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(3,6-Dimethyl-1,2,4,5-tetrazine-1,4-diyl)-bis[(morpholin-4-yl)methanone]

Na-Bo Sun,[a] Yan-Mei Guo[b] and Guo-Wu Rao[b]*

[a]College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou 310015, People's Republic of China, and [b]College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China
Correspondence e-mail: rgw@zjut.edu.cn

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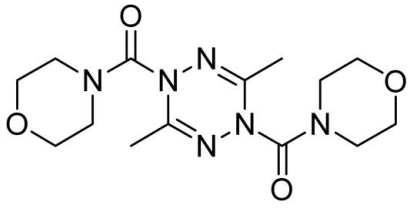
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.049; wR factor = 0.142; data-to-parameter ratio = 16.9.

In the title molecule, $C_{14}H_{22}N_6O_4$, the amide-substituted N atoms of the tetrazine ring deviate from the approximate plane of the four other atoms in the ring by 0.160 (2) and 0.243 (2) Å, forming a slight boat conformation. The morpholine rings are in chair conformations.

Related literature

For chemical reactions of 1,2,4,5-tetrazine derivatives, see: Domingo *et al.* (2009); Lorincz *et al.* (2010). For their biological activities, see: Devaraj *et al.* (2009); Eremeev *et al.* (1978, 1980); Han *et al.* (2010); Neunhoeffer (1984); Sauer (1996). For anti-tumor activity of 1,2,4,5-tetrazine derivatives, see: Hu *et al.* (2002, 2004); Rao & Hu, (2005, 2006). For details of the synthesis, see: Hu *et al.* (2004); Skorianetz & Kováts (1970, 1971); Sun *et al.* (2003). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{14}H_{22}N_6O_4$
M_r = 338.38
Monoclinic, $P2_1/n$
a = 15.285 (3) Å
b = 6.5977 (14) Å
c = 16.729 (4) Å
β = 106.576 (3)°
V = 1617.0 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 K
0.55 × 0.42 × 0.28 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.944, T_{max} = 0.971
9248 measured reflections
3714 independent reflections
2908 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.142
S = 1.03
3714 reflections
220 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5412).

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(3,6-Dimethyl-1,2,4,5-tetrazine-1,4-diyl)bis[(morpholin-4-yl)methanone]

Na-Bo Sun, Yan-Mei Guo and Guo-Wu Rao

S1. Comment

Tetrazine derivatives have high activity in chemical reactions (Domingo *et al.*, 2009; Lorincz *et al.*, 2010), and have been widely used in pesticides and medicines (Devaraj *et al.*, 2009; Eremeev *et al.*, 1978, 1980; Han *et al.*, 2010; Neunhoeffer, 1984; Sauer, 1996). In a continuation of our studies of antitumor activities in 1,2,4,5-tetrazine derivatives (Hu *et al.*, 2002, 2004; Rao & Hu, 2005, 2006), we have obtained a yellow crystalline compound, (I). The structure was confirmed by single-crystal X-ray diffraction.

The molecular structure of (I) is illustrated in Fig. 1. The N2═C3 [1.2730 (17) Å] and N5═C6 [1.2748 (18) Å] bonds lengths are typical for double bonds, as are the C3—N4 [1.3821 (17) Å], N4—N5 [1.4235 (17) Å], C6—N1 [1.3728 (17) Å] and N1—N2 [1.4207 (16) Å] bond lengths (Allen *et al.*, 1987). The tetrazine ring is a 1,4-dihydro structure with the N-substituted groups at the 1,4-positions.

In (I), atoms N2, C3, N5 and C6 are approximately planar, with the largest deviation from this plane being 0.0137 (6) Å. Atoms N1 and N4 deviate from this plane by 0.1604 (21) and 0.2429 (20) Å, respectively. The dihedral angle between the N2/C3/N5/C6 plane and the N1/N2/C6 plane is 13.37 (24)°, and between the N2/C3/N5/C6 plane and the N4/N5/C3 plane is 19.79 (21)°. The tetrazine ring has a slight boat conformation. Atoms C7, C8, C9 and C10 are approximately planar, with the largest deviation from this plane being 0.0114 (9) Å. Atoms O3 and N3 deviate from this plane by 0.6616 (23) and -0.5938 (21) Å, respectively. Atoms C11, C12, C13 and C14 are approximately planar, with the largest deviation from this plane being 0.0137 (9) Å. Atoms O4 and N6 deviate from this plane by 0.6576 (20) and -0.5953 (21) Å, respectively. The two morpholine rings exhibit chair conformations.

S2. Experimental

The title compound was the product of the reaction of bis(trichloromethyl) carbonate, morpholine, and 3,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine according to the procedure (Hu *et al.*, 2004; Sun *et al.*, 2003; Skorianetz & Kováts, 1970, 1971). A solution of the title compound in acetone was concentrated gradually at room temperature to afford yellow blocks.

S3. Refinement

H atoms were included in calculated positions and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameters of their parent atoms, and C—H distances were set to 0.96Å for methyl H atoms and 0.97 Å for methylene H atoms.

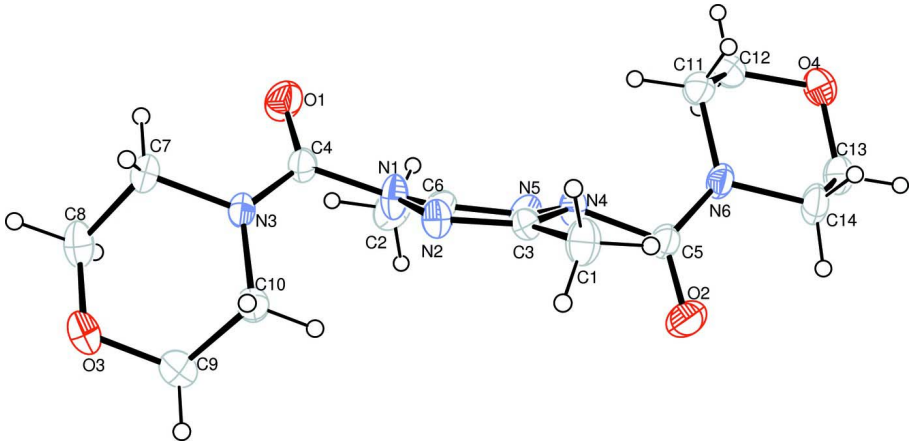

Figure 1

The molecular structure of (I), shown with 30% probability displacement ellipsoids.

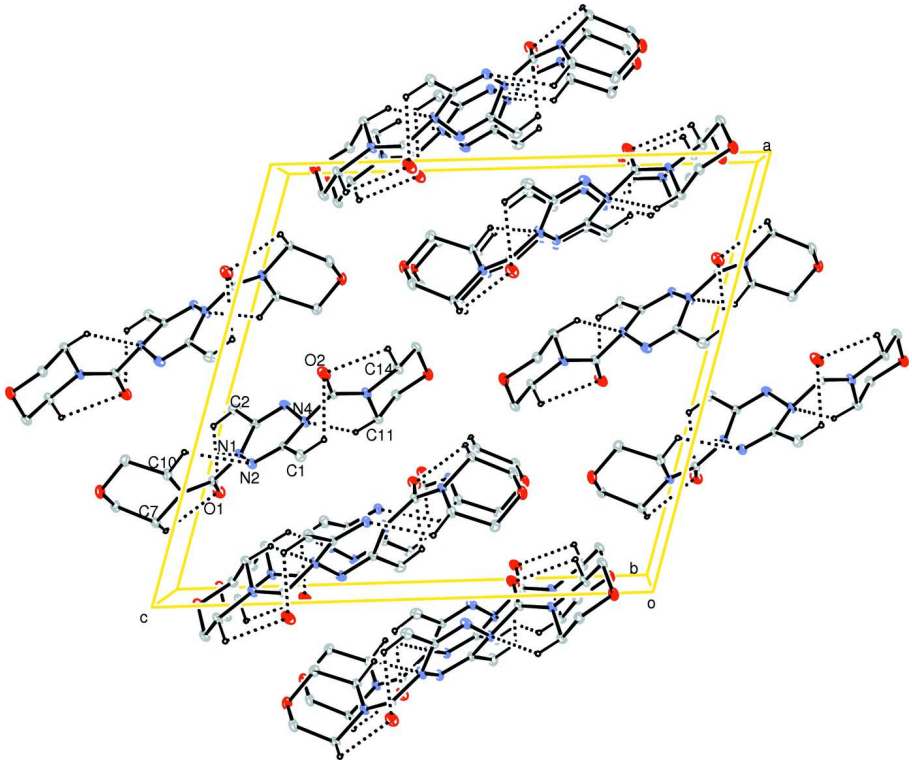

Figure 2

The crystal packing of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding were omitted for clarity.

(3,6-Dimethyl-1,2,4,5-tetrazine-1,4-diyl)bis[(morpholin-4-yl)methanone]

Crystal data

$C_{14}H_{22}N_6O_4$	a = 15.285 (3) Å
M_r = 338.38	b = 6.5977 (14) Å
Monoclinic, $P2_1/n$	c = 16.729 (4) Å
Hall symbol: -P 2yn	β = 106.576 (3)°

V = 1617.0 (6) Å^3
Z = 4
F(000) = 720
D_x = 1.390 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6920 reflections

θ = 2.9–28.2°
μ = 0.10 mm^{-1}
T = 298 K
Block, yellow
0.55 × 0.42 × 0.28 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.944, T_{max} = 0.971

9248 measured reflections
3714 independent reflections
2908 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 28.3°, θ_{min} = 2.1°
h = −15→20
k = −8→8
l = −18→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.142
S = 1.03
3714 reflections
220 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
$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.2523P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.036 (3)

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.

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 $F^2 > 2$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}
N2	0.68618 (8)	0.70860 (18)	0.11259 (7)	0.0374 (3)
N4	0.59388 (8)	0.60296 (19)	0.19430 (7)	0.0409 (3)
N5	0.55633 (9)	0.43942 (18)	0.13981 (8)	0.0450 (3)
N1	0.66936 (9)	0.51243 (19)	0.07644 (8)	0.0456 (3)
O4	0.49306 (9)	0.2853 (2)	0.41742 (7)	0.0586 (3)
O3	0.74085 (9)	0.7091 (2)	−0.18200 (7)	0.0620 (4)
N6	0.53166 (9)	0.5633 (2)	0.30490 (8)	0.0444 (3)
C6	0.59824 (9)	0.3973 (2)	0.08605 (8)	0.0359 (3)
N3	0.75197 (8)	0.57709 (19)	−0.01932 (7)	0.0416 (3)

O1	0.75909 (9)	0.27148 (18)	0.04345 (9)	0.0643 (4)
C3	0.64652 (9)	0.7449 (2)	0.16842 (8)	0.0333 (3)
O2	0.48046 (10)	0.8161 (2)	0.21322 (9)	0.0764 (5)
C4	0.72971 (10)	0.4435 (2)	0.03193 (8)	0.0397 (3)
C5	0.52962 (10)	0.6716 (2)	0.23773 (9)	0.0415 (3)
C11	0.59485 (10)	0.3983 (2)	0.33971 (10)	0.0461 (4)
H11A	0.6405	0.4442	0.3895	0.055*
H11B	0.6258	0.3549	0.2994	0.055*
C12	0.54193 (11)	0.2249 (3)	0.36082 (10)	0.0492 (4)
H12A	0.4994	0.1738	0.3101	0.059*
H12B	0.5836	0.1161	0.3854	0.059*
C7	0.82145 (11)	0.5206 (3)	−0.06011 (10)	0.0490 (4)
H7A	0.8456	0.3874	−0.0413	0.059*
H7B	0.8714	0.6170	−0.0455	0.059*
C10	0.70416 (11)	0.7647 (2)	−0.05175 (9)	0.0461 (4)
H10A	0.7453	0.8788	−0.0350	0.055*
H10B	0.6533	0.7839	−0.0287	0.055*
C14	0.47410 (12)	0.6227 (3)	0.35760 (11)	0.0531 (4)
H14A	0.4279	0.7179	0.3278	0.064*
H14B	0.5111	0.6889	0.4076	0.064*
C1	0.66582 (12)	0.9416 (3)	0.21394 (11)	0.0535 (4)
H1A	0.6875	0.9164	0.2728	0.080*
H1B	0.6109	1.0208	0.2020	0.080*
H1C	0.7115	1.0143	0.1963	0.080*
C13	0.42906 (12)	0.4385 (3)	0.38095 (11)	0.0548 (4)
H13A	0.3958	0.4774	0.4200	0.066*
H13B	0.3854	0.3847	0.3315	0.066*
C2	0.56523 (12)	0.2236 (3)	0.02845 (12)	0.0594 (5)
H2A	0.5571	0.2667	−0.0280	0.089*
H2B	0.5081	0.1761	0.0345	0.089*
H2C	0.6093	0.1159	0.0418	0.089*
C9	0.66960 (12)	0.7561 (3)	−0.14556 (10)	0.0588 (5)
H9A	0.6222	0.6540	−0.1618	0.071*
H9B	0.6429	0.8858	−0.1666	0.071*
C8	0.77950 (13)	0.5188 (3)	−0.15316 (10)	0.0581 (5)
H8A	0.8259	0.4854	−0.1803	0.070*
H8B	0.7326	0.4153	−0.1678	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0443 (6)	0.0343 (6)	0.0378 (6)	−0.0095 (5)	0.0183 (5)	−0.0074 (5)
N4	0.0480 (7)	0.0397 (7)	0.0428 (6)	−0.0052 (5)	0.0255 (5)	−0.0037 (5)
N5	0.0469 (7)	0.0330 (6)	0.0625 (8)	−0.0085 (5)	0.0278 (6)	−0.0075 (5)
N1	0.0601 (8)	0.0379 (7)	0.0506 (7)	−0.0152 (6)	0.0346 (6)	−0.0145 (5)
O4	0.0659 (7)	0.0694 (8)	0.0489 (6)	0.0032 (6)	0.0302 (6)	0.0145 (6)
O3	0.0741 (8)	0.0787 (9)	0.0390 (6)	0.0023 (7)	0.0255 (6)	0.0062 (6)
N6	0.0515 (7)	0.0449 (7)	0.0471 (7)	0.0098 (6)	0.0306 (6)	0.0054 (5)

C6	0.0375 (7)	0.0288 (7)	0.0417 (7)	−0.0002 (5)	0.0119 (6)	−0.0014 (5)
N3	0.0471 (7)	0.0461 (7)	0.0390 (6)	0.0091 (5)	0.0239 (5)	0.0036 (5)
O1	0.0768 (8)	0.0459 (7)	0.0819 (9)	0.0174 (6)	0.0417 (7)	0.0147 (6)
C3	0.0353 (6)	0.0348 (7)	0.0297 (6)	−0.0013 (5)	0.0089 (5)	−0.0013 (5)
O2	0.0777 (9)	0.0787 (9)	0.0906 (10)	0.0378 (8)	0.0525 (8)	0.0386 (8)
C4	0.0438 (7)	0.0405 (8)	0.0376 (7)	0.0007 (6)	0.0163 (6)	−0.0037 (6)
C5	0.0431 (7)	0.0416 (8)	0.0456 (8)	0.0033 (6)	0.0221 (6)	0.0017 (6)
C11	0.0434 (8)	0.0514 (9)	0.0468 (8)	0.0064 (7)	0.0182 (6)	0.0062 (7)
C12	0.0541 (9)	0.0496 (9)	0.0457 (8)	0.0062 (7)	0.0173 (7)	0.0079 (7)
C7	0.0487 (8)	0.0588 (10)	0.0483 (8)	0.0086 (7)	0.0278 (7)	0.0008 (7)
C10	0.0564 (9)	0.0445 (8)	0.0424 (8)	0.0095 (7)	0.0223 (7)	0.0053 (6)
C14	0.0653 (10)	0.0531 (10)	0.0544 (9)	0.0064 (8)	0.0386 (8)	−0.0022 (7)
C1	0.0623 (10)	0.0481 (9)	0.0552 (9)	−0.0113 (8)	0.0248 (8)	−0.0196 (7)
C13	0.0541 (9)	0.0674 (11)	0.0531 (9)	0.0012 (8)	0.0316 (8)	0.0028 (8)
C2	0.0529 (9)	0.0473 (9)	0.0776 (12)	−0.0106 (7)	0.0179 (9)	−0.0261 (8)
C9	0.0598 (10)	0.0707 (12)	0.0452 (9)	0.0083 (9)	0.0138 (8)	0.0096 (8)
C8	0.0704 (11)	0.0663 (11)	0.0470 (9)	−0.0035 (9)	0.0318 (8)	−0.0119 (8)

Geometric parameters (Å, º)

N2—C3	1.2730 (17)	C11—H11B	0.9700
N2—N1	1.4207 (16)	C12—H12A	0.9700
N4—C3	1.3821 (17)	C12—H12B	0.9700
N4—N5	1.4235 (17)	C7—C8	1.505 (2)
N4—C5	1.4509 (17)	C7—H7A	0.9700
N5—C6	1.2748 (18)	C7—H7B	0.9700
N1—C6	1.3728 (17)	C10—C9	1.507 (2)
N1—C4	1.4155 (17)	C10—H10A	0.9700
O4—C13	1.418 (2)	C10—H10B	0.9700
O4—C12	1.4201 (19)	C14—C13	1.502 (2)
O3—C8	1.413 (2)	C14—H14A	0.9700
O3—C9	1.426 (2)	C14—H14B	0.9700
N6—C5	1.3245 (19)	C1—H1A	0.9600
N6—C11	1.4620 (19)	C1—H1B	0.9600
N6—C14	1.4653 (17)	C1—H1C	0.9600
C6—C2	1.490 (2)	C13—H13A	0.9700
N3—C4	1.3392 (18)	C13—H13B	0.9700
N3—C10	1.4609 (19)	C2—H2A	0.9600
N3—C7	1.4650 (17)	C2—H2B	0.9600
O1—C4	1.2158 (18)	C2—H2C	0.9600
C3—C1	1.4911 (19)	C9—H9A	0.9700
O2—C5	1.2104 (19)	C9—H9B	0.9700
C11—C12	1.500 (2)	C8—H8A	0.9700
C11—H11A	0.9700	C8—H8B	0.9700
C3—N2—N1	114.67 (11)	C8—C7—H7B	109.8
C3—N4—N5	118.51 (11)	H7A—C7—H7B	108.2
C3—N4—C5	118.88 (12)	N3—C10—C9	110.14 (13)

N5—N4—C5	110.52 (11)	N3—C10—H10A	109.6
C6—N5—N4	115.15 (11)	C9—C10—H10A	109.6
C6—N1—C4	122.73 (12)	N3—C10—H10B	109.6
C6—N1—N2	120.49 (11)	C9—C10—H10B	109.6
C4—N1—N2	116.78 (11)	H10A—C10—H10B	108.1
C13—O4—C12	110.04 (12)	N6—C14—C13	109.79 (13)
C8—O3—C9	110.07 (13)	N6—C14—H14A	109.7
C5—N6—C11	126.36 (12)	C13—C14—H14A	109.7
C5—N6—C14	119.56 (13)	N6—C14—H14B	109.7
C11—N6—C14	113.66 (12)	C13—C14—H14B	109.7
N5—C6—N1	122.43 (12)	H14A—C14—H14B	108.2
N5—C6—C2	118.58 (13)	C3—C1—H1A	109.5
N1—C6—C2	118.90 (13)	C3—C1—H1B	109.5
C4—N3—C10	127.14 (12)	H1A—C1—H1B	109.5
C4—N3—C7	118.76 (13)	C3—C1—H1C	109.5
C10—N3—C7	113.26 (12)	H1A—C1—H1C	109.5
N2—C3—N4	122.96 (12)	H1B—C1—H1C	109.5
N2—C3—C1	118.17 (12)	O4—C13—C14	112.17 (14)
N4—C3—C1	118.54 (12)	O4—C13—H13A	109.2
O1—C4—N3	124.47 (13)	C14—C13—H13A	109.2
O1—C4—N1	118.89 (13)	O4—C13—H13B	109.2
N3—C4—N1	116.62 (13)	C14—C13—H13B	109.2
O2—C5—N6	125.04 (13)	H13A—C13—H13B	107.9
O2—C5—N4	121.32 (13)	C6—C2—H2A	109.5
N6—C5—N4	113.63 (12)	C6—C2—H2B	109.5
N6—C11—C12	108.81 (12)	H2A—C2—H2B	109.5
N6—C11—H11A	109.9	C6—C2—H2C	109.5
C12—C11—H11A	109.9	H2A—C2—H2C	109.5
N6—C11—H11B	109.9	H2B—C2—H2C	109.5
C12—C11—H11B	109.9	O3—C9—C10	111.70 (14)
H11A—C11—H11B	108.3	O3—C9—H9A	109.3
O4—C12—C11	111.39 (14)	C10—C9—H9A	109.3
O4—C12—H12A	109.4	O3—C9—H9B	109.3
C11—C12—H12A	109.4	C10—C9—H9B	109.3
O4—C12—H12B	109.4	H9A—C9—H9B	107.9
C11—C12—H12B	109.4	O3—C8—C7	111.07 (14)
H12A—C12—H12B	108.0	O3—C8—H8A	109.4
N3—C7—C8	109.40 (13)	C7—C8—H8A	109.4
N3—C7—H7A	109.8	O3—C8—H8B	109.4
C8—C7—H7A	109.8	C7—C8—H8B	109.4
N3—C7—H7B	109.8	H8A—C8—H8B	108.0

C3—N4—N5—C6	23.26 (19)	C11—N6—C5—O2	−174.99 (17)
C5—N4—N5—C6	165.46 (12)	C14—N6—C5—O2	−2.9 (3)
C3—N2—N1—C6	16.02 (19)	C11—N6—C5—N4	4.4 (2)
C3—N2—N1—C4	−163.17 (13)	C14—N6—C5—N4	176.51 (13)
N4—N5—C6—N1	−5.6 (2)	C3—N4—C5—O2	44.9 (2)
N4—N5—C6—C2	177.96 (14)	N5—N4—C5—O2	−97.15 (18)

C4—N1—C6—N5	164.79 (14)	C3—N4—C5—N6	−134.55 (14)
N2—N1—C6—N5	−14.4 (2)	N5—N4—C5—N6	83.42 (15)
C4—N1—C6—C2	−18.8 (2)	C5—N6—C11—C12	−134.69 (16)
N2—N1—C6—C2	162.09 (14)	C14—N6—C11—C12	52.82 (18)
N1—N2—C3—N4	2.27 (19)	C13—O4—C12—C11	61.50 (17)
N1—N2—C3—C1	175.66 (13)	N6—C11—C12—O4	−57.44 (17)
N5—N4—C3—N2	−22.2 (2)	C4—N3—C7—C8	117.84 (16)
C5—N4—C3—N2	−161.22 (13)	C10—N3—C7—C8	−52.37 (18)
N5—N4—C3—C1	164.45 (13)	C4—N3—C10—C9	−118.42 (16)
C5—N4—C3—C1	25.42 (19)	C7—N3—C10—C9	50.80 (18)
C10—N3—C4—O1	163.86 (16)	C5—N6—C14—C13	135.96 (16)
C7—N3—C4—O1	−4.8 (2)	C11—N6—C14—C13	−50.99 (19)
C10—N3—C4—N1	−17.6 (2)	C12—O4—C13—C14	−59.39 (18)
C7—N3—C4—N1	173.67 (13)	N6—C14—C13—O4	53.49 (19)
C6—N1—C4—O1	−44.3 (2)	C8—O3—C9—C10	59.94 (19)
N2—N1—C4—O1	134.89 (16)	N3—C10—C9—O3	−53.83 (19)
C6—N1—C4—N3	137.12 (15)	C9—O3—C8—C7	−61.71 (18)
N2—N1—C4—N3	−43.71 (18)	N3—C7—C8—O3	57.37 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*A*···O2	0.97	2.37	2.758 (2)	103
C1—H1*B*···O2	0.96	2.46	2.949 (2)	111
C2—H2*C*···O1	0.96	2.50	2.919 (2)	106
C7—H7*A*···O1	0.97	2.33	2.748 (2)	105
C10—H10*B*···N1	0.97	2.47	2.881 (2)	105
C10—H10*B*···N2	0.97	2.33	2.8640 (19)	114
C11—H11*B*···N4	0.97	2.35	2.7787 (19)	106