IUCrData

ISSN 2414-3146

4-Amino-5-{[cyclohexyl(methyl)amino]methyl}isophthalonitrile

Muhammad Sharif,[a]* Rauf Razzaq,[b] Ralf Jackstell[b] and Anke Spannenberg[b]

[a]Department of Chemistry, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Kingdom of , Saudi Arabia, and [b]Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany. *Correspondence e-mail: msharif@kfupm.edu.sa

Received 18 September 2019
Accepted 8 October 2019

Edited by J. Simpson, University of Otago, New Zealand

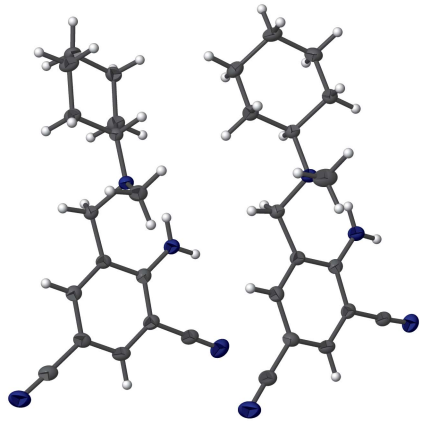
Keywords: crystal structure; cyanation; bromhexine.

CCDC references: 1957989; 1957989

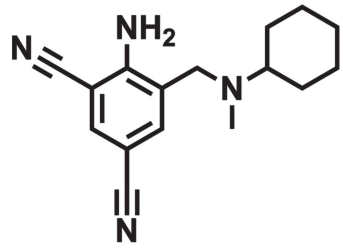
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_{20}N_4$, was synthesized by cyanation of bromhexine. The compound crystallizes with two unique molecules in the asymmetric unit. The substituted aniline and cyclohexane rings are inclined to one another by 37.26 (6)° in one molecule and by 22.84 (7)° in the other. In the crystal packing, intra- and intermolecular N—H···N hydrogen bonds and an intermolecular C—H···N contact were observed.

3D view



Chemical scheme



Structure description

The title compound is an aniline derivative with two cyano groups at the *ortho* and *para* positions. The other *ortho* position of the aniline core is occupied by a [cyclohexyl(methyl)amino]methyl substituent. Two unique molecules are present in the asymmetric unit, with intramolecular N2—H2*A*···N1 and N6—H6*A*···N5 hydrogen bonds (Fig. 1 and Table 1). The cyclohexyl ring adopts a chair conformation. In the crystal, intermolecular N—H···N and C—H···N hydrogen bonds (Table 1) stack the molecules along the *a*-axis direction (Fig. 2).

Synthesis and crystallization

The title compound was obtained as the main product while synthesizing the mono- and dicyano derivatives of the biologically active known mucolytic drug bromhexine (Bateman, 1971; Sharif *et al.*, 2014; Zanasi *et al.*, 2017).

The reaction was carried out in an Ace pressure tube. A mixture of bromhexine (2.0 mmol, 752 mg), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.8 mmol, 338 mg), Na_2CO_3 (2.4 mmol, 254 mg), CuI (0.2 mmol, 38 mg), 1-butylimidazole (4.0 mmol, 497 mg) and *o*-xylene (2.0 ml) was stirred at 433 K for 24 h. Next the reaction mixture was quenched with water

OPEN ACCESS

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1	0.909 (15)	2.205 (15)	2.8867 (14)	131.3 (12)
N6—H6A···N5	0.871 (15)	2.242 (15)	2.8824 (14)	130.3 (13)
N2—H2B···N7^{i}	0.889 (15)	2.122 (15)	2.9894 (15)	164.8 (12)
N6—H6A···N4^{ii}	0.871 (15)	2.457 (14)	3.0268 (14)	123.5 (11)
N6—H6B···N3^{i}	0.887 (14)	2.526 (15)	3.3780 (17)	161.3 (12)
C16—H16B···N8^{iii}	0.99	2.42	3.4095 (18)	177

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

and diluted with dichloromethane. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 20 ml). The combined organic layers were dried on anhydrous Na_2SO_4. After filtering, the solvent was removed *in vacuo* and the product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane) (yield 62%, 332 mg). Crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of ethyl acetate and *n*-heptane (1:1 *v*/*v*).

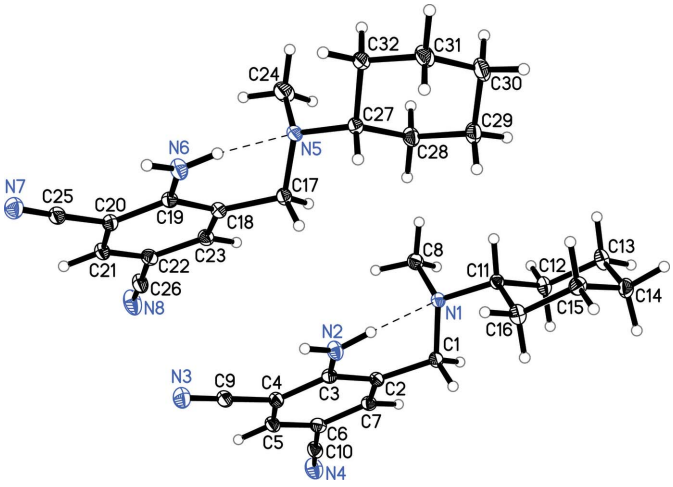


Figure 1
The asymmetric unit of the title compound, with intramolecular hydrogen bonds drawn as dashed lines. Displacement ellipsoids are shown at the 30% probability level.

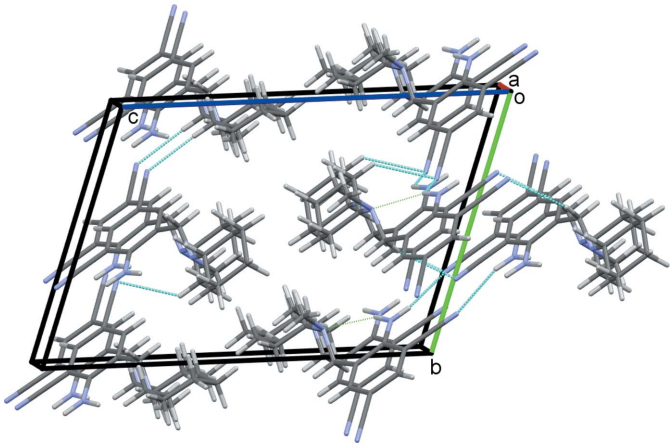


Figure 2
The overall packing of the title compound, with hydrogen bonds drawn as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{20}N_4$
M_r	268.36
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	8.7319 (4), 11.3091 (5), 16.1220 (7)
α, β, γ (°)	69.599 (3), 77.168 (4), 81.042 (4)
V (Å^3)	1449.57 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.50 × 0.44 × 0.26
Data collection	
Diffractometer	Stoe IPDS II
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27082, 7789, 5101
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.091, 0.85
No. of reflections	7789
No. of parameters	379
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.22

Computer programs: *X-AREA* (Stoe & Cie, 2005), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04–1.54 (*m*, 6H), 1.73 (*t*, 4H, J = 13.7 Hz), 2.09 (*s*, 3H), 2.04 (*t*, 1H, J = 10.3 Hz), 3.68 (*s*, 2H), 5.07 (*s*, 2H, NH_2), 7.12–7.18 (*m*, 2H); ^{13}C NMR ($CDCl_3$): δ 24.7 ($2CH_2$), 25.1 (CH_2), 27.0 ($2CH_2$), 35.4 (CH_3), 56.4 (CH_2), 60.1 (CH), 95.2 (C), 98.3 (C), 114.9 (C), 116.2 (C), 123.2 (C), 134.8 (CH), 135.1 (CH), 152.7 (C); GC—MS (EI, 70 eV): m/z = 268 (M^+, 29), 225 (74), 197 (31), 185 (32), 156 (49), 70 (100); HRMS (ESI): calculated for $C_{16}H_{20}N_4$ ($[M + H]^+$) 268,16880 found 268.16810.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

Funding for this research was provided by: Deanship of Scientific Research (DSR) at King Fahd University of Petroleum and Minerals (KFUPM) *via* project number IN161012.

References

Bateman, P. P. (1971). *Med. J. Aust.* **1**, 963–965.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Sharif, M., Pews-Davtyan, A., Lukas, J., Schranck, J., Langer, P., Rolfs, A. & Beller, M. (2014). *Eur. J. Org. Chem.* **2014**, 222–230.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Stoe & Cie (2005). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zanasi, A., Mazzolini, M. & Kantar, A. (2017). *Multidiscip. Respir. Med.* **12**, article No. 7.

full crystallographic data

IUCrData (2019). **4**, x191369 [https://doi.org/10.1107/S2414314619013695]

4-Amino-5-{[cyclohexyl(methyl)amino]methyl}isophthalonitrile

Muhammad Sharif, Rauf Razzaq, Ralf Jackstell and Anke Spannenberg

4-Amino-5-{[cyclohexyl(methyl)amino]methyl}isophthalonitrile

Crystal data

$C_{16}H_{20}N_4$
$M_r = 268.36$
Triclinic, $P\overline{1}$
$a = 8.7319$ (4) Å
$b = 11.3091$ (5) Å
$c = 16.1220$ (7) Å
$\alpha = 69.599$ (3)°
$\beta = 77.168$ (4)°
$\gamma = 81.042$ (4)°
$V = 1449.57$ (12) Å^3
$Z = 4$
$F(000) = 576$
$D_x = 1.230$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 508 reflections
$\theta = 1.9$–29.6°
$\mu = 0.08$ mm^{-1}
$T = 150$ K
Prism, colourless
0.50 × 0.44 × 0.26 mm

Data collection

Stoe IPDS II diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
27082 measured reflections
7789 independent reflections
5101 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 29.2°$, $\theta_{min} = 1.9°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.091$
$S = 0.85$
7789 reflections
379 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.01262 (12)	1.01919 (10)	0.24558 (7)	0.0222 (2)
H1A	0.0827	1.0552	0.2036	0.027*
H1B	−0.0509	1.0712	0.2856	0.027*
C2	−0.13801 (12)	1.02839 (10)	0.19187 (7)	0.0208 (2)
C3	−0.11999 (12)	0.95410 (10)	0.13430 (7)	0.0213 (2)
C4	−0.23642 (12)	0.97527 (11)	0.08020 (7)	0.0236 (2)
C5	−0.36355 (12)	1.06504 (11)	0.08291 (7)	0.0254 (2)
H5	−0.4393	1.0783	0.0457	0.030*
C6	−0.37958 (12)	1.13498 (11)	0.13990 (7)	0.0243 (2)
C7	−0.26577 (12)	1.11506 (11)	0.19415 (7)	0.0225 (2)
H7	−0.2780	1.1632	0.2335	0.027*
C8	−0.10479 (12)	0.83245 (11)	0.36453 (7)	0.0263 (2)
H8A	−0.1505	0.8852	0.4024	0.039*
H8B	−0.0713	0.7477	0.4024	0.039*
H8C	−0.1838	0.8259	0.3320	0.039*
C9	−0.22145 (13)	0.90380 (11)	0.02018 (7)	0.0266 (2)
C10	−0.50693 (13)	1.23112 (12)	0.14213 (8)	0.0285 (3)
C11	0.16669 (11)	0.87861 (10)	0.34391 (7)	0.0195 (2)
H11	0.1816	0.7876	0.3813	0.023*
C12	0.14675 (12)	0.95503 (12)	0.40779 (7)	0.0247 (2)
H12A	0.0489	0.9349	0.4529	0.030*
H12B	0.1373	1.0466	0.3734	0.030*
C13	0.28799 (13)	0.92430 (13)	0.45572 (8)	0.0308 (3)
H13A	0.2760	0.9783	0.4941	0.037*
H13B	0.2902	0.8348	0.4952	0.037*
C14	0.44315 (13)	0.94597 (12)	0.38886 (8)	0.0289 (3)
H14A	0.4474	1.0376	0.3552	0.035*
H14B	0.5322	0.9178	0.4220	0.035*
C15	0.45983 (12)	0.87413 (11)	0.32331 (8)	0.0263 (2)
H15A	0.4685	0.7820	0.3562	0.032*
H15B	0.5576	0.8947	0.2782	0.032*
C16	0.31880 (12)	0.90780 (12)	0.27543 (7)	0.0262 (2)
H16A	0.3136	0.9989	0.2395	0.031*
H16B	0.3315	0.8585	0.2338	0.031*
C17	−0.01014 (13)	0.52836 (11)	0.24386 (7)	0.0239 (2)
H17A	0.0779	0.5734	0.2000	0.029*
H17B	−0.0610	0.5811	0.2818	0.029*
C18	−0.12872 (12)	0.51462 (10)	0.19315 (7)	0.0219 (2)
C19	−0.08922 (12)	0.43587 (10)	0.13786 (7)	0.0211 (2)
C20	−0.19522 (12)	0.44230 (11)	0.08108 (7)	0.0223 (2)
C21	−0.33528 (12)	0.51940 (11)	0.08063 (7)	0.0246 (2)
H21	−0.4036	0.5230	0.0413	0.030*
C22	−0.37496 (12)	0.59069 (11)	0.13733 (7)	0.0246 (2)
C23	−0.26946 (13)	0.58799 (11)	0.19267 (7)	0.0239 (2)
H23	−0.2966	0.6386	0.2309	0.029*

C24	−0.06570 (14)	0.34748 (14)	0.37635 (8)	0.0376 (3)
H24A	−0.1018	0.4016	0.4142	0.056*
H24B	−0.0208	0.2654	0.4120	0.056*
H24C	−0.1551	0.3348	0.3537	0.056*
C25	−0.15260 (13)	0.36861 (11)	0.02185 (7)	0.0241 (2)
C26	−0.52121 (14)	0.66902 (12)	0.13769 (8)	0.0304 (3)
C27	0.20241 (12)	0.42067 (10)	0.32479 (7)	0.0214 (2)
H27	0.2718	0.4642	0.2670	0.026*
C28	0.18887 (14)	0.50117 (12)	0.38536 (8)	0.0284 (2)
H28A	0.1232	0.4607	0.4444	0.034*
H28B	0.1365	0.5858	0.3577	0.034*
C29	0.35188 (15)	0.51571 (12)	0.39894 (9)	0.0331 (3)
H29A	0.4128	0.5652	0.3408	0.040*
H29B	0.3400	0.5633	0.4415	0.040*
C30	0.44236 (15)	0.38784 (13)	0.43528 (9)	0.0363 (3)
H30A	0.5502	0.4009	0.4383	0.044*
H30B	0.3891	0.3429	0.4970	0.044*
C31	0.45189 (14)	0.30724 (13)	0.37569 (9)	0.0342 (3)
H31A	0.5053	0.2229	0.4027	0.041*
H31B	0.5153	0.3477	0.3159	0.041*
C32	0.28789 (13)	0.29169 (11)	0.36465 (8)	0.0271 (2)
H32A	0.2970	0.2406	0.3246	0.033*
H32B	0.2265	0.2463	0.4239	0.033*
N1	0.03069 (10)	0.88957 (8)	0.30035 (6)	0.02006 (18)
N2	0.00398 (11)	0.86860 (10)	0.13082 (7)	0.0268 (2)
N3	−0.20948 (13)	0.84663 (11)	−0.02760 (7)	0.0370 (3)
N4	−0.60595 (12)	1.30916 (12)	0.14443 (8)	0.0395 (3)
N5	0.05375 (10)	0.40784 (9)	0.30093 (6)	0.02239 (19)
N6	0.04566 (11)	0.36081 (10)	0.13743 (7)	0.0273 (2)
N7	−0.11321 (12)	0.30789 (10)	−0.02396 (7)	0.0317 (2)
N8	−0.63810 (13)	0.72932 (12)	0.13812 (8)	0.0451 (3)
H2A	0.0688 (16)	0.8538 (13)	0.1710 (10)	0.037 (4)*
H2B	0.0211 (16)	0.8229 (14)	0.0941 (10)	0.037 (4)*
H6A	0.1067 (17)	0.3564 (14)	0.1746 (10)	0.037 (4)*
H6B	0.0743 (15)	0.3178 (13)	0.0990 (9)	0.031 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0239 (5)	0.0222 (6)	0.0228 (5)	−0.0015 (4)	−0.0081 (4)	−0.0080 (4)
C2	0.0213 (5)	0.0223 (5)	0.0184 (5)	−0.0028 (4)	−0.0047 (4)	−0.0052 (4)
C3	0.0220 (5)	0.0226 (6)	0.0184 (5)	−0.0049 (4)	−0.0024 (4)	−0.0049 (4)
C4	0.0249 (5)	0.0270 (6)	0.0193 (5)	−0.0066 (4)	−0.0042 (4)	−0.0062 (4)
C5	0.0228 (5)	0.0308 (6)	0.0215 (5)	−0.0053 (4)	−0.0075 (4)	−0.0038 (5)
C6	0.0201 (5)	0.0265 (6)	0.0229 (5)	−0.0018 (4)	−0.0039 (4)	−0.0039 (4)
C7	0.0229 (5)	0.0239 (6)	0.0195 (5)	−0.0035 (4)	−0.0028 (4)	−0.0058 (4)
C8	0.0220 (5)	0.0297 (6)	0.0255 (5)	−0.0042 (4)	−0.0050 (4)	−0.0056 (5)
C9	0.0274 (5)	0.0304 (6)	0.0222 (5)	−0.0070 (5)	−0.0069 (4)	−0.0053 (5)

C10	0.0234 (5)	0.0353 (7)	0.0271 (6)	−0.0030 (5)	−0.0077 (4)	−0.0086 (5)
C11	0.0187 (5)	0.0195 (5)	0.0215 (5)	0.0002 (4)	−0.0061 (4)	−0.0073 (4)
C12	0.0214 (5)	0.0314 (6)	0.0253 (5)	0.0009 (4)	−0.0061 (4)	−0.0146 (5)
C13	0.0284 (6)	0.0421 (7)	0.0284 (6)	−0.0011 (5)	−0.0103 (5)	−0.0171 (5)
C14	0.0230 (5)	0.0301 (6)	0.0375 (6)	−0.0023 (5)	−0.0126 (5)	−0.0113 (5)
C15	0.0186 (5)	0.0262 (6)	0.0330 (6)	−0.0003 (4)	−0.0048 (4)	−0.0090 (5)
C16	0.0202 (5)	0.0353 (7)	0.0251 (5)	−0.0018 (4)	−0.0017 (4)	−0.0139 (5)
C17	0.0256 (5)	0.0235 (6)	0.0252 (5)	−0.0007 (4)	−0.0100 (4)	−0.0085 (4)
C18	0.0235 (5)	0.0225 (6)	0.0202 (5)	−0.0024 (4)	−0.0064 (4)	−0.0058 (4)
C19	0.0220 (5)	0.0212 (5)	0.0195 (5)	−0.0036 (4)	−0.0037 (4)	−0.0050 (4)
C20	0.0256 (5)	0.0227 (6)	0.0199 (5)	−0.0045 (4)	−0.0043 (4)	−0.0072 (4)
C21	0.0244 (5)	0.0270 (6)	0.0240 (5)	−0.0033 (4)	−0.0097 (4)	−0.0064 (5)
C22	0.0229 (5)	0.0254 (6)	0.0251 (5)	0.0008 (4)	−0.0078 (4)	−0.0066 (5)
C23	0.0270 (5)	0.0232 (6)	0.0223 (5)	−0.0001 (4)	−0.0064 (4)	−0.0082 (4)
C24	0.0301 (6)	0.0475 (8)	0.0292 (6)	−0.0124 (6)	−0.0064 (5)	−0.0006 (6)
C25	0.0245 (5)	0.0255 (6)	0.0223 (5)	−0.0051 (4)	−0.0062 (4)	−0.0056 (5)
C26	0.0314 (6)	0.0335 (7)	0.0313 (6)	0.0032 (5)	−0.0134 (5)	−0.0146 (5)
C27	0.0215 (5)	0.0226 (5)	0.0215 (5)	−0.0016 (4)	−0.0069 (4)	−0.0072 (4)
C28	0.0309 (6)	0.0284 (6)	0.0315 (6)	0.0034 (5)	−0.0126 (5)	−0.0151 (5)
C29	0.0388 (7)	0.0327 (7)	0.0368 (6)	−0.0026 (5)	−0.0173 (5)	−0.0163 (6)
C30	0.0362 (6)	0.0405 (8)	0.0409 (7)	0.0015 (5)	−0.0227 (6)	−0.0163 (6)
C31	0.0327 (6)	0.0333 (7)	0.0414 (7)	0.0077 (5)	−0.0200 (5)	−0.0146 (6)
C32	0.0323 (6)	0.0232 (6)	0.0287 (6)	0.0011 (5)	−0.0136 (5)	−0.0084 (5)
N1	0.0187 (4)	0.0215 (5)	0.0206 (4)	−0.0019 (3)	−0.0054 (3)	−0.0065 (4)
N2	0.0279 (5)	0.0298 (5)	0.0276 (5)	0.0026 (4)	−0.0090 (4)	−0.0153 (4)
N3	0.0451 (6)	0.0405 (7)	0.0303 (5)	−0.0107 (5)	−0.0088 (5)	−0.0136 (5)
N4	0.0289 (5)	0.0463 (7)	0.0464 (7)	0.0073 (5)	−0.0152 (5)	−0.0182 (6)
N5	0.0224 (4)	0.0239 (5)	0.0209 (4)	−0.0034 (4)	−0.0080 (3)	−0.0042 (4)
N6	0.0256 (5)	0.0316 (6)	0.0294 (5)	0.0038 (4)	−0.0096 (4)	−0.0154 (5)
N7	0.0367 (5)	0.0329 (6)	0.0282 (5)	−0.0056 (4)	−0.0044 (4)	−0.0133 (5)
N8	0.0387 (6)	0.0550 (8)	0.0541 (7)	0.0177 (6)	−0.0243 (5)	−0.0326 (6)

Geometric parameters (Å, º)

C1—N1	1.4644 (14)	C17—H17A	0.9900
C1—C2	1.5107 (14)	C17—H17B	0.9900
C1—H1A	0.9900	C18—C23	1.3714 (15)
C1—H1B	0.9900	C18—C19	1.4241 (15)
C2—C7	1.3686 (15)	C19—N6	1.3405 (14)
C2—C3	1.4248 (15)	C19—C20	1.4174 (14)
C3—N2	1.3397 (14)	C20—C21	1.3869 (15)
C3—C4	1.4226 (14)	C20—C25	1.4301 (16)
C4—C5	1.3868 (16)	C21—C22	1.3754 (16)
C4—C9	1.4363 (16)	C21—H21	0.9500
C5—C6	1.3801 (16)	C22—C23	1.4082 (15)
C5—H5	0.9500	C22—C26	1.4365 (15)
C6—C7	1.4079 (14)	C23—H23	0.9500
C6—C10	1.4328 (16)	C24—N5	1.4533 (15)

C7—H7	0.9500	C24—H24A	0.9800
C8—N1	1.4546 (14)	C24—H24B	0.9800
C8—H8A	0.9800	C24—H24C	0.9800
C8—H8B	0.9800	C25—N7	1.1412 (15)
C8—H8C	0.9800	C26—N8	1.1359 (15)
C9—N3	1.1457 (15)	C27—N5	1.4743 (13)
C10—N4	1.1397 (15)	C27—C32	1.5226 (15)
C11—N1	1.4774 (12)	C27—C28	1.5268 (15)
C11—C16	1.5241 (14)	C27—H27	1.0000
C11—C12	1.5271 (15)	C28—C29	1.5289 (16)
C11—H11	1.0000	C28—H28A	0.9900
C12—C13	1.5302 (14)	C28—H28B	0.9900
C12—H12A	0.9900	C29—C30	1.5224 (18)
C12—H12B	0.9900	C29—H29A	0.9900
C13—C14	1.5258 (17)	C29—H29B	0.9900
C13—H13A	0.9900	C30—C31	1.5205 (18)
C13—H13B	0.9900	C30—H30A	0.9900
C14—C15	1.5137 (17)	C30—H30B	0.9900
C14—H14A	0.9900	C31—C32	1.5255 (16)
C14—H14B	0.9900	C31—H31A	0.9900
C15—C16	1.5261 (15)	C31—H31B	0.9900
C15—H15A	0.9900	C32—H32A	0.9900
C15—H15B	0.9900	C32—H32B	0.9900
C16—H16A	0.9900	N2—H2A	0.909 (15)
C16—H16B	0.9900	N2—H2B	0.889 (15)
C17—N5	1.4603 (14)	N6—H6A	0.871 (15)
C17—C18	1.5098 (14)	N6—H6B	0.887 (14)

N1—C1—C2	113.66 (9)	C23—C18—C19	119.23 (9)
N1—C1—H1A	108.8	C23—C18—C17	119.98 (10)
C2—C1—H1A	108.8	C19—C18—C17	120.45 (9)
N1—C1—H1B	108.8	N6—C19—C20	120.95 (10)
C2—C1—H1B	108.8	N6—C19—C18	121.30 (10)
H1A—C1—H1B	107.7	C20—C19—C18	117.73 (9)
C7—C2—C3	119.48 (9)	C21—C20—C19	121.74 (10)
C7—C2—C1	119.49 (10)	C21—C20—C25	120.11 (10)
C3—C2—C1	120.90 (9)	C19—C20—C25	118.13 (10)
N2—C3—C4	121.56 (10)	C22—C21—C20	119.79 (10)
N2—C3—C2	120.66 (9)	C22—C21—H21	120.1
C4—C3—C2	117.77 (9)	C20—C21—H21	120.1
C5—C4—C3	121.53 (10)	C21—C22—C23	119.32 (10)
C5—C4—C9	118.89 (10)	C21—C22—C26	119.67 (10)
C3—C4—C9	119.57 (10)	C23—C22—C26	121.00 (10)
C6—C5—C4	119.72 (10)	C18—C23—C22	122.11 (10)
C6—C5—H5	120.1	C18—C23—H23	118.9
C4—C5—H5	120.1	C22—C23—H23	118.9
C5—C6—C7	119.55 (10)	N5—C24—H24A	109.5
C5—C6—C10	120.99 (10)	N5—C24—H24B	109.5

C7—C6—C10	119.41 (10)	H24A—C24—H24B	109.5
C2—C7—C6	121.94 (10)	N5—C24—H24C	109.5
C2—C7—H7	119.0	H24A—C24—H24C	109.5
C6—C7—H7	119.0	H24B—C24—H24C	109.5
N1—C8—H8A	109.5	N7—C25—C20	177.23 (12)
N1—C8—H8B	109.5	N8—C26—C22	178.88 (14)
H8A—C8—H8B	109.5	N5—C27—C32	111.22 (9)
N1—C8—H8C	109.5	N5—C27—C28	115.77 (9)
H8A—C8—H8C	109.5	C32—C27—C28	110.22 (9)
H8B—C8—H8C	109.5	N5—C27—H27	106.3
N3—C9—C4	179.90 (15)	C32—C27—H27	106.3
N4—C10—C6	178.36 (13)	C28—C27—H27	106.3
N1—C11—C16	111.93 (8)	C27—C28—C29	110.63 (9)
N1—C11—C12	115.86 (8)	C27—C28—H28A	109.5
C16—C11—C12	109.60 (9)	C29—C28—H28A	109.5
N1—C11—H11	106.3	C27—C28—H28B	109.5
C16—C11—H11	106.3	C29—C28—H28B	109.5
C12—C11—H11	106.3	H28A—C28—H28B	108.1
C11—C12—C13	110.45 (9)	C30—C29—C28	111.73 (10)
C11—C12—H12A	109.6	C30—C29—H29A	109.3
C13—C12—H12A	109.6	C28—C29—H29A	109.3
C11—C12—H12B	109.6	C30—C29—H29B	109.3
C13—C12—H12B	109.6	C28—C29—H29B	109.3
H12A—C12—H12B	108.1	H29A—C29—H29B	107.9
C14—C13—C12	111.63 (9)	C31—C30—C29	111.03 (10)
C14—C13—H13A	109.3	C31—C30—H30A	109.4
C12—C13—H13A	109.3	C29—C30—H30A	109.4
C14—C13—H13B	109.3	C31—C30—H30B	109.4
C12—C13—H13B	109.3	C29—C30—H30B	109.4
H13A—C13—H13B	108.0	H30A—C30—H30B	108.0
C15—C14—C13	111.16 (10)	C30—C31—C32	110.99 (10)
C15—C14—H14A	109.4	C30—C31—H31A	109.4
C13—C14—H14A	109.4	C32—C31—H31A	109.4
C15—C14—H14B	109.4	C30—C31—H31B	109.4
C13—C14—H14B	109.4	C32—C31—H31B	109.4
H14A—C14—H14B	108.0	H31A—C31—H31B	108.0
C14—C15—C16	111.16 (9)	C27—C32—C31	110.27 (10)
C14—C15—H15A	109.4	C27—C32—H32A	109.6
C16—C15—H15A	109.4	C31—C32—H32A	109.6
C14—C15—H15B	109.4	C27—C32—H32B	109.6
C16—C15—H15B	109.4	C31—C32—H32B	109.6
H15A—C15—H15B	108.0	H32A—C32—H32B	108.1
C11—C16—C15	110.21 (9)	C8—N1—C1	111.26 (8)
C11—C16—H16A	109.6	C8—N1—C11	112.12 (8)
C15—C16—H16A	109.6	C1—N1—C11	113.63 (8)
C11—C16—H16B	109.6	C3—N2—H2A	117.3 (9)
C15—C16—H16B	109.6	C3—N2—H2B	123.1 (9)
H16A—C16—H16B	108.1	H2A—N2—H2B	119.4 (13)

N5—C17—C18	113.69 (9)	C24—N5—C17	111.28 (9)
N5—C17—H17A	108.8	C24—N5—C27	115.29 (9)
C18—C17—H17A	108.8	C17—N5—C27	111.64 (9)
N5—C17—H17B	108.8	C19—N6—H6A	119.0 (9)
C18—C17—H17B	108.8	C19—N6—H6B	121.0 (8)
H17A—C17—H17B	107.7	H6A—N6—H6B	120.0 (12)
N1—C1—C2—C7	131.11 (11)	N6—C19—C20—C21	179.99 (11)
N1—C1—C2—C3	−53.09 (13)	C18—C19—C20—C21	−1.88 (16)
C7—C2—C3—N2	−179.99 (10)	N6—C19—C20—C25	−1.37 (16)
C1—C2—C3—N2	4.21 (16)	C18—C19—C20—C25	176.76 (10)
C7—C2—C3—C4	0.87 (15)	C19—C20—C21—C22	−0.93 (17)
C1—C2—C3—C4	−174.92 (10)	C25—C20—C21—C22	−179.54 (11)
N2—C3—C4—C5	−179.08 (11)	C20—C21—C22—C23	2.44 (17)
C2—C3—C4—C5	0.04 (15)	C20—C21—C22—C26	−179.08 (11)
N2—C3—C4—C9	−0.09 (16)	C19—C18—C23—C22	−1.72 (17)
C2—C3—C4—C9	179.04 (10)	C17—C18—C23—C22	171.65 (10)
C3—C4—C5—C6	−0.74 (17)	C21—C22—C23—C18	−1.13 (17)
C9—C4—C5—C6	−179.74 (10)	C26—C22—C23—C18	−179.59 (11)
C4—C5—C6—C7	0.53 (17)	N5—C27—C28—C29	−175.50 (9)
C4—C5—C6—C10	178.04 (11)	C32—C27—C28—C29	57.20 (13)
C3—C2—C7—C6	−1.12 (16)	C27—C28—C29—C30	−55.22 (14)
C1—C2—C7—C6	174.74 (10)	C28—C29—C30—C31	54.35 (15)
C5—C6—C7—C2	0.41 (16)	C29—C30—C31—C32	−55.62 (15)
C10—C6—C7—C2	−177.14 (11)	N5—C27—C32—C31	171.53 (9)
N1—C11—C12—C13	173.93 (9)	C28—C27—C32—C31	−58.69 (12)
C16—C11—C12—C13	−58.25 (12)	C30—C31—C32—C27	58.03 (14)
C11—C12—C13—C14	55.70 (14)	C2—C1—N1—C8	−59.53 (11)
C12—C13—C14—C15	−53.95 (14)	C2—C1—N1—C11	172.79 (8)
C13—C14—C15—C16	55.06 (13)	C16—C11—N1—C8	165.75 (9)
N1—C11—C16—C15	−170.51 (9)	C12—C11—N1—C8	−67.60 (12)
C12—C11—C16—C15	59.51 (12)	C16—C11—N1—C1	−67.01 (11)
C14—C15—C16—C11	−58.24 (13)	C12—C11—N1—C1	59.64 (12)
N5—C17—C18—C23	132.38 (11)	C18—C17—N5—C24	−68.52 (12)
N5—C17—C18—C19	−54.33 (14)	C18—C17—N5—C27	161.11 (9)
C23—C18—C19—N6	−178.74 (11)	C32—C27—N5—C24	65.28 (13)
C17—C18—C19—N6	7.93 (17)	C28—C27—N5—C24	−61.52 (14)
C23—C18—C19—C20	3.15 (16)	C32—C27—N5—C17	−166.45 (9)
C17—C18—C19—C20	−170.19 (10)	C28—C27—N5—C17	66.75 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1	0.909 (15)	2.205 (15)	2.8867 (14)	131.3 (12)
N6—H6*A*···N5	0.871 (15)	2.242 (15)	2.8824 (14)	130.3 (13)
N2—H2*B*···N7^{i}	0.889 (15)	2.122 (15)	2.9894 (15)	164.8 (12)
N6—H6*A*···N4^{ii}	0.871 (15)	2.457 (14)	3.0268 (14)	123.5 (11)

N6—H6*B*···N3^{i}	0.887 (14)	2.526 (15)	3.3780 (17)	161.3 (12)
C16—H16*B*···N8^{iii}	0.99	2.42	3.4095 (18)	177

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