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4-Chloro-6,7-dimethoxyquinoline

Min Wu

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People's Republic of China
Correspondence e-mail: wuminj@163.com

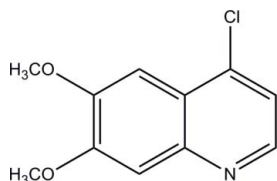
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.115; data-to-parameter ratio = 13.0.

The title molecule, $\text{C}_{11}\text{H}_{10}\text{ClNO}_2$, is almost planar with the C atoms of the methoxy groups deviating by -0.082 (2) and 0.020 (2) Å from the least-squares plane defined by the atoms of the quinoline ring system (r.m.s. deviation = 0.002 Å). An intramolecular $\text{C}-\text{H}\cdots\text{Cl}$ interaction generates an $S(5)$ ring motif.

Related literature

For related structures, see: Davies & Bond (2001); Yathirajan *et al.* (2007). For biological properties of quinoline derivatives, see: Franck *et al.* (2004); Moret *et al.* (2006); Furuta *et al.* (2006); Ilovich *et al.* (2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{10}\text{ClNO}_2$
 $M_r = 223.65$
Monoclinic, $P2_1/c$
 $a = 12.5530$ (17) Å
 $b = 4.6499$ (7) Å
 $c = 18.274$ (3) Å
 $\beta = 105.786$ (2)°

$V = 1026.4$ (3) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.35$ mm⁻¹
 $T = 296$ K
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Rigaku SCXmini diffractometer
6840 measured reflections
1808 independent reflections
1542 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$
3 standard reflections every 150 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.115$
 $S = 1.08$
1808 reflections
139 parameters

1 restraint
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C8}-\text{H8}\cdots\text{Cl1}$	0.93	2.70	3.0827 (17)	105

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LR2029).

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supporting information

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4-Chloro-6,7-dimethoxyquinoline

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S1. Comment

Quinoline derivatives have been interesting to researchers for many years because a large number of natural products contain these heterocycles and also because their varied biological activities (Franck *et al.* 2004; Moret *et al.* 2006; Furuta *et al.* 2006 & Ilovich *et al.* 2008).

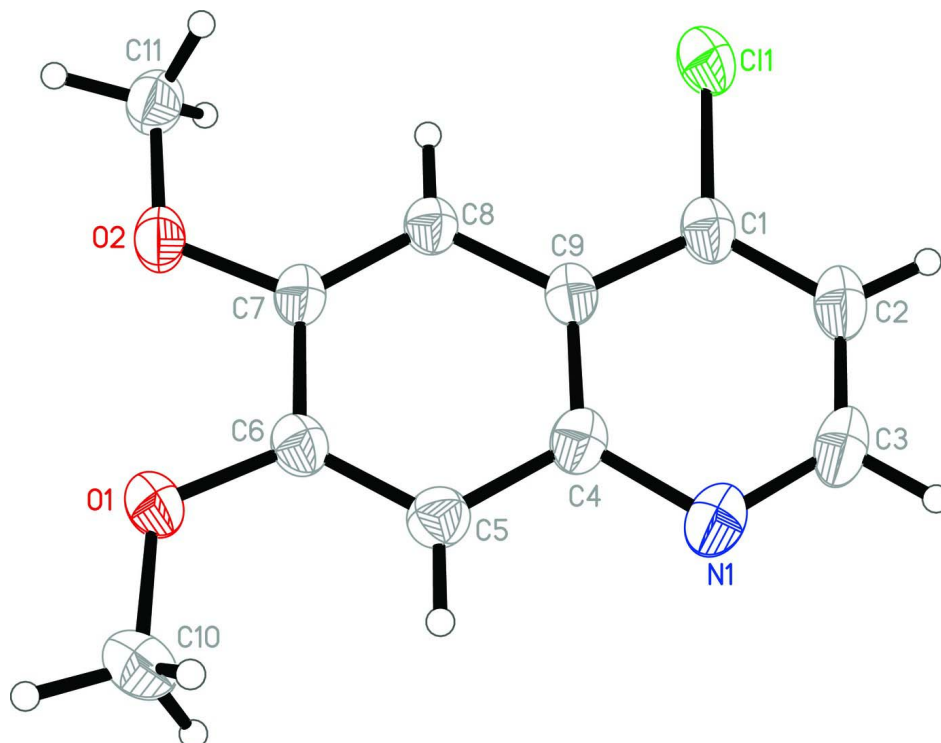
Prompted by the properties of quinoline derivatives, the title compound, C₁₁H₁₀ClNO₂, has been synthesized. Bond lengths and angles are in the usual range (Davies & Bond 2001 & Yathirajan *et al.* 2007) and the whole molecule is almost planar with the carbon atoms of the methoxyl groups deviating 0.08 (C10) and 0.02 Å (C11) from the least-square plane defined by the atoms of the quinoline ring. There are intramolecular C8 — H8 ...C11 interactions (Table 1) generating S(5) ring motifs (Bernstein *et al.* 1995) . Figure 1 shows the molecular structure of the title compound and Figure 2 is a partial packing view of the crystal structure down the *b* axis.

S2. Experimental

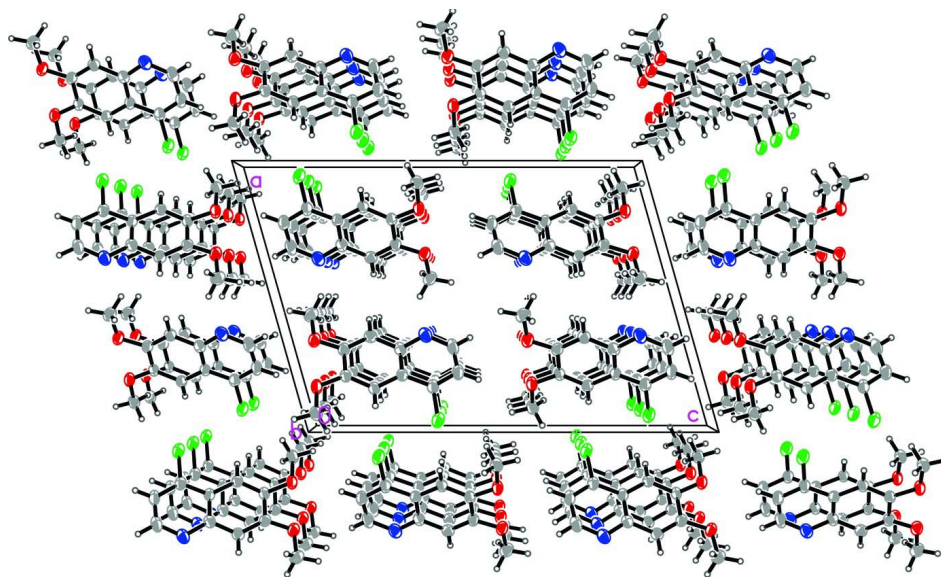
A mixture of 6,7- dimethoxynaphthalen-1-ol (20.4 g, 100 mmol) and POCl₃ (60 ml, 640 mmol) was heated under reflux for 6 h. The excess of phosphorus oxychloride was distilled out under reduced pressure. 200 g crush ice was added to the residue followed by 50% aqueous NaOH until the pH was adjusted to 8. The resulting solid was collected by filtration and washed with water to give the crude product. Purification of the crude product by a column chromatography (petroleum ether: EtOAc = 8:1 v.v) afforded the title compound (15.6 g, 70%) as pink crystals. The purity of the product, 4- chloro- 6, 7- dimethoxy- quinoline, was determined using a reversed- phase C-18 analytical HPLC column (99% purity). Crystals of the title compound suitable for *X*- ray diffraction were obtained by slow evaporation of methanol solution at room temperature. m. p. 403- 404 K; ¹H NMR (DMSO- d₆): δ8.57 (d, J = 5.1 Hz, 1H), 7.40 (d, J = 4.8 Hz, 1H), 7.37 (s, 1H), 7.32 (s, 1H), 4.04 (s, 3H), 4.03 (s, 3H). MS (ESI, *m/z*): 224 (*M*+1).

S3. Refinement

All H atoms were placed at calculated positions; C—H = 0.93 Å for aromatic H, C—H = 0.96 Å for methoxyl H. They were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$, respectively.

**Figure 1**

The molecular structure of the title compound, displacement ellipsoids are drawn at the 30% probability level.

**Figure 2**

Partial packing view of the title compound, viewed down the *b* axis.

4-Chloro-6,7-dimethoxyquinoline

Crystal data

C₁₁H₁₀ClNO₂ $M_r = 223.65$ Monoclinic, $P2_1/c$ $a = 12.5530$ (17) Å $b = 4.6499$ (7) Å $c = 18.274$ (3) Å $\beta = 105.786$ (2)° $V = 1026.4$ (3) Å³ $Z = 4$ $F(000) = 464$ $D_x = 1.447$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 30 reflections

 $\theta = 3\text{--}25^\circ$ $\mu = 0.35$ mm⁻¹ $T = 296$ K

Block, pink

 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω scans

6840 measured reflections

1808 independent reflections

1542 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$ $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 1.7^\circ$ $h = -14 \rightarrow 14$ $k = -5 \rightarrow 5$ $l = -21 \rightarrow 21$

3 standard reflections every 150 reflections

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.115$ $S = 1.08$

1808 reflections

139 parameters

1 restraint

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.1562P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.029 (4)

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. 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 $F^2 > \sigma(F^2)$ 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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.18445 (16)	0.9064 (4)	0.34245 (10)	0.0508 (5)
C2	0.23248 (18)	0.7745 (5)	0.40978 (11)	0.0608 (5)
H2	0.2071	0.8077	0.4523	0.073*

C3	0.32020 (19)	0.5895 (5)	0.41333 (12)	0.0668 (6)
H3	0.3522	0.4999	0.4596	0.080*
C4	0.31375 (16)	0.6656 (4)	0.28823 (10)	0.0486 (5)
C5	0.35750 (15)	0.6077 (4)	0.22615 (11)	0.0503 (5)
H5	0.4173	0.4832	0.2326	0.060*
C6	0.31298 (14)	0.7325 (4)	0.15691 (10)	0.0469 (4)
C7	0.22217 (14)	0.9277 (4)	0.14727 (9)	0.0443 (4)
C8	0.17947 (14)	0.9890 (4)	0.20641 (9)	0.0441 (4)
H8	0.1208	1.1173	0.1997	0.053*
C9	0.22416 (14)	0.8581 (3)	0.27829 (9)	0.0437 (4)
C10	0.43422 (17)	0.4878 (5)	0.09810 (13)	0.0659 (6)
H10A	0.4997	0.5563	0.1344	0.099*
H10B	0.4482	0.4703	0.0492	0.099*
H10C	0.4142	0.3033	0.1139	0.099*
C11	0.09705 (17)	1.2379 (5)	0.06201 (12)	0.0580 (5)
H11A	0.0339	1.1499	0.0729	0.087*
H11B	0.0780	1.2972	0.0097	0.087*
H11C	0.1195	1.4025	0.0942	0.087*
Cl1	0.07193 (4)	1.13418 (12)	0.33477 (3)	0.0656 (3)
N1	0.36194 (14)	0.5307 (4)	0.35576 (9)	0.0623 (5)
O1	0.34547 (11)	0.6869 (3)	0.09331 (7)	0.0585 (4)
O2	0.18526 (11)	1.0371 (3)	0.07552 (7)	0.0561 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0588 (11)	0.0528 (10)	0.0423 (10)	-0.0142 (9)	0.0164 (8)	-0.0043 (8)
C2	0.0742 (13)	0.0699 (12)	0.0404 (11)	-0.0112 (10)	0.0193 (10)	0.0013 (9)
C3	0.0824 (14)	0.0736 (13)	0.0398 (11)	-0.0076 (11)	0.0088 (10)	0.0115 (10)
C4	0.0543 (10)	0.0463 (10)	0.0428 (10)	-0.0079 (8)	0.0094 (8)	0.0014 (8)
C5	0.0505 (10)	0.0487 (10)	0.0506 (11)	0.0030 (8)	0.0120 (8)	0.0001 (8)
C6	0.0498 (10)	0.0491 (9)	0.0438 (10)	-0.0047 (8)	0.0162 (8)	-0.0054 (8)
C7	0.0504 (10)	0.0460 (9)	0.0363 (9)	-0.0045 (7)	0.0114 (7)	-0.0014 (7)
C8	0.0467 (9)	0.0452 (9)	0.0405 (9)	-0.0029 (7)	0.0121 (7)	-0.0012 (7)
C9	0.0487 (9)	0.0445 (9)	0.0381 (9)	-0.0113 (7)	0.0123 (7)	-0.0036 (7)
C10	0.0635 (12)	0.0696 (13)	0.0717 (14)	0.0061 (11)	0.0303 (10)	-0.0091 (11)
C11	0.0643 (12)	0.0611 (11)	0.0474 (11)	0.0071 (10)	0.0134 (9)	0.0054 (9)
Cl1	0.0735 (4)	0.0778 (4)	0.0532 (4)	0.0040 (3)	0.0302 (3)	-0.0051 (2)
N1	0.0685 (11)	0.0630 (10)	0.0506 (10)	-0.0002 (8)	0.0083 (8)	0.0112 (8)
O1	0.0633 (8)	0.0695 (9)	0.0478 (8)	0.0123 (7)	0.0239 (6)	-0.0024 (6)
O2	0.0675 (8)	0.0654 (8)	0.0380 (7)	0.0129 (7)	0.0188 (6)	0.0068 (6)

Geometric parameters (Å, °)

C1—C2	1.360 (3)	C6—C7	1.430 (3)
C1—C9	1.411 (3)	C7—C8	1.361 (2)
C1—Cl1	1.740 (2)	C7—O2	1.365 (2)
C2—C3	1.385 (3)	C8—C9	1.418 (2)

C2—H2	0.9300	C8—H8	0.9300
C3—N1	1.325 (3)	C10—O1	1.433 (2)
C3—H3	0.9300	C10—H10A	0.9600
C4—N1	1.370 (2)	C10—H10B	0.9600
C4—C9	1.410 (3)	C10—H10C	0.9600
C4—C5	1.414 (3)	C11—O2	1.418 (2)
C5—C6	1.366 (3)	C11—H11A	0.9600
C5—H5	0.9300	C11—H11B	0.9600
C6—O1	1.349 (2)	C11—H11C	0.9600
C2—C1—C9	120.67 (19)	C7—C8—C9	120.25 (17)
C2—C1—C11	119.85 (16)	C7—C8—H8	119.9
C9—C1—C11	119.48 (14)	C9—C8—H8	119.9
C1—C2—C3	118.27 (19)	C4—C9—C1	116.33 (16)
C1—C2—H2	120.9	C4—C9—C8	119.53 (16)
C3—C2—H2	120.9	C1—C9—C8	124.14 (17)
N1—C3—C2	124.90 (18)	O1—C10—H10A	109.5
N1—C3—H3	117.6	O1—C10—H10B	109.5
C2—C3—H3	117.6	H10A—C10—H10B	109.5
N1—C4—C9	123.24 (18)	O1—C10—H10C	109.5
N1—C4—C5	117.57 (17)	H10A—C10—H10C	109.5
C9—C4—C5	119.19 (16)	H10B—C10—H10C	109.5
C6—C5—C4	120.80 (17)	O2—C11—H11A	109.5
C6—C5—H5	119.6	O2—C11—H11B	109.5
C4—C5—H5	119.6	H11A—C11—H11B	109.5
O1—C6—C5	126.01 (17)	O2—C11—H11C	109.5
O1—C6—C7	114.29 (15)	H11A—C11—H11C	109.5
C5—C6—C7	119.69 (17)	H11B—C11—H11C	109.5
C8—C7—O2	125.52 (16)	C3—N1—C4	116.59 (18)
C8—C7—C6	120.54 (15)	C6—O1—C10	117.47 (15)
O2—C7—C6	113.94 (15)	C7—O2—C11	117.24 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8...C11	0.93	2.70	3.0827 (17)	105