

Ethyl 2-methyl-4-phenylquinoline-3-carboxylate

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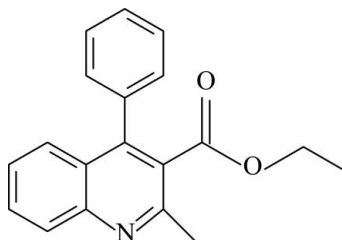
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 Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å;
 R factor = 0.065; wR factor = 0.194; data-to-parameter ratio = 20.1.

In the molecule of the title compound, $\text{C}_{19}\text{H}_{17}\text{NO}_2$, the quinoline ring system is planar [maximum deviation 0.021 (3) Å] and oriented with respect to the phenyl ring at a dihedral angle of 80.44 (4)°. Intramolecular $\text{C}-\text{H}\cdots\text{O}$ interactions result in the formation of five- and six-membered rings having planar and envelope conformations, respectively. In the crystal structure, intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions link the molecules into centrosymmetric dimers forming $R_2^2(12)$ ring motifs. $\pi-\pi$ contacts between the rings of the quinoline system [centroid-to-centroid distance = 3.812 (1) Å] may further stabilize the structure. Two weak $\text{C}-\text{H}\cdots\pi$ interactions are also found.

Related literature

For general background, see: Doube *et al.* (1998). For ring-motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

 $\text{C}_{19}\text{H}_{17}\text{NO}_2$
 $M_r = 291.34$
 Triclinic, $P\bar{1}$
 $a = 9.0282$ (10) Å
 $b = 9.362$ (1) Å
 $c = 10.7258$ (10) Å

 $\alpha = 69.765$ (8)°
 $\beta = 66.733$ (8)°
 $\gamma = 70.605$ (8)°
 $V = 761.08$ (15) Å³
 $Z = 2$

 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 120$ K
 $0.35 \times 0.32 \times 0.25$ mm

Data collection

 Bruker SMART CCD area-detector
 diffractometer
 Absorption correction: none
 8164 measured reflections

 3995 independent reflections
 3410 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.194$
 $S = 1.09$
 3995 reflections

 199 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C16—H16A ⁱ ···O1	0.97	2.32	2.711 (3)	103
C19—H19B ^j ···O2 ⁱ	0.96	2.52	3.374 (3)	147
C19—H19C ^j ···O2	0.96	2.59	3.212 (3)	122
C12—H12 ^j ···Cg2 ⁱⁱ	0.93	2.95	3.750 (3)	145
C17—H17C ^j ···Cg3 ⁱⁱⁱ	0.96	2.97	3.883 (3)	160

Symmetry codes: (i) $-x + 1, -y - 2, -z + 1$; (ii) $-x + 2, -y, -z + 1$; (iii) $-x + 2, -y, -z$. Cg2 and Cg3 are the centroids of rings C1–C6 and C8–C13, respectively.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2681).

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supplementary materials

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Comment

The quinoline moiety is probably the most well known heterocycle, a common and important feature of a variety of natural products and medicinal agents. They have emerged as antimalarial, antiasthmatic, anti-inflammatory, antibacterial, antihypertensive and tyrosine kinase PDGF-RTK inhibiting agents (Doube *et al.*, 1998). Moreover, polyquinolines are found to undergo hierarchical self-assembly into a variety of nano and *meso* structures with enhanced electronic and photonic functions. We report herein the synthesis and crystal structure of the title compound.

In the molecule of the title compound (Fig. 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The quinoline ring system A (N1/C1–C7/C14/C18) is planar with a maximum deviation of $-0.021(3)$ Å for atom C18, and oriented with respect to the phenyl ring B (C8–C13) at a dihedral angle of $A/B = 80.44(4)^\circ$. Intramolecular C—H \cdots O interactions result in the formations of five- and six-membered rings C (O1/O2/C15/C16/H16A) and D (O2/C14/C15/C18/C19/H19C). Ring C is planar, while ring D adopts envelope conformation, with atom O2 displaced by $-1.166(4)$ Å from the plane of the other ring atoms.

In the crystal structure, intermolecular C—H \cdots O interactions (Table 1) link the molecules into centrosymmetric dimers forming $R_2^2(12)$ ring motifs (Fig. 2) (Bernstein *et al.*, 1995), in which they may be effective in the stabilization of the structure. The π – π contact between the rings of the quinoline ring system, $Cg1\cdots Cg2^i$ [symmetry code: (i) $1 - x, -1 - y, 1 - z$, where Cg1 and Cg2 are centroids of the rings (N1/C1/C6/C7/C14/C18) and (C1–C6), respectively] may further stabilize the structure, with centroid-centroid distance of $3.812(1)$ Å. There also exist two weak C—H \cdots π interactions (Table 1).

Experimental

For the preparation of the title compound, a mixture of ethyl acetoacetate (0.13 g, 1 mmol), (2-aminophenyl)(phenyl)methanone (0.20 g, 1 mmol) and *p*-toluene sulfonic acid (0.1 g, 5.8 mmol) in water (5 ml) was stirred at reflux for 4 h. After completion of reaction (monitored by TLC) the reaction mixture was filtered and the precipitate washed with water (15 ml) and then recrystallized from EtOH/water (1:2) to afford the pure product (yield; 75%, 0.218 g).

Refinement

H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Hydrogen bonds are shown as dotted lines.

Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

Ethyl 2-methyl-4-phenylquinoline-3-carboxylate

Crystal data

$C_{19}H_{17}N_1O_2$	$Z = 2$
$M_r = 291.34$	$F_{000} = 308$
Triclinic, $P\bar{1}$	$D_x = 1.271 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 9.0282 (10) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 9.362 (1) \text{ \AA}$	Cell parameters from 1548 reflections
$c = 10.7258 (10) \text{ \AA}$	$\theta = 2.4\text{--}29.2^\circ$
$\alpha = 69.765 (8)^\circ$	$\mu = 0.08 \text{ mm}^{-1}$
$\beta = 66.733 (8)^\circ$	$T = 120 \text{ K}$
$\gamma = 70.605 (8)^\circ$	Block, colourless
$V = 761.08 (15) \text{ \AA}^3$	$0.35 \times 0.32 \times 0.25 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{\text{int}} = 0.044$
φ and ω scans	$\theta_{\text{max}} = 29.2^\circ$
Absorption correction: none	$\theta_{\text{min}} = 2.4^\circ$
8164 measured reflections	$h = -12 \rightarrow 12$
3995 independent reflections	$k = -12 \rightarrow 12$
3410 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0955P)^2 + 0.1587P]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.194$	$(\Delta/\sigma)_{\text{max}} = 0.01$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
3995 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
199 parameters	Extinction correction: none

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.6903 (3)	-0.70878 (17)	0.11893 (14)	0.0879 (5)
O2	0.6965 (2)	-0.95151 (14)	0.24871 (13)	0.0696 (4)
N1	0.44256 (15)	-0.71135 (15)	0.57975 (13)	0.0470 (3)
C1	0.56342 (18)	-0.68228 (16)	0.60840 (15)	0.0438 (3)
C2	0.5192 (2)	-0.6418 (2)	0.73600 (17)	0.0551 (4)
H2	0.4104	-0.6328	0.7953	0.066*
C3	0.6347 (3)	-0.6159 (2)	0.77284 (19)	0.0622 (5)
H3	0.6046	-0.5907	0.8575	0.075*
C4	0.7988 (2)	-0.6273 (2)	0.6834 (2)	0.0615 (4)
H4	0.8767	-0.6096	0.7094	0.074*
C5	0.8456 (2)	-0.66413 (19)	0.55808 (18)	0.0523 (4)
H5	0.9545	-0.6702	0.4994	0.063*
C6	0.72854 (17)	-0.69295 (15)	0.51769 (15)	0.0420 (3)
C7	0.76870 (17)	-0.73393 (15)	0.38991 (14)	0.0402 (3)
C8	0.94211 (17)	-0.75008 (16)	0.29187 (15)	0.0423 (3)
C9	1.0023 (2)	-0.61966 (19)	0.20110 (18)	0.0546 (4)
H9	0.9326	-0.5206	0.1985	0.066*
C10	1.1658 (2)	-0.6361 (2)	0.11427 (19)	0.0619 (4)
H10	1.2049	-0.5483	0.0535	0.074*
C11	1.2697 (2)	-0.7819 (2)	0.11829 (18)	0.0612 (5)
H11	1.3796	-0.7925	0.0614	0.073*
C12	1.2116 (2)	-0.9125 (2)	0.20633 (19)	0.0622 (4)
H12	1.2818	-1.0112	0.2081	0.075*
C13	1.0480 (2)	-0.89658 (18)	0.29248 (17)	0.0526 (4)
H13	1.009	-0.9851	0.3512	0.063*
C14	0.64476 (17)	-0.76184 (16)	0.36344 (14)	0.0410 (3)
C15	0.67936 (18)	-0.80112 (17)	0.22859 (15)	0.0451 (3)
C16	0.7336 (3)	-1.0130 (2)	0.12943 (19)	0.0640 (5)
H16A	0.7594	-0.9331	0.0428	0.077*
H16B	0.6389	-1.0461	0.1365	0.077*
C17	0.8780 (3)	-1.1482 (3)	0.1307 (2)	0.0694 (5)
H17A	0.8511	-1.2265	0.2168	0.083*
H17B	0.9711	-1.114	0.1231	0.083*
H17C	0.905	-1.1913	0.0532	0.083*
C18	0.48148 (18)	-0.75086 (17)	0.46289 (15)	0.0441 (3)
C19	0.3470 (2)	-0.7867 (2)	0.43737 (19)	0.0577 (4)
H19A	0.2567	-0.6965	0.4356	0.069*
H19B	0.3086	-0.8727	0.511	0.069*
H19C	0.3897	-0.8138	0.3491	0.069*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1583 (17)	0.0598 (8)	0.0463 (7)	-0.0329 (9)	-0.0344 (9)	-0.0036 (6)

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O2	0.1184 (12)	0.0481 (6)	0.0487 (6)	-0.0242 (7)	-0.0284 (7)	-0.0121 (5)
N1	0.0443 (6)	0.0499 (7)	0.0454 (6)	-0.0124 (5)	-0.0135 (5)	-0.0091 (5)
C1	0.0471 (7)	0.0398 (6)	0.0437 (7)	-0.0072 (5)	-0.0161 (6)	-0.0096 (5)
C2	0.0607 (9)	0.0556 (9)	0.0460 (8)	-0.0086 (7)	-0.0143 (7)	-0.0166 (6)
C3	0.0786 (12)	0.0623 (10)	0.0558 (9)	-0.0085 (8)	-0.0288 (9)	-0.0248 (8)
C4	0.0684 (11)	0.0631 (10)	0.0709 (11)	-0.0092 (8)	-0.0375 (9)	-0.0251 (8)
C5	0.0494 (8)	0.0540 (8)	0.0629 (9)	-0.0071 (6)	-0.0261 (7)	-0.0203 (7)
C6	0.0437 (7)	0.0376 (6)	0.0472 (7)	-0.0052 (5)	-0.0191 (6)	-0.0117 (5)
C7	0.0408 (6)	0.0364 (6)	0.0433 (7)	-0.0082 (5)	-0.0146 (5)	-0.0087 (5)
C8	0.0411 (6)	0.0440 (7)	0.0442 (7)	-0.0097 (5)	-0.0151 (5)	-0.0119 (5)
C9	0.0563 (9)	0.0464 (8)	0.0594 (9)	-0.0154 (6)	-0.0170 (7)	-0.0090 (6)
C10	0.0627 (10)	0.0744 (11)	0.0509 (9)	-0.0347 (9)	-0.0119 (7)	-0.0071 (8)
C11	0.0454 (8)	0.0894 (13)	0.0472 (8)	-0.0166 (8)	-0.0103 (6)	-0.0190 (8)
C12	0.0497 (9)	0.0676 (10)	0.0589 (9)	0.0023 (7)	-0.0163 (7)	-0.0192 (8)
C13	0.0499 (8)	0.0455 (7)	0.0544 (8)	-0.0070 (6)	-0.0147 (6)	-0.0086 (6)
C14	0.0442 (7)	0.0394 (6)	0.0405 (6)	-0.0110 (5)	-0.0151 (5)	-0.0075 (5)
C15	0.0476 (7)	0.0471 (7)	0.0435 (7)	-0.0142 (6)	-0.0163 (6)	-0.0089 (5)
C16	0.0854 (13)	0.0621 (10)	0.0558 (9)	-0.0166 (9)	-0.0259 (9)	-0.0238 (8)
C17	0.0650 (11)	0.0801 (13)	0.0642 (11)	-0.0162 (9)	-0.0143 (9)	-0.0266 (9)
C18	0.0433 (7)	0.0452 (7)	0.0439 (7)	-0.0124 (5)	-0.0162 (5)	-0.0060 (5)
C19	0.0497 (8)	0.0728 (11)	0.0576 (9)	-0.0221 (8)	-0.0213 (7)	-0.0115 (8)

Geometric parameters (\AA , $^\circ$)

C1—N1	1.3708 (19)	C11—H11	0.93
C1—C6	1.415 (2)	C12—C13	1.388 (2)
C1—C2	1.415 (2)	C12—H12	0.93
C2—C3	1.365 (3)	C13—H13	0.93
C2—H2	0.93	C14—C18	1.433 (2)
C3—C4	1.403 (3)	C14—C15	1.5031 (19)
C3—H3	0.93	C15—O1	1.1841 (19)
C4—C5	1.371 (2)	C15—O2	1.3132 (19)
C4—H4	0.93	C16—O2	1.457 (2)
C5—C6	1.417 (2)	C16—C17	1.485 (3)
C5—H5	0.93	C16—H16A	0.97
C6—C7	1.4268 (19)	C16—H16B	0.97
C7—C14	1.3775 (19)	C17—H17A	0.96
C7—C8	1.4939 (19)	C17—H17B	0.96
C8—C13	1.387 (2)	C17—H17C	0.96
C8—C9	1.391 (2)	C18—N1	1.311 (2)
C9—C10	1.390 (2)	C18—C19	1.503 (2)
C9—H9	0.93	C19—H19A	0.96
C10—C11	1.373 (3)	C19—H19B	0.96
C10—H10	0.93	C19—H19C	0.96
C11—C12	1.378 (3)		
N1—C1—C6	123.08 (13)	C11—C12—H12	120
N1—C1—C2	117.62 (14)	C13—C12—H12	120
C6—C1—C2	119.30 (14)	C8—C13—C12	120.70 (15)
C3—C2—C1	120.59 (16)	C8—C13—H13	119.7

C3—C2—H2	119.7	C12—C13—H13	119.7
C1—C2—H2	119.7	C7—C14—C18	120.33 (13)
C2—C3—C4	120.20 (16)	C7—C14—C15	120.08 (12)
C2—C3—H3	119.9	C18—C14—C15	119.58 (12)
C4—C3—H3	119.9	O1—C15—O2	124.63 (15)
C5—C4—C3	120.81 (15)	O1—C15—C14	124.46 (14)
C5—C4—H4	119.6	O2—C15—C14	110.91 (12)
C3—C4—H4	119.6	O2—C16—C17	107.69 (15)
C4—C5—C6	120.21 (16)	O2—C16—H16A	110.2
C4—C5—H5	119.9	C17—C16—H16A	110.2
C6—C5—H5	119.9	O2—C16—H16B	110.2
C1—C6—C5	118.89 (13)	C17—C16—H16B	110.2
C1—C6—C7	117.77 (12)	H16A—C16—H16B	108.5
C5—C6—C7	123.35 (13)	C16—C17—H17A	109.5
C14—C7—C6	117.96 (12)	C16—C17—H17B	109.5
C14—C7—C8	122.12 (12)	H17A—C17—H17B	109.5
C6—C7—C8	119.89 (12)	C16—C17—H17C	109.5
C13—C8—C9	118.59 (14)	H17A—C17—H17C	109.5
C13—C8—C7	120.19 (13)	H17B—C17—H17C	109.5
C9—C8—C7	121.21 (13)	N1—C18—C14	122.27 (13)
C10—C9—C8	120.56 (16)	N1—C18—C19	117.00 (14)
C10—C9—H9	119.7	C14—C18—C19	120.73 (13)
C8—C9—H9	119.7	C18—C19—H19A	109.5
C11—C10—C9	120.00 (16)	C18—C19—H19B	109.5
C11—C10—H10	120	H19A—C19—H19B	109.5
C9—C10—H10	120	C18—C19—H19C	109.5
C10—C11—C12	120.20 (16)	H19A—C19—H19C	109.5
C10—C11—H11	119.9	H19B—C19—H19C	109.5
C12—C11—H11	119.9	C18—N1—C1	118.58 (13)
C11—C12—C13	119.94 (16)	C15—O2—C16	119.11 (13)
N1—C1—C2—C3	178.06 (15)	C10—C11—C12—C13	-0.8 (3)
C6—C1—C2—C3	-1.1 (2)	C9—C8—C13—C12	1.3 (2)
C1—C2—C3—C4	0.8 (3)	C7—C8—C13—C12	-177.08 (15)
C2—C3—C4—C5	0.1 (3)	C11—C12—C13—C8	-0.5 (3)
C3—C4—C5—C6	-0.6 (3)	C6—C7—C14—C18	-0.5 (2)
N1—C1—C6—C5	-178.56 (13)	C8—C7—C14—C18	177.58 (12)
C2—C1—C6—C5	0.6 (2)	C6—C7—C14—C15	178.33 (11)
N1—C1—C6—C7	0.9 (2)	C8—C7—C14—C15	-3.6 (2)
C2—C1—C6—C7	-179.97 (12)	C7—C14—C15—O1	-76.8 (2)
C4—C5—C6—C1	0.3 (2)	C18—C14—C15—O1	102.0 (2)
C4—C5—C6—C7	-179.12 (14)	C7—C14—C15—O2	102.89 (16)
C1—C6—C7—C14	-0.56 (19)	C18—C14—C15—O2	-78.24 (17)
C5—C6—C7—C14	178.85 (13)	C7—C14—C18—N1	1.5 (2)
C1—C6—C7—C8	-178.70 (12)	C15—C14—C18—N1	-177.41 (13)
C5—C6—C7—C8	0.7 (2)	C7—C14—C18—C19	-177.80 (14)
C14—C7—C8—C13	-79.78 (18)	C15—C14—C18—C19	3.3 (2)
C6—C7—C8—C13	98.29 (17)	C14—C18—N1—C1	-1.1 (2)
C14—C7—C8—C9	101.92 (17)	C19—C18—N1—C1	178.13 (13)
C6—C7—C8—C9	-80.01 (18)	C6—C1—N1—C18	0.0 (2)

supplementary materials

C13—C8—C9—C10	-0.8 (2)	C2—C1—N1—C18	-179.18 (13)
C7—C8—C9—C10	177.53 (15)	O1—C15—O2—C16	0.8 (3)
C8—C9—C10—C11	-0.4 (3)	C14—C15—O2—C16	-178.93 (15)
C9—C10—C11—C12	1.2 (3)	C17—C16—O2—C15	129.54 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C16—H16A \cdots O1	0.97	2.32	2.711 (3)	103
C19—H19B \cdots O2 ⁱ	0.96	2.52	3.374 (3)	147
C19—H19C \cdots O2	0.96	2.59	3.212 (3)	122
C12—H12 \cdots Cg2 ⁱⁱ	0.93	2.95	3.750 (3)	145
C17—H17C \cdots Cg3 ⁱⁱⁱ	0.96	2.97	3.883 (3)	160

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

Fig. 1

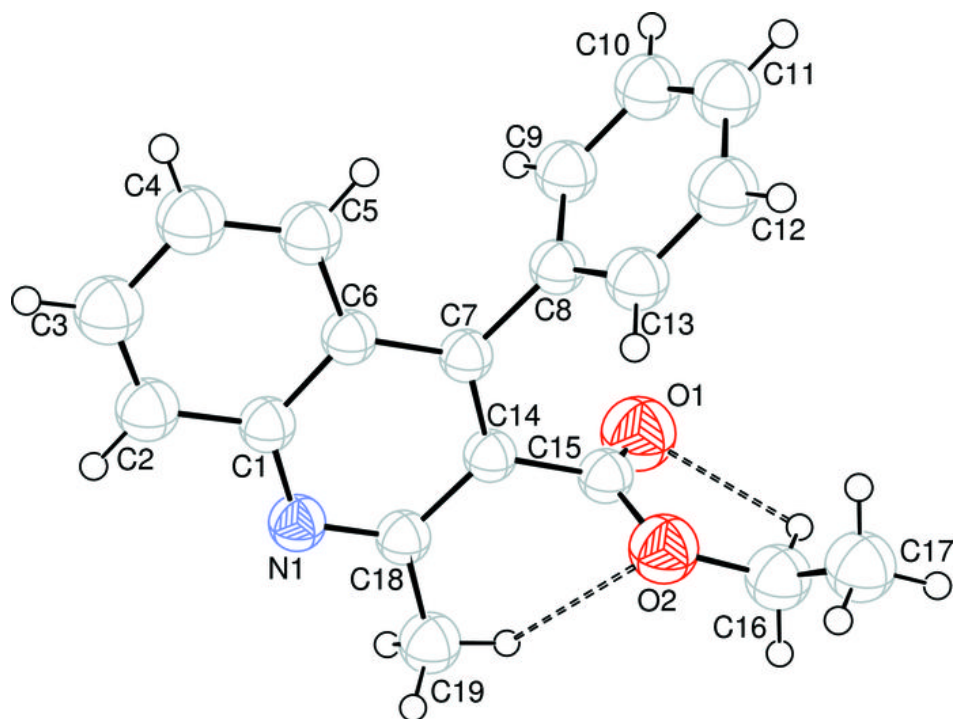


Fig. 2

