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tert-Butyl *N*-benzyl-*N*-(4-methyl-2-pyridyl)carbamate

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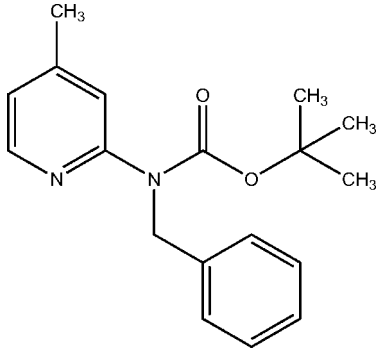
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.003 Å; R factor = 0.055; wR factor = 0.209; data-to-parameter ratio = 15.1.

In the crystal structure of the title compound, $C_{18}H_{22}N_2O_2$, the pyridine ring makes dihedral angles of 83.71 (6) and 9.2 (1)° with the phenyl ring and the carbamate plane, respectively. The phenyl ring and the carbamate plane are nearly perpendicular to one another, with a dihedral angle of 87.17 (7)°.

Related literature

For the preparation of the title compound, see: Koch *et al.* (2008). For applications of *N*-benzyl-2-aminopyridines, see, for example: Laufer & Koch (2008); Koch *et al.* (2008); Lipinski *et al.* (1985); Miwatashi *et al.* (2005); Stevens *et al.* (2005).



Experimental

Crystal data

$C_{18}H_{22}N_2O_2$
M_r = 298.38
Triclinic, $P\overline{1}$
a = 5.9090 (10) Å
b = 9.7779 (18) Å
c = 14.199 (7) Å
α = 89.683 (13)°
β = 87.968 (14)°
γ = 83.963 (15)°
V = 815.3 (5) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.63 mm^{-1}
T = 193 (2) K
0.45 × 0.45 × 0.33 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
5914 measured reflections
3074 independent reflections
2747 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.209
S = 1.12
3074 reflections
204 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2149).

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supplementary materials

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tert-Butyl *N*-benzyl-*N*-(4-methyl-2-pyridyl)carbamate

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Comment

N-Benzyl-2-aminopyridin-4-yl derivatives can be found in different p38 MAP kinase inhibitors, like the imidazolopyridines (Laufer & Koch 2008; Koch *et al.* 2008), thiazolopyridines (Miwatashi *et al.* 2005) or pyrazolopyridines (Stevens *et al.* 2005) and in histamine H_2-receptor antagonists (Lipinski *et al.* 1985).

The title compound, *tert*-butyl *N*-benzyl-*N*-(4-methylpyridin-2-yl)carbamate (**I**), was obtaineded as an intermediate in the synthesis of 2-alkylsulfanyl-5-(2-aminopyridin-4-yl)-4-(4-fluorophenyl)imidazoles as potent p38 MAP kinase inhibitors (Laufer & Koch 2008; Koch *et al.* 2008).

In the crystal structure of the title compound **I** the pyridine ring makes dihedral angles of 83.71 (6)° and 9.2 (1)° to the phenyl ring and the carbamate plane, respectively. The phenyl ring and the carbamate plane are nearly perpendicular to one another with a dihedral angle of 87.17 (7)°. The N1—C2 bond [1.383 (2) Å] of the carbamte function is shorter than the normal N1—C16-bond [1.475 (2) Å] to the benzyl moiety, indicating the partial double bond character of the amide bond of the carbamate.

Experimental

To a solution of *tert*-butyl 4-methylpyridin-2-ylcarbamate (0.75 g, 3.6 mmol) in dry DMF (11 ml) was added under an argon-atmosphere sodium hydride (0.18 g, 4.5 mmol, 60% oil dispersion) at 273 K in such a manner that the temperature was kept below 278 K. The reaction mixture was kept at 273 K for 20 min followed by the addition of benzyl bromide (0.71 g, 4.1 mmol) at the same temperature. After additional stirring at 273 K for 30 min the mixture was allowed to warm to room temperature within 1 h, after which water and ethyl acetate were added. The organic layer was washed subsequently with HCl (0.1 *M*), sodium bicarbonate and brine, dried (sodium sulfate) and concentrated *in vacuo*. The residue was purified by flash-chromatography (silica gel, *n*-hexane/ethyl acetate 3:1) to yield 0.60 g (56%) of **I** as a colourless solid (Koch *et al.* 2008). Recrystallization from hot *n*-hexane/ethyl acetate afforded colourless crystals.

Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (sp^3 C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the U_{eq} of the parent atom).

Figures

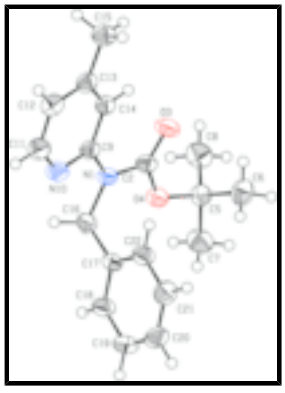


Fig. 1. View of compound I. Displacement ellipsoids are drawn at the 50% probability level. H atoms are depicted as circles of arbitrary size.

tert-Butyl *N*-benzyl-*N*-(4-methyl-2-pyridyl)carbamate

Crystal data

$C_{18}H_{22}N_2O_2$	$Z = 2$
$M_r = 298.38$	$F_{000} = 320$
Triclinic, $P\overline{1}$	$D_x = 1.215$ Mg m^{-3}
Hall symbol: -P 1	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å
$a = 5.9090$ (10) Å	Cell parameters from 25 reflections
$b = 9.7779$ (18) Å	$\theta = 65$–70^o
$c = 14.199$ (7) Å	$\mu = 0.63$ mm^{-1}
$\alpha = 89.683$ (13)º	$T = 193$ (2) K
$\beta = 87.968$ (14)º	Block, yellow
$\gamma = 83.963$ (15)º	0.45 × 0.45 × 0.33 mm
$V = 815.3$ (5) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 69.9^o$
Monochromator: graphite	$\theta_{min} = 3.1^o$
$T = 193$(2) K	$h = -7 \rightarrow 7$
$\omega/2\theta$ scans	$k = -11 \rightarrow 11$
Absorption correction: none	$l = -17 \rightarrow 17$
5914 measured reflections	3 standard reflections
3074 independent reflections	every 60 min
2747 reflections with $I > 2\sigma(I)$	intensity decay: 3%
$R_{int} = 0.090$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.209$

$S = 1.12$

3074 reflections

204 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1082P)^2 + 0.2701P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.31$ e Å^{-3}

$\Delta\rho_{min} = -0.37$ e Å^{-3}

Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.034 (4)

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}
N1	0.6712 (3)	0.71560 (15)	0.31250 (11)	0.0319 (4)
C2	0.6184 (3)	0.78127 (18)	0.22834 (14)	0.0333 (5)
O3	0.7015 (3)	0.88142 (15)	0.19760 (11)	0.0464 (4)
O4	0.4607 (2)	0.71849 (14)	0.18563 (10)	0.0359 (4)
C5	0.3936 (3)	0.7575 (2)	0.08933 (14)	0.0347 (5)
C6	0.6005 (4)	0.7399 (3)	0.02209 (16)	0.0487 (6)
H6A	0.7010	0.8107	0.0348	0.073*
H6B	0.5510	0.7488	−0.0430	0.073*
H6C	0.6829	0.6487	0.0311	0.073*
C7	0.2306 (4)	0.6529 (3)	0.06899 (18)	0.0539 (6)
H7A	0.1826	0.6636	0.0038	0.081*
H7B	0.0970	0.6673	0.1120	0.081*
H7C	0.3068	0.5600	0.0780	0.081*
C8	0.2739 (4)	0.9025 (2)	0.08803 (19)	0.0518 (6)
H8A	0.3828	0.9681	0.1016	0.078*
H8B	0.1497	0.9108	0.1359	0.078*
H8C	0.2119	0.9222	0.0257	0.078*
C9	0.8500 (3)	0.75070 (19)	0.36948 (13)	0.0321 (5)
N10	0.8999 (3)	0.66158 (17)	0.43875 (12)	0.0392 (5)
C11	1.0670 (4)	0.6864 (2)	0.49585 (15)	0.0422 (5)
H11	1.1012	0.6238	0.5460	0.051*

C12	1.1917 (3)	0.7972 (2)	0.48605 (15)	0.0405 (5)
H12	1.3094	0.8102	0.5280	0.049*
C13	1.1410 (3)	0.8897 (2)	0.41319 (14)	0.0352 (5)
C14	0.9660 (3)	0.86750 (19)	0.35502 (13)	0.0337 (5)
H14	0.9247	0.9305	0.3059	0.040*
C15	1.2734 (3)	1.0119 (2)	0.39721 (16)	0.0434 (5)
H15A	1.2841	1.0599	0.4570	0.065*
H15B	1.1955	1.0747	0.3519	0.065*
H15C	1.4268	0.9805	0.3723	0.065*
C16	0.5592 (3)	0.59215 (19)	0.33849 (14)	0.0331 (5)
H16A	0.3957	0.6093	0.3245	0.040*
H16B	0.5700	0.5772	0.4073	0.040*
C17	0.6591 (3)	0.46264 (18)	0.28813 (13)	0.0306 (4)
C18	0.5344 (3)	0.3499 (2)	0.28782 (15)	0.0404 (5)
H18	0.3877	0.3563	0.3181	0.048*
C19	0.6209 (4)	0.2281 (2)	0.24390 (18)	0.0492 (6)
H19	0.5331	0.1521	0.2441	0.059*
C20	0.8339 (4)	0.2171 (2)	0.19997 (16)	0.0463 (6)
H20	0.8937	0.1338	0.1700	0.056*
C21	0.9597 (4)	0.3287 (2)	0.20003 (16)	0.0449 (5)
H21	1.1061	0.3220	0.1695	0.054*
C22	0.8739 (3)	0.4502 (2)	0.24424 (15)	0.0382 (5)
H22	0.9629	0.5256	0.2445	0.046*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0366 (8)	0.0237 (8)	0.0358 (9)	−0.0040 (6)	−0.0036 (6)	0.0012 (6)
C2	0.0361 (9)	0.0232 (9)	0.0401 (10)	−0.0003 (7)	−0.0008 (7)	−0.0005 (7)
O3	0.0612 (9)	0.0325 (8)	0.0488 (9)	−0.0166 (6)	−0.0133 (7)	0.0106 (7)
O4	0.0377 (7)	0.0326 (7)	0.0384 (8)	−0.0070 (5)	−0.0082 (5)	0.0039 (6)
C5	0.0322 (9)	0.0366 (11)	0.0349 (10)	−0.0008 (7)	−0.0054 (7)	0.0024 (8)
C6	0.0409 (11)	0.0610 (14)	0.0431 (12)	−0.0011 (9)	0.0011 (9)	−0.0060 (10)
C7	0.0515 (12)	0.0581 (15)	0.0557 (14)	−0.0194 (11)	−0.0143 (10)	0.0072 (11)
C8	0.0484 (11)	0.0431 (13)	0.0608 (14)	0.0107 (9)	−0.0046 (10)	0.0099 (11)
C9	0.0365 (9)	0.0251 (9)	0.0336 (10)	0.0014 (7)	−0.0004 (7)	−0.0021 (7)
N10	0.0486 (9)	0.0289 (9)	0.0402 (9)	−0.0023 (7)	−0.0088 (7)	0.0047 (7)
C11	0.0506 (11)	0.0353 (11)	0.0405 (11)	−0.0003 (8)	−0.0120 (9)	0.0034 (9)
C12	0.0399 (10)	0.0392 (11)	0.0419 (11)	−0.0002 (8)	−0.0060 (8)	−0.0039 (9)
C13	0.0336 (9)	0.0324 (10)	0.0387 (10)	−0.0003 (7)	0.0023 (7)	−0.0060 (8)
C14	0.0379 (9)	0.0290 (9)	0.0340 (10)	−0.0026 (7)	−0.0004 (7)	−0.0013 (8)
C15	0.0376 (10)	0.0429 (12)	0.0509 (12)	−0.0095 (8)	−0.0014 (8)	−0.0022 (10)
C16	0.0338 (9)	0.0273 (9)	0.0380 (10)	−0.0042 (7)	0.0030 (7)	0.0027 (8)
C17	0.0316 (8)	0.0256 (9)	0.0351 (9)	−0.0043 (7)	−0.0032 (7)	0.0043 (7)
C18	0.0398 (10)	0.0342 (10)	0.0486 (12)	−0.0117 (8)	0.0006 (8)	0.0005 (9)
C19	0.0628 (13)	0.0295 (11)	0.0572 (14)	−0.0143 (9)	−0.0015 (10)	0.0012 (10)
C20	0.0620 (13)	0.0291 (10)	0.0458 (12)	0.0055 (9)	−0.0047 (10)	−0.0037 (9)
C21	0.0407 (10)	0.0443 (12)	0.0478 (12)	0.0025 (8)	0.0027 (9)	−0.0048 (10)

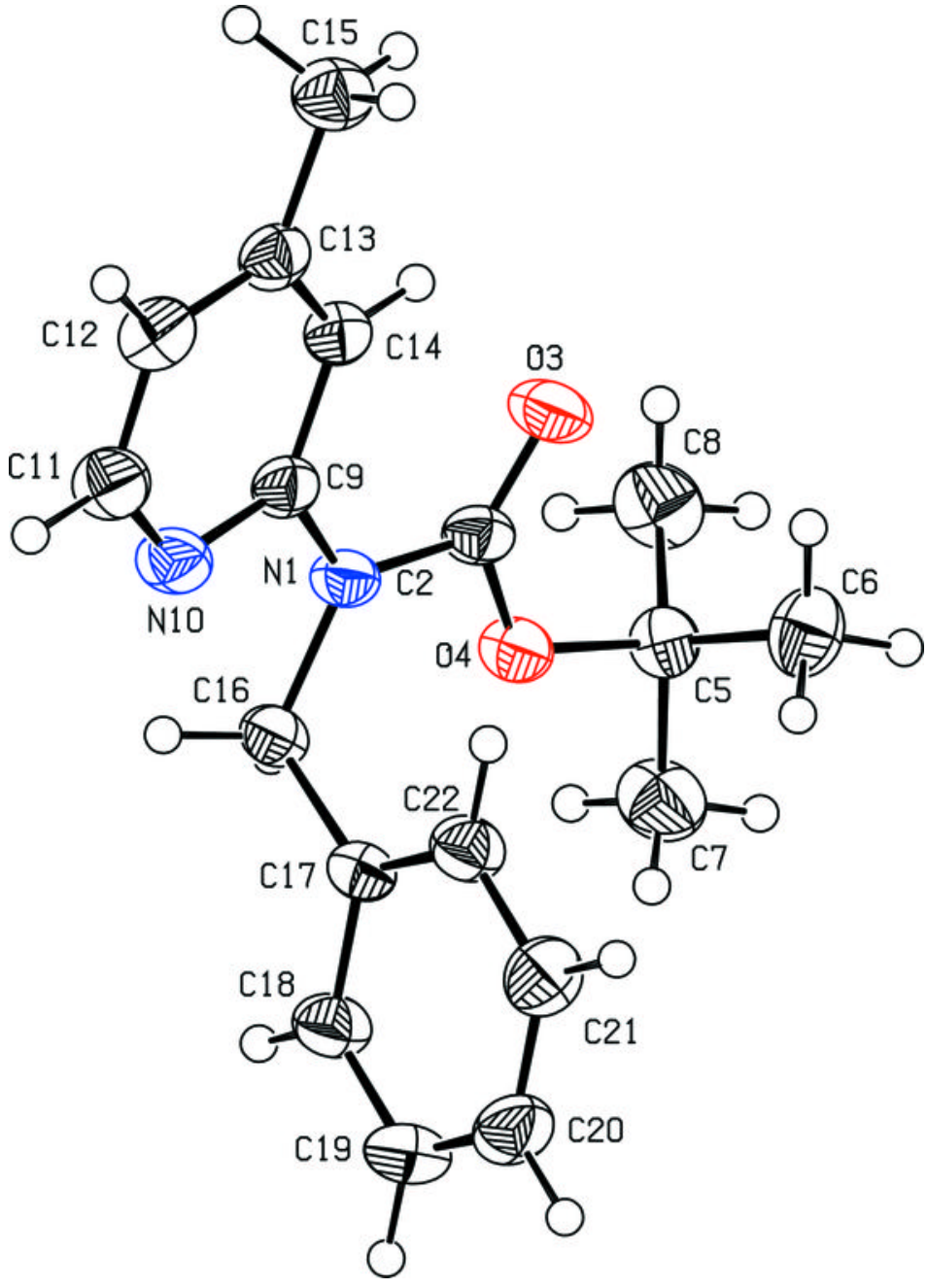
C22	0.0359 (9)	0.0337 (10)	0.0454 (12)	−0.0068 (7)	0.0041 (8)	0.0002 (9)

Geometric parameters (Å, °)

N1—C2	1.383 (3)	C12—C13	1.390 (3)
N1—C9	1.424 (3)	C12—H12	0.9500
N1—C16	1.475 (2)	C13—C14	1.381 (3)
C2—O3	1.213 (2)	C13—C15	1.507 (3)
C2—O4	1.333 (2)	C14—H14	0.9500
O4—C5	1.474 (2)	C15—H15A	0.9800
C5—C7	1.512 (3)	C15—H15B	0.9800
C5—C8	1.516 (3)	C15—H15C	0.9800
C5—C6	1.520 (3)	C16—C17	1.512 (3)
C6—H6A	0.9800	C16—H16A	0.9900
C6—H6B	0.9800	C16—H16B	0.9900
C6—H6C	0.9800	C17—C22	1.388 (3)
C7—H7A	0.9800	C17—C18	1.389 (3)
C7—H7B	0.9800	C18—C19	1.388 (3)
C7—H7C	0.9800	C18—H18	0.9500
C8—H8A	0.9800	C19—C20	1.379 (3)
C8—H8B	0.9800	C19—H19	0.9500
C8—H8C	0.9800	C20—C21	1.383 (3)
C9—N10	1.331 (3)	C20—H20	0.9500
C9—C14	1.403 (3)	C21—C22	1.386 (3)
N10—C11	1.342 (3)	C21—H21	0.9500
C11—C12	1.377 (3)	C22—H22	0.9500
C11—H11	0.9500		
C2—N1—C9	122.86 (15)	C11—C12—H12	120.9
C2—N1—C16	118.75 (16)	C13—C12—H12	120.9
C9—N1—C16	117.88 (15)	C14—C13—C12	118.64 (18)
O3—C2—O4	124.64 (19)	C14—C13—C15	120.26 (18)
O3—C2—N1	125.50 (18)	C12—C13—C15	121.11 (19)
O4—C2—N1	109.86 (15)	C13—C14—C9	119.18 (18)
C2—O4—C5	120.92 (14)	C13—C14—H14	120.4
O4—C5—C7	101.60 (15)	C9—C14—H14	120.4
O4—C5—C8	110.50 (17)	C13—C15—H15A	109.5
C7—C5—C8	111.09 (18)	C13—C15—H15B	109.5
O4—C5—C6	109.95 (15)	H15A—C15—H15B	109.5
C7—C5—C6	110.71 (19)	C13—C15—H15C	109.5
C8—C5—C6	112.47 (17)	H15A—C15—H15C	109.5
C5—C6—H6A	109.5	H15B—C15—H15C	109.5
C5—C6—H6B	109.5	N1—C16—C17	114.19 (14)
H6A—C6—H6B	109.5	N1—C16—H16A	108.7
C5—C6—H6C	109.5	C17—C16—H16A	108.7
H6A—C6—H6C	109.5	N1—C16—H16B	108.7
H6B—C6—H6C	109.5	C17—C16—H16B	108.7
C5—C7—H7A	109.5	H16A—C16—H16B	107.6
C5—C7—H7B	109.5	C22—C17—C18	118.39 (18)
H7A—C7—H7B	109.5	C22—C17—C16	122.65 (16)

C5—C7—H7C	109.5	C18—C17—C16	118.94 (16)
H7A—C7—H7C	109.5	C19—C18—C17	120.95 (18)
H7B—C7—H7C	109.5	C19—C18—H18	119.5
C5—C8—H8A	109.5	C17—C18—H18	119.5
C5—C8—H8B	109.5	C20—C19—C18	120.19 (19)
H8A—C8—H8B	109.5	C20—C19—H19	119.9
C5—C8—H8C	109.5	C18—C19—H19	119.9
H8A—C8—H8C	109.5	C19—C20—C21	119.30 (19)
H8B—C8—H8C	109.5	C19—C20—H20	120.3
N10—C9—C14	122.13 (19)	C21—C20—H20	120.3
N10—C9—N1	113.83 (16)	C20—C21—C22	120.57 (19)
C14—C9—N1	124.04 (17)	C20—C21—H21	119.7
C9—N10—C11	117.88 (18)	C22—C21—H21	119.7
N10—C11—C12	123.88 (19)	C21—C22—C17	120.60 (18)
N10—C11—H11	118.1	C21—C22—H22	119.7
C12—C11—H11	118.1	C17—C22—H22	119.7
C11—C12—C13	118.26 (19)		
C9—N1—C2—O3	−6.7 (3)	C11—C12—C13—C15	−178.86 (18)
C16—N1—C2—O3	−178.23 (17)	C12—C13—C14—C9	−1.9 (3)
C9—N1—C2—O4	173.65 (15)	C15—C13—C14—C9	177.99 (16)
C16—N1—C2—O4	2.1 (2)	N10—C9—C14—C13	1.4 (3)
O3—C2—O4—C5	7.6 (3)	N1—C9—C14—C13	−178.34 (15)
N1—C2—O4—C5	−172.67 (14)	C2—N1—C16—C17	78.3 (2)
C2—O4—C5—C7	175.46 (17)	C9—N1—C16—C17	−93.7 (2)
C2—O4—C5—C8	−66.6 (2)	N1—C16—C17—C22	18.4 (3)
C2—O4—C5—C6	58.2 (2)	N1—C16—C17—C18	−163.51 (17)
C2—N1—C9—N10	−169.13 (16)	C22—C17—C18—C19	−0.7 (3)
C16—N1—C9—N10	2.5 (2)	C16—C17—C18—C19	−178.88 (19)
C2—N1—C9—C14	10.6 (3)	C17—C18—C19—C20	0.3 (4)
C16—N1—C9—C14	−177.75 (16)	C18—C19—C20—C21	−0.1 (4)
C14—C9—N10—C11	0.1 (3)	C19—C20—C21—C22	0.4 (3)
N1—C9—N10—C11	179.83 (16)	C20—C21—C22—C17	−0.9 (3)
C9—N10—C11—C12	−1.1 (3)	C18—C17—C22—C21	1.0 (3)
N10—C11—C12—C13	0.5 (3)	C16—C17—C22—C21	179.10 (19)
C11—C12—C13—C14	1.0 (3)		

Fig. 1


C15
C13
C12
C14
O3
C8
C11
C9
N1
C2
C6
N10
O4
C5
C16
C22
C7
C17
C18
C21
C19
C20