Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-(6-Methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-ylidene)propanedinitrile

M. Sekar,[a] R. Velmurugan,[a] A. Chandramohan,[a] P. Ramesh[b] and M. N. Ponnuswamy[b]*

[a]Post Graduate and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore 641 020, India, and [b]Centre of Advanced Study in Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India
Correspondence e-mail: mnpsy2004@yahoo.com

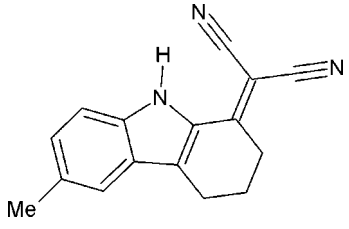
Received 19 October 2011; accepted 4 November 2011

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.050; wR factor = 0.154; data-to-parameter ratio = 20.9.

In the title compound, $C_{16}H_{13}N_3$, the cyclohexene ring adopts a sofa conformation. An intramolecular N—H···N hydrogen bond generates an $S(7)$ ring motif. In the crystal, the molecules are linked by pairs of N—H···N interactions, forming centrosymmetric dimers with an $R_2^2(14)$ motif.

Related literature

For the biological activity of carbazole derivatives, see: Magnus *et al.* (1992); Abraham (1975); Saxton (1983); Phillipson & Zenk (1980); Bergman & Pelcman (1990); Bonesi *et al.* (2004); Chakraborty *et al.* (1965); Kirtikar & Basu (1933); Chakraborty *et al.* (1973). For puckering parameters, see: Cremer & Pople (1975). For asymmetry parameters, see: Nardelli (1983). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{16}H_{13}N_3$
M_r = 247.29
Triclinic, $P\overline{1}$
a = 7.6396 (9) Å
b = 8.4381 (8) Å
c = 10.8967 (13) Å
α = 88.395 (6)°
β = 71.392 (7)°
γ = 71.217 (6)°
V = 628.08 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 296 K
0.17 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX CCD detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.986, T_{max} = 0.988
12507 measured reflections
3692 independent reflections
2815 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.154
S = 1.03
3692 reflections
177 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N16	0.86 (2)	2.59 (2)	3.3099 (17)	141.4 (16)
N1—H1···N16^{i}	0.86 (2)	2.49 (2)	3.2150 (17)	142.8 (16)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors thank Solid State Unit, Indian Institute of Science, Bangalore, India, for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5683).

References

Abraham, D. J. (1975). *The Catharanthus Alkaloids*, edited by W. I. Taylor & N. R. Farnsworth, chs. 7 and 8. New York: Marcel Decker.
Bergman, J. & Pelcman, B. (1990). *Pure Appl. Chem.* **62**, 1967–1976.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bonesi, S. M., Crevatin, L. K. & Erra-Balsells, R. (2004). *Photochem. Photobiol. Sci.* **3**, 381–388.
Bruker (1998). *SMART*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconcin, USA.
Chakraborty, D. P., Barman, B. K. & Bose, P. K. (1965). *Tetrahedron*, **21**, 681–685.
Chakraborty, D. P., Das, K. C., Das, B. P. & Chowdhury, B. K. (1973). *Trans. Bose Res. Inst.* **38**, 1–10.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Kirtikar, K. R. & Basu, B. D. (1933). *Indian Medicinal Plants*, edited by L. M. Basu, 2nd ed., pp. 2131–2133. Allahabad: Central Council for Research in Ayurveda & Siddha (Deptt. of AYUSH, Min. of Health & Family Welfare), Govt. of India.
Magnus, P., Sear, N. L., Kim, C. S. & Vicker, N. (1992). *J. Org. Chem.* **57**, 70–78.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Phillipson, J. D. & Zenk, M. H. (1980). *Indole and Biogenetically Related Alkaloids*, ch 3. New York: Academic Press.
Saxton, J. E. (1983). Editor. *Heterocyclic Compounds*, Vol. 25, *The Monoterpenoid Indole Alkaloids*, chs. 8 and 11. New York: Wiley.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2011). E**67**, o3270 [https://doi.org/10.1107/S160053681104654X]

2-(6-Methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-ylidene)propanedinitrile

M. Sekar, R. Velmurugan, A. Chandramohan, P. Ramesh and M. N. Ponnuswamy

S1. Comment

Carbazole alkaloids obtained from naturally occurring sources have been the subject of extensive research, mainly because of their widespread applications in traditional medicine (Bergman & Pelcman, 1990; Bonesi *et al.*, 2004; Chakraborty *et al.*, 1965; Kirtikar & Basu, 1933). Tetrahydrocarbazole systems are present in the framework of a number of indole-type alkaloids of biological interest (Magnus *et al.*, 1992; Abraham, 1975; Saxton, 1983; Phillipson *et al.*, 1980). These types of compounds possess significant antibiotic, anti-carcinogenic, antiviral and anti-inflammatory properties (Chakraborty *et al.*, 1973). Against this background and to ascertain the molecular structure and conformation, the X-ray crystal structure determination of the title compound has been carried out.

The *ORTEP* plot of the molecule is shown in Fig. 1. The cyclohexane ring in the carbazole ring system adopts envelope conformation with the puckering parameters (Cremer & Pople, 1975) and the asymmetry parameters (Nardelli, 1983) are: q_2=0.330 (1) Å, q_3 = 0.262 (1) Å, φ_2 = 168.7 (2)° and Δ_s(C2 & C5)= 8.6 (2)°. The sum of the bond angles around N1 [359.8°] is in accordance with sp^2 hybridization. The bond lengths and bond angles of (C15—N16) 1.148 (2) Å, (C17—N18) 1.145 (2) Å, (C14—C15—N16) 178.8 (2)° and (C14—C17—N18) 178.6 (2)° show linear character of the cyano group, a feature observed in carbonitrile compounds.

The crystal packing reveals that symmetry-related molecules are linked by N—H···N interactions. The intramolecular N1—H1···N16 hydrogen bond generates a S(7) ring motif. The molecules at (*x*, *y*, *z*) and (2 - *x*, -1 - *y*, 1 - *z*) are linked by N1—H1···N16 hydrogen bonds into cyclic centrosymmetric $R_2^2(14)$ dimer.

S2. Experimental

A mixture of 6-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (7.5 mmol), and melanonitrile (7.5 mmol), ammonium acetate (0.57 g, 8.125 mmol) and acetic acid (1.5 ml, 24.75 mmol) in 12.5 ml of toluene was stirred at 105°C for 5 h. On cooling the precipitate that formed was filtered off, washed with hexane (20 ml) and dried at 100°C to give a crude product of 6-Methyl-2-(1,2,3,4- tetrahydro-9*H*-carbazol-1-ylidene)propanedinitrile.The crystals of the title compound suitable for single XRD analysis were obtained by the slow evaporation method by using dichloroethane as solvent at room temperature.

S3. Refinement

The N-bound H atom was located in a difference map and refined isotropically. C-bound H atoms were positioned geometrically (C–H = 0.93–0.97 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for all other H atoms.

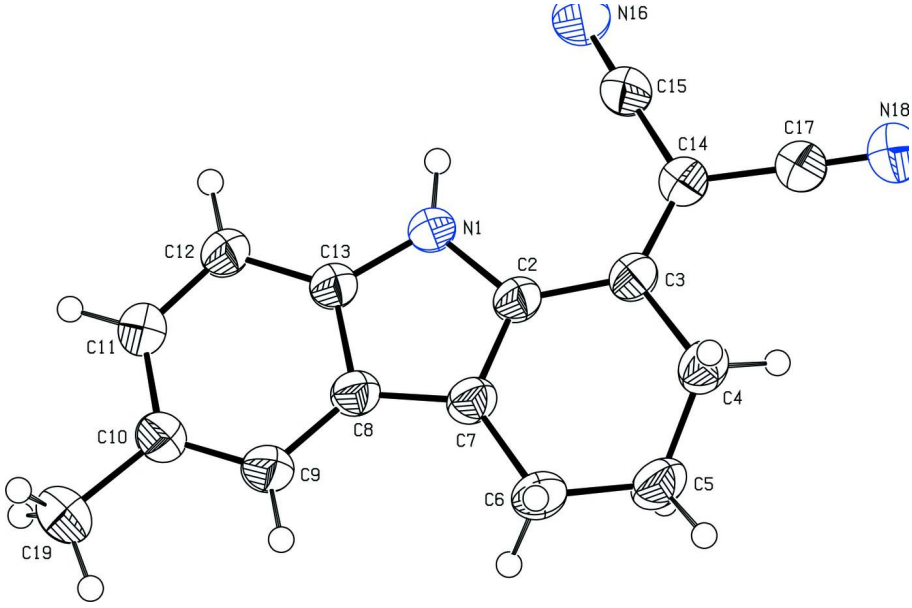


Figure 1

The molecular structure of the title compound, showing the atomic numbering and displacement ellipsoids drawn at the 50% probability level.

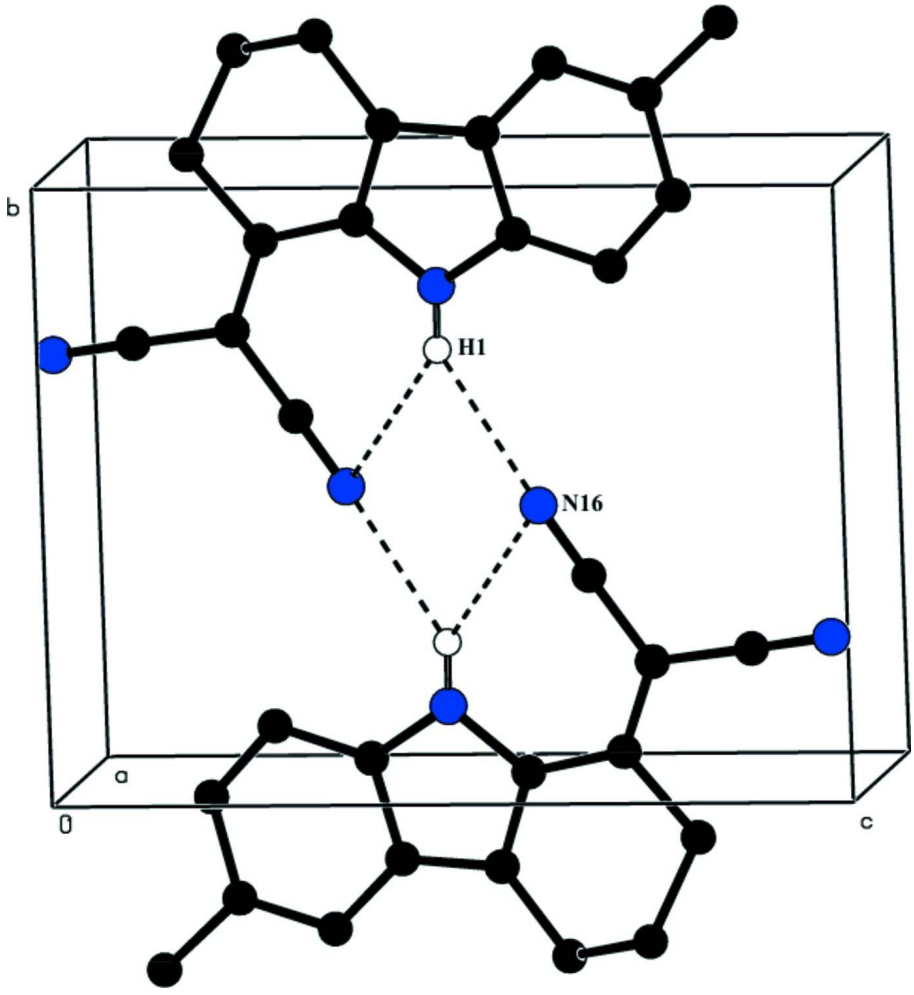


Figure 2

The crystal packing of the title compound. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity.

2-(6-Methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-ylidene)propanedinitrile

Crystal data

$C_{16}H_{13}N_3$
$M_r = 247.29$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.6396\ (9)$ Å
$b = 8.4381\ (8)$ Å
$c = 10.8967\ (13)$ Å
$\alpha = 88.395\ (6)°$
$\beta = 71.392\ (7)°$
$\gamma = 71.217\ (6)°$
$V = 628.08\ (12)$ Å^3
$Z = 2$
$F(000) = 260$
$D_x = 1.308$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1675 reflections
$\theta = 2.0–30.6°$
$\mu = 0.08$ mm^{-1}
$T = 296$ K
Block, brown
0.17 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX CCD detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.986, T_{max} = 0.988
12507 measured reflections
3692 independent reflections
2815 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 30.6°, θ_{min} = 2.0°
h = −10→10
k = −12→11
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.154
S = 1.03
3692 reflections
177 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 0.0632P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.19262 (15)	1.14409 (12)	0.48492 (9)	0.0374 (2)
H1	0.140 (3)	1.251 (3)	0.4900 (18)	0.073 (5)*
C2	0.16168 (16)	1.03889 (13)	0.58442 (11)	0.0348 (2)
C3	0.02788 (16)	1.08208 (13)	0.71382 (10)	0.0352 (2)
C4	0.04245 (19)	0.94137 (16)	0.80188 (12)	0.0446 (3)
H4A	−0.0838	0.9623	0.8687	0.054*
H4B	0.1358	0.9420	0.8447	0.054*
C5	0.1046 (2)	0.76799 (16)	0.73322 (13)	0.0480 (3)
H5A	0.1234	0.6840	0.7947	0.058*
H5B	0.0007	0.7603	0.7033	0.058*
C6	0.29157 (19)	0.73000 (15)	0.61842 (13)	0.0452 (3)
H6A	0.4026	0.7046	0.6494	0.054*
H6B	0.3079	0.6323	0.5656	0.054*
C7	0.28556 (17)	0.87609 (14)	0.53817 (11)	0.0370 (2)
C8	0.39448 (16)	0.88053 (13)	0.40647 (11)	0.0363 (2)

C9	0.53599 (18)	0.75647 (15)	0.30953 (12)	0.0429 (3)
H9	0.5779	0.6452	0.3286	0.051*
C10	0.61190 (18)	0.80110 (15)	0.18626 (12)	0.0430 (3)
C11	0.54686 (18)	0.97060 (16)	0.15997 (12)	0.0427 (3)
H11	0.5987	0.9992	0.0763	0.051*
C12	0.41057 (17)	1.09577 (15)	0.25181 (11)	0.0400 (3)
H12	0.3713	1.2069	0.2319	0.048*
C13	0.33323 (16)	1.04906 (14)	0.37662 (11)	0.0350 (2)
C14	−0.10538 (18)	1.23850 (15)	0.76265 (11)	0.0402 (3)
C15	−0.1323 (2)	1.38051 (16)	0.68896 (13)	0.0507 (3)
N16	−0.1573 (2)	1.49658 (16)	0.63094 (14)	0.0757 (4)
C17	−0.2293 (2)	1.26880 (16)	0.89586 (12)	0.0459 (3)
N18	−0.3258 (2)	1.29469 (17)	1.00271 (12)	0.0639 (4)
C19	0.7624 (2)	0.67329 (19)	0.07853 (15)	0.0603 (4)
H19A	0.8867	0.6900	0.0587	0.090*
H19B	0.7228	0.6862	0.0026	0.090*
H19C	0.7735	0.5623	0.1057	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0432 (5)	0.0282 (5)	0.0350 (5)	−0.0081 (4)	−0.0091 (4)	0.0063 (4)
C2	0.0378 (5)	0.0310 (5)	0.0351 (5)	−0.0105 (4)	−0.0126 (4)	0.0079 (4)
C3	0.0371 (6)	0.0354 (5)	0.0354 (6)	−0.0134 (4)	−0.0140 (4)	0.0074 (4)
C4	0.0483 (7)	0.0428 (6)	0.0390 (6)	−0.0122 (5)	−0.0131 (5)	0.0138 (5)
C5	0.0533 (7)	0.0390 (6)	0.0503 (7)	−0.0155 (5)	−0.0161 (6)	0.0180 (5)
C6	0.0508 (7)	0.0323 (5)	0.0477 (7)	−0.0084 (5)	−0.0161 (5)	0.0126 (5)
C7	0.0387 (6)	0.0325 (5)	0.0394 (6)	−0.0109 (4)	−0.0134 (4)	0.0084 (4)
C8	0.0372 (6)	0.0308 (5)	0.0394 (6)	−0.0102 (4)	−0.0119 (4)	0.0059 (4)
C9	0.0421 (6)	0.0322 (5)	0.0473 (7)	−0.0083 (5)	−0.0095 (5)	0.0034 (5)
C10	0.0411 (6)	0.0385 (6)	0.0435 (6)	−0.0111 (5)	−0.0075 (5)	−0.0010 (5)
C11	0.0436 (6)	0.0428 (6)	0.0383 (6)	−0.0153 (5)	−0.0081 (5)	0.0044 (5)
C12	0.0436 (6)	0.0345 (5)	0.0384 (6)	−0.0118 (5)	−0.0104 (5)	0.0087 (4)
C13	0.0364 (5)	0.0314 (5)	0.0355 (5)	−0.0104 (4)	−0.0110 (4)	0.0051 (4)
C14	0.0452 (6)	0.0370 (6)	0.0361 (6)	−0.0138 (5)	−0.0100 (5)	0.0040 (4)
C15	0.0575 (8)	0.0348 (6)	0.0448 (7)	−0.0081 (5)	−0.0038 (6)	0.0020 (5)
N16	0.0935 (10)	0.0380 (6)	0.0602 (8)	−0.0035 (6)	0.0026 (7)	0.0117 (5)
C17	0.0528 (7)	0.0391 (6)	0.0413 (6)	−0.0140 (5)	−0.0107 (5)	0.0027 (5)
N18	0.0785 (9)	0.0543 (7)	0.0450 (7)	−0.0193 (6)	−0.0046 (6)	0.0014 (5)
C19	0.0588 (9)	0.0472 (8)	0.0544 (8)	−0.0072 (6)	−0.0008 (7)	−0.0068 (6)

Geometric parameters (Å, º)

N1—C13	1.3708 (15)	C8—C9	1.4088 (16)
N1—C2	1.3918 (14)	C8—C13	1.4106 (15)
N1—H1	0.86 (2)	C9—C10	1.3775 (18)
C2—C7	1.3906 (16)	C9—H9	0.9300
C2—C3	1.4265 (16)	C10—C11	1.4088 (17)

C3—C14	1.3747 (16)	C10—C19	1.5081 (18)
C3—C4	1.5040 (15)	C11—C12	1.3738 (17)
C4—C5	1.5209 (18)	C11—H11	0.9300
C4—H4A	0.9700	C12—C13	1.4004 (16)
C4—H4B	0.9700	C12—H12	0.9300
C5—C6	1.5150 (19)	C14—C15	1.4198 (17)
C5—H5A	0.9700	C14—C17	1.4340 (17)
C5—H5B	0.9700	C15—N16	1.1478 (18)
C6—C7	1.4884 (15)	C17—N18	1.1445 (17)
C6—H6A	0.9700	C19—H19A	0.9600
C6—H6B	0.9700	C19—H19B	0.9600
C7—C8	1.4172 (16)	C19—H19C	0.9600

C13—N1—C2	108.39 (9)	C9—C8—C13	119.72 (10)
C13—N1—H1	124.4 (13)	C9—C8—C7	133.50 (11)
C2—N1—H1	127.0 (13)	C13—C8—C7	106.76 (10)
C7—C2—N1	108.68 (10)	C10—C9—C8	119.53 (11)
C7—C2—C3	123.14 (10)	C10—C9—H9	120.2
N1—C2—C3	128.18 (10)	C8—C9—H9	120.2
C14—C3—C2	125.69 (10)	C9—C10—C11	119.15 (11)
C14—C3—C4	119.19 (10)	C9—C10—C19	121.77 (12)
C2—C3—C4	115.11 (10)	C11—C10—C19	119.08 (12)
C3—C4—C5	114.33 (10)	C12—C11—C10	123.24 (11)
C3—C4—H4A	108.7	C12—C11—H11	118.4
C5—C4—H4A	108.7	C10—C11—H11	118.4
C3—C4—H4B	108.7	C11—C12—C13	117.21 (11)
C5—C4—H4B	108.7	C11—C12—H12	121.4
H4A—C4—H4B	107.6	C13—C12—H12	121.4
C6—C5—C4	112.68 (11)	N1—C13—C12	130.09 (10)
C6—C5—H5A	109.1	N1—C13—C8	108.75 (10)
C4—C5—H5A	109.1	C12—C13—C8	121.14 (10)
C6—C5—H5B	109.1	C3—C14—C15	124.22 (11)
C4—C5—H5B	109.1	C3—C14—C17	120.91 (11)
H5A—C5—H5B	107.8	C15—C14—C17	114.87 (11)
C7—C6—C5	110.49 (10)	N16—C15—C14	178.80 (16)
C7—C6—H6A	109.6	N18—C17—C14	178.61 (15)
C5—C6—H6A	109.6	C10—C19—H19A	109.5
C7—C6—H6B	109.6	C10—C19—H19B	109.5
C5—C6—H6B	109.6	H19A—C19—H19B	109.5
H6A—C6—H6B	108.1	C10—C19—H19C	109.5
C2—C7—C8	107.42 (10)	H19A—C19—H19C	109.5
C2—C7—C6	123.45 (11)	H19B—C19—H19C	109.5
C8—C7—C6	129.13 (11)		

C13—N1—C2—C7	0.46 (13)	C8—C9—C10—C11	0.34 (19)
C13—N1—C2—C3	−179.37 (11)	C8—C9—C10—C19	−179.48 (12)
C7—C2—C3—C14	−176.13 (11)	C9—C10—C11—C12	0.3 (2)
N1—C2—C3—C14	3.69 (19)	C19—C10—C11—C12	−179.91 (13)

C7—C2—C3—C4	5.41 (16)	C10—C11—C12—C13	−0.68 (19)
N1—C2—C3—C4	−174.77 (10)	C2—N1—C13—C12	178.08 (11)
C14—C3—C4—C5	149.75 (12)	C2—N1—C13—C8	−0.20 (13)
C2—C3—C4—C5	−31.69 (15)	C11—C12—C13—N1	−177.58 (11)
C3—C4—C5—C6	52.95 (15)	C11—C12—C13—C8	0.51 (18)
C4—C5—C6—C7	−45.23 (15)	C9—C8—C13—N1	178.52 (10)
N1—C2—C7—C8	−0.54 (13)	C7—C8—C13—N1	−0.13 (13)
C3—C2—C7—C8	179.31 (10)	C9—C8—C13—C12	0.06 (17)
N1—C2—C7—C6	−179.76 (10)	C7—C8—C13—C12	−178.59 (10)
C3—C2—C7—C6	0.08 (18)	C2—C3—C14—C15	1.6 (2)
C5—C6—C7—C2	20.28 (17)	C4—C3—C14—C15	−179.95 (12)
C5—C6—C7—C8	−158.76 (12)	C2—C3—C14—C17	−178.17 (11)
C2—C7—C8—C9	−177.97 (13)	C4—C3—C14—C17	0.23 (17)
C6—C7—C8—C9	1.2 (2)	C3—C14—C15—N16	159 (8)
C2—C7—C8—C13	0.41 (13)	C17—C14—C15—N16	−22 (9)
C6—C7—C8—C13	179.58 (11)	C3—C14—C17—N18	105 (7)
C13—C8—C9—C10	−0.50 (18)	C15—C14—C17—N18	−74 (7)
C7—C8—C9—C10	177.73 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N16	0.86 (2)	2.59 (2)	3.3099 (17)	141.4 (16)
N1—H1···N16^{i}	0.86 (2)	2.49 (2)	3.2150 (17)	142.8 (16)

Symmetry code: (i) −*x*, −*y*+3, −*z*+1.