Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Amino-4-(2-fluorophenyl)-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile

Wei Wang,[a] Shi-gui Tang,[b] Cheng Guo,[c]* Chang-jun Luan[a] and Ren-jun Du[a]

[a]Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China, [b]Department of Biotechnology and Pharmaceutical Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China, and [c]College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China
Correspondence e-mail: guocheng@njut.edu.cn

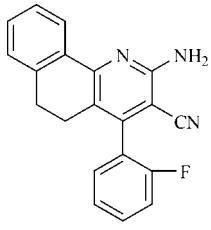
Received 19 November 2010; accepted 3 December 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; disorder in main residue; R factor = 0.052; wR factor = 0.161; data-to-parameter ratio = 7.3.

In the title compound, $C_{20}H_{14}FN_3$, the F atom of the fluoro-substituted benzene ring in the 4-position of the 5,6-dihydrobenzo[*h*]quinoline system is disordered over two positions (0.80 and 0.20 occupancy). The dihedral angle between the pyridine and fluorobenzene rings is 73.2 (2) Å. The crystal structure is established by intermolecular N—H···N hydrogen bonds, forming a three-dimensional network.

Related literature

For use of the title compound as an intermediate, see Shi *et al.* (2005). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{20}H_{14}FN_3$ M_r = 315.34
Orthorhombic, $P2_12_12_1$
a = 6.9690 (14) Å
b = 12.716 (3) Å
c = 17.379 (4) Å
V = 1540.1 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North et al., 1998)
T_{min} = 0.973, T_{max} = 0.982
1641 measured reflections
1641 independent reflections
1231 reflections with $I > 2\sigma(I)$
R_{int} = 0.0315
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.161
S = 1.02
1641 reflections
226 parameters
12 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N3^{i}	0.86	2.45	3.215 (5)	150

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We gratefully acknowledge the Analysis Center of Nanjing University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2252).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shi, F., Tu, S. J., Fang, F. & Li, T. J. (2005). *Arkivoc*, pp. 137–142.

supporting information

Acta Cryst. (2011). E**67**, o96 [https://doi.org/10.1107/S1600536810050695]

2-Amino-4-(2-fluorophenyl)-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile

Wei Wang, Shi-gui Tang, Cheng Guo, Chang-jun Luan and Ren-jun Du

S1. Comment

The title compound, $C_{20}H_{14}F_1N_3$, (I), is an important intermediate in the preparation of heterocyclic compounds (Shi *et al.*, 2005). Thus, it's crystal structure is reported herein.

The fundamental buliding unit of I is composed of one fluorine substituted benzene ring attached to a 5,6-dihydrobenzo[*h*]quinoline ring in 4-position. In addition, there is an amino group in 2-position and a nitrile function in 3-position (Fig 1). The o-fluoro-phenyl group is disordered over two positions. Bond lengths and angles of the compound are within normal ranges (Allen *et al.*, 1987). The crystal structure of the title compound is established by intermolecular N—H···N hydrogen bonds forming a three dimensional network (Fig 2).

S2. Experimental

The title compound, (I) was prepared under microwave irradiation, an environmentally friendly method. 2 mmol of 2-fluorobenzaldehyde, 2 mmol of malononitrile, 16 mmol of ammonium acetate and 2 mmol of 1,2,3,4-tetrahydronaphthalen-1-one were dissolved in 3 mL absolute ethanol. The reaction mixture was stirred at 90°C additionally irradiating the mixture with microwaves (400 W, 6 h). After cooling down to room temperature pure (I) was obtained directly from the solution. Crystals suitable for X-ray analysis were obtained by dissolving (I) (0.5 g) in methanol (20 ml) and slowly evaporating the solvent at the room temperature for about 7 days.

S3. Refinement

In the absence of anomalous scattering effects, Friedel pairs were merged. H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H, 0.97 Å for alkyl H and 0.86 Å for N—H, respectively. They were constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C, N), where x = 1.2 for aromatic H, and x = 1.5 for other H.

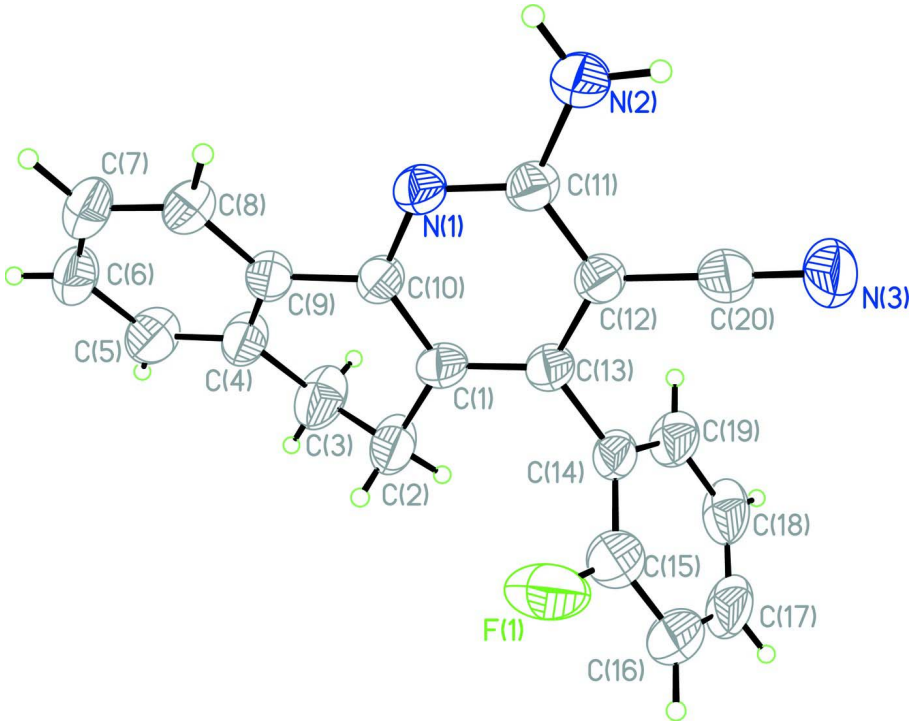


Figure 1

Molecular structure of (I), with the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

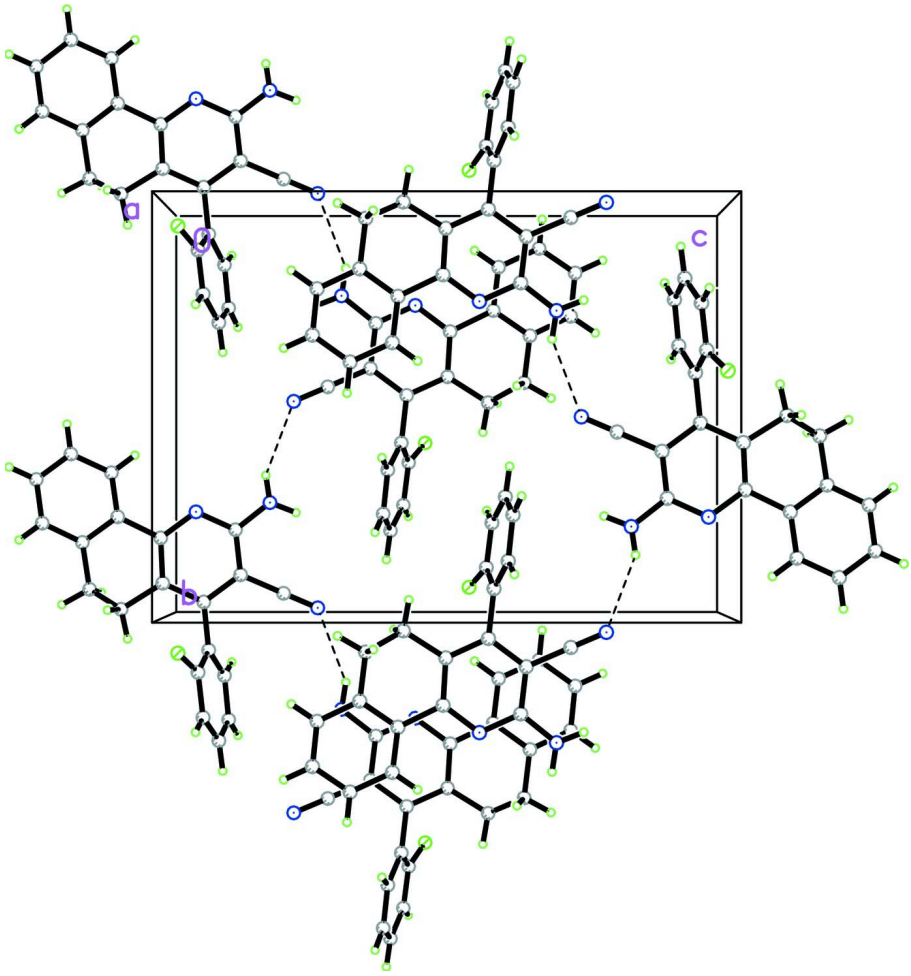


Figure 2

Packing diagram of (I). Hydrogen bonds are shown as dashed lines.

2-Amino-4-(2-fluorophenyl)-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile

Crystal data

$C_{20}H_{14}FN_3$
$M_r = 315.34$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 6.9690\ (14)$ Å
$b = 12.716\ (3)$ Å
$c = 17.379\ (4)$ Å
$V = 1540.1\ (5)$ Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.360$ Mg m^{-3}
Melting point: 438.15 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–13°
$\mu = 0.09$ mm^{-1}
$T = 293$ K
Block, yellow
0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North et al., 1998)
$T_{min} = 0.973$, $T_{max} = 0.982$
1641 measured reflections
1641 independent reflections

1231 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 25.3°$, $\theta_{min} = 2.0°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.161$
$S = 1.02$
1641 reflections
226 parameters
12 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
$w = 1/[\sigma^2(F_o^2) + (0.109P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.9531 (6)	0.0831 (3)	0.49848 (19)	0.0426 (9)	
N1	0.9958 (5)	0.2550 (2)	0.55568 (16)	0.0401 (8)	
N2	1.0177 (6)	0.2774 (2)	0.68616 (17)	0.0522 (9)	
H2A	1.0349	0.3435	0.6784	0.063*	
H2B	1.0166	0.2530	0.7323	0.063*	
N3	0.9601 (7)	0.0234 (3)	0.77208 (18)	0.0676 (12)	
C2	0.9338 (9)	0.0206 (3)	0.4259 (2)	0.0649 (13)	
H2C	0.8013	0.0217	0.4089	0.078*	
H2D	0.9695	−0.0519	0.4356	0.078*	
C3	1.0620 (9)	0.0662 (3)	0.3634 (2)	0.0734 (16)	
H3A	1.1955	0.0561	0.3773	0.088*	
H3B	1.0389	0.0294	0.3154	0.088*	
C4	1.0233 (7)	0.1807 (3)	0.3527 (2)	0.0518 (11)	
C5	1.0325 (8)	0.2273 (3)	0.2808 (2)	0.0642 (13)	
H5A	1.0595	0.1862	0.2378	0.077*	
C6	1.0010 (7)	0.3334 (3)	0.2722 (2)	0.0590 (11)	
H6A	1.0047	0.3636	0.2235	0.071*	
C7	0.9642 (7)	0.3947 (3)	0.3356 (2)	0.0557 (11)	
H7A	0.9440	0.4666	0.3299	0.067*	
C8	0.9571 (6)	0.3495 (3)	0.4076 (2)	0.0449 (9)	
H8A	0.9324	0.3914	0.4503	0.054*	

C9	0.9862 (6)	0.2430 (3)	0.41728 (19)	0.0407 (9)	
C10	0.9766 (5)	0.1922 (3)	0.49386 (19)	0.0390 (8)	
C11	0.9925 (6)	0.2118 (3)	0.62584 (19)	0.0382 (8)	
C12	0.9689 (6)	0.1031 (3)	0.63549 (19)	0.0382 (8)	
C13	0.9470 (6)	0.0380 (3)	0.5712 (2)	0.0398 (9)	
C14	0.9174 (6)	−0.0773 (3)	0.5810 (2)	0.0446 (10)	
C15	0.7404 (8)	−0.1240 (4)	0.5688 (3)	0.0615 (12)	
H15	0.6394	−0.0781	0.5591	0.074*	0.80
C16	0.7092 (9)	−0.2297 (4)	0.5788 (3)	0.0739 (16)	
H16A	0.5881	−0.2583	0.5705	0.089*	
C17	0.8575 (10)	−0.2917 (4)	0.6009 (2)	0.0757 (17)	
H17A	0.8376	−0.3633	0.6084	0.091*	
C18	1.0355 (9)	−0.2501 (3)	0.6122 (2)	0.0641 (14)	
H18A	1.1378	−0.2934	0.6255	0.077*	
C19	1.0625 (8)	−0.1438 (3)	0.6038 (2)	0.0557 (12)	
H19	1.1833	−0.1153	0.6130	0.067*	0.20
C20	0.9635 (7)	0.0585 (3)	0.7116 (2)	0.0479 (10)	
F1	0.610 (2)	−0.0743 (11)	0.5394 (10)	0.083 (4)	0.21
F1′	1.2344 (6)	−0.1074 (3)	0.6101 (3)	0.0917 (13)	0.80

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.053 (2)	0.0301 (17)	0.0443 (18)	−0.0026 (18)	−0.0015 (19)	−0.0052 (15)
N1	0.0467 (19)	0.0329 (14)	0.0408 (15)	−0.0002 (15)	0.0006 (15)	−0.0022 (13)
N2	0.077 (3)	0.0393 (16)	0.0398 (16)	−0.0077 (19)	0.0009 (17)	−0.0049 (13)
N3	0.115 (3)	0.0460 (18)	0.0422 (18)	−0.006 (2)	−0.004 (2)	0.0062 (15)
C2	0.115 (4)	0.039 (2)	0.0409 (19)	−0.004 (3)	−0.002 (2)	0.0032 (17)
C3	0.126 (5)	0.043 (2)	0.052 (2)	0.006 (3)	0.014 (3)	−0.003 (2)
C4	0.076 (3)	0.0390 (19)	0.0403 (19)	0.002 (2)	0.004 (2)	0.0021 (16)
C5	0.099 (4)	0.052 (2)	0.041 (2)	−0.005 (3)	0.008 (3)	−0.0039 (19)
C6	0.076 (3)	0.052 (2)	0.050 (2)	−0.003 (3)	−0.001 (2)	0.0174 (19)
C7	0.064 (3)	0.043 (2)	0.061 (2)	0.000 (2)	0.003 (2)	0.0166 (19)
C8	0.049 (2)	0.0356 (19)	0.050 (2)	0.0020 (19)	0.003 (2)	0.0013 (16)
C9	0.045 (2)	0.0386 (18)	0.0385 (18)	0.0020 (19)	0.0000 (17)	0.0019 (15)
C10	0.044 (2)	0.0339 (18)	0.0386 (17)	−0.0025 (18)	0.0015 (18)	0.0023 (15)
C11	0.042 (2)	0.0331 (16)	0.0397 (17)	−0.0027 (17)	0.0033 (17)	−0.0017 (15)
C12	0.041 (2)	0.0346 (17)	0.0391 (17)	−0.0020 (17)	0.0015 (18)	0.0003 (15)
C13	0.050 (2)	0.0295 (17)	0.0399 (17)	−0.0002 (18)	−0.0013 (19)	−0.0017 (14)
C14	0.066 (3)	0.0326 (19)	0.0353 (19)	−0.005 (2)	−0.0021 (19)	0.0018 (16)
C15	0.076 (3)	0.047 (2)	0.061 (3)	−0.007 (2)	−0.010 (3)	0.003 (2)
C16	0.100 (4)	0.052 (3)	0.069 (3)	−0.030 (3)	−0.013 (3)	0.013 (2)
C17	0.135 (5)	0.040 (2)	0.052 (3)	−0.022 (3)	−0.003 (3)	0.011 (2)
C18	0.102 (4)	0.038 (2)	0.052 (2)	0.017 (3)	−0.001 (3)	0.0077 (19)
C19	0.079 (3)	0.034 (2)	0.054 (2)	0.004 (2)	0.000 (2)	0.0033 (18)
C20	0.067 (3)	0.0336 (17)	0.043 (2)	−0.002 (2)	−0.004 (2)	−0.0037 (17)
F1	0.062 (8)	0.058 (8)	0.130 (12)	−0.007 (7)	−0.034 (8)	−0.002 (8)
F1′	0.071 (2)	0.056 (2)	0.148 (4)	0.002 (2)	−0.024 (2)	0.010 (2)

Geometric parameters (Å, º)

C1—C13	1.389 (5)	C7—C8	1.378 (5)
C1—C10	1.399 (5)	C7—H7A	0.9300
C1—C2	1.496 (5)	C8—C9	1.380 (5)
N1—C11	1.338 (4)	C8—H8A	0.9300
N1—C10	1.345 (4)	C9—C10	1.481 (4)
N2—C11	1.351 (4)	C11—C12	1.401 (5)
N2—H2A	0.8600	C12—C13	1.398 (5)
N2—H2B	0.8600	C12—C20	1.439 (5)
N3—C20	1.143 (4)	C13—C14	1.490 (5)
C2—C3	1.522 (7)	C14—C19	1.376 (6)
C2—H2C	0.9700	C14—C15	1.385 (6)
C2—H2D	0.9700	C15—F1	1.217 (14)
C3—C4	1.492 (6)	C15—C16	1.373 (6)
C3—H3A	0.9700	C15—H15	0.9300
C3—H3B	0.9700	C16—C17	1.356 (8)
C4—C5	1.386 (5)	C16—H16A	0.9300
C4—C9	1.397 (5)	C17—C18	1.362 (8)
C5—C6	1.374 (6)	C17—H17A	0.9300
C5—H5A	0.9300	C18—C19	1.373 (6)
C6—C7	1.374 (6)	C18—H18A	0.9300
C6—H6A	0.9300	C19—F1′	1.289 (6)
C13—C1—C10	117.7 (3)	C4—C9—C10	118.9 (3)
C13—C1—C2	123.0 (3)	N1—C10—C1	123.6 (3)
C10—C1—C2	119.2 (3)	N1—C10—C9	117.1 (3)
C11—N1—C10	118.9 (3)	C1—C10—C9	119.3 (3)
C11—N2—H2A	120.0	N1—C11—N2	116.8 (3)
C11—N2—H2B	120.0	N1—C11—C12	121.1 (3)
H2A—N2—H2B	120.0	N2—C11—C12	122.1 (3)
C1—C2—C3	110.3 (4)	C13—C12—C11	120.1 (3)
C1—C2—H2C	109.6	C13—C12—C20	119.8 (3)
C3—C2—H2C	109.6	C11—C12—C20	120.1 (3)
C1—C2—H2D	109.6	C1—C13—C12	118.6 (3)
C3—C2—H2D	109.6	C1—C13—C14	120.9 (3)
H2C—C2—H2D	108.1	C12—C13—C14	120.5 (3)
C4—C3—C2	110.7 (4)	C19—C14—C15	115.8 (4)
C4—C3—H3A	109.5	C19—C14—C13	122.4 (4)
C2—C3—H3A	109.5	C15—C14—C13	121.8 (4)
C4—C3—H3B	109.5	F1—C15—C16	116.3 (8)
C2—C3—H3B	109.5	F1—C15—C14	120.3 (8)
H3A—C3—H3B	108.1	C16—C15—C14	122.8 (5)
C5—C4—C9	119.4 (3)	C16—C15—H15	121.2
C5—C4—C3	121.4 (3)	C14—C15—H15	115.6
C9—C4—C3	119.1 (3)	C17—C16—C15	119.0 (6)
C6—C5—C4	120.6 (4)	C17—C16—H16A	120.5
C6—C5—H5A	119.8	C15—C16—H16A	120.5

C4—C5—H5A	119.5	C16—C17—C18	120.6 (4)
C5—C6—C7	120.1 (3)	C16—C17—H17A	119.7
C5—C6—H6A	120.0	C18—C17—H17A	119.7
C7—C6—H6A	120.0	C17—C18—C19	119.4 (5)
C6—C7—C8	119.8 (3)	C17—C18—H18A	120.3
C6—C7—H7A	120.1	C19—C18—H18A	120.3
C8—C7—H7A	120.1	F1′—C19—C18	118.1 (5)
C7—C8—C9	121.0 (3)	F1′—C19—C14	119.2 (4)
C7—C8—H8A	119.5	C18—C19—C14	122.3 (5)
C9—C8—H8A	119.5	C18—C19—H19	119.3
C8—C9—C4	119.1 (3)	C14—C19—H19	118.3
C8—C9—C10	122.1 (3)	N3—C20—C12	179.6 (5)

C13—C1—C2—C3	−144.0 (4)	N2—C11—C12—C13	−178.8 (4)
C10—C1—C2—C3	36.6 (6)	N1—C11—C12—C20	−179.3 (4)
C1—C2—C3—C4	−53.6 (6)	N2—C11—C12—C20	2.5 (7)
C2—C3—C4—C5	−144.6 (5)	C10—C1—C13—C12	−1.5 (6)
C2—C3—C4—C9	38.6 (7)	C2—C1—C13—C12	179.2 (4)
C9—C4—C5—C6	−1.5 (8)	C10—C1—C13—C14	178.5 (4)
C3—C4—C5—C6	−178.4 (5)	C2—C1—C13—C14	−0.9 (6)
C4—C5—C6—C7	1.4 (8)	C11—C12—C13—C1	1.3 (6)
C5—C6—C7—C8	−0.6 (8)	C20—C12—C13—C1	−179.9 (4)
C6—C7—C8—C9	−0.1 (7)	C11—C12—C13—C14	−178.6 (4)
C7—C8—C9—C4	0.0 (7)	C20—C12—C13—C14	0.2 (6)
C7—C8—C9—C10	−179.1 (4)	C1—C13—C14—C19	107.6 (5)
C5—C4—C9—C8	0.8 (7)	C12—C13—C14—C19	−72.5 (5)
C3—C4—C9—C8	177.7 (5)	C1—C13—C14—C15	−73.7 (5)
C5—C4—C9—C10	180.0 (4)	C12—C13—C14—C15	106.3 (5)
C3—C4—C9—C10	−3.1 (7)	C19—C14—C15—F1	−170.7 (10)
C11—N1—C10—C1	0.0 (6)	C13—C14—C15—F1	10.5 (12)
C11—N1—C10—C9	−178.4 (3)	C19—C14—C15—C16	0.0 (7)
C13—C1—C10—N1	0.9 (6)	C13—C14—C15—C16	−178.8 (4)
C2—C1—C10—N1	−179.8 (4)	F1—C15—C16—C17	170.6 (10)
C13—C1—C10—C9	179.3 (3)	C14—C15—C16—C17	−0.5 (8)
C2—C1—C10—C9	−1.4 (6)	C15—C16—C17—C18	−0.8 (8)
C8—C9—C10—N1	−19.4 (6)	C16—C17—C18—C19	2.4 (8)
C4—C9—C10—N1	161.5 (4)	C17—C18—C19—F1′	−175.7 (4)
C8—C9—C10—C1	162.1 (4)	C17—C18—C19—C14	−2.9 (7)
C4—C9—C10—C1	−17.0 (6)	C15—C14—C19—F1′	174.4 (4)
C10—N1—C11—N2	178.2 (3)	C13—C14—C19—F1′	−6.8 (6)
C10—N1—C11—C12	−0.2 (6)	C15—C14—C19—C18	1.7 (6)
N1—C11—C12—C13	−0.5 (6)	C13—C14—C19—C18	−179.5 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N2—H2*A*···N3^{i}	0.86	2.45	3.215 (5)	150

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