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(*E*)-3-[4-[(7-Chloroquinolin-4-yl)oxy]-3-methoxyphenyl]-1-(4-methylphenyl)prop-2-en-1-one: a ladder-like structure resulting solely from π - π stacking interactions

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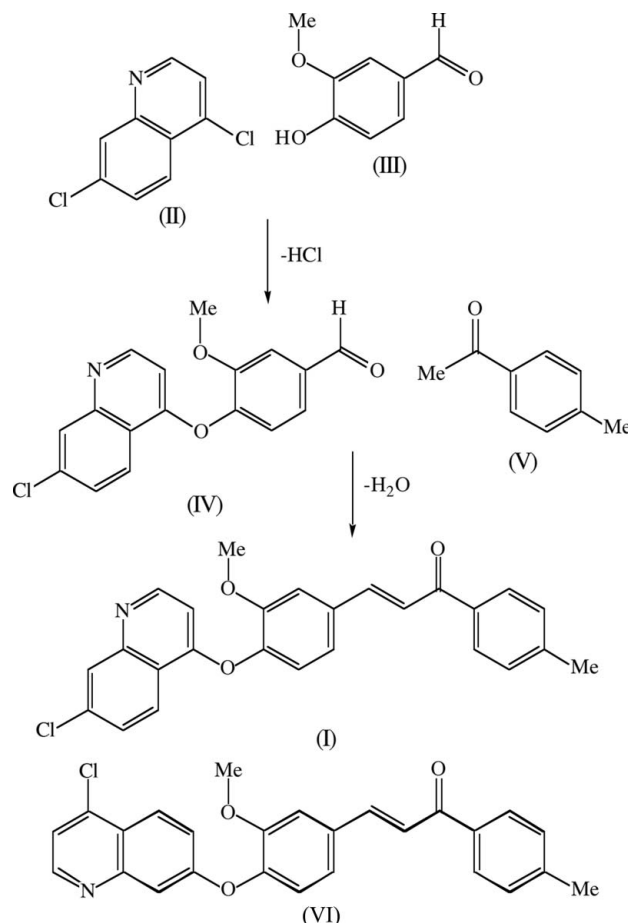
In the title compound, C₂₆H₂₀ClNO₃, the quinoline fragment is nearly orthogonal to the adjacent aryl ring, while the rest of the molecular skeleton is close to being planar. The crystal structure contains no hydrogen bonds of any sort, but there are two π - π stacking interactions present. One, involving the quinoline ring, links molecules related by inversion, while the other, involving the two nonfused aryl rings, links molecules related by translation, so together forming a ladder-type arrangement

Keywords: crystal structure; π - π stacking interactions; ladder-like structure; prop-2-en-1-one; (7-chloroquinolin-4-yl)oxy; nucleophilic aromatic substitution; Claisen–Schmidt condensation; chalcone.

1. Introduction

Many natural or synthetic chalcones containing the 1,3-diarylprop-2-en-1-one skeleton are highly active in pharmaceutical and medicinal applications, and they have been found to be effective as antimicrobial, antifungal, antimalarial, antioxidant, anti-angiogenic, antitumour and anti-inflammatory agents (Dimmock *et al.*, 1999; Kontogiorgis *et al.*, 2008; Echeverria *et al.*, 2009). Several strategies for the synthesis of these systems based on the formation of new carbon–carbon bonds have been reported, and among them the direct Aldol and Claisen–Schmidt condensations still occupy prominent positions (Kreher *et al.*, 2003). The present investigation is a continuation of our broad programme of work on the synthesis and structural study of chalcones and their derivatives, as investigation of these structures may be helpful in the design and synthesis of new compounds with interesting biological properties (Abonía *et al.*, 2012; Insuasty *et al.*, 2013). In order

to obtain the new key chalcone derivative (*E*)-3-[4-[(7-chloroquinolin-4-yl)oxy]-3-methoxyphenyl]-1-(4-methylphenyl)prop-2-en-1-one, (I) (see Scheme), the synthesis of the precursor 4-(7-chloroquinolin-4-yloxy)-3-methoxybenzaldehyde, (IV), was performed by the selective nucleophilic aromatic substitution (S_NAr) of the 4-chloro substituent in 4,7-dichloroquinoline, (II), by 4-hydroxy-3-methoxybenzaldehyde [vanillin, (III)]. This S_NAr process was carried out using microwave irradiation, and Claisen–Schmidt condensation of the resulting intermediate, (IV), with 4'-methylacetophenone, (V), then led to the formation of the title compound, (I), the molecular and supramolecular structure of which we report here. The purposes of the present study were therefore to confirm the regiochemistry of the S_NAr reaction, leading to the formation of (I) rather than to its isomer (VI) (see Scheme), and to explore the supramolecular assembly of (I), where the molecular constitution offers scope for a rich variety of C–H...X interactions, based on the presence of a pyridine-type N atom, two different types of O atom (ether and ketonic) and four independent aromatic rings.



2. Experimental

2.1. Synthesis and crystallization

A mixture of 4,7-dichloroquinoline, (II) (2.5 mmol), 4-hydroxy-3-methoxybenzaldehyde, (III) (2.5 mmol), and potassium carbonate (7 mmol) in *N,N*-dimethylformamide (0.2 ml)

Table 1

Experimental details.

Crystal data	
Chemical formula	C ₂₆ H ₂₀ ClNO ₃
<i>M_r</i>	429.88
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.9521 (9), 32.170 (3), 8.5382 (10)
β (°)	108.240 (16)
<i>V</i> (Å ³)	2074.5 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.21
Crystal size (mm)	0.39 × 0.32 × 0.19
Data collection	
Diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.882, 0.960
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	24962, 4747, 2666
<i>R_{int}</i>	0.069
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.055, 0.155, 1.07
No. of reflections	4747
No. of parameters	282
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.30, -0.37

Computer programs: *COLLECT* (Nonius, 1999), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

was subjected to microwave irradiation for 6 min at a maximum power of 100 W and a temperature of 373 K (see Scheme). The reaction mixture was allowed to cool to ambient temperature and then poured into excess ice-cold water. The resulting solid product was collected by filtration and recrystallized from ethanol to give the intermediate 4-(7-chloroquinolin-4-yloxy)-3-methoxybenzaldehyde, (IV). A mixture of (IV) (1 mmol) and 4'-methylacetophenone, (V) (1 mmol), dissolved in a mixture of aqueous sodium hydroxide solution (20% w/w, 0.8 ml) and aqueous ethanol (95% w/w, 30 ml), was then stirred at room temperature for 2 h. The resulting solid product was collected by filtration and washed with ethanol. No further purification was necessary and the desired chalcone, (I), was obtained in good yield as a yellow solid. Yellow crystals of (I) suitable for single-crystal X-ray diffraction were

grown by slow evaporation, at ambient temperature and in the presence of air, of a solution in chloroform–methanol (5:1 v/v) [yield 85%; m.p. 455–456 K (with decomposition)]. MS (70 eV) *m/z* (%): 429 (61, *M*⁺), 313 (76), 176 (100), 135 (32), 119 (64), 91 (58). Analysis found: C 72.6, H 4.6, N 3.3%; C₂₆H₂₀ClNO₃ requires: C 72.6, H 4.7, N 3.3%.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in a difference map and then treated as riding in geometrically idealized positions, with C–H = 0.95 (alkenyl, aromatic and heteroaromatic) or 0.98 Å (methyl), and with *U*_{iso}(H) = *kU*_{eq}(C), where *k* = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms. Six low-angle reflections ($\bar{1}01$, 120, 021, 031, $\bar{1}11$ and $\bar{1}21$), which had been wholly or partially attenuated by the beam stop, were omitted from the refinements. Examination of the refined structure using *PLATON* (Spek, 2009) showed that there were no solvent-accessible voids present.

3. Comment

The molecular constitution of (I) confirms that the S_NAr reaction has occurred at the 4-position of the quinoline component rather than at the 7-position, which would have produced the alternative isomer, (VI) (see Scheme). The molecular conformation of (I) can be specified in terms of the six torsion angles about the C1–C2, C1–C11, C3–C31, C33–O33, C34–O34 and O34–C44 single bonds (Table 2). The spacer unit between atoms C11 and C31 is essentially planar, with an all-*trans* chain-extended conformation; the maximum deviation from the mean plane through these atoms is 0.022 (2) Å for atom C2. However, the planes of the two adjacent aryl rings (C11–C16 and C31–C36) are both rotated out of the plane of the spacer unit, making dihedral angles with the spacer plane of 7.6 (3) and 7.7 (3)°, respectively. These rotations occur in disrotatory fashion, such that the dihedral angle between the two ring planes is only 1.40 (13)°.

Methoxy atom C37 lies close to the plane of the adjacent C31–C36 aryl ring, with a displacement from the ring plane of 0.136 (5) Å. Similarly, aryl atom C34 lies close to the plane of

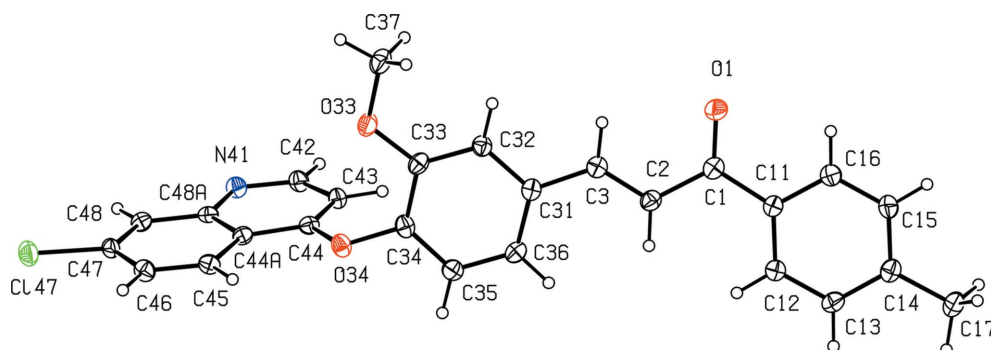


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 2Selected bond and torsion angles ($^{\circ}$).

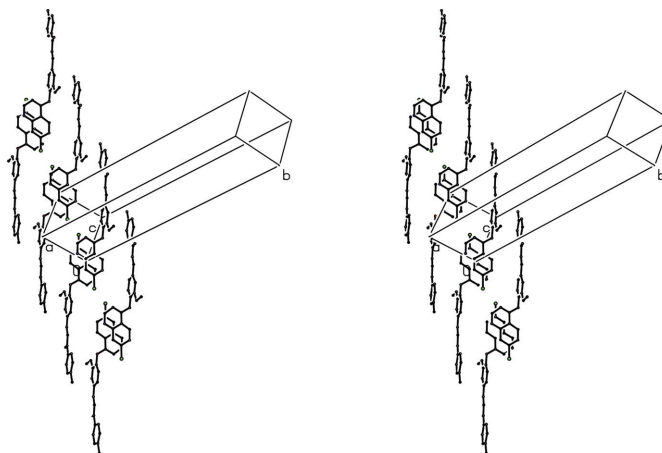
O33—C33—C32	125.5 (2)	O34—C44—C43	124.4 (2)
O33—C33—C34	116.3 (2)	O34—C44—C44a	115.5 (2)
O34—C34—C35	119.6 (2)	C33—O33—C37	116.8 (2)
O34—C34—C33	119.2 (2)	C34—O34—C44	116.79 (19)
C12—C11—C1—C2	9.7 (4)	C32—C33—O33—C37	-4.8 (4)
C11—C1—C2—C3	-179.3 (2)	C33—C34—O34—C44	76.2 (3)
C2—C3—C31—C32	174.2 (3)	C34—O34—C44—C43	12.3 (4)

the adjacent quinoline system, with a displacement from the plane of the pyridine component of 0.249 (3) Å. By contrast, the projection of the O34—C44 bond is nearly orthogonal to the C31—C36 aryl ring and atom C44 is displaced by 1.153 (2) Å from the plane of the C31—C36 ring. Accordingly, the dihedral angle between the plane of the pyridine ring and that of the C31—C36 aryl ring is 81.03 (12) $^{\circ}$. Consequently, the molecules of (I) have no internal symmetry and hence they are conformationally chiral. However, the centrosymmetric space group accommodates equal numbers of the two conformational enantiomers.

The two exocyclic C—C—O angles at atom C33 (Table 2) differ by almost 10 $^{\circ}$. This behaviour seems to be typical for methoxyarene systems where the methoxy C atoms lies in, or close to, the plane of the arene ring (Seip & Seip, 1973; Ferguson *et al.*, 1996; Gallagher *et al.*, 2001, 2004; Peralta *et al.*, 2007; Cuervo *et al.*, 2009), and a similar pattern is observed for the exocyclic C—C—O angles at atom C44, consistent with the location of atom C34 close to the plane of the pyridine ring, as noted above. By contrast, the exocyclic C—C—O angles at atom C34 are almost identical, typical of such angles where the α -C atom of the alkoxy substituent is significantly displaced from the plane of the adjacent ring (Peralta *et al.*, 2007; Cuervo *et al.*, 2009). Both of the C—O—C angles are somewhat larger than the ideal tetrahedral value as found, for example, in dimethyl ether, (CH₃)₂O, where the C—O—C angle is 111.5 (15) $^{\circ}$ (Kimura & Kubo, 1959).

Despite the presence in the molecule of (I) of several potential acceptors of hydrogen bonds which are sterically unencumbered, particularly atoms O1 and N41, there are, in fact, no hydrogen bonds of C—H \cdots O or C—H \cdots N types present in the crystal structure of (I). Nor, despite the presence of four independent aromatic rings, are there any hydrogen bonds of C—H \cdots π type.

However, there are several independent π - π stacking interactions present, and these determine the form of the supramolecular assembly. The planes of the fused C44a/C45—C48/C48a aryl rings in the molecules at (x , y , z) and ($-x$, $-y$, $-z$) are strictly parallel, with an interplanar spacing of 3.467 Å. The ring-centroid separation is 3.6288 (15) Å, corresponding to a ring-centroid offset of 1.071 Å. In addition, the planes of the pyridine ring in the molecule at (x , y , z) and the fused aryl ring in the molecule at ($-x$, $-y$, $-z$), *i.e.* the two components of the quinoline system, make a dihedral angle of 1.66 (12) $^{\circ}$. The ring-centroid separation is 3.7341 (15) Å and the shortest perpendicular distance from the centroid of one ring to the plane of the other is 3.479 Å, corresponding to a

**Figure 2**

A stereoview of part of the crystal structure of (I), showing the formation of a ladder-type structure running parallel to the [101] direction and built from π - π stacking interactions between molecules which are related either by inversion or by translation. For the sake of clarity, all of the H atoms have been omitted.

ring-centroid offset of *ca* 1.36 Å. Hence, these π - π interactions between the quinoline components link molecules related by inversion to form a dimer centred at the origin (Fig. 2).

The third π - π stacking interaction involves the two nonfused aryl rings. As noted earlier, the dihedral angle between the planes of these two rings within the molecule of (I) is 1.40 (13) $^{\circ}$. Similarly, the dihedral angle between the plane of the C11—C16 ring at (x , y , z) and that of the C31—C36 ring in the molecule at ($x + 1$, y , $z + 1$) is also 1.40 (13) $^{\circ}$. The associated ring-centroid separation is 3.7391 (17) Å, and the shortest perpendicular distance between the centroid of one ring and the plane of the other is 3.485 Å, corresponding to a ring-centroid offset of *ca* 1.36 Å. The effect of this interaction is to link molecules related by translation into a chain running parallel to the [101] direction. The combination of the three stacking interactions, which link molecules related by inversion in two cases and by translation in the third, generates a ladder-type arrangement running parallel to the [101] direction (Fig. 2).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: YF3063).

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supporting information

Acta Cryst. (2014). **C70**, 677-680 [doi:10.1107/S2053229614013588]

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Computing details

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(E)-3-{4-[(7-Chloroquinolin-4-yl)oxy]-3-methoxyphenyl}-1-(4-methylphenyl)prop-2-en-1-one

Crystal data

C₂₆H₂₀ClNO₃

M_r = 429.88

Monoclinic, *P2₁/n*

Hall symbol: -P 2yn

a = 7.9521 (9) Å

b = 32.170 (3) Å

c = 8.5382 (10) Å

β = 108.240 (16)°

V = 2074.5 (4) Å³

Z = 4

F(000) = 896

D_x = 1.376 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 4753 reflections

θ = 2.8–27.5°

μ = 0.21 mm⁻¹

T = 120 K

Block, yellow

0.39 × 0.32 × 0.19 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer

Radiation source: Bruker Nonius FR591 rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)

T_{min} = 0.882, *T_{max}* = 0.960

24962 measured reflections

4747 independent reflections

2666 reflections with *I* > 2 σ (*I*)

R_{int} = 0.069

θ_{\max} = 27.5°, θ_{\min} = 3.3°

h = -10→10

k = -41→41

l = -11→11

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.055

wR(*F*²) = 0.155

S = 1.07

4747 reflections

282 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.7161P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7614 (4)	0.19510 (8)	1.0948 (3)	0.0322 (6)
C2	0.6259 (4)	0.16948 (8)	0.9750 (3)	0.0321 (6)
H2	0.5737	0.1467	1.0132	0.039*
C3	0.5766 (3)	0.17803 (8)	0.8148 (3)	0.0301 (6)
H3	0.6298	0.2019	0.7848	0.036*
O1	0.8280 (3)	0.22494 (6)	1.0457 (2)	0.0408 (5)
C11	0.8162 (3)	0.18483 (8)	1.2727 (3)	0.0285 (6)
C12	0.7683 (4)	0.14875 (9)	1.3371 (3)	0.0348 (7)
H12	0.6924	0.1293	1.2650	0.042*
C13	0.8295 (4)	0.14070 (9)	1.5046 (3)	0.0365 (7)
H13	0.7952	0.1157	1.5458	0.044*
C14	0.9406 (4)	0.16864 (9)	1.6139 (3)	0.0331 (7)
C15	0.9879 (4)	0.20457 (9)	1.5499 (3)	0.0380 (7)
H15	1.0635	0.2241	1.6219	0.046*
C16	0.9268 (4)	0.21254 (9)	1.3829 (3)	0.0372 (7)
H16	0.9611	0.2376	1.3421	0.045*
C17	1.0095 (4)	0.16017 (10)	1.7960 (3)	0.0424 (7)
H17A	1.1387	0.1576	1.8303	0.064*
H17B	0.9580	0.1342	1.8204	0.064*
H17C	0.9767	0.1832	1.8559	0.064*
C31	0.4519 (3)	0.15576 (8)	0.6787 (3)	0.0286 (6)
C32	0.4087 (3)	0.17295 (8)	0.5205 (3)	0.0297 (6)
H32	0.4567	0.1992	0.5060	0.036*
C33	0.2974 (4)	0.15249 (8)	0.3847 (3)	0.0309 (6)
C34	0.2289 (3)	0.11402 (8)	0.4094 (3)	0.0307 (6)
C35	0.2670 (3)	0.09714 (9)	0.5638 (3)	0.0326 (6)
H35	0.2167	0.0712	0.5781	0.039*
C36	0.3782 (3)	0.11762 (8)	0.6986 (3)	0.0316 (6)
H36	0.4044	0.1057	0.8054	0.038*
O33	0.2479 (3)	0.16673 (5)	0.2266 (2)	0.0381 (5)
C37	0.3059 (4)	0.20758 (9)	0.2013 (3)	0.0419 (7)
H37A	0.2695	0.2274	0.2717	0.063*
H37B	0.2528	0.2155	0.0854	0.063*
H37C	0.4352	0.2078	0.2295	0.063*
O34	0.1135 (2)	0.09325 (6)	0.2747 (2)	0.0335 (5)
N41	0.3189 (3)	0.03318 (7)	-0.0597 (3)	0.0303 (5)
C42	0.4223 (3)	0.04635 (8)	0.0840 (3)	0.0301 (6)
H42	0.5456	0.0412	0.1101	0.036*
C43	0.3650 (3)	0.06740 (8)	0.2018 (3)	0.0288 (6)
H43	0.4474	0.0769	0.3019	0.035*
C44	0.1879 (3)	0.07392 (7)	0.1690 (3)	0.0265 (6)

C44a	0.0673 (3)	0.05947 (7)	0.0199 (3)	0.0265 (6)
C45	-0.1180 (3)	0.06409 (8)	-0.0232 (3)	0.0303 (6)
H45	-0.1680	0.0767	0.0526	0.036*
C46	-0.2264 (4)	0.05072 (8)	-0.1722 (3)	0.0324 (6)
H46	-0.3511	0.0539	-0.2000	0.039*
C47	-0.1522 (3)	0.03234 (8)	-0.2837 (3)	0.0291 (6)
Cl47	-0.29032 (9)	0.01742 (2)	-0.47598 (9)	0.0412 (2)
C48	0.0261 (3)	0.02615 (8)	-0.2449 (3)	0.0295 (6)
H48	0.0726	0.0126	-0.3213	0.035*
C48a	0.1414 (3)	0.03969 (7)	-0.0921 (3)	0.0254 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0351 (16)	0.0311 (15)	0.0310 (16)	0.0059 (13)	0.0113 (13)	0.0008 (12)
C2	0.0370 (16)	0.0298 (15)	0.0304 (16)	0.0021 (12)	0.0119 (13)	0.0016 (12)
C3	0.0323 (16)	0.0270 (14)	0.0314 (16)	0.0054 (12)	0.0107 (13)	-0.0010 (12)
O1	0.0522 (13)	0.0331 (11)	0.0363 (12)	-0.0056 (10)	0.0129 (10)	0.0032 (9)
C11	0.0276 (15)	0.0297 (14)	0.0280 (15)	0.0049 (11)	0.0084 (12)	0.0003 (11)
C12	0.0353 (16)	0.0358 (16)	0.0314 (16)	-0.0033 (13)	0.0078 (13)	0.0015 (12)
C13	0.0409 (17)	0.0357 (16)	0.0334 (17)	0.0011 (13)	0.0125 (14)	0.0073 (13)
C14	0.0300 (16)	0.0413 (17)	0.0294 (15)	0.0068 (13)	0.0114 (12)	-0.0004 (13)
C15	0.0410 (17)	0.0398 (17)	0.0314 (17)	-0.0060 (14)	0.0089 (13)	-0.0068 (13)
C16	0.0415 (17)	0.0362 (16)	0.0338 (17)	-0.0048 (13)	0.0117 (14)	-0.0021 (13)
C17	0.0426 (18)	0.054 (2)	0.0294 (16)	0.0034 (15)	0.0098 (14)	0.0034 (14)
C31	0.0285 (15)	0.0295 (14)	0.0279 (15)	0.0058 (12)	0.0091 (12)	-0.0017 (11)
C32	0.0322 (16)	0.0266 (14)	0.0294 (15)	0.0014 (12)	0.0085 (12)	-0.0017 (11)
C33	0.0363 (16)	0.0311 (15)	0.0268 (15)	0.0076 (12)	0.0120 (13)	0.0024 (11)
C34	0.0279 (15)	0.0323 (15)	0.0319 (16)	0.0019 (12)	0.0093 (12)	-0.0083 (12)
C35	0.0329 (16)	0.0327 (15)	0.0345 (16)	-0.0009 (12)	0.0139 (13)	-0.0032 (12)
C36	0.0357 (16)	0.0318 (15)	0.0293 (15)	0.0058 (12)	0.0130 (13)	0.0031 (12)
O33	0.0508 (12)	0.0336 (11)	0.0262 (11)	-0.0004 (9)	0.0066 (9)	0.0003 (8)
C37	0.055 (2)	0.0376 (17)	0.0304 (17)	0.0059 (15)	0.0086 (14)	0.0036 (13)
O34	0.0294 (10)	0.0393 (11)	0.0332 (11)	-0.0021 (8)	0.0118 (9)	-0.0110 (9)
N41	0.0257 (13)	0.0328 (12)	0.0327 (13)	0.0017 (10)	0.0095 (10)	-0.0012 (10)
C42	0.0214 (14)	0.0346 (15)	0.0331 (16)	0.0018 (12)	0.0066 (12)	-0.0001 (12)
C43	0.0258 (15)	0.0311 (15)	0.0272 (15)	-0.0013 (11)	0.0050 (12)	-0.0015 (11)
C44	0.0298 (15)	0.0236 (13)	0.0285 (15)	0.0005 (11)	0.0127 (12)	0.0003 (11)
C44a	0.0280 (15)	0.0252 (14)	0.0275 (14)	0.0020 (11)	0.0103 (12)	0.0021 (11)
C45	0.0273 (15)	0.0301 (15)	0.0355 (16)	0.0007 (12)	0.0126 (12)	-0.0005 (12)
C46	0.0243 (15)	0.0335 (15)	0.0368 (17)	0.0034 (12)	0.0057 (13)	0.0020 (12)
C47	0.0264 (15)	0.0292 (14)	0.0268 (15)	-0.0025 (11)	0.0014 (12)	0.0023 (11)
Cl47	0.0353 (4)	0.0456 (4)	0.0351 (4)	-0.0030 (3)	0.0000 (3)	-0.0028 (3)
C48	0.0305 (16)	0.0309 (15)	0.0291 (15)	0.0011 (12)	0.0124 (12)	0.0018 (11)
C48a	0.0245 (14)	0.0236 (13)	0.0295 (15)	-0.0003 (11)	0.0106 (12)	0.0051 (11)

Geometric parameters (Å, °)

C1—O1	1.231 (3)	C34—C35	1.369 (4)
C1—C11	1.481 (4)	C34—O34	1.397 (3)
C1—C2	1.482 (4)	C35—C36	1.380 (4)
C2—C3	1.328 (3)	C35—H35	0.9500
C2—H2	0.9500	C36—H36	0.9500
C3—C31	1.458 (4)	O33—C37	1.431 (3)
C3—H3	0.9500	C37—H37A	0.9800
C11—C12	1.387 (4)	C37—H37B	0.9800
C11—C16	1.391 (4)	C37—H37C	0.9800
C12—C13	1.383 (4)	O34—C44	1.373 (3)
C12—H12	0.9500	N41—C42	1.315 (3)
C13—C14	1.394 (4)	N41—C48a	1.367 (3)
C13—H13	0.9500	C42—C43	1.402 (4)
C14—C15	1.380 (4)	C42—H42	0.9500
C14—C17	1.503 (4)	C43—C44	1.363 (3)
C15—C16	1.379 (4)	C43—H43	0.9500
C15—H15	0.9500	C44—C44a	1.412 (3)
C16—H16	0.9500	C44a—C45	1.411 (4)
C17—H17A	0.9800	C44a—C48a	1.420 (3)
C17—H17B	0.9800	C45—C46	1.364 (4)
C17—H17C	0.9800	C45—H45	0.9500
C31—C36	1.393 (4)	C46—C47	1.398 (4)
C31—C32	1.399 (3)	C46—H46	0.9500
C32—C33	1.385 (4)	C47—C48	1.366 (4)
C32—H32	0.9500	C47—C147	1.733 (3)
C33—O33	1.362 (3)	C48—C48a	1.408 (4)
C33—C34	1.395 (4)	C48—H48	0.9500
O1—C1—C11	120.2 (2)	O34—C34—C33	119.2 (2)
O1—C1—C2	119.7 (2)	C34—C35—C36	120.3 (3)
C11—C1—C2	120.1 (2)	C34—C35—H35	119.8
C3—C2—C1	120.8 (3)	C36—C35—H35	119.8
C3—C2—H2	119.6	C35—C36—C31	120.2 (3)
C1—C2—H2	119.6	C35—C36—H36	119.9
C2—C3—C31	128.8 (3)	C31—C36—H36	119.9
C2—C3—H3	115.6	O33—C37—H37A	109.5
C31—C3—H3	115.6	O33—C37—H37B	109.5
C12—C11—C16	117.5 (2)	H37A—C37—H37B	109.5
C12—C11—C1	124.3 (2)	O33—C37—H37C	109.5
C16—C11—C1	118.1 (2)	H37A—C37—H37C	109.5
C13—C12—C11	121.0 (3)	H37B—C37—H37C	109.5
C13—C12—H12	119.5	C42—N41—C48a	116.3 (2)
C11—C12—H12	119.5	N41—C42—C43	125.2 (2)
C12—C13—C14	121.0 (3)	N41—C42—H42	117.4
C12—C13—H13	119.5	C43—C42—H42	117.4
C14—C13—H13	119.5	C44—C43—C42	118.3 (2)

C15—C14—C13	118.0 (3)	C44—C43—H43	120.9
C15—C14—C17	120.3 (3)	C42—C43—H43	120.9
C13—C14—C17	121.7 (3)	O34—C44—C43	124.4 (2)
C16—C15—C14	120.9 (3)	C43—C44—C44a	120.1 (2)
C16—C15—H15	119.5	O34—C44—C44a	115.5 (2)
C14—C15—H15	119.5	C33—O33—C37	116.8 (2)
C15—C16—C11	121.6 (3)	C34—O34—C44	116.79 (19)
C15—C16—H16	119.2	C45—C44a—C44	124.0 (2)
C11—C16—H16	119.2	C45—C44a—C48a	119.4 (2)
C14—C17—H17A	109.5	C44—C44a—C48a	116.5 (2)
C14—C17—H17B	109.5	C46—C45—C44a	120.9 (2)
H17A—C17—H17B	109.5	C46—C45—H45	119.5
C14—C17—H17C	109.5	C44a—C45—H45	119.5
H17A—C17—H17C	109.5	C45—C46—C47	119.4 (2)
H17B—C17—H17C	109.5	C45—C46—H46	120.3
C36—C31—C32	118.7 (2)	C47—C46—H46	120.3
C36—C31—C3	122.8 (2)	C48—C47—C46	121.6 (2)
C32—C31—C3	118.4 (2)	C48—C47—C147	119.5 (2)
C33—C32—C31	121.3 (3)	C46—C47—C147	119.0 (2)
C33—C32—H32	119.3	C47—C48—C48a	120.3 (2)
C31—C32—H32	119.3	C47—C48—H48	119.8
O33—C33—C32	125.5 (2)	C48a—C48—H48	119.8
O33—C33—C34	116.3 (2)	N41—C48a—C48	118.1 (2)
C32—C33—C34	118.2 (2)	N41—C48a—C44a	123.5 (2)
C35—C34—C33	121.2 (2)	C48—C48a—C44a	118.4 (2)
O34—C34—C35	119.6 (2)		
O1—C1—C2—C3	0.7 (4)	C3—C31—C36—C35	-177.1 (2)
C12—C11—C1—C2	9.7 (4)	C32—C33—O33—C37	-4.8 (4)
C11—C1—C2—C3	-179.3 (2)	C34—C33—O33—C37	175.2 (2)
C1—C2—C3—C31	177.4 (2)	C35—C34—O34—C44	-106.4 (3)
O1—C1—C11—C12	-170.4 (3)	C33—C34—O34—C44	76.2 (3)
O1—C1—C11—C16	7.8 (4)	C48a—N41—C42—C43	-2.2 (4)
C2—C1—C11—C16	-172.1 (2)	N41—C42—C43—C44	2.1 (4)
C16—C11—C12—C13	-0.3 (4)	C42—C43—C44—O34	178.5 (2)
C1—C11—C12—C13	177.9 (2)	C42—C43—C44—C44a	0.3 (4)
C11—C12—C13—C14	0.2 (4)	C34—O34—C44—C43	12.3 (4)
C12—C13—C14—C15	0.0 (4)	C34—O34—C44—C44a	-169.4 (2)
C12—C13—C14—C17	-179.4 (3)	C43—C44—C44a—C45	178.7 (2)
C13—C14—C15—C16	0.0 (4)	O34—C44—C44a—C45	0.3 (4)
C17—C14—C15—C16	179.4 (2)	C43—C44—C44a—C48a	-2.1 (4)
C14—C15—C16—C11	-0.2 (4)	O34—C44—C44a—C48a	179.5 (2)
C12—C11—C16—C15	0.3 (4)	C44—C44a—C45—C46	177.6 (2)
C1—C11—C16—C15	-178.0 (2)	C48a—C44a—C45—C46	-1.6 (4)
C2—C3—C31—C36	-7.7 (4)	C44a—C45—C46—C47	-0.3 (4)
C2—C3—C31—C32	174.2 (3)	C45—C46—C47—C48	2.3 (4)
C36—C31—C32—C33	-1.1 (4)	C45—C46—C47—C147	-177.4 (2)
C3—C31—C32—C33	177.1 (2)	C46—C47—C48—C48a	-2.4 (4)

C31—C32—C33—O33	180.0 (2)	C147—C47—C48—C48a	177.23 (19)
C31—C32—C33—C34	0.0 (4)	C42—N41—C48a—C48	179.8 (2)
O33—C33—C34—C35	-178.7 (2)	C42—N41—C48a—C44a	0.1 (4)
C32—C33—C34—C35	1.3 (4)	C47—C48—C48a—N41	-179.3 (2)
O33—C33—C34—O34	-1.3 (3)	C47—C48—C48a—C44a	0.5 (4)
C32—C33—C34—O34	178.7 (2)	C45—C44a—C48a—N41	-178.8 (2)
C33—C34—C35—C36	-1.4 (4)	C44—C44a—C48a—N41	2.0 (4)
O34—C34—C35—C36	-178.8 (2)	C45—C44a—C48a—C48	1.4 (4)
C34—C35—C36—C31	0.2 (4)	C44—C44a—C48a—C48	-177.8 (2)
C32—C31—C36—C35	1.0 (4)		
