

# Crystal structure of ethyl (1*RS*,6*SR*)-4-(2-methyl-1*H*-imidazol-4-yl)-2-oxo-6-(2,3,5-trichlorophenyl)-cyclohex-3-ene-1-carboxylate

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**Keywords:** crystal structure; cyclocondensation reaction; molecular stereochemistry; molecular conformation; hydrogen bonding

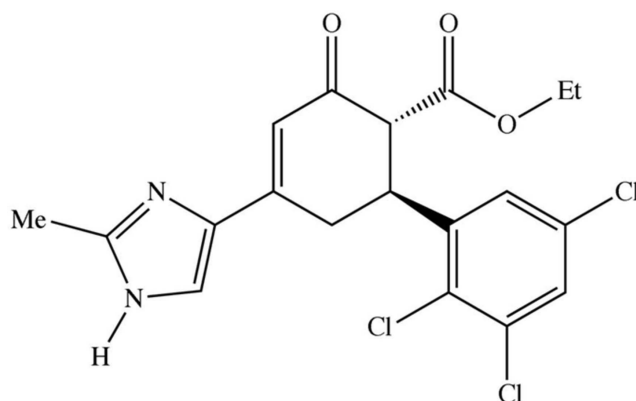
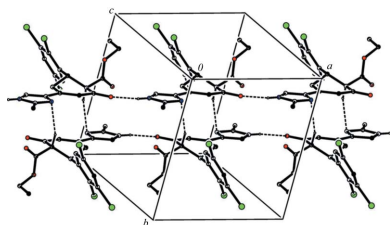
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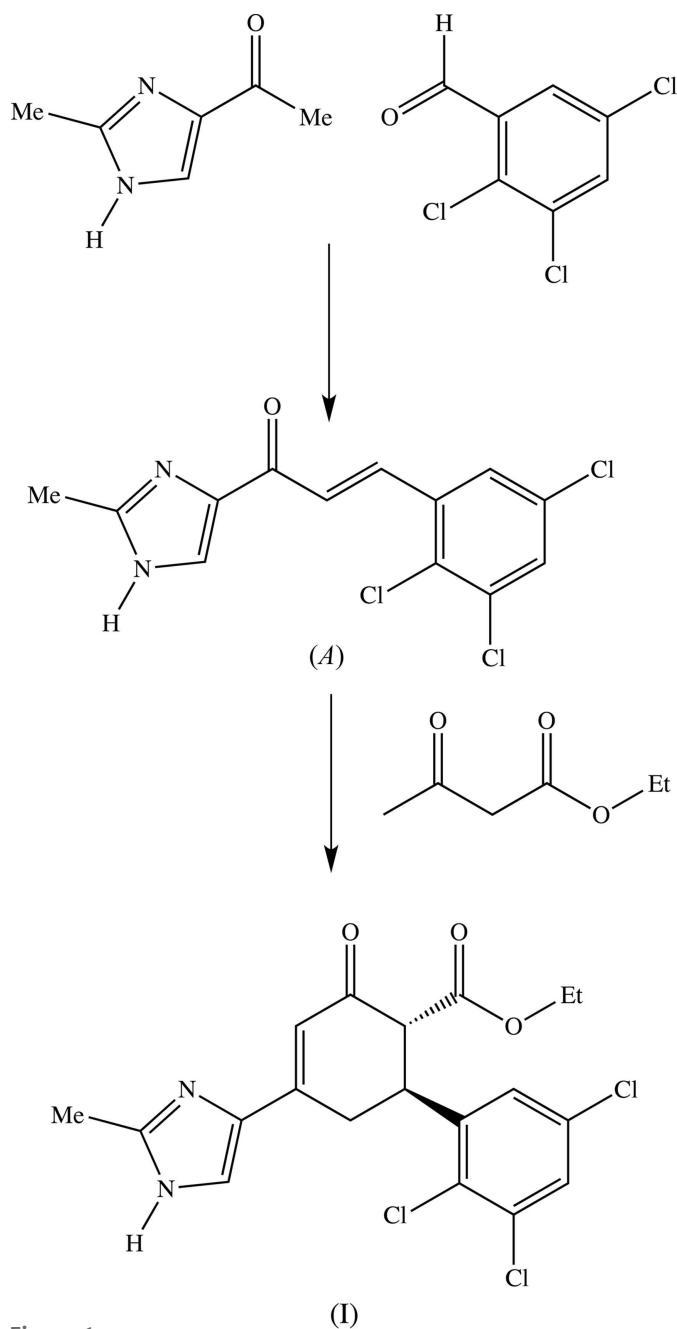
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The title compound, C<sub>19</sub>H<sub>17</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>3</sub>, has been prepared in a cyclocondensation reaction between 2,3,5-trichlorobenzaldehyde and 4-acetyl-2-methyl-1*H*-imidazole. The cyclohexenone ring adopts an envelope conformation with the C atom substituted by the trichlorophenyl ring as the flap. The mutually *trans* ester and aryl substituents both occupy equatorial sites. In the crystal, a combination of N—H···O and C—H···N hydrogen bonds links the molecules into ribbons of edge-fused centrosymmetric rings, which enclose *R*<sub>2</sub><sup>2</sup>(14) and *R*<sub>4</sub><sup>4</sup>(16) alternate ring motifs, propagating along the *b*-axis direction.

## 1. Chemical context

We have recently reported (Salian *et al.*, 2015) a simple and versatile synthesis of substituted 1,1':3'1''-terphenyls based upon the two-electron oxidation of substituted cyclohex-2-en-1-ones, themselves readily synthesized in reactions between 1,3-diarylprop-2-en-1-ones (chalcones) and compounds containing activated methylene units. This method points to a similar routes to substituted biphenyls carrying a wide range of substituents, including heterocyclic units. To this end, we have now synthesized the title compound (I) as a key intermediate in this proposed pathway. It was prepared by reaction of ethyl 3-oxobutanoate with the chalcone intermediate (A) (Fig. 1), which was itself prepared by base-catalysed condensation between 2,3,5-trichlorobenzaldehyde and 4-acetyl-2-methyl-1*H*-imidazole. The conversion of the intermediate (A) to the final product (I) is a two-step, but one-pot, process involving both Michael addition and a condensation reaction.





**Figure 1**  
The synthesis of the title compound (I).

## 2. Structural commentary

The molecule of compound (I) contains two stereogenic centres at atoms C1 and C6 (Fig. 2). The reference molecule was selected as one having the *R*-configuration at atom C1 and in this molecule atom C6 has the *S*-configuration; the centrosymmetric space group confirms that the compound has crystallized as a racemic mixture of the (1*R*,6*S*) and (1*S*,6*R*) diastereoisomers.

The central cyclohexenone ring (C1–C6), has puckering parameters of  $Q = 0.497$  (3) Å,  $\theta = 124.1$  (3)° and  $\varphi = 123.6$  (3)°, indicating an almost ideal envelope conformation with atom C6 as the flap. The maximum deviation from the

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N41-H41\cdots O2^i$	0.79 (4)	2.10 (4)	2.878 (3)	167 (3)
$C1-H1\cdots N43^{ii}$	0.98	2.60	3.538 (4)	161

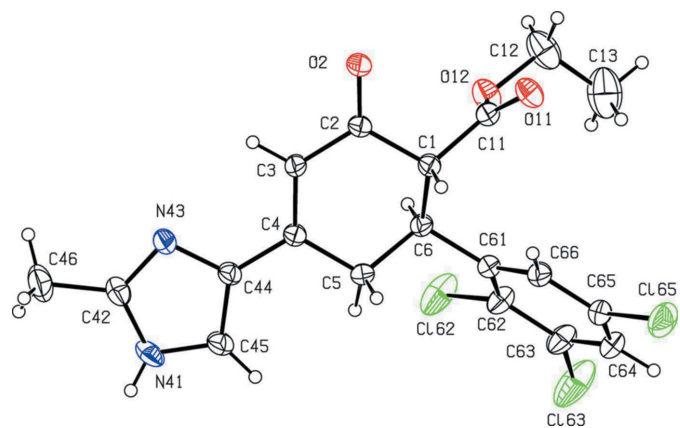
Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .

mean plane through atoms (C1–C5) is 0.023 (2) Å for atom C4, with an r.m.s. deviation of 0.0144 Å, and with the flap atom C6 displaced by 0.684 (3) Å.

The ester and aryl substituents at atoms C1 and C6, respectively, are *trans* to one another and both occupy equatorial sites (Fig. 2). The dihedral angle between the mean plane through atoms (C1–C5) and the adjacent imidazole ring is only 2.18 (16)° but, despite this, the bond lengths in the imidazolyl-cyclohexenone portion of the molecule, atoms (N41, C45, C44, C4, C3, C2, O2), provide no evidence for delocalization of the lone pair from the planar atom N41 through the vinylogous amide fragment onto atom O2. In contrast, the dihedral angle between the mean plane through atoms (C1–C5) and the carboxyl group (C11/O11/O12) is 89.0 (3)°.

## 3. Supramolecular interactions

In the crystal of compound (I), molecules related by translation along [100] are linked by nearly linear  $N-H\cdots O$  hydrogen bonds (Table 1 and Fig. 3), forming  $C(8)$  chains, and inversion-related pairs of such chains are linked by  $C-H\cdots N$  hydrogen bonds, forming ribbons or molecular ladders of edge-fused centrosymmetric rings, in which  $R_2^2(14)$  rings centred at  $(n + 1/2, 1/2, 1/2)$  alternate with  $R_4^4(16)$  rings centred at  $(n, 1/2, 1/2)$ ; where  $n$  represents an integer in each case (Fig. 3). There are no direction-specific interactions between adjacent ribbons.



**Figure 2**  
The molecular structure of the (1*R*,6*S*) enantiomer of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

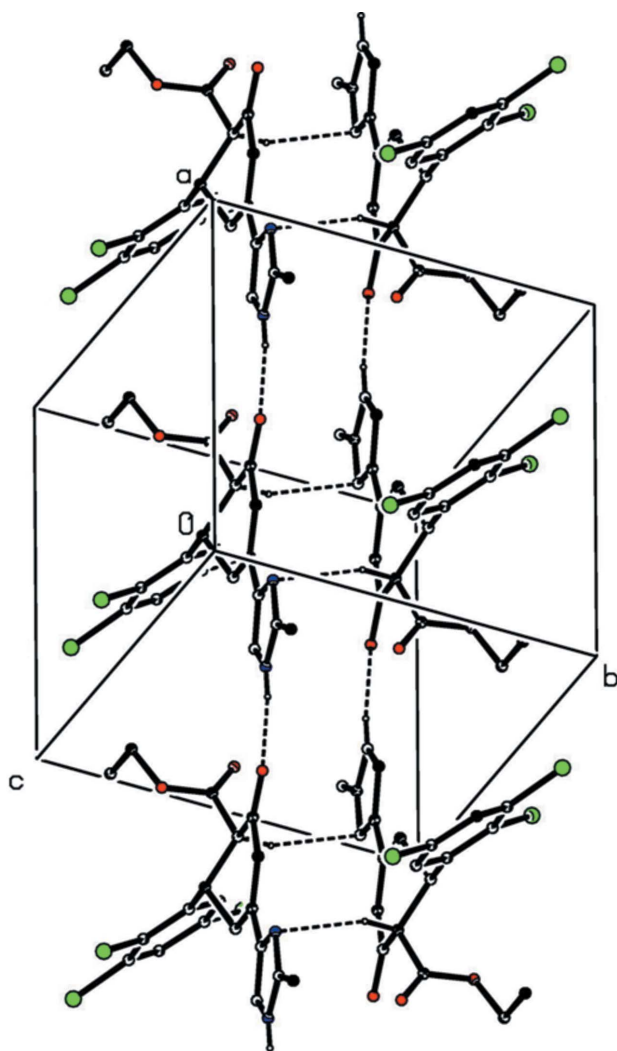


Figure 3

A partial view of the crystal packing of compound (I), showing the formation of a ribbon of edge-fused hydrogen-bonded  $R_2^2(14)$  and  $R_4^1(16)$  rings running parallel to the  $[100]$  direction (see Table 1). Hydrogen bonds are shown as dashed lines and, for the sake of clarity, the H atoms not involved in the motifs shown have been omitted.

#### 4. Database survey

The structures of a number of analogues of compound (I), usually carrying aryl substituents on atoms C4 and C6, have been reported in recent years (Fischer *et al.*, 2008; Fun *et al.*, 2008, 2012; Dutkiewicz *et al.*, 2011*a,b,c*; Kant *et al.*, 2012; Salian *et al.*, 2015). Without exception, these compounds all crystallize as racemic mixtures of the (1*R*,6*S*) and (1*S*,6*R*) forms, with mutually *trans* substituents at the sites corresponding to atoms C1 and C6 in compound (I), although in quite a number of these reports, the stereochemistry is not mentioned at all. The consistency of the stereochemistry indicates that the first step in the reaction between the chalcone and ester reagents is condensation between the chalcone and the acyl group of the ester component, followed by the Michael addition step, whose transition state is organized to minimize steric repulsions, leading to the mutually *trans*

Table 2

Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{17}Cl_3N_2O_3$
$M_r$	427.70
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	295
$a, b, c$ (Å)	9.753 (5), 10.029 (6), 11.099 (5)
$\alpha, \beta, \gamma$ (°)	106.281 (4), 96.420 (5), 104.913 (5)
$V$ (Å <sup>3</sup> )	987.0 (9)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.49
Crystal size (mm)	0.26 × 0.21 × 0.18
Data collection	
Diffractometer	Bruker APEXII area detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)
$T_{\min}$ , $T_{\max}$	0.789, 0.916
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	18900, 4534, 3178
$R_{\text{int}}$	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.050, 0.146, 1.03
No. of reflections	4534
No. of parameters	249
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.58, -0.54

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

disposition of the substituents at sites C1 and C6. Of particular interest is the structure of methyl (1*R*,6*S*)-4-(4-chlorophenyl)-6-[4-(propan-2-yl)phenyl]-2-oxocyclohex-3-ene-1-carboxylate, which exhibits enantiomeric disorder where the reference site contains both (1*R*,6*S*) and (1*S*,6*R*) forms with occupancies of 0.923 (3) and 0.077 (3), respectively (Salian *et al.*, 2015). There appears to be no evidence for such disorder in the structure reported earlier nor, indeed, in the structure of compound (I) reported here.

#### 5. Synthesis and crystallization

The synthesis of the title compound is illustrated in Fig. 1. For the synthesis of 1-(2-methyl-1*H*-imidazol-4-yl)-3-(2,3,5-trichlorophenyl)prop-2-en-1-one (*A*), aqueous sodium hydroxide solution (10% *w/v*, 30 cm<sup>3</sup>) was added to a mixture of 2,3,5-trichlorobenzaldehyde (0.02 mol) and 4-acetyl-2-methyl-1*H*-imidazole (0.02 mol), and the mixture was stirred at 275 K for 3 h. The resulting solid product was collected by filtration and recrystallized from ethanol. For the synthesis of the title compound, (I), a mixture of compound *A* (3.15 g, 0.01 mol) and ethyl 3-oxobutanoate (1.30 g, 0.01 mol) in methanol (30 cm<sup>3</sup>) containing aqueous sodium hydroxide (10% *w/v*, 0.8 cm<sup>3</sup>) was heated under reflux for 10 h. The reaction mixture was then cooled to ambient temperature and the resulting solid product (I) was collected by filtration. Crystals 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 methanol.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were located in difference-Fourier maps. For the H atom bonded to atom N41, the atomic coordinates were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ , giving an N–H distance of 0.79 (3) Å. The C-bound H atoms were subsequently treated as riding atoms in geometrically idealized positions: C–H distances 0.93–98 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$  and  $1.2U_{\text{eq}}(\text{C})$  for other H atoms.

## Acknowledgements

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## supporting information

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## Crystal structure of ethyl (1*RS*,6*SR*)-4-(2-methyl-1*H*-imidazol-4-yl)-2-oxo-6-(2,3,5-trichlorophenyl)cyclohex-3-ene-1-carboxylate

**Billava J. Mohan, Balladka K. Sarojini, Hemmige S. Yathirajan, Ravindranath Rathore and Christopher Glidewell**

### Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2* (Bruker, 2012); data reduction: *SAINT-Plus* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

**Ethyl (1*RS*,6*SR*)-4-(2-methyl-1*H*-imidazol-4-yl)-2-oxo-6-(2,3,5-trichlorophenyl)cyclohex-3-ene-1-carboxylate**

#### Crystal data

$C_{19}H_{17}Cl_3N_2O_3$

$M_r = 427.70$

Triclinic,  $P\bar{1}$

$a = 9.753$  (5) Å

$b = 10.029$  (6) Å

$c = 11.099$  (5) Å

$\alpha = 106.281$  (4)°

$\beta = 96.420$  (5)°

$\gamma = 104.913$  (5)°

$V = 987.0$  (9) Å<sup>3</sup>

$Z = 2$

$F(000) = 440$

$D_x = 1.439$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5020 reflections

$\theta = 2.7$ – $28.7$ °

$\mu = 0.49$  mm<sup>-1</sup>

$T = 295$  K

Block, colourless

$0.26 \times 0.21 \times 0.18$  mm

#### Data collection

Bruker APEXII area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

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

$T_{\min} = 0.789$ ,  $T_{\max} = 0.916$

18900 measured reflections

4534 independent reflections

3178 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 27.6$ °,  $\theta_{\min} = 2.2$ °

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 13$

$l = -14 \rightarrow 14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.146$

$S = 1.03$

4534 reflections

249 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.9642P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$$

*Special details*

**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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6401 (2)	0.3358 (2)	0.5952 (2)	0.0332 (5)
H1	0.6710	0.4417	0.6366	0.040*
C2	0.6017 (2)	0.3076 (3)	0.4517 (2)	0.0343 (5)
O2	0.69386 (18)	0.3027 (2)	0.38603 (16)	0.0473 (4)
C3	0.4555 (2)	0.2959 (3)	0.3987 (2)	0.0354 (5)
H3	0.4295	0.2757	0.3108	0.042*
C4	0.3547 (2)	0.3129 (2)	0.4705 (2)	0.0331 (5)
C5	0.3877 (2)	0.3355 (3)	0.6115 (2)	0.0370 (5)
H5A	0.3007	0.2896	0.6373	0.044*
H5B	0.4171	0.4391	0.6583	0.044*
C6	0.5070 (2)	0.2725 (3)	0.6461 (2)	0.0336 (5)
H6	0.4723	0.1671	0.6021	0.040*
C11	0.7669 (3)	0.2835 (3)	0.6267 (2)	0.0378 (5)
O11	0.88835 (19)	0.3608 (2)	0.66651 (19)	0.0516 (5)
O12	0.7266 (2)	0.1410 (2)	0.6038 (2)	0.0547 (5)
C12	0.8381 (4)	0.0789 (4)	0.6394 (4)	0.0731 (10)
H12A	0.9302	0.1321	0.6260	0.088*
H12B	0.8140	-0.0219	0.5857	0.088*
C13	0.8502 (6)	0.0866 (5)	0.7739 (5)	0.1074 (16)
H13A	0.7588	0.0341	0.7870	0.161*
H13B	0.8767	0.1867	0.8270	0.161*
H13C	0.9229	0.0441	0.7961	0.161*
N41	-0.0094 (2)	0.3117 (3)	0.3823 (2)	0.0491 (6)
H41	-0.086 (4)	0.321 (3)	0.393 (3)	0.059*
C42	0.0373 (3)	0.2879 (3)	0.2703 (3)	0.0452 (6)
N43	0.1716 (2)	0.2869 (2)	0.28599 (19)	0.0404 (5)
C44	0.2128 (2)	0.3098 (3)	0.4154 (2)	0.0344 (5)
C45	0.1003 (3)	0.3263 (3)	0.4751 (3)	0.0435 (6)
H45	0.0996	0.3440	0.5618	0.052*
C46	-0.0557 (3)	0.2675 (4)	0.1471 (3)	0.0726 (10)
H46A	-0.0195	0.2161	0.0773	0.109*
H46B	-0.0548	0.3609	0.1399	0.109*
H46C	-0.1530	0.2122	0.1442	0.109*
C61	0.5373 (2)	0.2972 (3)	0.7887 (2)	0.0351 (5)
C62	0.4533 (3)	0.2008 (3)	0.8401 (2)	0.0453 (6)
Cl62	0.31485 (11)	0.05093 (9)	0.74148 (7)	0.0798 (3)

C63	0.4784 (3)	0.2242 (3)	0.9712 (3)	0.0538 (7)
Cl63	0.37058 (14)	0.10827 (13)	1.03524 (9)	0.1058 (5)
C64	0.5884 (3)	0.3421 (3)	1.0529 (2)	0.0508 (7)
H64	0.6071	0.3565	1.1404	0.061*
C65	0.6695 (3)	0.4379 (3)	1.0018 (2)	0.0454 (6)
Cl65	0.80666 (9)	0.58707 (10)	1.10331 (7)	0.0736 (3)
C66	0.6450 (3)	0.4174 (3)	0.8725 (2)	0.0401 (5)
H66	0.7012	0.4848	0.8410	0.048*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0278 (10)	0.0376 (12)	0.0331 (11)	0.0076 (9)	0.0063 (9)	0.0118 (9)
C2	0.0283 (11)	0.0410 (12)	0.0354 (12)	0.0108 (9)	0.0097 (9)	0.0134 (10)
O2	0.0297 (8)	0.0772 (13)	0.0393 (9)	0.0183 (8)	0.0135 (7)	0.0209 (9)
C3	0.0285 (11)	0.0505 (14)	0.0285 (11)	0.0115 (10)	0.0070 (8)	0.0144 (10)
C4	0.0287 (11)	0.0377 (12)	0.0328 (11)	0.0086 (9)	0.0073 (9)	0.0121 (9)
C5	0.0330 (12)	0.0501 (14)	0.0313 (11)	0.0154 (10)	0.0118 (9)	0.0140 (10)
C6	0.0309 (11)	0.0405 (12)	0.0293 (11)	0.0088 (9)	0.0077 (9)	0.0123 (9)
C11	0.0357 (12)	0.0470 (14)	0.0335 (12)	0.0142 (10)	0.0089 (9)	0.0150 (10)
O11	0.0310 (9)	0.0553 (11)	0.0652 (12)	0.0095 (8)	0.0048 (8)	0.0193 (9)
O12	0.0439 (10)	0.0450 (11)	0.0700 (13)	0.0124 (8)	−0.0010 (9)	0.0161 (9)
C12	0.063 (2)	0.0548 (19)	0.107 (3)	0.0243 (16)	0.0036 (19)	0.0332 (19)
C13	0.121 (4)	0.098 (3)	0.113 (4)	0.033 (3)	−0.008 (3)	0.061 (3)
N41	0.0257 (10)	0.0629 (15)	0.0679 (15)	0.0175 (10)	0.0148 (10)	0.0295 (12)
C42	0.0323 (12)	0.0508 (15)	0.0526 (15)	0.0106 (11)	0.0030 (11)	0.0208 (12)
N43	0.0308 (10)	0.0521 (12)	0.0397 (11)	0.0137 (9)	0.0050 (8)	0.0166 (9)
C44	0.0268 (10)	0.0400 (12)	0.0375 (12)	0.0091 (9)	0.0082 (9)	0.0144 (10)
C45	0.0312 (12)	0.0572 (16)	0.0476 (14)	0.0154 (11)	0.0142 (10)	0.0209 (12)
C46	0.0450 (17)	0.099 (3)	0.070 (2)	0.0196 (17)	−0.0092 (15)	0.0305 (19)
C61	0.0336 (11)	0.0425 (13)	0.0310 (11)	0.0139 (9)	0.0075 (9)	0.0120 (10)
C62	0.0542 (15)	0.0442 (14)	0.0324 (12)	0.0069 (11)	0.0110 (11)	0.0109 (10)
Cl62	0.0963 (7)	0.0659 (5)	0.0445 (4)	−0.0258 (4)	0.0122 (4)	0.0142 (4)
C63	0.0669 (18)	0.0590 (17)	0.0371 (14)	0.0121 (14)	0.0189 (13)	0.0212 (13)
Cl63	0.1377 (10)	0.1048 (8)	0.0488 (5)	−0.0215 (7)	0.0276 (5)	0.0344 (5)
C64	0.0556 (16)	0.0693 (18)	0.0284 (12)	0.0232 (14)	0.0089 (11)	0.0132 (12)
C65	0.0390 (13)	0.0565 (16)	0.0340 (12)	0.0166 (11)	0.0019 (10)	0.0044 (11)
Cl65	0.0584 (5)	0.0874 (6)	0.0435 (4)	−0.0011 (4)	−0.0029 (3)	−0.0008 (4)
C66	0.0354 (12)	0.0484 (14)	0.0353 (12)	0.0111 (10)	0.0077 (10)	0.0130 (10)

*Geometric parameters (Å, °)*

C1—C11	1.506 (3)	C13—H13C	0.9600
C1—C2	1.522 (3)	N41—C45	1.348 (3)
C1—C6	1.532 (3)	N41—C42	1.351 (4)
C1—H1	0.9800	N41—H41	0.79 (3)
C2—O2	1.221 (3)	C42—N43	1.306 (3)
C2—C3	1.443 (3)	C42—C46	1.485 (4)

C3—C4	1.347 (3)	N43—C44	1.384 (3)
C3—H3	0.9300	C44—C45	1.365 (3)
C4—C44	1.438 (3)	C45—H45	0.9300
C4—C5	1.502 (3)	C46—H46A	0.9600
C5—C6	1.521 (3)	C46—H46B	0.9600
C5—H5A	0.9700	C46—H46C	0.9600
C5—H5B	0.9700	C61—C66	1.387 (3)
C6—C61	1.514 (3)	C61—C62	1.391 (3)
C6—H6	0.9800	C62—C63	1.390 (4)
C11—O11	1.191 (3)	C62—Cl62	1.727 (3)
C11—O12	1.322 (3)	C63—C64	1.378 (4)
O12—C12	1.454 (4)	C63—Cl63	1.722 (3)
C12—C13	1.463 (6)	C64—C65	1.373 (4)
C12—H12A	0.9700	C64—H64	0.9300
C12—H12B	0.9700	C65—C66	1.376 (3)
C13—H13A	0.9600	C65—Cl65	1.727 (3)
C13—H13B	0.9600	C66—H66	0.9300
C11—C1—C2	110.53 (18)	C12—C13—H13C	109.5
C11—C1—C6	113.77 (19)	H13A—C13—H13C	109.5
C2—C1—C6	110.99 (18)	H13B—C13—H13C	109.5
C11—C1—H1	107.1	C45—N41—C42	108.0 (2)
C2—C1—H1	107.1	C45—N41—H41	125 (2)
C6—C1—H1	107.1	C42—N41—H41	127 (2)
O2—C2—C3	121.8 (2)	N43—C42—N41	111.5 (2)
O2—C2—C1	120.7 (2)	N43—C42—C46	125.8 (3)
C3—C2—C1	117.43 (18)	N41—C42—C46	122.7 (3)
C4—C3—C2	123.1 (2)	C42—N43—C44	105.2 (2)
C4—C3—H3	118.4	C45—C44—N43	109.6 (2)
C2—C3—H3	118.4	C45—C44—C4	128.4 (2)
C3—C4—C44	121.5 (2)	N43—C44—C4	121.97 (19)
C3—C4—C5	120.7 (2)	N41—C45—C44	105.8 (2)
C44—C4—C5	117.83 (19)	N41—C45—H45	127.1
C4—C5—C6	111.86 (18)	C44—C45—H45	127.1
C4—C5—H5A	109.2	C42—C46—H46A	109.5
C6—C5—H5A	109.2	C42—C46—H46B	109.5
C4—C5—H5B	109.2	H46A—C46—H46B	109.5
C6—C5—H5B	109.2	C42—C46—H46C	109.5
H5A—C5—H5B	107.9	H46A—C46—H46C	109.5
C61—C6—C5	110.43 (18)	H46B—C46—H46C	109.5
C61—C6—C1	113.84 (18)	C66—C61—C62	117.8 (2)
C5—C6—C1	109.12 (19)	C66—C61—C6	121.8 (2)
C61—C6—H6	107.7	C62—C61—C6	120.3 (2)
C5—C6—H6	107.7	C63—C62—C61	120.7 (2)
C1—C6—H6	107.7	C63—C62—Cl62	119.0 (2)
O11—C11—O12	124.3 (2)	C61—C62—Cl62	120.26 (19)
O11—C11—C1	124.2 (2)	C64—C63—C62	120.7 (2)
O12—C11—C1	111.6 (2)	C64—C63—Cl63	118.6 (2)



C11—O12—C12	116.6 (2)	C62—C63—C163	120.7 (2)
O12—C12—C13	110.1 (3)	C65—C64—C63	118.3 (2)
O12—C12—H12A	109.6	C65—C64—H64	120.9
C13—C12—H12A	109.6	C63—C64—H64	120.9
O12—C12—H12B	109.6	C64—C65—C66	121.7 (2)
C13—C12—H12B	109.6	C64—C65—C165	118.8 (2)
H12A—C12—H12B	108.1	C66—C65—C165	119.5 (2)
C12—C13—H13A	109.5	C65—C66—C61	120.7 (2)
C12—C13—H13B	109.5	C65—C66—H66	119.7
H13A—C13—H13B	109.5	C61—C66—H66	119.7
C11—C1—C2—O2	-27.7 (3)	C42—N43—C44—C4	178.7 (2)
C6—C1—C2—O2	-154.8 (2)	C3—C4—C44—C45	-179.5 (3)
C11—C1—C2—C3	156.0 (2)	C5—C4—C44—C45	0.7 (4)
C6—C1—C2—C3	28.9 (3)	C3—C4—C44—N43	1.1 (4)
O2—C2—C3—C4	-174.3 (2)	C5—C4—C44—N43	-178.8 (2)
C1—C2—C3—C4	1.9 (3)	C42—N41—C45—C44	-0.3 (3)
C2—C3—C4—C44	175.9 (2)	N43—C44—C45—N41	0.8 (3)
C2—C3—C4—C5	-4.2 (4)	C4—C44—C45—N41	-178.8 (2)
C3—C4—C5—C6	-24.9 (3)	C5—C6—C61—C66	-93.7 (3)
C44—C4—C5—C6	154.9 (2)	C1—C6—C61—C66	29.5 (3)
C4—C5—C6—C61	-179.98 (19)	C5—C6—C61—C62	84.2 (3)
C4—C5—C6—C1	54.2 (3)	C1—C6—C61—C62	-152.7 (2)
C11—C1—C6—C61	54.8 (3)	C66—C61—C62—C63	-0.7 (4)
C2—C1—C6—C61	-179.81 (19)	C6—C61—C62—C63	-178.6 (2)
C11—C1—C6—C5	178.64 (19)	C66—C61—C62—C162	178.65 (19)
C2—C1—C6—C5	-56.0 (2)	C6—C61—C62—C162	0.7 (3)
C2—C1—C11—O11	99.8 (3)	C61—C62—C63—C64	-1.0 (4)
C6—C1—C11—O11	-134.6 (2)	C162—C62—C63—C64	179.6 (2)
C2—C1—C11—O12	-79.8 (2)	C61—C62—C63—C163	177.8 (2)
C6—C1—C11—O12	45.8 (3)	C162—C62—C63—C163	-1.5 (4)
O11—C11—O12—C12	4.8 (4)	C62—C63—C64—C65	1.9 (4)
C1—C11—O12—C12	-175.6 (2)	C163—C63—C64—C65	-177.0 (2)
C11—O12—C12—C13	86.1 (4)	C63—C64—C65—C66	-1.1 (4)
C45—N41—C42—N43	-0.2 (3)	C63—C64—C65—C165	179.4 (2)
C45—N41—C42—C46	-179.7 (3)	C64—C65—C66—C61	-0.7 (4)
N41—C42—N43—C44	0.7 (3)	C165—C65—C66—C61	178.85 (19)
C46—C42—N43—C44	-179.9 (3)	C62—C61—C66—C65	1.5 (4)
C42—N43—C44—C45	-0.9 (3)	C6—C61—C66—C65	179.4 (2)

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>
N41—H41...O2 <sup>i</sup>	0.79 (4)	2.10 (4)	2.878 (3)	167 (3)
C1—H1...N43 <sup>ii</sup>	0.98	2.60	3.538 (4)	161

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