Crystal structure, Hirshfeld surface analysis, inter-action energy and DFT calculations and energy frameworks of methyl 6-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate

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In the title compound, C_{12}H_{10}ClNO_{3}, the dihydroquinoline moiety is not planar with a dihedral angle between the two ring planes of 1.61 (6)°. An intramolecular C—H···O hydrogen bond helps to establish the rotational orientation of the carboxyl group. In the crystal, sheets of molecules parallel to (101) are generated by C—H···O and C—H···Cl hydrogen bonds, and are stacked through slipped π-stacking interactions between inversion-related dihydroquinoline units. A Hirshfeld surface analysis of the crystal structure indicates that the most important contributions for the crystal packing are from H···H (34.2%), H···O/O···H (19.9%), H···Cl/Cl···H (12.8%), H···C/C···H (10.3%) and C···C (9.7%) interactions. Computational chemistry indicates that in the crystal, the C—H···Cl hydrogen-bond energy is −37.4 kJ mol⁻¹, while the C—H···O hydrogen-bond energies are −45.4 and −29.2 kJ mol⁻¹. An evaluation of the electrostatic, dispersion and total energy frameworks revealed that the stabilization is dominated via the dispersion energy contribution. Density functional theory (DFT) optimized structures at the B3LYP/6–311 G(d,p) level are compared with the experimentally determined molecular structure in the solid state, and the HOMO—LUMO behaviour was elucidated to determine the energy gap.

1. Chemical context

Over the past few decades, heterocyclic chemistry has received increasing interest because of the pharmacological importance of the majority of heterocyclic compounds, especially N-containing heterocycles such as quinoline derivatives (Filali Baba et al., 2019; Hayani et al., 2021). Quinoline derivatives possess numerous biological properties, including antibacterial (Katoh et al., 2004; Abdel-Wahab et al., 2012), anti-inflammatory (Leatham et al., 1983), antihypertensive (Muruganantham et al., 2004), antibiotic (Mahamoud et al., 2006), anti-HIV (Wilson et al., 1992; Strekowski et al., 1991) and corrosion-inhibitive activities (Filali Baba et al., 2016a,b).
They are also considered to be important scaffolds for the development of new molecules of pharmaceutical interest (Filali Baba et al., 2020; Bouzian et al., 2018).

In a continuation of our research work devoted to the study of O- and N-alkylation reactions involving quinoline derivatives, we report here the synthesis and crystal structure of methyl 6-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate obtained by the alkylation reaction of 6-chloro-2-oxo-1,2-dihydroquinoline-4-carboxylic acid with an excess of methyl iodide as an alkylating reagent in phase transfer catalysis (PTC). The molecular and crystal structure as well as the Hirshfeld surface analysis of the title compound are reported. The results obtained using density functional theory (DFT) calculations, performed at the B3LYP/6-311G(d,p) level, are compared with the experimental results determined from the molecular and crystal structures in the solid state of the title compound, (I).

2. Structural commentary

The bicyclic molecular core is not planar as there is a dihedral angle of 1.61 (6)° between the mean planes of its constituent rings. The dihedral angle between the mean plane of the (C1/N1/C6–C9) ring and the plane defined by atoms C7, C11, O2 and O3 is 4.08 (8)° with the near coplanarity of the carboxyl group and the heterocyclic ring being caused, in part, by the intramolecular C5—H5···O2 hydrogen bond (Table 1, Fig. 1).

3. Supramolecular features

In the crystal, C2—H2···O2iii hydrogen bonds (Table 1) form ribbons of molecules extending along [010], which are further linked into sheets parallel to (101) by C12—H12···O1ii and weak C8—H8···Cl1iv (H···Cl is 0.11 Å less than the sum of the van der Waals radii) hydrogen bonds (Table 1, Fig. 2). The sheets are stacked along the direction of the normal to (101) by slipped π-stacking interactions between inversion-related
Table 1
Hydrogen-bond geometry (Å, °).

|       | D—H · · · A  | D—H  | H · · · A  | D···A  | D—H · · · A  |
|-------|-------------|-------|-----------|--------|-------------|
| C2—H2—O2ii | 0.95      | 2.57  | 3.5146 (16) | 178    |             |
| C5—H5—O2   | 0.95      | 2.19  | 2.8496 (16) | 126    |             |
| C8—H8—Cl1m | 0.95      | 2.84  | 3.7786 (13) | 170    |             |
| C12—H12C—O1ii | 0.98   | 2.36  | 3.0016 (16) | 122    |             |

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

dihydroquinoline moieties [centroid-centroid distance = 3.7140 (7) Å, dihedral angle = 1.61 (6)°, slippage = 1.63 Å] (Fig. 3).

4. Hirshfeld surface analysis
In order to visualize the intermolecular interactions in the crystal of (I), a Hirshfeld surface (HS) analysis (Hirshfeld, 1977) was carried out by using CrystalExplorer17.5 (Turner et al., 2017). In the HS plotted over $d_{norm}$ (Fig. 4a), the white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contact) than the van der Waals radii (Venkatesan et al., 2016). Selected contacts are given in Table 2. The bright-red spots indicate their roles as the respective donors and/or acceptors; they also appear as blue and red regions corresponding to positive and negative potentials on the HS mapped over electrostatic potential (Spackman et al., 2008; Jayatilaka et al., 2005) shown in Fig. 4b. The blue regions indicate a positive electrostatic potential (hydrogen-bond donors), while the red regions indicate a negative electrostatic potential (hydrogen-bond acceptors). The shape-index of the HS is a tool to visualize π–π stacking by the presence of adjacent red and blue triangles: if there are no adjacent red and/or blue triangles, then there are no π–π interactions. Fig. 4c clearly suggests that there are π–π interactions in (I). The overall two-dimensional fingerprint plot is shown in Fig. 5a, and those delineated into H···H, H···O/O···H, H···Cl/Cl···H, H···C/ C···H, C···C, C···O/O···C, C···Cl/Cl···C, O···Cl/Cl···O, O···O, H···N/N···H, N···Cl/Cl···N, C···N/N···C, Cl···Cl and N···O/O···N contacts (McKinnon et al., 2007) are illustrated in Fig. 5b–o, respectively, together with their relative

![Figure 4](image1)

(a) View of the three-dimensional Hirshfeld surface of the title compound, plotted over $d_{norm}$ in the range of −0.2172 to 0.9151 a.u.; (b) view of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential energy in the range −0.0500 to 0.0500 a.u. using the STO-3 G basis set at the Hartree–Fock level of theory; (c) Hirshfeld surface of the title compound plotted over shape-index.

![Figure 5](image2)

The full two-dimensional fingerprint plots for the title compound, showing (a) H···H interactions and delineated into (b) H···H, (c) H···O/O···H, (d) H···Cl/Cl···H, (e) H···C/C···H, (f) C···C, (g) C···O/O···C, (h) C···Cl/Cl···C, (i) O···Cl/Cl···O, (j) O···O, (k) H···N/N···H, (l) N···Cl/Cl···N, (m) C···N/N···C, (n) Cl···Cl and (o) N···O/O···N interactions. The $d_i$ and $d_e$ values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.
contributions to the Hirshfeld surface. The most important interaction is H⋯H, contributing 34.2% to the overall crystal packing, which is reflected in Fig. 5b as widely scattered points of high density due to the large hydrogen content of the molecule with the tip at $d_e = d_l = 1.24 \text{Å}$. The pair of the scattered points of spikes in the fingerprint plot delineated into H⋯O or O⋯H contacts, Fig. 5c, with a 19.9% contribution to the HS has a distribution of points with the tips at $d_e + d_l = 2.28 \text{Å}$. The H⋯Cl or Cl⋯H contacts, Fig. 5d, with a 12.8% contribution to the HS have a symmetric distribution of points with the tips at $d_e + d_l = 2.68 \text{Å}$. In the absence of C—H⋯π interactions, the pair of characteristic wings in the fingerprint plot delineated into H⋯C or C⋯H contacts, Fig. 5e, with a 10.3% contribution to the HS has the tips at $d_e + d_l = 3.01 \text{Å}$. The C⋯C contacts, Fig. 5f, with a 9.7% contribution to the HS have a bullet-shaped distribution of points with the tip at $d_e = d_l = 1.67 \text{Å}$. The C⋯O or O⋯C contacts, Fig. 5g, with a 3.4% contribution to the HS have the tips at $d_e + d_l = 3.32 \text{Å}$ and $d_e + d_l = 3.45 \text{Å}$ for sharp and tiny distributions of points. The symmetric distribution of points of the C⋯Cl or Cl⋯C contacts, Fig. 5h, with a 3.0% contribution to the HS appear as scattered points with a tiny pair of spikes with the tips at $d_e + d_l = 3.48 \text{Å}$. Finally, the contributions of the remaining O⋯Cl or Cl⋯O, O⋯O, H⋯N or N⋯H, N⋯Cl or Cl⋯N, C⋯N or N⋯C, Cl⋯Cl and N⋯O or O⋯N contacts (Fig. 5i–o) are smaller than 3.0% to the HS with low densities of points.

The Hirshfeld surface representations with the function $d_{\text{norm}}$ plotted onto the surface are shown for the H⋯H, H⋯O or O⋯H, H⋯Cl or Cl⋯H, H⋯C or C⋯H and C⋯C interactions in Fig. 6a–e, respectively.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number of H⋯H, H⋯O or O⋯H, H⋯Cl or Cl⋯H and H⋯C or C⋯H interactions suggest that van der Waals interactions play the major role in the crystal packing (Hathwar et al., 2015).

5. Interaction energy calculations

The intermolecular interaction energies were calculated using the CE-B3LYP/6-31G(d,p) energy model available in CrystalExplorer17.5 (Turner et al., 2017), where a cluster of molecules would be needed by applying crystallographic symmetry operations with respect to a selected central molecule within the radius of 3.8 Å by default (Turner et al., 2014). The total intermolecular energy ($E_{\text{tot}}$) is the sum of electrostatic ($E_{\text{ele}}$), polarization ($E_{\text{pol}}$), dispersion ($E_{\text{dis}}$) and exchange-repulsion ($E_{\text{rep}}$) energies (Turner et al., 2015) with scale factors of 1.057, 0.740, 0.871 and 0.618, respectively (Mackenzie et al., 2017). Hydrogen-bonding interaction energies (in kJ mol$^{-1}$) were calculated to be $-10.4$ ($E_{\text{ele}}$), $-1.6$ ($E_{\text{pol}}$), $-51.9$ ($E_{\text{dis}}$), $32.4$ ($E_{\text{rep}}$) and $-37.4$ ($E_{\text{tot}}$) [for the C8⋯H8⋯Cl11$^+$ hydrogen-bonding interaction]. $-0.9$ ($E_{\text{ele}}$), $-2.8$ ($E_{\text{pol}}$), $-84.0$ ($E_{\text{dis}}$), $49.9$ ($E_{\text{rep}}$) and $-45.4$ ($E_{\text{tot}}$) (for C2⋯H2⋯O2$^{ii}$) and $-6.0$ ($E_{\text{ele}}$), $-4.1$ ($E_{\text{pol}}$), $-37.0$ ($E_{\text{dis}}$), $20.2$ ($E_{\text{rep}}$) and $-29.2$ ($E_{\text{tot}}$) (for C12⋯H12C⋯O1$^{ii}$).

Table 2

| Selected interatomic distances (Å) | C1⋯O3 | 3.1903 (10) | H2⋯O2$^{ii}$ | 2.57 |
|-----------------------------------|-------|-------------|--------------|------|
| C1⋯H8$^{iii}$                    | 2.84  | O3⋯H8      | 2.25         |      |
| C2⋯O1                         | 3.0016 (16) | C2⋯H10C | 2.78         |      |
| O2⋯C5                          | 2.8496 (17) | C2⋯H10B  | 2.74         |      |
| O1⋯H10A                       | 2.26  | C1O⋯H2     | 2.46         |      |
| H12C⋯O1$^{ii}$                  | 2.36  | C1⋯H5      | 2.71         |      |
| O2⋯H12A                       | 2.64  | H2⋯H10B    | 2.24         |      |
| O2⋯H5                         | 2.19  | H2⋯H10C    | 2.29         |      |
| O2⋯H12B                       | 2.55  |              |              |      |

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

6. Energy frameworks

Energy frameworks combine the calculation of intermolecular interaction energies with a graphical representation of their magnitude (Turner et al., 2015). Energies between molecular pairs are represented as cylinders joining the centroids of pairs of molecules with the cylinder radius proportional to the relative strength of the corresponding interaction energy. Energy frameworks were constructed for $E_{\text{ele}}$ (red cylinders), $E_{\text{dis}}$ (green cylinders) and $E_{\text{tot}}$ (blue cylinders) (Fig. 7a–c). The evaluation of the electrostatic, dispersion and total energy...
frameworks indicates that the stabilization is dominated by the dispersion energy contributions in (I).

7. DFT calculations

The geometrical parameters and energies of (I) in the gas phase were computed via density functional theory (DFT) using the standard B3LYP functional and 6–311G(d,p) basis-set calculations (Becke, 1993) as implemented in GAUSSIAN 09 (Frisch et al., 2009), see Table 3. The theoretical bond lengths and angles are in good agreement with those based on the X-ray analysis. However, a few differences exists in case of some dihedral angles (N1—C1—C6—C7; C10—N1—C1—C6; O1—C9—N1—C1; O2—C11—C7—C6; O3—C11—C7—C6; C12—O3—C11—C7), because in the DFT calculations there is only one molecule treated in the gas phase whereas in the solid state several molecules interact by hydrogen-bonding interactions (Fig. 2, Table 1). The torsion angles show that the conformation of the molecule in the gas phase has $C_1$ symmetry.

The infrared spectrum of (I) on basis of the B3LYP/6-311G calculation is shown in the supporting information. All harmonic frequencies are positive, demonstrating the minimal signature of (I). The spectrum mainly constitutes 75 vibration

| Bonds/angles     | X-ray     | B3LYP/6-311G(d,p) |
|------------------|-----------|-------------------|
| C2—C1            | 1.4070 (17) | 1.4562            |
| C3—C2            | 1.3547 (18) | 1.3547            |
| C4—C3            | 1.3836 (17) | 1.3933            |
| C5—C4            | 1.3807 (17) | 1.3798            |
| C6—C5            | 1.4098 (16) | 1.4086            |
| C7—C6            | 1.4514 (16) | 1.4562            |
| C8—C7            | 1.3510 (16) | 1.3547            |
| C9—C8            | 1.4513 (17) | 1.4563            |
| N1—C1            | 1.3920 (15) | 1.3914            |
| H2—C2            | 0.95       | 1.07965           |
| H3—C3            | 0.95       | 1.0822            |
| C11—C4           | 1.7397 (13) | 1.7594            |
| H5—C5            | 0.9500     | 1.0777            |
| C11—C7           | 1.5022 (16) | 1.5077            |
| H8—C8            | 0.9500     | 1.0792            |
| O1—C9            | 1.2319 (15) | 1.2227            |
| O2—C11           | 1.2040 (16) | 1.2086            |
| O3—O3            | 1.3525 (15) | 1.3452            |
| C12—O3           | 1.4485 (15) | 1.4400            |
| H12A—C12         | 0.98       | 1.0907            |
| H12B—C12         | 0.98       | 1.0907            |
| H12C—C12         | 0.98       | 1.0872            |
| H10A—C10         | 0.98       | 1.0824            |
| H10B—C10         | 0.98       | 1.0859            |
| H10C—C10         | 0.98       | 1.0924            |
| C3—C2—C1         | 120.15 (11) | 121.15            |
| C4—C3—C2         | 120.29 (12) | 119.41            |
| C5—C4—C3         | 121.22 (12) | 121.07            |
| C6—C5—C4         | 120.00 (11) | 120.57            |
| C7—C6—C5         | 123.66 (11) | 123.69            |
| C8—C7—C6         | 119.52 (11) | 119.54            |
| C9—C8—C7         | 123.22 (11) | 123.86            |
| N1—C1—C6         | 119.77 (10) | 120.37            |
| H2—C2—C1         | 119.9      | 120.30            |
| H3—C3—C4         | 119.9      | 120.32            |
| C11—C4—C5        | 118.82 (10) | 119.62            |
| H5—C5—C6         | 120.00     | 119.03            |
| C11—C7—C6        | 122.02 (10) | 122.01            |
| F8—C8—C9         | 118.40     | 114.79            |
| O1—C9—N1         | 122.17 (12) | 122.09            |
| O2—C11—C7        | 125.71 (11) | 125.86            |
| O3—C11—C7        | 111.59 (10) | 111.75            |
| C12—O3—C11       | 116.08 (11) | 115.75            |
| H12A—C12—C3      | 109.5      | 110.40            |
| H12B—C12—O3      | 109.5      | 110.40            |
| H12C—C12—O3      | 109.5      | 110.31            |
| H10A—C10—N1      | 109.5      | 110.62            |
| H10B—C10—N1      | 109.5      | 107.00            |
| H10C—C10—N1      | 109.5      | 110.40            |
| C4—C3—C2—C1      | 0.40 (19)  | 0.00              |
| C5—C4—C3—C2      | 0.32 (19)  | 0.00              |
| C6—C5—C4—C3      | −0.25 (19) | 0.00              |
| C7—C6—C5—C4      | −179.83 (11) | −180.00        |
| C8—C7—C6—C5      | −1.59 (17)  | 0.00              |
| C9—C8—C7—C6      | 0.23 (18)  | 0.00              |
| N1—C1—C6—C7      | 0.69 (17)  | 0.00              |
| C10—N1—C1—C6     | −178.45 (12) | −180.00        |
| C11—C4—C5—C6     | −179.81 (9)  | −180.00          |
| O1—C9—N1—C1      | 177.48 (12) | 179.99          |
| O2—C11—C7—C6     | 4.6 (2)     | −0.01             |
| O3—C11—C7—C6     | 175.14 (11) | −179.99          |
| C12—O3—C11—C7    | −179.85 (11) | 179.99          |
modes. The CH₃ torsion appears in the 17–119 cm⁻¹ region, the ν C≡C stretching mode is at 1363 cm⁻¹, the vibrations of the aromatic N—CH₃ appear at 1091 cm⁻¹, and the O—CH₃ and the C—Cl stretching bands are observed, respectively, at 1033 cm⁻¹ and 1124 cm⁻¹. The C—H stretch of the CH₃ group appears at 3182 cm⁻¹, however the aromatic C—H stretches appear in the 3208-3256 cm⁻¹ region. The bending of CH₃ appear between 1528 cm⁻¹ and 1556 cm⁻¹, Finally, the band positions of the bending of the HCC, HCN and HCO groups are respectively at 1169 cm⁻¹, 1119 cm⁻¹ and 1204 cm⁻¹.

The HOMO and LUMO energies are predicted with the B3LYP method in combination of basis sets 6-31G(d,p). This molecule contains 65 occupied molecular orbitals and 309 unoccupied virtual molecular orbitals. The frontier molecular orbitals are shown in Fig. 8. The positive phase is shown in red and the negative phase is shown in green. The HOMO-LUMO energy gap of (I) reflects the chemical activity and was calculated by the DFT/B3LYP/6-31G(d,p) method (Table 4). The high value of the energy gap (3.68 eV) implies a high electronic stability and low reactivity. In general, low values mean that it will be easier to remove an electron from the HOMO orbital towards the LUMO orbital.

8. Molecular electrostatic potential (MESP) analysis

The study of MESP is a useful tool in the investigation of the molecular structure with its relation to physico-chemical properties. The MESP analysis of (I) was performed with the functional B3LYP and the basis set 6-311G (d,P). The different values of the electrostatic potential are represented by different colours (Seminario, 1996; Murray & Sen, 1996) such that red represents the region of the most negative electrostatic potential (electrophilic sites), blue represents the region of the most positive electrostatic potential (the nucleophilic reactivity) and green represents the region of zero potential. The potential increases in the following order: red < orange < yellow < green < blue. Fig. 9 reveals that the negative potential sites are on oxygen and chlorine atoms, as well as the positive potential site is around hydrogen atoms. From these results, we can deduce that the H atoms show the strongest attraction and the oxygen and chlorine atoms show the strongest repulsion in the density curve. The H atom of the methoxy and amine group has a higher positive value than the other H atoms.

9. Database survey

A search of the Cambridge Crystallographic Database (updated to Dec. 31, 2021; Groom et al., 2016) using the fragment shown in the scheme below yielded 20 hits of which 16 contained an ester group attached to C7 (the remainder contained an alkyl group at this position) and, of these, only two, ROKCIG (Filali Baba et al., 2019) and REYREV (Filali Baba et al., 2018) contain a halogen atom attached to the aromatic ring. The former is more closely related to the title molecule by having an ethyl group attached to nitrogen and also in the ester substituent. In contrast to the title molecule, that in ROKCIG forms inversion dimers through C—H···O hydrogen bonds (rather than ribbons), which are connected into layers approximately parallel to (104), but there are no

| Molecular Energy (eV) | Compound (I) |
|-----------------------|--------------|
| Total Energy TE (eV)  | -32759.86    |
| $E_{\text{HOMO}}$ (eV) | -6.50        |
| $E_{\text{LUMO}}$ (eV) | -2.82        |
| Gap, $\Delta E$ (eV)  | 3.68         |
| Dipole moment, $\mu$ (Debye) | 0.6065 |
| Ionization potential, $I$ (eV) | 6.50 |
| Electron affinity, $A$ | 2.82 |
| Electronegativity, $\chi$ | 1.84 |
| Hardness, $\eta$ | 3.68 |
| Softness, $\sigma$ | 0.27 |
| Electrophilicity index, $\omega$ | -0.68 |

Table 4
Calculated energies.
C—H⋯Cl hydrogen bonds or π-stacking interactions. In the non-halogenated analog of ROKCIG (ROKCOM; Filali Baba et al., 2019) C—H⋯O hydrogen bonds form ribbons of molecules along [001], which are connected by weak π-stacking interactions.

10. Synthesis and crystallization

To a solution of 6-chloro-2-oxo-1,2-dihydroquinoline-4-carboxylic acid (1 g, 4.47 mmol) in 10 ml of DMF were added 3.30 ml (9.83 mmol) of methyl iodide, 3.17 g (22.36 mmol) of K2CO3 and 0.17 g (0.5 mmol) of tetra-n-butylammonium bromide (TBAB). The reaction mixture was stirred at room temperature in DMF for 6 h. After removal of salts, the solvent was evaporated under reduced pressure and the residue obtained was dissolved in dichloromethane. The organic phase was dried over Na2SO4 and then concentrated in vacuo. A pure compound was obtained after recrystallization from dichloromethane/hexane (v/v 1/3).

11. Refinement

Crystal, data collection and refinement details are presented in Table 5. Hydrogen atoms were included as riding contributions in idealized positions with isotropic displacement parameters tied to those of the attached atoms. Two reflections obscured by the beamstop were omitted from the final refinement.

Funding information

JTM thanks Tulane University for support of the Tulane Crystallography Laboratory. TH is grateful to Hacettepe University Scientific Research Project Unit (grant No. 013 D04 602 004).

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Table 5

Table 5: Experimental details.

| Property                           | Value               |
|-----------------------------------|---------------------|
| Chemical formula                  | C12H10ClNO3         |
| M, g/mol                          | 251.66              |
| Crystall system, space group      | Monoclinic, P21/c    |
| Temperature (K)                   | 150                 |
| a, b, c (Å)                       | 8.3515 (3), 16.6672 (6), 7.9705 (3) |
| V (Å³)                            | 1059.90 (7)         |
| μ (mm⁻¹)                          | 0.36                |
| Crystal size (mm)                 | 0.35 × 0.19 × 0.04  |
| Data collection                   | Bruker D8 QUEST PHOTON 3 diffractometer |
| Absorption correction            | Multi-scan (SADABS: Krause et al., 2015) |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 3544 |
| Refinement                        |                     |
| R | 0.041, 0.115, 1.06 |
| wR | 0.040, 0.737 |
| S | 0.54, –0.30 |

Computer programs: APEX3 and SAINT (Bruker, 2020), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 2012) and pubCIF (Westrip, 2010).

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Crystal structure, Hirshfeld surface analysis, interaction energy and DFT calculations and energy frameworks of methyl 6-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate

Yassir Filali Baba, Sonia Hayani, Samira Dalbouha, Tuncer Hökelek, Fouad Ouazzani Chahdi, Joel T. Mague, Youssef Kandri Rodi, Nada Kheira Sebbar and El Mokhtar Essassi

Computing details
Data collection: APEX3 (Bruker, 2020); cell refinement: SAINT (Bruker, 2020); data reduction: SAINT (Bruker, 2020); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: DIAMOND (Brandenburg & Putz, 2012); software used to prepare material for publication: pubCIF (Westrip, 2010).

Methyl 6-chloro-1-methyl-2-oxo-1,2-dihydroquinoline-4-carboxylate

Crystal data
C₁₂H₁₀ClNO₃  
Formula
Mr = 251.66  

Monoclinic, P2₁/c  
a = 8.3515 (3) Å  
b = 16.6672 (6) Å  
c = 7.9705 (3) Å  
β = 107.191 (2)°  

V = 1059.90 (7) Å³  
Z = 4  

F(000) = 520  
D_x = 1.577 Mg m⁻³  

Cell parameters from 9727 reflections  
θ = 2.6–31.5°  
μ = 0.36 mm⁻¹  

T = 150 K  
Plate, pale blue  

0.35 × 0.19 × 0.04 mm

Data collection
Bruker D8 QUEST PHOTON 3  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
Detector resolution: 7.3910 pixels mm⁻¹  
φ and ω scans  
Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)  
T_min = 0.94, T_max = 0.99

70718 measured reflections  
3544 independent reflections  
2977 reflections with I > 2σ(I)  
R_obs = 0.040  
θ_max = 31.6°, θ_min = 2.8°  
k = −24→24  
l = −11→11

Refinement
Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.041  
wR(F²) = 0.115  
S = 1.06

3544 reflections  
156 parameters  
0 restraints  
Primary atom site location: dual
## Supporting Information

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

### Special details

**Experimental.** The diffraction data were obtained from 12 sets of frames, each of width 0.5° in ω or φ, collected with scan parameters determined by the "strategy" routine in *APEX3*. The scan time was 15 sec/frame.

**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.** Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on $F$, and R- factors based on ALL data will be even larger. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Two reflections obscured by the beamstop were omitted from the final refinement.

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

| Atom | x      | y      | z      | $U_{eq}$/$U_{iso}$ |
|------|--------|--------|--------|---------------------|
| Cl1  | 0.84517 (4) | 0.57446 (2) | 1.07652 (4) | 0.02841 (10) |
| O1   | 0.11119 (15) | 0.35446 (6) | 0.34782 (14) | 0.0330 (2) |
| O2   | 0.33909 (15) | 0.67466 (6) | 0.64348 (17) | 0.0415 (3) |
| O3   | 0.12761 (13) | 0.64014 (6) | 0.41182 (12) | 0.0279 (2) |
| N1   | 0.34559 (13) | 0.36878 (6) | 0.58343 (13) | 0.0213 (2) |
| C1   | 0.46120 (15) | 0.41783 (7) | 0.70040 (16) | 0.0199 (2) |
| C2   | 0.59973 (16) | 0.38341 (8) | 0.82548 (17) | 0.0236 (2) |
| H2   | 0.612806 | 0.326763 | 0.831409 | 0.028* |
| C3   | 0.71602 (16) | 0.43149 (7) | 0.93894 (17) | 0.0226 (2) |
| H3   | 0.809737 | 0.407995 | 1.022678 | 0.027* |
| C4   | 0.69735 (16) | 0.51402 (8) | 0.93189 (16) | 0.0223 (2) |
| C5   | 0.56211 (15) | 0.54992 (7) | 0.81228 (16) | 0.0205 (2) |
| H5   | 0.551223 | 0.606682 | 0.809742 | 0.025* |
| C6   | 0.44019 (14) | 0.50236 (7) | 0.69390 (15) | 0.0187 (2) |
| C7   | 0.29453 (15) | 0.53504 (7) | 0.56374 (15) | 0.0186 (2) |
| C8   | 0.18725 (16) | 0.48494 (7) | 0.45164 (16) | 0.0213 (2) |
| H8   | 0.092808 | 0.507382 | 0.367006 | 0.026* |
| C9   | 0.20920 (16) | 0.39853 (8) | 0.45415 (16) | 0.0228 (2) |
| C10  | 0.36647 (19) | 0.28134 (8) | 0.59449 (19) | 0.0288 (3) |
| H10A | 0.272556 | 0.255765 | 0.506926 | 0.043* |
| H10B | 0.369000 | 0.263150 | 0.712165 | 0.043* |
| H10C | 0.471808 | 0.266706 | 0.571760 | 0.043* |
| C11  | 0.25956 (15) | 0.62357 (7) | 0.54768 (16) | 0.0209 (2) |
| C12  | 0.08323 (19) | 0.72398 (8) | 0.3841 (2) | 0.0304 (3) |
| H12A | 0.174601 | 0.753257 | 0.357605 | 0.046* |
| H12B | 0.064284 | 0.746230 | 0.490485 | 0.046* |
Supporting information

Atomic displacement parameters (Å²)

|    | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|----|-----|-----|-----|-----|-----|-----|
| C11| 0.02388 (16) | 0.02942 (17) | 0.02545 (16) | −0.00297 (11) | −0.00271 (12) | −0.00145 (11) |
| O1 | 0.0406 (6) | 0.0229 (5) | 0.0279 (5) | −0.0084 (4) | −0.0016 (4) | −0.0034 (4) |
| O2 | 0.0370 (6) | 0.0184 (4) | 0.0512 (7) | 0.0009 (4) | −0.0147 (5) | −0.0053 (4) |
| O3 | 0.0309 (5) | 0.0208 (4) | 0.0250 (5) | 0.0054 (4) | −0.0028 (4) | 0.0003 (3) |
| N1 | 0.0261 (5) | 0.0153 (4) | 0.0205 (5) | 0.0001 (4) | 0.0041 (4) | −0.0008 (3) |
| C1 | 0.0217 (5) | 0.0175 (5) | 0.0201 (5) | −0.0002 (4) | 0.0056 (4) | −0.0002 (4) |
| C2 | 0.0249 (6) | 0.0198 (5) | 0.0251 (6) | 0.0033 (4) | 0.0061 (5) | 0.0024 (4) |
| C3 | 0.0222 (6) | 0.0223 (5) | 0.0222 (5) | 0.0027 (4) | 0.0048 (4) | 0.0022 (4) |
| C4 | 0.0202 (5) | 0.0242 (5) | 0.0200 (5) | −0.0009 (4) | 0.0023 (4) | −0.0003 (4) |
| C5 | 0.0205 (5) | 0.0186 (5) | 0.0210 (5) | 0.0002 (4) | 0.0039 (4) | 0.0001 (4) |
| C6 | 0.0189 (5) | 0.0178 (5) | 0.0182 (5) | 0.0002 (4) | 0.0035 (4) | −0.0002 (4) |
| C7 | 0.0196 (5) | 0.0162 (5) | 0.0188 (5) | 0.0000 (4) | 0.0041 (4) | 0.0002 (4) |
| C8 | 0.0221 (5) | 0.0188 (5) | 0.0206 (5) | −0.0012 (4) | 0.0027 (4) | 0.0004 (4) |
| C9 | 0.0262 (6) | 0.0202 (5) | 0.0203 (5) | −0.0025 (4) | 0.0043 (4) | 0.0001 (4) |
| C10| 0.0364 (7) | 0.0153 (5) | 0.0323 (7) | 0.0006 (5) | 0.0063 (6) | 0.0007 (4) |
| C11| 0.0206 (5) | 0.0176 (5) | 0.0221 (5) | 0.0008 (4) | 0.0027 (4) | 0.0008 (4) |
| C12| 0.0334 (7) | 0.0221 (6) | 0.0314 (7) | 0.0077 (5) | 0.0030 (5) | 0.0055 (5) |

Geometric parameters (Å, °)

|    | Cl1—C4 | Cl4—C5 | Cl1—C9 | Cl5—H5 | Cl4—C6 | Cl5—C6 |
|----|--------|--------|--------|--------|--------|--------|
| Cl1—C4 | 1.7397 (13) | Cl4—C5 | 1.3807 (17) | Cl5—H5 | 0.9500 | Cl4—C6 |
| Cl1—C11 | 1.2040 (16) | Cl5—C6 | 1.4098 (16) | Cl1—C9 | 1.3825 (16) | Cl—C7 |
| Cl1—C11 | 1.3258 (15) | Cl6—C7 | 1.4514 (16) | Cl1—C9 | 1.3920 (15) | Cl7—C8 |
| Cl1—C12 | 1.4458 (15) | Cl7—C8 | 1.3510 (16) | Cl1—C10 | 1.4673 (16) | Cl8—C9 |
| Cl1—C2 | 1.4070 (17) | Cl9—H10A | 0.9800 | Cl1—C6 | 1.4189 (16) | Cl10—H10B |
| Cl1—C2 | 1.3726 (18) | Cl10—H10B | 0.9800 | Cl1—C10 | 1.4070 (17) | Cl11—H10C |
| Cl1—C2 | 1.3726 (18) | Cl2—H10C | 0.9800 | Cl2—H2 | 0.9500 | Cl12—H12A |
| Cl1—C2 | 1.3836 (17) | Cl2—H12A | 0.9800 | Cl3—C4 | 0.9500 | Cl12—H12C |
| Cl1—O3^i | 3.1903 (10) | H2—O2^iii | 2.57 | Cl3—H3 | 0.9500 | C11—O1^ii |
| Cl1—O8 | 2.84 | O3—H8 | 2.25 | Cl3—H3 | 0.9500 | C12—O1^ia |
| Cl2—O1^i | 3.0016 (16) | C2—H10C | 2.78 | O2—C5 | 2.8496 (17) | C11—H5 |
| O1—H10A | 2.26 | C2—H10B | 2.74 | O1—H10A | 2.26 | C11—H5 |
| H12C—O1^ia | 2.36 | C10—H2 | 2.46 | O2—H12A | 2.64 | H2—H10B |
| O2—H5 | 2.19 | H2—H10C | 2.29 | O2—H5 | 2.19 | 0.046^e |
### Supporting Information

| Bond          | Length (Å) | Angle (°)   | Symmetry Code          |
|---------------|------------|-------------|------------------------|
| O2···H12B     | 2.55       |             |                        |
| C11—O3—C12   | 116.08 (11)| C8—C7—C11  |                        |
| C9—N1—C1     | 122.97 (10)| C6—C7—C11  |                        |
| C9—N1—C10    | 117.27 (10)| C7—C8—C9   |                        |
| C1—N1—C10    | 119.77 (10)| C7—C8—H8   |                        |
| N1—C1—C2     | 119.83 (11)| C9—C8—H8   |                        |
| N1—C1—C6     | 120.32 (11)| O1—C9—N1   | 122.17 (12)            |
| C2—C1—C6     | 119.85 (11)| O1—C9—C8   | 121.78 (12)            |
| C3—C2—C1     | 120.15 (11)| N1—C9—C8   | 116.05 (11)            |
| C3—C2—H2     | 119.9      | N1—C10—H10A| 109.5                  |
| C1—C2—H2     | 119.9      | N1—C10—H10B| 109.5                  |
| C2—C3—C4     | 120.29 (12)| H10A—C10—H10B| 109.5              |
| C2—C3—H3     | 119.9      | N1—C10—H10C| 109.5                  |
| C4—C3—H3     | 119.9      | H10A—C10—H10C| 109.5           |
| C5—C4—C3     | 121.22 (12)| H10B—C10—H10C| 109.5            |
| C5—C4—Cl1    | 118.82 (10)| O2—C11—O3  | 122.70 (12)            |
| C3—C4—Cl1    | 119.96 (10)| O2—C11—C7  | 125.71 (11)            |
| C4—C5—C6     | 120.00 (11)| O3—C11—C7  | 111.59 (10)            |
| C4—C5—H5     | 120.0      | O3—C12—H12A| 109.5                  |
| C6—C5—H5     | 120.0      | O3—C12—H12B| 109.5                  |
| C5—C6—C1     | 118.48 (11)| H12A—C12—H12B| 109.5           |
| C5—C6—C7     | 123.66 (11)| O3—C12—H12C| 109.5                  |
| C1—C6—C7     | 117.86 (10)| H12A—C12—H12C| 109.5            |
| C8—C7—C6     | 119.52 (11)| H12B—C12—H12C| 109.5           |

Symmetry codes: (i) \(x+1, y, z+1\); (ii) \(-x, y+1/2, -z+1/2\); (iii) \(-x+1, y-1/2, -z+3/2\).
Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A      | D—H···A |
|-------------|------|-------|------------|---------|
| C2—H2···O2
  iii        | 0.95 | 2.57  | 3.5146 (16)| 178     |
| C5—H5···O2  | 0.95 | 2.19  | 2.8496 (16)| 126     |
| C8—H8···Cl1
  iv         | 0.95 | 2.84  | 3.7786 (13)| 170     |
| C12—H12C···O1
  ii         | 0.98 | 2.36  | 3.0016 (16)| 122     |

Symmetry codes: (ii) −x, y+1/2, −z+1/2; (iii) −x+1, y−1/2, −z+3/2; (iv) x−1, y, z−1.