

Crystal structure and Hirshfeld surface analysis of (*E*)-4-{2,2-dichloro-1-[(3,5-dimethylphenyl)diazenyl]ethenyl}-*N,N*-dimethylaniline

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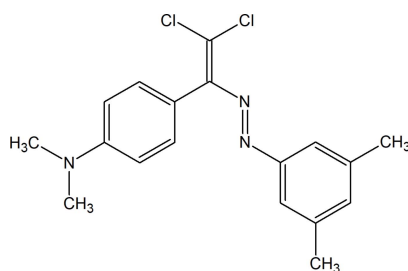
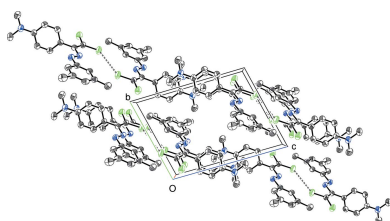
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In the title compound, C₁₈H₁₉Cl₂N₃, the planes of the benzene rings subtend a dihedral angle of 77.07 (10)°. In the crystal, molecules are associated into inversion dimers *via* short Cl...Cl contacts [3.3763 (9) Å]. A Hirshfeld surface analysis indicates that the most important contact percentages for the different types of interactions are H...H (43.9%), Cl...H/H...Cl (22.9%), C...H/H...C (20.8%) and N...H/H...N (8.0%).

1. Chemical context

Aromatic azo compounds provide ubiquitous motifs in organic chemistry and are widely used as organic dyes, indicators, pigments, food additives, ligands, radical reaction initiators, therapeutic agents, *etc.* (Maharramov *et al.*, 2010; Mahmudov *et al.*, 2013). On the other hand, the study of both inter- and intramolecular non-covalent interactions in azo compounds is important for our understanding of the factors governing the assembly of the molecules into supramolecular systems (see, for example, Mahmudov *et al.*, 2015; Shikhaliyev *et al.*, 2014). When compared to well-explored hydrogen-bonding and π -interactions (see, for example, Akbari *et al.*, 2017; Mahmoudi *et al.*, 2018), the exploration of new intermolecular interactions such as halogen, chalcogen, pnictogen, tetrel and triel bonds is in progress. Thus, decorating the structure of azo compounds with tailored functionalities (halogen, chalcogen and tetrel bond-donor centres) can be an important strategy to control and tune their functional properties such as their analytical and solvatochromic behaviour (Mahmudov *et al.*, 2010; Mahmudov & Pombeiro, 2016).



In order to continue our work in this direction, we now describe the synthesis and structure of the title compound, C₁₈H₁₉Cl₂N₃ (I) and its Hirshfeld surface analysis.

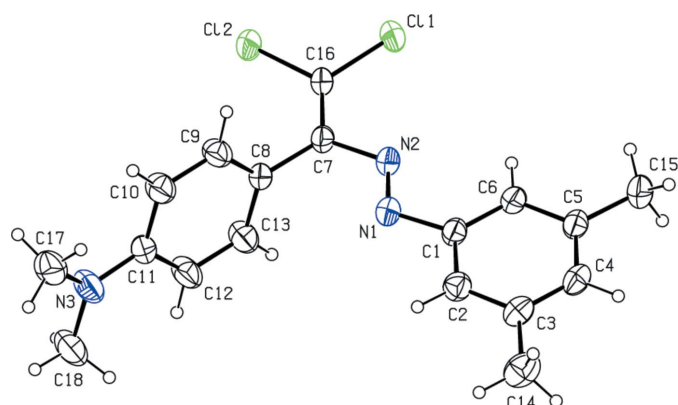


Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level.

2. Structural commentary

The title compound has a non-planar molecular conformation (Fig. 1); the dihedral angle between the planes of the C1–C6 and C8–C13 aromatic rings is 77.07 (10)°. The amine N atom as well as the directly adjacent arene C atom are displaced out of the plane of the other five aromatic C atoms: the deviations are –0.009 (2) for C11 and –0.065 (2) Å for N3. Some key torsion angles describing the molecular conformation are C6–C1–N1–N2 [–0.5 (3)°], C1–N1–N2–C7 [–178.40 (15)°], N1–N2–C7–C8 [–6.1 (3)°], N1–N2–C7–C16 [–173.27 (17)°], N2–C7–C8–C13 [–72.1 (3)°], N2–C7–C16–C11 [–0.9 (3)°], N2–C7–C16–Cl2 [179.97 (14)°] and C8–C7–C16–Cl2 [–0.6 (3)°]. All of the C=C, N=N, C–Cl bond lengths in (I) are similar to those in the related azocompounds reported in the *Database survey*.

3. Supramolecular features

In the crystal, molecules of (I) are linked into inversion dimers *via* short halogen···halogen contacts [Cl1···Cl1ⁱ = 3.3763 (9) Å C16–Cl1···Cl1ⁱ = 141.47 (7)°; symmetry code: (i) = 2 – x, 1 – y, 2 – z] compared to the van der Waals radius sum of 3.50 Å. No other directional contacts could be identi-

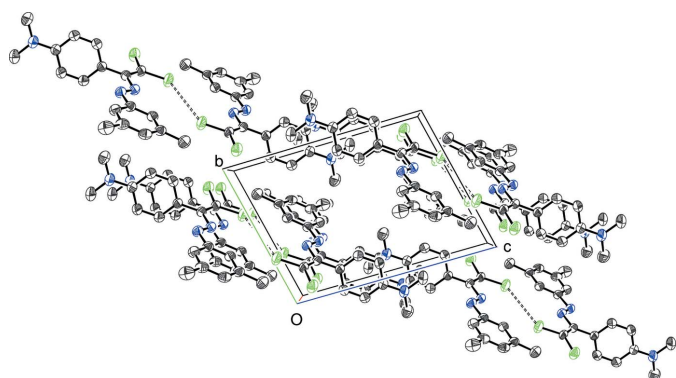


Figure 2
Crystal packing for (I) viewed along the *a*-axis direction.

Table 1
Percentage contributions of interatomic contacts to the Hirshfeld surface for (I).

Contact	Percentage contribution
H···H	43.9
Cl···H/H···Cl	22.9
C···H/H···C	20.8
N···H/H···N	8.0
Cl···C/C···Cl	2.3
Cl···Cl	1.4
N···C/C···N	0.3
C···C	0.3

fied and the shortest aromatic-ring-centroid separation is greater than 5.25 Å. The packing for (I) is shown in Fig. 2.

4. Hirshfeld surface analysis

The Hirshfeld surface (McKinnon *et al.*, 2007) for (I) and its associated two-dimensional fingerprint plots (Spackman & McKinnon, 2002) were calculated using *CrystalExplorer17* (Turner *et al.*, 2017). Red, white and blue regions visible on the d_{norm} surface indicate contacts with distances shorter, longer and approximately equal to the van der Waals radii: the surface for (I) (Fig. 3) is almost featureless, indicating a lack of directional interactions.

The overall two-dimensional fingerprint plot (Fig. 4a) and those delineated into H···H, Cl···H/H···Cl and C···H/H···C contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 4b–d, respectively and percentage contributions to the Hirshfeld surface are given in Table 1. The most important interaction is H···H, contributing 43.9% to the overall surface, which is reflected in Fig. 4b as widely scattered points of high density due to the large hydrogen content of the molecule, with the tip at $d_e = d_i = 1.15$ Å. The reciprocal Cl···H/H···Cl interactions appear as two symmetrical broad wings with $d_e + d_i \approx 3.05$ Å and contribute 22.9% to the Hirshfeld surface (Fig. 4c). The pair of characteristic wings in the fingerprint plot delineated

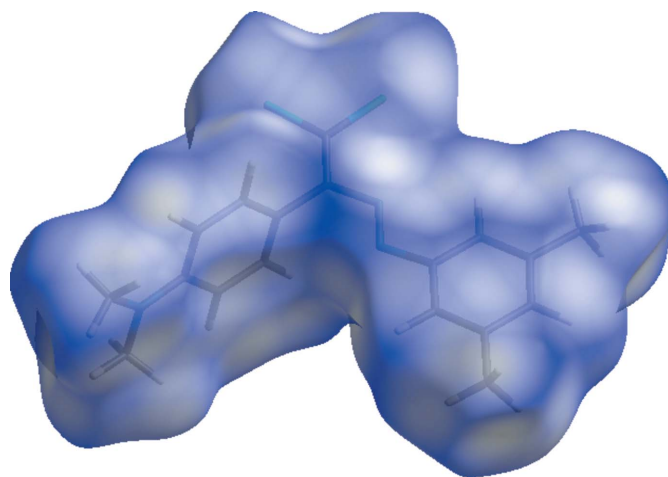


Figure 3
A view of the three-dimensional Hirshfeld surface for (I) plotted over d_{norm} in the range –0.07 to 1.33 a.u.

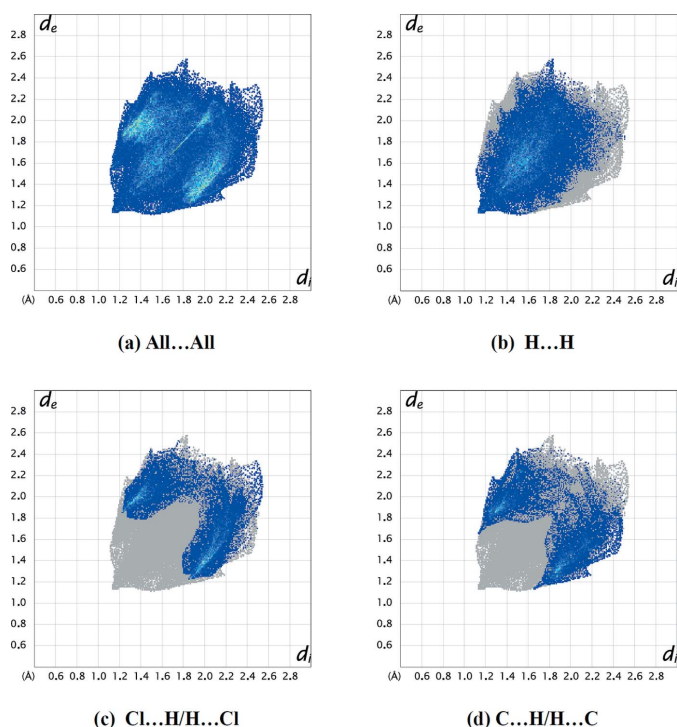


Figure 4
A view of the two-dimensional fingerprint plots for (I) showing (a) all interactions, and separated into (b) H...H, (c) Cl...H/H...Cl and (d) C...H/H...C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

into C...H/H...C contacts (Fig. 4d; 20.8% contribution to the Hirshfeld surface), have the tips at $d_e + d_i \approx 2.80$ Å. The remaining contributions from the other different interatomic contacts to the Hirshfeld surfaces are listed in Table 1. The small contribution of the other weak intermolecular N...H/H...N, Cl...C/C...Cl, Cl...Cl, N...C/C...N and C...C contacts suggest a negligible effect on the packing. The dominance of H-atom contacts suggest that van der Waals interactions play the major role in establishing the crystal packing for (I) (Hathwar *et al.*, 2015).

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, update of November 2019; Groom *et al.*, 2016) the (*E*)-1-(2,2-dichloro-1-phenylethenyl)-2-phenyldiazene unit resulted in 25 hits. Six compounds are closely related to the title compound, *viz.* 1-(4-bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (CSD refcode HONBOE; Akkurt *et al.*, 2019), 1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (HONBUK; Akkurt *et al.*, 2019), 1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-fluorophenyl)ethenyl]diazene (HODQAV; Shikhaliyev *et al.*, 2019), 1-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]-2-(4-fluorophenyl)diazene (XIZREG; Atioğlu *et al.*, 2019), 1,1-[methylenebis(4,1-phenylene)]bis[(2,2-dichloro-1-(4-nitrophenyl)ethenyl)diazene (LEQXIR; Shikhaliyev *et al.*, 2018) and 1,1-[methyl-

enebis(4,1-phenylene)]bis[[2,2-dichloro-1-(4-chlorophenyl)ethenyl]diazene] (LEQXOX; Shikhaliyev *et al.*, 2018).

In the crystals of HONBOE and HONBUK, the aromatic rings form dihedral angles of 60.9 (2) and 64.1 (2)°, respectively. Molecules are linked through weak $X \cdots Cl$ contacts ($X = Br$ for HONBOE and Cl for HONBUK), $C-H \cdots Cl$ and $C-Cl \cdots \pi$ interactions into sheets parallel to the *ab* plane. Additional van der Waals interactions consolidate the three-dimensional packing. In the crystal of HODQAV, the planes of the benzene rings make a dihedral angle of 56.13 (13)°. Molecules are stacked in columns along the *a*-axis direction *via* weak $C-H \cdots Cl$ hydrogen bonds and face-to-face $\pi-\pi$ stacking interactions. The crystal packing is further consolidated by short $Cl \cdots Cl$ contacts. In XIZREG, the benzene rings form a dihedral angle of 63.29 (8)°. Molecules are linked by $C-H \cdots O$ hydrogen bonds into zigzag chains running along the *c*-axis direction. The crystal packing also features $C-Cl \cdots \pi$, $C-F \cdots \pi$ and $N-O \cdots \pi$ interactions. In the crystals of LEQXIR and LEQXOX, the dihedral angles between the aromatic rings are 56.18 (12) and 60.31 (14)°, respectively. In LEQXIR, $C-H \cdots N$ and $C-H \cdots O$ hydrogen bonds and short $Cl \cdots O$ contacts occur and in LEQXOX $C-H \cdots N$ and short $Cl \cdots Cl$ contacts are observed.

6. Synthesis and crystallization

A 20 ml screw-neck vial was charged with DMSO (10 ml), (*Z*)-4-[[2-(3,5-dimethylphenyl)hydrazineylidene]methyl]-*N,N*-dimethylaniline (267 mg, 1.00 mmol), tetramethylethylenediamine (TMEDA) (295 mg, 2.50 mmol), $CuCl$ (2 mg, 0.02 mmol) and CCl_4 (20 mmol, 10 equiv). After 1–3 h (until TLC analysis showed complete consumption of the corresponding Schiff base) the reaction mixture was poured into ~0.01 *M* solution of HCl (100 ml, $pH = 2-3$) and extracted with dichloromethane (3×20 ml). The combined organic phase was washed with water (3×50 ml), brine (30 ml), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* using a rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3:1–1:1) to form a red solid in 85% yield (m.p. 429 K). Orange plates of (I) were obtained by the slow evaporation of an ethanol solution. Analysis calculated for $C_{18}H_{19}Cl_2N_3$: C 62.08, H 5.50, N 12.07; found: C 62.01, H 5.48, N 12.03%. 1H NMR (300 MHz, $CDCl_3$) δ 2.38 (6H, $ArMe_2$), 3.05 (6H, NMe_2), 6.88–7.43 (7H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.57, 153.15, 151.94, 147.03, 142.69, 138.64, 137.97, 133.14, 131.20, 127.08, 121.02, 21.20. ESI-MS: m/z : 349.18 $[M+H]^+$.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound H atoms were placed in idealized locations and refined using a riding model with $C-H = 0.93-0.96$ Å. The constraint $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(\text{methyl C})$ was applied in all cases.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₈ H ₁₉ Cl ₂ N ₃
<i>M_r</i>	348.26
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.1035 (4), 9.1965 (5), 12.3665 (7)
α , β , γ (°)	102.421 (2), 95.880 (2), 91.105 (2)
<i>V</i> (Å ³)	894.48 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.37
Crystal size (mm)	0.28 × 0.22 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.897, 0.924
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13675, 3339, 2786
<i>R</i> _{int}	0.039
(sin θ / λ) _{max} (Å ⁻¹)	0.611
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.045, 0.125, 1.03
No. of reflections	3339
No. of parameters	212
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.30, -0.21

Computer programs: *APEX3* and *SAINT* (Bruker, 2007), *SHELXS* (Sheldrick, 2008), *SHELXL2016/6* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

Funding information

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Computing details

Data collection: *APEX3* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

(*E*)-4-{2,2-Dichloro-1-[(3,5-dimethylphenyl)diazenyl]ethenyl}-*N,N*-dimethylaniline

Crystal data

$C_{18}H_{19}Cl_2N_3$

$M_r = 348.26$

Triclinic, $P\bar{1}$

$a = 8.1035$ (4) Å

$b = 9.1965$ (5) Å

$c = 12.3665$ (7) Å

$\alpha = 102.421$ (2)°

$\beta = 95.880$ (2)°

$\gamma = 91.105$ (2)°

$V = 894.48$ (8) Å³

$Z = 2$

$F(000) = 364$

$D_x = 1.293$ Mg m⁻³

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

Cell parameters from 7784 reflections

$\theta = 2.3$ – 25.7 °

$\mu = 0.37$ mm⁻¹

$T = 296$ K

Plate, orange

$0.28 \times 0.22 \times 0.18$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.897$, $T_{\max} = 0.924$

13675 measured reflections

3339 independent reflections

2786 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 25.8$ °, $\theta_{\min} = 2.3$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 11$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.125$

$S = 1.03$

3339 reflections

212 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.3599P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4932 (2)	0.5319 (2)	0.78212 (16)	0.0507 (4)
C2	0.3377 (3)	0.5251 (2)	0.72287 (17)	0.0572 (5)
H2A	0.313279	0.592879	0.678105	0.069*
C3	0.2180 (2)	0.4186 (2)	0.72940 (19)	0.0586 (5)
C4	0.2585 (2)	0.3198 (2)	0.79718 (18)	0.0578 (5)
H4A	0.179261	0.247628	0.801995	0.069*
C5	0.4136 (2)	0.3245 (2)	0.85843 (16)	0.0528 (4)
C6	0.5313 (2)	0.4323 (2)	0.85097 (16)	0.0515 (4)
H6A	0.635267	0.438287	0.891630	0.062*
C7	0.8563 (2)	0.7644 (2)	0.81327 (15)	0.0486 (4)
C8	0.8188 (2)	0.8616 (2)	0.73299 (15)	0.0470 (4)
C9	0.7799 (3)	1.0079 (2)	0.76813 (17)	0.0624 (5)
H9A	0.780539	1.047283	0.844019	0.075*
C10	0.7401 (3)	1.0978 (2)	0.69421 (18)	0.0663 (6)
H10A	0.713687	1.195886	0.721428	0.080*
C11	0.7385 (2)	1.0455 (2)	0.58013 (16)	0.0530 (4)
C12	0.7818 (4)	0.8986 (3)	0.54516 (18)	0.0731 (7)
H12A	0.785747	0.859575	0.469609	0.088*
C13	0.8188 (3)	0.8099 (2)	0.61981 (18)	0.0705 (6)
H13A	0.844835	0.711493	0.593078	0.085*
C14	0.0476 (3)	0.4121 (3)	0.6668 (3)	0.0815 (7)
H14A	0.015539	0.310513	0.631791	0.122*
H14B	0.049299	0.470111	0.610925	0.122*
H14C	-0.030567	0.451581	0.717658	0.122*
C15	0.4523 (3)	0.2146 (3)	0.9306 (2)	0.0681 (6)
H15A	0.553126	0.246587	0.978497	0.102*
H15B	0.465759	0.118284	0.884317	0.102*
H15C	0.362933	0.208661	0.974908	0.102*
C16	0.9971 (2)	0.7786 (2)	0.88186 (16)	0.0520 (4)
C17	0.6238 (4)	1.2751 (3)	0.5403 (2)	0.0806 (7)
H17A	0.556425	1.271764	0.599308	0.121*
H17B	0.556809	1.299516	0.478616	0.121*
H17C	0.711966	1.349476	0.566573	0.121*
C18	0.6996 (5)	1.0776 (3)	0.3882 (2)	0.0944 (9)
H18A	0.639013	0.983527	0.364268	0.142*
H18B	0.813161	1.065188	0.373532	0.142*
H18C	0.651020	1.147779	0.348239	0.142*
Cl1	1.04137 (8)	0.67088 (7)	0.97728 (5)	0.0734 (2)

C12	1.15092 (7)	0.90973 (7)	0.88372 (5)	0.0707 (2)
N1	0.6056 (2)	0.64606 (18)	0.76759 (14)	0.0552 (4)
N2	0.7438 (2)	0.64937 (17)	0.82395 (13)	0.0523 (4)
N3	0.6932 (3)	1.1321 (2)	0.50518 (15)	0.0745 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0541 (10)	0.0443 (9)	0.0535 (10)	−0.0068 (8)	0.0080 (8)	0.0098 (8)
C2	0.0576 (11)	0.0520 (11)	0.0617 (12)	0.0014 (8)	0.0037 (9)	0.0127 (9)
C3	0.0487 (10)	0.0522 (11)	0.0701 (12)	−0.0004 (8)	0.0069 (9)	0.0031 (9)
C4	0.0515 (11)	0.0497 (11)	0.0695 (13)	−0.0095 (8)	0.0145 (9)	0.0044 (9)
C5	0.0587 (11)	0.0445 (10)	0.0555 (11)	−0.0058 (8)	0.0135 (9)	0.0085 (8)
C6	0.0522 (10)	0.0489 (10)	0.0524 (10)	−0.0075 (8)	0.0047 (8)	0.0104 (8)
C7	0.0573 (10)	0.0433 (9)	0.0470 (9)	−0.0069 (8)	0.0098 (8)	0.0127 (7)
C8	0.0526 (10)	0.0438 (9)	0.0462 (9)	−0.0061 (7)	0.0053 (7)	0.0139 (7)
C9	0.0852 (15)	0.0571 (12)	0.0450 (10)	0.0091 (10)	0.0075 (10)	0.0105 (9)
C10	0.0933 (16)	0.0507 (11)	0.0555 (11)	0.0152 (11)	0.0078 (11)	0.0116 (9)
C11	0.0605 (11)	0.0506 (10)	0.0509 (10)	0.0002 (8)	0.0071 (8)	0.0173 (8)
C12	0.116 (2)	0.0619 (13)	0.0454 (11)	0.0188 (13)	0.0177 (11)	0.0156 (9)
C13	0.1110 (19)	0.0516 (11)	0.0516 (11)	0.0172 (12)	0.0162 (11)	0.0124 (9)
C14	0.0548 (13)	0.0765 (16)	0.107 (2)	0.0020 (11)	−0.0048 (12)	0.0125 (14)
C15	0.0748 (14)	0.0611 (13)	0.0729 (14)	−0.0112 (10)	0.0133 (11)	0.0237 (11)
C16	0.0617 (11)	0.0470 (10)	0.0501 (10)	−0.0114 (8)	0.0049 (8)	0.0187 (8)
C17	0.0918 (18)	0.0726 (15)	0.0815 (16)	0.0185 (13)	−0.0053 (13)	0.0312 (13)
C18	0.147 (3)	0.0867 (18)	0.0594 (14)	0.0169 (18)	0.0137 (15)	0.0345 (13)
C11	0.0839 (4)	0.0724 (4)	0.0705 (4)	−0.0174 (3)	−0.0110 (3)	0.0408 (3)
C12	0.0679 (4)	0.0737 (4)	0.0743 (4)	−0.0273 (3)	−0.0064 (3)	0.0340 (3)
N1	0.0584 (10)	0.0498 (9)	0.0589 (9)	−0.0091 (7)	0.0039 (8)	0.0170 (7)
N2	0.0568 (9)	0.0478 (8)	0.0543 (9)	−0.0093 (7)	0.0075 (7)	0.0161 (7)
N3	0.1083 (16)	0.0659 (11)	0.0564 (10)	0.0201 (11)	0.0110 (10)	0.0269 (9)

Geometric parameters (Å, °)

C1—C2	1.384 (3)	C11—C12	1.391 (3)
C1—C6	1.397 (3)	C12—C13	1.373 (3)
C1—N1	1.429 (2)	C12—H12A	0.9300
C2—C3	1.385 (3)	C13—H13A	0.9300
C2—H2A	0.9300	C14—H14A	0.9600
C3—C4	1.385 (3)	C14—H14B	0.9600
C3—C14	1.506 (3)	C14—H14C	0.9600
C4—C5	1.394 (3)	C15—H15A	0.9600
C4—H4A	0.9300	C15—H15B	0.9600
C5—C6	1.387 (3)	C15—H15C	0.9600
C5—C15	1.503 (3)	C16—C11	1.7123 (19)
C6—H6A	0.9300	C16—C12	1.7129 (18)
C7—C16	1.336 (3)	C17—N3	1.438 (3)
C7—N2	1.420 (2)	C17—H17A	0.9600

C7—C8	1.485 (2)	C17—H17B	0.9600
C8—C9	1.375 (3)	C17—H17C	0.9600
C8—C13	1.378 (3)	C18—N3	1.433 (3)
C9—C10	1.378 (3)	C18—H18A	0.9600
C9—H9A	0.9300	C18—H18B	0.9600
C10—C11	1.388 (3)	C18—H18C	0.9600
C10—H10A	0.9300	N1—N2	1.254 (2)
C11—N3	1.374 (3)		
C2—C1—C6	120.38 (17)	C12—C13—C8	122.3 (2)
C2—C1—N1	115.34 (17)	C12—C13—H13A	118.9
C6—C1—N1	124.28 (17)	C8—C13—H13A	118.9
C1—C2—C3	120.85 (19)	C3—C14—H14A	109.5
C1—C2—H2A	119.6	C3—C14—H14B	109.5
C3—C2—H2A	119.6	H14A—C14—H14B	109.5
C4—C3—C2	118.00 (19)	C3—C14—H14C	109.5
C4—C3—C14	120.8 (2)	H14A—C14—H14C	109.5
C2—C3—C14	121.2 (2)	H14B—C14—H14C	109.5
C3—C4—C5	122.48 (18)	C5—C15—H15A	109.5
C3—C4—H4A	118.8	C5—C15—H15B	109.5
C5—C4—H4A	118.8	H15A—C15—H15B	109.5
C6—C5—C4	118.55 (18)	C5—C15—H15C	109.5
C6—C5—C15	120.77 (19)	H15A—C15—H15C	109.5
C4—C5—C15	120.67 (18)	H15B—C15—H15C	109.5
C5—C6—C1	119.72 (18)	C7—C16—C11	124.05 (14)
C5—C6—H6A	120.1	C7—C16—C12	122.70 (14)
C1—C6—H6A	120.1	C11—C16—C12	113.24 (11)
C16—C7—N2	114.49 (16)	N3—C17—H17A	109.5
C16—C7—C8	123.12 (16)	N3—C17—H17B	109.5
N2—C7—C8	122.39 (16)	H17A—C17—H17B	109.5
C9—C8—C13	116.53 (18)	N3—C17—H17C	109.5
C9—C8—C7	121.42 (17)	H17A—C17—H17C	109.5
C13—C8—C7	122.04 (17)	H17B—C17—H17C	109.5
C8—C9—C10	121.94 (18)	N3—C18—H18A	109.5
C8—C9—H9A	119.0	N3—C18—H18B	109.5
C10—C9—H9A	119.0	H18A—C18—H18B	109.5
C9—C10—C11	121.60 (19)	N3—C18—H18C	109.5
C9—C10—H10A	119.2	H18A—C18—H18C	109.5
C11—C10—H10A	119.2	H18B—C18—H18C	109.5
N3—C11—C10	122.27 (19)	N2—N1—C1	113.12 (16)
N3—C11—C12	121.46 (18)	N1—N2—C7	114.22 (16)
C10—C11—C12	116.26 (18)	C11—N3—C18	121.15 (19)
C13—C12—C11	121.38 (19)	C11—N3—C17	121.07 (19)
C13—C12—H12A	119.3	C18—N3—C17	117.6 (2)
C11—C12—H12A	119.3		
C6—C1—C2—C3	-0.9 (3)	C9—C10—C11—C12	-1.0 (4)
N1—C1—C2—C3	179.58 (18)	N3—C11—C12—C13	-176.6 (2)

C1—C2—C3—C4	0.2 (3)	C10—C11—C12—C13	1.9 (4)
C1—C2—C3—C14	178.9 (2)	C11—C12—C13—C8	-1.4 (4)
C2—C3—C4—C5	0.2 (3)	C9—C8—C13—C12	-0.2 (4)
C14—C3—C4—C5	-178.5 (2)	C7—C8—C13—C12	179.0 (2)
C3—C4—C5—C6	0.0 (3)	N2—C7—C16—C11	-0.9 (3)
C3—C4—C5—C15	-179.74 (19)	C8—C7—C16—C11	178.48 (14)
C4—C5—C6—C1	-0.6 (3)	N2—C7—C16—C12	179.97 (14)
C15—C5—C6—C1	179.08 (18)	C8—C7—C16—C12	-0.6 (3)
C2—C1—C6—C5	1.1 (3)	C2—C1—N1—N2	179.06 (17)
N1—C1—C6—C5	-179.40 (17)	C6—C1—N1—N2	-0.5 (3)
C16—C7—C8—C9	-72.4 (3)	C1—N1—N2—C7	-178.40 (15)
N2—C7—C8—C9	107.0 (2)	C16—C7—N2—N1	-173.27 (17)
C16—C7—C8—C13	108.5 (3)	C8—C7—N2—N1	-6.1 (3)
N2—C7—C8—C13	-72.1 (3)	C10—C11—N3—C18	177.2 (3)
C13—C8—C9—C10	1.1 (3)	C12—C11—N3—C18	-4.4 (4)
C7—C8—C9—C10	-178.0 (2)	C10—C11—N3—C17	-8.3 (4)
C8—C9—C10—C11	-0.5 (4)	C12—C11—N3—C17	170.1 (3)
C9—C10—C11—N3	177.5 (2)		
