

(Z)-4,6-Dichloro-N-(4-chlorophenyl)quinoline-3-carbimidoyl chloride

Matthias Weil,^{a*} David Chan Bodin Siebert^b and Michael Schnürch^b

^aInstitute for Chemical Technologies and Analytics, Division of Structural Chemistry, TU Wien, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria, and ^bInstitute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163, A-1060 Vienna, Austria. *Correspondence e-mail: matthias.weil@tuwien.ac.at

Received 16 February 2017

Accepted 17 February 2017

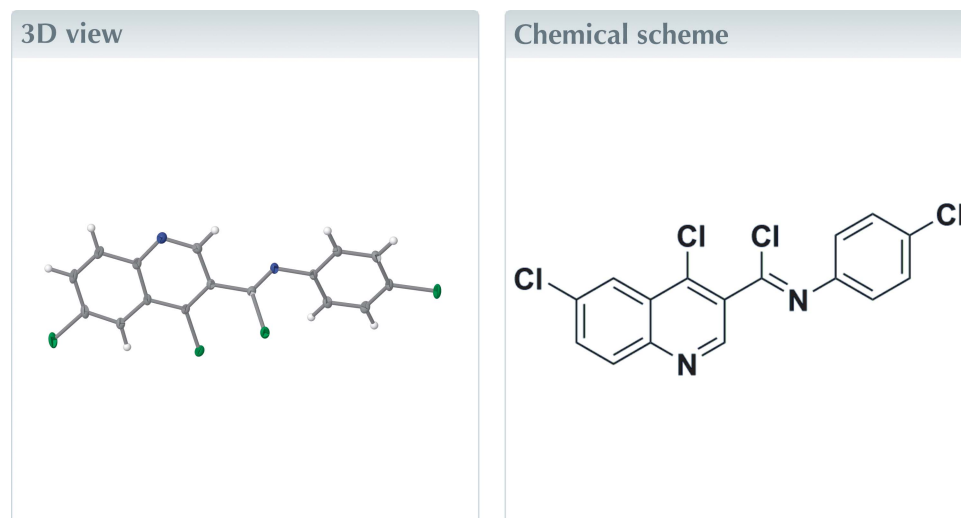
Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

Keywords: crystal structure; quinoline derivative; imidoyl chloride.

CCDC reference: 1533438

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

The title imidoyl chloride, C₁₆H₈Cl₄N₂, has formed accidentally as a side product during the synthesis of a quinolin-3-one derivative. The molecule is not flat [the dihedral angle between the 4,6-dichloroquinoline and the imidoyl chloride planes is 53.43 (5)°], preventing π -conjugation over the complete entity. In the crystal, C—H...N hydrogen bonding between a chlorophenyl C—H group and the quinoline N atom, as well as π – π stacking between neighbouring quinoline rings, consolidate the packing.



Structure description

Pyrazoloquinolinones are reported as highly active compounds (agonists, antagonists and partial agonists) for the benzodiazepine binding site at the GABA_A receptor (Yokoyama *et al.*, 1982). Additionally, they act as allosteric modulators *via* the α + β -interface (Ramerstorfer *et al.*, 2011; Varagic *et al.*, 2013). In the context of this research, we obtained the title compound, (III), as a by-product during the synthesis of ethyl 4,6-dichloroquinoline-3-carboxylate, (II) (Fig. 1).

The molecular structure of the title compound is displayed in Fig. 2. The 4,6-dichloroquinoline moiety is essentially planar (r.m.s. deviation = 0.0198 Å), with one of the substituted Cl atoms having the largest deviation from the mean plane [Cl2, 0.0468 (6) Å]. The complete molecule is not flat, with the imidoyl chloride moiety twisted out of the 4,6-dichloroquinoline plane by 53.43 (5)°. The dihedral angles between the imidoyl chloride moiety and the attached 3-chlorophenyl ring and between the 4,6-dichloroquinoline and the 3-chlorophenyl ring are 71.30 (14) and 18.20 (4)°, respectively. The torsion angle of the backbone connecting the three moieties, *i.e.* C8—C10—N2—C11, is –178.03 (13)°.

Individual molecules are arranged in layers parallel to (10 $\bar{1}$). Within a layer, π – π stacking between parallel quinoline rings (centroid-to-centroid distance between phenyl

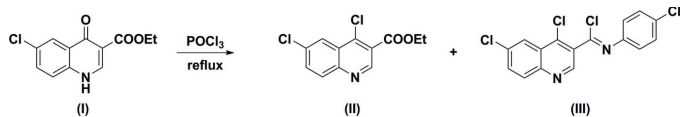


Figure 1
The reaction scheme for the synthesis of the title compound, (III), and the originally intended product (II).

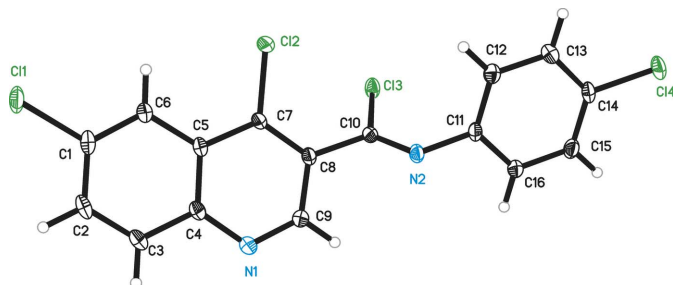


Figure 2
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are given as spheres of arbitrary radius.

and pyridine rings = 3.595 Å; plane-to-plane distance = 3.446 Å) stabilize this arrangement. Mutual intermolecular C—H···N hydrogen-bonding interactions between a C—H group of the chlorophenyl ring and the quinoline N atom of two molecules in neighbouring layers leads to the formation of inversion dimers (Fig. 3 and Table 1), with an $R_2^2(16)$ ring motif.

Further intermolecular halogen–halogen contacts, *i.e.* Cl3···Cl3(−*x* + 1, −*y* + 1, −*z*), with a distance of 3.3453 (7) Å, might also help to consolidate the crystal structure.

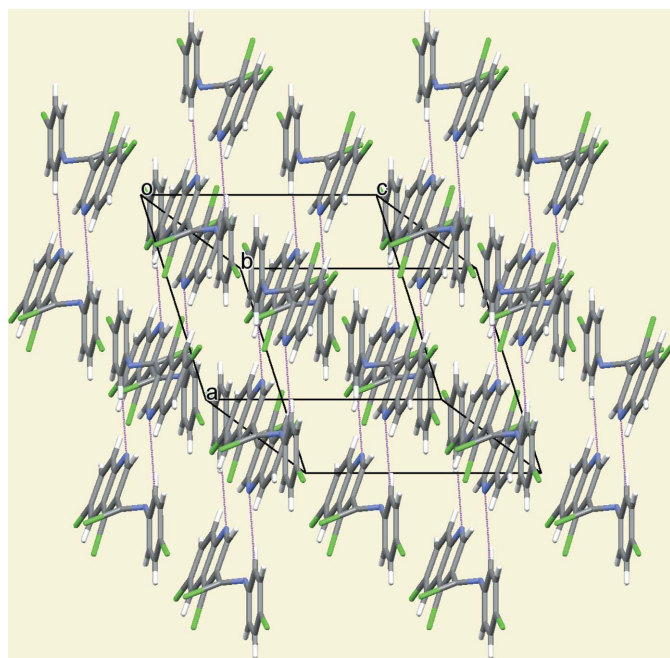


Figure 3
The packing of the molecules in the crystal structure of the title compound in a view along the b^* axis. C—H···N interactions are shown as magenta dashed lines.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C16—H16···N1 ⁱ	0.95	2.55	3.453 (2)	159

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₈ Cl ₄ N ₂
<i>M_r</i>	370.04
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.2595 (14), 9.9204 (15), 10.1731 (15)
α , β , γ (°)	64.259 (4), 72.322 (5), 64.093 (4)
<i>V</i> (Å ³)	749.6 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.78
Crystal size (mm)	0.30 × 0.20 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.689, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	26858, 4335, 3750
<i>R_{int}</i>	0.033
(sin θ/λ) _{max} (Å ^{−1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.025, 0.068, 1.04
No. of reflections	4335
No. of parameters	199
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.46, −0.20

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *XP* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

Ethyl 6-chloro-4-oxo-1,4-dihydroquinoline-3-carboxylate, (I), was prepared *via* the Gould–Jacobs reaction (Gould & Jacobs, 1939). 2 g of the crude product were dispersed in 10 ml phosphoryl chloride and refluxed for 2 h. The reaction mixture was then poured on ice, neutralized with saturated NaHCO₃ solution and extracted with CH₂Cl₂ (3 × 40 ml). The organic layer was washed with water (1 × 40 ml) and brine (1 × 40 ml), dried over Na₂SO₄, filtered and evaporated. The residue was purified *via* flash column chromatography (5–20% EtOAc in petroleum ether) to give a colourless solid (yield: 1.74 g, 6.45 mmol, 81%) of (II). The side product (III), representing the title compound, consisted of a light-yellow solid (32 mg). We assume that for formation of (III), the 3-chloroaniline employed in the synthesis of (I) was still present in the crude product and reacted in the following step with (II) to give (III) as a minor by-product.

¹H NMR (400 MHz, CDCl₃) for (III): δ 7.11 (*d*, *J* = 8.6 Hz, 2H, H_{2'} and H_{6'}), 7.44 (*d*, *J* = 8.5 Hz, 2H, H_{3'} and H_{5'}), 7.80 (*dd*,

$J = 8.9, 2.3$ Hz, 1H, H₇), 8.13 ($d, J = 9.0$ Hz, 1H, H₈), 8.37 ($d, J = 2.3$ Hz, 1H, H₅), 9.06 ($s, 1H, H_2$).

Refinement

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

Acknowledgements

The X-ray centre of TU Wien is acknowledged for financial support and providing access to the single-crystal diffractometer.

References

Bruker (2015). *APEX3, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

- Gould, R. G. Jr & Jacobs, W. A. (1939). *J. Am. Chem. Soc.* **61**, 2890–2895.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Ramerstorfer, J., Furtmüller, R., Sarto-Jackson, I., Varagic, Z., Sieghart, W. & Ernst, M. (2011). *J. Neurosci.* **31**, 870–877.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Varagic, Z., Wimmer, L., Schnürch, M., Mihovilovic, M. D., Huang, S., Rallapalli, S., Cook, J. M., Mirheydari, P., Ecker, G. F., Sieghart, W. & Ernst, M. (2013). *Br. J. Pharmacol.* **169**, 371–383.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yokoyama, N., Ritter, B. & Neubert, A. D. (1982). *J. Med. Chem.* **25**, 337–339.

full crystallographic data

IUCrData (2017). 2, x170274 [https://doi.org/10.1107/S2414314617002747]

(Z)-4,6-Dichloro-N-(4-chlorophenyl)quinoline-3-carbimidoyl chloride

Matthias Weil, David Chan Bodin Siebert and Michael Schnürch

(Z)-4,6-Dichloro-N-(4-chlorophenyl)quinoline-3-carbimidoyl chloride*Crystal data*

$C_{16}H_8Cl_4N_2$	$Z = 2$
$M_r = 370.04$	$F(000) = 372$
Triclinic, $P\bar{1}$	$D_x = 1.639 \text{ Mg m}^{-3}$
$a = 9.2595 (14) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 9.9204 (15) \text{ \AA}$	Cell parameters from 9901 reflections
$c = 10.1731 (15) \text{ \AA}$	$\theta = 2.3\text{--}29.9^\circ$
$\alpha = 64.259 (4)^\circ$	$\mu = 0.78 \text{ mm}^{-1}$
$\beta = 72.322 (5)^\circ$	$T = 100 \text{ K}$
$\gamma = 64.093 (4)^\circ$	Plate, light yellow
$V = 749.6 (2) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	4335 independent reflections
ω - and φ -scans	3750 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2015)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.689$, $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$
26858 measured reflections	$h = -12 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.2338P]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4335 reflections	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
199 parameters	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
0 restraints	

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl2	0.47318 (3)	0.78291 (3)	0.06212 (3)	0.02002 (7)
Cl3	0.44918 (4)	0.43177 (3)	0.18302 (3)	0.01907 (7)
Cl4	0.82948 (4)	-0.21042 (3)	0.69589 (3)	0.02329 (8)
Cl1	0.10737 (4)	1.41289 (3)	-0.17857 (4)	0.02702 (8)
N2	0.36407 (12)	0.44659 (11)	0.45370 (11)	0.01588 (19)
N1	-0.03955 (12)	0.86631 (12)	0.30708 (11)	0.0181 (2)
C8	0.23627 (14)	0.68779 (13)	0.26551 (12)	0.0139 (2)
C5	0.15842 (13)	0.96888 (12)	0.11060 (12)	0.0136 (2)
C10	0.34979 (13)	0.52050 (13)	0.31946 (12)	0.0140 (2)
C4	0.00070 (14)	0.98888 (13)	0.19243 (13)	0.0154 (2)
C11	0.47579 (14)	0.28773 (13)	0.50743 (12)	0.0144 (2)
C9	0.07433 (14)	0.72394 (14)	0.34052 (13)	0.0172 (2)
H9	0.0469	0.6389	0.4204	0.021*
C12	0.64151 (15)	0.25868 (14)	0.47403 (13)	0.0178 (2)
H12	0.6800	0.3437	0.4112	0.021*
C7	0.27708 (13)	0.81186 (13)	0.15223 (12)	0.0132 (2)
C13	0.75057 (15)	0.10521 (14)	0.53263 (14)	0.0186 (2)
H13	0.8639	0.0846	0.5109	0.022*
C1	0.06808 (15)	1.24874 (13)	-0.03627 (13)	0.0186 (2)
C2	-0.08890 (15)	1.27159 (14)	0.04404 (14)	0.0195 (2)
H2	-0.1711	1.3749	0.0209	0.023*
C14	0.69239 (14)	-0.01764 (13)	0.62317 (13)	0.0166 (2)
C3	-0.12176 (14)	1.14356 (14)	0.15572 (14)	0.0186 (2)
H3	-0.2278	1.1582	0.2094	0.022*
C6	0.19062 (14)	1.10229 (13)	-0.00598 (13)	0.0159 (2)
H6	0.2954	1.0902	-0.0621	0.019*
C15	0.52756 (15)	0.00998 (14)	0.65689 (13)	0.0191 (2)
H15	0.4897	-0.0757	0.7184	0.023*
C16	0.41786 (15)	0.16421 (13)	0.59996 (13)	0.0179 (2)
H16	0.3045	0.1851	0.6240	0.021*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.01386 (13)	0.01335 (12)	0.02513 (15)	-0.00307 (10)	0.00064 (10)	-0.00410 (10)
Cl3	0.02500 (15)	0.01218 (12)	0.01400 (13)	-0.00016 (10)	-0.00392 (10)	-0.00510 (10)
Cl4	0.02391 (15)	0.01314 (13)	0.02437 (15)	0.00239 (10)	-0.01131 (12)	-0.00309 (11)
Cl1	0.03162 (17)	0.01036 (12)	0.03095 (17)	-0.00513 (11)	-0.01023 (13)	0.00125 (11)
N2	0.0173 (5)	0.0109 (4)	0.0146 (5)	-0.0015 (3)	-0.0033 (4)	-0.0031 (3)
N1	0.0156 (5)	0.0163 (5)	0.0182 (5)	-0.0027 (4)	-0.0028 (4)	-0.0051 (4)
C8	0.0153 (5)	0.0107 (4)	0.0132 (5)	-0.0019 (4)	-0.0037 (4)	-0.0038 (4)
C5	0.0160 (5)	0.0104 (4)	0.0139 (5)	-0.0016 (4)	-0.0061 (4)	-0.0042 (4)
C10	0.0137 (5)	0.0113 (4)	0.0143 (5)	-0.0025 (4)	-0.0013 (4)	-0.0047 (4)
C4	0.0151 (5)	0.0138 (5)	0.0161 (5)	-0.0013 (4)	-0.0059 (4)	-0.0056 (4)
C11	0.0181 (5)	0.0107 (5)	0.0109 (5)	-0.0010 (4)	-0.0043 (4)	-0.0033 (4)

C9	0.0164 (5)	0.0152 (5)	0.0153 (5)	-0.0042 (4)	-0.0016 (4)	-0.0031 (4)
C12	0.0198 (6)	0.0131 (5)	0.0183 (5)	-0.0052 (4)	-0.0042 (4)	-0.0034 (4)
C7	0.0123 (5)	0.0117 (5)	0.0139 (5)	-0.0016 (4)	-0.0033 (4)	-0.0048 (4)
C13	0.0159 (5)	0.0167 (5)	0.0212 (6)	-0.0026 (4)	-0.0059 (4)	-0.0061 (4)
C1	0.0254 (6)	0.0106 (5)	0.0193 (6)	-0.0038 (4)	-0.0105 (5)	-0.0025 (4)
C2	0.0206 (6)	0.0123 (5)	0.0239 (6)	0.0021 (4)	-0.0117 (5)	-0.0072 (4)
C14	0.0207 (6)	0.0113 (5)	0.0143 (5)	0.0002 (4)	-0.0081 (4)	-0.0036 (4)
C3	0.0154 (5)	0.0163 (5)	0.0218 (6)	0.0009 (4)	-0.0065 (4)	-0.0087 (4)
C6	0.0179 (5)	0.0117 (5)	0.0168 (5)	-0.0035 (4)	-0.0050 (4)	-0.0040 (4)
C15	0.0228 (6)	0.0128 (5)	0.0160 (5)	-0.0050 (4)	-0.0033 (4)	-0.0012 (4)
C16	0.0172 (5)	0.0142 (5)	0.0160 (5)	-0.0028 (4)	-0.0024 (4)	-0.0027 (4)

Geometric parameters (Å, °)

C12—C7	1.7268 (12)	C11—C16	1.3933 (16)
C13—C10	1.7680 (11)	C9—H9	0.9500
C14—C14	1.7424 (11)	C12—C13	1.3881 (15)
C11—C1	1.7407 (12)	C12—H12	0.9500
N2—C10	1.2551 (15)	C13—C14	1.3861 (17)
N2—C11	1.4224 (13)	C13—H13	0.9500
N1—C9	1.3121 (14)	C1—C6	1.3698 (15)
N1—C4	1.3704 (15)	C1—C2	1.4083 (18)
C8—C7	1.3768 (15)	C2—C3	1.3678 (17)
C8—C9	1.4255 (16)	C2—H2	0.9500
C8—C10	1.4817 (14)	C14—C15	1.3858 (17)
C5—C6	1.4190 (15)	C3—H3	0.9500
C5—C4	1.4202 (16)	C6—H6	0.9500
C5—C7	1.4237 (14)	C15—C16	1.3920 (15)
C4—C3	1.4209 (15)	C15—H15	0.9500
C11—C12	1.3911 (17)	C16—H16	0.9500
C10—N2—C11	122.47 (10)	C5—C7—C12	118.57 (8)
C9—N1—C4	117.52 (10)	C14—C13—C12	119.30 (11)
C7—C8—C9	117.66 (10)	C14—C13—H13	120.4
C7—C8—C10	124.91 (10)	C12—C13—H13	120.4
C9—C8—C10	117.38 (10)	C6—C1—C2	122.32 (11)
C6—C5—C4	119.79 (10)	C6—C1—C11	119.01 (10)
C6—C5—C7	123.51 (10)	C2—C1—C11	118.67 (9)
C4—C5—C7	116.71 (10)	C3—C2—C1	119.32 (10)
N2—C10—C8	121.50 (10)	C3—C2—H2	120.3
N2—C10—C13	123.61 (9)	C1—C2—H2	120.3
C8—C10—C13	114.73 (8)	C15—C14—C13	121.29 (10)
N1—C4—C5	123.25 (10)	C15—C14—C14	119.47 (9)
N1—C4—C3	117.90 (11)	C13—C14—C14	119.25 (9)
C5—C4—C3	118.85 (10)	C2—C3—C4	120.85 (11)
C12—C11—C16	120.60 (10)	C2—C3—H3	119.6
C12—C11—N2	119.73 (10)	C4—C3—H3	119.6
C16—C11—N2	119.57 (10)	C1—C6—C5	118.87 (11)

N1—C9—C8	124.64 (11)	C1—C6—H6	120.6
N1—C9—H9	117.7	C5—C6—H6	120.6
C8—C9—H9	117.7	C14—C15—C16	119.52 (11)
C13—C12—C11	119.87 (11)	C14—C15—H15	120.2
C13—C12—H12	120.1	C16—C15—H15	120.2
C11—C12—H12	120.1	C15—C16—C11	119.41 (11)
C8—C7—C5	120.21 (10)	C15—C16—H16	120.3
C8—C7—C12	121.19 (8)	C11—C16—H16	120.3

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>
C16—H16 \cdots N1 ⁱ	0.95	2.55	3.453 (2)	159

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