Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(4*R*)-4-(Biphenyl-4-yl)-7-chloro-1,2,3,4-tetrahydroquinoline

Thomas Theissmann[a] and Michael Bolte[b]*

[a]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany, and [b]Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt/Main, Germany
Correspondence e-mail: bolte@chemie.uni-frankfurt.de

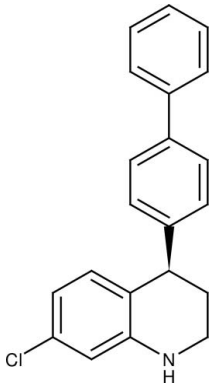
Received 9 September 2011; accepted 19 September 2011

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.079; data-to-parameter ratio = 14.4.

The title compound, $C_{21}H_{18}ClN$, was synthesized by an enantioselective Brønsted acid-catalysed transfer hydrogenation reaction. The six-membered heterocycle adopts a half-chair conformation. It has the biphenyl residue in an axial position. The two rings of the biphenyl residue are almost coplanar [dihedral angle = 2.65 (9)°]. The crystal packing is stabilized by N—H···Cl hydrogen bonds, which connect the molecules into chains running along the *a* axis.

Related literature

For organocatalysed processes, see: Rueping, Sugiono & Schoepke (2010); Rueping, Dufour & Schoepke (2011). For Brønsted acid-catalysed transfer hydrogenations, see: Rueping *et al.* (2008); Rueping, Stoeckel *et al.* (2010). For the synthesis of the title compound, see: Rueping, Theissmann *et al.* (2011).



Experimental

Crystal data

$C_{21}H_{18}ClN$
M_r = 319.81
Orthorhombic, $P2_12_12_1$
a = 5.5354 (4) Å
b = 8.0039 (4) Å
c = 35.8207 (17) Å
V = 1587.03 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 173 K
0.35 × 0.21 × 0.11 mm

Data collection

STOE IPDS II two-circle-diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)
T_{min} = 0.921, T_{max} = 0.984
18042 measured reflections
3071 independent reflections
2867 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.079
S = 1.05
3071 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Absolute structure: Flack (1983), 1240 Friedel pairs
Flack parameter: 0.01 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^{i}	0.90 (3)	2.66 (3)	3.5466 (17)	171 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LR2028).

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Rueping, M., Dufour, J. & Schoepke, F. R. (2011). *Green Chem.* **13**, 1084–1105.
Rueping, M., Stoeckel, M., Sugiono, E. & Theissmann, T. (2010). *Tetrahedron*, **66**, 6565–6568.
Rueping, M., Sugiono, E. & Schoepke, F. R. (2010). *Synlett*, pp. 852–865.
Rueping, M., Theissmann, T., Raja, S. & Bats, J. B. (2008). *Adv. Synth. Catal.* **350**, 1001–1006.
Rueping, M., Theissmann, T., Stoeckel, M. & Antonchick, A. P. (2011). *Org. Biomol. Chem.* **9**, 6844–6850
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.

supporting information

Acta Cryst. (2011). E**67**, o2747 [https://doi.org/10.1107/S160053681103830X]

(4*R*)-4-(Biphenyl-4-yl)-7-chloro-1,2,3,4-tetrahydroquinoline

Thomas Theissmann and Michael Bolte

S1. Comment

Tetrahydroquinolines are widely distributed in nature. Due to their importance as synthetic intermediates in the preparation of pharmaceuticals, agrochemicals, and in material science, considerable effort has been made to prepare these important molecules. Recently organocatalyzed processes have found widespread applications (Rueping, Sugiono & Schoepke, 2010; Rueping, Dufour & Schoepke, 2011). In particular Brønsted acid catalyzed transfer hydrogenations have been reported to provide a series of N-heterocyclic compounds with highest enantioselectivities (Rueping *et al.*, 2008; Rueping, Stoeckel *et al.*, 2010). The title compound was synthesized for the first time following this methodology (Rueping, Theissmann *et al.*, 2011) and colourless plates suitable for crystal structure determination were obtained.

The six-membered heterocycle in the title compound adopts a half chair conformation. It has the biphenyl residue in an axial position. The two rings of the biphenyl residue are almost coplanar [dihedral angle 2.65 (9)°]. The crystal packing is stabilized by N—H···Cl hydrogen bonds connecting the molecules to chains running along the *a* axis.

S2. Experimental

The title compound has been synthesized as described by Rueping, Theissmann *et al.* (2011).

S3. Refinement

All H atoms could be located by difference Fourier synthesis. Those bonded to C were refined with fixed individual displacement parameters [U(H) = 1.2 U_{eq}(C)] using a riding model with C—H ranging from 0.95Å to 1.00 Å. The H atom bonded to N was freely refined.

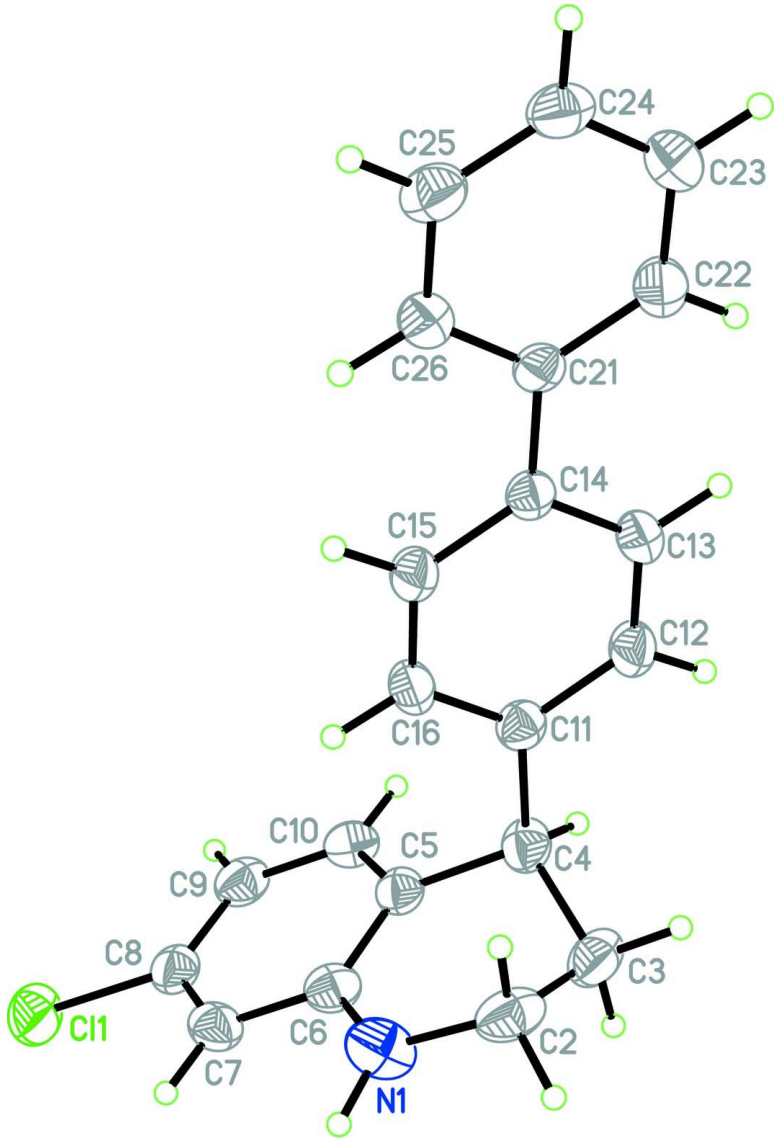


Figure 1

Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

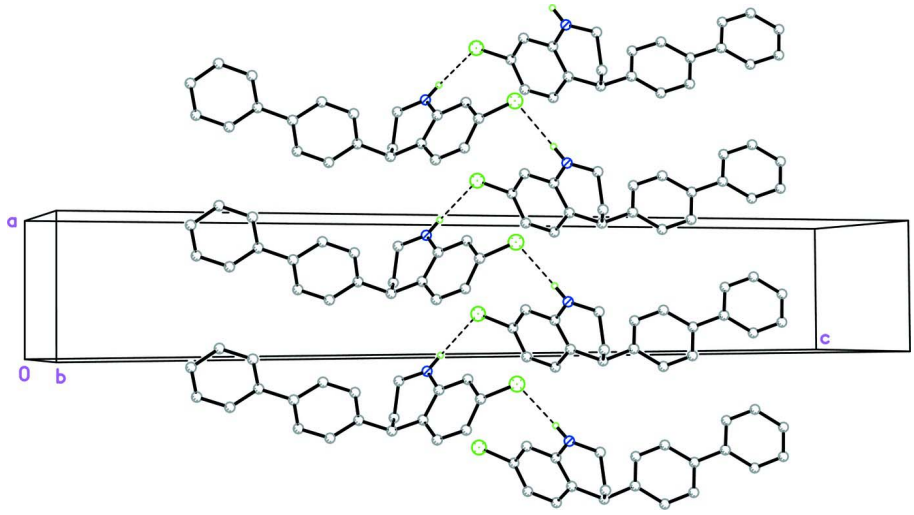


Figure 2

Packing diagram of the title compound. Hydrogen atoms bonded to C have been omitted for clarity. Hydrogen bonds are drawn as dashed lines.

(4*R*)-4-(biphenyl-4-yl)-7-chloro-1,2,3,4-tetrahydroquinoline

Crystal data

$C_{21}H_{18}ClN$
$M_r = 319.81$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 5.5354$ (4) Å
$b = 8.0039$ (4) Å
$c = 35.8207$ (17) Å
$V = 1587.03$ (16) Å^3
$Z = 4$
$F(000) = 672$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 18030 reflections
$\theta = 2.3$–$26.4°$
$\mu = 0.24$ mm^{-1}
$T = 173$ K
Plate, colourless
0.35 × 0.21 × 0.11 mm

Data collection

STOE IPDS II two-circle-diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)
$T_{min} = 0.921$, $T_{max} = 0.984$
18042 measured reflections
3071 independent reflections
2867 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 25.9°$, $\theta_{min} = 2.3°$
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -43 \rightarrow 44$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.05$
3071 reflections
213 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

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1208P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.026 (2)
Absolute structure: Flack (1983), 1240 Friedel pairs
Absolute structure parameter: 0.01 (5)

Special details

Experimental. ;

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}
Cl1	0.19210 (10)	0.59051 (5)	0.005768 (11)	0.04965 (15)
N1	0.1122 (3)	0.01504 (19)	0.06517 (4)	0.0428 (4)
H1	−0.002 (5)	0.000 (3)	0.0477 (7)	0.059 (6)*
C2	0.1862 (4)	−0.12356 (19)	0.08883 (4)	0.0407 (4)
H2A	0.1373	−0.2302	0.0771	0.049*
H2B	0.1034	−0.1151	0.1133	0.049*
C3	0.4575 (4)	−0.12319 (19)	0.09483 (5)	0.0406 (4)
H3A	0.5403	−0.1469	0.0709	0.049*
H3B	0.5017	−0.2120	0.1128	0.049*
C4	0.5406 (3)	0.04765 (18)	0.10990 (4)	0.0317 (3)
H4	0.7213	0.0481	0.1100	0.038*
C5	0.4573 (3)	0.18288 (17)	0.08315 (4)	0.0281 (3)
C6	0.2442 (3)	0.15963 (19)	0.06229 (4)	0.0308 (3)
C7	0.1654 (3)	0.28714 (19)	0.03814 (4)	0.0331 (3)
H7	0.0211	0.2739	0.0241	0.040*
C8	0.3000 (3)	0.43151 (18)	0.03507 (4)	0.0337 (3)
C9	0.5160 (3)	0.45488 (18)	0.05393 (4)	0.0349 (3)
H9	0.6092	0.5534	0.0506	0.042*
C10	0.5906 (3)	0.32869 (19)	0.07781 (4)	0.0327 (3)
H10	0.7381	0.3421	0.0910	0.039*
C11	0.4564 (3)	0.07013 (17)	0.15017 (4)	0.0277 (3)
C12	0.5861 (3)	−0.00906 (19)	0.17846 (4)	0.0319 (3)
H12	0.7295	−0.0682	0.1723	0.038*
C13	0.5108 (3)	−0.00350 (18)	0.21525 (4)	0.0311 (3)
H13	0.6035	−0.0590	0.2338	0.037*
C14	0.3006 (3)	0.08229 (16)	0.22576 (4)	0.0248 (3)
C15	0.1743 (3)	0.16460 (19)	0.19743 (4)	0.0304 (3)
H15	0.0325	0.2257	0.2035	0.037*

C16	0.2518 (3)	0.15902 (19)	0.16041 (4)	0.0310 (3)
H16	0.1628	0.2172	0.1418	0.037*
C21	0.2160 (3)	0.08270 (16)	0.26536 (4)	0.0249 (3)
C22	0.3477 (3)	0.00061 (19)	0.29322 (4)	0.0351 (4)
H22	0.4934	−0.0551	0.2868	0.042*
C23	0.2701 (3)	−0.0012 (2)	0.33005 (4)	0.0403 (4)
H23	0.3632	−0.0577	0.3484	0.048*
C24	0.0585 (3)	0.07846 (19)	0.34030 (4)	0.0357 (4)
H24	0.0048	0.0762	0.3655	0.043*
C25	−0.0739 (3)	0.1618 (2)	0.31320 (5)	0.0371 (4)
H25	−0.2188	0.2178	0.3199	0.045*
C26	0.0041 (3)	0.16382 (19)	0.27635 (4)	0.0321 (3)
H26	−0.0888	0.2217	0.2582	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0746 (3)	0.0413 (2)	0.0330 (2)	0.0169 (2)	0.0022 (2)	0.00881 (16)
N1	0.0445 (8)	0.0444 (8)	0.0394 (8)	−0.0146 (7)	−0.0043 (7)	0.0067 (6)
C2	0.0615 (11)	0.0297 (7)	0.0309 (8)	−0.0111 (8)	0.0079 (8)	−0.0035 (6)
C3	0.0623 (11)	0.0287 (8)	0.0309 (8)	0.0079 (8)	0.0097 (8)	−0.0005 (6)
C4	0.0329 (7)	0.0325 (7)	0.0296 (7)	0.0056 (6)	0.0058 (6)	0.0022 (6)
C5	0.0316 (8)	0.0290 (7)	0.0237 (7)	0.0038 (6)	0.0040 (6)	−0.0007 (5)
C6	0.0341 (8)	0.0337 (7)	0.0246 (7)	−0.0020 (6)	0.0060 (6)	−0.0018 (5)
C7	0.0337 (8)	0.0420 (8)	0.0237 (7)	0.0033 (7)	0.0008 (6)	−0.0011 (6)
C8	0.0473 (9)	0.0304 (7)	0.0235 (7)	0.0083 (7)	0.0045 (7)	0.0002 (5)
C9	0.0461 (9)	0.0271 (7)	0.0315 (7)	−0.0031 (7)	0.0041 (7)	−0.0018 (6)
C10	0.0351 (8)	0.0345 (7)	0.0284 (7)	−0.0023 (6)	0.0025 (6)	−0.0044 (6)
C11	0.0301 (7)	0.0250 (6)	0.0280 (7)	−0.0008 (6)	0.0016 (6)	0.0003 (6)
C12	0.0287 (7)	0.0335 (8)	0.0336 (8)	0.0093 (6)	0.0012 (6)	0.0005 (6)
C13	0.0312 (7)	0.0327 (7)	0.0294 (7)	0.0073 (6)	−0.0046 (6)	0.0016 (6)
C14	0.0253 (6)	0.0214 (6)	0.0278 (6)	−0.0025 (6)	−0.0017 (6)	−0.0012 (5)
C15	0.0278 (7)	0.0329 (7)	0.0306 (7)	0.0083 (6)	0.0009 (6)	−0.0003 (6)
C16	0.0312 (8)	0.0334 (7)	0.0285 (7)	0.0079 (6)	−0.0021 (6)	0.0037 (6)
C21	0.0281 (7)	0.0201 (6)	0.0266 (6)	−0.0038 (6)	−0.0018 (5)	−0.0023 (5)
C22	0.0377 (8)	0.0345 (8)	0.0330 (8)	0.0069 (7)	0.0011 (7)	0.0025 (6)
C23	0.0523 (10)	0.0389 (8)	0.0296 (8)	0.0077 (7)	−0.0025 (7)	0.0058 (6)
C24	0.0491 (9)	0.0307 (7)	0.0273 (7)	−0.0037 (7)	0.0057 (7)	−0.0027 (6)
C25	0.0374 (9)	0.0396 (8)	0.0344 (8)	0.0023 (7)	0.0045 (7)	−0.0068 (7)
C26	0.0317 (8)	0.0345 (7)	0.0302 (7)	0.0036 (7)	−0.0027 (6)	−0.0013 (6)

Geometric parameters (Å, º)

Cl1—C8	1.7545 (15)	C11—C16	1.387 (2)
N1—C6	1.372 (2)	C11—C12	1.394 (2)
N1—C2	1.455 (2)	C12—C13	1.383 (2)
N1—H1	0.90 (3)	C12—H12	0.9500
C2—C3	1.517 (3)	C13—C14	1.402 (2)

C2—H2A	0.9900	C13—H13	0.9500
C2—H2B	0.9900	C14—C15	1.397 (2)
C3—C4	1.540 (2)	C14—C21	1.4937 (19)
C3—H3A	0.9900	C15—C16	1.395 (2)
C3—H3B	0.9900	C15—H15	0.9500
C4—C5	1.5175 (19)	C16—H16	0.9500
C4—C11	1.5267 (19)	C21—C26	1.398 (2)
C4—H4	1.0000	C21—C22	1.399 (2)
C5—C10	1.394 (2)	C22—C23	1.388 (2)
C5—C6	1.409 (2)	C22—H22	0.9500
C6—C7	1.407 (2)	C23—C24	1.383 (2)
C7—C8	1.379 (2)	C23—H23	0.9500
C7—H7	0.9500	C24—C25	1.387 (2)
C8—C9	1.386 (2)	C24—H24	0.9500
C9—C10	1.386 (2)	C25—C26	1.389 (2)
C9—H9	0.9500	C25—H25	0.9500
C10—H10	0.9500	C26—H26	0.9500

C6—N1—C2	122.48 (15)	C5—C10—H10	118.8
C6—N1—H1	115.7 (15)	C16—C11—C12	117.50 (13)
C2—N1—H1	120.3 (15)	C16—C11—C4	124.03 (13)
N1—C2—C3	111.07 (14)	C12—C11—C4	118.41 (13)
N1—C2—H2A	109.4	C13—C12—C11	121.50 (13)
C3—C2—H2A	109.4	C13—C12—H12	119.2
N1—C2—H2B	109.4	C11—C12—H12	119.2
C3—C2—H2B	109.4	C12—C13—C14	121.44 (13)
H2A—C2—H2B	108.0	C12—C13—H13	119.3
C2—C3—C4	110.31 (13)	C14—C13—H13	119.3
C2—C3—H3A	109.6	C15—C14—C13	116.80 (13)
C4—C3—H3A	109.6	C15—C14—C21	122.13 (12)
C2—C3—H3B	109.6	C13—C14—C21	121.06 (12)
C4—C3—H3B	109.6	C16—C15—C14	121.43 (13)
H3A—C3—H3B	108.1	C16—C15—H15	119.3
C5—C4—C11	114.82 (12)	C14—C15—H15	119.3
C5—C4—C3	108.73 (13)	C11—C16—C15	121.28 (13)
C11—C4—C3	110.15 (12)	C11—C16—H16	119.4
C5—C4—H4	107.6	C15—C16—H16	119.4
C11—C4—H4	107.6	C26—C21—C22	117.03 (13)
C3—C4—H4	107.6	C26—C21—C14	122.11 (12)
C10—C5—C6	118.75 (14)	C22—C21—C14	120.86 (13)
C10—C5—C4	121.53 (14)	C23—C22—C21	121.44 (15)
C6—C5—C4	119.69 (13)	C23—C22—H22	119.3
N1—C6—C7	119.52 (15)	C21—C22—H22	119.3
N1—C6—C5	121.15 (14)	C24—C23—C22	120.65 (15)
C7—C6—C5	119.33 (14)	C24—C23—H23	119.7
C8—C7—C6	119.28 (14)	C22—C23—H23	119.7
C8—C7—H7	120.4	C23—C24—C25	118.89 (14)
C6—C7—H7	120.4	C23—C24—H24	120.6

C7—C8—C9	122.71 (14)	C25—C24—H24	120.6
C7—C8—Cl1	118.13 (13)	C24—C25—C26	120.44 (15)
C9—C8—Cl1	119.17 (12)	C24—C25—H25	119.8
C8—C9—C10	117.34 (14)	C26—C25—H25	119.8
C8—C9—H9	121.3	C25—C26—C21	121.54 (14)
C10—C9—H9	121.3	C25—C26—H26	119.2
C9—C10—C5	122.47 (15)	C21—C26—H26	119.2
C9—C10—H10	118.8		

C6—N1—C2—C3	−25.4 (2)	C5—C4—C11—C12	−157.97 (14)
N1—C2—C3—C4	54.08 (17)	C3—C4—C11—C12	78.90 (17)
C2—C3—C4—C5	−55.71 (17)	C16—C11—C12—C13	1.8 (2)
C2—C3—C4—C11	70.92 (17)	C4—C11—C12—C13	−175.56 (15)
C11—C4—C5—C10	88.01 (17)	C11—C12—C13—C14	−0.1 (2)
C3—C4—C5—C10	−148.10 (14)	C12—C13—C14—C15	−1.3 (2)
C11—C4—C5—C6	−93.87 (16)	C12—C13—C14—C21	177.88 (14)
C3—C4—C5—C6	30.02 (18)	C13—C14—C15—C16	1.1 (2)
C2—N1—C6—C7	178.40 (14)	C21—C14—C15—C16	−178.13 (13)
C2—N1—C6—C5	−1.7 (2)	C12—C11—C16—C15	−2.0 (2)
C10—C5—C6—N1	176.93 (14)	C4—C11—C16—C15	175.14 (14)
C4—C5—C6—N1	−1.2 (2)	C14—C15—C16—C11	0.6 (2)
C10—C5—C6—C7	−3.2 (2)	C15—C14—C21—C26	0.8 (2)
C4—C5—C6—C7	178.64 (13)	C13—C14—C21—C26	−178.40 (13)
N1—C6—C7—C8	−179.37 (14)	C15—C14—C21—C22	−179.32 (14)
C5—C6—C7—C8	0.7 (2)	C13—C14—C21—C22	1.5 (2)
C6—C7—C8—C9	2.3 (2)	C26—C21—C22—C23	0.5 (2)
C6—C7—C8—Cl1	−178.17 (11)	C14—C21—C22—C23	−179.43 (14)
C7—C8—C9—C10	−2.6 (2)	C21—C22—C23—C24	0.1 (2)
Cl1—C8—C9—C10	177.80 (11)	C22—C23—C24—C25	−0.6 (2)
C8—C9—C10—C5	0.0 (2)	C23—C24—C25—C26	0.5 (2)
C6—C5—C10—C9	2.8 (2)	C24—C25—C26—C21	0.1 (2)
C4—C5—C10—C9	−179.01 (14)	C22—C21—C26—C25	−0.6 (2)
C5—C4—C11—C16	24.9 (2)	C14—C21—C26—C25	179.31 (14)
C3—C4—C11—C16	−98.23 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{i}	0.90 (3)	2.66 (3)	3.5466 (17)	171 (2)

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