |
| N1—C101—C106—C108 | 0.99 (16) | N2—C201—C206—C205 | 178.44 (11) |
| C102—C101—C106—C108 | −178.94 (10) | C202—C201—C206—C205 | −0.74 (18) |
| C104—C105—C106—C101 | −0.69 (17) | N2—C201—C206—C208 | −1.05 (17) |
| C104—C105—C106—C108 | 179.60 (11) | C202—C201—C206—C208 | 179.77 (11) |
| C103—C102—C107—F13 | −4.70 (18) | C203—C202—C207—F23 | −2.68 (18) |
| C101—C102—C107—F13 | 176.48 (11) | C201—C202—C207—F23 | 177.71 (12) |
| C103—C102—C107—F11 | −125.94 (13) | C203—C202—C207—F21 | −123.94 (14) |
| C101—C102—C107—F11 | 55.24 (16) | C201—C202—C207—F21 | 56.46 (16) |
| C103—C102—C107—F12 | 115.27 (14) | C203—C202—C207—F22 | 117.68 (14) |
| C101—C102—C107—F12 | −63.55 (15) | C201—C202—C207—F22 | −61.92 (16) |

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| C101—C106—C108—O11 | −179.90 (11) | C205—C206—C208—O21 | 3.99 (18) |
| C105—C106—C108—O11 | −0.19 (17) | C201—C206—C208—O21 | −176.53 (12) |
| C101—C106—C108—C109 | 0.70 (16) | C205—C206—C208—C209 | −175.03 (11) |
| C105—C106—C108—C109 | −179.60 (10) | C201—C206—C208—C209 | 4.46 (17) |
| O11—C108—C109—C110 | 179.19 (12) | O21—C208—C209—C210 | 177.19 (12) |
| C106—C108—C109—C110 | −1.43 (15) | C206—C208—C209—C210 | −3.86 (16) |
| O11—C108—C109—C111 | −1.12 (18) | O21—C208—C209—C211 | −5.5 (2) |
| C106—C108—C109—C111 | 178.25 (10) | C206—C208—C209—C211 | 173.49 (11) |
| C101—N1—C110—C109 | 1.34 (17) | C201—N2—C210—C209 | 3.95 (18) |
| C108—C109—C110—N1 | 0.50 (17) | C208—C209—C210—N2 | −0.11 (18) |
| C111—C109—C110—N1 | −179.19 (10) | C211—C209—C210—N2 | −177.50 (11) |
| C112—O13—C111—O12 | −3.68 (18) | C212—O23—C211—O22 | −7.8 (2) |
| C112—O13—C111—C109 | 175.91 (10) | C212—O23—C211—C209 | 171.24 (11) |
| C110—C109—C111—O12 | −176.54 (12) | C210—C209—C211—O22 | −177.47 (13) |
| C108—C109—C111—O12 | 3.78 (19) | C208—C209—C211—O22 | 5.2 (2) |
| C110—C109—C111—O13 | 3.89 (15) | C210—C209—C211—O23 | 3.55 (16) |
| C108—C109—C111—O13 | −175.80 (10) | C208—C209—C211—O23 | −173.77 (11) |
| C111—O13—C112—C113 | −90.46 (14) | C211—O23—C212—C213 | −91.90 (16) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O21$^{i}$ | 0.892 (19) | 1.875 (19) | 2.6588 (13) | 145.5 (16) |
| N2—H2···O11$^{ii}$ | 0.851 (18) | 2.011 (17) | 2.7178 (13) | 139.9 (16) |
| N2—H2···O12$^{ii}$ | 0.851 (18) | 2.487 (17) | 3.0380 (15) | 123.2 (14) |
| C212—H21*B*···F22$^{iii}$ | 0.99 | 2.46 | 3.0909 (18) | 121 |
| C204—H204···O13$^{iv}$ | 0.95 | 2.60 | 3.4691 (18) | 153 |

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