



Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(Z)-2,3-Dichloro-1,4-bis(4-chlorophenyl)but-2-ene-1,4-dioneRam K. Tittal,^{a*} Satish Kumar^b and R. N. Ram^a^aDepartment of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India, and ^bDepartment of Chemistry, St. Stephen's College, University Enclave, Delhi 110 007, IndiaCorrespondence e-mail: rkittaliitd@nitkr.ac.in

Received 9 June 2014; accepted 2 July 2014

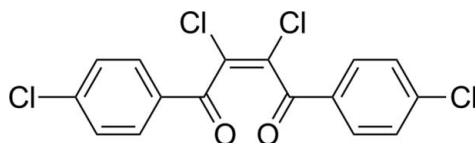
Edited by L. Farrugia, University of Glasgow, Scotland

Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.065; wR factor = 0.145; data-to-parameter ratio = 15.2.

The title compound, $\text{C}_{16}\text{H}_8\text{Cl}_4\text{O}_2$, crystallizes with two independent molecules in the asymmetric unit. Both molecules have a *Z* conformation around the central double bond and they show significantly different C—C—O torsion angles between the aromatic ring and the carbonyl group [30.1 (7) and 3.9 (7)° in one molecule and 23.5 (7) and 9.3 (8)° in the other]. The crystal packing shows short halogen Cl \cdots O [3.003 (5) and 3.246 (4) Å] and Cl \cdots Cl [3.452 (2) Å] contacts and aromatic C—H \cdots Cl and C—H \cdots O interactions link the molecules, resulting in chains propagating along [100]. The crystal structure also features π – π stacking interactions between aromatic units of the two independent molecules, with a centroid–centroid distance of 3.9264 (6) Å.

Related literature

For general background and details of the synthesis, see: Clark (2002); Martin *et al.* (1985); Matyjaszewski & Xia (2001); Ram & Charles (1999); Ram & Kumar (2008); Ram & Tittal (2014a,b); Ram & Manoj (2008); Ram & Meher (2003); Ram *et al.* (2007); Tomislav & Matyjaszewski (2008). For halogen-bond interactions, see: Agarwal *et al.* (2014); Gonnade *et al.* (2008); Pedireddi *et al.* (1992). For short aromatic interactions, see: Warad *et al.* (2013).



* Present Address: Department of Chemistry, National Institute of Technology, Kurukshetra, Haryana 136 119, India.

Experimental

Crystal data

$\text{C}_{16}\text{H}_8\text{Cl}_4\text{O}_2$
 $M_r = 374.02$
 Orthorhombic, *Ab*a2
 $a = 19.065$ (2) Å
 $b = 28.668$ (4) Å
 $c = 11.8800$ (14) Å
 $V = 6493.1$ (14) Å³
 $Z = 16$
 Mo $K\alpha$ radiation
 $\mu = 0.73$ mm⁻¹
 $T = 273$ K
 $0.37 \times 0.28 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.782$, $T_{\max} = 0.863$
 31827 measured reflections
 6044 independent reflections
 5194 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.145$
 $S = 1.13$
 6044 reflections
 397 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³
 Absolute structure: Flack (1983), 1939 Friedel pairs
 Absolute structure parameter: 0.08 (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots Cl7	0.93	2.74	3.160 (5)	109
C28—H28 \cdots Cl2	0.93	2.72	3.191 (5)	112
C3—H3 \cdots O1 ⁱ	0.93	2.55	3.290 (6)	137
C5—H5 \cdots O3 ⁱⁱ	0.93	2.75	3.418 (6)	129
C6—H6 \cdots O3 ⁱⁱⁱ	0.93	2.91	3.502 (6)	122
C13—H13 \cdots O2 ⁱⁱⁱ	0.93	2.45	3.302 (7)	152
C29—H29 \cdots Cl8 ^{iv}	0.93	2.81	3.645 (5)	149

Symmetry codes: (i) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (ii) $x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (iv) $x, y + \frac{1}{2}, z + \frac{3}{2}$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2008) and SHELXTL (Sheldrick, 2008); software used to prepare material for publication: publCIF (Westrip, 2010), PLATON (Spek, 2009) and SHELXTL.

The authors are thankful to Shailesh Upreti for providing assistance in solving the crystal structure.

Supporting information for this paper is available from the IUCr electronic archives (Reference: FJ2678).

References

- Agarwal, P., Mishra, P., Gupta, N., Neelam., Sahoo, P. & Kumar, S. (2014). *Acta Cryst.* **E70**, o418.
 Bruker (2000). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Clark, A. J. (2002). *Chem. Soc. Rev.* **31**, 1–11.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Gonnade, R. G., Bhadbhade, M. M. & Shashidhar, M. S. (2008). *CrystEngComm*, **10**, 288–296.
 Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

- Martin, P., Steiner, E., Streith, J., Winkler, T. & Bellus, D. (1985). *Tetrahedron*, **41**, 4057–4078.
- Matyjaszewski, K. & Xia, J. (2001). *Chem. Rev.* **101**, 2921–2990.
- Pedireddi, V. R., Sarma, J. A. R. P. & Desiraju, G. R. (1992). *J. Chem. Soc. Perkin Trans. 2*, pp. 311–320.
- Ram, R. N. & Charles, I. (1999). *Chem. Commun.* pp. 2267–2268.
- Ram, R. N. & Kumar, N. (2008). *Tetrahedron Lett.* **49**, 799–802.
- Ram, R. N. & Manoj, T. P. (2008). *J. Org. Chem.* **73**, 5633–5635.
- Ram, R. N. & Meher, N. K. (2003). *Org. Lett.* **5**, 145–147.
- Ram, R. N. & Tittal, R. K. (2014a). *Tetrahedron Lett.* Submitted. <http://dx.doi.org/10.1016/j.tetlet.2014.06.008>
- Ram, R. N. & Tittal, R. K. (2014b). *Tetrahedron Lett.* Submitted. <http://dx.doi.org/10.1016/j.tetlet.2014.05.097>
- Ram, R. N., Tittal, R. K. & Upreti, S. (2007). *Tetrahedron Lett.* **48**, 7994–7997.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tomislav, P. T. & Matyjaszewski, K. (2008). *Chem. Soc. Rev.* **37**, 1087–1097.
- Warad, I., Al-Noaimi, M., Haddad, S. F., Al-Demeri, Y. & Hammouti, B. (2013). *Acta Cryst.* **E69**, o1075.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2014). E70, o861–o862 [doi:10.1107/S1600536814015463]

(Z)-2,3-Dichloro-1,4-bis(4-chlorophenyl)but-2-ene-1,4-dione**Ram K. Tittal, Satish Kumar and R. N. Ram****S1. Structural commentary**

Free radical reactions are intimately involved in the chemistry of trichloromethyl compounds. Generation of free radicals from trichloromethyl group by homolysis of a C—Cl bond is relatively easy. Free radicals can easily be generated by the action of UV-light, radical initiators or redox active metal salts or its complexes. Considerable amount of information is available in the literature on radical reactions involving trichloromethyl group containing compounds. For example, the radical generated by reaction of a trichloromethyl group substituted compound under non reducing condition with CuCl or its complexes with bpy or with other bi- or tridentate tertiary amine ligands readily undergo intermolecular (Martin *et al.*, 1985) or intramolecular (Clark, 2002), (Ram & Kumar, 2008) addition/cyclization on to a suitably substituted carbon-carbon double bond. The formation of mono-and/or di-reduction product are also reported under non reducing conditions along with cyclization products (Ram *et al.*, 2007). Such radicals also acts as radical initiator in atom transfer radical polymerization reactions (Tomislav & Matyjaszewski, 2008), (Matyjaszewski & Xia, 2001). However, if the carbon-carbon double bond in such radical centre is replaced by any weak or relatively better leaving group at the β -position of the radical centre, it underwent predominantly rearrangement and/or fragmentation by the intermediate formation of contact ion pair (Ram & Meher, 2003). It is worthwhile to mention that 2,2,2-trichloroethylalkyl ethers and trichloromethyl carbinols having no suitably located carbon-carbon double bond or a leaving group β -position to the trichloromethyl carbon underwent 1,2-H shift under similar conditions through the intermediacy of a copper-carbenoid species (Ram & Charles, 1999), (Ram & Manoj, 2008). In this context, we have decided to explore the behavior of the radicals derived from trichloromethyl compounds which neither contains any suitably located carbon-carbon double bond nor any leaving group or any hydrogen atom at the β -position of the radical centre so as to restrict the above transformations i.e. intermolecular or intramolecular addition; ATRP; rearrangement and/or fragmentation or 1,2-H shift. The major product obtained under such reaction conditions is reported here. The asymmetric unit (Fig. 1) consists of the two formula units of the compound. Each formula unit adopts Z conformation about the C=C bond: C₈=C₉ and C₂₄=C₂₅. The aromatic ring of two units are nearly coplanar with a dihedral angle of 12.73° (C₁₂—C₁₅—C₂₁—C₁₈). A centroid to centroid distance of 3.9264 (6) Å between aromatic units of two independent molecules present in the asymmetric unit is observed indicating the presence of π - π stacking interactions (Fig. 1). The structure is stabilized by short intermolecular C—H \cdots Cl [3.160 (5), 3.191 (5) and 3.645 (5)Å], C—H \cdots O [3.290 (6), 3.418 (6), 3.502 (6) and 3.302 (7)Å] interactions [Warad *et al.* (2013)] (Fig. 2). In addition, the crystal packing also features short Cl \cdots O {O₂ \cdots Cl₃ [3.003 (5)] Å and O₄ \cdots Cl₈ [3.246 (4) Å]} and Cl₂ \cdots Cl₆ [3.452 (2)Å] halogen bond interactions (Fig. 3) (Gonnade *et al.*, 2008), (Pedireddi *et al.*, 1992), Agarwal *et al.* (2014).

S2. Synthesis and crystallization

A two-neck round bottom flask fitted with a rubber septum was charged with CuCl (0.8 g, 0.008mol), 2,2'-bipyridine (1.25 g, 0.008 mol). Nitrogen was introduced into the flask followed by addition of 15 mL dry DCE or benzene into the

flask to ensure the formation of the brown colored CuCl-bpy complex. To the reaction flask a solution of the 2,2,2-trichloro-1-(4-chloro-phenyl)-ethanone(0.004 mol) in dry DCE or benzene (5 mL) was added with the with the help of a syringe and the reaction mixture was heated to reflux with stirring under a slow and continuous flow of nitrogen. After the completion of the reaction as indicated by TLC (1-2 h), the reaction mixture was cooled and filtered through a celite pad. The filtrate was evaporated under reduced pressure on a rotary evaporator and purified by column chromatography using silica gel as the solid support. A solution of *n*-hexane and ethylacetate was used as the solvent for elution to get **1** in 52 or 60 % isolated yields in DCE or benzene respectively. Suitable crystals were obtained from chloroform/hexane. Melting point 110 °C.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed at their ideal position with C—H = 0.93 Å.

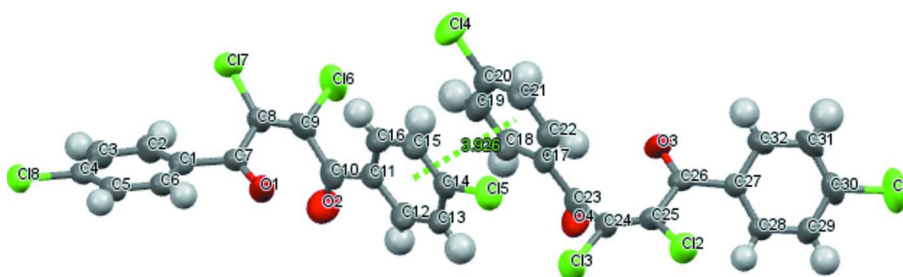


Figure 1

The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms showing π - π stacking interactions.

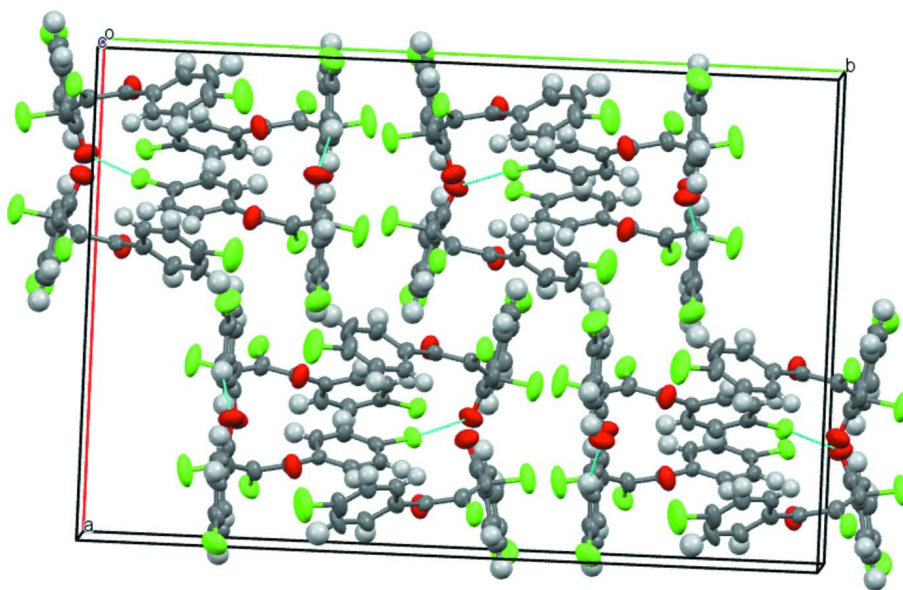
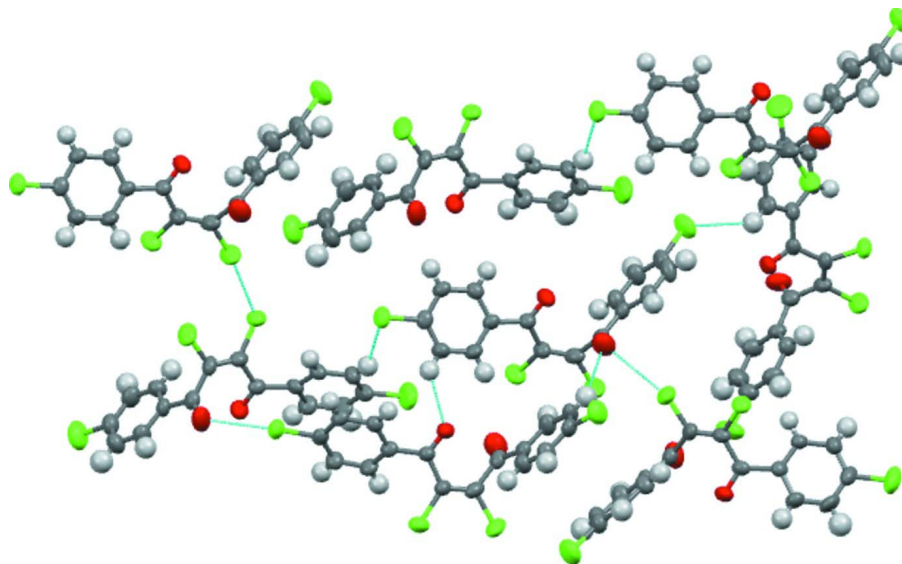


Figure 2

The packing diagram of the title compound showing short intermolecular halogen bond Cl...O interactions.

**Figure 3**

Structure of the title compound showing Cl...Cl, O...Cl, C—H...Cl and C—H...O interactions.

(Z)-2,3-Dichloro-1,4-bis(4-chlorophenyl)but-2-ene-1,4-dione

Crystal data

$C_{16}H_8Cl_4O_2$

$M_r = 374.02$

Orthorhombic, *Aba2*

Hall symbol: A 2 -2ac

$a = 19.065$ (2) Å

$b = 28.668$ (4) Å

$c = 11.8800$ (14) Å

$V = 6493.1$ (14) Å³

$Z = 16$

$F(000) = 3008$

$D_x = 1.530$ Mg m⁻³

Melting point: 383 K

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

Cell parameters from 5754 reflections

$\theta = 3.2$ – 26.1°

$\mu = 0.73$ mm⁻¹

$T = 273$ K

Block, colourless

$0.37 \times 0.28 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

$T_{\min} = 0.782$, $T_{\max} = 0.863$

31827 measured reflections

6044 independent reflections

5194 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 1.4^\circ$

$h = -23 \rightarrow 23$

$k = -34 \rightarrow 34$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.145$

$S = 1.13$

6044 reflections

397 parameters

1 restraint

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

$$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack (1983), 1939 Friedel pairs
 Absolute structure parameter: 0.08 (7)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1802 (2)	0.18216 (14)	0.0202 (4)	0.0441 (10)
C2	0.2138 (3)	0.18813 (16)	−0.0820 (4)	0.0560 (12)
H2	0.2257	0.2180	−0.1056	0.067*
C3	0.2296 (2)	0.15075 (16)	−0.1490 (4)	0.0553 (12)
H3	0.2540	0.1549	−0.2160	0.066*
C4	0.2091 (2)	0.10726 (15)	−0.1158 (4)	0.0479 (11)
C5	0.1760 (2)	0.09998 (15)	−0.0130 (4)	0.0491 (11)
H5	0.1631	0.0701	0.0094	0.059*
C6	0.1627 (2)	0.13761 (17)	0.0547 (4)	0.0493 (11)
H6	0.1418	0.1332	0.1246	0.059*
C7	0.1635 (2)	0.22072 (15)	0.0995 (4)	0.0458 (10)
C8	0.1486 (3)	0.26865 (17)	0.0565 (4)	0.0520 (12)
C9	0.1600 (3)	0.30479 (17)	0.1200 (5)	0.0584 (13)
C10	0.1935 (3)	0.30333 (16)	0.2379 (5)	0.0543 (12)
C11	0.1455 (2)	0.30832 (14)	0.3351 (4)	0.0471 (11)
C12	0.1746 (3)	0.31256 (18)	0.4422 (5)	0.0612 (14)
H12	0.2231	0.3141	0.4499	0.073*
C13	0.1333 (3)	0.3145 (2)	0.5364 (5)	0.0653 (15)
H13	0.1531	0.3172	0.6077	0.078*
C14	0.0618 (3)	0.31252 (17)	0.5223 (4)	0.0595 (14)
C15	0.0316 (3)	0.30947 (19)	0.4183 (5)	0.0645 (14)
H15	−0.0169	0.3092	0.4113	0.077*
C16	0.0730 (3)	0.30681 (17)	0.3243 (5)	0.0586 (13)
H16	0.0526	0.3040	0.2535	0.070*
C17	0.1304 (3)	0.45602 (16)	0.5455 (4)	0.0494 (11)
C18	0.1596 (3)	0.4566 (2)	0.4390 (5)	0.0661 (15)
H18	0.2072	0.4631	0.4313	0.079*
C19	0.1208 (3)	0.4480 (2)	0.3454 (5)	0.0743 (16)
H19	0.1416	0.4484	0.2746	0.089*
C20	0.0506 (3)	0.43870 (19)	0.3565 (5)	0.0653 (14)
C21	0.0195 (3)	0.43733 (19)	0.4611 (5)	0.0681 (15)

H21	-0.0280	0.4306	0.4682	0.082*
C22	0.0595 (3)	0.44599 (18)	0.5550 (5)	0.0604 (13)
H22	0.0388	0.4451	0.6259	0.072*
C23	0.1738 (3)	0.46744 (16)	0.6438 (4)	0.0543 (12)
C24	0.1466 (3)	0.45532 (16)	0.7593 (4)	0.0552 (12)
C25	0.1170 (2)	0.48387 (16)	0.8325 (4)	0.0514 (12)
C26	0.1019 (2)	0.53398 (15)	0.8002 (4)	0.0462 (10)
C27	0.0991 (2)	0.57237 (16)	0.8868 (4)	0.0459 (11)
C28	0.1346 (2)	0.57170 (15)	0.9873 (4)	0.0466 (11)
H28	0.1594	0.5451	1.0085	0.056*
C29	0.1339 (3)	0.60992 (17)	1.0567 (4)	0.0584 (13)
H29	0.1595	0.6097	1.1234	0.070*
C30	0.0961 (3)	0.64784 (18)	1.0281 (5)	0.0671 (15)
C31	0.0593 (3)	0.64972 (18)	0.9285 (6)	0.0768 (17)
H31	0.0335	0.6761	0.9097	0.092*
C32	0.0614 (3)	0.61211 (17)	0.8578 (4)	0.0597 (13)
H32	0.0373	0.6131	0.7897	0.072*
Cl1	0.09338 (14)	0.69524 (6)	1.11846 (19)	0.1247 (8)
Cl2	0.08763 (8)	0.46534 (4)	0.96328 (11)	0.0696 (4)
Cl3	0.16115 (10)	0.39746 (4)	0.79049 (14)	0.0897 (5)
Cl4	-0.00090 (11)	0.42888 (7)	0.23804 (16)	0.1048 (6)
Cl5	0.00905 (9)	0.31287 (6)	0.64225 (14)	0.0877 (5)
Cl6	0.14301 (12)	0.36143 (5)	0.08012 (14)	0.0981 (6)
Cl7	0.11250 (8)	0.27538 (5)	-0.07659 (12)	0.0712 (4)
Cl8	0.22478 (7)	0.05907 (4)	-0.20286 (12)	0.0635 (3)
O1	0.1630 (2)	0.21511 (12)	0.1997 (3)	0.0657 (10)
O2	0.2555 (2)	0.30041 (15)	0.2467 (4)	0.0835 (12)
O3	0.0931 (2)	0.54208 (12)	0.7004 (3)	0.0653 (9)
O4	0.2329 (2)	0.48314 (14)	0.6368 (4)	0.0807 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.039 (2)	0.040 (2)	0.053 (3)	-0.0054 (18)	-0.001 (2)	0.005 (2)
C2	0.072 (3)	0.038 (2)	0.059 (3)	-0.005 (2)	0.006 (3)	0.009 (2)
C3	0.063 (3)	0.051 (3)	0.052 (3)	-0.005 (2)	0.010 (2)	0.005 (2)
C4	0.039 (2)	0.049 (3)	0.056 (3)	0.007 (2)	-0.009 (2)	-0.004 (2)
C5	0.048 (3)	0.039 (2)	0.061 (3)	-0.0011 (19)	0.002 (2)	0.007 (2)
C6	0.048 (3)	0.054 (3)	0.045 (3)	0.004 (2)	0.000 (2)	0.003 (2)
C7	0.050 (3)	0.043 (2)	0.044 (3)	0.003 (2)	-0.003 (2)	0.005 (2)
C8	0.065 (3)	0.044 (3)	0.047 (3)	0.011 (2)	0.003 (2)	0.004 (2)
C9	0.066 (3)	0.044 (3)	0.065 (3)	0.014 (2)	0.016 (3)	0.014 (2)
C10	0.062 (3)	0.037 (2)	0.063 (3)	-0.009 (2)	0.012 (3)	-0.004 (2)
C11	0.050 (3)	0.037 (2)	0.055 (3)	-0.0023 (19)	0.000 (2)	-0.006 (2)
C12	0.047 (3)	0.068 (3)	0.069 (4)	0.000 (2)	-0.008 (3)	-0.016 (3)
C13	0.066 (4)	0.075 (4)	0.054 (3)	0.025 (3)	-0.012 (3)	-0.020 (3)
C14	0.070 (3)	0.052 (3)	0.056 (3)	0.018 (2)	0.005 (3)	-0.009 (2)
C15	0.051 (3)	0.082 (4)	0.061 (3)	0.002 (3)	0.004 (3)	-0.011 (3)

C16	0.056 (3)	0.067 (3)	0.053 (3)	0.004 (2)	-0.008 (2)	-0.008 (2)
C17	0.054 (3)	0.041 (3)	0.052 (3)	-0.002 (2)	-0.003 (2)	-0.012 (2)
C18	0.056 (3)	0.075 (4)	0.067 (4)	-0.015 (3)	0.005 (3)	-0.012 (3)
C19	0.087 (4)	0.085 (4)	0.051 (3)	-0.006 (3)	0.005 (3)	-0.010 (3)
C20	0.076 (4)	0.062 (3)	0.058 (3)	0.001 (3)	-0.008 (3)	-0.011 (3)
C21	0.053 (3)	0.069 (3)	0.082 (4)	-0.012 (3)	-0.001 (3)	-0.010 (3)
C22	0.065 (3)	0.064 (3)	0.053 (3)	-0.009 (3)	0.006 (3)	0.004 (3)
C23	0.063 (3)	0.043 (3)	0.058 (3)	0.004 (2)	-0.001 (3)	-0.008 (2)
C24	0.071 (3)	0.039 (3)	0.055 (3)	0.004 (2)	-0.012 (2)	-0.009 (2)
C25	0.060 (3)	0.048 (3)	0.047 (3)	-0.004 (2)	-0.007 (2)	0.012 (2)
C26	0.043 (2)	0.048 (3)	0.047 (3)	-0.0041 (19)	-0.009 (2)	0.009 (2)
C27	0.051 (3)	0.049 (3)	0.038 (2)	0.006 (2)	0.009 (2)	0.005 (2)
C28	0.053 (3)	0.045 (2)	0.041 (2)	0.009 (2)	0.001 (2)	0.006 (2)
C29	0.079 (3)	0.053 (3)	0.043 (3)	0.003 (3)	-0.003 (3)	-0.002 (2)
C30	0.099 (4)	0.046 (3)	0.057 (3)	0.014 (3)	0.024 (3)	0.001 (2)
C31	0.096 (4)	0.048 (3)	0.086 (4)	0.036 (3)	0.004 (3)	0.006 (3)
C32	0.064 (3)	0.051 (3)	0.064 (3)	0.016 (2)	-0.008 (2)	0.004 (3)
C11	0.204 (2)	0.0658 (10)	0.1046 (15)	0.0227 (12)	0.0211 (15)	-0.0310 (10)
C12	0.1076 (11)	0.0476 (6)	0.0537 (8)	-0.0028 (7)	0.0051 (7)	0.0125 (6)
C13	0.1506 (14)	0.0439 (7)	0.0746 (10)	0.0210 (8)	-0.0108 (11)	-0.0020 (7)
C14	0.1133 (14)	0.1214 (15)	0.0795 (11)	-0.0006 (11)	-0.0345 (10)	-0.0287 (10)
C15	0.0900 (10)	0.1093 (13)	0.0638 (9)	0.0236 (9)	0.0217 (8)	-0.0129 (9)
C16	0.1784 (18)	0.0426 (7)	0.0734 (10)	0.0264 (9)	0.0176 (11)	0.0112 (7)
C17	0.0909 (10)	0.0691 (8)	0.0534 (7)	0.0193 (7)	-0.0084 (7)	0.0110 (6)
C18	0.0727 (8)	0.0537 (7)	0.0641 (8)	0.0115 (6)	-0.0026 (7)	-0.0138 (6)
O1	0.101 (3)	0.052 (2)	0.044 (2)	0.0158 (18)	0.0010 (19)	0.0062 (16)
O2	0.056 (2)	0.114 (3)	0.080 (3)	-0.010 (2)	0.011 (2)	-0.006 (2)
O3	0.095 (3)	0.055 (2)	0.046 (2)	0.0059 (18)	-0.0172 (19)	0.0064 (16)
O4	0.063 (2)	0.097 (3)	0.082 (3)	-0.016 (2)	-0.002 (2)	-0.028 (2)

Geometric parameters (Å, °)

C1—C6	1.382 (6)	C17—C18	1.382 (7)
C1—C2	1.383 (7)	C17—C22	1.386 (7)
C1—C7	1.487 (6)	C17—C23	1.468 (7)
C2—C3	1.368 (7)	C18—C19	1.359 (8)
C2—H2	0.9300	C18—H18	0.9300
C3—C4	1.365 (6)	C19—C20	1.372 (8)
C3—H3	0.9300	C19—H19	0.9300
C4—C5	1.390 (7)	C20—C21	1.377 (8)
C4—C18	1.751 (5)	C20—C14	1.738 (6)
C5—C6	1.369 (7)	C21—C22	1.374 (8)
C5—H5	0.9300	C21—H21	0.9300
C6—H6	0.9300	C22—H22	0.9300
C7—O1	1.201 (5)	C23—O4	1.216 (6)
C7—C8	1.493 (6)	C23—C24	1.508 (7)
C8—C9	1.299 (7)	C24—C25	1.322 (7)
C8—C17	1.736 (5)	C24—C13	1.722 (5)

C9—C10	1.541 (8)	C25—C26	1.514 (6)
C9—C16	1.722 (5)	C25—C12	1.735 (5)
C10—O2	1.190 (6)	C26—O3	1.220 (6)
C10—C11	1.479 (7)	C26—C27	1.507 (7)
C11—C16	1.389 (7)	C27—C28	1.373 (7)
C11—C12	1.393 (7)	C27—C32	1.390 (6)
C12—C13	1.369 (8)	C28—C29	1.371 (7)
C12—H12	0.9300	C28—H28	0.9300
C13—C14	1.375 (7)	C29—C30	1.348 (7)
C13—H13	0.9300	C29—H29	0.9300
C14—C15	1.366 (8)	C30—C31	1.377 (9)
C14—C15	1.744 (6)	C30—C11	1.733 (6)
C15—C16	1.369 (8)	C31—C32	1.367 (8)
C15—H15	0.9300	C31—H31	0.9300
C16—H16	0.9300	C32—H32	0.9300
C6—C1—C2	119.1 (4)	C18—C17—C22	118.0 (5)
C6—C1—C7	116.6 (4)	C18—C17—C23	119.9 (5)
C2—C1—C7	124.3 (4)	C22—C17—C23	122.1 (5)
C3—C2—C1	121.0 (4)	C19—C18—C17	121.9 (5)
C3—C2—H2	119.5	C19—C18—H18	119.1
C1—C2—H2	119.5	C17—C18—H18	119.1
C4—C3—C2	119.0 (5)	C18—C19—C20	119.2 (6)
C4—C3—H3	120.5	C18—C19—H19	120.4
C2—C3—H3	120.5	C20—C19—H19	120.4
C3—C4—C5	121.4 (4)	C19—C20—C21	120.8 (5)
C3—C4—C18	120.1 (4)	C19—C20—C14	120.3 (5)
C5—C4—C18	118.5 (4)	C21—C20—C14	118.9 (5)
C6—C5—C4	118.8 (4)	C22—C21—C20	119.3 (5)
C6—C5—H5	120.6	C22—C21—H21	120.4
C4—C5—H5	120.6	C20—C21—H21	120.4
C5—C6—C1	120.6 (4)	C21—C22—C17	120.8 (5)
C5—C6—H6	119.7	C21—C22—H22	119.6
C1—C6—H6	119.7	C17—C22—H22	119.6
O1—C7—C1	122.0 (4)	O4—C23—C17	123.4 (5)
O1—C7—C8	117.4 (4)	O4—C23—C24	117.8 (5)
C1—C7—C8	120.6 (4)	C17—C23—C24	118.6 (4)
C9—C8—C7	120.3 (4)	C25—C24—C23	127.1 (4)
C9—C8—C17	120.4 (4)	C25—C24—C13	121.6 (4)
C7—C8—C17	119.3 (4)	C23—C24—C13	111.3 (3)
C8—C9—C10	125.1 (4)	C24—C25—C26	120.1 (4)
C8—C9—C16	124.1 (4)	C24—C25—C12	122.5 (4)
C10—C9—C16	110.7 (4)	C26—C25—C12	117.1 (4)
O2—C10—C11	123.6 (5)	O3—C26—C27	121.3 (4)
O2—C10—C9	119.5 (5)	O3—C26—C25	116.9 (4)
C11—C10—C9	116.8 (4)	C27—C26—C25	121.8 (4)
C16—C11—C12	118.9 (5)	C28—C27—C32	118.8 (5)
C16—C11—C10	122.7 (5)	C28—C27—C26	124.4 (4)

C12—C11—C10	118.4 (4)	C32—C27—C26	116.6 (4)
C13—C12—C11	121.4 (5)	C29—C28—C27	120.4 (4)
C13—C12—H12	119.3	C29—C28—H28	119.8
C11—C12—H12	119.3	C27—C28—H28	119.8
C12—C13—C14	118.0 (5)	C30—C29—C28	119.9 (5)
C12—C13—H13	121.0	C30—C29—H29	120.1
C14—C13—H13	121.0	C28—C29—H29	120.1
C15—C14—C13	122.0 (5)	C29—C30—C31	121.4 (5)
C15—C14—C15	119.8 (4)	C29—C30—C11	119.5 (5)
C13—C14—C15	118.2 (4)	C31—C30—C11	119.1 (4)
C14—C15—C16	119.9 (5)	C32—C31—C30	118.8 (5)
C14—C15—H15	120.0	C32—C31—H31	120.6
C16—C15—H15	120.0	C30—C31—H31	120.6
C15—C16—C11	119.8 (5)	C31—C32—C27	120.6 (5)
C15—C16—H16	120.1	C31—C32—H32	119.7
C11—C16—H16	120.1	C27—C32—H32	119.7
C6—C1—C2—C3	0.1 (7)	C22—C17—C18—C19	0.4 (9)
C7—C1—C2—C3	177.8 (4)	C23—C17—C18—C19	-177.5 (5)
C1—C2—C3—C4	2.8 (8)	C17—C18—C19—C20	0.4 (9)
C2—C3—C4—C5	-3.6 (7)	C18—C19—C20—C21	-1.0 (9)
C2—C3—C4—C18	176.9 (4)	C18—C19—C20—C14	178.5 (5)
C3—C4—C5—C6	1.3 (7)	C19—C20—C21—C22	0.8 (9)
C18—C4—C5—C6	-179.2 (3)	C14—C20—C21—C22	-178.7 (4)
C4—C5—C6—C1	1.7 (7)	C20—C21—C22—C17	0.0 (8)
C2—C1—C6—C5	-2.4 (7)	C18—C17—C22—C21	-0.6 (8)
C7—C1—C6—C5	179.8 (4)	C23—C17—C22—C21	177.3 (5)
C6—C1—C7—O1	30.1 (7)	C18—C17—C23—O4	9.3 (8)
C2—C1—C7—O1	-147.6 (5)	C22—C17—C23—O4	-168.5 (5)
C6—C1—C7—C8	-151.7 (4)	C18—C17—C23—C24	-165.2 (5)
C2—C1—C7—C8	30.5 (7)	C22—C17—C23—C24	17.0 (7)
O1—C7—C8—C9	24.3 (7)	O4—C23—C24—C25	84.3 (7)
C1—C7—C8—C9	-153.9 (5)	C17—C23—C24—C25	-100.9 (6)
O1—C7—C8—C17	-153.0 (4)	O4—C23—C24—C13	-93.7 (5)
C1—C7—C8—C17	28.8 (6)	C17—C23—C24—C13	81.1 (5)
C7—C8—C9—C10	4.4 (8)	C23—C24—C25—C26	5.1 (8)
C17—C8—C9—C10	-178.3 (4)	C13—C24—C25—C26	-177.1 (3)
C7—C8—C9—C16	-178.6 (4)	C23—C24—C25—C12	179.9 (4)
C17—C8—C9—C16	-1.3 (7)	C13—C24—C25—C12	-2.3 (6)
C8—C9—C10—O2	80.1 (7)	C24—C25—C26—O3	26.5 (7)
C16—C9—C10—O2	-97.3 (5)	C12—C25—C26—O3	-148.6 (4)
C8—C9—C10—C11	-103.2 (6)	C24—C25—C26—C27	-152.6 (5)
C16—C9—C10—C11	79.5 (5)	C12—C25—C26—C27	32.3 (5)
O2—C10—C11—C16	-173.1 (5)	O3—C26—C27—C28	-152.0 (5)
C9—C10—C11—C16	10.3 (6)	C25—C26—C27—C28	27.0 (7)
O2—C10—C11—C12	3.9 (7)	O3—C26—C27—C32	23.5 (7)
C9—C10—C11—C12	-172.7 (4)	C25—C26—C27—C32	-157.5 (4)
C16—C11—C12—C13	1.0 (7)	C32—C27—C28—C29	-1.2 (7)

C10—C11—C12—C13	-176.1 (5)	C26—C27—C28—C29	174.2 (4)
C11—C12—C13—C14	-0.4 (8)	C27—C28—C29—C30	2.3 (8)
C12—C13—C14—C15	-1.2 (8)	C28—C29—C30—C31	-1.7 (9)
C12—C13—C14—C15	177.7 (4)	C28—C29—C30—C11	178.0 (4)
C13—C14—C15—C16	2.2 (9)	C29—C30—C31—C32	0.1 (9)
C15—C14—C15—C16	-176.7 (4)	C11—C30—C31—C32	-179.6 (5)
C14—C15—C16—C11	-1.5 (8)	C30—C31—C32—C27	1.0 (9)
C12—C11—C16—C15	0.0 (7)	C28—C27—C32—C31	-0.5 (8)
C10—C11—C16—C15	177.0 (5)	C26—C27—C32—C31	-176.3 (5)

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>
C2—H2...C17	0.93	2.74	3.160 (5)	109
C28—H28...C12	0.93	2.72	3.191 (5)	112
C3—H3...O1 ⁱ	0.93	2.55	3.290 (6)	137
C5—H5...O3 ⁱⁱ	0.93	2.75	3.418 (6)	129
C6—H6...O3 ⁱⁱ	0.93	2.91	3.502 (6)	122
C13—H13...O2 ⁱⁱⁱ	0.93	2.45	3.302 (7)	152
C29—H29...C18 ^{iv}	0.93	2.81	3.645 (5)	149

Symmetry codes: (i) $-x+1/2, y, z-1/2$; (ii) $x, y-1/2, z-1/2$; (iii) $-x+1/2, y, z+1/2$; (iv) $x, y+1/2, z+3/2$.