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1-(2-Bromo-5-methoxyphenyl)-8-chloro-6-(2-fluorophenyl)-4*H*-1,2,4-triazolo[4,3-*a*][1,4]benzodiazepine

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.075
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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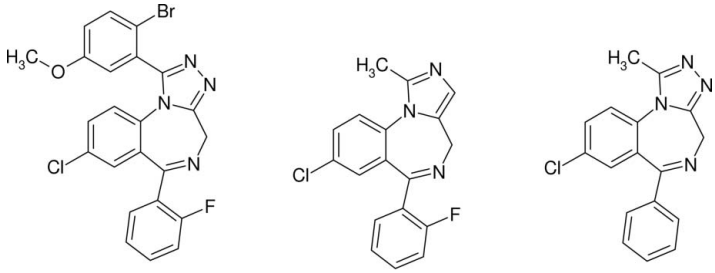
The title compound, $C_{23}H_{15}BrClFN_4O$, is an analogue of sedatives such as midazolam and alprazolam. Its geometrical parameters are normal and comparable with those of related compounds. The only possible significant intermolecular interaction is a C—H···O bond.

Comment

1,4-Benzodiazepine derivatives are widely used as daytime sedatives, tranquilizers, sleep inducers, anaesthetics, anticonvulsants and muscle relaxants (Block *et al.*, 1989; Di Braccio *et al.*, 2001; Hollister, 1983; Moroz, 2004). Five-atom heterocyclic fused benzodiazepine ring systems occupy a prominent place among drugs for treatment of central nervous system (CNS) disorders (Robol *et al.*, 1996; Wang *et al.*, 1999; Novelli *et al.*, 1999; Evans *et al.*, 2001).



(I) (II) (III)

The title compound, (I), $C_{23}H_{15}BrClFN_4O$, (Fig. 1), which appears to have promising physiological properties, comparable with those of diazepam (Valium), is a structural analogue of well known CNS depressant drugs such as midazolam, (II),

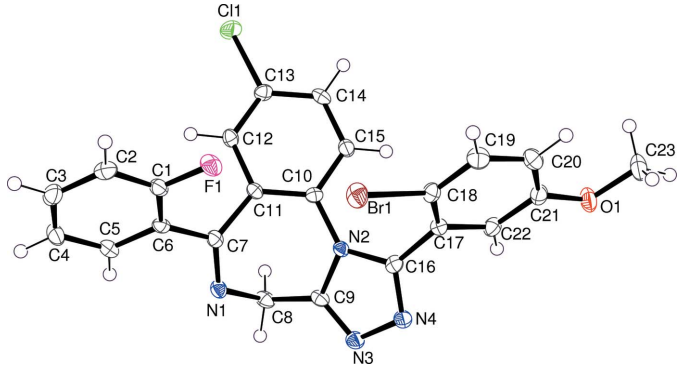


Figure 1
View of (I), showing 30% probability displacement ellipsoids and arbitrary spheres for the H atoms.

and alprazolam, $C_{17}H_{13}ClN_4$, (III). To confirm the structural relationship of (I) to these drugs, its crystal structure is presented here.

The geometrical parameters for (I) fall within their expected ranges (Allen *et al.*, 1995), although the C10—N2—C16 bond angle of 131.51 (18)° is notably obtuse. Atom C7 is displaced from the fluorobenzene mean plane by 0.108 (4) Å. The Br atom is significantly displaced [by 0.154 (3) Å] from the plane of the benzenel ring to which it is attached. The dihedral angles between the various rings in (I) are as follows, where a single atom is used to identify its five- or six-membered ring: C1/C12 62.23 (10); C1/C17 6.12 (11); C1/N3 50.99 (11); C12/C17 64.24 (10); C12/N3 38.05 (11); N3/C17 56.43 (11)°.

The bond distances within the five-membered ring (Table 1) suggest that the C9—N3 and C16—N4 bonds have far more double-bond character than do N3—N4, C9—N2 and C16—N2, *i.e.* the canonical form shown in the scheme is probably the most significant contributor to the overall structure. The bond angle sums about atoms C7 (359.6°), C9 (360.0°), C16 (360.0°) and N2 (359.7°) suggest that all these atoms are well regarded as being sp^2 hybridized.

The seven-membered diazepine ring (C7/C11/C10/N2/C9/C8/N1) in (I) is far from planar, and its shape approximates to a twist chair (Hendrickson, 1967) with a pseudo-twofold axis passing through C9 and the C7—C11 bond midpoint, if such a description is valid for a seven-membered ring containing multiple bonds. However, the pattern of the torsion angles of the seven-membered ring is also close to reflecting C_s symmetry. In the structure of alprazolam dihydrate (Vega *et al.*, 1999), a similar ring conformation was described as a boat. In this description applied to (I), atoms C7, C9, N1 and N2 form the bottom of the boat (r.m.s. deviation from the mean plane = 0.017 Å), C8 the prow, and C10 and C11 the stern [deviations from the C7/C9/N1/N2 mean plane = 0.686 (3), 0.666 (3) and 0.698 (3) Å, respectively].

The crystal packing in (I), shown in Fig. 2, results in $(10\bar{1})$ sheets of molecules. Apart from a possible C—H···N interaction (Table 2), which might help to provide coherence between adjacent $(10\bar{1})$ sheets, there are few significant intermolecular interactions in (I). Any π–π stacking must be extremely weak, the smallest centroid···centroid separation being 4.11 Å. No C—H···π interactions were identified in a *PLATON* (Spek, 2003) analysis of (I).

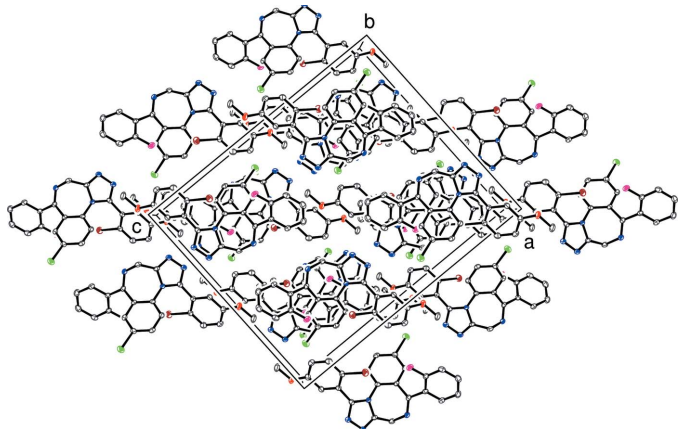


Figure 2
The packing in (I), viewed approximately down [010]. H atoms have been omitted.

Experimental

7-Chloro-5-(2-fluorophenyl)-1,3-dihydro-2*H*-1,4-benzodiazepine-2-thione (3.06 g, 0.01 mol) was reacted with 2-bromo-5-methoxy benzoic hydrazide (2.45 g, 0.01 mol) by refluxing in *n*-butanol (50 ml) with a catalytic amount of acetic acid (0.1 ml) to result in crude (I). The crude product was purified by silica-gel column chromatograpy using dichloromethane as eluent (yield 78%) and recrystallized from acetone as pale-yellow crystals (m.p. 493 K). FT–IR (KBr, cm^{-1}): 3055 and 2926 (–CH), 1609 (–C═N), 1482 ($-CH_2$), 1297 (Ar—F), 1018 (Ar—Cl). ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 3.82 (*s*, 3H, $-OCH_3$), 4.22 (*d*, *J* = 13.2 Hz, 1H, $-CH_2$), 5.64 (*d*, *J* = 13.2 Hz, 1H, $-CH_2$), 6.85 (*d*, *J* = 8.4 Hz, 1H, ArH), 6.95 (*dd*, *J* = 8.7 and 9.3 Hz, 2H, Ar—H), 7.07 (*t*, 1H, Ar—H), 7.16–7.32 (*m*, 1H, Ar—H), 7.45–7.52 (*m*, 4H, Ar—H), 7.67 (*t*, 1H, Ar—H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, p.p.m.): 46.34, 55.70, 116.23, 116.53, 118.93, 124.64, 129.24, 130.25, 131.58, 132.58, 133.37, 134.29, 155.30, 159.15, 165.38.

Crystal data

$C_{23}H_{15}BrClFN_4O$
M_r = 497.75
Monoclinic, *C*2/*c*
a = 17.0109 (6) Å
b = 11.5436 (4) Å
c = 20.6095 (6) Å
β = 92.2816 (17)°
V = 4043.8 (2) Å^3
Z = 8
D_x = 1.635 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 4476 reflections
θ = 2.9–27.5°
μ = 2.20 mm^{-1}
T = 120 (2) K
Block, pale yellow
0.36 × 0.32 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.505, T_{max} = 0.620
17959 measured reflections
4636 independent reflections
3545 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.5°
h = −19 → 22
k = −14 → 14
l = −26 → 26

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.075
S = 1.03
4636 reflections
282 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 3.972P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00038 (7)

Table 1
Selected geometric parameters (Å, °).

C6—C7	1.493 (3)	C9—N2	1.380 (3)
C7—N1	1.283 (3)	C16—N4	1.314 (3)
C7—C11	1.496 (3)	C16—N2	1.383 (3)
C9—N3	1.302 (3)	N3—N4	1.390 (3)
F1—C1—C6—C7	−6.3 (3)	C16—C17—C18—Br1	1.2 (3)
N1—C8—C9—N3	113.4 (2)	C15—C10—N2—C16	34.3 (3)
N1—C8—C9—N2	−66.0 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···N4^{i}	0.95	2.42	3.244 (3)	145

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

H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl carrier). The methyl group was rotated to fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*, *DENZO* (Otwinowski & Minor, 1997) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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$Z = 8$
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$T = 120$ K
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17959 measured reflections
4636 independent reflections
3545 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.5°$
$h = -19\rightarrow22$
$k = -14\rightarrow14$
$l = -26\rightarrow26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.075$
$S = 1.03$
4636 reflections
282 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
$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 3.972P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00038 (7)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.29527 (13)	0.03453 (19)	0.14939 (10)	0.0186 (5)
C2	0.31284 (15)	−0.01748 (19)	0.09168 (11)	0.0225 (5)
H2	0.2740	−0.0598	0.0672	0.027*
C3	0.38893 (15)	−0.0064 (2)	0.07022 (11)	0.0256 (6)
H3	0.4024	−0.0406	0.0303	0.031*
C4	0.44510 (15)	0.0543 (2)	0.10690 (11)	0.0254 (6)
H4	0.4974	0.0600	0.0927	0.030*
C5	0.42487 (14)	0.10679 (19)	0.16437 (11)	0.0201 (5)
H5	0.4637	0.1488	0.1891	0.024*
C6	0.34883 (13)	0.09925 (18)	0.18672 (10)	0.0162 (5)
C7	0.32824 (13)	0.16341 (18)	0.24659 (10)	0.0160 (5)
C8	0.36680 (13)	0.2444 (2)	0.34771 (10)	0.0197 (5)
H8A	0.3527	0.3230	0.3320	0.024*
H8B	0.4151	0.2506	0.3759	0.024*
C9	0.30212 (13)	0.19739 (18)	0.38564 (10)	0.0166 (5)
C10	0.20196 (13)	0.23708 (18)	0.29772 (10)	0.0148 (5)
C11	0.25103 (13)	0.22564 (18)	0.24509 (10)	0.0145 (4)
C12	0.22626 (13)	0.27568 (18)	0.18603 (10)	0.0168 (5)
H12	0.2584	0.2690	0.1495	0.020*
C13	0.15616 (13)	0.33444 (18)	0.18002 (10)	0.0177 (5)
C14	0.10730 (13)	0.34409 (19)	0.23184 (10)	0.0194 (5)
H14	0.0585	0.3837	0.2271	0.023*
C15	0.13075 (13)	0.29515 (19)	0.29064 (10)	0.0177 (5)
H15	0.0978	0.3013	0.3266	0.021*
C16	0.18369 (13)	0.14398 (18)	0.40899 (10)	0.0167 (5)
C17	0.09854 (13)	0.12232 (18)	0.40969 (10)	0.0168 (5)
C18	0.05775 (14)	0.04967 (19)	0.36588 (10)	0.0190 (5)
C19	−0.02163 (14)	0.0307 (2)	0.37113 (11)	0.0244 (5)
H19	−0.0489	−0.0174	0.3404	0.029*
C20	−0.06211 (14)	0.0812 (2)	0.42102 (11)	0.0250 (5)
H20	−0.1169	0.0677	0.4245	0.030*
C21	−0.02190 (14)	0.1514 (2)	0.46569 (10)	0.0209 (5)
C22	0.05765 (14)	0.17254 (19)	0.45944 (10)	0.0192 (5)
H22	0.0846	0.2222	0.4896	0.023*
C23	−0.13683 (15)	0.1847 (2)	0.52609 (12)	0.0305 (6)

H23A	−0.1532	0.2276	0.5643	0.046*
H23B	−0.1463	0.1018	0.5323	0.046*
H23C	−0.1672	0.2117	0.4876	0.046*
N1	0.38193 (11)	0.16916 (15)	0.29199 (8)	0.0176 (4)
N2	0.22620 (10)	0.19133 (15)	0.35967 (8)	0.0154 (4)
N3	0.30634 (11)	0.15665 (16)	0.44457 (8)	0.0200 (4)
N4	0.23087 (11)	0.12220 (16)	0.45954 (8)	0.0199 (4)
F1	0.22125 (8)	0.01895 (11)	0.17111 (6)	0.0242 (3)
O1	−0.05502 (10)	0.20385 (14)	0.51736 (7)	0.0278 (4)
Cl1	0.12993 (4)	0.39768 (5)	0.10587 (3)	0.02819 (16)
Br1	0.112657 (15)	−0.03066 (2)	0.301251 (11)	0.02696 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0155 (12)	0.0191 (12)	0.0213 (11)	0.0029 (10)	0.0009 (9)	0.0025 (9)
C2	0.0272 (14)	0.0195 (12)	0.0204 (11)	0.0029 (10)	−0.0045 (10)	−0.0002 (9)
C3	0.0326 (15)	0.0258 (13)	0.0186 (11)	0.0089 (11)	0.0038 (11)	0.0000 (10)
C4	0.0210 (13)	0.0285 (14)	0.0272 (12)	0.0074 (11)	0.0068 (10)	0.0007 (11)
C5	0.0146 (12)	0.0207 (12)	0.0250 (12)	0.0022 (10)	−0.0002 (9)	0.0006 (10)
C6	0.0151 (12)	0.0150 (12)	0.0183 (10)	0.0023 (9)	−0.0012 (9)	0.0029 (9)
C7	0.0141 (12)	0.0146 (11)	0.0194 (11)	−0.0016 (9)	0.0026 (9)	0.0024 (9)
C8	0.0147 (12)	0.0203 (12)	0.0238 (11)	−0.0004 (10)	−0.0033 (10)	−0.0039 (9)
C9	0.0140 (12)	0.0161 (12)	0.0195 (11)	0.0006 (9)	−0.0030 (9)	−0.0056 (9)
C10	0.0148 (12)	0.0136 (11)	0.0156 (10)	−0.0026 (9)	−0.0023 (9)	−0.0003 (8)
C11	0.0117 (11)	0.0133 (11)	0.0185 (10)	−0.0015 (9)	0.0001 (9)	−0.0010 (9)
C12	0.0148 (12)	0.0166 (12)	0.0194 (11)	−0.0016 (9)	0.0034 (9)	0.0010 (9)
C13	0.0195 (13)	0.0152 (12)	0.0183 (11)	−0.0002 (9)	−0.0006 (9)	0.0041 (9)
C14	0.0132 (12)	0.0200 (12)	0.0249 (11)	0.0046 (10)	−0.0015 (9)	−0.0003 (10)
C15	0.0149 (12)	0.0203 (12)	0.0182 (11)	0.0000 (9)	0.0021 (9)	−0.0021 (9)
C16	0.0207 (13)	0.0149 (11)	0.0146 (10)	0.0001 (9)	0.0001 (9)	−0.0039 (9)
C17	0.0161 (12)	0.0180 (12)	0.0162 (10)	0.0002 (9)	0.0006 (9)	0.0008 (9)
C18	0.0210 (13)	0.0196 (12)	0.0165 (10)	0.0007 (10)	0.0025 (9)	−0.0023 (9)
C19	0.0234 (14)	0.0256 (14)	0.0238 (12)	−0.0061 (11)	−0.0027 (10)	−0.0055 (10)
C20	0.0165 (13)	0.0310 (14)	0.0274 (12)	−0.0050 (11)	0.0011 (10)	0.0009 (11)
C21	0.0219 (13)	0.0225 (13)	0.0188 (11)	−0.0009 (10)	0.0044 (10)	0.0021 (9)
C22	0.0210 (13)	0.0214 (12)	0.0153 (10)	−0.0033 (10)	0.0009 (9)	−0.0008 (9)
C23	0.0224 (14)	0.0385 (15)	0.0313 (13)	−0.0028 (12)	0.0122 (11)	−0.0005 (12)
N1	0.0138 (10)	0.0200 (10)	0.0193 (9)	−0.0012 (8)	0.0019 (8)	−0.0009 (8)
N2	0.0121 (10)	0.0188 (10)	0.0152 (9)	0.0001 (8)	−0.0003 (7)	−0.0022 (7)
N3	0.0172 (11)	0.0243 (11)	0.0181 (9)	0.0004 (8)	−0.0020 (8)	−0.0035 (8)
N4	0.0173 (11)	0.0254 (11)	0.0169 (9)	−0.0001 (8)	−0.0009 (8)	−0.0021 (8)
F1	0.0158 (7)	0.0282 (8)	0.0286 (7)	−0.0040 (6)	−0.0011 (6)	−0.0051 (6)
O1	0.0202 (10)	0.0389 (10)	0.0248 (8)	−0.0015 (8)	0.0083 (7)	−0.0073 (8)
Cl1	0.0323 (4)	0.0294 (3)	0.0227 (3)	0.0115 (3)	0.0001 (3)	0.0086 (2)
Br1	0.02801 (15)	0.02872 (16)	0.02428 (13)	−0.00058 (11)	0.00281 (10)	−0.01096 (10)

Geometric parameters (Å, º)

C1—F1	1.365 (3)	C12—H12	0.9500
C1—C2	1.376 (3)	C13—C14	1.384 (3)
C1—C6	1.387 (3)	C13—Cl1	1.736 (2)
C2—C3	1.390 (3)	C14—C15	1.382 (3)
C2—H2	0.9500	C14—H14	0.9500
C3—C4	1.385 (3)	C15—H15	0.9500
C3—H3	0.9500	C16—N4	1.314 (3)
C4—C5	1.386 (3)	C16—N2	1.383 (3)
C4—H4	0.9500	C16—C17	1.471 (3)
C5—C6	1.393 (3)	C17—C22	1.388 (3)
C5—H5	0.9500	C17—C18	1.397 (3)
C6—C7	1.493 (3)	C18—C19	1.377 (3)
C7—N1	1.283 (3)	C18—Br1	1.899 (2)
C7—C11	1.496 (3)	C19—C20	1.388 (3)
C8—N1	1.471 (3)	C19—H19	0.9500
C8—C9	1.478 (3)	C20—C21	1.386 (3)
C8—H8A	0.9900	C20—H20	0.9500
C8—H8B	0.9900	C21—O1	1.366 (3)
C9—N3	1.302 (3)	C21—C22	1.386 (3)
C9—N2	1.380 (3)	C22—H22	0.9500
C10—C15	1.387 (3)	C23—O1	1.428 (3)
C10—C11	1.401 (3)	C23—H23A	0.9800
C10—N2	1.427 (3)	C23—H23B	0.9800
C11—C12	1.397 (3)	C23—H23C	0.9800
C12—C13	1.373 (3)	N3—N4	1.390 (3)
F1—C1—C2	117.5 (2)	C14—C13—Cl1	120.29 (17)
F1—C1—C6	118.89 (19)	C15—C14—C13	118.9 (2)
C2—C1—C6	123.6 (2)	C15—C14—H14	120.6
C1—C2—C3	118.2 (2)	C13—C14—H14	120.6
C1—C2—H2	120.9	C14—C15—C10	120.7 (2)
C3—C2—H2	120.9	C14—C15—H15	119.7
C4—C3—C2	120.2 (2)	C10—C15—H15	119.7
C4—C3—H3	119.9	N4—C16—N2	109.73 (19)
C2—C3—H3	119.9	N4—C16—C17	122.04 (19)
C3—C4—C5	119.9 (2)	N2—C16—C17	128.20 (18)
C3—C4—H4	120.1	C22—C17—C18	118.5 (2)
C5—C4—H4	120.1	C22—C17—C16	117.31 (19)
C4—C5—C6	121.4 (2)	C18—C17—C16	124.05 (19)
C4—C5—H5	119.3	C19—C18—C17	120.6 (2)
C6—C5—H5	119.3	C19—C18—Br1	119.27 (17)
C1—C6—C5	116.6 (2)	C17—C18—Br1	120.09 (17)
C1—C6—C7	123.7 (2)	C18—C19—C20	120.6 (2)
C5—C6—C7	119.60 (19)	C18—C19—H19	119.7
N1—C7—C6	116.41 (19)	C20—C19—H19	119.7
N1—C7—C11	126.09 (19)	C21—C20—C19	119.4 (2)

C6—C7—C11	117.12 (18)	C21—C20—H20	120.3
N1—C8—C9	110.69 (18)	C19—C20—H20	120.3
N1—C8—H8A	109.5	O1—C21—C22	115.4 (2)
C9—C8—H8A	109.5	O1—C21—C20	124.7 (2)
N1—C8—H8B	109.5	C22—C21—C20	119.9 (2)
C9—C8—H8B	109.5	C21—C22—C17	121.0 (2)
H8A—C8—H8B	108.1	C21—C22—H22	119.5
N3—C9—N2	111.07 (19)	C17—C22—H22	119.5
N3—C9—C8	127.7 (2)	O1—C23—H23A	109.5
N2—C9—C8	121.23 (18)	O1—C23—H23B	109.5
C15—C10—C11	120.59 (19)	H23A—C23—H23B	109.5
C15—C10—N2	119.53 (19)	O1—C23—H23C	109.5
C11—C10—N2	119.86 (19)	H23A—C23—H23C	109.5
C12—C11—C10	117.9 (2)	H23B—C23—H23C	109.5
C12—C11—C7	116.78 (19)	C7—N1—C8	117.28 (19)
C10—C11—C7	125.37 (18)	C9—N2—C16	104.10 (17)
C13—C12—C11	120.9 (2)	C9—N2—C10	124.10 (18)
C13—C12—H12	119.6	C16—N2—C10	131.51 (18)
C11—C12—H12	119.6	C9—N3—N4	107.05 (17)
C12—C13—C14	121.1 (2)	C16—N4—N3	108.04 (17)
C12—C13—Cl1	118.62 (17)	C21—O1—C23	117.65 (18)

F1—C1—C2—C3	−177.41 (19)	N2—C16—C17—C18	60.2 (3)
C6—C1—C2—C3	1.3 (3)	C22—C17—C18—C19	1.5 (3)
C1—C2—C3—C4	0.8 (3)	C16—C17—C18—C19	177.7 (2)
C2—C3—C4—C5	−1.7 (3)	C22—C17—C18—Br1	−175.01 (16)
C3—C4—C5—C6	0.5 (3)	C16—C17—C18—Br1	1.2 (3)
F1—C1—C6—C5	176.28 (18)	C17—C18—C19—C20	−1.6 (3)
C2—C1—C6—C5	−2.4 (3)	Br1—C18—C19—C20	174.98 (18)
F1—C1—C6—C7	−6.3 (3)	C18—C19—C20—C21	0.1 (4)
C2—C1—C6—C7	175.0 (2)	C19—C20—C21—O1	−178.7 (2)
C4—C5—C6—C1	1.5 (3)	C19—C20—C21—C22	1.4 (3)
C4—C5—C6—C7	−176.0 (2)	O1—C21—C22—C17	178.68 (19)
C1—C6—C7—N1	146.1 (2)	C20—C21—C22—C17	−1.4 (3)
C5—C6—C7—N1	−36.6 (3)	C18—C17—C22—C21	0.0 (3)
C1—C6—C7—C11	−40.6 (3)	C16—C17—C22—C21	−176.5 (2)
C5—C6—C7—C11	136.8 (2)	C6—C7—N1—C8	172.24 (18)
N1—C8—C9—N3	113.4 (2)	C11—C7—N1—C8	−0.4 (3)
N1—C8—C9—N2	−66.0 (3)	C9—C8—N1—C7	67.5 (2)
C15—C10—C11—C12	0.8 (3)	N3—C9—N2—C16	0.8 (2)
N2—C10—C11—C12	−177.56 (18)	C8—C9—N2—C16	−179.76 (19)
C15—C10—C11—C7	−178.9 (2)	N3—C9—N2—C10	175.23 (19)
N2—C10—C11—C7	2.7 (3)	C8—C9—N2—C10	−5.3 (3)
N1—C7—C11—C12	137.3 (2)	N4—C16—N2—C9	−0.9 (2)
C6—C7—C11—C12	−35.4 (3)	C17—C16—N2—C9	177.0 (2)
N1—C7—C11—C10	−43.0 (3)	N4—C16—N2—C10	−174.8 (2)
C6—C7—C11—C10	144.3 (2)	C17—C16—N2—C10	3.1 (4)
C10—C11—C12—C13	0.2 (3)	C15—C10—N2—C9	−138.5 (2)

C7—C11—C12—C13	179.93 (19)	C11—C10—N2—C9	39.8 (3)
C11—C12—C13—C14	−1.2 (3)	C15—C10—N2—C16	34.3 (3)
C11—C12—C13—Cl1	178.42 (16)	C11—C10—N2—C16	−147.3 (2)
C12—C13—C14—C15	1.1 (3)	N2—C9—N3—N4	−0.3 (2)
Cl1—C13—C14—C15	−178.47 (17)	C8—C9—N3—N4	−179.8 (2)
C13—C14—C15—C10	−0.1 (3)	N2—C16—N4—N3	0.7 (2)
C11—C10—C15—C14	−0.8 (3)	C17—C16—N4—N3	−177.34 (19)
N2—C10—C15—C14	177.52 (19)	C9—N3—N4—C16	−0.3 (2)
N4—C16—C17—C22	54.2 (3)	C22—C21—O1—C23	−179.9 (2)
N2—C16—C17—C22	−123.5 (2)	C20—C21—O1—C23	0.2 (3)
N4—C16—C17—C18	−122.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N4^{i}	0.95	2.42	3.244 (3)	145

Symmetry code: (i) $x, -y, z-1/2$.