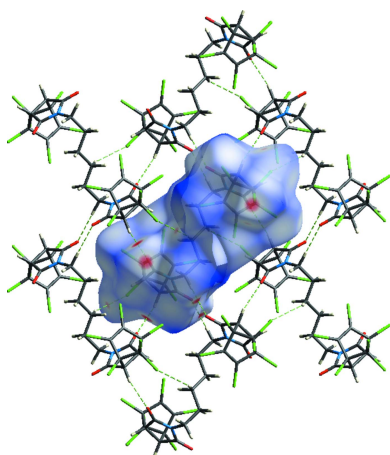


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# Crystal structure and Hirshfeld surface analysis of (3aR,4S,7S,7aS)-4,5,6,7,8,8-hexachloro-2-[6-[(3aR,4R,7R,7aS)-4,5,6,7,8,8-hexachloro-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl]hexyl]-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione

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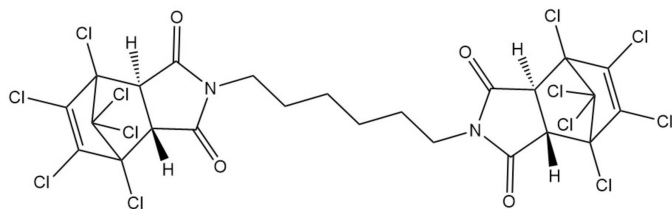
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The molecule of the title compound, C<sub>24</sub>H<sub>16</sub>Cl<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, is generated by a crystallographic inversion centre at the midpoint of the central C—C bond. A kink in the molecule is defined by a torsion angle of  $-169.86(15)^\circ$  about this central bond of the alkyl bridge. The pyrrolidine ring is essentially planar [max. deviation = 0.014(1) Å]. The cyclohexane ring has a boat conformation, while both cyclopentane rings adopt an envelope conformation. In the crystal structure, molecules are linked by intermolecular C—H $\cdots$ O, C—H $\cdots$ Cl and C—Cl $\cdots$  $\pi$  interactions, and short intermolecular Cl $\cdots$ O and Cl $\cdots$ Cl contacts, forming a three-dimensional network.

## 1. Chemical context

*N*-heterocyclic compounds are of interest in the fields of synthetic organic chemistry, coordination chemistry and medicinal chemistry because of their important biological properties (Mahmoudi *et al.*, 2016, 2017*a,b,c*, 2018*a,b*; 2019; Viswanathan *et al.*, 2019). For this reason, many approaches have been developed for their efficient and versatile synthesis (Gurbanov *et al.*, 2017, 2018*a,b*; Ma *et al.*, 2017*a,b*). On the other hand, *N*-heterocycles or *N*-ligands can also be used as precursors in the synthesis of coordination compounds (Ma *et al.*, 2020, 2021; Mahmudov *et al.*, 2013), and as building blocks in the construction of supramolecular structures as they have both hydrogen-bond donor and acceptor capabilities (Gurbanov *et al.*, 2020*a*; Kopylovich *et al.*, 2011*a,b*; Asgarova *et al.*, 2019). In fact, attachment of suitable functional groups to *N*-ligands can improve their solubility and the catalytic activity of the corresponding coordination compounds (Mizar *et al.*, 2012; Gurbanov *et al.*, 2020*b*; Khalilov *et al.*, 2011, 2018*a,b*; Maharramov *et al.*, 2019; Shikhaliyev *et al.*, 2019; Shixaliyev *et al.*, 2014). Intermolecular halogen bonds and other types of non-covalent interactions in halogenated *N*-heterocyclic compounds can improve their solubility and other functional properties. In order to continue our work in this perspective, we have synthesized a new halogenated *N*-heterocyclic compound, (3aR,4S,7S,7aS)-4,5,6,7,8,8-hexachloro-2-[6-

[(3*aR*,4*R*,7*R*,7*aS*)-4,5,6,7,8,8-hexachloro-1,3-dioxo-1,3,3*a*,4,7,7*a*-hexahydro-2*H*-4,7-methanoisindol-2-yl]hexyl]-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione, which provides multiple intermolecular non-covalent interactions.



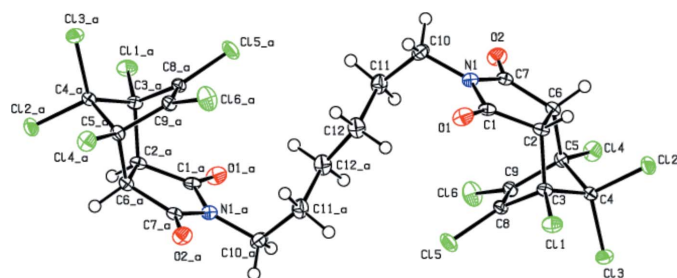
## 2. Structural commentary

The molecule of the title compound is generated by a crystallographic inversion centre at the midpoint of the central C—C bond. A kink in the molecule is defined by the C10—C11—C12—C12<sub>a</sub> torsion angle of  $-169.86(15)^\circ$  about this central bond of the alkyl bridge (Fig. 1). The pyrrolidine ring (N1/C1/C2/C6/C7) is essentially planar [maximum deviation =  $-0.014(1)$  Å for N1]. The cyclohexane ring (C2/C3/C5/C6/C8/C9) has a boat conformation [the puckering parameters (Cremer and Pople, 1975) are  $Q_T = 0.9300(14)$  Å,  $\theta = 89.99(9)^\circ$ ,  $\varphi = 59.37(9)^\circ$ ], while both the cyclopentane rings (C2—C6 and C3—C5/C8/C9) adopt an envelope conformation [ $Q(2) = 0.6308(14)$  Å,  $\varphi(2) = 252.44(13)^\circ$  and  $Q(2) = 0.5835(14)$  Å,  $\varphi(2) = 215.53(14)^\circ$ , respectively] with the C4 atom bearing the dichloromethane group as the flap.

## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal structure, molecules are linked by intermolecular C—H...O, C—H...Cl and C—Cl... $\pi$  interactions (Table 1), and short intermolecular contacts, listed in Table 2, forming a three-dimensional network (Figs. 2 and 3).

In order to visualize the intermolecular interactions (Table 2) in the crystal of the title compound, a Hirshfeld surface analysis was carried out using *Crystal Explorer 17.5* (Turner *et al.*, 2017). Fig. 4 shows the Hirshfeld surface plotted over  $d_{\text{norm}}$  in the range  $-0.1922$  to  $1.7149$  a.u. The red spots on the Hirshfeld surface represent C—H...O and C—H...Cl



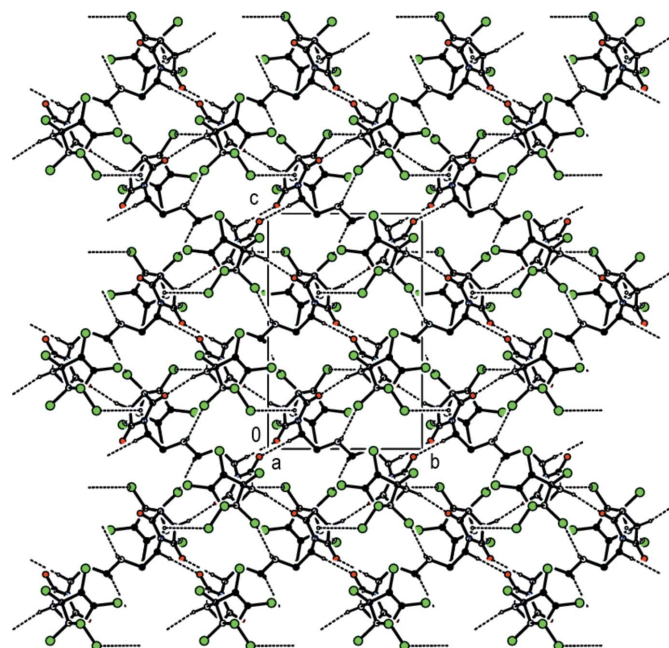
**Figure 1**  
The molecular structure of the title compound with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level. [Symmetry code: (a)  $2 - x, 1 - y, -z$ ].

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

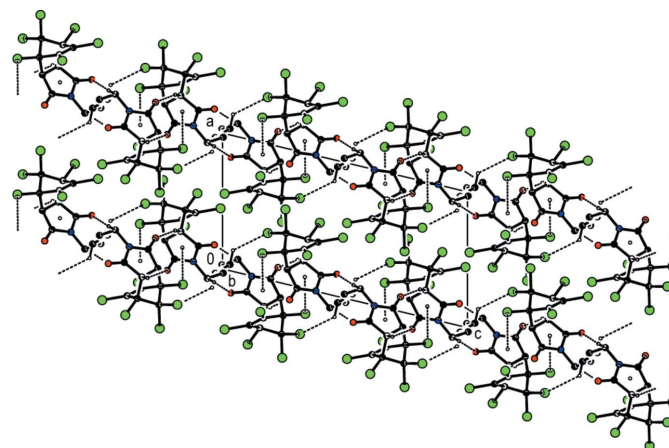
Cg1 is the centroid of the N1/C1/C2/C6/C7 pyrrolidine ring.

<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>
C6—H6...O1 <sup>i</sup>	1.00	2.43	3.3867 (16)	161
C10—H10A...O2 <sup>ii</sup>	0.99	2.45	3.4402 (17)	178
C12—H12B...Cl2 <sup>iii</sup>	0.99	2.80	3.5299 (15)	131
C3—Cl1...Cg1 <sup>iii</sup>	1.75 (1)	3.89 (1)	4.9389 (14)	117 (1)

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



**Figure 2**  
Crystal packing of the title compound viewed along the *a*-axis direction. C—H...O, C—H...Cl hydrogen bonds and C—Cl... $\pi$  interactions (Table 1) are represented by dashed lines. H atoms not involved in hydrogen bonding are omitted for clarity.



**Figure 3**  
Crystal packing viewed along the *b* axis, with intermolecular interactions shown as in Fig. 2. H atoms not involved in hydrogen bonding are omitted for clarity.

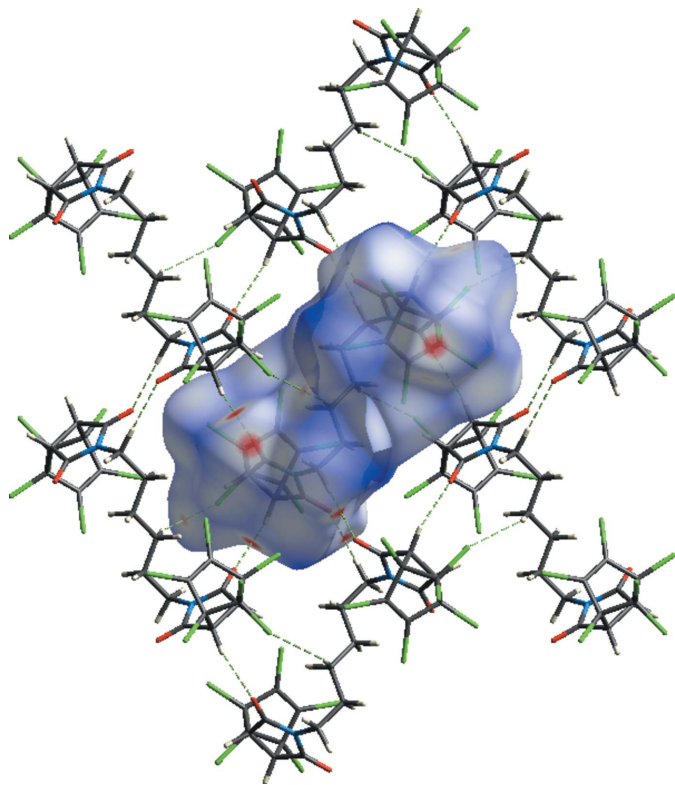
**Table 2**  
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
Cl3...Cl2	3.4333 (5)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
O1...H6	2.43	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
Cl1...H11B	2.99	$x, \frac{1}{2} - y, \frac{1}{2} + z$
Cl3...H10B	2.96	$-1 + x, y, z$
O2...Cl4	3.4606 (11)	$1 - x, -y, -z$
H10A...O2	2.45	$2 - x, -y, -z$

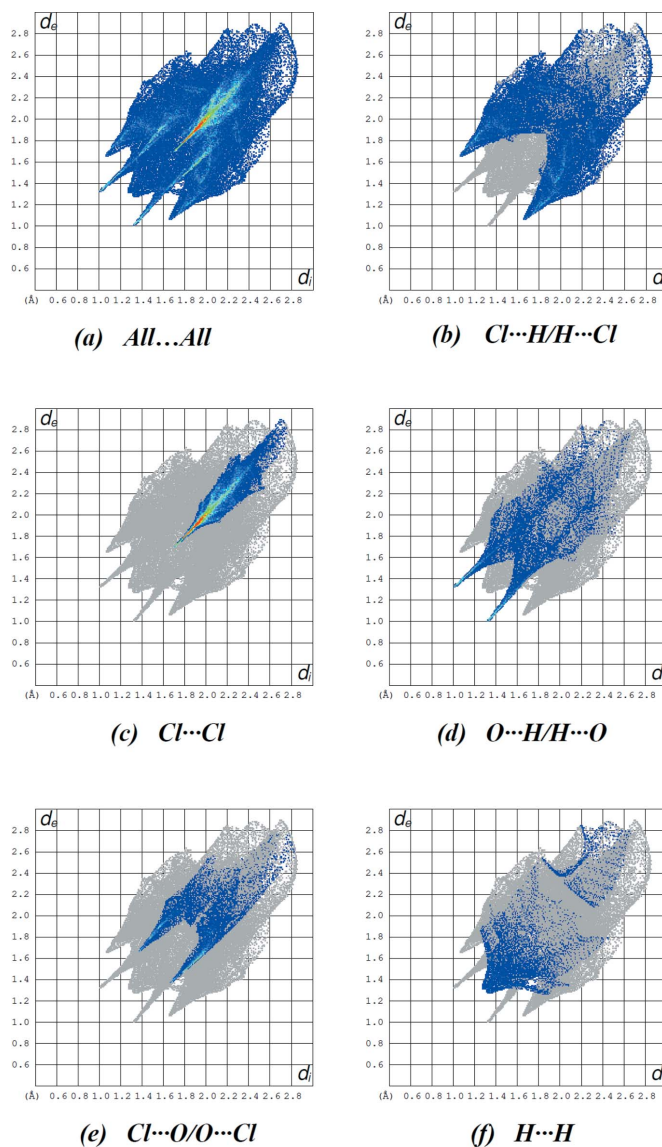
contacts. Fig. 5 shows the full two-dimensional fingerprint plot and those delineated into the major contacts: Cl...H/H...Cl (33.6%; Fig. 5b), Cl...Cl (29.3%; Fig. 5c), O...H/H...O (13.9%; Fig. 5d), Cl...O/O...Cl (11.4%; Fig. 5e) and H...H (7.0%; Fig. 5f) interactions. The remaining other weak interactions (contribution percentages) are Cl...C/C...Cl (3.2%), Cl...N/N...Cl (1.4%) and C...H/H...C (0.2%).

#### 4. Database survey

Four related compounds containing the methanoisindole moiety were found in the Cambridge Structural Database (CSD, version 5.42, update of November 2020; Groom *et al.*, 2016): 4,5,6,7,8,8-hexachloro-2-[2-(3,4-dimethoxyphenyl)ethyl]-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (refcode COHTUR; Manohar *et al.*, 2019), 5-hydroxy-4-



**Figure 4**  
A view of the Hirshfeld surface for the title compound, plotted over  $d_{\text{norm}}$  in the range  $-0.1922$  to  $1.7149$  a.u. together with interacting neighbouring molecules.



**Figure 5**

A view of the two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) Cl...H/H...Cl, (c) Cl...Cl and (d) O...H/H...O, (e) Cl...O/O...Cl and (f) H...H interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

(4-methylphenyl)-4-azatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (QOVCAH; Aslantaş *et al.*, 2015), (3aR,4S,7R,7aS)-2-(perfluoropyridin-4-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (MOJFUP; Peloquin *et al.*, 2019) and (3aR,4S,7R,7aS)-2-[(perfluoropyridin-4-yl)oxy]-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (MOJGAW; Peloquin *et al.*, 2019).

In COHTUR, the six-membered ring of the norbornene moiety adopts a boat conformation and the two five-membered rings have envelope conformations. The pyrrolidine ring makes a dihedral angle of  $14.83$  (12) $^\circ$  with the 3,4-dimethoxyphenyl ring, which are attached to each other by an extended N—CH<sub>2</sub>—CH<sub>2</sub>—C<sub>ar</sub> bridge. In the crystal of COHTUR, weak C—H...O hydrogen bonds link the mol-



ecules, forming a cyclic  $R_4^4(48)$  ring motif (Bernstein *et al.*, 1995). The molecules are stacked in layers held together by offset  $\pi$ - $\pi$  interactions, with a centroid-centroid distance of 3.564 (1) Å for the pyrrolidine and benzene rings. There is also an intermolecular C-Cl... $\pi$  interaction present.

In the crystal of QOVCAH, the cyclohexene ring adopts a boat conformation, and the five-membered rings have envelope conformations with the bridging atom as the flap. Their mean planes are oriented at a dihedral angle of 86.51 (7)°. The molecular structure is stabilized by a short intramolecular C-H...O contact. In the crystal, molecules are linked by O-H...O hydrogen bonds, forming chains propagating along [100]. The chains are linked by C-H... $\pi$  interactions, forming slabs parallel to (001).

The compound MOJFUP crystallizes in the triclinic space group  $P\bar{1}$  with two molecules, *A* and *B*, in the asymmetric unit, and MOJGAW in the monoclinic space group  $P2_1/n$  with one molecule per asymmetric unit. The synthesis of both compounds is conducted using *endo* starting materials, and the same configuration is observed in the resulting crystal structures. In MOJFUP, steric interactions between the *ortho*-fluorine atoms and the carbonyl oxygen atoms prevents free rotation about the nitrogen-*ipso*-carbon bond, which is evidenced by separate  $^{19}\text{F}$  NMR peaks in solution for the *ortho*-F atoms. In molecule *A*, the 2,3,5,6-tetrafluoropyridine plane is rotated by 58.05 (5)° relative to the pyrrolidine plane and the corresponding dihedral angle for molecule *B* is 61.65 (7)°. The addition of an oxygen atom between N and C in the bridge between the ring systems in MOJGAW alleviates this steric restriction and only one  $^{19}\text{F}$  NMR peak in solution is observed for the *ortho*-F atoms; even so, the dihedral angle between the 2,3,5,6-tetrafluoropyridine and pyrrolidine planes in the crystal of MOJGAW of 84.01 (5)° is larger than that found in MOJFUP.

The main directional interactions in the crystal structures of MOJFUP and MOJGAW are of the type C-H...O, C-H...F, C-O... $\pi$ , and C-F... $\pi$ . In both compounds, weak hydrogen-bonding interactions are observed for the hydrogen atom(s)  $\alpha$  to the carbonyl groups (C-H...O and C-H...F in MOJFUP; C-H...O in MOJGAW) and the olefinic hydrogen atoms (C-H...F in MOJFUP; C-H...O in MOJGAW). A weak interaction is also observed for a bridge hydrogen atom in MOJGAW, C-H...F. The packing is further aided by  $\pi$ -interactions with the pyridine ring in MOJGAW.

## 5. Synthesis and crystallization

To 741 mg (2 mmol) of (3*aR*,4*R*,7*R*,7*aS*)-4,5,6,7,8,8-hexachloro-3*a*,4,7,7*a*-tetrahydro-4,7-methanoisobenzofuran-1,3-dione were added 0.12 mL (1 mmol) of hexane-1,6-diamine and 25 mL of dimethylformamide, and the mixture was stirred for 6 h at 373 K. Then, the reaction mixture was cooled to room temperature and poured into cold water. The obtained precipitate was filtered off, washed with water, recrystallized from chloroform and dried under vacuum. Yellow powder, yield 92%, m.p 404–405 K (decomp.). Analysis calculated for  $\text{C}_{24}\text{H}_{16}\text{Cl}_{12}\text{N}_2\text{O}_4$  ( $M_r = 821.80$ ): C 35.08, H 1.96, N 3.41%;

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{24}\text{H}_{16}\text{Cl}_{12}\text{N}_2\text{O}_4$
$M_r$	821.79
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
$a, b, c$ (Å)	8.9549 (3), 10.5908 (4), 16.6043 (6)
$\beta$ (°)	103.499 (1)
$V$ (Å <sup>3</sup> )	1531.24 (10)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.12
Crystal size (mm)	0.34 × 0.32 × 0.28
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}$ , $T_{\text{max}}$	0.684, 0.736
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12567, 3403, 3141
$R_{\text{int}}$	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.643
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.021, 0.053, 1.04
No. of reflections	3403
No. of parameters	190
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.33, -0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

found: C 35.03, H 2.00, N 3.35%. ESI-MS:  $m/z$ : 822.9 [ $M_r + \text{H}$ ]<sup>+</sup>.  $^1\text{H}$  NMR (300.130 MHz) in acetone- $d_6$ , internal TMS,  $\delta$  (ppm): 1.29–3.43 (12H, 6CH<sub>2</sub>), 3.86 (4H, CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.468 MHz, acetone- $d_6$ ).  $\delta$ : 25.8 (2CH<sub>2</sub>), 27.2 (2CH<sub>2</sub>), 39.3 (4C-H), 52.0 (2CH<sub>2</sub>), 79.3 (4CCl), 104.4 (2CCl<sub>2</sub>), 130.9 (2C=C-Cl) and 170.2 (4C=O). Off-white prismatic crystals suitable for X-ray analysis were obtained by slow evaporation of a chloroform-hexane (1/1,  $v/v$ ) mixture.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound H atoms were positioned geometrically and refined using a riding model, with C-H = 0.99 (methylene) and 1.00 Å (methine), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Two reflections (100 and 002), affected by the incident beam-stop, and owing to poor agreement between observed and calculated intensities, two outliers (136 and 118) were omitted in the final cycles of refinement.

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The authors' contributions are as follows. Conceptualization, AIA and MA; methodology, AIA and ZA; investigation, AIA, ZA, and SM; writing (original draft), MA and SM; writing (review and editing of the manuscript), MA and SM; visualization, AIA and ZA; funding acquisition, AIA; resources, AIA, ZA and SHM; supervision, MA and SM.

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of (3a*R*,4*S*,7*S*,7a*S*)-4,5,6,7,8,8-hexachloro-2-{6-[(3a*R*,4*R*,7*R*,7a*S*)-4,5,6,7,8,8-hexachloro-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisindol-2-yl]hexyl}-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione

Aygun I. Alikhanova, Zeliha Atioğlu, Mehmet Akkurt and Sixberth Mlowe

### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

(3a*R*,4*S*,7*S*,7a*S*)-4,5,6,7,8,8-Hexachloro-2-{6-[(3a*R*,4*R*,7*R*,7a*S*)-4,5,6,7,8,8-hexachloro-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisindol-2-yl]hexyl}-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione

### Crystal data

C<sub>24</sub>H<sub>16</sub>Cl<sub>12</sub>N<sub>2</sub>O<sub>4</sub>  
*M<sub>r</sub>* = 821.79  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 8.9549 (3) Å  
*b* = 10.5908 (4) Å  
*c* = 16.6043 (6) Å  
 $\beta$  = 103.499 (1)°  
*V* = 1531.24 (10) Å<sup>3</sup>  
*Z* = 2

*F*(000) = 820  
*D<sub>x</sub>* = 1.782 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 7701 reflections  
 $\theta$  = 2.3–27.2°  
 $\mu$  = 1.12 mm<sup>-1</sup>  
*T* = 150 K  
 Block, colourless  
 0.34 × 0.32 × 0.28 mm

### Data collection

Bruker APEXII CCD  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Krause *et al.*, 2015)  
*T<sub>min</sub>* = 0.684, *T<sub>max</sub>* = 0.736  
 12567 measured reflections

3403 independent reflections  
 3141 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.023  
 $\theta_{\max}$  = 27.2°,  $\theta_{\min}$  = 2.3°  
*h* = -8→11  
*k* = -13→13  
*l* = -21→21

### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.021  
*wR*(*F*<sup>2</sup>) = 0.053  
*S* = 1.04

3403 reflections  
 190 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

$$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.7545P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.81506 (4)	0.38645 (3)	0.33748 (2)	0.02092 (8)
Cl2	0.65657 (4)	0.08552 (3)	0.31569 (2)	0.02036 (8)
Cl3	0.45141 (4)	0.28198 (3)	0.24334 (2)	0.01993 (8)
Cl4	0.48797 (4)	0.05628 (3)	0.10287 (2)	0.02218 (8)
Cl5	0.75019 (4)	0.52267 (3)	0.15453 (2)	0.02455 (9)
Cl6	0.55737 (5)	0.31532 (4)	0.00843 (2)	0.02966 (9)
O1	1.10843 (11)	0.32935 (10)	0.22625 (6)	0.0224 (2)
O2	0.83761 (12)	0.05643 (10)	0.03360 (6)	0.0220 (2)
N1	0.99701 (12)	0.19567 (11)	0.11936 (7)	0.0156 (2)
C1	1.01234 (15)	0.25177 (13)	0.19624 (8)	0.0152 (3)
C2	0.88902 (15)	0.19800 (12)	0.23555 (8)	0.0139 (2)
H2	0.935586	0.153877	0.288724	0.017*
C3	0.76483 (15)	0.29560 (12)	0.24743 (8)	0.0142 (2)
C4	0.62421 (15)	0.20595 (12)	0.24022 (8)	0.0142 (2)
C5	0.63197 (15)	0.15971 (12)	0.15208 (8)	0.0140 (2)
C6	0.79769 (15)	0.10488 (12)	0.17088 (8)	0.0142 (2)
H6	0.801142	0.017191	0.193567	0.017*
C7	0.87382 (15)	0.11223 (12)	0.09843 (8)	0.0153 (3)
C8	0.71121 (15)	0.36779 (12)	0.16671 (8)	0.0153 (3)
C9	0.63396 (15)	0.28797 (13)	0.11034 (8)	0.0157 (3)
C10	1.09720 (16)	0.21915 (14)	0.06241 (8)	0.0200 (3)
H10A	1.112615	0.139247	0.034488	0.024*
H10B	1.198763	0.248383	0.094445	0.024*
C11	1.02959 (17)	0.31780 (14)	-0.00267 (8)	0.0213 (3)
H11A	1.081293	0.311153	-0.049094	0.026*
H11B	0.919312	0.299100	-0.024805	0.026*
C12	1.04563 (18)	0.45260 (13)	0.03013 (8)	0.0223 (3)
H12A	1.010849	0.455925	0.082477	0.027*
H12B	1.155427	0.476794	0.042781	0.027*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.02260 (17)	0.01966 (17)	0.01950 (16)	0.00008 (13)	0.00287 (13)	-0.00824 (12)

C12	0.02766 (18)	0.01698 (16)	0.01742 (15)	0.00127 (13)	0.00727 (13)	0.00505 (12)
C13	0.01596 (15)	0.01944 (17)	0.02574 (17)	0.00286 (12)	0.00760 (13)	-0.00038 (12)
C14	0.01995 (16)	0.02252 (18)	0.02291 (16)	-0.00783 (13)	0.00266 (13)	-0.00581 (13)
C15	0.02410 (18)	0.01230 (16)	0.0374 (2)	-0.00025 (13)	0.00750 (15)	0.00650 (13)
C16	0.0340 (2)	0.0339 (2)	0.01635 (16)	0.00063 (16)	-0.00359 (14)	0.00900 (14)
O1	0.0162 (5)	0.0248 (5)	0.0257 (5)	-0.0038 (4)	0.0037 (4)	-0.0082 (4)
O2	0.0253 (5)	0.0215 (5)	0.0197 (5)	-0.0021 (4)	0.0061 (4)	-0.0076 (4)
N1	0.0153 (5)	0.0151 (6)	0.0165 (5)	0.0019 (4)	0.0043 (4)	-0.0011 (4)
C1	0.0124 (6)	0.0151 (6)	0.0168 (6)	0.0048 (5)	0.0008 (5)	-0.0006 (5)
C2	0.0146 (6)	0.0121 (6)	0.0139 (6)	0.0031 (5)	0.0008 (5)	-0.0012 (5)
C3	0.0147 (6)	0.0129 (6)	0.0145 (6)	0.0014 (5)	0.0021 (5)	-0.0018 (5)
C4	0.0153 (6)	0.0118 (6)	0.0154 (6)	0.0020 (5)	0.0037 (5)	0.0016 (5)
C5	0.0144 (6)	0.0128 (6)	0.0138 (6)	-0.0016 (5)	0.0015 (5)	-0.0002 (5)
C6	0.0163 (6)	0.0116 (6)	0.0142 (6)	0.0007 (5)	0.0023 (5)	0.0003 (5)
C7	0.0163 (6)	0.0117 (6)	0.0177 (6)	0.0035 (5)	0.0036 (5)	0.0000 (5)
C8	0.0135 (6)	0.0129 (6)	0.0200 (6)	0.0024 (5)	0.0049 (5)	0.0037 (5)
C9	0.0146 (6)	0.0173 (6)	0.0146 (6)	0.0036 (5)	0.0021 (5)	0.0049 (5)
C10	0.0189 (7)	0.0217 (7)	0.0220 (7)	-0.0003 (6)	0.0100 (5)	-0.0032 (5)
C11	0.0262 (7)	0.0211 (7)	0.0172 (6)	-0.0055 (6)	0.0067 (6)	-0.0023 (5)
C12	0.0274 (7)	0.0209 (7)	0.0178 (6)	-0.0054 (6)	0.0037 (6)	-0.0022 (5)

*Geometric parameters (Å, °)*

C11—C3	1.7464 (13)	C3—C4	1.5592 (18)
C12—C4	1.7639 (13)	C4—C5	1.5599 (17)
C13—C4	1.7558 (13)	C5—C9	1.5269 (18)
C14—C5	1.7432 (13)	C5—C6	1.5559 (18)
C15—C8	1.6989 (14)	C6—C7	1.5168 (18)
C16—C9	1.6958 (13)	C6—H6	1.0000
O1—C1	1.2098 (17)	C8—C9	1.3293 (19)
O2—C7	1.2042 (16)	C10—C11	1.523 (2)
N1—C1	1.3855 (16)	C10—H10A	0.9900
N1—C7	1.3927 (17)	C10—H10B	0.9900
N1—C10	1.4686 (17)	C11—C12	1.5228 (19)
C1—C2	1.5186 (19)	C11—H11A	0.9900
C2—C6	1.5442 (17)	C11—H11B	0.9900
C2—C3	1.5642 (17)	C12—C12 <sup>i</sup>	1.515 (3)
C2—H2	1.0000	C12—H12A	0.9900
C3—C8	1.5203 (17)	C12—H12B	0.9900
C1—N1—C7	113.85 (11)	C2—C6—C5	103.10 (10)
C1—N1—C10	125.21 (11)	C7—C6—H6	111.5
C7—N1—C10	120.94 (11)	C2—C6—H6	111.5
O1—C1—N1	125.37 (13)	C5—C6—H6	111.5
O1—C1—C2	126.60 (12)	O2—C7—N1	124.52 (13)
N1—C1—C2	108.03 (11)	O2—C7—C6	127.35 (12)
C1—C2—C6	105.12 (10)	N1—C7—C6	108.13 (11)
C1—C2—C3	114.59 (11)	C9—C8—C3	107.83 (11)



C6—C2—C3	103.47 (10)	C9—C8—C15	128.16 (11)
C1—C2—H2	111.1	C3—C8—C15	124.00 (10)
C6—C2—H2	111.1	C8—C9—C5	107.78 (11)
C3—C2—H2	111.1	C8—C9—C16	128.08 (11)
C8—C3—C4	98.94 (10)	C5—C9—C16	124.06 (10)
C8—C3—C2	107.98 (10)	N1—C10—C11	111.81 (11)
C4—C3—C2	99.97 (10)	N1—C10—H10A	109.3
C8—C3—C11	116.29 (9)	C11—C10—H10A	109.3
C4—C3—C11	116.31 (9)	N1—C10—H10B	109.3
C2—C3—C11	115.05 (9)	C11—C10—H10B	109.3
C3—C4—C5	92.94 (9)	H10A—C10—H10B	107.9
C3—C4—C13	114.83 (9)	C12—C11—C10	113.62 (11)
C5—C4—C13	113.84 (9)	C12—C11—H11A	108.8
C3—C4—C12	112.95 (9)	C10—C11—H11A	108.8
C5—C4—C12	113.80 (9)	C12—C11—H11B	108.8
C13—C4—C12	108.08 (7)	C10—C11—H11B	108.8
C9—C5—C6	108.14 (10)	H11A—C11—H11B	107.7
C9—C5—C4	98.88 (10)	C12 <sup>i</sup> —C12—C11	113.19 (14)
C6—C5—C4	100.27 (9)	C12 <sup>i</sup> —C12—H12A	108.9
C9—C5—C14	115.59 (9)	C11—C12—H12A	108.9
C6—C5—C14	115.22 (9)	C12 <sup>i</sup> —C12—H12B	108.9
C4—C5—C14	116.55 (9)	C11—C12—H12B	108.9
C7—C6—C2	104.81 (10)	H12A—C12—H12B	107.8
C7—C6—C5	113.96 (10)		
C7—N1—C1—O1	-178.12 (13)	C3—C2—C6—C5	0.55 (12)
C10—N1—C1—O1	1.4 (2)	C9—C5—C6—C7	-47.46 (14)
C7—N1—C1—C2	2.31 (14)	C4—C5—C6—C7	-150.44 (11)
C10—N1—C1—C2	-178.13 (11)	C14—C5—C6—C7	83.59 (12)
O1—C1—C2—C6	179.44 (13)	C9—C5—C6—C2	65.53 (12)
N1—C1—C2—C6	-1.01 (13)	C4—C5—C6—C2	-37.45 (12)
O1—C1—C2—C3	66.54 (17)	C14—C5—C6—C2	-163.42 (9)
N1—C1—C2—C3	-113.90 (12)	C1—N1—C7—O2	177.78 (13)
C1—C2—C3—C8	47.50 (14)	C10—N1—C7—O2	-1.8 (2)
C6—C2—C3—C8	-66.37 (12)	C1—N1—C7—C6	-2.63 (15)
C1—C2—C3—C4	150.38 (10)	C10—N1—C7—C6	177.79 (11)
C6—C2—C3—C4	36.51 (11)	C2—C6—C7—O2	-178.64 (13)
C1—C2—C3—C11	-84.24 (12)	C5—C6—C7—O2	-66.68 (18)
C6—C2—C3—C11	161.89 (9)	C2—C6—C7—N1	1.79 (13)
C8—C3—C4—C5	52.32 (10)	C5—C6—C7—N1	113.75 (12)
C2—C3—C4—C5	-57.86 (10)	C4—C3—C8—C9	-35.34 (13)
C11—C3—C4—C5	177.63 (9)	C2—C3—C8—C9	68.27 (13)
C8—C3—C4—C13	-65.69 (11)	C11—C3—C8—C9	-160.66 (10)
C2—C3—C4—C13	-175.87 (8)	C4—C3—C8—C15	145.71 (10)
C11—C3—C4—C13	59.62 (12)	C2—C3—C8—C15	-110.68 (11)
C8—C3—C4—C12	169.74 (9)	C11—C3—C8—C15	20.39 (15)
C2—C3—C4—C12	59.57 (11)	C3—C8—C9—C5	0.64 (14)
C11—C3—C4—C12	-64.95 (11)	C15—C8—C9—C5	179.54 (10)

C3—C4—C5—C9	-51.85 (10)	C3—C8—C9—C16	-176.19 (10)
C13—C4—C5—C9	66.99 (11)	C15—C8—C9—C16	2.7 (2)
C12—C4—C5—C9	-168.55 (9)	C6—C5—C9—C8	-69.69 (13)
C3—C4—C5—C6	58.55 (10)	C4—C5—C9—C8	34.26 (13)
C13—C4—C5—C6	177.40 (9)	C14—C5—C9—C8	159.47 (10)
C12—C4—C5—C6	-58.15 (11)	C6—C5—C9—C16	107.30 (11)
C3—C4—C5—C14	-176.38 (9)	C4—C5—C9—C16	-148.75 (10)
C13—C4—C5—C14	-57.54 (12)	C14—C5—C9—C16	-23.54 (15)
C12—C4—C5—C14	66.92 (11)	C1—N1—C10—C11	-96.26 (15)
C1—C2—C6—C7	-0.47 (13)	C7—N1—C10—C11	83.27 (15)
C3—C2—C6—C7	120.07 (11)	N1—C10—C11—C12	76.43 (15)
C1—C2—C6—C5	-119.99 (10)	C10—C11—C12—C12 <sup>i</sup>	-169.86 (15)

Symmetry code: (i)  $-x+2, -y+1, -z$ .

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 is the centroid of the N1/C1/C2/C6/C7 pyrrolidine ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 $\cdots$ O1 <sup>ii</sup>	1.00	2.43	3.3867 (16)	161
C10—H10A $\cdots$ O2 <sup>iii</sup>	0.99	2.45	3.4402 (17)	178
C12—H12B $\cdots$ C12 <sup>iv</sup>	0.99	2.80	3.5299 (15)	131
C3—C11 $\cdots$ Cg1 <sup>iv</sup>	1.75 (1)	3.89 (1)	4.9389 (14)	117 (1)

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