

## 2-(Cyclohexylamino)-1,4-naphthoquinone

 James C. Knight,\* Thomas  
 Tatchell and Ian A. Fallis

 Main Building, School of Chemistry, Cardiff  
 University, Park Place, Cardiff CF10 3AT, Wales

Correspondence e-mail: knightjc@cardiff.ac.uk

## Key indicators

 Single-crystal X-ray study  
 T = 150 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
 R factor = 0.049  
 wR factor = 0.136  
 Data-to-parameter ratio = 17.1

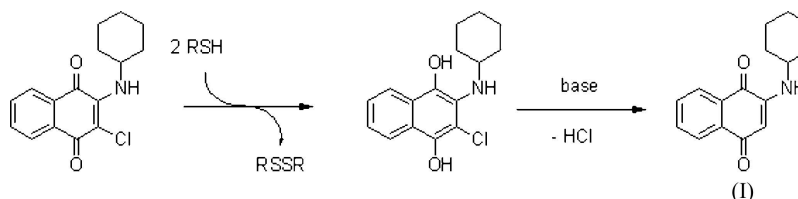
 For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

 The molecules of the title compound,  $\text{C}_{16}\text{H}_{17}\text{NO}_2$ , interact by  
 $\pi$ - $\pi$  stacking between the naphthoquinone ring systems.

 Received 31 January 2007  
 Accepted 1 February 2007

## Comment

In research focusing on the development of redox-active naphthoquinone-based healing agents we have observed unexpected reactivity of amine-substituted chloronaphthoquinones and we report here a by-product from one of our syntheses. In an attempt to prepare 3-(cyclohexylamino)-2-(*p*-tolylsulfanyl)naphthalene-1,4-dione by reaction of 2-chloro-3-(cyclohexylamino)naphthalene-1,4-dione with thiocresol under basic conditions, we isolated the title compound, (I), in modest yield. We postulate that the dechlorinated product was obtained *via* a quinolic intermediate obtained after oxidation of thiocresol to the corresponding disulfide. The reduction of chloronaphthoquinones has been described before (Reynolds *et al.*, 1964), but what is unusual here is that a low-potential aminoquinone is acting as an oxidant. Elimination of HCl from the intermediate 2-chloro-3-(cyclohexylamino)naphthalene-1,4-diol would be readily achieved under the basic conditions employed to afford the title compound.

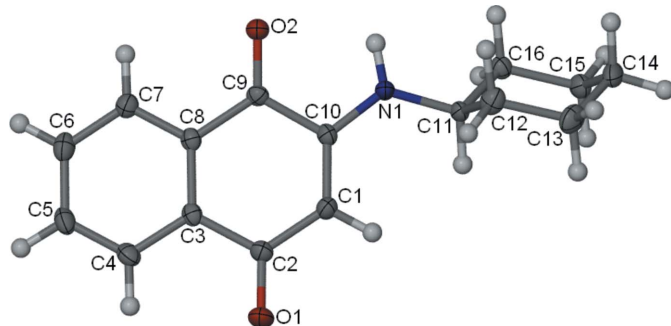


In (I), the naphthoquinone system is substituted with a cyclohexylamino group in position 2 (Fig. 1). The cyclohexyl group is in the chair conformation with an average C—C bond length of 1.496 (2) Å which lies well within the range of classical values. The central C10—N1—C11 angle is 126.73 (12)°, a value which is slightly more obtuse than that found in the related compound 3-chloro-2-pyrrolidino-1,4-naphthoquinone (Lynch *et al.*, 2002). An acute intramolecular N—H...O bond (Table 1) helps to establish the molecular conformation of (I).

The molecular packing diagram (Fig. 2) shows the occurrence of centrosymmetric intermolecular  $\pi$ - $\pi$  stacking of the C1/C2/C3/C8/C9/C10 aromatic ring, with a centroid-centroid distance of 3.8694 (8) Å.

## Experimental

3-Chloro-2-(cyclohexylamino)-1,4-naphthoquinone (0.5 g, 1.73 mmol), potassium carbonate (365 mg, 2.64 mmol) and *p*-thioltoluene (241 mg, 2.54 mmol) were reacted in acetonitrile (40 ml). The solu-

**Figure 1**

View of the molecular structure of (I), showing 50% displacement ellipsoids (H atoms are represented by spheres of arbitrary radius).

tion mixture was refluxed overnight under an inert nitrogen atmosphere. This solution was filtered, dried and purified by flash column chromatography ( $\text{SiO}_2$ ) using  $\text{CHCl}_3$  as the eluant. The title compound was found at  $R_F = 0.36$ . Ruby-red blocks of (I) were obtained by slow evaporation of a  $\text{CHCl}_3$  solution (yield 185 mg, 42%).

**Crystal data**

$\text{C}_{16}\text{H}_{17}\text{NO}_2$   
 $M_r = 255.31$   
 Monoclinic,  $P2_1/c$   
 $a = 10.3204$  (3) Å  
 $b = 6.3380$  (2) Å  
 $c = 18.9664$  (7) Å  
 $\beta = 96.179$  (1)°  
 $V = 1233.40$  (7) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.375$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, red  
 $0.52 \times 0.40 \times 0.22$  mm

**Data collection**

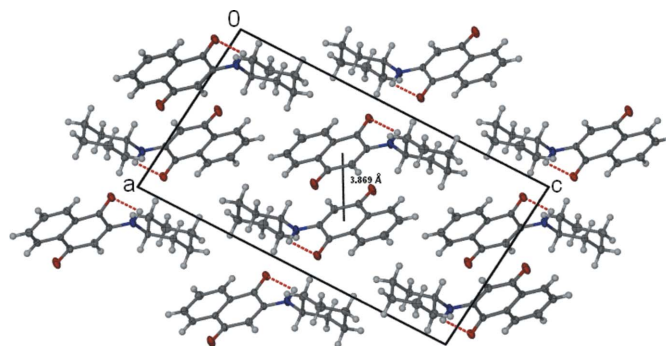
Bruker–Nonius KappaCCD  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.954$ ,  $T_{\max} = 0.980$

11095 measured reflections  
 3094 independent reflections  
 2075 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.068$   
 $\theta_{\text{max}} = 28.7^\circ$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.136$   
 $S = 1.05$   
 3094 reflections  
 172 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.0683P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.28$  e Å<sup>-3</sup>

**Figure 2**

The packing of (I) showing the  $\pi$ - $\pi$  stacking. The dashed line indicates the intramolecular hydrogen bond.

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1-H1}\cdots\text{O2}$	0.88	2.19	2.5917 (16)	107

The H atoms were placed in calculated positions ( $\text{C-H} = 0.95$ – $1.00$  and  $\text{N-H} = 0.88$  Å) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ .

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

**References**

- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.  
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Lynch, D. E. & McClenaghan, I. (2002). *Acta Cryst.* **C58**, o704–o707.  
 Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Reynolds, G. A. & Van Allan, J. A. (1964). *J. Org. Chem.* **29**, 3591–3593.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

## supporting information

*Acta Cryst.* (2007). E63, o1226–o1227 [https://doi.org/10.1107/S1600536807005466]

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Hall symbol:  $-P\ 2_1/c$

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$c = 18.9664$  (7) Å

$\beta = 96.179$  (1)°

$V = 1233.40$  (7) Å<sup>3</sup>

$Z = 4$

$F(000) = 544$

$D_x = 1.375$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6520 reflections

$\theta = 2.9$ – $27.5$ °

$\mu = 0.09$  mm<sup>-1</sup>

$T = 150$  K

Block, red

$0.52 \times 0.40 \times 0.22$  mm

*Data collection*

Bruker–Nonius KappaCCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SORTAV; Blessing, 1995)

$T_{\min} = 0.954$ ,  $T_{\max} = 0.980$

11095 measured reflections

3094 independent reflections

2075 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 28.7$ °,  $\theta_{\min} = 3.1$ °

$h = -13 \rightarrow 12$

$k = -8 \rightarrow 8$

$l = -23 \rightarrow 24$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.136$

$S = 1.05$

2944 reflections

172 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

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.0683P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.21$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.28$  e Å<sup>-3</sup>

## Special details

**Experimental.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.10–1.35 (*m*, 5H, Cy ring), 1.55 (*m*, 1H, Cy ring), 1.70 (*m*, 2H, Cy ring), 1.95 [*dd*, ( $J_{\text{HH}} = 1.70 + 3.40$  Hz), 2H, Cy ring], 3.20 [quintet, ( $J_{\text{HH}} = 3.20$  Hz), 1H, Cy ring], 5.65 (*s*, 1H, Ar), 5.75 [*d*, ( $J_{\text{HH}} = 5.77$  Hz), 1H, NH], 7.45 [*t*, ( $J_{\text{HH}} = 7.50$  Hz), 1H, Ar], 7.60 [*t*, ( $J_{\text{HH}} = 7.60$  Hz), 1H, Ar], 7.90 [*d*, ( $J_{\text{HH}} = 7.90$  Hz), 1H, Ar] and 7.95 [*d*, ( $J_{\text{HH}} = 8.00$  Hz), 1H, Ar].  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  24.56, 25.46, 31.64, 31.86, 51.12, 100.73, 126.07, 126.21, 130.56, 131.56, 133.66, 134.67, 146.67, 182.09, 182.82. IR (KBr)  $\text{cm}^{-1}$ : 3342, 3041, 2926, 2856, 1671, 1619, 1597, 1571, 1522, 1441, 1350, 1304, 1267, 1250, 1120, 1098, 1002, 952, 890, 862, 778, 726, 669, 635 and 565.

**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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.62825 (14)	0.2358 (2)	1.01432 (8)	0.0225 (3)
H1A	0.6059	0.1130	0.9870	0.027*
C2	0.54304 (13)	0.3009 (2)	1.06508 (8)	0.0218 (3)
C3	0.57619 (13)	0.4910 (2)	1.10630 (7)	0.0188 (3)
C4	0.49385 (14)	0.5627 (2)	1.15364 (8)	0.0243 (4)
H4	0.4178	0.4850	1.1610	0.029*
C5	0.52166 (15)	0.7429 (2)	1.18922 (8)	0.0272 (4)
H5	0.4660	0.7931	1.2223	0.033*
C6	0.63093 (15)	0.8536 (3)	1.17734 (8)	0.0279 (4)
H6	0.6487	0.9837	1.2014	0.033*
C7	0.71608 (14)	0.7814 (2)	1.13138 (8)	0.0233 (3)
H7	0.7925	0.8591	1.1246	0.028*
C8	0.68908 (13)	0.5990 (2)	1.09624 (7)	0.0189 (3)
C9	0.78112 (13)	0.5186 (2)	1.04880 (8)	0.0189 (3)
C10	0.73880 (13)	0.3397 (2)	1.00320 (7)	0.0192 (3)
C11	0.80372 (14)	0.1429 (2)	0.89982 (8)	0.0205 (3)
H11	0.7102	0.0986	0.8930	0.025*
C12	0.88468 (16)	−0.0420 (2)	0.92266 (9)	0.0280 (4)
H12A	0.8546	−0.1035	0.9660	0.034*
H12B	0.9767	0.0019	0.9338	0.034*
C13	0.87457 (16)	−0.2031 (2)	0.86481 (9)	0.0318 (4)
H13A	0.7837	−0.2553	0.8573	0.038*
H13B	0.9314	−0.3242	0.8799	0.038*
C14	0.91285 (15)	−0.1184 (3)	0.79535 (9)	0.0290 (4)
H14A	1.0056	−0.0755	0.8014	0.035*
H14B	0.9021	−0.2302	0.7587	0.035*
C15	0.83056 (15)	0.0644 (2)	0.77231 (8)	0.0264 (4)
H15A	0.7386	0.0192	0.7621	0.032*
H15B	0.8592	0.1251	0.7284	0.032*
C16	0.84189 (14)	0.2266 (2)	0.82992 (8)	0.0219 (3)

H16A	0.7854	0.3481	0.8148	0.026*
H16B	0.9330	0.2779	0.8371	0.026*
N1	0.81963 (11)	0.30046 (19)	0.95388 (7)	0.0238 (3)
H1	0.8897	0.3801	0.9550	0.029*
O1	0.44263 (10)	0.20911 (18)	1.07492 (6)	0.0347 (3)
O2	0.88904 (9)	0.59166 (16)	1.04622 (6)	0.0265 (3)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0255 (8)	0.0203 (7)	0.0222 (8)	-0.0047 (6)	0.0055 (6)	-0.0034 (6)
C2	0.0224 (8)	0.0225 (7)	0.0214 (8)	-0.0028 (6)	0.0058 (6)	0.0004 (6)
C3	0.0203 (7)	0.0209 (7)	0.0151 (8)	0.0024 (6)	0.0014 (6)	0.0004 (6)
C4	0.0195 (7)	0.0299 (8)	0.0240 (9)	0.0020 (6)	0.0046 (6)	-0.0011 (7)
C5	0.0254 (8)	0.0322 (8)	0.0244 (9)	0.0057 (7)	0.0048 (6)	-0.0066 (7)
C6	0.0312 (8)	0.0256 (8)	0.0262 (9)	0.0045 (7)	0.0005 (7)	-0.0063 (7)
C7	0.0256 (8)	0.0216 (7)	0.0226 (8)	-0.0006 (6)	0.0023 (6)	-0.0013 (6)
C8	0.0211 (7)	0.0204 (7)	0.0150 (8)	0.0017 (6)	0.0015 (6)	0.0008 (6)
C9	0.0208 (7)	0.0196 (7)	0.0167 (8)	-0.0028 (6)	0.0036 (6)	0.0026 (6)
C10	0.0205 (7)	0.0211 (7)	0.0166 (8)	0.0001 (6)	0.0042 (6)	-0.0008 (6)
C11	0.0220 (7)	0.0221 (7)	0.0187 (8)	-0.0049 (6)	0.0075 (6)	-0.0048 (6)
C12	0.0358 (9)	0.0242 (8)	0.0235 (9)	-0.0030 (7)	0.0015 (7)	0.0015 (6)
C13	0.0363 (9)	0.0198 (8)	0.0387 (11)	0.0008 (7)	0.0015 (8)	-0.0048 (7)
C14	0.0238 (8)	0.0290 (8)	0.0347 (10)	0.0001 (7)	0.0056 (7)	-0.0136 (7)
C15	0.0281 (8)	0.0308 (8)	0.0212 (9)	-0.0047 (7)	0.0067 (6)	-0.0051 (7)
C16	0.0246 (7)	0.0207 (7)	0.0212 (8)	-0.0008 (6)	0.0055 (6)	-0.0005 (6)
N1	0.0245 (7)	0.0239 (6)	0.0249 (7)	-0.0095 (5)	0.0112 (5)	-0.0086 (5)
O1	0.0315 (6)	0.0334 (6)	0.0423 (8)	-0.0142 (5)	0.0190 (5)	-0.0103 (5)
O2	0.0237 (6)	0.0269 (6)	0.0301 (7)	-0.0069 (5)	0.0092 (4)	-0.0069 (5)

*Geometric parameters (Å, °)*

C1—C10	1.3535 (19)	C11—N1	1.4281 (18)
C1—C2	1.433 (2)	C11—C12	1.477 (2)
C1—H1A	0.9500	C11—C16	1.519 (2)
C2—O1	1.2201 (16)	C11—H11	1.0000
C2—C3	1.457 (2)	C12—C13	1.494 (2)
C3—C4	1.378 (2)	C12—H12A	0.9900
C3—C8	1.3820 (19)	C12—H12B	0.9900
C4—C5	1.342 (2)	C13—C14	1.514 (2)
C4—H4	0.9500	C13—H13A	0.9900
C5—C6	1.367 (2)	C13—H13B	0.9900
C5—H5	0.9500	C14—C15	1.475 (2)
C6—C7	1.381 (2)	C14—H14A	0.9900
C6—H6	0.9500	C14—H14B	0.9900
C7—C8	1.349 (2)	C15—C16	1.495 (2)
C7—H7	0.9500	C15—H15A	0.9900
C8—C9	1.468 (2)	C15—H15B	0.9900

C9—O2	1.2120 (16)	C16—H16A	0.9900
C9—C10	1.464 (2)	C16—H16B	0.9900
C10—N1	1.3419 (18)	N1—H1	0.8800
C10—C1—C2	123.59 (13)	C16—C11—H11	108.8
C10—C1—H1A	118.2	C11—C12—C13	109.52 (13)
C2—C1—H1A	118.2	C11—C12—H12A	109.8
O1—C2—C1	123.94 (13)	C13—C12—H12A	109.8
O1—C2—C3	117.81 (13)	C11—C12—H12B	109.8
C1—C2—C3	118.23 (12)	C13—C12—H12B	109.8
C4—C3—C8	120.97 (13)	H12A—C12—H12B	108.2
C4—C3—C2	119.79 (13)	C12—C13—C14	113.14 (13)
C8—C3—C2	119.23 (13)	C12—C13—H13A	109.0
C5—C4—C3	119.67 (14)	C14—C13—H13A	108.9
C5—C4—H4	120.2	C12—C13—H13B	108.9
C3—C4—H4	120.2	C14—C13—H13B	108.9
C4—C5—C6	119.30 (15)	H13A—C13—H13B	107.8
C4—C5—H5	120.4	C15—C14—C13	109.90 (13)
C6—C5—H5	120.4	C15—C14—H14A	109.7
C5—C6—C7	121.76 (15)	C13—C14—H14A	109.7
C5—C6—H6	119.1	C15—C14—H14B	109.7
C7—C6—H6	119.1	C13—C14—H14B	109.7
C8—C7—C6	118.97 (14)	H14A—C14—H14B	108.2
C8—C7—H7	120.5	C14—C15—C16	109.05 (13)
C6—C7—H7	120.5	C14—C15—H15A	109.9
C7—C8—C3	119.27 (14)	C16—C15—H15A	109.9
C7—C8—C9	119.16 (13)	C14—C15—H15B	109.9
C3—C8—C9	121.57 (13)	C16—C15—H15B	109.9
O2—C9—C10	119.27 (13)	H15A—C15—H15B	108.3
O2—C9—C8	123.40 (13)	C15—C16—C11	112.98 (12)
C10—C9—C8	117.33 (12)	C15—C16—H16A	109.0
N1—C10—C1	128.03 (14)	C11—C16—H16A	109.0
N1—C10—C9	112.78 (12)	C15—C16—H16B	109.0
C1—C10—C9	119.19 (13)	C11—C16—H16B	109.0
N1—C11—C12	109.08 (12)	H16A—C16—H16B	107.8
N1—C11—C16	111.20 (12)	C10—N1—C11	126.73 (12)
C12—C11—C16	109.97 (12)	C10—N1—H1	116.6
N1—C11—H11	108.8	C11—N1—H1	116.6
C12—C11—H11	108.8		
C10—C1—C2—O1	179.28 (14)	C3—C8—C9—C10	10.3 (2)
C10—C1—C2—C3	0.9 (2)	C2—C1—C10—N1	-174.88 (14)
O1—C2—C3—C4	-1.0 (2)	C2—C1—C10—C9	5.2 (2)
C1—C2—C3—C4	177.50 (14)	O2—C9—C10—N1	-11.0 (2)
O1—C2—C3—C8	-179.79 (13)	C8—C9—C10—N1	169.59 (12)
C1—C2—C3—C8	-1.3 (2)	O2—C9—C10—C1	168.95 (13)
C8—C3—C4—C5	1.7 (2)	C8—C9—C10—C1	-10.5 (2)
C2—C3—C4—C5	-177.05 (13)	N1—C11—C12—C13	-176.86 (12)

C3—C4—C5—C6	0.6 (2)	C16—C11—C12—C13	-54.66 (16)
C4—C5—C6—C7	-2.2 (2)	C11—C12—C13—C14	56.74 (18)
C5—C6—C7—C8	1.4 (2)	C12—C13—C14—C15	-57.82 (17)
C6—C7—C8—C3	1.0 (2)	C13—C14—C15—C16	56.06 (16)
C6—C7—C8—C9	-178.34 (13)	C14—C15—C16—C11	-57.67 (17)
C4—C3—C8—C7	-2.5 (2)	N1—C11—C16—C15	178.25 (12)
C2—C3—C8—C7	176.24 (13)	C12—C11—C16—C15	57.32 (16)
C4—C3—C8—C9	176.77 (13)	C1—C10—N1—C11	2.6 (2)
C2—C3—C8—C9	-4.4 (2)	C9—C10—N1—C11	-177.49 (13)
C7—C8—C9—O2	10.2 (2)	C12—C11—N1—C10	-99.26 (17)
C3—C8—C9—O2	-169.11 (13)	C16—C11—N1—C10	139.29 (15)
C7—C8—C9—C10	-170.40 (12)		

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...O2	0.88	2.19	2.5917 (16)	107