

CRYSTALLOGRAPHIC  
COMMUNICATIONS

ISSN 2056-9890

# Syntheses and crystal structure of 4-[(pyridin-3-yl)diazenyl]morpholine and 1-[(pyridin-3-yl)diazenyl]-1,2,3,4-tetrahydroquinoline

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Received 28 November 2022

Accepted 4 January 2023

Edited by J. Ellena, Universidade de São Paulo, Brazil

**Keywords:** 1,2,3-triazenes; morpholine; 1,2,3,4-tetrahydroquinoline; pyridine; crystal structure.

**CCDC references:** 2234291; 2234292

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

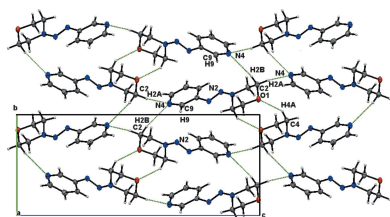
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Two new heterocyclic 1,2,3-triazenes were synthesized by diazotation of 3-aminopyridine following respectively by coupling with morpholine or 1,2,3,4-tetrahydroquinoline. 4-[(Pyridin-3-yl)diazenyl]morpholine (**I**), C<sub>9</sub>H<sub>12</sub>N<sub>4</sub>O, has monoclinic *P*2<sub>1</sub>/*c* symmetry at 100 K, while 1-[(pyridin-3-yl)diazenyl]-1,2,3,4-tetrahydroquinoline (**II**), C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>, has monoclinic *P*2<sub>1</sub>/*n* symmetry at 100 K. These 1,2,3-triazene derivatives were synthesized by the organic medium method by coupling reactions of 3-aminopyridine with morpholine and 1,2,3,4-tetrahydroquinoline, respectively, and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, mass spectrometry, and single-crystal X-ray diffraction. The molecule of compound **I** consists of pyridine and morpholine rings connected by an azo moiety (–N=N–). In the molecule of **II**, the pyridine ring and the 1,2,3,4-tetrahydroquinoline unit are also connected by an azo moiety. The double- and single-bond distances in the triazene chain are comparable for the two compounds. In both crystal structures, the molecules are connected by C–H⋯N interactions, forming infinite chains for **I** and layers parallel to the *bc* plane for **II**.

## 1. Chemical context

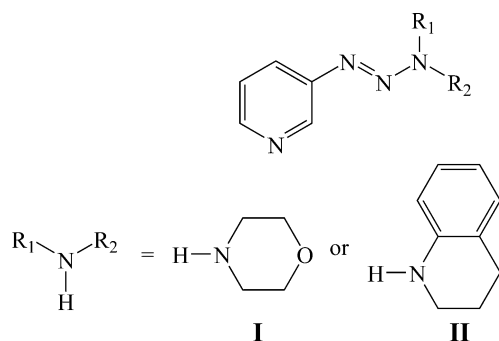
1,2,3-Triazenes are versatile compounds in preparative chemistry because of their stable and highly modular nature (Patil & Bugarin, 2016). 1,2,3-Triazene derivatives have been studied for their potential anticancer properties (Rouzer *et al.*, 1996; Connors *et al.*, 1976), used as a protecting group in natural product synthesis (Nicolaou *et al.*, 1999) and combinatorial chemistry (Bräse *et al.*, 2000), incorporated into polymers (Jones *et al.*, 1997) and oligomer synthesis (Moore, 1997), and used to prepare heterocycles (Wirschun *et al.*, 1998). 1,2,3-Triazenes are some of the most important compounds proposed for electrochromic materials that change color in the presence of the missing light in response to electrochemical switching (Monk *et al.*, 2007). This phenomenon has potential utility in protective eyewear and data storage devices applications (Mortimer, 1997, 1999; Argun *et al.* 2004; Lampert, 1984). These molecules constitute a unique class of compounds containing three adjacent nitrogen atoms



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in an acyclic arrangement (Kimball & Haley, 2002; Nwajiobi *et al.*, 2022; Bormann *et al.*, 2022). 1,2,3-Triazenes can be prepared by diazo coupling between a diazonium salt and primary, or secondary amines (Sadchikova & Mokrushin, 2002) or Grignard reagents coupled with azides (Kirk, 1978). The synthesis of this type of compound in water as solvent is one of the most important challenges in green chemistry as the reaction conditions minimize environmental hazards and chemical waste (Zhang *et al.*, 2018). 1,2,3-Triazenes can exist as a mixture of tautomers. The nature of the mixture and equilibrium position can be defined by crystallographic studies. It is in this context that we synthesized two triazene derivatives and determined their structures by XRD.



## 2. Structural commentary

Compound **I** was synthesized *via* reaction of the diazonium salt of 3-aminopyridine and morpholine. The resulting compound was recrystallized from ethanol to yield orange single crystals. Compound **I** crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$ , with the asymmetric unit consisting of one 1-morpholino-2-(pyridin-3-yl)diazene molecule (Fig. 1). The molecule consists of six-membered pyridine and morpholine rings connected by an  $-N=N-$  moiety through the nitrogen atom of the morpholine ring and a carbon atom of the pyridine ring. Thus a 1,2,3-triazene moiety

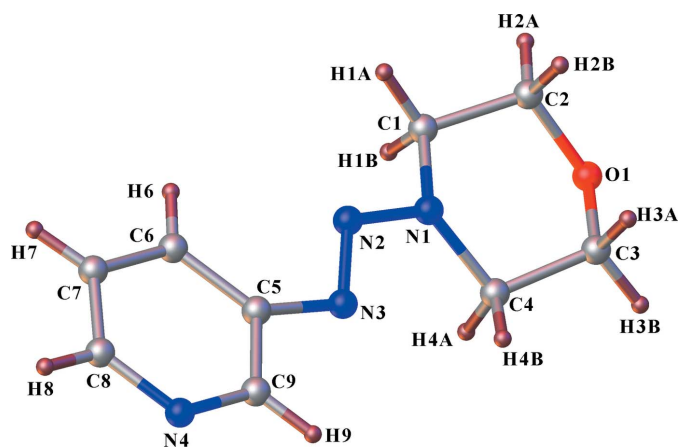


Figure 1

A view of the title compound **I**, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level.

( $-N=N-N-$ ) is formed in which the double-bond character of the azo moiety is indicated by the bond distance of 1.2640 (12) Å for N2–N3. The bond distance of 1.3350 (11) Å is indicative of single-bond character for N1–N2 moiety. The N2–N3 bond adopts an (*E*)-configuration. The pyridyl group is *trans* with respect to the morpholino group across the N2–N3 bond. The morpholine ring has a chair conformation with N1 and O1 situated, respectively, 0.192 (1) Å to one side of the mean plane through all ring atoms and 0.273 (1) Å to the other. Thus, O1 and N1 atoms are in a *syn* conformation with respect to the C1–C2 link [N1–C1–C2–O1 = 55.81 (11)°] and C3–C4 link [N1–C4–C3–O1 = –54.11 (11)°]. The pyridine ring forms dihedral angles of 8.80 (10) and 12.46 (5)° with the triazene moiety and the mean plane of the morpholine ring, respectively. The C–C bond lengths in the pyridine ring are in the normal range [1.33–1.39 Å]. In fact, the C5–C6 and C8–N4 bond lengths [1.3928 (14) and 1.3351 (15) Å, respectively] are characteristic of a delocalized pyridine ring (Wahedy *et al.*, 2017). The C–C–C bond angles in the ring measure almost 120°, with a maximum deviation of less than 2°, indicating that the atoms involved are  $sp^2$ -hybridized. All the bond angles involving the morpholine heterocyclic ring atoms, which fall in the range 108.17 (8)–116.08 (8)°, are close of the ideal value of 109° for a perfect tetrahedral carbon atom, and are indicative of  $sp^3$ -hybridized carbon atoms in the heterocyclic ring. The values of the bond distances in the chain, N3–N2 = 1.2640 (12) Å and N2–N1 = 1.3350 (11) Å, indicate their respective double- and single-bond characters. The N3–N2–N1 angle of 114.09 (8)° confirms the formation of the triazene compound (Fig. 2).

Compound **II** crystallizes in the centrosymmetric monoclinic space group  $P2_1/n$ , with the asymmetric unit consisting of one 1-[3,4-dihydroquinolin-1(2H)-yl]-2-(pyridin-3-yl)diazene molecule. The molecule consists of a pyridine ring and a tetrahydroquinoline moiety connected by an azo unit ( $-N=N-$ ) through the nitrogen atom of the 1,2,3,4-tetrahydroquinoline ring and a carbon atom of the pyridine ring. Thus a 1,2,3-triazene moiety ( $-N=N-N-$ ) is formed in which the double-bond character of the azo moiety is indicated by the bond distance of 1.2737 (13) Å for N2–N3 while the bond

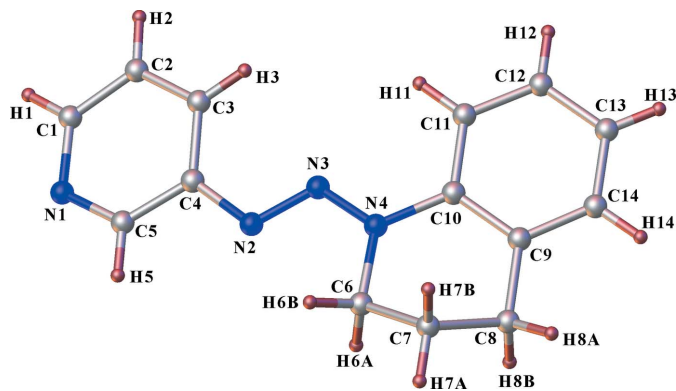


Figure 2

A view of the title compound **II**, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2A\cdots N4^i$	0.99	2.67	3.5465 (14)	148
$C2-H2B\cdots N4^{ii}$	0.99	2.68	3.5607 (14)	149
$C3-H3A\cdots N2^{iii}$	0.99	2.57	3.4149 (13)	143
$C7-H7\cdots N3^{iv}$	0.95	2.70	3.5168 (14)	145

Symmetry codes: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $x + 1, y, z$ ; (iv)  $-x, y + \frac{1}{2}, -z + \frac{3}{2}$ .

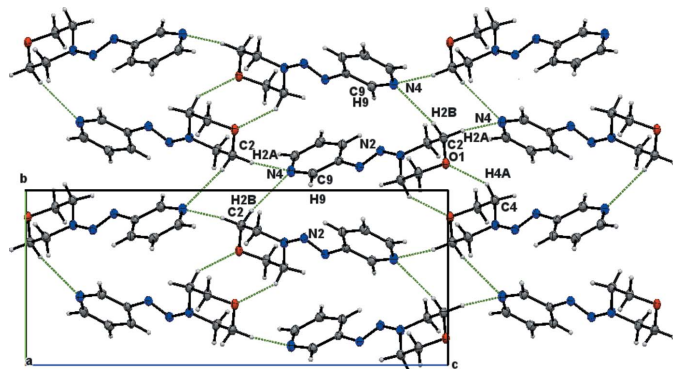
distance of 1.3341 (12) Å shows the single-bond character of N3–N4. The N2–N3 bond adopts an (*E*)-configuration. The pyridyl group is *trans* with respect to the tetraquinolyl group across the N2–N3 bond. The mean planes of the fused benzene and piperidine rings are not coplanar and form a dihedral angle of 10.79 (5)°. The pyridine ring forms dihedral angles of 12.12 (10), 22.07 (5) and 25.72 (5)° with the triazine moiety, the benzene ring and the piperidine ring, respectively. In the fused piperidine ring, two types of hybridized atoms exist as shown by the different angle values. The angles whose vertices are C9, C10 and N4 are in the range 118.39 (10)–120.41 (10)°, close to the ideal angle of 120° for  $sp^2$ -hybridized atoms. The angles whose vertices are C6, C7 and C8 are in the range 109.95 (9)–110.68 (13)°, close to the ideal angle of 109° for  $sp^3$ -hybridized atoms.

### 3. Supramolecular features

The the crystal of **I**, non-classical C–H $\cdots$ N interactions link the molecules into chains: C3–H3A $\cdots$ N2<sup>iii</sup> bonds form chains parallel to the *a* axis, C2–H2B $\cdots$ N4<sup>ii</sup> and C7–H7 $\cdots$ N3<sup>iv</sup> bonds form chains parallel to the *b* axis and C2–H2A $\cdots$ N4<sup>i</sup> bonds form chains parallel to the *c* axis (Table 1, Fig. 3). In the crystal of **II**, C12–H12 $\cdots$ N3<sup>i</sup> interactions link the molecules, forming layers in the *bc* plane (Table 2, Fig. 4).

### 4. Database survey

A search of the CSD database (Version 5.43, November 2021; Groom *et al.*, 2016) gave 48 hits for compounds including



**Figure 3**  
Infinite chains of compound **I** parallel to the *a* axis.

**Table 2**  
Hydrogen-bond geometry (Å, °) for **II**.

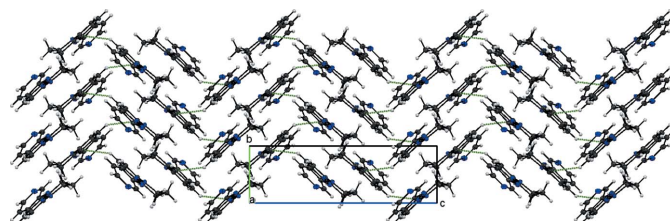
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C12-H12\cdots N3^i$	0.95	2.58	3.3890 (14)	143

Symmetry code: (i)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

morpholino 1,2,3-triazene derivatives similar to compound **I**. Three hits of compounds including the tetrahydroquinoline triazine moiety as in compound **II** were found: TADLOB (Huang *et al.* 2010), VAQMAC and VAQMEG (Katritzky *et al.*, 2003). Arylmorpholino 1,2,3-triazenes have structural characteristics like those of compound **I** and contain a 1,2,3-triazine unit consisting of three consecutive conjugated nitrogen atoms, as seen in **I**. Examination of the structure of EMUDEX (Lee *et al.*, 2016) suggests that a degree of  $\pi$ -delocalization across the linear triazine moiety of **I** was observed. The N2–N3 double-bond distance of 1.2679 (13) Å and the N1–N2 single-bond distance of 1.3501 (12) Å in EMUDEX are in accordance with those reported for OFUBUO (Mukai *et al.*, 2013), EZEXEN (Gholivand *et al.*, 2010), FUZLUI (Pye *et al.*, 2010). The structures of HAHQOZ (Johnson *et al.* 2016), HUHGEZ (Isovitich & Fronczek, 2020), IJEVUR (Gangwar *et al.*, 2021), OPAVUX (Chin *et al.*, 2011) and RUJQIX (Chin *et al.*, 2009) feature similar intermolecular hydrogen-bonding interactions to those in **I**, resulting in supramolecular networks.

### 5. Synthesis and crystallization

Several methods are known for the synthesis of 1,2,3-triazenes, but the most known is the diazo-coupling method where the diazonium salt is formed by the action of NaNO<sub>2</sub> in an acid medium on a primary amine and coupling of this salt with a primary or secondary amine. In this part of the work, a certain number of difficulties were encountered, in particular concerning the solubility of the synthesized 1,2,3-triazenes in the solvents used for analysis (CDCl<sub>3</sub> and acetone-*d*<sub>6</sub>). Known by the strong presence of a dipole moment, the analysis of these compounds requires the use of very polar solvents such as DMSO-*d*<sub>6</sub> or MeOD. The compounds were prepared according to the reaction sequence presented in Fig. 5. We tried several methods for the synthesis of diazonium salts of aminopyridine derivatives. Finally, we succeeded in obtaining the diazonium salt of 3-aminopyridine using isoamyl nitrite



**Figure 4**  
Layers of compound **II** parallel to the *bc* plane.

**Table 3**  
Experimental details.

	<b>I</b>	<b>II</b>
Crystal data		
Chemical formula	C <sub>9</sub> H <sub>12</sub> N <sub>4</sub> O	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub>
<i>M<sub>r</sub></i>	192.23	238.29
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.6889 (3), 8.3058 (4), 20.3063 (8)	15.4187 (2), 4.8130 (1), 15.9993 (3)
β (°)	97.370 (4)	96.115 (2)
<i>V</i> (Å <sup>3</sup> )	951.56 (8)	1180.56 (4)
<i>Z</i>	4	4
Radiation type	Mo Kα	Cu Kα
μ (mm <sup>-1</sup> )	0.09	0.66
Crystal size (mm)	0.26 × 0.16 × 0.14	0.24 × 0.13 × 0.05
Data collection		
Diffractometer	Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector	Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector
Absorption correction	Analytical ( <i>CrysAlis PRO</i> ; Rigaku OD, 2020)	Analytical ( <i>CrysAlis PRO</i> ; Rigaku OD, 2020)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.187, 1.000	0.187, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	47217, 2464, 2280	12295, 2142, 2010
<i>R</i> <sub>int</sub>	0.032	0.023
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.676	0.602
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.038, 0.104, 1.05	0.034, 0.094, 1.07
No. of reflections	2464	2142
No. of parameters	127	163
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.39, -0.20	0.22, -0.19

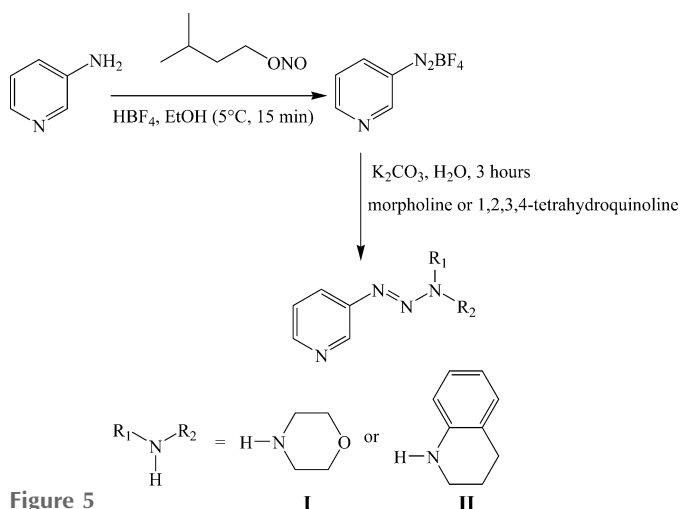
Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *CrysAlis PRO* (Rigaku OD, 2020), *OLEX2.solve* (Bourhis *et al.*, 2015), *SHELXL2018/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

instead of sodium nitrite and ethanol as solvent with good yield. We witnessed an explosion of this salt because of its instability. In a 100 mL flask, 3-aminopyridine (5 mmol), ethanol (3 mL), HBF<sub>4</sub> acid (50%, 1.5 mL) and isoamyl nitrite (5 mmol) were added. The mixture was kept under stirring for 15 min at 268 K. To this solution containing the diazonium salt, morpholine or 1,2,3,4-tetrahydroquinoline (5 mmol) in water (5 mL) was added and the mixture was stirred for 1 h at 273 K. A solution of potassium carbonate in water (5 mL) was

added to the flask and the reaction kept under stirring for 3 h at room temperature. The resulting product was extracted with ethyl acetate, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. Compounds **I** and **II** were obtained in a crystalline form with this synthetic method.

**Compound I.** Yield: 72%. Orange crystal, m.p. 356–358 K, HPLC purity: 99.67%. <sup>1</sup>H MNR (400 MHz, δ (ppm), DMSO-*d*<sub>6</sub>): 8.59 (*d*, *J* = 2.5 Hz, 1 H), 8.40 (*dd*, *J* = 4.7, 1.7 Hz, 1 H), 7.74 (*d*, *J* = 8.3 Hz, 1 H), 7.39 (*dd*, *J* = 8.4, 4.7 Hz, 1 H), 3.78 (*s*, 8 H). <sup>13</sup>C MNR (100 MHz, δ (ppm), DMSO-*d*<sub>6</sub>): 147.41, 146.07, 143.68, 126.44, 124.3. MS (ESI) (*m/z*, %): 194.25 (12), 193.2 ([*M*+1], 100).

**Compound II.** Yield: 28%. Orange crystal, m.p. 343–350 K, HPLC purity: 99.82%. <sup>1</sup>H MNR (400 MHz, δ (ppm), CDCl<sub>3</sub>): 8.86 (*s*, 1 H), 8.45 (*d*, *J* = 4.8 Hz, 1 H), 7.90 (*dd*, *J* = 8.4, 2; 7 Hz, 1 H), 7.83 (*d*, *J* = 8.3 Hz, 1 H), 7.34 (*dd*, *J* = 8.2, 4.8 Hz, 1 H), 7.30–7.23 (*m*, 1 H), 7.17 (*d*, *J* = 7.5 Hz, 1 H), 7.05 (*d*, *J* = 8.2, 1 H), 4.13 (*t*, *J* = 5.9 Hz, 2 H), 2.85 (*t*, *J* = 6.1 Hz, 2 H), 2.21–2.10 (*m*, 2H). <sup>13</sup>C MNR (100 MHz, δ (ppm), CDCl<sub>3</sub>): 147.41, 146.42, 144.76, 139.96, 128.93, 127.52, 126.77, 126.14, 123.75, 123.16, 115.47. MS (ESI) (*m/z*, %): 240.29 (21), 477.29 (7), 239.17 ([*M*+1], 100).



**Figure 5**  
Reaction scheme.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were optimized

geometrically ( $C-H = 0.95-0.99 \text{ \AA}$ ) and refined as riding with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

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## supporting information

*Acta Cryst.* (2023). E79, 74-78 [https://doi.org/10.1107/S2056989023000129]

## Syntheses and crystal structure of 4-[(pyridin-3-yl)diazenyl]morpholine and 1-[(pyridin-3-yl)diazenyl]-1,2,3,4-tetrahydroquinoline

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### Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2020); cell refinement: *CrysAlis PRO* (Rigaku OD, 2020); data reduction: *CrysAlis PRO* (Rigaku OD, 2020); program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *Olex2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009).

### 4-[(Pyridin-3-yl)diazenyl]morpholine (I)

#### Crystal data

$C_9H_{12}N_4O$

$M_r = 192.23$

Monoclinic,  $P2_1/c$

$a = 5.6889$  (3) Å

$b = 8.3058$  (4) Å

$c = 20.3063$  (8) Å

$\beta = 97.370$  (4)°

$V = 951.56$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 408$

$D_x = 1.342$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 10944 reflections

$\theta = 2.0\text{--}36.0^\circ$

$\mu = 0.09$  mm<sup>-1</sup>

$T = 100$  K

(cut) irregular block, colourless

$0.26 \times 0.16 \times 0.14$  mm

#### Data collection

Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector diffractometer

Detector resolution: 10 pixels mm<sup>-1</sup>

profile data from  $\omega$ -scans

Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.187$ ,  $T_{\max} = 1.000$

47217 measured reflections

2464 independent reflections

2280 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 28.7^\circ$ ,  $\theta_{\min} = 2.0^\circ$

$h = -7 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -27 \rightarrow 27$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.104$

$S = 1.05$

2464 reflections

127 parameters

0 restraints

Primary atom site location: iterative

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.3578P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C2	0.62623 (19)	0.79887 (13)	0.51038 (5)	0.0239 (2)
H2A	0.569056	0.840631	0.465513	0.029*
H2B	0.731480	0.881059	0.533953	0.029*
C1	0.41701 (18)	0.76924 (14)	0.54796 (5)	0.0245 (2)
H1A	0.334523	0.872026	0.554175	0.029*
H1B	0.303268	0.695170	0.522423	0.029*
C4	0.65470 (18)	0.55810 (12)	0.61131 (5)	0.0220 (2)
H4A	0.561459	0.464763	0.592211	0.026*
H4B	0.724736	0.530281	0.657060	0.026*
C3	0.84953 (18)	0.59792 (14)	0.56928 (5)	0.0240 (2)
H3A	0.953897	0.681815	0.591964	0.029*
H3B	0.946831	0.500602	0.564925	0.029*
C5	0.25737 (17)	0.66881 (12)	0.75890 (5)	0.0195 (2)
C6	0.05135 (18)	0.76118 (13)	0.75068 (5)	0.0224 (2)
H6	0.000875	0.814030	0.709820	0.027*
C7	−0.07817 (18)	0.77375 (13)	0.80398 (5)	0.0248 (2)
H7	−0.220732	0.834549	0.800057	0.030*
C8	0.00371 (19)	0.69618 (14)	0.86306 (5)	0.0258 (2)
H8	−0.086330	0.706044	0.899152	0.031*
N1	0.50202 (15)	0.69888 (11)	0.61229 (4)	0.02041 (19)
N2	0.36372 (14)	0.72537 (10)	0.65955 (4)	0.01964 (18)
N3	0.40585 (14)	0.63392 (10)	0.70942 (4)	0.01969 (18)
O1	0.75628 (13)	0.65370 (9)	0.50469 (3)	0.02197 (17)
N4	0.20195 (17)	0.60850 (12)	0.87196 (4)	0.0274 (2)
C9	0.32349 (18)	0.59528 (13)	0.82007 (5)	0.0239 (2)
H9	0.463560	0.531802	0.825257	0.029*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C2	0.0285 (5)	0.0252 (5)	0.0193 (4)	0.0003 (4)	0.0080 (4)	0.0021 (4)
C1	0.0244 (5)	0.0300 (5)	0.0202 (4)	0.0050 (4)	0.0068 (4)	0.0045 (4)
C4	0.0239 (5)	0.0249 (5)	0.0182 (4)	0.0031 (4)	0.0070 (3)	0.0021 (4)
C3	0.0213 (4)	0.0339 (5)	0.0175 (4)	0.0037 (4)	0.0051 (3)	0.0012 (4)
C5	0.0211 (4)	0.0214 (4)	0.0169 (4)	−0.0034 (3)	0.0054 (3)	−0.0031 (3)
C6	0.0250 (5)	0.0250 (5)	0.0174 (4)	0.0003 (4)	0.0038 (4)	−0.0003 (4)

C7	0.0237 (5)	0.0264 (5)	0.0254 (5)	0.0014 (4)	0.0075 (4)	−0.0040 (4)
C8	0.0306 (5)	0.0286 (5)	0.0206 (5)	−0.0037 (4)	0.0126 (4)	−0.0036 (4)
N1	0.0214 (4)	0.0245 (4)	0.0167 (4)	0.0018 (3)	0.0074 (3)	0.0006 (3)
N2	0.0195 (4)	0.0225 (4)	0.0176 (4)	−0.0012 (3)	0.0048 (3)	−0.0005 (3)
N3	0.0200 (4)	0.0220 (4)	0.0175 (4)	0.0002 (3)	0.0037 (3)	−0.0005 (3)
O1	0.0243 (4)	0.0279 (4)	0.0147 (3)	0.0010 (3)	0.0064 (3)	−0.0008 (3)
N4	0.0344 (5)	0.0304 (5)	0.0185 (4)	0.0003 (4)	0.0073 (3)	0.0015 (3)
C9	0.0253 (5)	0.0265 (5)	0.0203 (5)	0.0017 (4)	0.0048 (4)	0.0000 (4)

*Geometric parameters (Å, °)*

C2—H2A	0.9900	C5—C6	1.3928 (14)
C2—H2B	0.9900	C5—N3	1.4230 (12)
C2—C1	1.5142 (14)	C5—C9	1.3918 (14)
C2—O1	1.4271 (12)	C6—H6	0.9500
C1—H1A	0.9900	C6—C7	1.3891 (13)
C1—H1B	0.9900	C7—H7	0.9500
C1—N1	1.4559 (12)	C7—C8	1.3886 (15)
C4—H4A	0.9900	C8—H8	0.9500
C4—H4B	0.9900	C8—N4	1.3351 (15)
C4—C3	1.5195 (13)	N1—N2	1.3350 (11)
C4—N1	1.4583 (13)	N2—N3	1.2640 (12)
C3—H3A	0.9900	N4—C9	1.3370 (13)
C3—H3B	0.9900	C9—H9	0.9500
C3—O1	1.4275 (12)		
H2A—C2—H2B	108.1	O1—C3—H3B	109.2
C1—C2—H2A	109.5	C6—C5—N3	126.45 (9)
C1—C2—H2B	109.5	C9—C5—C6	118.40 (9)
O1—C2—H2A	109.5	C9—C5—N3	115.07 (9)
O1—C2—H2B	109.5	C5—C6—H6	121.0
O1—C2—C1	110.65 (8)	C7—C6—C5	118.06 (9)
C2—C1—H1A	109.9	C7—C6—H6	121.0
C2—C1—H1B	109.9	C6—C7—H7	120.5
H1A—C1—H1B	108.3	C8—C7—C6	119.05 (10)
N1—C1—C2	108.99 (8)	C8—C7—H7	120.5
N1—C1—H1A	109.9	C7—C8—H8	118.2
N1—C1—H1B	109.9	N4—C8—C7	123.64 (9)
H4A—C4—H4B	108.4	N4—C8—H8	118.2
C3—C4—H4A	110.1	C1—N1—C4	116.08 (8)
C3—C4—H4B	110.1	N2—N1—C1	114.85 (8)
N1—C4—H4A	110.1	N2—N1—C4	123.29 (8)
N1—C4—H4B	110.1	N3—N2—N1	114.09 (8)
N1—C4—C3	108.17 (8)	N2—N3—C5	112.00 (8)
C4—C3—H3A	109.2	C2—O1—C3	109.59 (7)
C4—C3—H3B	109.2	C8—N4—C9	116.83 (9)
H3A—C3—H3B	107.9	C5—C9—H9	118.0
O1—C3—C4	112.02 (8)	N4—C9—C5	124.01 (10)



O1—C3—H3A	109.2	N4—C9—H9	118.0
C2—C1—N1—C4	−51.60 (12)	C6—C7—C8—N4	−0.19 (17)
C2—C1—N1—N2	154.23 (9)	C7—C8—N4—C9	−0.74 (17)
C1—C2—O1—C3	−62.24 (10)	C8—N4—C9—C5	1.07 (16)
C1—N1—N2—N3	163.81 (9)	N1—C4—C3—O1	−54.11 (11)
C4—C3—O1—C2	61.98 (11)	N1—N2—N3—C5	178.85 (8)
C4—N1—N2—N3	11.73 (13)	N3—C5—C6—C7	176.15 (9)
C3—C4—N1—C1	50.22 (11)	N3—C5—C9—N4	−177.49 (10)
C3—C4—N1—N2	−158.00 (9)	O1—C2—C1—N1	55.81 (11)
C5—C6—C7—C8	0.81 (16)	C9—C5—C6—C7	−0.52 (15)
C6—C5—N3—N2	15.17 (14)	C9—C5—N3—N2	−168.06 (9)
C6—C5—C9—N4	−0.45 (16)		

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
C2—H2A $\cdots$ N4 <sup>i</sup>	0.99	2.67	3.5465 (14)	148
C2—H2B $\cdots$ N4 <sup>ii</sup>	0.99	2.68	3.5607 (14)	149
C3—H3A $\cdots$ N2 <sup>iii</sup>	0.99	2.57	3.4149 (13)	143
C7—H7 $\cdots$ N3 <sup>iv</sup>	0.95	2.70	3.5168 (14)	145

Symmetry codes: (i)  $x, -y+3/2, z-1/2$ ; (ii)  $-x+1, y+1/2, -z+3/2$ ; (iii)  $x+1, y, z$ ; (iv)  $-x, y+1/2, -z+3/2$ .

### 1-[(Pyridin-3-yl)diazenyl]-1,2,3,4-tetrahydroquinoline (II)

#### Crystal data

$\text{C}_{14}\text{H}_{14}\text{N}_4$

$M_r = 238.29$

Monoclinic,  $P2_1/n$

$a = 15.4187$  (2)  $\text{\AA}$

$b = 4.8130$  (1)  $\text{\AA}$

$c = 15.9993$  (3)  $\text{\AA}$

$\beta = 96.115$  (2) $^\circ$

$V = 1180.56$  (4)  $\text{\AA}^3$

$Z = 4$

$F(000) = 504$

$D_x = 1.341$   $\text{Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.54178$   $\text{\AA}$

Cell parameters from 7895 reflections

$\theta = 2.0\text{--}36.0^\circ$

$\mu = 0.66$   $\text{mm}^{-1}$

$T = 100$  K

(cut) irregular block, colourless

$0.24 \times 0.13 \times 0.05$  mm

#### Data collection

Rigaku FRE+ equipped with VHF Varimax  
confocal mirrors and an AFC12 goniometer and  
HyPix 6000 detector  
diffractometer

Detector resolution: 10 pixels  $\text{mm}^{-1}$

profile data from  $\omega$ -scans

Absorption correction: analytical

(CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.187$ ,  $T_{\max} = 1.000$

12295 measured reflections

2142 independent reflections

2010 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 68.2^\circ$ ,  $\theta_{\min} = 5.8^\circ$

$h = -18 \rightarrow 17$

$k = -5 \rightarrow 5$

$l = -19 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.094$

$S = 1.07$

2142 reflections

163 parameters  
 0 restraints  
 Primary atom site location: iterative  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.4022P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

### 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.33530 (7)	0.4875 (2)	0.29703 (7)	0.0231 (3)
H1	0.279699	0.515484	0.266503	0.028*
C2	0.40405 (7)	0.6536 (2)	0.27811 (7)	0.0233 (3)
H2	0.394906	0.793635	0.236253	0.028*
C3	0.48588 (7)	0.6140 (2)	0.32051 (7)	0.0220 (3)
H3	0.533766	0.726560	0.308860	0.026*
C4	0.49636 (7)	0.4040 (2)	0.38099 (7)	0.0190 (3)
C5	0.42285 (7)	0.2529 (2)	0.39706 (7)	0.0222 (3)
H5	0.429669	0.115020	0.439742	0.027*
C6	0.72221 (7)	0.1768 (2)	0.51239 (7)	0.0207 (3)
H6A	0.709233	−0.014174	0.491712	0.025*
H6B	0.677731	0.229166	0.549830	0.025*
C7	0.81190 (7)	0.1837 (2)	0.56141 (7)	0.0226 (3)
H7A	0.815446	0.040449	0.606052	0.027*
H7B	0.821715	0.367432	0.588596	0.027*
C8	0.88195 (7)	0.1301 (2)	0.50322 (7)	0.0206 (3)
H8A	0.940339	0.144430	0.535296	0.025*
H8B	0.875328	−0.060116	0.479846	0.025*
C9	0.87424 (7)	0.3391 (2)	0.43253 (7)	0.0183 (3)
C10	0.79318 (7)	0.4562 (2)	0.40429 (7)	0.0181 (2)
C11	0.78684 (7)	0.6578 (2)	0.34059 (7)	0.0203 (3)
H11	0.732038	0.740036	0.322463	0.024*
C12	0.86059 (7)	0.7368 (2)	0.30415 (7)	0.0219 (3)
H12	0.856037	0.871900	0.260628	0.026*
C13	0.94119 (7)	0.6197 (2)	0.33081 (7)	0.0223 (3)
H13	0.991636	0.673085	0.305469	0.027*
C14	0.94718 (7)	0.4242 (2)	0.39480 (7)	0.0210 (3)
H14	1.002478	0.346140	0.413404	0.025*
N1	0.34340 (6)	0.2893 (2)	0.35634 (6)	0.0251 (2)
N2	0.57576 (6)	0.32558 (19)	0.42816 (6)	0.0196 (2)
N3	0.64124 (6)	0.43689 (19)	0.39911 (6)	0.0189 (2)
N4	0.71783 (6)	0.36903 (19)	0.44088 (6)	0.0187 (2)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0221 (5)	0.0212 (6)	0.0257 (6)	0.0030 (5)	0.0019 (4)	−0.0037 (5)
C2	0.0265 (6)	0.0207 (6)	0.0233 (6)	0.0034 (5)	0.0050 (5)	0.0010 (5)
C3	0.0227 (5)	0.0193 (6)	0.0248 (6)	−0.0010 (4)	0.0066 (4)	−0.0001 (5)
C4	0.0207 (5)	0.0174 (5)	0.0194 (5)	0.0011 (4)	0.0048 (4)	−0.0039 (4)
C5	0.0232 (6)	0.0188 (6)	0.0252 (6)	0.0005 (5)	0.0048 (4)	0.0007 (5)
C6	0.0235 (6)	0.0191 (6)	0.0200 (5)	−0.0015 (4)	0.0052 (4)	0.0030 (4)
C7	0.0257 (6)	0.0220 (6)	0.0198 (5)	−0.0017 (5)	0.0016 (4)	0.0039 (5)
C8	0.0224 (5)	0.0157 (6)	0.0235 (6)	−0.0009 (4)	0.0012 (4)	0.0017 (4)
C9	0.0228 (5)	0.0129 (5)	0.0193 (5)	−0.0013 (4)	0.0023 (4)	−0.0028 (4)
C10	0.0209 (5)	0.0155 (5)	0.0180 (5)	−0.0033 (4)	0.0035 (4)	−0.0029 (4)
C11	0.0222 (5)	0.0178 (6)	0.0206 (5)	−0.0004 (4)	0.0008 (4)	0.0001 (4)
C12	0.0282 (6)	0.0190 (6)	0.0188 (6)	−0.0034 (5)	0.0033 (4)	0.0018 (4)
C13	0.0235 (6)	0.0210 (6)	0.0234 (6)	−0.0033 (5)	0.0076 (4)	−0.0013 (5)
C14	0.0210 (5)	0.0175 (6)	0.0250 (6)	0.0010 (4)	0.0041 (4)	−0.0021 (4)
N1	0.0225 (5)	0.0215 (5)	0.0314 (6)	−0.0004 (4)	0.0031 (4)	0.0000 (4)
N2	0.0204 (5)	0.0177 (5)	0.0213 (5)	−0.0014 (4)	0.0052 (4)	−0.0014 (4)
N3	0.0199 (5)	0.0171 (5)	0.0199 (5)	−0.0007 (4)	0.0033 (4)	−0.0020 (4)
N4	0.0192 (5)	0.0181 (5)	0.0188 (5)	−0.0011 (4)	0.0022 (4)	0.0021 (4)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C1—H1	0.9500	C7—C8	1.5212 (15)
C1—C2	1.3865 (16)	C8—H8A	0.9900
C1—N1	1.3422 (16)	C8—H8B	0.9900
C2—H2	0.9500	C8—C9	1.5090 (15)
C2—C3	1.3807 (16)	C9—C10	1.4013 (15)
C3—H3	0.9500	C9—C14	1.3934 (15)
C3—C4	1.3967 (16)	C10—C11	1.4030 (15)
C4—C5	1.3935 (16)	C10—N4	1.4189 (13)
C4—N2	1.4192 (14)	C11—H11	0.9500
C5—H5	0.9500	C11—C12	1.3851 (16)
C5—N1	1.3363 (15)	C12—H12	0.9500
C6—H6A	0.9900	C12—C13	1.3895 (16)
C6—H6B	0.9900	C13—H13	0.9500
C6—C7	1.5159 (15)	C13—C14	1.3864 (16)
C6—N4	1.4674 (14)	C14—H14	0.9500
C7—H7A	0.9900	N2—N3	1.2737 (13)
C7—H7B	0.9900	N3—N4	1.3341 (12)
C2—C1—H1	118.4	H8A—C8—H8B	108.2
N1—C1—H1	118.4	C9—C8—C7	109.95 (9)
N1—C1—C2	123.27 (10)	C9—C8—H8A	109.7
C1—C2—H2	120.2	C9—C8—H8B	109.7
C3—C2—C1	119.54 (11)	C10—C9—C8	120.41 (10)
C3—C2—H2	120.2	C14—C9—C8	121.19 (10)

C2—C3—H3	120.9	C14—C9—C10	118.39 (10)
C2—C3—C4	118.19 (10)	C9—C10—C11	120.21 (10)
C4—C3—H3	120.9	C9—C10—N4	119.30 (10)
C3—C4—N2	126.19 (10)	C11—C10—N4	120.49 (10)
C5—C4—C3	117.99 (10)	C10—C11—H11	120.0
C5—C4—N2	115.82 (10)	C12—C11—C10	119.91 (10)
C4—C5—H5	117.9	C12—C11—H11	120.0
N1—C5—C4	124.27 (11)	C11—C12—H12	119.8
N1—C5—H5	117.9	C11—C12—C13	120.47 (10)
H6A—C6—H6B	108.1	C13—C12—H12	119.8
C7—C6—H6A	109.5	C12—C13—H13	120.4
C7—C6—H6B	109.5	C14—C13—C12	119.27 (10)
N4—C6—H6A	109.5	C14—C13—H13	120.4
N4—C6—H6B	109.5	C9—C14—H14	119.1
N4—C6—C7	110.68 (9)	C13—C14—C9	121.74 (10)
C6—C7—H7A	109.6	C13—C14—H14	119.1
C6—C7—H7B	109.6	C5—N1—C1	116.69 (10)
C6—C7—C8	110.35 (9)	N3—N2—C4	111.49 (9)
H7A—C7—H7B	108.1	N2—N3—N4	114.08 (9)
C8—C7—H7A	109.6	C10—N4—C6	122.45 (9)
C8—C7—H7B	109.6	N3—N4—C6	120.64 (9)
C7—C8—H8A	109.7	N3—N4—C10	116.17 (9)
C7—C8—H8B	109.7		
C1—C2—C3—C4	0.55 (17)	C9—C10—C11—C12	1.46 (16)
C2—C1—N1—C5	−1.03 (17)	C9—C10—N4—C6	5.22 (15)
C2—C3—C4—C5	−2.17 (16)	C9—C10—N4—N3	−164.91 (9)
C2—C3—C4—N2	177.24 (10)	C10—C9—C14—C13	0.03 (16)
C3—C4—C5—N1	2.38 (17)	C10—C11—C12—C13	−0.64 (17)
C3—C4—N2—N3	−11.45 (15)	C11—C10—N4—C6	−174.70 (10)
C4—C5—N1—C1	−0.77 (17)	C11—C10—N4—N3	15.17 (15)
C4—N2—N3—N4	−179.67 (8)	C11—C12—C13—C14	−0.47 (17)
C5—C4—N2—N3	167.97 (10)	C12—C13—C14—C9	0.78 (17)
C6—C7—C8—C9	56.49 (12)	C14—C9—C10—C11	−1.15 (16)
C7—C6—N4—C10	23.41 (14)	C14—C9—C10—N4	178.93 (9)
C7—C6—N4—N3	−166.89 (9)	N1—C1—C2—C3	1.13 (18)
C7—C8—C9—C10	−28.76 (14)	N2—C4—C5—N1	−177.08 (10)
C7—C8—C9—C14	150.10 (10)	N2—N3—N4—C6	1.30 (14)
C8—C9—C10—C11	177.73 (10)	N2—N3—N4—C10	171.63 (9)
C8—C9—C10—N4	−2.19 (15)	N4—C6—C7—C8	−53.93 (12)
C8—C9—C14—C13	−178.84 (10)	N4—C10—C11—C12	−178.62 (10)

## 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>
C12—H12 $\cdots$ N3 <sup>i</sup>	0.95	2.58	3.3890 (14)	143

Symmetry code: (i)  $-x+3/2, y+1/2, -z+1/2$ .