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2-[(*Z*)-4,7-Dichloro-3,3-dimethyl-2,3-dihydro-1*H*-indol-2-ylidene]-3-oxopropanenitrile

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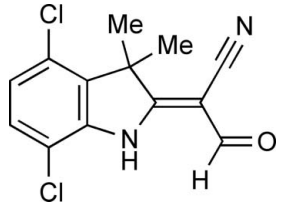
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.046; wR factor = 0.127; data-to-parameter ratio = 13.4.

In the title compound, $C_{13}H_{10}Cl_2N_2O$, the ring N atom and its three attached atoms are essentially coplanar with angles adding to 359.8°, indicating conjugation with the 2-formylacrylonitrile subunit. The aldehyde group is oriented to place the carbonyl O atom 2.02 (3) Å from the N—H hydrogen atom. Intramolecular N—H···O and C—H···Cl interactions occur. The geometry of the exocyclic double bond is *Z*. In the crystal, weak C—H···N hydrogen bonds link the molecules into chains along [1$\bar{1}$0].

Related literature

For related structures, see: Baradarani *et al.* (2006); Helliwell *et al.* (2010) Rashidi *et al.* (2009). For the chemistry of complexes of (2*H*-indol-2-ylidene)propanedials, see: Rashidi *et al.* (2011).



Experimental

Crystal data

$C_{13}H_{10}Cl_2N_2O$
M_r = 281.13
Triclinic, $P\bar{1}$
a = 7.0535 (8) Å
b = 7.9455 (10) Å
c = 12.2883 (15) Å
α = 105.151 (2)°
β = 104.855 (2)°
γ = 95.296 (2)°
V = 633.09 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.50 mm^{-1}
T = 100 K
0.60 × 0.60 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.724, T_{max} = 1.000
3237 measured reflections
2268 independent reflections
2028 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.127
S = 1.05
2268 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N2^{i}	0.93	2.56	3.256 (3)	132
C10—H10B···Cl2	0.96	2.83	3.473 (2)	125
N1—H1N···O1	0.88 (3)	2.02 (3)	2.678 (3)	131 (2)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2144).

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supporting information

Acta Cryst. (2012). E**68**, o233 [doi:10.1107/S1600536811053906]

2-[(*Z*)-4,7-Dichloro-3,3-dimethyl-2,3-dihydro-1*H*-indol-2-ylidene]-3-oxopropanenitrile

Madeleine Helliwell, Mehdi M. Baradarani, Razieh Mohammadnejadaghdam, Arash Afghan and John A. Joule

S1. Comment

We showed that the interaction of 2,3,3-trimethyl-3*H*-indoles with the Vilsmeier reagent produces (1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)propanedials (Baradarani *et al.*, 2006). 2,3,3-Trimethyl-2*H*-pyrrolo[2,3-*f*]quinoline, 2,3,3-trimethyl-3*H*-pyrrolo[3,2-*h*]quinoline (Rashidi *et al.*, 2009), 2,2′,3,3,3′,3′-hexamethyl-3*H*,3′*H*-5,5′-biindole and 2,3,3,7,8,8-hexamethyl-3*H*,8*H*-indolo[7,6-*g*]indole (Rashidi *et al.*, 2011) behave analogously. The (1,3-dihydroindol-2-ylidene)propanedials were shown to react with arylhydrazines (or hydrazine) to produce 3,3-dimethyl-2-[1-aryl-1*H*-pyrazol-4-yl]-3*H*-indoles (Baradarani *et al.*, 2006; Rashidi *et al.*, 2009; Helliwell *et al.* 2010; Rashidi *et al.*, 2011).

In anticipation that the (1,3-dihydroindol-2-ylidene)propanedials would react with hydroxylamine to produce isoxazol-4-yl-3*H*-indoles, 2-(4,7-dichloro-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)propanedial was treated with hydroxylamine hydrochloride in refluxing ethanol. The unexpected product of the reaction was 2-(4,7-dichloro-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)-3-oxopropanenitrile as shown by this X-ray diffraction analysis. We interpret this transformation as involving firstly formation of the monooxime **1** which cyclizes to generate hemiacetal **2**, fragmentation of which (arrows on **2**) would then give the product **3** (Fig. 3).

The sum of the angles of the bonds at the ring nitrogen in the title compound is 359.8 ° showing the extensive conjugation of the nitrogen with the 2-formylacrylonitrile subunit. The geometry of the double bond linking the two heterocyclic subunits is *Z*. In the crystal structure, there are intramolecular N—H···O and C—H···Cl interactions and weak intermolecular C—H···N hydrogen bonds which link the molecules into chains.

S2. Experimental

A mixture of 2-(4,7-dichloro-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)propanedial (100 mg, 0.35 mmol) and hydroxylamine hydrochloride (24 mg, 0.35 mmol) in absolute EtOH (10 ml) was heated at reflux for 12 h. The solvent was evaporated and resulting mixture dissolved in water and neutralized with aq. NaOH (2 N). The resulting precipitate was filtered off, washed with water, dried in air and recrystallized from EtOH. Yield 70%, mp 451–456 K, FT—IR (KBr) ν_{max} 3199, 2989, 2941, 2205, 1642, 1539, 1156, 928 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 6H, 2CH_3), 7.07 (d, J = 8.7 Hz, 1H, ArH), 7.25 (d, J = 8.7 Hz, 1H, ArH), 9.45 (s, 1H, CHO), 12.32 (bs, 1H, NH), ^{13}C NMR ($CDCl_3$) δ 20.3, 52.9, 81.6, 115.8, 117.8, 125.6, 127.1, 128.7, 129.7, 134.6, 139.4, 177.2, 188.0.

S3. Refinement

H atoms bonded to C were included in calculated positions using the riding method, with C—H distances of 0.96 Å and U_{eq} values set at 1.5 times those of the parent atoms for methyl H atoms and C—H distances of 0.93 Å and U_{eq} values of 1.2 times the parent atom for all other H atoms. The H atom bonded to N1 was found by difference Fourier methods and

refined isotropically with the N1—H1N distance refined to 0.88 (3) Å.

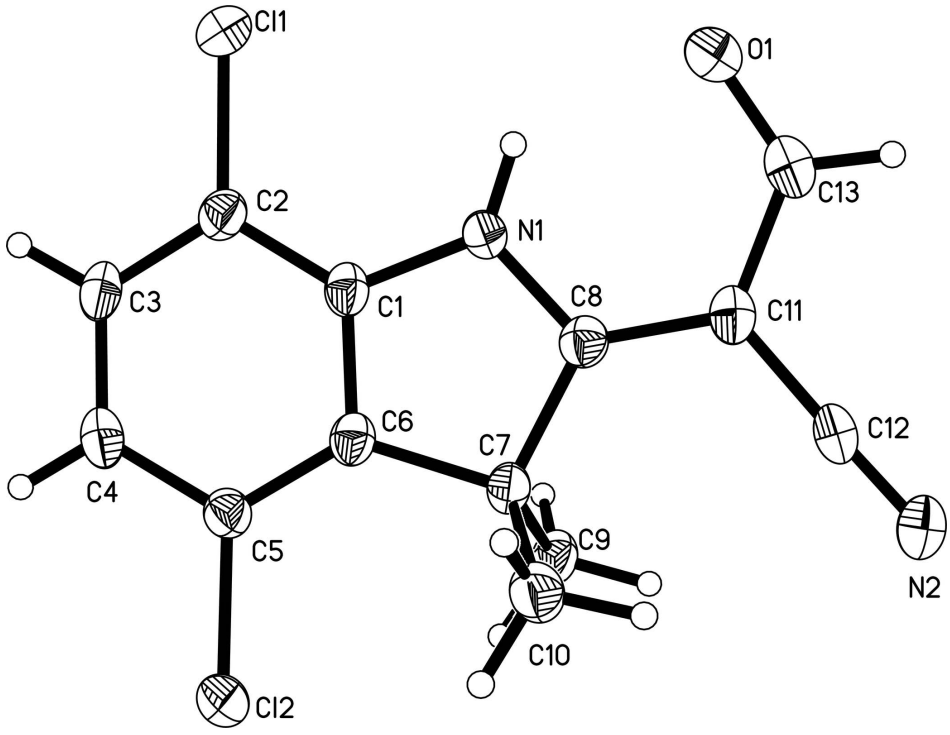

Figure 1

Plot of the title compound with ellipsoids drawn at the 50% probability level.

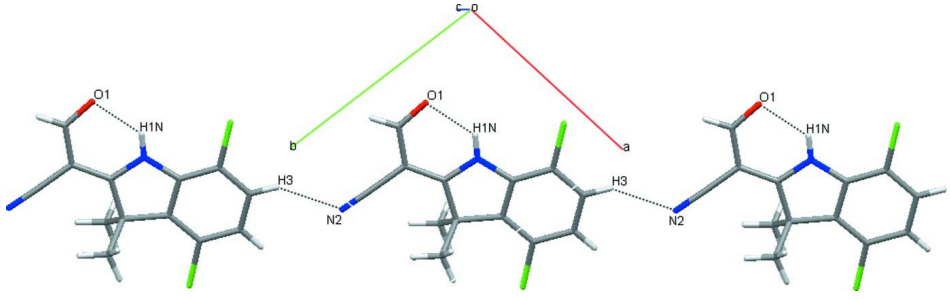

Figure 2

Packing diagram showing the intramolecular N—H···O hydrogen bonds and the weak intermolecular C—H···N hydrogen bonds, which link the molecules into chains.

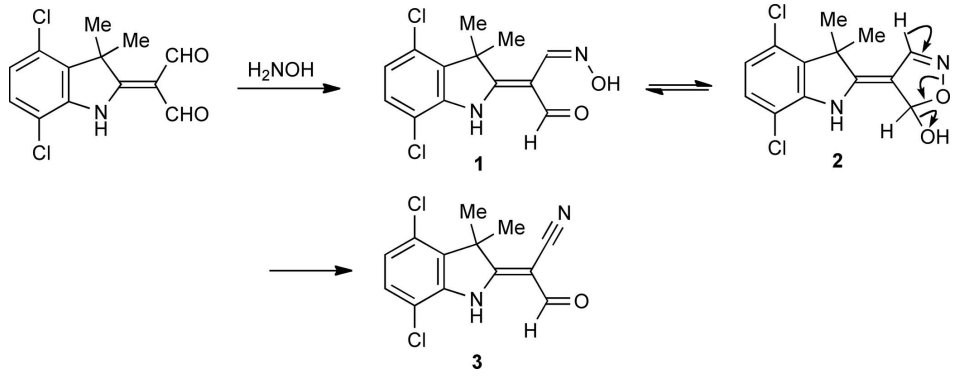

Figure 3

Reaction scheme.

2-[(*Z*)-4,7-Dichloro-3,3-dimethyl-2,3-dihydro-1*H*-indol-2- ylidene]-3-oxopropanenitrile

Crystal data

$C_{13}H_{10}Cl_2N_2O$
$M_r = 281.13$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.0535\ (8)$ Å
$b = 7.9455\ (10)$ Å
$c = 12.2883\ (15)$ Å
$\alpha = 105.151\ (2)°$
$\beta = 104.855\ (2)°$
$\gamma = 95.296\ (2)°$
$V = 633.09\ (13)$ Å^3
$Z = 2$
$F(000) = 288$
$D_x = 1.475$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 954 reflections
$\theta = 2.7–26.6°$
$\mu = 0.50$ mm^{-1}
$T = 100$ K
Irregular, colourless
0.60 × 0.60 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.724$, $T_{max} = 1.000$
3237 measured reflections
2268 independent reflections
2028 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.4°$, $\theta_{min} = 1.8°$
$h = -7\rightarrow8$
$k = -9\rightarrow7$
$l = -13\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.127$
$S = 1.05$
2268 reflections
169 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.3121P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

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)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl2	1.27782 (8)	0.70384 (7)	0.97251 (5)	0.0315 (2)
Cl1	0.74564 (9)	0.06883 (7)	0.53899 (5)	0.0352 (2)
O1	0.2509 (2)	0.4169 (2)	0.53396 (14)	0.0312 (4)
N1	0.6292 (3)	0.4367 (2)	0.65761 (17)	0.0229 (4)
N2	0.4289 (3)	1.0032 (3)	0.7934 (2)	0.0421 (6)
C1	0.8201 (3)	0.3982 (3)	0.69974 (19)	0.0226 (5)
C2	0.8935 (3)	0.2435 (3)	0.6587 (2)	0.0246 (5)
C3	1.0883 (3)	0.2341 (3)	0.7155 (2)	0.0264 (5)
H3	1.1416	0.1333	0.6900	0.032*
C4	1.2042 (3)	0.3757 (3)	0.8108 (2)	0.0265 (5)
H4	1.3336	0.3674	0.8489	0.032*
C5	1.1276 (3)	0.5315 (3)	0.85021 (19)	0.0233 (5)
C6	0.9348 (3)	0.5444 (3)	0.79314 (19)	0.0222 (5)
C7	0.8125 (3)	0.6947 (3)	0.80972 (19)	0.0225 (5)
C8	0.6153 (3)	0.6045 (3)	0.71454 (19)	0.0225 (5)
C9	0.9066 (3)	0.8550 (3)	0.7818 (2)	0.0278 (5)
H9A	0.9145	0.8194	0.7024	0.042*
H9B	1.0379	0.8997	0.8353	0.042*
H9C	0.8261	0.9459	0.7902	0.042*
C10	0.7818 (4)	0.7484 (3)	0.9349 (2)	0.0298 (5)
H10A	0.6960	0.8355	0.9390	0.045*
H10B	0.9082	0.7970	0.9932	0.045*
H10C	0.7224	0.6460	0.9494	0.045*
C11	0.4428 (3)	0.6762 (3)	0.68668 (19)	0.0249 (5)
C12	0.4373 (3)	0.8573 (3)	0.7470 (2)	0.0295 (5)
C13	0.2650 (3)	0.5725 (3)	0.5954 (2)	0.0280 (5)
H13	0.1531	0.6262	0.5818	0.034*
H1N	0.528 (4)	0.371 (4)	0.599 (2)	0.033 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0233 (3)	0.0289 (3)	0.0350 (4)	0.0044 (2)	0.0003 (2)	0.0051 (2)
Cl1	0.0351 (4)	0.0219 (3)	0.0396 (4)	0.0050 (2)	0.0025 (3)	0.0021 (2)
O1	0.0254 (9)	0.0304 (9)	0.0331 (9)	0.0027 (7)	0.0033 (7)	0.0075 (7)
N1	0.0186 (9)	0.0207 (9)	0.0273 (10)	0.0042 (7)	0.0030 (8)	0.0070 (7)

N2	0.0358 (12)	0.0330 (12)	0.0495 (13)	0.0176 (9)	0.0022 (10)	0.0045 (10)
C1	0.0215 (11)	0.0220 (10)	0.0280 (11)	0.0062 (8)	0.0082 (9)	0.0117 (9)
C2	0.0260 (11)	0.0200 (10)	0.0283 (11)	0.0047 (9)	0.0077 (9)	0.0082 (9)
C3	0.0259 (12)	0.0230 (11)	0.0358 (12)	0.0108 (9)	0.0113 (10)	0.0132 (9)
C4	0.0213 (11)	0.0296 (11)	0.0341 (12)	0.0092 (9)	0.0085 (9)	0.0163 (9)
C5	0.0213 (11)	0.0223 (10)	0.0258 (11)	0.0032 (8)	0.0052 (9)	0.0081 (9)
C6	0.0226 (11)	0.0204 (10)	0.0266 (11)	0.0055 (8)	0.0086 (9)	0.0103 (8)
C7	0.0211 (11)	0.0205 (10)	0.0265 (11)	0.0068 (8)	0.0063 (9)	0.0073 (8)
C8	0.0227 (11)	0.0206 (10)	0.0259 (11)	0.0037 (8)	0.0081 (9)	0.0091 (8)
C9	0.0262 (12)	0.0201 (10)	0.0383 (13)	0.0054 (9)	0.0084 (10)	0.0110 (9)
C10	0.0266 (12)	0.0346 (12)	0.0278 (12)	0.0098 (10)	0.0071 (9)	0.0077 (9)
C11	0.0232 (11)	0.0259 (11)	0.0295 (12)	0.0087 (9)	0.0090 (9)	0.0119 (9)
C12	0.0211 (11)	0.0326 (13)	0.0338 (12)	0.0110 (9)	0.0035 (9)	0.0101 (10)
C13	0.0224 (11)	0.0342 (12)	0.0305 (12)	0.0078 (9)	0.0074 (9)	0.0143 (10)

Geometric parameters (Å, º)

Cl2—C5	1.760 (2)	C6—C7	1.538 (3)
Cl1—C2	1.749 (2)	C7—C8	1.536 (3)
O1—C13	1.249 (3)	C7—C9	1.540 (3)
N1—C8	1.359 (3)	C7—C10	1.561 (3)
N1—C1	1.406 (3)	C8—C11	1.393 (3)
N1—H1N	0.88 (3)	C9—H9A	0.9600
N2—C12	1.165 (3)	C9—H9B	0.9600
C1—C2	1.400 (3)	C9—H9C	0.9600
C1—C6	1.405 (3)	C10—H10A	0.9600
C2—C3	1.392 (3)	C10—H10B	0.9600
C3—C4	1.399 (3)	C10—H10C	0.9600
C3—H3	0.9300	C11—C12	1.446 (3)
C4—C5	1.415 (3)	C11—C13	1.454 (3)
C4—H4	0.9300	C13—H13	0.9300
C5—C6	1.388 (3)		
C8—N1—C1	111.42 (18)	C6—C7—C10	112.45 (17)
C8—N1—H1N	119.7 (18)	C9—C7—C10	111.53 (18)
C1—N1—H1N	128.7 (18)	N1—C8—C11	122.6 (2)
C2—C1—C6	123.2 (2)	N1—C8—C7	110.02 (18)
C2—C1—N1	128.0 (2)	C11—C8—C7	127.41 (19)
C6—C1—N1	108.87 (18)	C7—C9—H9A	109.5
C3—C2—C1	117.9 (2)	C7—C9—H9B	109.5
C3—C2—Cl1	121.11 (17)	H9A—C9—H9B	109.5
C1—C2—Cl1	120.99 (17)	C7—C9—H9C	109.5
C2—C3—C4	120.1 (2)	H9A—C9—H9C	109.5
C2—C3—H3	119.9	H9B—C9—H9C	109.5
C4—C3—H3	119.9	C7—C10—H10A	109.5
C3—C4—C5	121.0 (2)	C7—C10—H10B	109.5
C3—C4—H4	119.5	H10A—C10—H10B	109.5
C5—C4—H4	119.5	C7—C10—H10C	109.5

C6—C5—C4	119.5 (2)	H10A—C10—H10C	109.5
C6—C5—Cl2	121.27 (16)	H10B—C10—H10C	109.5
C4—C5—Cl2	119.19 (17)	C8—C11—C12	120.6 (2)
C5—C6—C1	118.17 (19)	C8—C11—C13	121.2 (2)
C5—C6—C7	132.44 (19)	C12—C11—C13	118.26 (19)
C1—C6—C7	109.38 (18)	N2—C12—C11	178.4 (3)
C8—C7—C6	100.22 (16)	O1—C13—C11	125.0 (2)
C8—C7—C9	110.43 (18)	O1—C13—H13	117.5
C6—C7—C9	110.65 (17)	C11—C13—H13	117.5
C8—C7—C10	111.05 (18)		

C8—N1—C1—C2	−176.3 (2)	C1—C6—C7—C8	1.8 (2)
C8—N1—C1—C6	3.2 (2)	C5—C6—C7—C9	64.1 (3)
C6—C1—C2—C3	1.4 (3)	C1—C6—C7—C9	−114.8 (2)
N1—C1—C2—C3	−179.2 (2)	C5—C6—C7—C10	−61.3 (3)
C6—C1—C2—Cl1	−177.94 (16)	C1—C6—C7—C10	119.75 (19)
N1—C1—C2—Cl1	1.5 (3)	C1—N1—C8—C11	178.22 (19)
C1—C2—C3—C4	0.4 (3)	C1—N1—C8—C7	−2.0 (2)
Cl1—C2—C3—C4	179.71 (16)	C6—C7—C8—N1	0.1 (2)
C2—C3—C4—C5	−0.9 (3)	C9—C7—C8—N1	116.83 (19)
C3—C4—C5—C6	−0.3 (3)	C10—C7—C8—N1	−118.90 (19)
C3—C4—C5—Cl2	178.64 (17)	C6—C7—C8—C11	179.9 (2)
C4—C5—C6—C1	2.0 (3)	C9—C7—C8—C11	−63.4 (3)
Cl2—C5—C6—C1	−176.95 (15)	C10—C7—C8—C11	60.9 (3)
C4—C5—C6—C7	−176.9 (2)	N1—C8—C11—C12	−177.9 (2)
Cl2—C5—C6—C7	4.2 (3)	C7—C8—C11—C12	2.3 (3)
C2—C1—C6—C5	−2.6 (3)	N1—C8—C11—C13	1.2 (3)
N1—C1—C6—C5	177.89 (18)	C7—C8—C11—C13	−178.6 (2)
C2—C1—C6—C7	176.50 (19)	C8—C11—C13—O1	−1.5 (3)
N1—C1—C6—C7	−3.0 (2)	C12—C11—C13—O1	177.7 (2)
C5—C6—C7—C8	−179.3 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N2^{i}	0.93	2.56	3.256 (3)	132
C10—H10*B*···Cl2	0.96	2.83	3.473 (2)	125
N1—H1*N*···O1	0.88 (3)	2.02 (3)	2.678 (3)	131 (2)

Symmetry code: (i) *x*+1, *y*−1, *z*.