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10-(4-Chlorophenyl)-7-methyl-5,6-dihydrobenzo[*h*]pyrazolo[5,1-*b*]quinazoline and 2-(4-chlorophenyl)-5-methyl-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]quinazoline: isomeric molecules linked into hydrogen-bonded dimers or π-stacked chains

John N. Low,[a] Justo Cobo,[b] Jairo Quiroga,[c] Jaime Portilla[c] and Christopher Glidewell[d]*

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [c]Grupo de Investigación de Compuestos Heterociclícos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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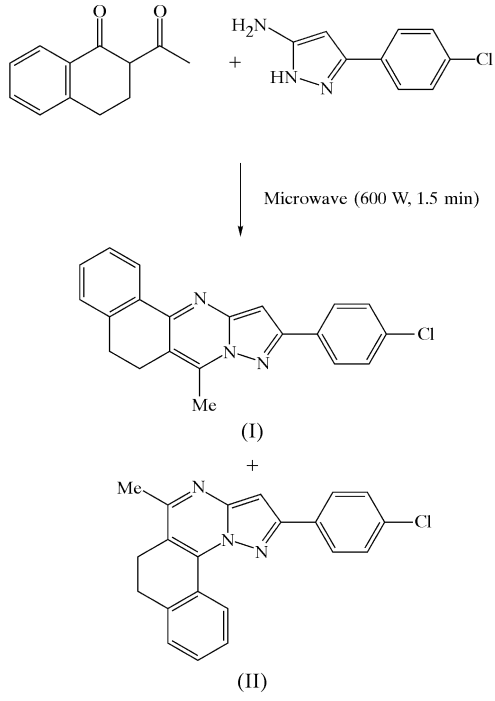
The isomeric title compounds 10-(4-chlorophenyl)-7-methyl-5,6-dihydrobenzo[*h*]pyrazolo[5,1-*b*]quinazoline, (I), and 2-(4-chlorophenyl)-5-methyl-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]-quinazoline, (II), both $C_{21}H_{16}ClN_3$, exhibit peripheral delocalization in the heteroaromatic portion of the fused ring system. The molecules of (I) are linked into centrosymmetric dimers by a single C—H···π(arene) hydrogen bond, and the molecules of (II), where $Z' = 2$, are linked by π–π stacking interactions into chains in which the two types of molecules alternate.

Comment

The quinazoline skeleton is an important pharmacophore which occurs frequently in medicinal chemistry literature (Fry *et al.*, 1994). In particular, pyrazolo[1,5-*c*]quinazolinones have been shown to be potent amino acid antagonists (McQuaid *et al.*, 1992), and anti-inflammatory, antiasthmatic and anti-allergenic agents and immunosuppressants (Casey *et al.*, 1980). Continuing our studies of the application of free-solvent cyclocondensation procedures under microwave irradiation, we have now prepared two benzo-fused pyrazolo[5,1-*b*]-quinazolines from a 5-aminopyrazole and 2-acetyl-1-tetralone, resulting in a regioisomeric mixture 10-(4-chlorophenyl)-7-methyl-5,6-dihydrobenzo[*h*]pyrazolo[5,1-*b*]quinazoline, (I), and 2-(4-chlorophenyl)-5-methyl-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]quinazoline, (II), in an approximate ratio of 1:4.

The isomeric compounds (I) and (II) both crystallize in space group $P\overline{1}$, but with Z' values of 1 and 2, respectively. Within the molecule of (I) (Fig. 1), the C10—C11 and C11—C12 bonds, which in the classically bond-localized form are double and single bonds, respectively, differ in length by only



ca 0.01 Å (Table 1). Similarly, the C12—N1 and N9—C10 bonds, which are formally double and single bonds, respectively, are nearly identical in length. At the same time, the N1a—C10 bond is much longer than the other formally single N—C bonds, N1a—C2 and N9—C10. Taken together, these observations indicate an important contribution to the overall molecular–electronic structure of the heterobicyclic portion of the molecule, of a fairly delocalized 10-π periphery with a rather weak cross-ring bond. A similar pattern of distances, leading to a similar conclusion, is apparent in each of the two independent molecules, 1 and 2, of compound (II) (Fig. 2 Table 3).

By contrast, the bond lengths in the terminal carbocyclic rings of the fused ring system, ring C4a/C5–C8/C8a in (I) and rings C*n*1c/C*n*2–C*n*5/C*n*5a in (II), where $n = 1$ or 2 for the

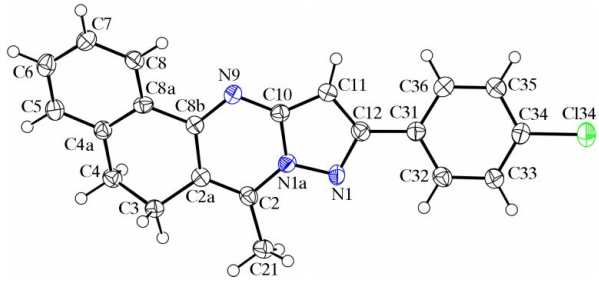


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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molecules of types 1 and 2 (Fig. 2), are consistent with typical aromatic delocalization. For the intervening non-planar rings, the ring-puckering parameters (Cremer & Pople, 1975) for the atom sequence C2a/C3/C4/C4a/C8a/C8b in (I), θ = 113.7 (4)° and φ = 268.4 (4)°, correspond to a conformation intermediate between the half-chair and screw-boat forms (Evans & Boeyens, 1989). For the atom sequences C*n*1b/C*n*1c/C*n*5a/C*n*6/C*n*7/C*n*7a in (II), the corresponding values are θ = 68.6 (4)° and φ = 205.6 (4)° for n = 1, and θ = 68.5 (4)° and φ = 206.6 (4)° for n = 2, corresponding very closely to the screw-boat conformation.

The molecules in (I) are linked into centrosymmetric dimers by means of a single C—H···π(arene) hydrogen bond (Table 2). Atom C3 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* the axial atom H3*A*, to the chlorinated ring (C31–C36) in the molecule at ($1-x$, $1-y$, $1-z$), so generating a dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 3). There are no direction-specific interactions between these dimers.

In compound (II), the molecules are linked into chains by the concerted action of two independent π–π stacking interactions. The heterocyclic ring containing atom N19 in the type 1 molecule at (x, y, z) makes a dihedral angle of 1.5 (2)° with each of the chlorinated rings in the two type 2 molecules at (x, y, z) and ($1+x$, y, z). The interplanar spacings are both *ca* 3.47 Å, and the ring-centroid separations are 3.544 (2) Å within the asymmetric unit, and 3.546 (2) Å to the molecule at ($1+x$, y, z). These interactions are augmented by an entirely complementary pair of interactions between the ring containing atom N29 in the type 2 molecules at (x, y, z) and ($1+x$, y, z), and the chlorinated ring in the type 1 molecule at (x, y, z). Here, the dihedral angles between adjacent ring planes are both 7.2 (2)°, with interplanar spacings of *ca* 3.5 Å within the asymmetric unit and *ca* 3.47 Å to the adjacent unit. The respective ring-centroid separations are 3.589 (2) and 3.503 (2) Å. The effect of these interactions is to link the molecules into a chain running parallel to the [100] direction,

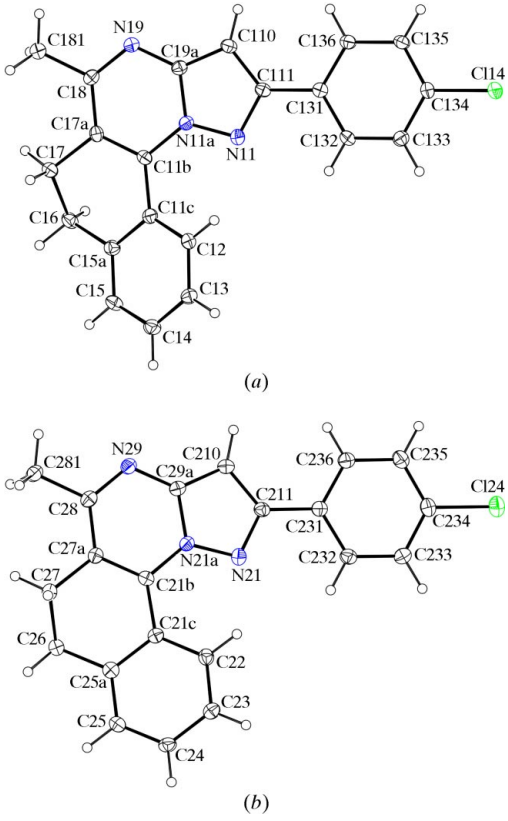

Figure 2
The two independent molecules of (II), showing the atom-labelling scheme in (*a*) a type 1 molecule and (*b*) a type 2 molecule. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

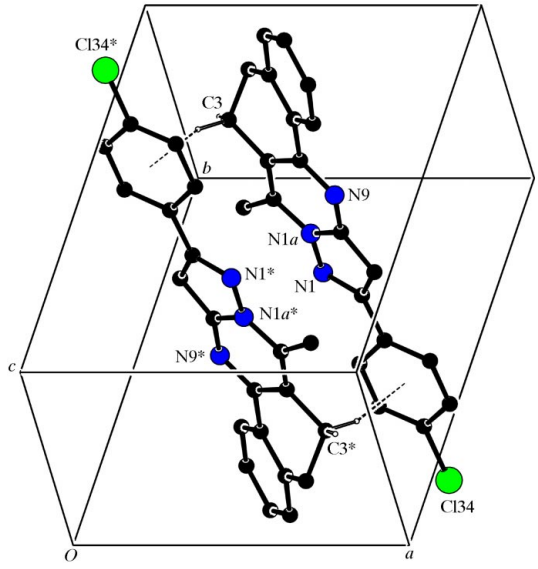

Figure 3
Part of the crystal structure of (I), showing the formation of a cyclic centrosymmetric dimer. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1-x$, $1-y$, $1-z$).

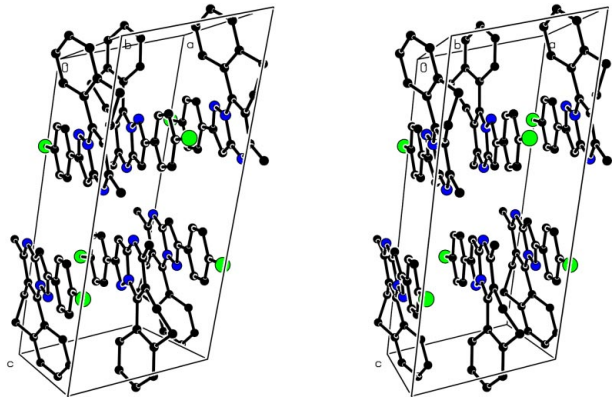

Figure 4
A stereoview of part of the crystal structure of (II), showing an anti-parallel pair of π-stacked chains along [100]. For the sake of clarity, H atoms have been omitted.

in which molecules of the two types alternate. Two antiparallel chains of this type pass through each unit cell (Fig. 4), but there are no direction-specific interactions between adjacent chains.

Experimental

Equimolar quantities of 5-amino-3-(4-chlorophenyl)-1*H*-pyrazole (500 mg, 2.6 mmol) and 2-acetyl-1-tetralone (485 mg, 2.6 mmol) were placed in Pyrex open vessels and irradiated in a domestic microwave oven for 1.5 min at 600 W. The product mixture was extracted with ethanol. After the solvent had been removed, the products were separated by column chromatography on silica gel, using hexane–ethyl acetate (3:1 *v*/*v*) as eluant. Compound (I) was obtained as the first fraction (yield 18%, m.p. 449 K). MS (EI, 70 eV, %): 348/346 (8/35, *M*+1), 347/345 (39/100, M^+), 344 (28), 166 (11), 75 (8). Analysis found: C 72.9, H 4.6, N 12.2%; $C_{21}H_{16}ClN_3$ requires: C 72.9, H 4.7, N 12.2%. Yellow crystals of (I) suitable for single-crystal X-ray diffraction were obtained by direct evaporation of the chromatographic eluate. Compound (II) was obtained as the second fraction (yield 70%, m.p. 505 K). MS (EI, 70 eV, %): 348/346 (8/32, *M*+1), 347/345 (37/100, M^+), 344 (24), 166 (22), 75 (30). Analysis found: C 72.8, H 4.6, N 12.1%; $C_{21}H_{16}ClN_3$ requires: C 72.9, H 4.7, N 12.2%. Brown crystals of (II) suitable for single-crystal X-ray diffraction were obtained by direct evaporation of the chromatographic eluate.

Compound (I)

Crystal data

$C_{21}H_{16}ClN_3$
M_r = 345.82
Triclinic, $P\overline{1}$
a = 9.2382 (8) Å
b = 10.3054 (8) Å
c = 10.3184 (9) Å
α = 62.720 (4)°
β = 83.098 (4)°
γ = 70.531 (5)°
V = 822.54 (12) Å^3
Z = 2
D_x = 1.396 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3763 reflections
θ = 3.3–27.6°
μ = 0.24 mm^{-1}
T = 120 (2) K
Plate, yellow
0.34 × 0.19 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.914, T_{max} = 0.981
17 454 measured reflections
3763 independent reflections
2156 reflections with $I > 2\sigma(I)$
R_{int} = 0.094
θ_{max} = 27.6°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.153
S = 0.96
3763 reflections
229 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.3108P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å) for (I).

N1—N1a	1.357 (3)	N9—C10	1.351 (3)
N1a—C2	1.365 (3)	C10—C11	1.381 (4)
C2—C2a	1.365 (4)	C11—C12	1.393 (4)
C2a—C8b	1.442 (4)	C12—N1	1.345 (3)
C8b—N9	1.319 (3)	N1a—C10	1.394 (3)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

*Cg*1 is the centroid of the C31–C36 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···*Cg*1^{i}	0.99	2.92	3.815 (3)	150

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

Compound (II)

Crystal data

$C_{21}H_{16}ClN_3$
M_r = 345.82
Triclinic, $P\overline{1}$
a = 7.0098 (3) Å
b = 15.0306 (7) Å
c = 17.0060 (8) Å
α = 111.492 (2)°
β = 101.406 (3)°
γ = 97.981 (3)°
V = 1589.81 (13) Å^3
Z = 4
D_x = 1.445 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7321 reflections
θ = 3.0–27.6°
μ = 0.25 mm^{-1}
T = 120 (2) K
Needle, pale brown
0.14 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.949, T_{max} = 0.993
35 785 measured reflections
7321 independent reflections
4073 reflections with $I > 2\sigma(I)$
R_{int} = 0.113
θ_{max} = 27.6°
$h = -8 \rightarrow 9$
$k = -19 \rightarrow 19$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.152
S = 1.03
7321 reflections
453 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.1965P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 3
Selected geometric parameters (Å) for (II).

N11—N11a	1.359 (3)	N21—N21a	1.355 (3)
N11a—C11b	1.381 (3)	N21a—C21b	1.378 (3)
C11b—C17a	1.378 (4)	C21b—C27a	1.381 (4)
C17a—C18	1.419 (4)	C27a—C28	1.422 (4)
C18—N19	1.321 (3)	C28—N29	1.316 (3)
N19—C19a	1.351 (3)	N29—C29a	1.350 (3)
C19a—C110	1.379 (4)	C29a—C210	1.377 (4)
C110—C111	1.398 (4)	C210—C211	1.390 (4)
C111—N11	1.348 (3)	C211—N21	1.348 (3)
N11a—C19a	1.393 (3)	N21a—C29a	1.403 (3)

Crystals of compounds (I) and (II) are triclinic. For each, the space group $P\overline{1}$ was selected and confirmed by the structure analysis. All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic and heteroaromatic), 0.98 (CH_3) or 0.99 Å (CH_2), and with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for the methyl groups.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s)

used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1742). Services for accessing these data are described at the back of the journal.

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supporting information

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Computing details

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

(I) 9-(4-Chlorophenyl)-7-methyl-5,6-dihydrobenzo[*h*]pyrazolo[3,2-*b*]quinazoline

Crystal data

$C_{21}H_{16}ClN_3$
$M_r = 345.82$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.2382\ (8)$ Å
$b = 10.3054\ (8)$ Å
$c = 10.3184\ (9)$ Å
$\alpha = 62.720\ (4)°$
$\beta = 83.098\ (4)°$
$\gamma = 70.531\ (5)°$
$V = 822.54\ (12)$ Å^3
$Z = 2$
$F(000) = 360$
$D_x = 1.396$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3763 reflections
$\theta = 3.3–27.6°$
$\mu = 0.24$ mm^{-1}
$T = 120$ K
Plate, yellow
0.34 × 0.19 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.914$, $T_{max} = 0.981$
17454 measured reflections
3763 independent reflections
2156 reflections with $I > 2\sigma(I)$
$R_{int} = 0.094$
$\theta_{max} = 27.6°$, $\theta_{min} = 3.3°$
$h = -11\rightarrow11$
$k = -13\rightarrow12$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.153$
$S = 0.96$
3763 reflections
229 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.3108P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.5577 (3)	0.6152 (2)	0.2713 (2)	0.0255 (5)
N1a	0.5130 (3)	0.6765 (2)	0.3669 (2)	0.0243 (5)
C2	0.3685 (3)	0.7693 (3)	0.3697 (3)	0.0255 (6)
C2a	0.3464 (3)	0.8265 (3)	0.4691 (3)	0.0242 (6)
C3	0.1939 (3)	0.9296 (3)	0.4859 (3)	0.0264 (6)
C4	0.2139 (3)	1.0496 (3)	0.5235 (3)	0.0270 (6)
C5	0.3036 (3)	1.0335 (3)	0.7534 (3)	0.0286 (7)
C4a	0.3231 (3)	0.9742 (3)	0.6536 (3)	0.0246 (6)
C6	0.4060 (3)	0.9650 (3)	0.8719 (3)	0.0319 (7)
C7	0.5291 (3)	0.8343 (3)	0.8922 (3)	0.0301 (7)
C8	0.5501 (3)	0.7751 (3)	0.7927 (3)	0.0276 (6)
C8a	0.4484 (3)	0.8441 (3)	0.6724 (3)	0.0245 (6)
C8b	0.4733 (3)	0.7819 (3)	0.5657 (3)	0.0227 (6)
N9	0.6107 (3)	0.6882 (2)	0.5635 (2)	0.0252 (5)
C10	0.6331 (3)	0.6356 (3)	0.4620 (3)	0.0238 (6)
C11	0.7595 (3)	0.5459 (3)	0.4217 (3)	0.0267 (6)
C12	0.7079 (3)	0.5372 (3)	0.3054 (3)	0.0264 (6)
C21	0.2530 (3)	0.7957 (3)	0.2637 (3)	0.0323 (7)
C31	0.7918 (3)	0.4546 (3)	0.2206 (3)	0.0250 (6)
C32	0.7111 (3)	0.4332 (3)	0.1301 (3)	0.0284 (7)
C33	0.7858 (3)	0.3537 (3)	0.0516 (3)	0.0295 (7)
C34	0.9444 (3)	0.2940 (3)	0.0637 (3)	0.0286 (7)
Cl34	1.04079 (9)	0.19353 (9)	−0.03472 (9)	0.0413 (3)
C35	1.0280 (3)	0.3134 (3)	0.1521 (3)	0.0305 (7)
C36	0.9516 (3)	0.3938 (3)	0.2302 (3)	0.0293 (7)
H3A	0.1381	0.8667	0.5641	0.032*
H3B	0.1315	0.9821	0.3938	0.032*
H4A	0.2541	1.1232	0.4388	0.045 (9)*
H4B	0.1129	1.1078	0.5452	0.030 (7)*
H5	0.2189	1.1223	0.7404	0.034*
H6	0.3919	1.0074	0.9389	0.038*
H7	0.5984	0.7858	0.9740	0.036*
H8	0.6350	0.6863	0.8063	0.033*
H11	0.8606	0.4997	0.4643	0.032*

H21A	0.2779	0.8591	0.1644	0.048*
H21B	0.1504	0.8486	0.2852	0.048*
H21C	0.2547	0.6966	0.2719	0.048*
H32	0.6022	0.4743	0.1223	0.034*
H33	0.7293	0.3402	−0.0098	0.035*
H35	1.1369	0.2720	0.1593	0.037*
H36	1.0086	0.4076	0.2910	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0274 (14)	0.0257 (12)	0.0236 (13)	−0.0049 (10)	0.0026 (10)	−0.0139 (10)
N1a	0.0261 (13)	0.0252 (12)	0.0228 (13)	−0.0078 (10)	0.0000 (10)	−0.0116 (10)
C2	0.0233 (16)	0.0258 (15)	0.0229 (15)	−0.0043 (12)	0.0008 (12)	−0.0095 (12)
C2a	0.0254 (15)	0.0225 (14)	0.0214 (15)	−0.0072 (12)	0.0010 (12)	−0.0073 (12)
C3	0.0231 (15)	0.0298 (15)	0.0253 (15)	−0.0052 (12)	−0.0020 (12)	−0.0130 (12)
C4	0.0251 (16)	0.0254 (15)	0.0294 (16)	−0.0071 (12)	0.0002 (12)	−0.0117 (13)
C5	0.0299 (16)	0.0282 (15)	0.0270 (16)	−0.0091 (13)	0.0042 (13)	−0.0126 (13)
C4a	0.0245 (15)	0.0252 (14)	0.0251 (15)	−0.0085 (12)	0.0024 (12)	−0.0120 (12)
C6	0.0373 (18)	0.0345 (16)	0.0274 (17)	−0.0139 (14)	0.0069 (14)	−0.0163 (14)
C7	0.0342 (17)	0.0339 (16)	0.0231 (16)	−0.0105 (13)	−0.0011 (13)	−0.0130 (13)
C8	0.0240 (15)	0.0287 (15)	0.0287 (16)	−0.0059 (12)	0.0003 (12)	−0.0131 (13)
C8a	0.0240 (15)	0.0279 (15)	0.0227 (15)	−0.0117 (12)	0.0005 (12)	−0.0096 (12)
C8b	0.0234 (15)	0.0219 (14)	0.0214 (15)	−0.0075 (12)	0.0017 (12)	−0.0084 (12)
N9	0.0275 (13)	0.0265 (12)	0.0244 (13)	−0.0088 (10)	0.0012 (10)	−0.0134 (11)
C10	0.0241 (15)	0.0223 (14)	0.0245 (15)	−0.0079 (12)	−0.0008 (12)	−0.0093 (12)
C11	0.0230 (15)	0.0281 (15)	0.0286 (16)	−0.0061 (12)	−0.0006 (12)	−0.0133 (13)
C12	0.0254 (16)	0.0244 (14)	0.0280 (16)	−0.0071 (12)	0.0012 (12)	−0.0112 (12)
C21	0.0261 (16)	0.0375 (17)	0.0315 (17)	−0.0047 (13)	−0.0033 (13)	−0.0166 (14)
C31	0.0273 (16)	0.0235 (14)	0.0211 (15)	−0.0060 (12)	−0.0011 (12)	−0.0081 (12)
C32	0.0261 (16)	0.0259 (15)	0.0277 (16)	−0.0036 (12)	−0.0006 (12)	−0.0104 (13)
C33	0.0279 (17)	0.0294 (15)	0.0311 (17)	−0.0061 (13)	0.0000 (13)	−0.0152 (13)
C34	0.0335 (17)	0.0266 (15)	0.0257 (16)	−0.0075 (13)	0.0011 (13)	−0.0131 (13)
Cl34	0.0385 (5)	0.0466 (5)	0.0441 (5)	−0.0042 (4)	0.0021 (4)	−0.0309 (4)
C35	0.0275 (16)	0.0299 (16)	0.0312 (17)	−0.0071 (13)	0.0010 (13)	−0.0127 (13)
C36	0.0334 (18)	0.0298 (15)	0.0275 (16)	−0.0120 (13)	−0.0001 (13)	−0.0132 (13)

Geometric parameters (Å, º)

N1—N1a	1.357 (3)	C5—H5	0.95
N1a—C2	1.365 (3)	C4a—C8a	1.399 (4)
C2—C2a	1.365 (4)	C6—C7	1.389 (4)
C2a—C8b	1.442 (4)	C6—H6	0.95
C8b—N9	1.319 (3)	C7—C8	1.381 (4)
N9—C10	1.351 (3)	C7—H7	0.95
C10—C11	1.381 (4)	C8—C8a	1.398 (4)
C11—C12	1.393 (4)	C8—H8	0.95
C12—N1	1.345 (3)	C8a—C8b	1.471 (4)

N1a—C10	1.394 (3)	C11—H11	0.95
C2—C21	1.492 (4)	C12—C31	1.473 (4)
C21—H21A	0.98	C31—C36	1.393 (4)
C21—H21B	0.98	C31—C32	1.394 (4)
C21—H21C	0.98	C32—C33	1.379 (4)
C2a—C3	1.502 (4)	C32—H32	0.95
C3—C4	1.524 (4)	C33—C34	1.383 (4)
C3—H3A	0.99	C33—H33	0.95
C3—H3B	0.99	C34—C35	1.382 (4)
C4—C4a	1.507 (4)	C34—Cl34	1.741 (3)
C4—H4A	0.99	C35—C36	1.385 (4)
C4—H4B	0.99	C35—H35	0.95
C5—C4a	1.387 (4)	C36—H36	0.95
C5—C6	1.390 (4)		

C12—N1—N1a	104.2 (2)	C6—C7—H7	120.2
N1—N1a—C2	124.6 (2)	C7—C8—C8a	121.0 (3)
N1—N1a—C10	112.1 (2)	C7—C8—H8	119.5
C2—N1a—C10	123.2 (2)	C8a—C8—H8	119.5
N1a—C2—C2a	116.5 (2)	C8—C8a—C4a	119.3 (2)
N1a—C2—C21	115.8 (2)	C8—C8a—C8b	120.6 (2)
C2a—C2—C21	127.7 (2)	C4a—C8a—C8b	120.1 (2)
C2—C21—H21A	109.5	N9—C8b—C2a	123.5 (2)
C2—C21—H21B	109.5	N9—C8b—C8a	118.2 (2)
H21A—C21—H21B	109.5	C2a—C8b—C8a	118.4 (2)
C2—C21—H21C	109.5	C8b—N9—C10	117.5 (2)
H21A—C21—H21C	109.5	N9—C10—C11	133.9 (2)
H21B—C21—H21C	109.5	N9—C10—N1a	120.5 (2)
C2—C2a—C8b	118.7 (2)	C11—C10—N1a	105.6 (2)
C2—C2a—C3	122.8 (2)	C10—C11—C12	105.6 (2)
C8b—C2a—C3	118.4 (2)	C10—C11—H11	127.2
C2a—C3—C4	111.3 (2)	C12—C11—H11	127.2
C2a—C3—H3A	109.4	N1—C12—C11	112.5 (2)
C4—C3—H3A	109.4	N1—C12—C31	117.8 (2)
C2a—C3—H3B	109.4	C11—C12—C31	129.7 (3)
C4—C3—H3B	109.4	C36—C31—C32	118.4 (3)
H3A—C3—H3B	108.0	C36—C31—C12	121.6 (2)
C4a—C4—C3	110.7 (2)	C32—C31—C12	119.9 (2)
C4a—C4—H4A	109.5	C33—C32—C31	121.5 (3)
C3—C4—H4A	109.5	C33—C32—H32	119.3
C4a—C4—H4B	109.5	C31—C32—H32	119.3
C3—C4—H4B	109.5	C32—C33—C34	118.9 (3)
H4A—C4—H4B	108.1	C32—C33—H33	120.6
C4a—C5—C6	121.0 (3)	C34—C33—H33	120.6
C4a—C5—H5	119.5	C35—C34—C33	121.2 (3)
C6—C5—H5	119.5	C35—C34—Cl34	119.3 (2)
C5—C4a—C8a	119.4 (2)	C33—C34—Cl34	119.6 (2)
C5—C4a—C4	121.2 (2)	C34—C35—C36	119.4 (3)

C8a—C4a—C4	119.5 (2)	C34—C35—H35	120.3
C7—C6—C5	119.8 (3)	C36—C35—H35	120.3
C7—C6—H6	120.1	C35—C36—C31	120.7 (3)
C5—C6—H6	120.1	C35—C36—H36	119.7
C8—C7—C6	119.7 (3)	C31—C36—H36	119.7
C8—C7—H7	120.2		

C12—N1—N1a—C2	178.2 (2)	C4a—C8a—C8b—N9	161.9 (2)
C12—N1—N1a—C10	−0.9 (3)	C8—C8a—C8b—C2a	162.6 (2)
N1—N1a—C2—C2a	−176.9 (2)	C4a—C8a—C8b—C2a	−18.0 (4)
C10—N1a—C2—C2a	2.1 (4)	C2a—C8b—N9—C10	1.9 (4)
N1—N1a—C2—C21	3.4 (4)	C8a—C8b—N9—C10	−178.1 (2)
C10—N1a—C2—C21	−177.7 (2)	C8b—N9—C10—C11	175.6 (3)
N1a—C2—C2a—C8b	−2.0 (4)	C8b—N9—C10—N1a	−1.8 (4)
C21—C2—C2a—C8b	177.7 (3)	N1—N1a—C10—N9	178.9 (2)
N1a—C2—C2a—C3	−179.7 (2)	C2—N1a—C10—N9	−0.2 (4)
C21—C2—C2a—C3	0.0 (4)	N1—N1a—C10—C11	0.8 (3)
C2—C2a—C3—C4	−144.8 (3)	C2—N1a—C10—C11	−178.3 (2)
C8b—C2a—C3—C4	37.5 (3)	N9—C10—C11—C12	−178.1 (3)
C2a—C3—C4—C4a	−52.6 (3)	N1a—C10—C11—C12	−0.4 (3)
C6—C5—C4a—C8a	−0.4 (4)	N1a—N1—C12—C11	0.6 (3)
C6—C5—C4a—C4	−179.0 (3)	N1a—N1—C12—C31	179.5 (2)
C3—C4—C4a—C5	−146.1 (3)	C10—C11—C12—N1	−0.2 (3)
C3—C4—C4a—C8a	35.4 (3)	C10—C11—C12—C31	−178.8 (3)
C4a—C5—C6—C7	−0.6 (4)	N1—C12—C31—C36	168.5 (2)
C5—C6—C7—C8	1.2 (4)	C11—C12—C31—C36	−12.8 (4)
C6—C7—C8—C8a	−0.6 (4)	N1—C12—C31—C32	−12.7 (4)
C7—C8—C8a—C4a	−0.5 (4)	C11—C12—C31—C32	165.9 (3)
C7—C8—C8a—C8b	178.9 (2)	C36—C31—C32—C33	0.1 (4)
C5—C4a—C8a—C8	1.0 (4)	C12—C31—C32—C33	−178.6 (2)
C4—C4a—C8a—C8	179.5 (2)	C31—C32—C33—C34	0.1 (4)
C5—C4a—C8a—C8b	−178.4 (2)	C32—C33—C34—C35	−0.3 (4)
C4—C4a—C8a—C8b	0.1 (4)	C32—C33—C34—Cl34	−179.9 (2)
C2—C2a—C8b—N9	0.1 (4)	C33—C34—C35—C36	0.1 (4)
C3—C2a—C8b—N9	177.9 (2)	Cl34—C34—C35—C36	179.8 (2)
C2—C2a—C8b—C8a	−180.0 (2)	C34—C35—C36—C31	0.1 (4)
C3—C2a—C8b—C8a	−2.2 (4)	C32—C31—C36—C35	−0.3 (4)
C8—C8a—C8b—N9	−17.5 (4)	C12—C31—C36—C35	178.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···*Cg*1^{i}	0.99	2.92	3.815 (3)	150

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

(II) 2-(4-Chlorophenyl)-5-methyl-6,7-dihydrobenzo[*e*]pyrazolo[2,3-*b*]quinazoline

Crystal data

$C_{21}H_{16}ClN_3$
$M_r = 345.82$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.0098$ (3) Å
$b = 15.0306$ (7) Å
$c = 17.0060$ (8) Å
$\alpha = 111.492$ (2)°
$\beta = 101.406$ (3)°
$\gamma = 97.981$ (3)°
$V = 1589.81$ (13) Å^3
$Z = 4$
$F(000) = 720$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7321 reflections
$\theta = 3.0$–$27.6°$
$\mu = 0.25$ mm^{-1}
$T = 120$ K
Needle, pale brown
0.14 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.949$, $T_{max} = 0.993$
35785 measured reflections
7321 independent reflections
4073 reflections with $I > 2\sigma(I)$
$R_{int} = 0.113$
$\theta_{max} = 27.6°$, $\theta_{min} = 3.0°$
$h = -8 \rightarrow 9$
$k = -19 \rightarrow 19$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.152$
$S = 1.03$
7321 reflections
453 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.1965P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl14	0.62859 (10)	0.90803 (5)	0.31741 (5)	0.0308 (2)
N11	0.5024 (3)	0.42836 (16)	0.24275 (15)	0.0256 (5)
N11a	0.4963 (3)	0.35103 (16)	0.26626 (14)	0.0227 (5)
N19	0.5274 (3)	0.31548 (17)	0.39424 (15)	0.0263 (5)
C11b	0.4606 (4)	0.2532 (2)	0.21034 (17)	0.0229 (6)
C11c	0.4432 (4)	0.2215 (2)	0.11577 (18)	0.0244 (6)
C12	0.5273 (4)	0.2821 (2)	0.07935 (18)	0.0265 (7)
C13	0.5161 (4)	0.2454 (2)	−0.00915 (18)	0.0283 (7)
C14	0.4190 (4)	0.1488 (2)	−0.06282 (19)	0.0311 (7)
C15	0.3350 (4)	0.0882 (2)	−0.02794 (18)	0.0296 (7)
C15a	0.3476 (4)	0.1226 (2)	0.06073 (18)	0.0263 (7)
C16	0.2648 (4)	0.0573 (2)	0.10087 (18)	0.0302 (7)

C17	0.4042 (4)	0.0786 (2)	0.18979 (18)	0.0290 (7)
C17a	0.4509 (4)	0.18713 (19)	0.24891 (18)	0.0237 (6)
C18	0.4903 (4)	0.2215 (2)	0.34146 (18)	0.0245 (6)
C19a	0.5276 (4)	0.3805 (2)	0.35650 (18)	0.0244 (6)
C110	0.5556 (4)	0.4814 (2)	0.39119 (18)	0.0261 (7)
C111	0.5387 (4)	0.5070 (2)	0.31936 (17)	0.0232 (6)
C131	0.5579 (4)	0.6054 (2)	0.31877 (18)	0.0232 (6)
C132	0.5459 (4)	0.6180 (2)	0.24087 (18)	0.0253 (6)
C133	0.5664 (4)	0.7099 (2)	0.23978 (18)	0.0274 (7)
C134	0.6000 (4)	0.79088 (19)	0.31782 (18)	0.0243 (6)
C135	0.6134 (4)	0.7813 (2)	0.39600 (18)	0.0276 (7)
C136	0.5913 (4)	0.6884 (2)	0.39648 (18)	0.0280 (7)
C181	0.4976 (4)	0.1508 (2)	0.38531 (19)	0.0319 (7)
Cl24	−0.05261 (11)	0.09943 (5)	0.27457 (5)	0.0378 (2)
N21	0.0130 (3)	0.53992 (16)	0.24916 (15)	0.0275 (6)
N21a	0.0454 (3)	0.63920 (16)	0.28162 (14)	0.0234 (5)
N29	0.1396 (3)	0.77941 (16)	0.42033 (15)	0.0271 (6)
C21b	0.0335 (4)	0.6966 (2)	0.23437 (18)	0.0236 (6)
C21c	−0.0385 (4)	0.6542 (2)	0.13807 (17)	0.0240 (6)
C22	−0.1612 (4)	0.5596 (2)	0.08740 (18)	0.0271 (7)
C23	−0.2294 (4)	0.5262 (2)	−0.00278 (18)	0.0285 (7)
C24	−0.1771 (4)	0.5858 (2)	−0.04435 (19)	0.0290 (7)
C25	−0.0588 (4)	0.6796 (2)	0.00475 (19)	0.0285 (7)
C25a	0.0096 (4)	0.7150 (2)	0.09532 (19)	0.0265 (7)
C26	0.1341 (4)	0.8176 (2)	0.14903 (18)	0.0301 (7)
C27	0.0763 (4)	0.8630 (2)	0.23393 (18)	0.0287 (7)
C27a	0.0839 (4)	0.7971 (2)	0.28284 (18)	0.0234 (6)
C28	0.1345 (4)	0.8352 (2)	0.37605 (18)	0.0272 (7)
C29a	0.0993 (4)	0.6813 (2)	0.37368 (18)	0.0256 (6)
C210	0.1005 (4)	0.6040 (2)	0.39874 (19)	0.0280 (7)
C211	0.0471 (4)	0.5199 (2)	0.32108 (18)	0.0242 (6)
C231	0.0242 (4)	0.4165 (2)	0.30983 (18)	0.0240 (6)
C232	−0.0117 (4)	0.3414 (2)	0.22687 (19)	0.0278 (7)
C233	−0.0363 (4)	0.2443 (2)	0.21597 (19)	0.0294 (7)
C234	−0.0228 (4)	0.2223 (2)	0.2884 (2)	0.0285 (7)
C235	0.0135 (4)	0.2947 (2)	0.3713 (2)	0.0321 (7)
C236	0.0357 (4)	0.3918 (2)	0.38153 (19)	0.0293 (7)
C281	0.1848 (4)	0.9444 (2)	0.42988 (19)	0.0319 (7)
H12	0.5924	0.3488	0.1158	0.032*
H13	0.5752	0.2865	−0.0332	0.034*
H14	0.4101	0.1241	−0.1238	0.037*
H15	0.2677	0.0222	−0.0654	0.036*
H16A	0.2473	−0.0124	0.0612	0.036*
H16B	0.1320	0.0680	0.1081	0.036*
H17A	0.3404	0.0399	0.2178	0.035*
H17B	0.5300	0.0585	0.1816	0.035*
H18A	0.5614	0.1872	0.4483	0.048*
H18B	0.5748	0.1035	0.3597	0.048*

H18C	0.3612	0.1156	0.3764	0.048*
H110	0.5809	0.5244	0.4512	0.031*
H132	0.5231	0.5620	0.1875	0.030*
H133	0.5576	0.7176	0.1863	0.033*
H135	0.6375	0.8378	0.4491	0.033*
H136	0.5989	0.6812	0.4502	0.034*
H22	−0.1977	0.5181	0.1154	0.033*
H23	−0.3125	0.4621	−0.0363	0.034*
H24	−0.2224	0.5623	−0.1064	0.035*
H25	−0.0237	0.7204	−0.0240	0.034*
H26A	0.1144	0.8583	0.1150	0.036*
H26B	0.2774	0.8162	0.1625	0.036*
H27A	0.1690	0.9277	0.2712	0.034*
H27B	−0.0606	0.8736	0.2207	0.034*
H210	0.1314	0.6074	0.4569	0.034*
H232	−0.0195	0.3571	0.1772	0.033*
H233	−0.0623	0.1934	0.1592	0.035*
H235	0.0231	0.2785	0.4207	0.038*
H236	0.0592	0.4422	0.4384	0.035*
H28A	0.1935	0.9571	0.4914	0.048*
H28B	0.0801	0.9731	0.4079	0.048*
H28C	0.3135	0.9741	0.4253	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.0283 (13)	0.0215 (13)	0.0271 (14)	0.0053 (10)	0.0072 (10)	0.0103 (11)
N11a	0.0233 (12)	0.0234 (13)	0.0212 (13)	0.0040 (10)	0.0052 (10)	0.0098 (11)
C11b	0.0216 (14)	0.0219 (15)	0.0219 (16)	0.0054 (11)	0.0049 (11)	0.0055 (13)
C11c	0.0234 (15)	0.0274 (16)	0.0245 (16)	0.0089 (12)	0.0072 (12)	0.0112 (13)
C12	0.0292 (16)	0.0247 (16)	0.0271 (17)	0.0096 (12)	0.0087 (13)	0.0104 (13)
C13	0.0316 (16)	0.0305 (17)	0.0268 (17)	0.0078 (13)	0.0117 (13)	0.0140 (14)
C14	0.0347 (17)	0.0341 (18)	0.0265 (17)	0.0128 (14)	0.0121 (13)	0.0110 (14)
C15	0.0323 (17)	0.0239 (16)	0.0247 (17)	0.0036 (13)	0.0068 (13)	0.0027 (13)
C15a	0.0255 (15)	0.0285 (16)	0.0255 (17)	0.0074 (12)	0.0084 (12)	0.0104 (13)
C16	0.0341 (17)	0.0218 (15)	0.0291 (18)	0.0028 (13)	0.0089 (13)	0.0052 (13)
C17	0.0364 (17)	0.0245 (16)	0.0255 (17)	0.0075 (13)	0.0107 (13)	0.0081 (13)
C17a	0.0217 (14)	0.0222 (15)	0.0284 (17)	0.0072 (12)	0.0075 (12)	0.0103 (13)
C18	0.0217 (15)	0.0293 (16)	0.0260 (17)	0.0063 (12)	0.0075 (12)	0.0142 (14)
C181	0.0383 (18)	0.0286 (17)	0.0285 (18)	0.0087 (14)	0.0079 (13)	0.0115 (14)
N19	0.0298 (13)	0.0268 (14)	0.0230 (13)	0.0076 (11)	0.0073 (10)	0.0105 (11)
C19a	0.0235 (15)	0.0262 (16)	0.0224 (16)	0.0038 (12)	0.0050 (12)	0.0099 (13)
C110	0.0290 (16)	0.0251 (16)	0.0213 (16)	0.0055 (12)	0.0077 (12)	0.0062 (13)
C111	0.0212 (14)	0.0234 (15)	0.0220 (16)	0.0032 (11)	0.0062 (12)	0.0065 (13)
C131	0.0206 (14)	0.0244 (15)	0.0241 (16)	0.0042 (12)	0.0066 (12)	0.0092 (13)
C132	0.0268 (15)	0.0204 (15)	0.0240 (16)	0.0040 (12)	0.0067 (12)	0.0045 (13)
C133	0.0292 (16)	0.0292 (17)	0.0258 (17)	0.0074 (13)	0.0081 (12)	0.0126 (14)
C134	0.0231 (15)	0.0206 (15)	0.0290 (17)	0.0052 (12)	0.0069 (12)	0.0099 (13)

Cl14	0.0388 (4)	0.0216 (4)	0.0313 (4)	0.0060 (3)	0.0095 (3)	0.0101 (3)
C135	0.0357 (17)	0.0227 (16)	0.0213 (16)	0.0051 (13)	0.0096 (13)	0.0050 (13)
C136	0.0351 (17)	0.0254 (16)	0.0222 (16)	0.0058 (13)	0.0096 (13)	0.0078 (13)
N21	0.0274 (13)	0.0242 (13)	0.0301 (15)	0.0044 (10)	0.0070 (11)	0.0110 (11)
N21a	0.0228 (12)	0.0221 (13)	0.0222 (14)	0.0038 (10)	0.0056 (10)	0.0064 (10)
C21b	0.0203 (14)	0.0285 (16)	0.0238 (16)	0.0060 (12)	0.0060 (12)	0.0123 (13)
C21c	0.0226 (15)	0.0253 (15)	0.0234 (16)	0.0075 (12)	0.0060 (12)	0.0085 (13)
C22	0.0264 (16)	0.0258 (16)	0.0300 (18)	0.0055 (12)	0.0093 (13)	0.0118 (13)
C23	0.0274 (16)	0.0281 (16)	0.0267 (17)	0.0069 (13)	0.0050 (13)	0.0083 (14)
C24	0.0316 (16)	0.0319 (17)	0.0212 (16)	0.0087 (13)	0.0036 (13)	0.0095 (14)
C25	0.0309 (16)	0.0308 (17)	0.0276 (17)	0.0078 (13)	0.0096 (13)	0.0151 (14)
C25a	0.0233 (15)	0.0288 (16)	0.0292 (17)	0.0084 (12)	0.0080 (12)	0.0124 (14)
C26	0.0354 (17)	0.0264 (16)	0.0286 (17)	0.0048 (13)	0.0092 (13)	0.0119 (14)
C27	0.0316 (16)	0.0238 (16)	0.0289 (17)	0.0043 (13)	0.0077 (13)	0.0096 (13)
C27a	0.0206 (14)	0.0235 (15)	0.0264 (17)	0.0066 (12)	0.0083 (12)	0.0087 (13)
C28	0.0235 (15)	0.0269 (16)	0.0282 (17)	0.0067 (12)	0.0077 (12)	0.0073 (14)
N29	0.0277 (13)	0.0248 (13)	0.0259 (14)	0.0050 (10)	0.0080 (10)	0.0072 (11)
C29a	0.0248 (15)	0.0273 (16)	0.0228 (16)	0.0058 (12)	0.0065 (12)	0.0081 (13)
C210	0.0313 (16)	0.0300 (17)	0.0213 (16)	0.0061 (13)	0.0055 (12)	0.0100 (14)
C211	0.0218 (15)	0.0282 (16)	0.0235 (16)	0.0043 (12)	0.0083 (12)	0.0107 (13)
C231	0.0180 (14)	0.0281 (16)	0.0249 (17)	0.0036 (12)	0.0056 (11)	0.0103 (13)
C232	0.0268 (16)	0.0318 (17)	0.0253 (17)	0.0061 (13)	0.0057 (12)	0.0130 (14)
C233	0.0294 (16)	0.0297 (17)	0.0266 (17)	0.0077 (13)	0.0076 (13)	0.0083 (14)
C234	0.0221 (15)	0.0286 (17)	0.0377 (19)	0.0059 (12)	0.0085 (13)	0.0163 (15)
Cl24	0.0397 (5)	0.0290 (4)	0.0461 (5)	0.0074 (3)	0.0098 (4)	0.0178 (4)
C235	0.0320 (17)	0.0332 (18)	0.0345 (19)	0.0067 (13)	0.0076 (14)	0.0184 (15)
C236	0.0307 (17)	0.0303 (17)	0.0262 (17)	0.0070 (13)	0.0083 (13)	0.0103 (14)
C281	0.0365 (18)	0.0262 (16)	0.0271 (17)	0.0060 (13)	0.0060 (13)	0.0060 (14)

Geometric parameters (Å, º)

N11—N11a	1.359 (3)	N21—N21a	1.355 (3)
N11a—C11b	1.381 (3)	N21a—C21b	1.378 (3)
C11b—C17a	1.378 (4)	C21b—C27a	1.381 (4)
C17a—C18	1.419 (4)	C27a—C28	1.422 (4)
C18—N19	1.321 (3)	C28—N29	1.316 (3)
N19—C19a	1.351 (3)	N29—C29a	1.350 (3)
C19a—C110	1.379 (4)	C29a—C210	1.377 (4)
C110—C111	1.398 (4)	C210—C211	1.390 (4)
C111—N11	1.348 (3)	C211—N21	1.348 (3)
N11a—C19a	1.393 (3)	N21a—C29a	1.403 (3)
C11b—C11c	1.474 (4)	C21b—C21c	1.470 (4)
C11c—C12	1.403 (4)	C21c—C22	1.405 (4)
C11c—C15a	1.412 (4)	C21c—C25a	1.406 (4)
C12—C13	1.381 (4)	C22—C23	1.383 (4)
C12—H12	0.95	C22—H22	0.95
C13—C14	1.382 (4)	C23—C24	1.382 (4)
C13—H13	0.95	C23—H23	0.95

C14—C15	1.383 (4)	C24—C25	1.383 (4)
C14—H14	0.95	C24—H24	0.95
C15—C15a	1.383 (4)	C25—C25a	1.386 (4)
C15—H15	0.95	C25—H25	0.95
C15a—C16	1.502 (4)	C25a—C26	1.501 (4)
C16—C17	1.522 (4)	C26—C27	1.517 (4)
C16—H16A	0.99	C26—H26A	0.99
C16—H16B	0.99	C26—H26B	0.99
C17—C17a	1.516 (4)	C27—C27a	1.509 (4)
C17—H17A	0.99	C27—H27A	0.99
C17—H17B	0.99	C27—H27B	0.99
C18—C181	1.507 (4)	C28—C281	1.506 (4)
C181—H18A	0.98	C210—H210	0.95
C181—H18B	0.98	C211—C231	1.477 (4)
C181—H18C	0.98	C231—C236	1.390 (4)
C110—H110	0.95	C231—C232	1.393 (4)
C111—C131	1.470 (4)	C232—C233	1.383 (4)
C131—C132	1.393 (4)	C232—H232	0.95
C131—C136	1.395 (4)	C233—C234	1.377 (4)
C132—C133	1.377 (4)	C233—H233	0.95
C132—H132	0.95	C234—C235	1.376 (4)
C133—C134	1.382 (4)	C234—Cl24	1.751 (3)
C133—H133	0.95	C235—C236	1.387 (4)
C134—C135	1.375 (4)	C235—H235	0.95
C134—Cl14	1.747 (3)	C236—H236	0.95
C135—C136	1.387 (4)	C281—H28A	0.98
C135—H135	0.95	C281—H28B	0.98
C136—H136	0.95	C281—H28C	0.98

C111—N11—N11a	104.0 (2)	C211—N21—N21a	104.2 (2)
N11—N11a—C11b	126.4 (2)	N21—N21a—C21b	127.1 (2)
N11—N11a—C19a	112.1 (2)	N21—N21a—C29a	111.6 (2)
C11b—N11a—C19a	121.6 (2)	C21b—N21a—C29a	121.3 (2)
C17a—C11b—N11a	115.9 (2)	N21a—C21b—C27a	116.2 (2)
C17a—C11b—C11c	121.8 (2)	N21a—C21b—C21c	122.3 (2)
N11a—C11b—C11c	122.2 (2)	C27a—C21b—C21c	121.4 (2)
C12—C11c—C15a	119.0 (2)	C22—C21c—C25a	118.6 (3)
C12—C11c—C11b	123.6 (2)	C22—C21c—C21b	124.1 (2)
C15a—C11c—C11b	117.2 (2)	C25a—C21c—C21b	117.3 (2)
C13—C12—C11c	120.4 (3)	C23—C22—C21c	120.7 (3)
C13—C12—H12	119.8	C23—C22—H22	119.6
C11c—C12—H12	119.8	C21c—C22—H22	119.6
C12—C13—C14	120.2 (3)	C24—C23—C22	120.2 (3)
C12—C13—H13	119.9	C24—C23—H23	119.9
C14—C13—H13	119.9	C22—C23—H23	119.9
C13—C14—C15	120.1 (3)	C23—C24—C25	119.7 (3)
C13—C14—H14	119.9	C23—C24—H24	120.1
C15—C14—H14	119.9	C25—C24—H24	120.1

C15a—C15—C14	120.9 (3)	C24—C25—C25a	121.0 (3)
C15a—C15—H15	119.6	C24—C25—H25	119.5
C14—C15—H15	119.6	C25a—C25—H25	119.5
C15—C15a—C11c	119.3 (3)	C25—C25a—C21c	119.7 (3)
C15—C15a—C16	122.0 (2)	C25—C25a—C26	121.2 (3)
C11c—C15a—C16	118.7 (2)	C21c—C25a—C26	119.1 (2)
C15a—C16—C17	110.9 (2)	C25a—C26—C27	110.6 (2)
C15a—C16—H16A	109.5	C25a—C26—H26A	109.5
C17—C16—H16A	109.5	C27—C26—H26A	109.5
C15a—C16—H16B	109.5	C25a—C26—H26B	109.5
C17—C16—H16B	109.5	C27—C26—H26B	109.5
H16A—C16—H16B	108.1	H26A—C26—H26B	108.1
C17a—C17—C16	110.7 (2)	C27a—C27—C26	110.8 (2)
C17a—C17—H17A	109.5	C27a—C27—H27A	109.5
C16—C17—H17A	109.5	C26—C27—H27A	109.5
C17a—C17—H17B	109.5	C27a—C27—H27B	109.5
C16—C17—H17B	109.5	C26—C27—H27B	109.5
H17A—C17—H17B	108.1	H27A—C27—H27B	108.1
C11b—C17a—C18	120.0 (2)	C21b—C27a—C28	119.8 (3)
C11b—C17a—C17	117.9 (2)	C21b—C27a—C27	118.1 (2)
C18—C17a—C17	122.1 (2)	C28—C27a—C27	122.1 (2)
N19—C18—C17a	123.3 (2)	N29—C28—C27a	123.4 (3)
N19—C18—C181	116.1 (2)	N29—C28—C281	116.1 (2)
C17a—C18—C181	120.7 (2)	C27a—C28—C281	120.5 (3)
C18—C181—H18A	109.5	C28—N29—C29a	117.3 (2)
C18—C181—H18B	109.5	N29—C29a—C210	132.1 (3)
H18A—C181—H18B	109.5	N29—C29a—N21a	122.0 (2)
C18—C181—H18C	109.5	C210—C29a—N21a	105.9 (2)
H18A—C181—H18C	109.5	C29a—C210—C211	105.5 (2)
H18B—C181—H18C	109.5	C29a—C210—H210	127.2
C18—N19—C19a	117.1 (2)	C211—C210—H210	127.2
N19—C19a—C110	132.0 (3)	N21—C211—C210	112.8 (2)
N19—C19a—N11a	122.1 (2)	N21—C211—C231	119.0 (2)
C110—C19a—N11a	106.0 (2)	C210—C211—C231	128.3 (3)
C19a—C110—C111	105.4 (2)	C236—C231—C232	118.6 (3)
C19a—C110—H110	127.3	C236—C231—C211	120.8 (3)
C111—C110—H110	127.3	C232—C231—C211	120.6 (3)
N11—C111—C110	112.6 (2)	C233—C232—C231	120.7 (3)
N11—C111—C131	119.0 (2)	C233—C232—H232	119.6
C110—C111—C131	128.5 (3)	C231—C232—H232	119.6
C132—C131—C136	118.6 (3)	C234—C233—C232	119.3 (3)
C132—C131—C111	120.8 (2)	C234—C233—H233	120.4
C136—C131—C111	120.6 (2)	C232—C233—H233	120.4
C133—C132—C131	121.2 (3)	C235—C234—C233	121.5 (3)
C133—C132—H132	119.4	C235—C234—Cl24	119.3 (2)
C131—C132—H132	119.4	C233—C234—Cl24	119.2 (2)
C132—C133—C134	118.9 (3)	C234—C235—C236	118.9 (3)
C132—C133—H133	120.5	C234—C235—H235	120.6

C134—C133—H133	120.5	C236—C235—H235	120.6
C135—C134—C133	121.4 (3)	C235—C236—C231	121.0 (3)
C135—C134—Cl14	119.2 (2)	C235—C236—H236	119.5
C133—C134—Cl14	119.4 (2)	C231—C236—H236	119.5
C134—C135—C136	119.3 (3)	C28—C281—H28A	109.5
C134—C135—H135	120.4	C28—C281—H28B	109.5
C136—C135—H135	120.4	H28A—C281—H28B	109.5
C135—C136—C131	120.5 (3)	C28—C281—H28C	109.5
C135—C136—H136	119.7	H28A—C281—H28C	109.5
C131—C136—H136	119.7	H28B—C281—H28C	109.5
C111—N11—N11a—C11b	179.2 (2)	C211—N21—N21a—C21b	178.7 (2)
C111—N11—N11a—C19a	0.3 (3)	C211—N21—N21a—C29a	−0.1 (3)
N11—N11a—C11b—C17a	−176.6 (2)	N21—N21a—C21b—C27a	−176.7 (2)
C19a—N11a—C11b—C17a	2.2 (3)	C29a—N21a—C21b—C27a	2.1 (3)
N11—N11a—C11b—C11c	6.2 (4)	N21—N21a—C21b—C21c	6.4 (4)
C19a—N11a—C11b—C11c	−175.0 (2)	C29a—N21a—C21b—C21c	−174.8 (2)
C17a—C11b—C11c—C12	−153.6 (3)	N21a—C21b—C21c—C22	22.3 (4)
N11a—C11b—C11c—C12	23.5 (4)	C27a—C21b—C21c—C22	−154.4 (3)
C17a—C11b—C11c—C15a	22.0 (4)	N21a—C21b—C21c—C25a	−161.7 (2)
N11a—C11b—C11c—C15a	−160.9 (2)	C27a—C21b—C21c—C25a	21.6 (4)
C15a—C11c—C12—C13	0.2 (4)	C25a—C21c—C22—C23	1.4 (4)
C11b—C11c—C12—C13	175.7 (2)	C21b—C21c—C22—C23	177.4 (2)
C11c—C12—C13—C14	1.0 (4)	C21c—C22—C23—C24	0.1 (4)
C12—C13—C14—C15	−0.8 (4)	C22—C23—C24—C25	−1.0 (4)
C13—C14—C15—C15a	−0.5 (4)	C23—C24—C25—C25a	0.3 (4)
C14—C15—C15a—C11c	1.7 (4)	C24—C25—C25a—C21c	1.3 (4)
C14—C15—C15a—C16	−177.5 (3)	C24—C25—C25a—C26	−178.5 (3)
C12—C11c—C15a—C15	−1.5 (4)	C22—C21c—C25a—C25	−2.1 (4)
C11b—C11c—C15a—C15	−177.3 (2)	C21b—C21c—C25a—C25	−178.4 (2)
C12—C11c—C15a—C16	177.7 (2)	C22—C21c—C25a—C26	177.7 (2)
C11b—C11c—C15a—C16	1.9 (4)	C21b—C21c—C25a—C26	1.4 (4)
C15—C15a—C16—C17	140.1 (3)	C25—C25a—C26—C27	141.3 (3)
C11c—C15a—C16—C17	−39.1 (3)	C21c—C25a—C26—C27	−38.5 (3)
C15a—C16—C17—C17a	53.3 (3)	C25a—C26—C27—C27a	53.2 (3)
N11a—C11b—C17a—C18	−4.3 (4)	N21a—C21b—C27a—C28	−3.0 (3)
C11c—C11b—C17a—C18	173.0 (2)	C21c—C21b—C27a—C28	174.0 (2)
N11a—C11b—C17a—C17	177.8 (2)	N21a—C21b—C27a—C27	179.0 (2)
C11c—C11b—C17a—C17	−5.0 (4)	C21c—C21b—C27a—C27	−4.0 (4)
C16—C17—C17a—C11b	−32.8 (3)	C26—C27—C27a—C21b	−33.7 (3)
C16—C17—C17a—C18	149.2 (2)	C26—C27—C27a—C28	148.3 (2)
C11b—C17a—C18—N19	3.5 (4)	C21b—C27a—C28—N29	1.1 (4)
C17—C17a—C18—N19	−178.6 (2)	C27—C27a—C28—N29	179.0 (2)
C11b—C17a—C18—C181	−174.8 (2)	C21b—C27a—C28—C281	−178.5 (2)
C17—C17a—C18—C181	3.1 (4)	C27—C27a—C28—C281	−0.5 (4)
C17a—C18—N19—C19a	−0.3 (4)	C27a—C28—N29—C29a	1.8 (4)
C181—C18—N19—C19a	178.1 (2)	C281—C28—N29—C29a	−178.6 (2)
C18—N19—C19a—C110	178.3 (3)	C28—N29—C29a—C210	176.7 (3)

C18—N19—C19a—N11a	−1.9 (4)	C28—N29—C29a—N21a	−2.7 (4)
N11—N11a—C19a—N19	179.9 (2)	N21—N21a—C29a—N29	179.7 (2)
C11b—N11a—C19a—N19	0.9 (4)	C21b—N21a—C29a—N29	0.8 (4)
N11—N11a—C19a—C110	−0.3 (3)	N21—N21a—C29a—C210	0.2 (3)
C11b—N11a—C19a—C110	−179.3 (2)	C21b—N21a—C29a—C210	−178.7 (2)
N19—C19a—C110—C111	−180.0 (3)	N29—C29a—C210—C211	−179.6 (3)
N11a—C19a—C110—C111	0.2 (3)	N21a—C29a—C210—C211	−0.2 (3)
N11a—N11—C111—C110	−0.1 (3)	N21a—N21—C211—C210	0.0 (3)
N11a—N11—C111—C131	179.2 (2)	N21a—N21—C211—C231	179.8 (2)
C19a—C110—C111—N11	0.0 (3)	C29a—C210—C211—N21	0.1 (3)
C19a—C110—C111—C131	−179.3 (3)	C29a—C210—C211—C231	−179.6 (3)
N11—C111—C131—C132	−2.2 (4)	N21—C211—C231—C236	−172.7 (2)
C110—C111—C131—C132	176.9 (3)	C210—C211—C231—C236	7.0 (4)
N11—C111—C131—C136	178.6 (2)	N21—C211—C231—C232	6.5 (4)
C110—C111—C131—C136	−2.2 (4)	C210—C211—C231—C232	−173.8 (3)
C136—C131—C132—C133	0.1 (4)	C236—C231—C232—C233	0.3 (4)
C111—C131—C132—C133	−179.1 (2)	C211—C231—C232—C233	−179.0 (2)
C131—C132—C133—C134	0.2 (4)	C231—C232—C233—C234	−0.7 (4)
C132—C133—C134—C135	0.0 (4)	C232—C233—C234—C235	0.4 (4)
C132—C133—C134—Cl14	179.4 (2)	C232—C233—C234—Cl24	−179.6 (2)
C133—C134—C135—C136	−0.4 (4)	C233—C234—C235—C236	0.3 (4)
Cl14—C134—C135—C136	−179.8 (2)	Cl24—C234—C235—C236	−179.6 (2)
C134—C135—C136—C131	0.7 (4)	C234—C235—C236—C231	−0.8 (4)
C132—C131—C136—C135	−0.5 (4)	C232—C231—C236—C235	0.5 (4)
C111—C131—C136—C135	178.7 (2)	C211—C231—C236—C235	179.7 (3)