



(*E*)-6,6'-(Diazene-1,2-diyl)bis(1,10-phenanthrolin-5-ol) trichloromethane disolvate: a superconjugated ligand

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Received 7 June 2019

Accepted 2 July 2019

Edited by J. Jasinski, Keene State College, USA

Keywords: crystal structure; diazo; phenanthroline; superconjugated ligand.

CCDC reference: 1937969

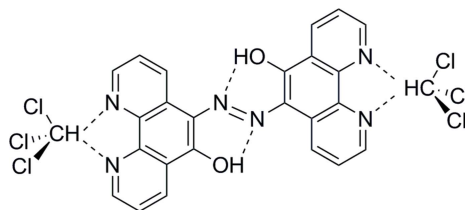
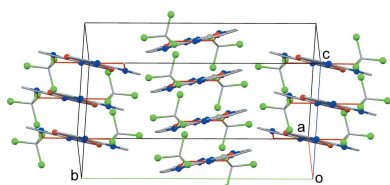
Supporting information: this article has supporting information at journals.iucr.org/e

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Phenanthroline ligands are important metal-binding molecules which have been extensively researched for applications in both material science and medicinal chemistry. Azobenzene and its derivatives have received significant attention because of their ability to be reversibly switched between the *E* and *Z* forms and so could have applications in optical memory and logic devices or as molecular machines. Herein we report the formation and crystal structure of a highly unusual novel diazo-diphenanthroline compound, C₂₄H₁₄N₆O₂·2CHCl₃.

1. Chemical context

The chemical versatility of 1,10-phenanthroline (phen), its substituted derivatives and corresponding metal complexes (Bencini & Lippolis, 2010) is exemplified by their uses as organic light-emitting diodes (OLED)/electroluminescent display and solid-state lighting materials (Li *et al.*, 2009), fluorescence molecular probes and imaging agents (Haraga *et al.*, 2018), ion sensors (Zheng *et al.*, 2012), solar energy converters (Freitag *et al.*, 2016), anti-cancer and antimicrobial cytotoxins (McCann *et al.*, 2012), DNA/RNA binding/cleavage (Kellett *et al.*, 2011), enzyme inhibitors (Zhu *et al.*, 2015), biomimetics (Casey *et al.*, 1994) and catalysts (Lu *et al.*, 2015). Given the resourcefulness of phenanthrolines, there is a continuing demand for new molecules containing this structural motif.



Herein, we detail the preparation and structural characterization of the purple diazo-diphenanthroline compound, (*E*)-6,6'-(diazene-1,2-diyl)bis(1,10-phenanthrolin-5-ol) (**1**), which was isolated in low yield from the reaction between 1,10-phenanthroline-5,6-dione (phendione) and isonicotinic acid hydrazide (isoniazid). Compound **1** crystallizes with two trichloromethane solvate molecules (**1**·2CHCl₃). The fully conjugated bis-phenanthroline molecule **1** is expected to offer exciting new physical and chemical properties as a stand-alone

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1A\cdots N2^i$	0.88 (3)	1.74 (3)	2.540 (3)	149 (3)
$C21-H21\cdots N1$	1.00	2.36	3.219 (3)	143
$C21-H21\cdots N3$	1.00	2.33	3.136 (4)	137

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

organic molecule, and it will also birth a plethora of interesting metal coordination complexes as a consequence of the dual N,N' -1,10-phenanthroline chelating moieties situated on the opposite ends of the molecule.

2. Structural commentary

Compound **1**·2CHCl₃ crystallizes with two molecules of trichloromethane solvate per diazo-diphenanthroline (Fig. 1). The molecule lies on a centre of symmetry and is essentially planar, the r.m.s. deviation from the plane of the atoms in the ring system is 0.259 Å. The molecules lie parallel to the (5 7 15) or (5 $\bar{7}$ 14) planes. There is a hydrogen bond between the alcohol and the diazo linker [$O1\cdots N2 = 2.540$ (3) Å under symmetry operation $-x + 2, -y + 1, -z + 1$, Table 1] and the trichloromethane molecule is oriented by a bifurcated C–H \cdots N interaction with the phenanthroline moiety [3.219 (3) and 3.136 (4) Å to N1 and N3, respectively]. The carbon atom of the trichloromethane molecule (C21) is 1.045 (3) Å from the mean plane of **1**·2CHCl₃. There are 40 examples in the Cambridge Structural Database (CSD, Version 5.40, update of May 2019; Groom *et al.*, 2016) showing similar interactions between trichloromethane and 1,10-phenanthroline derivatives and the geometry for **1**·2CHCl₃ is typical of the group [mean Cl₃CH \cdots N = 3.18 (5) Å].

The bond lengths indicate some delocalization through the central part of the molecule. The C6–O1 and C5–N2 bonds are short [1.318 (3) and 1.376 (3) Å, respectively] and the N=N bond, at 1.316 (4) Å, is significantly longer than in most free diazo molecules [mean of 1.24 (4) Å for 2730 CSD entries].

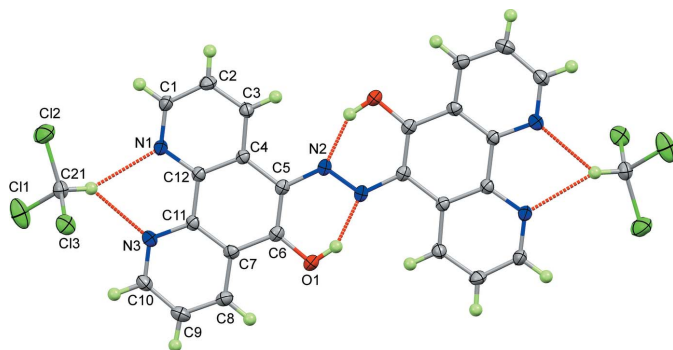


Figure 1
Perspective view of **1**·2CHCl₃ showing the labelling scheme for the asymmetric unit with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius and C–H \cdots N hydrogen bonds are indicated by dashed red lines.

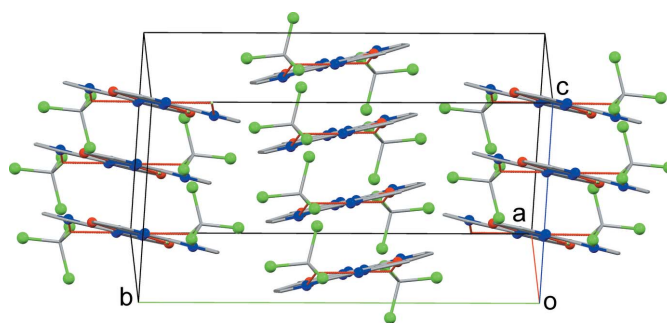


Figure 2
Unit-cell packing diagram viewed parallel to the plane of **1**·2CHCl₃. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

3. Supramolecular features

Fig. 2 shows the unit-cell packing, the molecules lie parallel to the (5 7 15) or (5 $\bar{7}$ 14) planes with a mean interplanar distance of 3.228 (2) Å (under $1 - x, 1 - y, 1 - z$) and the axis of the stack runs parallel to the a axis. The shortest ring centroid–centroid distance is 3.5154 (15) Å between the C₆ rings; however, there is a more direct overlap between the diazo group and an imine group in the next layer (*ca* 3.246 Å between the mid-point of the N=N bond and the mid-point of the C11=N3 bond under symmetry operation $1 - x, 1 - y, 1 - z$) (Fig. 3). The most notable interactions between stacks are type 1 $R-Cl\cdots Cl-R$ packing interactions (Mukherjee *et al.*, 2014; Cavallo *et al.*, 2016), the shortest Cl \cdots Cl distance being 3.5353 (11) Å for Cl1 \cdots Cl3 under symmetry operation $-1 + x, y, z$.

4. Database survey

There are three published examples of molecules containing the 2,2'-dihydroxyazobenzene core (Bougueria *et al.*, 2014; Evangelio *et al.*, 2008; Schilde *et al.*, 1994) and all of these are significantly less delocalized than **1**·2CHCl₃.

5. Spectroscopy studies of **1** in solution

Compound **1** has a very low solubility in all organic solvents investigated (CH₃Cl, CH₂Cl₂, DMSO, CH₃CN and alcohols).

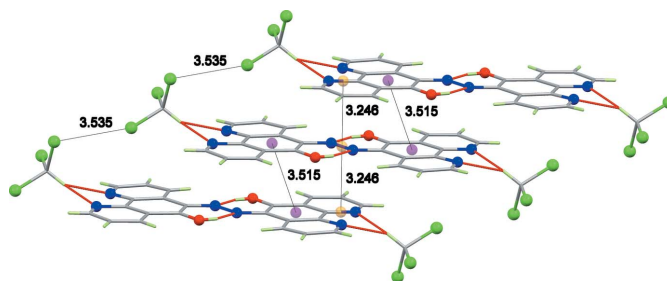
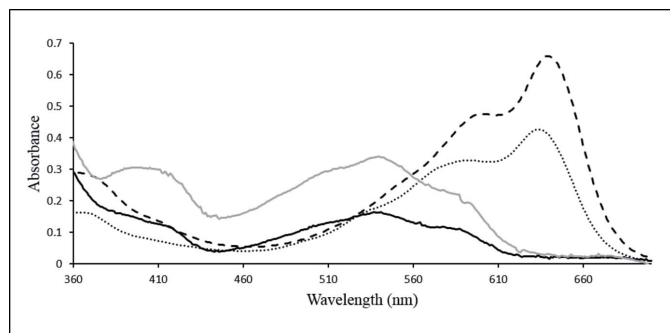


Figure 3
Principal intermolecular interactions in **1**·2CHCl₃. Purple spheres represent ring centroids and orange spheres show bond mid-points; distances in Å.


Figure 4

UV/vis spectra of $1 \cdot 2\text{CHCl}_3$ in (—) CHCl_3 , (---) ethanol, (· · · · ·) CH_2Cl_2 , and (- · · · ·) methanol. The absorbance axis is $\times 10$ for the CHCl_3 and CH_2Cl_2 solutions.

UV/vis spectra of $1 \cdot 2\text{CHCl}_3$ recorded in ethanol, methanol, CHCl_3 and CH_2Cl_2 are given in Fig. 4. Compound **1** exhibits significant solvatochromism showing a broad band in CHCl_3 and CH_2Cl_2 with λ_{max} at 543 nm. This band undergoes a bathochromic shift and separates into two bands in the alcohols with λ_{max} values at 643 nm and 600 nm in ethanol and at 636 nm and 591 nm in methanol. No accurate measurement of the extinction coefficient could be made as **1** was not fully soluble in the solvents and precipitation from the solvent occurred upon standing. The solubility of **1** was so low that only a very poorly resolved ^1H NMR of the compound was obtained in d^4 -methanol showing a series of peaks in the region expected for the phenanthroline H-atom signals and no definitive assignments of the peaks could be made. Interestingly, **1** was more soluble in strongly acidic solutions due to the protonation of one or more of the N atoms. Compound **1** dissolved in CF_3COOD to form a bright-red solution. Six signals are observed in the ^1H NMR spectrum in the region associated with the phenanthroline peaks. This finding is consistent with a compound which has a centre of symmetry, as found for the crystal structure, and suggests that at room temperature **1** remains in the *E* form in this solvent.

6. Synthesis and crystallization

The mechanism to form **1** from the reaction mixture is unclear; however, the formation of isonicotinic acid *N'*-(pyridine-4-carbonyl)-hydrazide (**2**) from the mixture is an indication that radical chemistry is occurring. Isoniazid is well known to react to form radical species and these radicals are important in its role as an anti-tuberculosis drug (Timmins *et al.* 2006). Significantly one LC-MS study has shown that isoniazid will photo-degrade to form **2** (Fig. 5) and radical intermediates are proposed in its formation (Bhutani, 2007). Attempts were made to try to favour the formation of **1** using UV irradiation and the radical initiators azobisisobutyronitrile and 2,2'-azobis(2-amidinopropane) dihydrochloride but these were unsuccessful. However, although the reaction to form **1** was low yielding, attempts to make **1** by reaction of 6-amino-1,10-phenanthroline-5-ol and 6-nitroso-1,10-phenanthroline-5-ol

using known conditions to form diazo compounds (Zhao *et al.* 2011) did not form the desired product. Studies are ongoing to improve the yield of the reaction to form **1**.

Phendione (0.210 g, 1.000 mmol) was added to solution of isoniazid (0.137 g, 1.000 mmol) in EtOH (25 cm^3). *p*-Tolouenesulfonic acid (10%, 0.02 g) was added and the solution refluxed for 6 h. The resulting suspension was filtered whilst hot and the filtrate allowed to stand in the dark overnight. Precipitated yellow (*Z*)-*N'*-(6-oxo-1,10-phenanthroline-5(6*H*)) ylidene)isonicotinohydrazide (0.263 g, 0.799 mmol, 80%) was filtered off and the bright-orange filtrate was concentrated to *ca* 10 cm^3 using rotary evaporation and then allowed to stand in the dark. Over a period of four weeks, the bright-orange filtrate changed to a dark-green suspension. This mixture was heated to reflux and filtered whilst hot to give a green filtrate (see below) and a dark-purple powder. The powder was dissolved in CHCl_3 and allowed to crystallize over several days to produce dark-purple crystals of (*E*)-6,6'-(diazene-1,2-diyl)bis(1,10-phenanthroline-5-ol) trichloromethane disolvate ($1 \cdot 2\text{CHCl}_3$) (0.026 g, 0.039 mmol, 6.2% based on isoniazid starting material). Upon leaving the above green filtrate to evaporate further white isonicotinic acid *N'*-(pyridine-4-carbonyl)-hydrazide (compound **2**) precipitated. The supernatant was decanted off and the solid dissolved in hot acetone. This colourless solution was evaporated to dryness on a rotary evaporator to give **2** (0.015 g, 0.062 mmol, 12.4% based on isoniazid starting material).

Compound **1**: IR (ATR, cm^{-1}) ($1 \cdot 2\text{CHCl}_3$): 3065, 2108, 1583, 1568, 1500, 1472, 1415, 1338, 1284, 1227, 1162, 1027, 795, 739, 717. ^1H NMR (protonated-1) (CF_3COOD , 500 MHz): δ 9.60 (*d*, $J = 8.5$ Hz, 2H, PhenH), 9.56 (*d*, $J = 8.5$ Hz, 2H, PhenH), 9.47 (*d*, $J = 5.0$ Hz, 2H, PhenH), 9.37 (*d*, $J = 5.0$ Hz, 2H, PhenH), 8.57 (*dd*, $J = 8.5, 5.0$ Hz, 2H, PhenH), 8.38 (*dd*, $J = 8.5, 5.0$ Hz, 2H, PhenH), 4.12 (*s*, 2H, OH). Elemental analysis calculated for $1 \cdot 2\text{CHCl}_3$ ($\text{C}_{26}\text{H}_{16}\text{Cl}_6\text{N}_6\text{O}_2$, 657.15 g mol^{-1}): C 47.52, H 2.45, N 12.79%; found: C 47.73, H 2.52, N 12.77%.

Compound **2** has been previously reported (Quiroga *et al.*, 2008; Bhutani *et al.*, 2007) and the characterization data given are consistent with the data recorded in the present study.

Compound **2**: IR (KBr, cm^{-1}) 3435, 3210, 3045, 1682, 1642, 1546, 1489, 1406, 1299, 838, 751. ^1H NMR (CD_3OD , 500 MHz): δ 8.80 (*d*, $J = 5$ Hz, 2H), 7.42 (*d*, $J = 5$ Hz, 2H). ^{13}C NMR (CD_3OD , 125 MHz): δ 165.6 (C=O), 150.0 (PyrC), 140.5 (PyrC), 121.8 (PyrC). MS: Calculated m/z for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$: ($M + \text{H}$) $^+$ 243.0877; found: ($M + \text{H}$) $^+$ 243.0882; difference (ppm): 2.15.

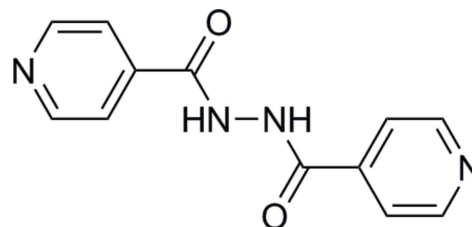


Figure 5
Chemical structure of **2**

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were included in calculated positions and treated as riding, with C–H = 0.95–1.00 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms or $1.2U_{\text{eq}}(\text{C})$ otherwise. The H atom (H1A) bonded to oxygen was located in a difference-Fourier map and its coordinates were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Acknowledgements

We gratefully acknowledge Maynooth University for a John and Pat Hume Scholarship for MA.

Funding information

Funding for this research was provided by: National University of Ireland, Maynooth Hume Scholarship (scholarship to Muhib Ahmed).

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₂₄ H ₁₄ N ₆ O ₂ ·2CHCl ₃
M_r	657.15
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	5.9406 (7), 18.856 (2), 12.2375 (16)
β (°)	96.863 (4)
V (Å ³)	1361.0 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.67
Crystal size (mm)	0.43 × 0.05 × 0.04
Data collection	
Diffractometer	Bruker–Nonius X8 APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2012)
$T_{\text{min}}, T_{\text{max}}$	0.657, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18529, 2732, 2068
R_{int}	0.045
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.620
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.111, 1.03
No. of reflections	2732
No. of parameters	184
H-atom treatment	Heterozyz
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.87, −0.59

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXT* (Sheldrick 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2019). E75, 1224-1227 [https://doi.org/10.1107/S205698901900954X]

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Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINTE* (Bruker, 2010); data reduction: *SAINTE* (Bruker, 2010); program(s) used to solve structure: *SHELXT* (Sheldrick 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(*E*)-6,6'-(Diazene-1,2-diyl)bis(1,10-phenanthrolin-5-ol) trichloromethane disolvate

Crystal data

$C_{24}H_{14}N_6O_2 \cdot 2CHCl_3$
 $M_r = 657.15$
 Monoclinic, $P2_1/c$
 $a = 5.9406$ (7) Å
 $b = 18.856$ (2) Å
 $c = 12.2375$ (16) Å
 $\beta = 96.863$ (4)°
 $V = 1361.0$ (3) Å³
 $Z = 2$

$F(000) = 664$
 $D_x = 1.604$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 5155 reflections
 $\theta = 2.7$ – 26.1 °
 $\mu = 0.67$ mm⁻¹
 $T = 150$ K
 Lath, purple
 $0.43 \times 0.05 \times 0.04$ mm

Data collection

Bruker–Nonius X8 APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed-tube
 Detector resolution: 9.1 pixels mm⁻¹
 thin-slice ω and φ scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2012)
 $T_{\min} = 0.657$, $T_{\max} = 0.745$

18529 measured reflections
 2732 independent reflections
 2068 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\max} = 26.2$ °, $\theta_{\min} = 2.7$ °
 $h = -5 \rightarrow 7$
 $k = -23 \rightarrow 23$
 $l = -15 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.111$
 $S = 1.02$
 2732 reflections
 184 parameters
 0 restraints
 Primary atom site location: dual

Secondary atom site location: difference Fourier map
 Hydrogen site location: mixed
 Heterozyz
 $w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 1.8407P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.87$ e Å⁻³
 $\Delta\rho_{\min} = -0.59$ e Å⁻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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.3174 (4)	0.63628 (11)	0.66898 (18)	0.0216 (5)
C1	0.3648 (5)	0.69741 (14)	0.6234 (2)	0.0240 (6)
H1	0.269904	0.736919	0.632910	0.029*
C2	0.5456 (5)	0.70706 (14)	0.5623 (2)	0.0255 (6)
H2	0.572645	0.752054	0.531450	0.031*
C3	0.6846 (4)	0.65044 (14)	0.5473 (2)	0.0219 (6)
H3	0.810516	0.656051	0.507047	0.026*
C4	0.6383 (4)	0.58421 (13)	0.5923 (2)	0.0174 (5)
C5	0.7702 (4)	0.52078 (13)	0.5757 (2)	0.0177 (5)
N2	0.9396 (3)	0.52817 (11)	0.50912 (17)	0.0195 (5)
C6	0.7175 (4)	0.45623 (14)	0.6231 (2)	0.0195 (5)
O1	0.8303 (3)	0.39726 (10)	0.61010 (16)	0.0246 (4)
H1A	0.937 (6)	0.4088 (17)	0.569 (3)	0.037*
C7	0.5313 (4)	0.45226 (13)	0.6889 (2)	0.0191 (5)
C8	0.4726 (5)	0.38783 (14)	0.7366 (2)	0.0239 (6)
H8	0.554738	0.345644	0.726050	0.029*
C9	0.2948 (5)	0.38714 (15)	0.7985 (2)	0.0274 (6)
H9	0.251833	0.344474	0.831710	0.033*
C10	0.1781 (5)	0.45015 (15)	0.8118 (2)	0.0253 (6)
H10	0.057433	0.449191	0.856178	0.030*
N3	0.2257 (4)	0.51143 (12)	0.76615 (18)	0.0224 (5)
C11	0.4006 (4)	0.51294 (13)	0.7050 (2)	0.0182 (5)
C12	0.4522 (4)	0.58002 (13)	0.6541 (2)	0.0185 (5)
C21	0.0382 (5)	0.64497 (15)	0.8784 (2)	0.0271 (6)
H21	0.087592	0.621547	0.811921	0.032*
Cl1	-0.23375 (13)	0.61485 (6)	0.89683 (7)	0.0493 (3)
Cl2	0.03861 (18)	0.73803 (4)	0.85952 (7)	0.0508 (3)
Cl3	0.23081 (12)	0.62261 (4)	0.99506 (6)	0.0333 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0234 (11)	0.0211 (12)	0.0208 (12)	0.0047 (9)	0.0050 (9)	-0.0007 (9)
C1	0.0290 (14)	0.0208 (15)	0.0229 (14)	0.0070 (11)	0.0065 (11)	-0.0003 (11)
C2	0.0330 (15)	0.0159 (13)	0.0279 (15)	0.0000 (11)	0.0054 (12)	0.0012 (11)
C3	0.0231 (13)	0.0216 (14)	0.0219 (14)	-0.0011 (11)	0.0064 (11)	-0.0016 (11)
C4	0.0192 (13)	0.0169 (13)	0.0160 (12)	0.0001 (10)	0.0008 (10)	-0.0016 (10)
C5	0.0158 (12)	0.0196 (13)	0.0169 (13)	0.0011 (10)	-0.0011 (10)	-0.0021 (10)
N2	0.0180 (11)	0.0213 (11)	0.0193 (11)	0.0023 (8)	0.0020 (9)	-0.0036 (9)

C6	0.0192 (13)	0.0203 (14)	0.0180 (13)	0.0023 (10)	-0.0011 (10)	-0.0020 (10)
O1	0.0258 (10)	0.0197 (10)	0.0293 (11)	0.0053 (8)	0.0072 (8)	0.0007 (8)
C7	0.0212 (13)	0.0203 (13)	0.0151 (13)	0.0003 (10)	-0.0007 (10)	0.0007 (10)
C8	0.0277 (14)	0.0199 (14)	0.0236 (14)	0.0023 (11)	0.0004 (11)	0.0027 (11)
C9	0.0319 (15)	0.0274 (15)	0.0230 (14)	-0.0046 (12)	0.0036 (12)	0.0063 (12)
C10	0.0244 (14)	0.0290 (15)	0.0236 (14)	-0.0027 (11)	0.0077 (11)	0.0032 (12)
N3	0.0235 (11)	0.0250 (12)	0.0190 (11)	-0.0009 (9)	0.0039 (9)	0.0005 (9)
C11	0.0207 (13)	0.0198 (13)	0.0141 (12)	0.0010 (10)	0.0016 (10)	-0.0020 (10)
C12	0.0199 (13)	0.0196 (13)	0.0156 (13)	0.0008 (10)	0.0008 (10)	-0.0015 (10)
C21	0.0290 (15)	0.0290 (16)	0.0242 (15)	0.0014 (12)	0.0077 (12)	-0.0021 (12)
C11	0.0258 (4)	0.0875 (7)	0.0346 (5)	-0.0121 (4)	0.0037 (3)	-0.0095 (4)
C12	0.0818 (7)	0.0295 (4)	0.0438 (5)	0.0156 (4)	0.0196 (5)	0.0009 (4)
C13	0.0273 (4)	0.0379 (4)	0.0339 (4)	-0.0051 (3)	0.0008 (3)	0.0002 (3)

Geometric parameters (Å, °)

N1—C1	1.326 (3)	O1—H1A	0.88 (3)
N1—C12	1.355 (3)	C7—C11	1.409 (4)
C1—C2	1.392 (4)	C7—C8	1.409 (4)
C1—H1	0.9500	C8—C9	1.371 (4)
C2—C3	1.375 (4)	C8—H8	0.9500
C2—H2	0.9500	C9—C10	1.395 (4)
C3—C4	1.405 (4)	C9—H9	0.9500
C3—H3	0.9500	C10—N3	1.328 (3)
C4—C12	1.414 (3)	C10—H10	0.9500
C4—C5	1.457 (3)	N3—C11	1.352 (3)
C5—N2	1.376 (3)	C11—C12	1.459 (4)
C5—C6	1.400 (4)	C21—C11	1.752 (3)
N2—N2 ⁱ	1.316 (4)	C21—C12	1.770 (3)
C6—O1	1.318 (3)	C21—C13	1.771 (3)
C6—C7	1.446 (4)	C21—H21	1.0000
C1—N1—C12	117.7 (2)	C8—C7—C6	121.2 (2)
N1—C1—C2	123.8 (2)	C9—C8—C7	118.8 (2)
N1—C1—H1	118.1	C9—C8—H8	120.6
C2—C1—H1	118.1	C7—C8—H8	120.6
C3—C2—C1	118.9 (3)	C8—C9—C10	118.9 (3)
C3—C2—H2	120.5	C8—C9—H9	120.6
C1—C2—H2	120.5	C10—C9—H9	120.6
C2—C3—C4	119.3 (2)	N3—C10—C9	123.9 (2)
C2—C3—H3	120.3	N3—C10—H10	118.0
C4—C3—H3	120.3	C9—C10—H10	118.0
C3—C4—C12	117.4 (2)	C10—N3—C11	117.9 (2)
C3—C4—C5	122.8 (2)	N3—C11—C7	122.2 (2)
C12—C4—C5	119.8 (2)	N3—C11—C12	118.0 (2)
N2—C5—C6	123.3 (2)	C7—C11—C12	119.8 (2)
N2—C5—C4	116.3 (2)	N1—C12—C4	122.7 (2)
C6—C5—C4	120.4 (2)	N1—C12—C11	117.6 (2)

N2 ⁱ —N2—C5	118.1 (3)	C4—C12—C11	119.6 (2)
O1—C6—C5	122.8 (2)	C11—C21—C12	110.73 (16)
O1—C6—C7	117.2 (2)	C11—C21—C13	109.64 (15)
C5—C6—C7	120.0 (2)	C12—C21—C13	109.29 (16)
C6—O1—H1A	106 (2)	C11—C21—H21	109.1
C11—C7—C8	118.3 (2)	C12—C21—H21	109.1
C11—C7—C6	120.4 (2)	C13—C21—H21	109.1

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1A \cdots N2 ⁱ	0.88 (3)	1.74 (3)	2.540 (3)	149 (3)
C21—H21 \cdots N1	1.00	2.36	3.219 (3)	143
C21—H21 \cdots N3	1.00	2.33	3.136 (4)	137

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