



Crystal structure and Hirshfeld surface analysis of 2-hydroxy-7-methoxy-1,8-bis(2,4,6-trichlorobenzoyl)naphthalene

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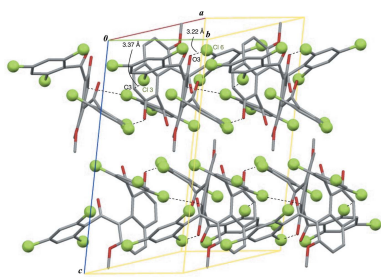
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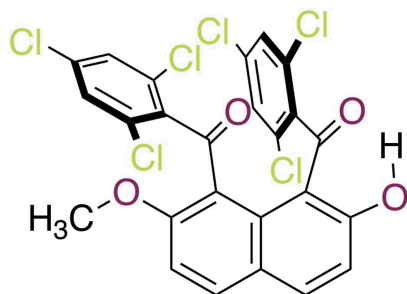
In the title compound, C₂₅H₁₂Cl₆O₄, the two carbonyl groups are oriented in a same direction with respect to the naphthalene ring system and are situated roughly parallel to each other, while the two 2,4,6-trichlorobenzene rings are orientated in opposite directions with respect to the naphthalene ring system: the carbonyl C—(C=O)—C planes subtend dihedral angles of 45.54 (15) and 30.02 (15)° to the naphthalene ring system are. The dihedral angles formed by the carbonyl groups and the benzene rings show larger differences, the C=O vectors being inclined to the benzene rings by 46.39 (16) and 79.78 (16)°. An intramolecular O—H···O=C hydrogen bond forms an S(6) ring motif. In the crystal, no effective intermolecular hydrogen bonds are found; instead, O···Cl and C···Cl close contacts are observed along the 2₁ helical-axis direction. The Hirshfeld surface analysis reveals several weak interactions, the major contributor being Cl···H/H···Cl contacts.

1. Chemical context

o-Hydroxyaryl ketones are generally recognized to be important precursors in the preparation of valuable products such as drugs, cosmetics, dyes and pesticides (Choy & Kwong, 2013; Naemi *et al.*, 2014; Nimmual *et al.*, 2015). The preparation methods reported include, for example, Fries rearrangement of phenolic esters (Murashige *et al.*, 2011), acylation of benzoquinone and derivatives (Schiel *et al.*, 2001), coupling reactions of nitriles with boronic acids (Zhou & Larock, 2004), direct C—H bond arylation of 2-hydroxybenzaldehydes (Lee & Yi, 2015; Weng *et al.*, 2010), and microwave-assisted direct benzoylation of phenols under solvent-free or ionic liquid conditions (Tran *et al.*, 2017). The neighbouring carbonyl and hydroxy groups contribute to the regio- and chemoselectivities in these reactions. Conformational studies of hydroxyaryl ketones in the solid state and in solution have attracted considerable interest (Siskos *et al.*, 2015; Nonhebel, 1968). Since the discovery of an effective method for diarylation at the 1,8(*peri*)-positions of the naphthalene ring core and the related reactions (Okamoto & Yonezawa, 2009; Okamoto *et al.*, 2011; Okamoto, Mitsui *et al.*, 2012), we have reported on the spatial organization of 1,8-diarylated naphthalenes and homologous compounds in both the solid state and solution (Okamoto, Watanabe *et al.*, 2012; Yoshiwaka *et al.*, 2015; Okamoto *et al.*, 2015; Ohisa *et al.*, 2018). In the crystal structures of these compounds, which have non-coplanar accumulated aromatic rings, molecules are arranged by weak



intermolecular interactions, such as non-classical hydrogen bonds and van der Waals interactions. Thus, the accumulation structures of 1,8-diaroylated naphthalenes are drastically changed by simple molecular modifications. Herein, we report on the crystal structure and Hirshfeld surface analysis of the title hydroxyaryl ketone, 2-hydroxy-7-methoxy-1,8-bis(2,4,6-trichlorobenzoyl)naphthalene.



2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. This compound consists of a naphthalene ring core with two 2,4,6-trichlorobenzoyl groups at the 1,8-positions, a hydroxy group at the 2-position, and a methoxy group at the 7-position of the naphthalene ring system, affording an unsymmetrical molecular structure.

Analogous aroylated unsymmetrical naphthalene compounds, for example, 1,8-bis(4-chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (Mitsui, Nagasawa, Noguchi *et al.*, 2010) and 1,8-bis(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (Nakaema *et al.*, 2007), have two aroyl groups at the 1,8-positions of the naphthalene ring system. The two 4-chlorobenzoyl groups have the same orientation with respect to the

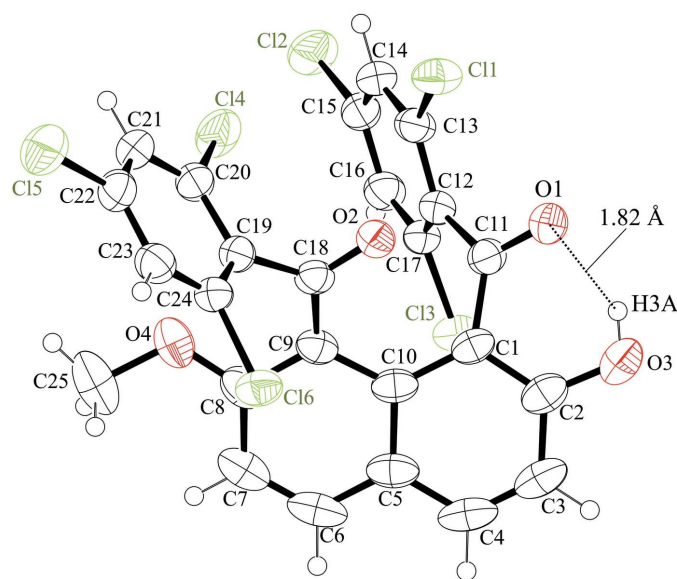


Figure 1

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Table 1

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>
O3—H3A...O1	0.84	1.82	2.551 (3)	145

naphthalene ring core in 1,8-bis(4-chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene, while they are in opposite directions in 1,8-bis(4-chlorobenzoyl)-2,7-dimethoxynaphthalene. In contrast, in the title compound the carbonyl groups and the benzene rings of the 2,4,6-trichlorobenzoyl groups are located in distinct orientations with respect to the naphthalene ring plane: the two carbonyl groups are oriented in the same direction and are located roughly parallel to the naphthalene ring, whereas the two 2,4,6-trichlorobenzene rings are twisted away in opposite directions (Fig. 2). The dihedral angles of the carbonyl C—(C=O)—C plane [C1—(C11=O1)—C12 and C9—(C18=O2)—C19] and the naphthalene ring are 45.54 (15) and 30.02 (15)°, respectively. The carbonyl C—(C=O)—C plane and the 2,4,6-trichlorobenzene ring in the 8-position of the naphthalene ring forms a larger dihedral angle than that in 1-position [C19—C24 ring and C12—C17 ring], 79.78 (16)° versus 46.39 (16)°. The two carbonyl C—(C=O)—C planes make a large dihedral angle, 73.68 (19)°. Furthermore, the naphthalene ring plane is somewhat distorted, the C6—C5—C10—C9 and C4—C5—C10—C1 torsion angles being 10.2 (4) and 6.1 (5)°, respectively.

The intramolecular O—H...O=C hydrogen bond forms a six-membered *S*(6) ring motif (O3—H3A...O1; Figs. 1 and 2, Table 1). In addition, one chloro atom of the trichlorobenzoyl group at the 1-position of the naphthalene ring system makes two short intramolecular Cl...O=C contacts [Cl1...O1 = 3.018 (2) Å and Cl1...O2 = 2.969 (2) Å]. 1-Aroyl-2-hydroxy-naphthalene homologues often form intramolecular O—H...O=C hydrogen bonds whether the second aroyl group is present or not, *e.g.*, 1-benzoyl-2-hydroxy-7-methoxynaphthalene (Nagasawa, Mitsui, Kato *et al.*, 2010), 2-hydroxy-7-methoxy-1-(4-methylbenzoyl)naphthalene (Nagasawa, Mitsui, Okamoto *et al.*, 2010), 1-(4-chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (Mitsui *et al.*, 2008) and 1,8-bis(4-

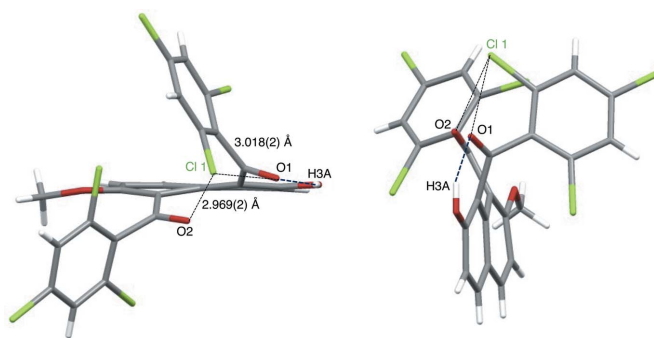


Figure 2

View of the title compound showing the intramolecular contacts; top view (left) and side view (right).

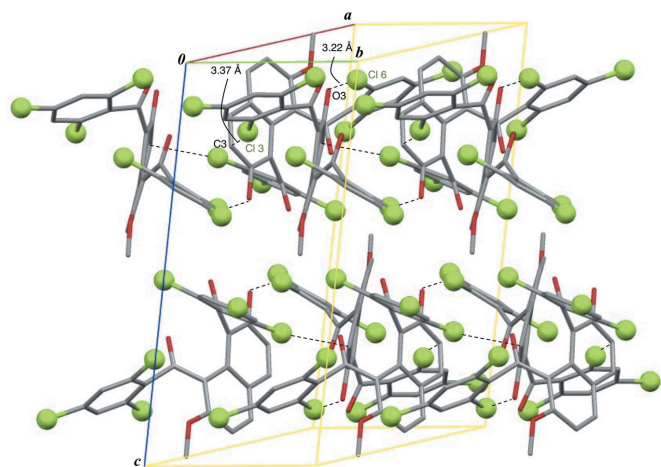


Figure 3
A view of the crystal packing of the title compound, showing the Cl \cdots O and Cl \cdots C short contacts. H atoms have been omitted for clarity.

chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (Mitsui, Nagasawa, Noguchi *et al.*, 2010). The 2,4,6-trisubstituents in the benzene ring tend to bring about intramolecular short contacts involving the carbonyl oxygen atom: intramolecular C–H \cdots O=C hydrogen bonds are observed in 2,7-dimethoxy-1,8-bis(2,4,6-trimethylbenzoyl)naphthalene (Muto *et al.*, 2012*a*) and 1-(4-chlorobenzoyl)-2,7-dimethoxy-8-(2,4,6-trimethylbenzoyl)naphthalene (Muto *et al.*, 2012*b*).

3. Supramolecular features

In the crystal, 2_1 helical molecular assemblies are observed along the *b*-axis direction (Fig. 3). The chloro groups in the assemblies are aligned in a herringbone pattern. There are no

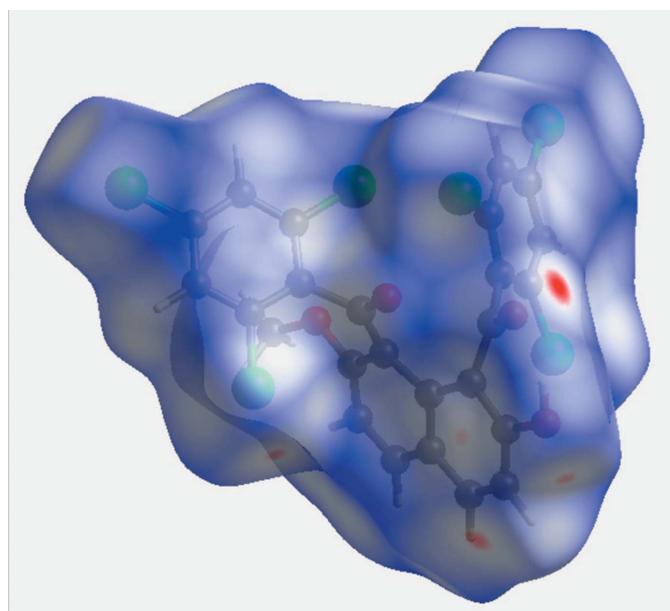


Figure 4
The Hirshfeld surface of the title compound mapped over d_{norm} , in the range -0.0895 to 1.1549 a.u.

effective hydrogen bonds, instead, two kinds of short contacts involving chlorine atoms are observed; Cl6 \cdots O3 i [$3.224(3)$ Å] and Cl3 \cdots C3 i [$3.370(3)$ Å], symmetry code: (i) $-x + 1, y + \frac{1}{2}, \frac{1}{2} - z$ (Fig. 3).

4. Hirshfeld surface analysis and two-dimensional fingerprint plots

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017). The Hirshfeld surfaces are colour-mapped with the normalized contact distance, d_{norm} , from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The Hirshfeld surface of the title compound mapped over d_{norm} in the range -0.0895 to 1.1549 a.u., is shown in Fig. 4. The red points represent close contacts and negative d_{norm} values on the surface. The largest red point corresponds to the short contact of $3.078(3)$ Å involving the carbonyl O atom, O1, and carbon atom C23 i [symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$], while the other red points around the naphthalene ring indicate short Cl \cdots H interactions.

The two-dimensional fingerprint plots from the Hirshfeld surface analysis are shown in Fig. 5, revealing the intermolecular contacts and their percentage distributions on the Hirshfeld surface. Not surprisingly the Cl \cdots H/H \cdots Cl contacts (31.0%) are present as a major contributor, while C \cdots H/H \cdots C (14.8%), H \cdots H (14.0%), O \cdots H/H \cdots O (12.8%), Cl \cdots Cl (11.0%), Cl \cdots C/C \cdots Cl (8.2%), Cl \cdots O/O \cdots Cl

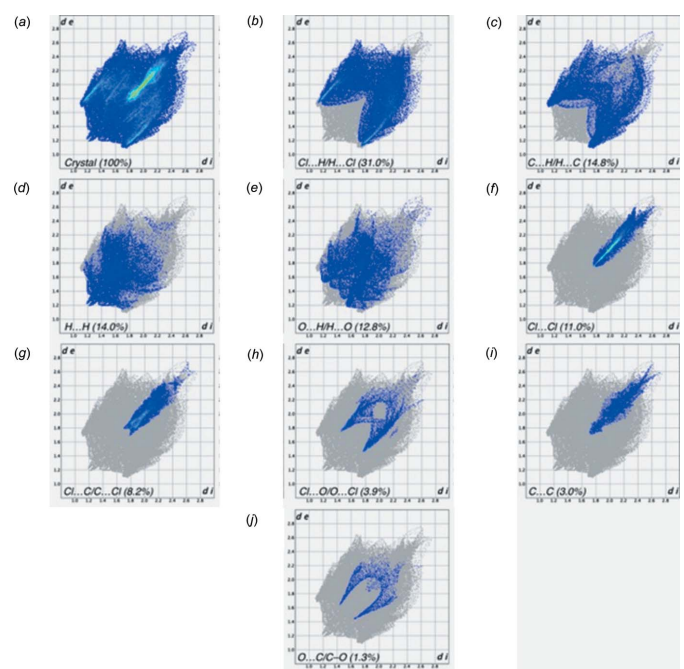


Figure 5
(a) The full two-dimensional fingerprint plot for the title compound, and those delineated into (b) Cl \cdots H/H \cdots Cl, (c) C \cdots H/H \cdots C, (d) H \cdots H, (e) O \cdots H/H \cdots O, (f) Cl \cdots Cl, (g) Cl \cdots C, (h) Cl \cdots O, (i) C \cdots C and (j) O \cdots C contacts.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₅ H ₁₂ Cl ₆ O ₄
<i>M_r</i>	589.05
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	193
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.9667 (4), 7.9150 (1), 17.6995 (5)
β (°)	110.673 (1)
<i>V</i> (Å ³)	2354.91 (9)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	6.95
Crystal size (mm)	0.40 × 0.40 × 0.20
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Numerical (NUMABS; Higashi, 1999)
<i>T</i> _{min} , <i>T</i> _{max}	0.168, 0.337
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	41619, 4300, 3737
<i>R</i> _{int}	0.110
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.602
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.045, 0.126, 1.06
No. of reflections	4300
No. of parameters	319
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.50, -0.26

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SIR2004* (Burla *et al.*, 2007), *SHELXL97* (Sheldrick, 2008) and *ORTEP3* (Burnett & Johnson, 1996).

(3.9%), C⋯C (3.0%) and O⋯C/C⋯O (1.3%) contacts also make significant contributions to the Hirshfeld surface.

5. Database survey

A search of the Cambridge Structural Database (CSD, version 5.40, last update November 2018; Groom *et al.*, 2016) of the 2-hydroxy-1-benzoylnaphthalene moiety of the title compound yield 16 hits. These include compounds with a similar aroylnaphthalene unit and other polycyclic aromatic hydrocarbon moieties (CSD refcode ITUXOM: Ji *et al.*, 2016; PIRLUX: Freeman *et al.*, 1994; VUDFAC: Luo & Yu, 2009; VUDFEG: Luo & Yu, 2009). A search with a 1-benzoyl group bonded to the 2-hydroxynaphthalene framework gave 12 hits. Among these, three had bromo group(s) at the 8-position, 3,8-positions, and 3,6-positions of the naphthalene ring core, *viz.* PUKGIM (Mitsui, Nakaema, Nagasawa *et al.*, 2010), YUNWOP (Mitsui, Watanabe *et al.*, 2010) and YUPWEM (Mitsui, Nagasawa, Watanabe *et al.*, 2010). Four compounds had an 8-benzoyl group, *i.e.*, 1,8-diaroylated naphthalene compounds, *viz.* CIQBUB (Mohri *et al.*, 2013), LESLOM (Hijikata *et al.*, 2013), YUQBOC (Mitsui, Nagasawa, Noguchi *et al.*, 2010) and YUQBOC1 (Okamoto, Mitsui *et al.*, 2012). The remaining five compounds have a single 1-benzoyl-2-hydroxynaphthalene moiety, *viz.* KABJUJ (Nagasawa, Mitsui, Kato *et al.*, 2010), UCUHAE (Okamoto *et al.*, 2014), VABBEH (Nagasawa, Mitsui, Okamoto *et al.*, 2010), VOJFOQ (Mitsui *et al.*, 2008) and VOJFQ01 (Okamoto, Mitsui *et al.*, 2012). These structures have *p*-substituted or

unsubstituted benzoyl group(s). The structure most similar to the title compound is 1,8-bis(4-chlorobenzoyl)-7-methoxynaphthalen-2-ol ethanol solvate, for which there are two reports; refcodes YUQBOC and YUQBOC01.

6. Synthesis and crystallization

To a 10 ml eggplant flask equipped with a nitrogen bulb, 2,4,6-trichlorobenzoyl chloride (0.0938 ml, 0.6 mmol), dichloromethane (0.5 ml), titanium tetrachloride (0.1972 ml, 1.8 mmol), and finally 2,7-dimethoxynaphthalene (37.6 mg, 0.2 mmol) were introduced sequentially. The reaction mixture was stirred at ambient temperature for 6 h, then it was poured into ice-water. The resulting mixture was extracted with chloroform (3 × 20 ml), then the organic layer was washed with saturated aqueous NaCl solution (3 × 20 ml) and dried over granular MgSO₄. The solvent was removed by evaporation to yield a crude product of purple viscous liquid, which was crystallized from hot (hexane/CHCl₃) to give yellow plate-like crystals (isolated yield 24%; m.p. 493–497 K).

¹H NMR δ (300 MHz, DMSO-*d*₆); 3.59 (3H, s), 7.01 (1H, *d*, *J* = 8.4 Hz), 7.34 (1H, *d*, *J* = 9.3 Hz), 7.66 (2H, s), 7.70 (2H, s), 8.04 (1H, *d*, *J* = 8.7 Hz), 8.09 (1H, *d*, *J* = 9.0 Hz) ppm.

¹H NMR δ (300 MHz, CDCl₃); 3.45 (3H, s), 6.95 (1H, *br*), 7.02 (1H, *d*, *J* = 8.7 Hz), 7.20 (2H, *br*), 7.21 (1H, *d*, *J* = 9.0 Hz), 7.42 (1H, *br*), 7.90 (1H, *d*, *J* = 8.4 Hz), 8.01 (1H, *d*, *J* = 9.0 Hz) ppm.

¹³C NMR δ (100 MHz, CDCl₃); 56.64, 110.35, 114.82, 117.67, 119.13, 119.38, 124.45, 127.37, 133.42, 133.68, 134.14, 135.42, 135.51, 136.69, 136.80, 139.15, 140.88, 165.60, 166.21, 185.98, 191.21 ppm.

IR (KBr); 1629 (C=O), 1600, 1510, 1442 (Ar, naphthalene), 1289 (=C–O–C) cm⁻¹.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All of the H atoms were found in a difference-Fourier map and were subsequently refined as riding atoms, with C–H = 0.95 (aromatic) and 0.96 (methyl) Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C).

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supporting information

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Crystal structure and Hirshfeld surface analysis of 2-hydroxy-7-methoxy-1,8-bis-(2,4,6-trichlorobenzoyl)naphthalene

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Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

7-Methoxy-1,8-bis[(2,4,6-trichlorophenyl)carbonyl]naphthalen-2-ol

Crystal data

$C_{25}H_{12}Cl_6O_4$

$M_r = 589.05$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 17.9667$ (4) Å

$b = 7.9150$ (1) Å

$c = 17.6995$ (5) Å

$\beta = 110.673$ (1)°

$V = 2354.91$ (9) Å³

$Z = 4$

$F(000) = 1184$

$D_x = 1.661$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54187$ Å

Cell parameters from 28116 reflections

$\theta = 3.0$ – 68.3 °

$\mu = 6.95$ mm⁻¹

$T = 193$ K

Platelet, yellow

$0.40 \times 0.40 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer

Radiation source: rotating anode

Graphite monochromator

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: numerical
(NUMABS; Higashi, 1999)

$T_{\min} = 0.168$, $T_{\max} = 0.337$

41619 measured reflections

4300 independent reflections

3737 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.110$

$\theta_{\max} = 68.3$ °, $\theta_{\min} = 5.1$ °

$h = -21 \rightarrow 21$

$k = -9 \rightarrow 9$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.126$

$S = 1.06$

4300 reflections

319 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

$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 1.5934P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{Å}^{-3}$

Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00166 (17)

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.13592 (4)	0.62787 (10)	0.05084 (5)	0.0543 (2)
C12	0.00708 (5)	0.06020 (13)	0.10904 (5)	0.0645 (3)
C13	0.32240 (4)	0.09099 (9)	0.20159 (4)	0.0477 (2)
C14	0.09824 (5)	0.59970 (12)	0.24340 (5)	0.0634 (3)
C15	0.10530 (6)	1.19664 (13)	0.39062 (6)	0.0703 (3)
C16	0.37761 (4)	0.90853 (10)	0.39693 (4)	0.0512 (2)
O1	0.30235 (12)	0.5154 (3)	0.07105 (12)	0.0517 (5)
O2	0.26606 (11)	0.6928 (3)	0.20713 (11)	0.0422 (5)
O3	0.44648 (13)	0.4173 (3)	0.11247 (14)	0.0589 (6)
H3A	0.4035	0.4583	0.0812	0.071*
O4	0.26290 (15)	0.5184 (3)	0.41656 (12)	0.0613 (6)
C1	0.37736 (16)	0.4494 (4)	0.20717 (17)	0.0413 (6)
C2	0.44482 (17)	0.4097 (4)	0.1885 (2)	0.0492 (7)
C3	0.51384 (17)	0.3460 (4)	0.2480 (2)	0.0571 (9)
H3	0.5593	0.3195	0.2347	0.069*
C4	0.51548 (18)	0.3226 (4)	0.3237 (2)	0.0584 (9)
H4	0.5612	0.2728	0.3625	0.070*
C5	0.45068 (18)	0.3702 (4)	0.34747 (19)	0.0509 (8)
C6	0.4532 (2)	0.3417 (4)	0.42678 (19)	0.0604 (9)
H6	0.4992	0.2905	0.4644	0.072*
C7	0.3920 (2)	0.3850 (4)	0.45164 (19)	0.0583 (9)
H7	0.3938	0.3581	0.5046	0.070*
C8	0.3262 (2)	0.4701 (4)	0.39744 (17)	0.0511 (8)
C9	0.32242 (16)	0.5103 (4)	0.31878 (16)	0.0409 (6)
C10	0.38174 (16)	0.4428 (4)	0.28935 (17)	0.0418 (6)
C11	0.30243 (16)	0.4589 (4)	0.13587 (16)	0.0403 (6)
C12	0.22876 (15)	0.3656 (4)	0.13489 (15)	0.0379 (6)
C13	0.15151 (17)	0.4292 (4)	0.09543 (16)	0.0431 (7)
C14	0.08428 (16)	0.3378 (4)	0.08818 (16)	0.0464 (7)
H14	0.0331	0.3860	0.0625	0.056*
C15	0.09164 (16)	0.1760 (4)	0.11843 (17)	0.0458 (7)
C16	0.16576 (17)	0.1018 (4)	0.15470 (16)	0.0457 (7)

H16	0.1706	-0.0115	0.1736	0.055*
C17	0.23220 (15)	0.1976 (4)	0.16237 (15)	0.0386 (6)
C18	0.27267 (15)	0.6515 (4)	0.27587 (16)	0.0395 (6)
C19	0.23318 (16)	0.7726 (4)	0.31692 (15)	0.0398 (6)
C20	0.15062 (16)	0.7704 (4)	0.29719 (16)	0.0452 (7)
C21	0.11036 (18)	0.8971 (4)	0.31971 (18)	0.0500 (7)
H21	0.0543	0.8925	0.3057	0.060*
C22	0.15427 (18)	1.0321 (4)	0.36357 (18)	0.0503 (7)
C23	0.23617 (18)	1.0364 (4)	0.38688 (17)	0.0480 (7)
H23	0.2656	1.1279	0.4180	0.058*
C24	0.27431 (16)	0.9059 (4)	0.36436 (16)	0.0424 (6)
C25	0.2684 (3)	0.5207 (6)	0.4997 (2)	0.0862 (14)
H25A	0.2202	0.5722	0.5036	0.103*
H25B	0.3150	0.5868	0.5317	0.103*
H25C	0.2736	0.4048	0.5205	0.103*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0419 (4)	0.0540 (5)	0.0572 (4)	0.0039 (3)	0.0054 (3)	0.0116 (3)
C12	0.0421 (4)	0.0769 (6)	0.0739 (5)	-0.0167 (4)	0.0198 (4)	0.0057 (4)
C13	0.0375 (4)	0.0437 (4)	0.0543 (4)	0.0019 (3)	0.0067 (3)	0.0027 (3)
C14	0.0434 (4)	0.0766 (6)	0.0739 (5)	-0.0202 (4)	0.0255 (4)	-0.0219 (4)
C15	0.0680 (6)	0.0673 (6)	0.0806 (6)	0.0184 (5)	0.0324 (5)	-0.0061 (4)
C16	0.0357 (4)	0.0568 (5)	0.0525 (4)	-0.0032 (3)	0.0049 (3)	-0.0037 (3)
O1	0.0434 (11)	0.0682 (15)	0.0466 (11)	-0.0015 (10)	0.0198 (9)	0.0071 (10)
O2	0.0418 (10)	0.0444 (11)	0.0401 (10)	0.0018 (9)	0.0139 (8)	0.0033 (8)
O3	0.0461 (12)	0.0644 (16)	0.0731 (15)	0.0009 (11)	0.0297 (11)	-0.0043 (12)
O4	0.0764 (16)	0.0679 (16)	0.0452 (12)	-0.0017 (13)	0.0284 (11)	0.0088 (11)
C1	0.0307 (13)	0.0372 (15)	0.0531 (16)	-0.0021 (11)	0.0111 (12)	-0.0008 (12)
C2	0.0356 (15)	0.0438 (18)	0.0666 (19)	-0.0069 (13)	0.0161 (14)	-0.0040 (14)
C3	0.0312 (15)	0.0483 (19)	0.086 (2)	-0.0005 (13)	0.0137 (15)	-0.0100 (17)
C4	0.0330 (15)	0.0430 (18)	0.079 (2)	0.0006 (13)	-0.0053 (15)	-0.0020 (16)
C5	0.0391 (16)	0.0430 (18)	0.0542 (17)	-0.0043 (13)	-0.0037 (13)	-0.0053 (13)
C6	0.057 (2)	0.0471 (19)	0.0503 (18)	-0.0023 (16)	-0.0145 (15)	0.0031 (14)
C7	0.069 (2)	0.052 (2)	0.0395 (16)	-0.0097 (17)	0.0013 (15)	0.0044 (14)
C8	0.0587 (19)	0.0451 (18)	0.0425 (15)	-0.0083 (15)	0.0093 (14)	0.0011 (13)
C9	0.0370 (14)	0.0414 (16)	0.0382 (14)	-0.0050 (12)	0.0057 (11)	0.0009 (12)
C10	0.0332 (14)	0.0337 (15)	0.0497 (15)	-0.0041 (11)	0.0036 (11)	0.0001 (12)
C11	0.0361 (14)	0.0421 (16)	0.0414 (14)	0.0020 (12)	0.0123 (11)	-0.0003 (12)
C12	0.0336 (13)	0.0445 (16)	0.0332 (13)	-0.0010 (12)	0.0090 (10)	-0.0010 (11)
C13	0.0384 (14)	0.0486 (17)	0.0371 (14)	0.0000 (13)	0.0068 (11)	0.0021 (12)
C14	0.0324 (14)	0.061 (2)	0.0421 (15)	0.0021 (13)	0.0085 (11)	-0.0004 (13)
C15	0.0350 (14)	0.059 (2)	0.0423 (15)	-0.0096 (13)	0.0124 (11)	-0.0020 (13)
C16	0.0418 (16)	0.0502 (19)	0.0429 (15)	-0.0053 (13)	0.0121 (12)	0.0032 (13)
C17	0.0329 (13)	0.0451 (16)	0.0351 (13)	0.0006 (12)	0.0088 (10)	-0.0021 (11)
C18	0.0312 (13)	0.0440 (16)	0.0398 (14)	-0.0047 (12)	0.0080 (11)	0.0000 (12)
C19	0.0358 (13)	0.0473 (17)	0.0367 (13)	-0.0022 (12)	0.0132 (11)	0.0027 (12)

C20	0.0366 (14)	0.0576 (19)	0.0413 (14)	-0.0087 (13)	0.0138 (11)	-0.0023 (13)
C21	0.0383 (15)	0.067 (2)	0.0480 (16)	0.0024 (14)	0.0186 (13)	0.0005 (15)
C22	0.0510 (17)	0.055 (2)	0.0489 (16)	0.0111 (15)	0.0225 (14)	0.0034 (14)
C23	0.0494 (17)	0.0501 (18)	0.0421 (15)	0.0006 (14)	0.0132 (13)	-0.0025 (13)
C24	0.0339 (14)	0.0523 (18)	0.0383 (14)	-0.0010 (12)	0.0096 (11)	0.0015 (12)
C25	0.127 (4)	0.090 (3)	0.049 (2)	-0.016 (3)	0.040 (2)	-0.003 (2)

Geometric parameters (Å, °)

C11—C13	1.737 (3)	C7—H7	0.9500
C12—C15	1.731 (3)	C8—C9	1.406 (4)
C13—C17	1.740 (3)	C9—C10	1.444 (4)
C14—C20	1.728 (3)	C9—C18	1.465 (4)
C15—C22	1.731 (3)	C11—C12	1.511 (4)
C16—C24	1.738 (3)	C12—C13	1.408 (4)
O1—C11	1.231 (3)	C12—C17	1.409 (4)
O2—C18	1.224 (3)	C13—C14	1.374 (4)
O3—C2	1.358 (4)	C14—C15	1.376 (5)
O3—H3A	0.8400	C14—H14	0.9500
O4—C8	1.351 (4)	C15—C16	1.388 (4)
O4—C25	1.441 (4)	C16—C17	1.380 (4)
C1—C2	1.400 (4)	C16—H16	0.9500
C1—C10	1.430 (4)	C18—C19	1.522 (4)
C1—C11	1.487 (4)	C19—C24	1.388 (4)
C2—C3	1.407 (4)	C19—C20	1.399 (4)
C3—C4	1.342 (5)	C20—C21	1.375 (4)
C3—H3	0.9500	C21—C22	1.391 (5)
C4—C5	1.421 (5)	C21—H21	0.9500
C4—H4	0.9500	C22—C23	1.381 (4)
C5—C6	1.407 (5)	C23—C24	1.374 (4)
C5—C10	1.422 (4)	C23—H23	0.9500
C6—C7	1.365 (5)	C25—H25A	0.9800
C6—H6	0.9500	C25—H25B	0.9800
C7—C8	1.403 (5)	C25—H25C	0.9800
C2—O3—H3A	109.5	C12—C13—C11	121.4 (2)
C8—O4—C25	120.0 (3)	C13—C14—C15	119.5 (3)
C2—C1—C10	119.4 (3)	C13—C14—H14	120.2
C2—C1—C11	114.3 (3)	C15—C14—H14	120.2
C10—C1—C11	125.0 (2)	C14—C15—C16	121.2 (3)
O3—C2—C1	123.2 (3)	C14—C15—C12	119.6 (2)
O3—C2—C3	115.8 (3)	C16—C15—C12	119.1 (3)
C1—C2—C3	120.8 (3)	C17—C16—C15	117.9 (3)
C4—C3—C2	120.0 (3)	C17—C16—H16	121.0
C4—C3—H3	120.0	C15—C16—H16	121.0
C2—C3—H3	120.0	C16—C17—C12	123.6 (3)
C3—C4—C5	121.8 (3)	C16—C17—C13	115.1 (2)
C3—C4—H4	119.1	C12—C17—C13	121.1 (2)

C5—C4—H4	119.1	O2—C18—C9	123.1 (3)
C6—C5—C4	120.7 (3)	O2—C18—C19	114.1 (2)
C6—C5—C10	120.0 (3)	C9—C18—C19	122.4 (2)
C4—C5—C10	119.2 (3)	C24—C19—C20	116.9 (3)
C7—C6—C5	122.4 (3)	C24—C19—C18	122.0 (2)
C7—C6—H6	118.8	C20—C19—C18	120.3 (2)
C5—C6—H6	118.8	C21—C20—C19	122.6 (3)
C6—C7—C8	118.7 (3)	C21—C20—C14	119.3 (2)
C6—C7—H7	120.7	C19—C20—C14	118.1 (2)
C8—C7—H7	120.7	C20—C21—C22	118.0 (3)
O4—C8—C7	123.0 (3)	C20—C21—H21	121.0
O4—C8—C9	115.7 (3)	C22—C21—H21	121.0
C7—C8—C9	121.3 (3)	C23—C22—C21	121.3 (3)
C8—C9—C10	119.3 (3)	C23—C22—C15	119.4 (3)
C8—C9—C18	119.6 (3)	C21—C22—C15	119.3 (2)
C10—C9—C18	119.2 (2)	C24—C23—C22	118.9 (3)
C5—C10—C1	118.1 (3)	C24—C23—H23	120.6
C5—C10—C9	117.0 (3)	C22—C23—H23	120.6
C1—C10—C9	124.8 (2)	C23—C24—C19	122.2 (3)
O1—C11—C1	120.8 (3)	C23—C24—C16	118.6 (2)
O1—C11—C12	117.0 (2)	C19—C24—C16	119.2 (2)
C1—C11—C12	120.8 (2)	O4—C25—H25A	109.5
C13—C12—C17	115.1 (3)	O4—C25—H25B	109.5
C13—C12—C11	122.5 (3)	H25A—C25—H25B	109.5
C17—C12—C11	121.7 (2)	O4—C25—H25C	109.5
C14—C13—C12	122.6 (3)	H25A—C25—H25C	109.5
C14—C13—C11	116.0 (2)	H25B—C25—H25C	109.5
C10—C1—C2—O3	-178.1 (3)	C17—C12—C13—C14	3.5 (4)
C11—C1—C2—O3	14.5 (4)	C11—C12—C13—C14	174.0 (3)
C10—C1—C2—C3	7.0 (4)	C17—C12—C13—C11	-175.0 (2)
C11—C1—C2—C3	-160.4 (3)	C11—C12—C13—C11	-4.6 (4)
O3—C2—C3—C4	-175.3 (3)	C12—C13—C14—C15	-1.8 (4)
C1—C2—C3—C4	0.0 (5)	C11—C13—C14—C15	176.8 (2)
C2—C3—C4—C5	-3.9 (5)	C13—C14—C15—C16	-1.4 (4)
C3—C4—C5—C6	178.9 (3)	C13—C14—C15—C12	-179.7 (2)
C3—C4—C5—C10	0.8 (5)	C14—C15—C16—C17	2.5 (4)
C4—C5—C6—C7	-179.7 (3)	C12—C15—C16—C17	-179.2 (2)
C10—C5—C6—C7	-1.6 (5)	C15—C16—C17—C12	-0.5 (4)
C5—C6—C7—C8	-3.9 (5)	C15—C16—C17—C13	-175.5 (2)
C25—O4—C8—C7	15.0 (5)	C13—C12—C17—C16	-2.3 (4)
C25—O4—C8—C9	-165.1 (3)	C11—C12—C17—C16	-172.9 (3)
C6—C7—C8—O4	-179.8 (3)	C13—C12—C17—C13	172.3 (2)
C6—C7—C8—C9	0.2 (5)	C11—C12—C17—C13	1.8 (4)
O4—C8—C9—C10	-171.3 (3)	C8—C9—C18—O2	-179.4 (3)
C7—C8—C9—C10	8.7 (4)	C10—C9—C18—O2	16.3 (4)
O4—C8—C9—C18	24.5 (4)	C8—C9—C18—C19	8.5 (4)
C7—C8—C9—C18	-155.6 (3)	C10—C9—C18—C19	-155.8 (3)

C6—C5—C10—C1	-172.0 (3)	O2—C18—C19—C24	-91.9 (3)
C4—C5—C10—C1	6.1 (4)	C9—C18—C19—C24	80.8 (4)
C6—C5—C10—C9	10.2 (4)	O2—C18—C19—C20	77.3 (3)
C4—C5—C10—C9	-171.7 (3)	C9—C18—C19—C20	-109.9 (3)
C2—C1—C10—C5	-9.9 (4)	C24—C19—C20—C21	3.1 (4)
C11—C1—C10—C5	156.1 (3)	C18—C19—C20—C21	-166.7 (3)
C2—C1—C10—C9	167.7 (3)	C24—C19—C20—C14	-176.2 (2)
C11—C1—C10—C9	-26.3 (4)	C18—C19—C20—C14	14.1 (4)
C8—C9—C10—C5	-13.6 (4)	C19—C20—C21—C22	0.2 (4)
C18—C9—C10—C5	150.6 (3)	C14—C20—C21—C22	179.5 (2)
C8—C9—C10—C1	168.7 (3)	C20—C21—C22—C23	-2.6 (4)
C18—C9—C10—C1	-27.0 (4)	C20—C21—C22—C15	178.3 (2)
C2—C1—C11—O1	-36.1 (4)	C21—C22—C23—C24	1.6 (4)
C10—C1—C11—O1	157.3 (3)	C15—C22—C23—C24	-179.3 (2)
C2—C1—C11—C12	130.2 (3)	C22—C23—C24—C19	2.0 (4)
C10—C1—C11—C12	-36.4 (4)	C22—C23—C24—C16	-177.8 (2)
O1—C11—C12—C13	-47.0 (4)	C20—C19—C24—C23	-4.2 (4)
C1—C11—C12—C13	146.3 (3)	C18—C19—C24—C23	165.4 (3)
O1—C11—C12—C17	122.9 (3)	C20—C19—C24—C16	175.5 (2)
C1—C11—C12—C17	-43.9 (4)	C18—C19—C24—C16	-14.9 (4)

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>
O3—H3A...O1	0.84	1.82	2.551 (3)	145