Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,2-Dimethyl-5-[(3-nitroanilino)-methylene]-1,3-dioxane-4,6-dione

Meng Zhou, Rui Li* and Zhen-Yu Ding

State Key Laboratory of Biotherapy, West China Hospital, Sichuan University, Chengdu 610041, People's Republic of China
Correspondence e-mail: lirui@scu.edu.cn

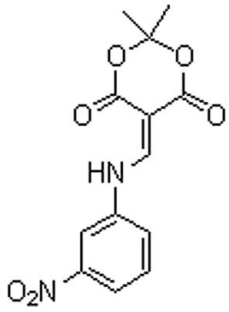
Received 29 July 2009; accepted 10 August 2009

Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.101; data-to-parameter ratio = 15.5.

The benzene ring of the title compound, $C_{13}H_{12}N_2O_6$, is twisted away from the planes of the aminomethylene unit and the dioxane ring by 30.13 (4) and 35.89 (4)°, respectively. The dioxane ring exhibits a half-boat conformation, in which the C atom between the dioxane O atoms is 0.553 (8) Å out-of-plane. An intramolecular N—H···O hydrogen bond stabilizes the conformation of the dioxane ring with the aminomethylene group [the dihedral angle between the mean planes of the dioxane ring and the aminomethylene group is 11.61 (4)°]. In the crystal, a three-dimensional framework is built *via* weak intermolecular N—H···O and C—H···O interactions.

Related literature

For the synthesis of related compounds, see: Cassis *et al.* (1985). For the synthesis of related antitumor precursors, see Ruchelman *et al.* (2003). For the crystal structures of related 5-arylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione derivatives, see Li *et al.* (2009*a*,*b*); Li, Shi *et al.* (2009).



Experimental

Crystal data

$C_{13}H_{12}N_2O_6$ M_r = 292.25
Monoclinic, $P2_1/c$
a = 11.7900 (13) Å
b = 8.7699 (9) Å
c = 14.0614 (15) Å
β = 113.8640 (10)°
V = 1329.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 153 K
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
8116 measured reflections
3052 independent reflections
2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.101
S = 1.05
3052 reflections
197 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3	0.882 (16)	2.150 (15)	2.7705 (14)	126.8 (13)
N1—H1···O3^{i}	0.882 (16)	2.308 (16)	3.1101 (14)	151.2 (13)
C7—H7···O4^{ii}	0.93	2.58	3.4527 (18)	156
C11—H11···O4^{iii}	0.93	2.39	3.242 (2)	152
C13—H13···O4^{ii}	0.93	2.36	3.205 (2)	151

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x, -y, -z+2$; (iii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); 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* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

This research was supported financially by the State Key Laboratory of Drug Research (Shanghai Institute of Materia Medica, Chinese Academy of Sciences).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2002).

References

Bruker (2000). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cassis, R., Tapia, R. & Valderrama, J. A. (1985). *Synth. Commun.* **15**, 125–133.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Li, R., Ding, Z.-Y., Wei, Y.-Q. & Ding, J. (2009*a*). *Acta Cryst.* E**65**, o1296.
Li, R., Ding, Z.-Y., Wei, Y.-Q. & Ding, J. (2009*b*). *Acta Cryst.* E**65**, o1297.
Li, R., Shi, J.-Y., Ding, Z.-Y., Wei, Y.-Q. & Ding, J. (2009). *Acta Cryst.* E**65**, o1298–o1299.
Ruchelman, A. L., Singh, S. K., Ray, A., Wu, X. H., Yang, J. M., Li, T. K., Liu, A., Liu, L. F. & LaVoie, E. J. (2003). *Bioorg. Med. Chem.* **11**, 2061–2073.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2009). E**65**, o2171 [doi:10.1107/S1600536809031535]

2,2-Dimethyl-5-[(3-nitroanilino)methylene]-1,3-dioxane-4,6-dione

Meng Zhou, Rui Li and Zhen-Yu Ding

S1. Comment

The 4(1*H*)quinolone structure have long attracted pharmacological interest as anticancer agents, anti-malarial agents and reversible (H+/K+) ATPase inhibitors (Ruchelman *et al.*, 2003). 5-Arylaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-diones are the key intermediates which can be used to synthesize the 4(1*H*)quinolone derivatives by thermolysis (Cassis *et al.*, 1985).

The molecular structure of the title compound is shown in Fig. 1. The dihedral angle between the mean planes formed by the benzyl and aminomethylene units is 30.13 (4)°, while the angle between the mean planes of the dioxane ring and the aminomethylene group is only 11.61 (4)° due to the intramolecular N1—H1···O3 hydrogen bond (Table 1). Apart from that, the dioxane ring exhibits a half-boat conformation, in which the C atom between the dioxane oxygen atoms is 0.553 (8) Å out-of-plane.

The three-dimensional framework is built by the weak intermolecular N1—H1···O3^{i}, C7—H7···O4^{ii}, C13—H13···O4^{ii} and C11—H11···O4^{iii} interactions (Fig. 2).

S2. Experimental

An ethanol solution (50 ml) of 2,2-dimethyl-1,3-dioxane-4,6-dione (1.44 g, 0.01 mol) and methylorthoformate (1.27 g, 0.012 mol) was heated to reflux for 1 h, then the 3-nitrobenzenamine (1.38 g, 0.01 mol) was added into the solution. The mixture was heated under reflux for another 8 h and then filtered. Single crystals were obtained from the filtrate after 3 days.

S3. Refinement

The imino H atom was located in a difference Fourier map and refined isotropically. The other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic, C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

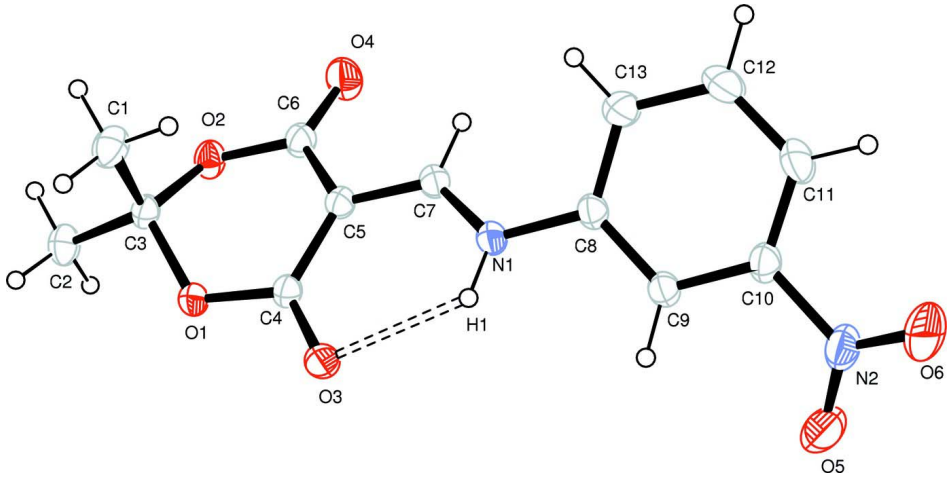


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. The intramolecular hydrogen bond is shown as a dashed line.

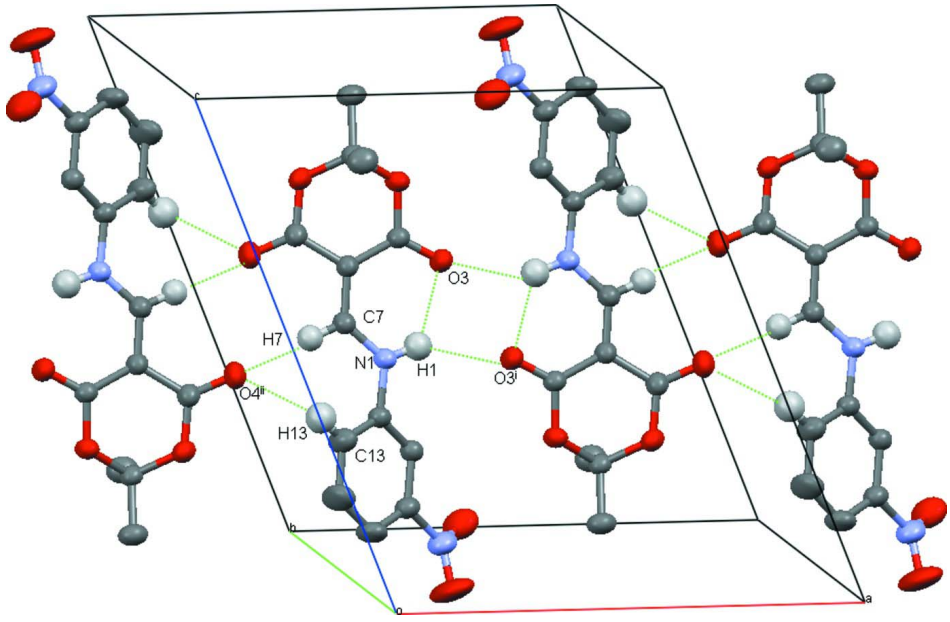


Figure 2

Crystal packing of the title compound, showing the intermolecular hydrogen bonds as dashed lines. [Symmetry codes: (i) -*x* + 1, -*y*, -*z* + 2; (ii) -*x*, -*y*, -*z* + 2].

2,2-Dimethyl-5-[(3-nitroanilino)methylene]-1,3-dioxane-4,6-dione

Crystal data

$C_{13}H_{12}N_2O_6$
M_r = 292.25
Monoclinic, $P2_1/c$
a = 11.7900 (13) Å
b = 8.7699 (9) Å
c = 14.0614 (15) Å
β = 113.864 (1)°
V = 1329.6 (2) Å^3
Z = 4
F(000) = 608
D_x = 1.460 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4305 reflections
θ = 2.3–27.6°

μ = 0.12 mm^{-1}
T = 153 K

Block, colourless
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
8116 measured reflections
3052 independent reflections

2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.6°, θ_{min} = 2.8°
h = −15→14
k = −11→10
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.101
S = 1.05
3052 reflections
197 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.3157P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0195 (18)

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}
O1	0.45433 (8)	−0.09916 (10)	1.23372 (6)	0.0370 (2)
O3	0.47419 (8)	−0.05487 (12)	1.08661 (7)	0.0440 (2)
O2	0.25826 (8)	−0.13984 (11)	1.23681 (6)	0.0401 (2)
C4	0.40464 (11)	−0.06725 (13)	1.13054 (9)	0.0322 (2)
N1	0.26298 (10)	0.01843 (13)	0.91248 (8)	0.0359 (2)
C8	0.19585 (11)	0.06369 (14)	0.80763 (9)	0.0342 (3)
C9	0.24224 (11)	0.02544 (14)	0.73506 (9)	0.0347 (3)
H9	0.3148	−0.0312	0.7538	0.042*
C3	0.37852 (11)	−0.07324 (14)	1.29110 (9)	0.0337 (3)
O4	0.08565 (9)	−0.12773 (15)	1.09442 (8)	0.0584 (3)
C7	0.21114 (11)	−0.01291 (14)	0.97781 (9)	0.0350 (3)
H7	0.1252	−0.0055	0.9519	0.042*
O5	0.30012 (13)	−0.07262 (15)	0.57581 (10)	0.0684 (3)

C6	0.19637 (11)	−0.10611 (15)	1.13438 (9)	0.0381 (3)
C5	0.27159 (11)	−0.05534 (14)	1.08029 (9)	0.0333 (3)
C10	0.17796 (12)	0.07365 (16)	0.63388 (9)	0.0403 (3)
C13	0.08587 (14)	0.14495 (19)	0.77793 (11)	0.0510 (4)
H13	0.0545	0.1705	0.8268	0.061*
C2	0.43836 (14)	−0.16096 (17)	1.39116 (10)	0.0459 (3)
H2A	0.3876	−0.1539	1.4299	0.069*
H2B	0.5188	−0.1189	1.4315	0.069*
H2C	0.4468	−0.2660	1.3759	0.069*
N2	0.22862 (12)	0.03454 (17)	0.55739 (9)	0.0535 (3)
C1	0.36712 (15)	0.09463 (15)	1.30692 (11)	0.0481 (3)
H1A	0.3285	0.1440	1.2406	0.072*
H1B	0.4481	0.1372	1.3444	0.072*
H1C	0.3174	0.1099	1.3459	0.072*
C11	0.06978 (15)	0.1552 (2)	0.60191 (11)	0.0586 (4)
H11	0.0293	0.1874	0.5334	0.070*
O6	0.19778 (16)	0.1124 (2)	0.47934 (10)	0.0992 (6)
C12	0.02320 (15)	0.1877 (2)	0.67512 (13)	0.0672 (5)
H12	−0.0518	0.2393	0.6550	0.081*
H1	0.3441 (15)	0.0100 (18)	0.9339 (12)	0.051 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0341 (4)	0.0496 (5)	0.0266 (4)	0.0047 (4)	0.0115 (3)	0.0028 (3)
O3	0.0338 (5)	0.0665 (6)	0.0354 (5)	0.0021 (4)	0.0177 (4)	0.0058 (4)
O2	0.0413 (5)	0.0500 (5)	0.0306 (4)	−0.0094 (4)	0.0164 (4)	0.0009 (4)
C4	0.0350 (6)	0.0351 (6)	0.0270 (5)	0.0005 (4)	0.0130 (5)	0.0007 (4)
N1	0.0313 (5)	0.0478 (6)	0.0274 (5)	0.0026 (4)	0.0106 (4)	0.0029 (4)
C8	0.0332 (6)	0.0396 (6)	0.0279 (5)	−0.0008 (5)	0.0105 (5)	0.0033 (5)
C9	0.0328 (6)	0.0388 (6)	0.0302 (6)	0.0001 (5)	0.0106 (5)	0.0030 (5)
C3	0.0375 (6)	0.0384 (6)	0.0263 (5)	−0.0019 (5)	0.0140 (5)	−0.0011 (4)
O4	0.0353 (5)	0.0966 (9)	0.0440 (6)	−0.0133 (5)	0.0167 (4)	0.0000 (5)
C7	0.0312 (6)	0.0427 (6)	0.0295 (6)	−0.0006 (5)	0.0108 (5)	−0.0006 (5)
O5	0.0855 (9)	0.0756 (8)	0.0587 (7)	0.0112 (7)	0.0443 (6)	−0.0031 (6)
C6	0.0352 (6)	0.0482 (7)	0.0324 (6)	−0.0042 (5)	0.0152 (5)	−0.0021 (5)
C5	0.0315 (6)	0.0409 (6)	0.0283 (5)	−0.0007 (5)	0.0128 (5)	−0.0004 (5)
C10	0.0420 (7)	0.0496 (7)	0.0294 (6)	−0.0030 (5)	0.0146 (5)	0.0032 (5)
C13	0.0479 (8)	0.0687 (10)	0.0417 (7)	0.0176 (7)	0.0235 (6)	0.0123 (7)
C2	0.0555 (8)	0.0499 (8)	0.0300 (6)	−0.0003 (6)	0.0147 (6)	0.0052 (5)
N2	0.0583 (8)	0.0716 (9)	0.0339 (6)	−0.0037 (7)	0.0218 (5)	0.0014 (6)
C1	0.0629 (9)	0.0392 (7)	0.0427 (7)	0.0011 (6)	0.0219 (7)	−0.0044 (6)
C11	0.0521 (9)	0.0833 (12)	0.0349 (7)	0.0148 (8)	0.0118 (6)	0.0209 (7)
O6	0.1211 (13)	0.1419 (14)	0.0516 (7)	0.0380 (11)	0.0524 (8)	0.0415 (8)
C12	0.0509 (9)	0.0965 (13)	0.0529 (9)	0.0351 (9)	0.0197 (7)	0.0271 (9)

Geometric parameters (Å, º)

O1—C4	1.3560 (14)	C7—H7	0.9300
O1—C3	1.4441 (14)	O5—N2	1.2183 (18)
O3—C4	1.2147 (14)	C6—C5	1.4524 (16)
O2—C6	1.3580 (15)	C10—C11	1.370 (2)
O2—C3	1.4348 (15)	C10—N2	1.4665 (17)
C4—C5	1.4401 (17)	C13—C12	1.383 (2)
N1—C7	1.3219 (15)	C13—H13	0.9300
N1—C8	1.4190 (15)	C2—H2A	0.9600
N1—H1	0.882 (16)	C2—H2B	0.9600
C8—C9	1.3800 (17)	C2—H2C	0.9600
C8—C13	1.3875 (18)	N2—O6	1.2164 (17)
C9—C10	1.3802 (17)	C1—H1A	0.9600
C9—H9	0.9300	C1—H1B	0.9600
C3—C1	1.5030 (18)	C1—H1C	0.9600
C3—C2	1.5053 (17)	C11—C12	1.378 (2)
O4—C6	1.2092 (16)	C11—H11	0.9300
C7—C5	1.3754 (16)	C12—H12	0.9300
C4—O1—C3	117.92 (9)	C4—C5—C6	119.70 (10)
C6—O2—C3	117.84 (9)	C11—C10—C9	123.24 (12)
O3—C4—O1	118.31 (11)	C11—C10—N2	118.87 (12)
O3—C4—C5	124.71 (11)	C9—C10—N2	117.88 (12)
O1—C4—C5	116.96 (10)	C12—C13—C8	119.52 (13)
C7—N1—C8	124.04 (10)	C12—C13—H13	120.2
C7—N1—H1	119.2 (10)	C8—C13—H13	120.2
C8—N1—H1	116.7 (10)	C3—C2—H2A	109.5
C9—C8—C13	120.26 (11)	C3—C2—H2B	109.5
C9—C8—N1	118.62 (11)	H2A—C2—H2B	109.5
C13—C8—N1	121.12 (11)	C3—C2—H2C	109.5
C8—C9—C10	118.11 (11)	H2A—C2—H2C	109.5
C8—C9—H9	120.9	H2B—C2—H2C	109.5
C10—C9—H9	120.9	O6—N2—O5	123.59 (14)
O2—C3—O1	109.91 (9)	O6—N2—C10	117.94 (14)
O2—C3—C1	110.44 (11)	O5—N2—C10	118.46 (12)
O1—C3—C1	110.45 (10)	C3—C1—H1A	109.5
O2—C3—C2	106.13 (10)	C3—C1—H1B	109.5
O1—C3—C2	106.25 (10)	H1A—C1—H1B	109.5
C1—C3—C2	113.48 (11)	C3—C1—H1C	109.5
N1—C7—C5	126.51 (11)	H1A—C1—H1C	109.5
N1—C7—H7	116.7	H1B—C1—H1C	109.5
C5—C7—H7	116.7	C10—C11—C12	117.54 (13)
O4—C6—O2	118.33 (11)	C10—C11—H11	121.2
O4—C6—C5	125.30 (12)	C12—C11—H11	121.2
O2—C6—C5	116.25 (10)	C11—C12—C13	121.26 (14)
C7—C5—C4	122.25 (10)	C11—C12—H12	119.4
C7—C5—C6	117.66 (11)	C13—C12—H12	119.4

C3—O1—C4—O3	163.48 (11)	O3—C4—C5—C6	165.88 (12)
C3—O1—C4—C5	−18.46 (15)	O1—C4—C5—C6	−12.04 (17)
C7—N1—C8—C9	−149.73 (12)	O4—C6—C5—C7	7.2 (2)
C7—N1—C8—C13	30.4 (2)	O2—C6—C5—C7	−176.78 (11)
C13—C8—C9—C10	1.64 (19)	O4—C6—C5—C4	−165.75 (14)
N1—C8—C9—C10	−178.26 (11)	O2—C6—C5—C4	10.23 (18)
C6—O2—C3—O1	−50.49 (14)	C8—C9—C10—C11	−1.1 (2)
C6—O2—C3—C1	71.61 (13)	C8—C9—C10—N2	179.15 (11)
C6—O2—C3—C2	−164.99 (10)	C9—C8—C13—C12	−0.1 (2)
C4—O1—C3—O2	48.46 (13)	N1—C8—C13—C12	179.74 (15)
C4—O1—C3—C1	−73.64 (14)	C11—C10—N2—O6	22.6 (2)
C4—O1—C3—C2	162.88 (10)	C9—C10—N2—O6	−157.58 (15)
C8—N1—C7—C5	−179.14 (12)	C11—C10—N2—O5	−158.17 (16)
C3—O2—C6—O4	−161.51 (12)	C9—C10—N2—O5	21.6 (2)
C3—O2—C6—C5	22.23 (16)	C9—C10—C11—C12	−1.0 (3)
N1—C7—C5—C4	1.6 (2)	N2—C10—C11—C12	178.78 (16)
N1—C7—C5—C6	−171.23 (12)	C10—C11—C12—C13	2.5 (3)
O3—C4—C5—C7	−6.8 (2)	C8—C13—C12—C11	−2.0 (3)
O1—C4—C5—C7	175.30 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3	0.882 (16)	2.150 (15)	2.7705 (14)	126.8 (13)
N1—H1···O3^{i}	0.882 (16)	2.308 (16)	3.1101 (14)	151.2 (13)
C7—H7···O4	0.93	2.48	2.8026 (18)	101
C7—H7···O4^{ii}	0.93	2.58	3.4527 (18)	156
C11—H11···O4^{iii}	0.93	2.39	3.242 (2)	152
C13—H13···O4^{ii}	0.93	2.36	3.205 (2)	151

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*, −*y*, −*z*+2; (iii) −*x*, *y*+1/2, −*z*+3/2.