organic compounds

2-[(3,3-Dimethylindolin-2-ylidene)methyl]-4-[(3,3-dimethyl-3H-indol-1-ium-2-yl)methylidene]-3-oxocyclobut-1-en-1-olate chloroform disolvate

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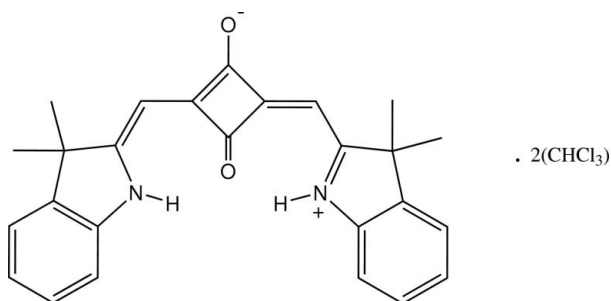Correspondence e-mail: g.smith@qut.edu.au

In the title squaraine dye solvate, $C_{26}H_{24}N_2O_2 \cdot 2CHCl_3$, the dye molecule is essentially planar, except for the methyl groups, having a maximum deviation over the 26-membered delocalized bond system of 0.060 (2) Å. It possesses crystallographic twofold rotational symmetry with the indole ring systems adopting a *syn* conformation. The molecular structure features intramolecular N—H···O hydrogen bonds enclosing conjoint S7 ring motifs about one of the dioxocyclobutene O atoms, while the two chloroform solvent molecules are linked to the second O atom through C—H···O hydrogen bonds.

Related literature

For the first report of bis(indolenine)squaraine dyes with alkyl substituents on the *N*-atom of each of the indolenine rings, see: Sprenger Von & Ziegenbein (1967). For background to bis(indolenine)squaraine dyes as biomarkers, see: Patsenker *et al.* (2011); Sameiro & Gonçalves (2009). For the structures of some analogues of the parent dye, see: Kobiyashi *et al.* (1986); Natsukawa & Nakazumi (1993); Tong & Peng (1999); Lynch & Byriel (1999); Lynch (2002); Arunkumar *et al.* (2007); Matsui *et al.* (2012); Lynch *et al.* (2012).

Experimental

Crystal data

$C_{26}H_{24}N_2O_2 \cdot 2CHCl_3$	V = 2978.5 (3) Å^3
M_r = 635.21	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 20.4724 (11) Å	μ = 0.61 mm^{-1}
b = 13.5433 (5) Å	T = 200 K
c = 11.4259 (5) Å	0.40 × 0.22 × 0.20 mm
β = 109.561 (5)°	

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	10054 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)	2926 independent reflections
	2415 reflections with $I > 2\sigma(I)$
T_{min} = 0.794, T_{max} = 0.888	R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	176 parameters
$wR(F^2)$ = 0.112	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
2926 reflections	$\Delta\rho_{min}$ = −0.50 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.88	1.96	2.7835 (18)	156
C15—H15···O1	0.98	2.13	3.075 (3)	161

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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supporting information

2-[(3,3-Dimethylindolin-2-ylidene)methyl]-4-[(3,3-dimethyl-3*H*-indol-1-ium-2-yl)methylidene]-3-oxocyclobut-1-en-1-olate chloroform disolvate

Graham Smith and Daniel E. Lynch

S1. Comment

Bis(indolenine)squaraine dyes, in which there is an alkyl substituent on the *N*-atom of each of the indolenine rings, were first reported on by Sprenger Von & Ziegenbein (1967) and have been studied since then for a range of opto-electronic applications such as long-wavelength protein-sensitive bioprobes (Lynch *et al.*, 2012; Patsenker *et al.*, 2011; Sameiro & Gonçalves, 2009). However, the parent dye compound 2,4-[(3,3-dimethyl-2-indolylidene)methyl]cyclobutenediylio-1,3-diolate, which has no *N*-alkyl substituent (*R*) on the indolenine ring, has remained relatively untouched in the literature, including reporting of the crystal structure. The crystal structures of a number of analogues with such substituents have been reported; for *e.g. R* = methyl (Kobiyashi *et al.*, 1986), ethyl (Natsukawa & Nakazumi, 1993), isopropyl (Tong & Peng, 1999), *n*-butyl (Matsui *et al.*, 2012), *n*-hexyl (Lynch & Byriel, 1999) and *n*-octyl (Lynch, 2002).

Evaporation of a solution of the dye in chloroform gave the title compound solvate as large green-black crystal prisms and its crystal structure is reported on herein. The dye molecule adopts the uncommon *syn*-conformation with respect to the indolenine rings, having crystallographic twofold rotational symmetry (Fig. 1). The structures of all other members of this series of *N*-alkyl-substituted squaraine dyes have the inversion-related *anti*-conformation.

The planarity of the delocalized 26-membered linked ring system in the overall molecule is indicated by maximum deviations of 0.059 (2) (C6 and C6[i]) and 0.060 (2) (C4 and C4[i]) from the least-squares plane [symmetry code (i): -*x*, *y*, -*z* + 3/2]. This planarity is further stabilized by the intramolecular N—H⋯O hydrogen bonds to O2 of the dioxocyclobutene ring (Table 1), closing conjoint *S*7 ring motifs.

Inter-species C—H⋯O hydrogen-bonding interactions link the two chloroform molecules to the second O-atom (O1). Although chloroform is a common solvent for the crystallization of squaraine dyes, chloroform solvates are uncommon with only three such structures reported on previously (Natsukawa & Nakazumi, 1993; Lynch & Byriel, 1999; Arunkumar *et al.*, 2007).

S2. Experimental

Squaric acid (200 mg, 1.75 mmol) was added to 2.0 molar equivalents of 2,3,3-trimethylindolenine (0.56 g, 3.5 mmol) and quinoline (0.45 g, 3.5 mmol) in a 1:1 *v/v* mix of 1-butanol:toluene (30 ml) and the mixture was then refluxed for 16 h using a Dean and Stark apparatus. Upon cooling, metallic green crystals were collected *in vacuo*, washed with petroleum ether (60/40), and were used without further purification [Yield: 0.31 g (45%)]. Spectroscopic data are available in the archived CIF. For the X-ray diffraction analysis large green-black lustrous crystal prisms of the title compound were obtained from the room temperature evaporation of a solution of the dye in chloroform. A cleaved crystal specimen was used for the actual analysis.

S3. Refinement

The H atom of the N—H group was located in a difference Fourier but was subsequently refined as a riding atom: N-H = 0.88 Å with $U_{iso}(H) = 1.2U_{eq}(N)$. C-bound H atoms were included in calculated positions and refined as riding atoms: C—H = 0.93 Å (aromatic or ethylenic), 0.96 Å (methyl) or 0.98 Å (methine) with $U_{iso}(H) = 1.5U_{eq}$(C-methyl) and = $1.2U_{eq}(C)$ for other H atoms.
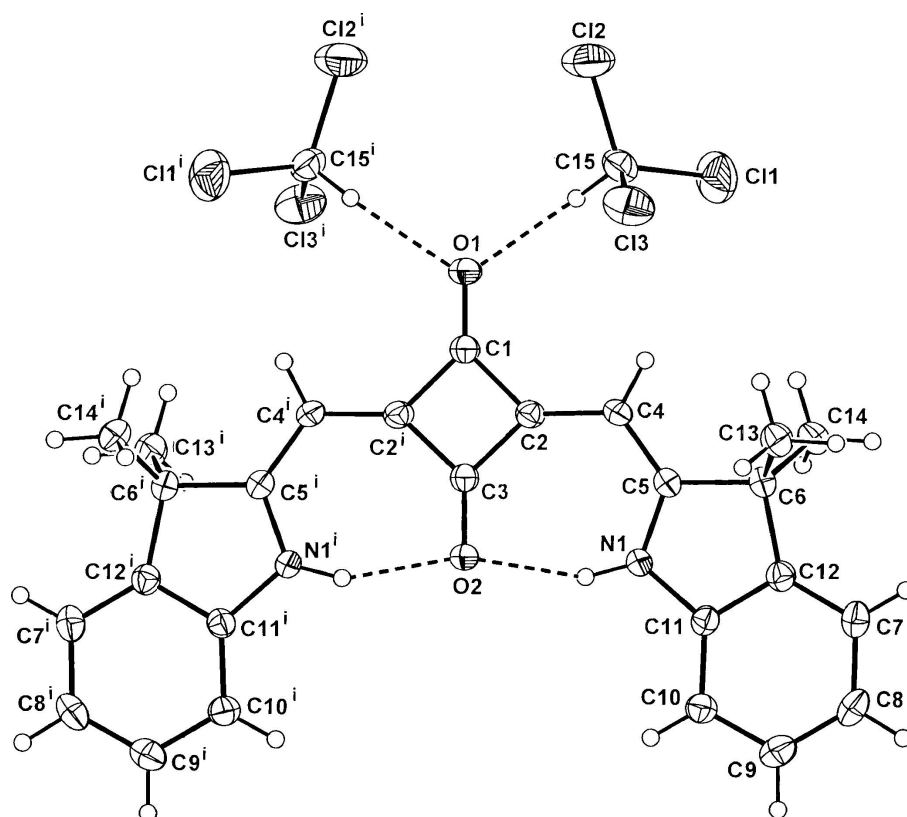
Figure 1

The molecular conformation and atom-numbering scheme for the title compound (symmetry code: (i) -x, y, -z + 3/2). The displacement ellipsoids are drawn at the 40% probability level. The intra- and inter-species N-H⋯O and C-H⋯O hydrogen bonds are shown as dashed lines.

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Crystal data

$C_{26}H_{24}N_2O_2 \cdot 2CHCl_3$	$F(000) = 1304$
$M_r = 635.21$	$D_x = 1.416$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2690 reflections
$a = 20.4270 (11)$ Å	$\theta = 3.3–28.8°$
$b = 13.5433 (5)$ Å	$\mu = 0.61$ mm^{-1}
$c = 11.4259 (5)$ Å	$T = 200$ K
$\beta = 109.561 (5)°$	Prism, green
$V = 2978.5 (3)$ Å^3	$0.40 \times 0.22 \times 0.20$ mm
$Z = 4$	

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer	10054 measured reflections
Radiation source: Enhance (Mo) X-ray source	2926 independent reflections
Graphite monochromator	2415 reflections with $I > 2\sigma(I)$
Detector resolution: 16.077 pixels mm^{-1}	$R_{int} = 0.027$
ω scans	$\theta_{max} = 26.0°, \theta_{min} = 3.5°$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)	$h = -22 \rightarrow 25$
	$k = -16 \rightarrow 16$
$T_{min} = 0.794, T_{max} = 0.888$	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.112$	
$S = 1.02$	H-atom parameters constrained
2926 reflections	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 4.0361P]$ where $P = (F_o^2 + 2F_c^2)/3$
176 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.54$ e Å^{-3}
	$\Delta\rho_{min} = -0.50$ e Å^{-3}

Special details

Experimental. Spectroscopic details of the as synthesized metallic green crystals of the title dye: UV/Vis (CHCl$_3$), recorded on a Nicolet 205 F T—IR spectrometer: λmax (log ε): 665(5.54). IR (KBr, cm^{-1}) recorded on a Unicam UV-4 spectrometer: λmax: 1623 (C—O). Electrospray mass spectra recorded in the the positive (ES+) ion mode: 397.1 [M+H]$^+$, 460.1 [M+Na+MeCN]$^+$, 815.3 [2M+Na]$^+$, 1211.6 [3M+Na]$^+$.

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
O1	0.00000	0.35895 (15)	0.75000	0.0420 (8)
O2	0.00000	0.02418 (14)	0.75000	0.0330 (7)
N1	0.08460 (9)	0.01681 (12)	0.60326 (15)	0.0292 (5)
C1	0.00000	0.2681 (2)	0.75000	0.0308 (9)
C2	0.03058 (10)	0.19196 (14)	0.69306 (18)	0.0283 (6)
C3	0.00000	0.1172 (2)	0.75000	0.0273 (8)
C4	0.07197 (11)	0.19354 (15)	0.61835 (19)	0.0300 (6)
C5	0.09788 (10)	0.11037 (14)	0.57941 (18)	0.0272 (6)
C6	0.14808 (11)	0.10979 (15)	0.50618 (19)	0.0298 (6)
C7	0.19200 (12)	−0.05112 (17)	0.4256 (2)	0.0364 (7)
C8	0.18945 (12)	−0.15368 (18)	0.4251 (2)	0.0400 (8)
C9	0.15195 (12)	−0.20386 (17)	0.4872 (2)	0.0390 (7)
C10	0.11502 (12)	−0.15347 (15)	0.55071 (19)	0.0333 (7)

C11	0.11792 (11)	−0.05144 (15)	0.54957 (18)	0.0278 (6)
C12	0.15568 (10)	−0.00001 (15)	0.48861 (18)	0.0293 (6)
C13	0.21729 (12)	0.15545 (17)	0.5872 (2)	0.0397 (7)
C14	0.11833 (13)	0.16552 (17)	0.3829 (2)	0.0400 (8)
Cl1	0.10014 (5)	0.46856 (7)	0.50703 (7)	0.0756 (3)
Cl2	0.09549 (5)	0.60290 (5)	0.70002 (8)	0.0724 (3)
Cl3	0.17949 (4)	0.42725 (6)	0.76203 (7)	0.0650 (3)
C15	0.10219 (14)	0.47904 (18)	0.6610 (2)	0.0444 (8)
H1	0.05820	0.00030	0.64720	0.0350*
H4	0.08300	0.25470	0.59290	0.0360*
H7	0.21760	−0.01770	0.38450	0.0440*
H8	0.21330	−0.18910	0.38230	0.0480*
H9	0.15150	−0.27250	0.48640	0.0470*
H10	0.08950	−0.18680	0.59210	0.0400*
H131	0.23420	0.12070	0.66480	0.0600*
H132	0.21030	0.22370	0.60240	0.0600*
H133	0.25060	0.15050	0.54490	0.0600*
H141	0.15020	0.16100	0.33750	0.0600*
H142	0.11160	0.23360	0.39920	0.0600*
H143	0.07460	0.13680	0.33480	0.0600*
H15	0.06270	0.44250	0.66990	0.0530*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0502 (14)	0.0225 (10)	0.0651 (15)	0.0000	0.0351 (12)	0.0000
O2	0.0396 (12)	0.0231 (10)	0.0439 (12)	0.0000	0.0240 (10)	0.0000
N1	0.0351 (9)	0.0247 (9)	0.0344 (9)	0.0005 (7)	0.0203 (8)	0.0024 (7)
C1	0.0302 (15)	0.0265 (15)	0.0392 (16)	0.0000	0.0161 (13)	0.0000
C2	0.0261 (10)	0.0252 (10)	0.0342 (11)	−0.0004 (8)	0.0111 (9)	0.0009 (8)
C3	0.0260 (14)	0.0265 (15)	0.0304 (14)	0.0000	0.0108 (12)	0.0000
C4	0.0336 (11)	0.0229 (10)	0.0377 (11)	−0.0023 (8)	0.0176 (9)	0.0028 (8)
C5	0.0268 (10)	0.0281 (10)	0.0272 (10)	−0.0018 (8)	0.0099 (8)	0.0017 (8)
C6	0.0315 (11)	0.0308 (11)	0.0310 (10)	−0.0012 (9)	0.0156 (9)	0.0018 (8)
C7	0.0336 (12)	0.0442 (13)	0.0349 (11)	0.0034 (10)	0.0162 (10)	0.0003 (9)
C8	0.0399 (13)	0.0444 (14)	0.0373 (12)	0.0119 (11)	0.0150 (10)	−0.0059 (10)
C9	0.0432 (13)	0.0337 (12)	0.0375 (12)	0.0079 (10)	0.0102 (10)	−0.0026 (9)
C10	0.0392 (12)	0.0288 (11)	0.0325 (11)	−0.0001 (9)	0.0127 (9)	0.0009 (8)
C11	0.0291 (10)	0.0295 (10)	0.0254 (9)	0.0031 (8)	0.0098 (8)	0.0002 (8)
C12	0.0272 (10)	0.0315 (11)	0.0303 (10)	0.0004 (9)	0.0110 (8)	0.0009 (8)
C13	0.0350 (12)	0.0408 (13)	0.0477 (13)	−0.0062 (10)	0.0196 (11)	−0.0029 (10)
C14	0.0524 (15)	0.0354 (12)	0.0366 (12)	0.0007 (11)	0.0206 (11)	0.0076 (9)
Cl1	0.0984 (7)	0.0894 (6)	0.0439 (4)	−0.0101 (5)	0.0303 (4)	−0.0026 (4)
Cl2	0.0981 (6)	0.0384 (4)	0.0764 (5)	−0.0049 (4)	0.0234 (5)	−0.0064 (3)
Cl3	0.0658 (5)	0.0531 (4)	0.0653 (5)	−0.0084 (4)	0.0077 (4)	0.0035 (3)
C15	0.0548 (15)	0.0384 (13)	0.0436 (13)	−0.0135 (12)	0.0214 (12)	−0.0011 (10)

Geometric parameters (Å, º)

Cl1—C15	1.751 (2)	C7—C8	1.390 (3)
Cl2—C15	1.753 (3)	C8—C9	1.384 (3)
Cl3—C15	1.760 (3)	C9—C10	1.389 (3)
O1—C1	1.230 (3)	C10—C11	1.383 (3)
O2—C3	1.260 (3)	C11—C12	1.387 (3)
N1—C5	1.343 (3)	C4—H4	0.9300
N1—C11	1.405 (3)	C7—H7	0.9300
N1—H1	0.8800	C8—H8	0.9300
C1—C2[i]	1.466 (3)	C9—H9	0.9300
C1—C2	1.466 (3)	C10—H10	0.9300
C2—C4	1.388 (3)	C13—H133	0.9600
C2—C3	1.453 (3)	C13—H131	0.9600
C4—C5	1.380 (3)	C13—H132	0.9600
C5—C6	1.525 (3)	C14—H141	0.9600
C6—C12	1.516 (3)	C14—H142	0.9600
C6—C13	1.537 (3)	C14—H143	0.9600
C6—C14	1.533 (3)	C15—H15	0.9800
C7—C12	1.380 (3)		
C5—N1—C11	111.84 (18)	C6—C12—C7	131.1 (2)
C11—N1—H1	124.00	C6—C12—C11	109.10 (18)
C5—N1—H1	124.00	C2—C4—H4	118.00
C2—C1—C2[i]	90.59 (19)	C5—C4—H4	118.00
O1—C1—C2[i]	134.70 (11)	C8—C7—H7	121.00
O1—C1—C2	134.70 (11)	C12—C7—H7	121.00
C1—C2—C3	88.88 (16)	C7—C8—H8	119.00
C1—C2—C4	134.41 (18)	C9—C8—H8	120.00
C3—C2—C4	136.70 (18)	C8—C9—H9	119.00
O2—C3—C2	134.18 (11)	C10—C9—H9	119.00
C2—C3—C2[i]	91.64 (19)	C9—C10—H10	122.00
O2—C3—C2[i]	134.18 (11)	C11—C10—H10	122.00
C2—C4—C5	124.33 (19)	C6—C13—H131	109.00
N1—C5—C4	125.4 (2)	C6—C13—H132	110.00
N1—C5—C6	108.97 (17)	C6—C13—H133	109.00
C4—C5—C6	125.59 (18)	H131—C13—H132	110.00
C5—C6—C12	101.26 (16)	H131—C13—H133	110.00
C12—C6—C13	111.12 (18)	H132—C13—H133	109.00
C12—C6—C14	112.84 (17)	C6—C14—H141	109.00
C13—C6—C14	110.92 (18)	C6—C14—H142	109.00
C5—C6—C13	108.62 (17)	C6—C14—H143	109.00
C5—C6—C14	111.66 (19)	H141—C14—H142	109.00
C8—C7—C12	118.5 (2)	H141—C14—H143	109.00
C7—C8—C9	121.0 (2)	H142—C14—H143	110.00
C8—C9—C10	121.2 (2)	Cl1—C15—Cl2	110.82 (13)
C9—C10—C11	117.0 (2)	Cl1—C15—Cl3	109.94 (16)
N1—C11—C12	108.72 (17)	Cl2—C15—Cl3	110.12 (13)

C10—C11—C12	122.6 (2)	Cl1—C15—H15	109.00
N1—C11—C10	128.7 (2)	Cl2—C15—H15	109.00
C7—C12—C11	119.8 (2)	Cl3—C15—H15	109.00
C11—N1—C5—C4	179.2 (2)	C4—C5—C6—C12	−178.6 (2)
C11—N1—C5—C6	−2.7 (2)	C4—C5—C6—C13	64.3 (3)
C5—N1—C11—C10	−177.9 (2)	C4—C5—C6—C14	−58.3 (3)
C5—N1—C11—C12	0.8 (2)	C5—C6—C12—C7	177.2 (2)
O1—C1—C2—C3	180.00 (2)	C5—C6—C12—C11	−2.8 (2)
O1—C1—C2—C4	0.9 (3)	C13—C6—C12—C7	−67.6 (3)
C2ⁱ—C1—C2—C3	0.00 (12)	C13—C6—C12—C11	112.4 (2)
C2ⁱ—C1—C2—C4	−179.1 (2)	C14—C6—C12—C7	57.7 (3)
C2—C1—C2ⁱ—C3	0.02 (16)	C14—C6—C12—C11	−122.3 (2)
C1—C2—C3—O2	180.00 (1)	C12—C7—C8—C9	−0.6 (3)
C1—C2—C3—C2ⁱ	0.00 (11)	C8—C7—C12—C6	−179.9 (2)
C4—C2—C3—O2	−0.9 (3)	C8—C7—C12—C11	0.1 (3)
C4—C2—C3—C2ⁱ	179.1 (3)	C7—C8—C9—C10	0.8 (4)
C1—C2—C4—C5	176.79 (19)	C8—C9—C10—C11	−0.4 (3)
C3—C2—C4—C5	−1.9 (4)	C9—C10—C11—N1	178.4 (2)
C2—C4—C5—N1	3.0 (3)	C9—C10—C11—C12	−0.1 (3)
C2—C4—C5—C6	−174.8 (2)	N1—C11—C12—C6	1.5 (2)
N1—C5—C6—C12	3.3 (2)	N1—C11—C12—C7	−178.52 (19)
N1—C5—C6—C13	−113.77 (19)	C10—C11—C12—C6	−179.7 (2)
N1—C5—C6—C14	123.59 (19)	C10—C11—C12—C7	0.2 (3)

Symmetry code: (i) −*x*, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.88	1.96	2.7835 (18)	156
C15—H15···O1	0.98	2.13	3.075 (3)	161