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Synthesis and crystal structure of *anti*-10-butyl-10,11,22,23-tetrahydro-9*H*,21*H*-5,8:15,12-bis(metheno)[1,5,11]triazacyclohexadecino[1,16-*a*:5,6-*a*′]diindole

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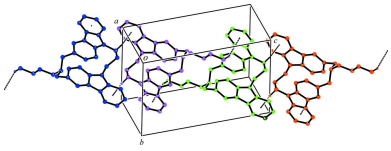
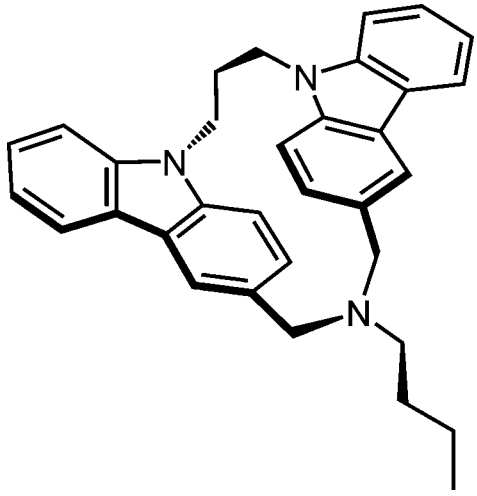
The title compound, $C_{33}H_{33}N_3$, is a carbazolophane, which is a cyclophane composed of two carbazole fragments. It has a planar chirality but crystallizes as a racemate in the space group $P\overline{1}$. The molecule adopts an *anti*-configuration, in which two carbazole fragments are partially overlapped. Both carbazole ring systems are slightly bent, with the C atoms at 3-positions showing the largest deviations from the mean planes. The dihedral angle between two carbazole fragments is 5.19 (3)°, allowing an intramolecular slipped π–π interaction [$Cg\cdots Cg$ = 3.2514 (8) Å]. In the crystal, the molecules are linked *via* intermolecular C—H···N hydrogen bonds and C—H···π interactions into a network sheet parallel to the *ab* plane. The molecules of different sheets form other C—H···π interactions, thus forming a three-dimensional network.

1. Chemical context

Carbazole is characterized not only as a molecule with electron-donating properties, but also as an emissive heteroaromatic chromophore (Wex *et al.*, 2017), so carbazole derivatives have attracted much attention for the construction of photofunctional devices such as solar cells (Gratia *et al.*, 2015) and organic light-emitting diodes (Kaji *et al.*, 2015). Poly(*N*-vinylcarbazole) is a widely used photoconductive aromatic polymer, in which the formation of two types of excimers, partially overlapped (PO) and fully overlapped (FO) (sandwich) ones, was proposed (Sakai *et al.*, 1996). Our group has reported various carbazolophanes, which are cyclophanes composed of two carbazole fragments, as the models of excimers. Among these, aza-bridged carbazolophanes synthesized so far by cyclization reaction are limited to cyanamide bridging (Tani *et al.*, 2001, 2007) and *o*-nitrophenylsulfonamide bridging (Tani *et al.*, 2020). These bridges act as polar functional groups with the resonance effect. In the aza-bridged carbazolophanes, the PO and FO isomers have been isolated and their distinct difference in fluorescence spectra provided the evidence for existence of two types of excimers (Tani *et al.*, 2001; Ohkita *et al.*, 2002). Recently, optical resolution of aza-bridged PO carbazolophanes and their chiroptical properties, including circularly polarized luminescence, were reported (Tani *et al.*, 2020). However, the



solubility of the aza-bridged carbazolophanes in common organic solvents is low, leading to difficulties in examining the solvent effect and in manufacturing photofunctional devices. Therefore, the title compound with an *N*-linear alkyl group, *anti*-10-butyl-10,11,22,23-tetrahydro-9*H*,21*H*-5,8:15,12-bis(metheno)[1,5,11]triazacyclohexadecino[1,16-a:5,6-a′]diindole (cyclophane nomenclature: *anti*-3-butyl-1^{9}*H*,5^{9}*H*-3-aza-1,5(3,9)-dicarbazolacyclooctaphane), having good solubility in organic solvents, is a promising candidate for investigation of the photophysical and chiroptical properties of the carbazole chromophore. Previously, our group reported the EPR spectrum of the title compound, but no other chemical properties were examined because of the very low yield (Saiful *et al.*, 2006). Here, the modified synthesis and crystal structure of the title compound are reported.



2. Structural commentary

The title compound has a planar chirality but crystallizes as a racemate in the centrosymmetric space group $P\overline{1}$. The molecular structure of the title compound is shown in Fig. 1. The molecule adopts an *anti*-configuration, in which two carbazole fragments are partially overlapped with parallel orientation. The two carbazole fragments are slightly bent, with r.m.s. deviations of 0.064 (1) Å for the N1/C4–C15 ring system and 0.062 (1)Å for N2/C16–C27 ring system. In both carbazole fragments, the C atoms at the 3-positions bridged through the dimethyleneamino group show the largest deviations from the mean planes [0.1177 (14) Å for C7 and −0.1082 (14) Å for C19]. The dihedral angle formed by two carbazole fragments is 5.19 (3)°, providing an intramolecular slipped parallel π–π interaction [*Cg*2···*Cg*5 = 3.2514 (8) Å; *Cg*2 and *Cg*5 are the centroids of the C4–C9 and C16–C21 rings, respectively; inter-planar distance = 3.0856 (6) Å; slippage = 1.099 Å]. In comparison, in the related PO compounds, the dihedral angles between two carbazole fragments and the centroid–centroid distances are 5.96 (6)° and 3.294 (4) Å for *N*-cyanamide-bridged [3.3](3,9)carbazolophane (BACKOG; Tani *et al.*, 2001), and 1.28 (7)° and 3.3259 (16) Å for *N*-*o*-nitrophenylsulfonamide-bridged [3.3](3,9)carbazolophane (YUKYEL; Tani *et al.*, 2020). The N1···N2 distance between the N atoms at the 9-positions of the carbazole ring systems is 3.3776 (17) Å, slightly shorter than those in the above-mentioned related compounds [3.414 (4) and 3.461 (4) Å for the cyanamide-bridged and *o*-nitrophenylsulfonamide-bridged carbazolophanes, respectively]. The bond angle C31—N3—C32 is 114.56 (11)°, smaller than those in the related compounds [119.9 (2) and 119.0 (3)° for the cyanamide-bridged and *o*-nitrophenylsulfonamide-bridged carbazolophanes, respectively], that is, the hybridization of N3 atom is closer to sp^3 than to sp^2, reflecting the difference in the resonance effect of the substituent at the N3 atom.

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

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the C22–C27, C4–C9, N2/C16/C17/C22/C23 and C10–C15 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···N3^{i}	0.95	2.56	3.4858 (18)	166
C28—H28*A*···*Cg*1^{ii}	0.99	2.72	3.4144 (15)	128
C30—H30*A*···*Cg*2^{iii}	0.99	2.62	3.5224 (16)	152
C31—H31*B*···*Cg*3^{iv}	0.99	2.83	3.7245 (15)	150
C36—H36*B*···*Cg*4^{v}	0.98	2.99	3.9151 (18)	159

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

3. Supramolecular features

In the crystal, molecules are linked by intermolecular C—H···N hydrogen bonds (Fig. 2, Table 1), forming a *C*(9) chain motif running parallel to the *b* axis. The molecules are further joined into columns along the *a*-axis direction by pairs of C—

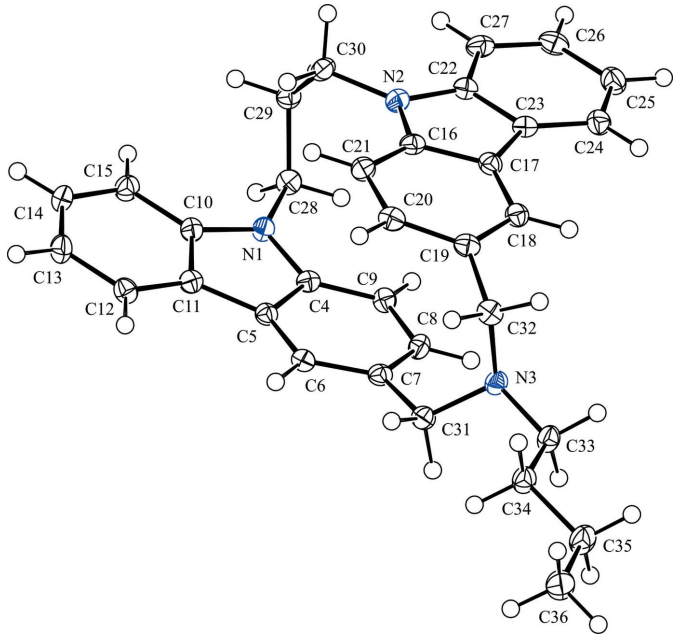


Figure 1
The molecular structure of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radius.

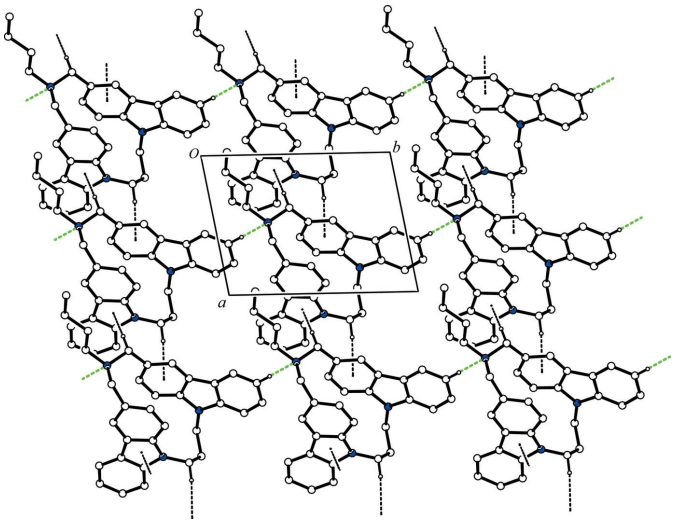


Figure 2
A packing diagram of the title compound viewed along the *c* axis, showing the two-dimensional network. The C—H···N hydrogen bonds and C—H···π interactions are shown as green and black dashed lines, respectively. H atoms not involved in these interactions have been omitted for clarity.

H···π interactions (C30—H30*A*···*Cg*2^{iii} and C31—H31*B*···*Cg*3^{iv}; *Cg*2 and *Cg*3 are the centroids of the C4–C9 and N2/C16/C17/C23/C22 rings, respectively; see Fig. 2 and Table 1), thus network sheets parallel to the *ab* plane are observed (Fig. 2). Besides this, the molecules belonging to different sheets are associated *via* a pair of C—H···π interactions (C28—H28*A*···*Cg*1^{ii}; *Cg*1 is the centroid of the C22–C27 ring), forming a centrosymmetric dimer (Fig. 3). Another pair of C—H···π interactions (C36—H36*B*···*Cg*4^{v}; *Cg*4 is the centroid of the C10–C15 ring) forms another centrosymmetric dimer (Fig. 3). As a result, a ribbon structure along [$\bar{1}$01] is formed (Fig. 3). Overall, the molecules are cross-linked *via* intermolecular C—H···N hydrogen bonds and C—H···π interactions into a three-dimensional network.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42; May 2021; Groom *et al.*, 2016) using *ConQuest* (Bruno *et al.*, 2002) for compounds containing a carbazole skeleton gave 4473 hits, and for those containing two 3,9-dimethylenecarbazole fragments gave 49 hits. Among those, a search for the carbazolophane skeleton gave seven hits. Of these seven compounds, three structures are [3.3](3,9) carbazolophanes, two being PO [3.3](3,9)carbazolophanes with the same skeleton as in the title compound: *anti*-10-(2-nitrobenzen-1-sulfonyl)-10,11,22,23-tetrahydro-9*H*,21*H*-5,8:15,12-bis(metheno)[1,5,11]triazacyclohexadecino[1,16-*a*:5,6-*a*′]-diindole (*N*-cyanamide-bridged PO [3.3](3,9)carbazolophane, YUKYEL; Tani *et al.*, 2020) and *anti*-3-cyano-3-aza-1(9,3),3(3,9)-dicarbazolacyclooctaphane (*N*-*o*-nitrophenylsulfonamide-bridged PO [3.3](3,9)carbazolophane, BACKOG; Tani *et al.*, 2001). One structure is *N*-cyanamide-bridged FO [3.3](3,9)carbazolophane, *syn*-3-cyano-3-aza-1(9,3),3(3,9)-dicarbazolacyclooctaphane benzene clathrate (BACKIA; Tani *et al.*, 2001), in which the dihedral angle between two carbazole rings is 8.48 (10)°, and intramolecular *Cg*···*Cg* distances are 3.322 (3) Å for the benzene rings bridged by cyanamide, 3.447 (2) Å for the central pyrrole rings and 3.792 (3) Å for the outer benzene rings. Three of the remaining four structures are PO [*m.n*](3,9)carbazolophanes; *anti*-ethenylene and 1,3-xylylene-bridged [2.5](3,9)carbazolophane (VELKON; Kumar *et al.*, 2006), *anti*-*N*-cyanamide-bridged [3.4](3,9)carbazolophane (KEYVAM; Tani *et al.*, 2007) and *anti*-*O*-oxa-bridged [3.5](3,9)carbazolophane (KEYVEG; Tani *et al.*, 2007). In these structures, the dihedral angles between two carbazole ring systems and intramolecular *Cg*···*Cg* distances in the partially overlapped benzene rings are 31.69 (6)° and 3.8062 (15) Å for ethenylene and 1,3-xylylene-bridged [2.5](3,9)carbazolophane; 15.04 (9)° and 3.732 (3) Å for cyanamide-bridged [3.4](3,9)carbazolophane; 24.87 (11)° and 3.901 (3) Å (the average value of two independent molecules) for oxa-bridged [3.5](3,9)carbazolophane.

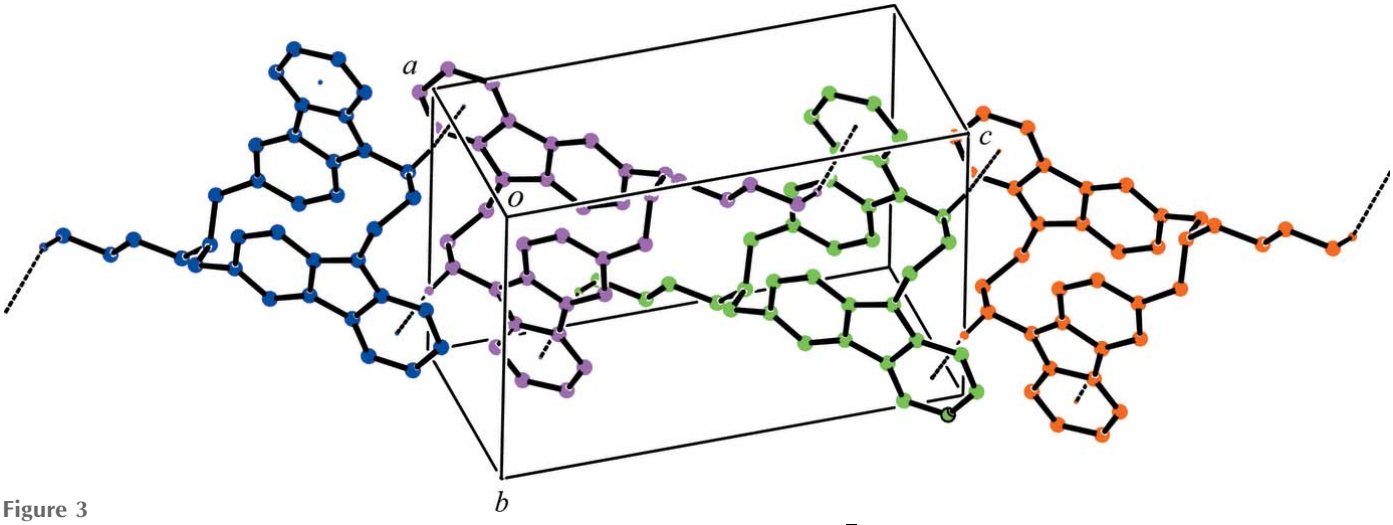


Figure 3
An excerpt of the crystal packing of the title compound showing the ribbon structure along [$\bar{1}$01]. The C—H···π interactions are shown as black dashed lines. H atoms not involved in these interactions have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{33}H_{33}N_3$
M_r	471.64
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	7.9106 (3), 10.4468 (4), 15.5735 (5)
α, β, γ (°)	79.988 (3), 77.717 (3), 77.909 (3)
V (Å^3)	1218.33 (8)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.58
Crystal size (mm)	0.40 × 0.13 × 0.05
Data collection	
Diffractometer	Rigaku XtaLAB Synergy
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2022)
T_{min}, T_{max}	0.451, 0.972
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	14067, 4827, 4383
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.118, 1.05
No. of reflections	4827
No. of parameters	326
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.31

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *CrystalStructure* (Rigaku, 2019).

The last of the seven compounds is a FO carbazolophane, *syn*-cyclobutane-bridged [2.4](3,9)carbazolophane (GOZGUX; Nakamura *et al.*, 1999) in which the dihedral angle between its carbazole fragments is 18.9 (2)°, and intramolecular $Cg\cdots Cg$ distances are 3.517 Å for the benzene rings bridged by cyanamide, 4.167 Å for the central pyrrole rings and 4.242 Å for the outer benzene rings.

5. Synthesis and crystallization

A solution of 9,9′-(1,3-propanediyl)bis[3-(bromomethyl)-9*H*-carbazole] (560 mg, 1.00 mmol; Tani, *et al.*, 2001) in dichloromethane (100 mL) was added to a 500 mL flask, which contained a mixture of tetrabutylammonium iodide (70.6 mg, 0.191 mmol) and *n*-butylamine (220 mg, 3.01 mmol) in dichloromethane (150 mL) and sodium hydroxide (1.00 g, 0.25 mol) in water (10 mL). Then, the flask was filled with argon and was stirred at room temperature for 3 d. The reaction mixtures were washed with water, then dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (Wako-gel C-200, 10 g). Elution from hexane:ethyl acetate (19:1) gave a white solid (41.5 mg, 9%). Elution from hexane:ethyl acetate (10:1) gave mixtures including a *syn*-configuration (FO isomer), but they were difficult to separate. A part of the title compound was recrystallized from dichloromethane:ethanol (1:3) to give a colorless crystal suitable for X-ray diffraction. Melting point: 482–484 K. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.08 (*t*, *J* = 7.6 Hz, 3H), 1.57–1.60 (*m*, 2H),1.78 (*quint*, *J* = 7.6 Hz, 2H), 2.81–2.97 (*m*, 4H), 3.74–3.90 (*m*, 6H), 4.10–4.17 (*m*, 2H), 5.34 (*d*, *J* = 8.1 Hz, 2H), 6.38 (*br*, 2H), 7.25-7.30 (*m*, 2H), 7.46–7.53 (*m*, 4H), 7.67 (*s*, 2H), 8.11 (*d*, *J* = 7.6 Hz, 2H).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were placed in geometrically calculated positions (C—H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C).

Funding information

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supporting information

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Synthesis and crystal structure of *anti*-10-butyl-10,11,22,23-tetrahydro-9*H*,21*H*-5,8:15,12-bis(metheno)[1,5,11]triazacyclohexadecino[1,16-*a*:5,6-*a*′]diindole

Koji Kubono, Keita Tani, Yukiyasu Kashiwagi, Fumito Tani and Taisuke Matsumoto

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2022); cell refinement: *CrysAlis PRO* (Rigaku OD, 2022); data reduction: *CrysAlis PRO* (Rigaku OD, 2022); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015*b*); molecular graphics: *CrystalStructure* (Rigaku, 2019); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2019).

anti-10-Butyl-10,11,22,23-tetrahydro-9*H*,21*H*-5,8:15,12-bis(metheno)[1,5,11]triazacyclohexadecino[1,16-*a*:5,6-*a*′]diindole

Crystal data

$C_{33}H_{33}N_3$
M_r = 471.64
Triclinic, $P\overline{1}$
a = 7.9106 (3) Å
b = 10.4468 (4) Å
c = 15.5735 (5) Å
α = 79.988 (3)°
β = 77.717 (3)°
γ = 77.909 (3)°
V = 1218.33 (8) Å^3
Z = 2
F(000) = 504.00
D_x = 1.286 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 9429 reflections
θ = 2.9–74.8°
μ = 0.58 mm^{-1}
T = 100 K
Prism, colourless
0.40 × 0.13 × 0.05 mm

Data collection

Rigaku XtaLAB Synergy diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2022)
T_{min} = 0.451, T_{max} = 0.972
14067 measured reflections
4827 independent reflections
4383 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.028
θ_{max} = 75.4°, θ_{min} = 2.9°
h = −9→9
k = −12→12
l = −19→15

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.118
S = 1.05
4827 reflections
326 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

$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.6261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ 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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.82658 (15)	0.71805 (11)	0.11798 (7)	0.0171 (2)
N2	1.15258 (15)	0.47838 (11)	0.18124 (8)	0.0188 (2)
N3	0.49011 (15)	0.28118 (11)	0.39375 (7)	0.0177 (2)
C4	0.71367 (17)	0.63439 (13)	0.16544 (8)	0.0158 (3)
C5	0.59504 (17)	0.69870 (13)	0.23257 (9)	0.0160 (3)
C6	0.48501 (17)	0.62693 (13)	0.29675 (9)	0.0165 (3)
H6	0.406279	0.668922	0.342939	0.020*
C7	0.49126 (17)	0.49443 (13)	0.29271 (9)	0.0171 (3)
C8	0.60034 (18)	0.43601 (13)	0.22033 (9)	0.0178 (3)
H8	0.596903	0.347337	0.215192	0.021*
C9	0.71166 (17)	0.50366 (13)	0.15691 (9)	0.0175 (3)
H9	0.784875	0.462725	0.108815	0.021*
C10	0.77834 (17)	0.83775 (13)	0.15155 (9)	0.0173 (3)
C11	0.63514 (17)	0.82992 (13)	0.22327 (9)	0.0174 (3)
C12	0.56582 (18)	0.93710 (13)	0.26950 (9)	0.0190 (3)
H12	0.470434	0.932256	0.317992	0.023*
C13	0.63778 (19)	1.05200 (14)	0.24394 (10)	0.0222 (3)
H13	0.592392	1.125523	0.275587	0.027*
C14	0.77841 (18)	1.05906 (13)	0.17086 (10)	0.0213 (3)
H14	0.824434	1.138552	0.153186	0.026*
C15	0.85017 (18)	0.95296 (14)	0.12471 (9)	0.0207 (3)
H15	0.945449	0.958064	0.076184	0.025*
C16	1.03369 (17)	0.44294 (13)	0.25712 (9)	0.0174 (3)
C17	1.02490 (17)	0.30775 (13)	0.26373 (9)	0.0175 (3)
C18	0.89825 (17)	0.25347 (13)	0.32861 (9)	0.0180 (3)
H18	0.890067	0.163128	0.332509	0.022*
C19	0.78436 (17)	0.33257 (14)	0.38739 (9)	0.0184 (3)
C20	0.80863 (18)	0.46273 (14)	0.38464 (9)	0.0196 (3)
H20	0.738393	0.513423	0.428779	0.024*
C21	0.93065 (18)	0.52035 (14)	0.32029 (9)	0.0193 (3)
H21	0.943592	0.609013	0.319239	0.023*

C22	1.22754 (17)	0.36575 (13)	0.14118 (9)	0.0182 (3)
C23	1.15213 (17)	0.25666 (13)	0.19060 (9)	0.0171 (3)
C24	1.20764 (18)	0.13269 (14)	0.16252 (9)	0.0209 (3)
H24	1.157845	0.059339	0.194712	0.025*
C25	1.33597 (19)	0.11695 (14)	0.08733 (10)	0.0238 (3)
H25	1.374559	0.032439	0.068095	0.029*
C26	1.40972 (18)	0.22603 (15)	0.03911 (9)	0.0226 (3)
H26	1.497276	0.213768	−0.012435	0.027*
C27	1.35725 (18)	0.34962 (14)	0.06532 (9)	0.0211 (3)
H27	1.407904	0.422325	0.032672	0.025*
C28	0.97116 (17)	0.68287 (14)	0.04623 (9)	0.0186 (3)
H28A	0.953335	0.746320	−0.007603	0.022*
H28B	0.966591	0.594228	0.033405	0.022*
C29	1.15445 (18)	0.68108 (14)	0.06399 (9)	0.0197 (3)
H29A	1.170947	0.773751	0.058267	0.024*
H29B	1.241895	0.639167	0.016749	0.024*
C30	1.19716 (18)	0.61029 (13)	0.15383 (9)	0.0198 (3)
H30A	1.324710	0.602970	0.151835	0.024*
H30B	1.134237	0.666442	0.199967	0.024*
C31	0.38822 (17)	0.41067 (13)	0.36585 (9)	0.0188 (3)
H31A	0.345645	0.459203	0.417797	0.023*
H31B	0.283955	0.397118	0.345283	0.023*
C32	0.62358 (18)	0.28555 (14)	0.44600 (9)	0.0198 (3)
H32A	0.659389	0.196276	0.477504	0.024*
H32B	0.571759	0.345842	0.491046	0.024*
C33	0.37437 (18)	0.18555 (13)	0.43519 (9)	0.0205 (3)
H33A	0.449751	0.099609	0.450472	0.025*
H33B	0.309815	0.173521	0.390086	0.025*
C34	0.23937 (18)	0.21747 (14)	0.51833 (9)	0.0211 (3)
H34A	0.301200	0.221478	0.566524	0.025*
H34B	0.165479	0.305036	0.505587	0.025*
C35	0.1226 (2)	0.11267 (15)	0.54839 (11)	0.0270 (3)
H35A	0.066395	0.106049	0.498681	0.032*
H35B	0.197237	0.026042	0.562874	0.032*
C36	−0.0194 (2)	0.14142 (16)	0.62842 (12)	0.0321 (4)
H36A	−0.091006	0.228698	0.615574	0.039*
H36B	0.035182	0.140059	0.679530	0.039*
H36C	−0.094333	0.074069	0.641870	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0183 (5)	0.0162 (5)	0.0162 (5)	−0.0042 (4)	−0.0001 (4)	−0.0030 (4)
N2	0.0177 (5)	0.0184 (6)	0.0202 (6)	−0.0048 (4)	−0.0022 (4)	−0.0021 (4)
N3	0.0188 (6)	0.0163 (5)	0.0176 (6)	−0.0054 (4)	−0.0021 (4)	0.0000 (4)
C4	0.0157 (6)	0.0183 (6)	0.0136 (6)	−0.0039 (5)	−0.0035 (5)	−0.0006 (5)
C5	0.0163 (6)	0.0163 (6)	0.0158 (6)	−0.0020 (5)	−0.0044 (5)	−0.0023 (5)
C6	0.0157 (6)	0.0184 (6)	0.0151 (6)	−0.0018 (5)	−0.0029 (5)	−0.0028 (5)

C7	0.0161 (6)	0.0192 (6)	0.0165 (6)	−0.0035 (5)	−0.0054 (5)	−0.0001 (5)
C8	0.0228 (7)	0.0151 (6)	0.0176 (6)	−0.0052 (5)	−0.0075 (5)	−0.0007 (5)
C9	0.0196 (6)	0.0177 (6)	0.0153 (6)	−0.0024 (5)	−0.0032 (5)	−0.0040 (5)
C10	0.0187 (6)	0.0162 (6)	0.0170 (6)	−0.0021 (5)	−0.0041 (5)	−0.0026 (5)
C11	0.0181 (6)	0.0182 (6)	0.0157 (6)	−0.0037 (5)	−0.0042 (5)	−0.0002 (5)
C12	0.0194 (6)	0.0185 (6)	0.0169 (6)	−0.0011 (5)	−0.0012 (5)	−0.0020 (5)
C13	0.0261 (7)	0.0159 (6)	0.0242 (7)	−0.0030 (5)	−0.0027 (6)	−0.0053 (5)
C14	0.0236 (7)	0.0148 (6)	0.0265 (7)	−0.0059 (5)	−0.0050 (6)	−0.0020 (5)
C15	0.0216 (7)	0.0195 (7)	0.0203 (7)	−0.0061 (5)	−0.0016 (5)	−0.0004 (5)
C16	0.0149 (6)	0.0210 (7)	0.0168 (6)	−0.0042 (5)	−0.0049 (5)	−0.0005 (5)
C17	0.0166 (6)	0.0181 (6)	0.0178 (6)	−0.0011 (5)	−0.0054 (5)	−0.0024 (5)
C18	0.0181 (6)	0.0175 (6)	0.0180 (6)	−0.0028 (5)	−0.0048 (5)	0.0004 (5)
C19	0.0178 (6)	0.0223 (7)	0.0152 (6)	−0.0027 (5)	−0.0054 (5)	−0.0005 (5)
C20	0.0185 (6)	0.0243 (7)	0.0167 (6)	−0.0019 (5)	−0.0042 (5)	−0.0054 (5)
C21	0.0201 (6)	0.0194 (7)	0.0201 (7)	−0.0033 (5)	−0.0061 (5)	−0.0043 (5)
C22	0.0157 (6)	0.0194 (6)	0.0198 (7)	−0.0027 (5)	−0.0044 (5)	−0.0026 (5)
C23	0.0146 (6)	0.0207 (7)	0.0164 (6)	−0.0037 (5)	−0.0032 (5)	−0.0022 (5)
C24	0.0197 (7)	0.0181 (7)	0.0235 (7)	−0.0027 (5)	−0.0034 (5)	−0.0003 (5)
C25	0.0217 (7)	0.0212 (7)	0.0262 (7)	0.0001 (5)	−0.0021 (6)	−0.0050 (6)
C26	0.0153 (6)	0.0298 (8)	0.0201 (7)	−0.0015 (5)	0.0003 (5)	−0.0033 (6)
C27	0.0162 (6)	0.0260 (7)	0.0209 (7)	−0.0070 (5)	−0.0021 (5)	0.0002 (5)
C28	0.0197 (7)	0.0211 (7)	0.0149 (6)	−0.0044 (5)	−0.0002 (5)	−0.0047 (5)
C29	0.0188 (6)	0.0195 (6)	0.0197 (7)	−0.0048 (5)	−0.0003 (5)	−0.0022 (5)
C30	0.0197 (6)	0.0189 (7)	0.0231 (7)	−0.0077 (5)	−0.0052 (5)	−0.0018 (5)
C31	0.0176 (6)	0.0185 (6)	0.0196 (7)	−0.0032 (5)	−0.0031 (5)	−0.0009 (5)
C32	0.0200 (7)	0.0220 (7)	0.0160 (6)	−0.0027 (5)	−0.0023 (5)	−0.0013 (5)
C33	0.0231 (7)	0.0166 (6)	0.0212 (7)	−0.0061 (5)	−0.0005 (5)	−0.0020 (5)
C34	0.0224 (7)	0.0183 (7)	0.0213 (7)	−0.0056 (5)	0.0005 (5)	−0.0018 (5)
C35	0.0272 (7)	0.0226 (7)	0.0292 (8)	−0.0096 (6)	0.0018 (6)	−0.0006 (6)
C36	0.0242 (8)	0.0263 (8)	0.0407 (9)	−0.0070 (6)	0.0067 (7)	−0.0031 (7)

Geometric parameters (Å, º)

N1—C10	1.3875 (17)	C20—C21	1.3858 (19)
N1—C4	1.3891 (17)	C20—H20	0.9500
N1—C28	1.4542 (17)	C21—H21	0.9500
N2—C22	1.3895 (18)	C22—C27	1.3993 (19)
N2—C16	1.3925 (17)	C22—C23	1.4253 (19)
N2—C30	1.4630 (17)	C23—C24	1.3923 (19)
N3—C31	1.4684 (17)	C24—C25	1.386 (2)
N3—C33	1.4698 (17)	C24—H24	0.9500
N3—C32	1.4756 (17)	C25—C26	1.413 (2)
C4—C9	1.3986 (18)	C25—H25	0.9500
C4—C5	1.4098 (18)	C26—C27	1.376 (2)
C5—C6	1.4005 (18)	C26—H26	0.9500
C5—C11	1.4472 (18)	C27—H27	0.9500
C6—C7	1.3866 (19)	C28—C29	1.5286 (19)
C6—H6	0.9500	C28—H28A	0.9900

C7—C8	1.4115 (19)	C28—H28B	0.9900
C7—C31	1.5115 (18)	C29—C30	1.5347 (19)
C8—C9	1.3778 (19)	C29—H29A	0.9900
C8—H8	0.9500	C29—H29B	0.9900
C9—H9	0.9500	C30—H30A	0.9900
C10—C15	1.3988 (19)	C30—H30B	0.9900
C10—C11	1.4164 (18)	C31—H31A	0.9900
C11—C12	1.3884 (19)	C31—H31B	0.9900
C12—C13	1.3954 (19)	C32—H32A	0.9900
C12—H12	0.9500	C32—H32B	0.9900
C13—C14	1.416 (2)	C33—C34	1.5299 (19)
C13—H13	0.9500	C33—H33A	0.9900
C14—C15	1.381 (2)	C33—H33B	0.9900
C14—H14	0.9500	C34—C35	1.5271 (19)
C15—H15	0.9500	C34—H34A	0.9900
C16—C21	1.3948 (19)	C34—H34B	0.9900
C16—C17	1.4133 (19)	C35—C36	1.516 (2)
C17—C18	1.3980 (19)	C35—H35A	0.9900
C17—C23	1.4468 (18)	C35—H35B	0.9900
C18—C19	1.3902 (19)	C36—H36A	0.9800
C18—H18	0.9500	C36—H36B	0.9800
C19—C20	1.405 (2)	C36—H36C	0.9800
C19—C32	1.5179 (18)		

C10—N1—C4	108.38 (11)	C22—C23—C17	106.30 (12)
C10—N1—C28	126.84 (11)	C25—C24—C23	119.59 (13)
C4—N1—C28	124.78 (11)	C25—C24—H24	120.2
C22—N2—C16	108.10 (11)	C23—C24—H24	120.2
C22—N2—C30	127.04 (11)	C24—C25—C26	120.31 (13)
C16—N2—C30	124.72 (11)	C24—C25—H25	119.8
C31—N3—C33	111.29 (10)	C26—C25—H25	119.8
C31—N3—C32	114.56 (11)	C27—C26—C25	121.32 (13)
C33—N3—C32	113.55 (11)	C27—C26—H26	119.3
N1—C4—C9	129.49 (12)	C25—C26—H26	119.3
N1—C4—C5	109.42 (11)	C26—C27—C22	118.46 (13)
C9—C4—C5	121.02 (12)	C26—C27—H27	120.8
C6—C5—C4	119.43 (12)	C22—C27—H27	120.8
C6—C5—C11	133.58 (12)	N1—C28—C29	115.26 (11)
C4—C5—C11	106.48 (11)	N1—C28—H28A	108.5
C7—C6—C5	119.85 (12)	C29—C28—H28A	108.5
C7—C6—H6	120.1	N1—C28—H28B	108.5
C5—C6—H6	120.1	C29—C28—H28B	108.5
C6—C7—C8	119.25 (12)	H28A—C28—H28B	107.5
C6—C7—C31	121.17 (12)	C28—C29—C30	117.30 (11)
C8—C7—C31	119.55 (12)	C28—C29—H29A	108.0
C9—C8—C7	122.01 (12)	C30—C29—H29A	108.0
C9—C8—H8	119.0	C28—C29—H29B	108.0
C7—C8—H8	119.0	C30—C29—H29B	108.0

C8—C9—C4	118.03 (12)	H29A—C29—H29B	107.2
C8—C9—H9	121.0	N2—C30—C29	116.16 (11)
C4—C9—H9	121.0	N2—C30—H30A	108.2
N1—C10—C15	129.63 (12)	C29—C30—H30A	108.2
N1—C10—C11	109.09 (12)	N2—C30—H30B	108.2
C15—C10—C11	121.29 (12)	C29—C30—H30B	108.2
C12—C11—C10	119.92 (12)	H30A—C30—H30B	107.4
C12—C11—C5	133.47 (13)	N3—C31—C7	113.67 (11)
C10—C11—C5	106.59 (12)	N3—C31—H31A	108.8
C11—C12—C13	119.27 (13)	C7—C31—H31A	108.8
C11—C12—H12	120.4	N3—C31—H31B	108.8
C13—C12—H12	120.4	C7—C31—H31B	108.8
C12—C13—C14	120.02 (13)	H31A—C31—H31B	107.7
C12—C13—H13	120.0	N3—C32—C19	111.50 (11)
C14—C13—H13	120.0	N3—C32—H32A	109.3
C15—C14—C13	121.47 (13)	C19—C32—H32A	109.3
C15—C14—H14	119.3	N3—C32—H32B	109.3
C13—C14—H14	119.3	C19—C32—H32B	109.3
C14—C15—C10	118.00 (13)	H32A—C32—H32B	108.0
C14—C15—H15	121.0	N3—C33—C34	117.93 (11)
C10—C15—H15	121.0	N3—C33—H33A	107.8
N2—C16—C21	129.47 (13)	C34—C33—H33A	107.8
N2—C16—C17	109.55 (12)	N3—C33—H33B	107.8
C21—C16—C17	120.97 (12)	C34—C33—H33B	107.8
C18—C17—C16	119.87 (12)	H33A—C33—H33B	107.2
C18—C17—C23	133.27 (13)	C35—C34—C33	110.75 (12)
C16—C17—C23	106.64 (12)	C35—C34—H34A	109.5
C19—C18—C17	119.56 (13)	C33—C34—H34A	109.5
C19—C18—H18	120.2	C35—C34—H34B	109.5
C17—C18—H18	120.2	C33—C34—H34B	109.5
C18—C19—C20	118.91 (13)	H34A—C34—H34B	108.1
C18—C19—C32	120.73 (12)	C36—C35—C34	113.48 (13)
C20—C19—C32	119.96 (12)	C36—C35—H35A	108.9
C21—C20—C19	122.81 (13)	C34—C35—H35A	108.9
C21—C20—H20	118.6	C36—C35—H35B	108.9
C19—C20—H20	118.6	C34—C35—H35B	108.9
C20—C21—C16	117.33 (13)	H35A—C35—H35B	107.7
C20—C21—H21	121.3	C35—C36—H36A	109.5
C16—C21—H21	121.3	C35—C36—H36B	109.5
N2—C22—C27	129.80 (13)	H36A—C36—H36B	109.5
N2—C22—C23	109.31 (12)	C35—C36—H36C	109.5
C27—C22—C23	120.88 (13)	H36A—C36—H36C	109.5
C24—C23—C22	119.43 (12)	H36B—C36—H36C	109.5
C24—C23—C17	134.27 (13)		

C10—N1—C4—C9	−178.96 (13)	C23—C17—C18—C19	−175.18 (13)
C28—N1—C4—C9	0.4 (2)	C17—C18—C19—C20	−5.06 (19)
C10—N1—C4—C5	−2.13 (14)	C17—C18—C19—C32	167.69 (12)

C28—N1—C4—C5	177.18 (12)	C18—C19—C20—C21	6.4 (2)
N1—C4—C5—C6	−171.01 (11)	C32—C19—C20—C21	−166.42 (12)
C9—C4—C5—C6	6.13 (19)	C19—C20—C21—C16	−0.9 (2)
N1—C4—C5—C11	1.85 (14)	N2—C16—C21—C20	173.16 (13)
C9—C4—C5—C11	178.99 (12)	C17—C16—C21—C20	−5.76 (19)
C4—C5—C6—C7	−1.25 (19)	C16—N2—C22—C27	−177.87 (13)
C11—C5—C6—C7	−171.78 (13)	C30—N2—C22—C27	−2.0 (2)
C5—C6—C7—C8	−4.24 (19)	C16—N2—C22—C23	1.67 (14)
C5—C6—C7—C31	173.68 (11)	C30—N2—C22—C23	177.56 (12)
C6—C7—C8—C9	5.2 (2)	N2—C22—C23—C24	179.96 (12)
C31—C7—C8—C9	−172.75 (12)	C27—C22—C23—C24	−0.45 (19)
C7—C8—C9—C4	−0.45 (19)	N2—C22—C23—C17	0.28 (14)
N1—C4—C9—C8	171.28 (12)	C27—C22—C23—C17	179.87 (12)
C5—C4—C9—C8	−5.22 (19)	C18—C17—C23—C24	−7.3 (3)
C4—N1—C10—C15	−178.79 (13)	C16—C17—C23—C24	178.31 (14)
C28—N1—C10—C15	1.9 (2)	C18—C17—C23—C22	172.30 (14)
C4—N1—C10—C11	1.55 (14)	C16—C17—C23—C22	−2.08 (14)
C28—N1—C10—C11	−177.74 (12)	C22—C23—C24—C25	0.4 (2)
N1—C10—C11—C12	178.38 (12)	C17—C23—C24—C25	179.95 (14)
C15—C10—C11—C12	−1.3 (2)	C23—C24—C25—C26	−0.3 (2)
N1—C10—C11—C5	−0.40 (14)	C24—C25—C26—C27	0.2 (2)
C15—C10—C11—C5	179.91 (12)	C25—C26—C27—C22	−0.3 (2)
C6—C5—C11—C12	−8.0 (3)	N2—C22—C27—C26	179.90 (13)
C4—C5—C11—C12	−179.42 (14)	C23—C22—C27—C26	0.4 (2)
C6—C5—C11—C10	170.53 (14)	C10—N1—C28—C29	63.32 (17)
C4—C5—C11—C10	−0.87 (14)	C4—N1—C28—C29	−115.87 (14)
C10—C11—C12—C13	0.5 (2)	N1—C28—C29—C30	46.67 (17)
C5—C11—C12—C13	178.94 (14)	C22—N2—C30—C29	66.13 (17)
C11—C12—C13—C14	0.8 (2)	C16—N2—C30—C29	−118.63 (14)
C12—C13—C14—C15	−1.5 (2)	C28—C29—C30—N2	48.00 (17)
C13—C14—C15—C10	0.8 (2)	C33—N3—C31—C7	−156.62 (11)
N1—C10—C15—C14	−178.98 (13)	C32—N3—C31—C7	72.88 (14)
C11—C10—C15—C14	0.6 (2)	C6—C7—C31—N3	−134.49 (13)
C22—N2—C16—C21	177.94 (13)	C8—C7—C31—N3	43.42 (17)
C30—N2—C16—C21	1.9 (2)	C31—N3—C32—C19	−76.51 (14)
C22—N2—C16—C17	−3.04 (14)	C33—N3—C32—C19	154.11 (11)
C30—N2—C16—C17	−179.04 (11)	C18—C19—C32—N3	−69.92 (16)
N2—C16—C17—C18	−172.11 (11)	C20—C19—C32—N3	102.75 (14)
C21—C16—C17—C18	7.01 (19)	C31—N3—C33—C34	−59.87 (16)
N2—C16—C17—C23	3.17 (14)	C32—N3—C33—C34	71.15 (15)
C21—C16—C17—C23	−177.71 (12)	N3—C33—C34—C35	176.03 (12)
C16—C17—C18—C19	−1.39 (19)	C33—C34—C35—C36	−177.56 (13)

Hydrogen-bond geometry (Å, º)

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the C22–C27, C4–C9, N2/C16/C17/C22/C23 and C10–C15 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···N3^{i}	0.95	2.56	3.4858 (18)	166

C28—H28*A*···*Cg*1^{ii}	0.99	2.72	3.4144 (15)	128
C30—H30*A*···*Cg*2^{iii}	0.99	2.62	3.5224 (16)	152
C31—H31*B*···*Cg*3^{iv}	0.99	2.83	3.7245 (15)	150
C36—H36*B*···*Cg*4^{v}	0.98	2.99	3.9151 (18)	159

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+2, −*y*+1, −*z*; (iii) *x*+1, *y*, *z*; (iv) *x*−1, *y*, *z*+1; (v) −*x*+1, −*y*+1, −*z*+1.