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1,4-Dihydroxy-2,3-dinitro-9,10-anthraquinone

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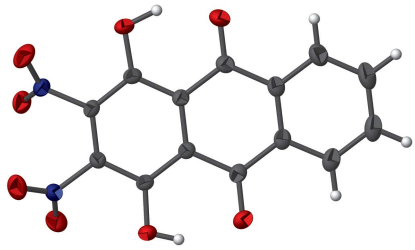
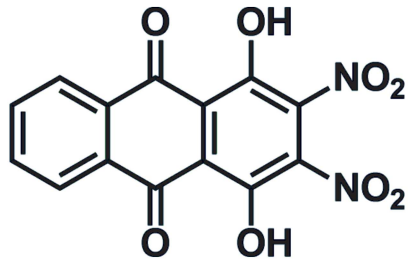
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{14}H_6N_2O_8$, the anthraquinone unit is essentially planar [maximum deviation = 0.0645 (10) Å], and there are two intramolecular O–H···O hydrogen bonds forming *S*(6) motifs. The planes of the two nitro substituents make dihedral angles of 54.77 (8) and 55.60 (3)° with the anthraquinone ring system. In the crystal, molecules are linked by short intermolecular O···O contacts, leading to a three-dimensional network structure.

3D view



Chemical scheme



Structure description

Various kinds of anthraquinone derivatives are manufactured as dyes and pigments. Among them, for example, hydroxyanthraquinones are used as mordant dyes for dyeing cotton. Recently, we have been interested in the effect of substitution of the aromatic ring on optical properties both in solution and in the solid state. We have previously reported several alkoxy-substituted anthraquinones (Kitamura *et al.* 2015*a*,*b*; Ohta *et al.* 2012*a*,*b*). We have also investigated the preparation of anthraquinone derivatives with hydroxyl substituents (Furukawa *et al.* 2014; Ohira *et al.* 2016). In this paper we report the treatment of 1,4-dihydroxy-9,10-anthraquinone with fuming HNO_3 to give a nitro compound. However, we failed to characterize this product by NMR techniques due to its low solubility. Thus to elucidate the structure of the title compound, an X-ray crystallographic study was carried out.

The molecular structure of the title compound is shown in Fig. 1. The anthraquinone ring is essentially planar [maximum deviation = 0.0645 (10) Å for C13], and there are two intramolecular O—H···O hydrogen bonds, each forming an *S*(6) ring motif (Table 1 and Fig. 1). The nitro group planes make dihedral angles of 54.77 (8) (N1/O5/O6) and 55.60 (3)° (N2/O7/O8) with the anthraquinone ring system.

There are not only short intramolecular O···O contacts [O1···O5 = 2.7960 (12), O2···O8 = 2.7833 (12) and O6···O7 = 2.9097 (12) Å] but also short intermolecular

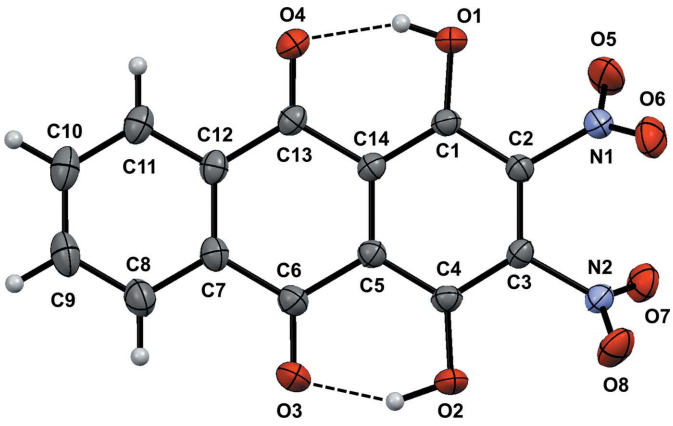


Figure 1
The molecular structure of the title compound, showing the atom-numbering and 50% probability displacement ellipsoids. The intramolecular hydrogen bonds are drawn as dashed lines.

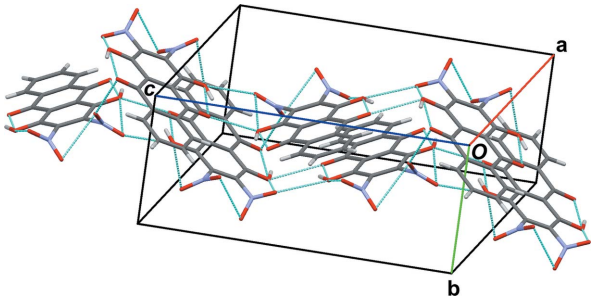


Figure 2
The crystal packing of the title compound. Short O···O contacts are shown as blue lines.

O···O contacts [O1···O3^{i} = 2.8305 (11), O5···O2^{i} = 2.8369 (11), and O6···O4^{ii} = 2.9796 (11) Å; symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$] in the crystal (Fig. 2). The latter O···O contacts form a three-dimensional network structure. No π–π stacking interactions are observed.

Synthesis and crystallization

A mixture of 1,4-dihydroxy-9,10-anthraquinone (502 mg, 2.09 mmol) and fuming HNO_3 (5 ml) was stirred at room temperature for 25 h (Fig. 3). Water (100 ml) was added to the reaction mixture, then the resulting solid was filtered off and dried under vacuum. After chromatography on silica gel with an eluent of dichloromethane-hexane (2:1), recrystallization from ethyl acetate (4 ml) afforded the title compound (35 mg, 5% yield) as red single crystals suitable for X-ray diffraction.

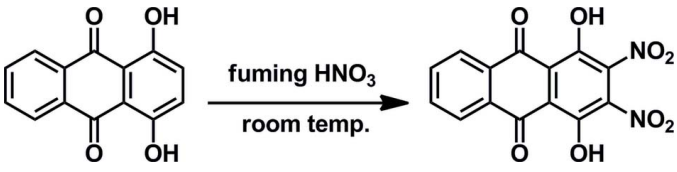


Figure 3
The reaction scheme for the synthesis of the title compound.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4	0.854 (19)	1.788 (18)	2.5691 (11)	151.0 (17)
O2—H2···O3	0.963 (18)	1.686 (19)	2.5480 (11)	146.9 (16)

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_6N_2O_8$
M_r	330.21
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	200
a, b, c (Å)	11.7590 (11), 7.2852 (6), 15.9670 (16)
β (°)	105.420 (3)
V (Å^3)	1318.6 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.14
Crystal size (mm)	0.6 × 0.35 × 0.2
Data collection	
Diffractometer	Rigaku R-Axis Rapid
Absorption correction	Numerical (*NUMABS*; Higashi, 1999)
T_{min}, T_{max}	0.938, 0.972
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12217, 3003, 2637
R_{int}	0.017
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.114, 1.06
No. of reflections	3003
No. of parameters	225
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.38

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SIR2004* (Burla *et al.*, 2005), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *WinGX* (Farrugia, 2012).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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References

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Furukawa, W., Takehara, M., Inoue, Y. & Kitamura, C. (2014). *Acta Cryst.* E**70**, o1130.
Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
Kitamura, C., Li, S., Takehara, M., Inoue, Y., Ono, K. & Kawase, T. (2015*a*). *Acta Cryst.* E**71**, o504–o505.
Kitamura, C., Li, S., Takehara, M., Inoue, Y., Ono, K., Kawase, T. & Fujimoto, K. J. (2015*b*). *Bull. Chem. Soc. Jpn*, **88**, 713–715.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Ohira, N., Takehara, M., Inoue, Y. & Kitamura, C. (2016). *IUCrData* **1**, x160753.
Ohta, A., Hattori, K., Kobayashi, T., Naito, H., Kawase, T. & Kitamura, C. (2012*a*). *Acta Cryst.* E**68**, o2843.
Ohta, A., Hattori, K., Kusumoto, Y., Kawase, T., Kobayashi, T., Naito, H. & Kitamura, C. (2012*b*). *Chem. Lett.* **41**, 674–676.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2016). **1**, x160906 [doi:10.1107/S2414314616009068]

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Crystal data

$C_{14}H_6N_2O_8$
M_r = 330.21
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.7590 (11) Å
b = 7.2852 (6) Å
c = 15.9670 (16) Å
β = 105.420 (3)°
V = 1318.6 (2) Å^3
Z = 4
$F(000)$ = 672
D_x = 1.663 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 10510 reflections
θ = 3.1–27.5°
μ = 0.14 mm^{-1}
T = 200 K
Prism, red
0.6 × 0.35 × 0.2 mm

Data collection

Rigaku R-Axis Rapid diffractometer
Radiation source: fine-focus sealed x-ray tube
Graphite monochromator
Detector resolution: 10 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.938, T_{max} = 0.972
12217 measured reflections
3003 independent reflections
2637 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −15→15
k = −9→9
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.114
S = 1.06
3003 reflections
225 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.1104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-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. All the H atoms except for the OH groups were positioned geometrically and refined using a riding model. The H atoms of the OH groups were located in a difference Fourier map and freely refined [O1—H1 = 0.854 (19) Å; O2—H2 = 0.963 (18) Å].

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.43626 (9)	0.09726 (13)	0.18654 (6)	0.0228 (2)
C2	0.55559 (8)	0.11243 (13)	0.18766 (6)	0.0226 (2)
C3	0.59008 (8)	0.17506 (13)	0.11682 (6)	0.0222 (2)
C4	0.50778 (9)	0.23341 (13)	0.04100 (6)	0.0238 (2)
C5	0.38757 (8)	0.22601 (13)	0.03995 (6)	0.0226 (2)
C6	0.29867 (9)	0.29396 (14)	−0.03798 (6)	0.0269 (2)
C7	0.17279 (9)	0.28732 (14)	−0.03954 (7)	0.0272 (2)
C8	0.08861 (10)	0.34966 (17)	−0.11327 (7)	0.0361 (3)
H8	0.1123	0.3943	−0.162	0.043*
C9	−0.03031 (10)	0.34580 (17)	−0.11475 (8)	0.0406 (3)
H9	−0.0879	0.3876	−0.1648	0.049*
C10	−0.06520 (10)	0.28146 (16)	−0.04380 (8)	0.0372 (3)
H10	−0.1465	0.2814	−0.0452	0.045*
C11	0.01757 (9)	0.21716 (14)	0.02919 (8)	0.0315 (2)
H11	−0.007	0.1719	0.0774	0.038*
C12	0.13735 (9)	0.21906 (13)	0.03167 (7)	0.0256 (2)
C13	0.22486 (9)	0.14497 (13)	0.10835 (6)	0.0241 (2)
C14	0.35224 (8)	0.15643 (12)	0.11118 (6)	0.0218 (2)
N1	0.64537 (7)	0.05360 (13)	0.26604 (6)	0.0291 (2)
N2	0.71694 (7)	0.19212 (11)	0.12268 (5)	0.0252 (2)
O1	0.40976 (7)	0.02703 (11)	0.25620 (5)	0.0314 (2)
O2	0.54693 (7)	0.29723 (12)	−0.02477 (5)	0.0335 (2)
O3	0.33025 (7)	0.35632 (13)	−0.09998 (5)	0.0401 (2)
O4	0.19430 (6)	0.07395 (11)	0.16893 (5)	0.0322 (2)
O5	0.64416 (8)	0.12276 (16)	0.33468 (5)	0.0491 (3)
O6	0.71535 (7)	−0.06315 (12)	0.25598 (6)	0.0403 (2)
O7	0.77730 (7)	0.27811 (11)	0.18428 (5)	0.0354 (2)
O8	0.75222 (7)	0.11905 (13)	0.06575 (6)	0.0408 (2)
H2	0.4783 (17)	0.333 (3)	−0.0697 (12)	0.072 (5)*
H1	0.3344 (17)	0.027 (3)	0.2432 (11)	0.067 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0236 (4)	0.0244 (4)	0.0221 (5)	0.0001 (4)	0.0091 (4)	0.0012 (3)
C2	0.0217 (4)	0.0251 (4)	0.0204 (4)	0.0012 (4)	0.0046 (3)	0.0006 (3)
C3	0.0193 (4)	0.0245 (4)	0.0238 (5)	−0.0006 (4)	0.0076 (3)	−0.0024 (3)
C4	0.0251 (5)	0.0279 (4)	0.0198 (4)	−0.0022 (4)	0.0086 (4)	−0.0011 (3)
C5	0.0220 (5)	0.0252 (4)	0.0206 (4)	−0.0011 (4)	0.0059 (4)	−0.0014 (3)
C6	0.0271 (5)	0.0308 (5)	0.0222 (5)	−0.0010 (4)	0.0053 (4)	0.0003 (4)
C7	0.0237 (5)	0.0280 (5)	0.0272 (5)	−0.0006 (4)	0.0020 (4)	−0.0014 (4)

C8	0.0302 (5)	0.0407 (6)	0.0324 (6)	0.0003 (5)	−0.0003 (4)	0.0032 (5)
C9	0.0280 (5)	0.0421 (6)	0.0429 (6)	0.0021 (5)	−0.0061 (5)	0.0005 (5)
C10	0.0223 (5)	0.0353 (6)	0.0501 (7)	−0.0008 (4)	0.0027 (5)	−0.0047 (5)
C11	0.0232 (5)	0.0294 (5)	0.0414 (6)	−0.0021 (4)	0.0075 (4)	−0.0035 (4)
C12	0.0218 (5)	0.0238 (4)	0.0300 (5)	−0.0014 (4)	0.0046 (4)	−0.0036 (4)
C13	0.0222 (4)	0.0235 (4)	0.0273 (5)	−0.0020 (4)	0.0077 (4)	−0.0028 (4)
C14	0.0217 (4)	0.0220 (4)	0.0224 (5)	−0.0009 (4)	0.0072 (4)	−0.0012 (3)
N1	0.0230 (4)	0.0370 (5)	0.0262 (4)	−0.0006 (4)	0.0048 (3)	0.0075 (3)
N2	0.0214 (4)	0.0270 (4)	0.0281 (4)	−0.0009 (3)	0.0085 (3)	0.0011 (3)
O1	0.0264 (4)	0.0437 (4)	0.0261 (4)	0.0018 (3)	0.0105 (3)	0.0114 (3)
O2	0.0285 (4)	0.0506 (5)	0.0240 (4)	−0.0017 (3)	0.0116 (3)	0.0074 (3)
O3	0.0338 (4)	0.0614 (6)	0.0245 (4)	0.0004 (4)	0.0066 (3)	0.0125 (4)
O4	0.0262 (4)	0.0392 (4)	0.0332 (4)	−0.0044 (3)	0.0114 (3)	0.0049 (3)
O5	0.0399 (5)	0.0836 (7)	0.0214 (4)	0.0060 (5)	0.0040 (3)	−0.0016 (4)
O6	0.0324 (4)	0.0363 (4)	0.0489 (5)	0.0093 (3)	0.0052 (4)	0.0093 (4)
O7	0.0254 (4)	0.0412 (4)	0.0371 (4)	−0.0070 (3)	0.0041 (3)	−0.0054 (3)
O8	0.0313 (4)	0.0539 (5)	0.0433 (5)	0.0014 (4)	0.0205 (4)	−0.0104 (4)

Geometric parameters (Å, º)

C1—O1	1.3343 (12)	C8—H8	0.95
C1—C2	1.4028 (13)	C9—C10	1.3851 (18)
C1—C14	1.4062 (13)	C9—H9	0.95
C2—C3	1.3770 (13)	C10—C11	1.3863 (16)
C2—N1	1.4703 (12)	C10—H10	0.95
C3—C4	1.4000 (13)	C11—C12	1.3984 (14)
C3—N2	1.4749 (12)	C11—H11	0.95
C4—O2	1.3372 (12)	C12—C13	1.4763 (14)
C4—C5	1.4102 (14)	C13—O4	1.2318 (12)
C5—C14	1.4052 (13)	C13—C14	1.4887 (13)
C5—C6	1.4815 (14)	N1—O5	1.2098 (12)
C6—O3	1.2328 (13)	N1—O6	1.2233 (13)
C6—C7	1.4745 (15)	N2—O8	1.2176 (11)
C7—C8	1.3973 (15)	N2—O7	1.2216 (11)
C7—C12	1.4022 (15)	O1—H1	0.854 (19)
C8—C9	1.3925 (17)	O2—H2	0.963 (18)
O1—C1—C2	118.30 (8)	C10—C9—H9	119.8
O1—C1—C14	124.34 (9)	C8—C9—H9	119.8
C2—C1—C14	117.37 (8)	C9—C10—C11	120.50 (11)
C3—C2—C1	121.85 (8)	C9—C10—H10	119.8
C3—C2—N1	119.60 (8)	C11—C10—H10	119.8
C1—C2—N1	118.51 (8)	C10—C11—C12	119.81 (11)
C2—C3—C4	121.61 (8)	C10—C11—H11	120.1
C2—C3—N2	119.32 (8)	C12—C11—H11	120.1
C4—C3—N2	118.96 (8)	C11—C12—C7	119.66 (10)
O2—C4—C3	118.79 (9)	C11—C12—C13	119.65 (10)
O2—C4—C5	123.87 (9)	C7—C12—C13	120.68 (9)

C3—C4—C5	117.32 (9)	O4—C13—C12	121.34 (9)
C14—C5—C4	121.02 (9)	O4—C13—C14	120.06 (9)
C14—C5—C6	120.39 (9)	C12—C13—C14	118.59 (9)
C4—C5—C6	118.58 (9)	C5—C14—C1	120.76 (9)
O3—C6—C7	120.92 (9)	C5—C14—C13	120.48 (9)
O3—C6—C5	120.11 (9)	C1—C14—C13	118.76 (8)
C7—C6—C5	118.96 (9)	O5—N1—O6	125.37 (9)
C8—C7—C12	120.12 (10)	O5—N1—C2	118.10 (9)
C8—C7—C6	119.12 (10)	O6—N1—C2	116.54 (9)
C12—C7—C6	120.76 (9)	O8—N2—O7	125.80 (9)
C9—C8—C7	119.40 (11)	O8—N2—C3	117.09 (8)
C9—C8—H8	120.3	O7—N2—C3	117.10 (8)
C7—C8—H8	120.3	C1—O1—H1	104.7 (12)
C10—C9—C8	120.50 (11)	C4—O2—H2	106.5 (11)

O1—C1—C2—C3	176.79 (9)	C10—C11—C12—C13	−178.04 (9)
C14—C1—C2—C3	−2.76 (14)	C8—C7—C12—C11	−1.28 (16)
O1—C1—C2—N1	−1.16 (14)	C6—C7—C12—C11	178.90 (9)
C14—C1—C2—N1	179.29 (8)	C8—C7—C12—C13	177.20 (9)
C1—C2—C3—C4	2.42 (15)	C6—C7—C12—C13	−2.62 (15)
N1—C2—C3—C4	−179.65 (9)	C11—C12—C13—O4	3.16 (15)
C1—C2—C3—N2	178.55 (8)	C7—C12—C13—O4	−175.32 (9)
N1—C2—C3—N2	−3.52 (14)	C11—C12—C13—C14	−177.22 (9)
C2—C3—C4—O2	178.29 (9)	C7—C12—C13—C14	4.30 (14)
N2—C3—C4—O2	2.15 (14)	C4—C5—C14—C1	1.90 (14)
C2—C3—C4—C5	0.15 (14)	C6—C5—C14—C1	−177.89 (8)
N2—C3—C4—C5	−176.00 (8)	C4—C5—C14—C13	−178.44 (8)
O2—C4—C5—C14	179.70 (9)	C6—C5—C14—C13	1.78 (14)
C3—C4—C5—C14	−2.26 (14)	O1—C1—C14—C5	−178.90 (9)
O2—C4—C5—C6	−0.51 (15)	C2—C1—C14—C5	0.61 (14)
C3—C4—C5—C6	177.53 (8)	O1—C1—C14—C13	1.42 (14)
C14—C5—C6—O3	179.38 (9)	C2—C1—C14—C13	−179.06 (8)
C4—C5—C6—O3	−0.42 (15)	O4—C13—C14—C5	175.75 (8)
C14—C5—C6—C7	−0.01 (14)	C12—C13—C14—C5	−3.87 (14)
C4—C5—C6—C7	−179.80 (8)	O4—C13—C14—C1	−4.57 (14)
O3—C6—C7—C8	1.22 (16)	C12—C13—C14—C1	175.80 (8)
C5—C6—C7—C8	−179.39 (9)	C3—C2—N1—O5	125.97 (11)
O3—C6—C7—C12	−178.95 (10)	C1—C2—N1—O5	−56.03 (13)
C5—C6—C7—C12	0.43 (15)	C3—C2—N1—O6	−54.34 (13)
C12—C7—C8—C9	0.94 (17)	C1—C2—N1—O6	123.66 (10)
C6—C7—C8—C9	−179.24 (10)	C2—C3—N2—O8	128.07 (10)
C7—C8—C9—C10	0.23 (19)	C4—C3—N2—O8	−55.70 (12)
C8—C9—C10—C11	−1.06 (18)	C2—C3—N2—O7	−51.84 (12)
C9—C10—C11—C12	0.71 (17)	C4—C3—N2—O7	124.39 (10)
C10—C11—C12—C7	0.46 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4	0.854 (19)	1.788 (18)	2.5691 (11)	151.0 (17)
O2—H2···O3	0.963 (18)	1.686 (19)	2.5480 (11)	146.9 (16)