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3-*tert*-Butyl-5,6,8-trinitronaphtho-[1,8a,8-*cd*][1,2]dithiole

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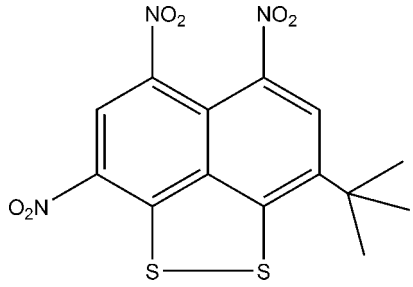
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.039; wR factor = 0.109; data-to-parameter ratio = 12.2.

Nitration of 2,7-di-*tert*-butylnaphthalene 1,8-disulfide with fuming nitric acid in 1:3 molar ratio gives the title compound, $C_{14}H_{11}N_3O_6S_2$. A tape motif is formed by weak head-to-tail interactions (3.131 Å) between S and NO_2 O atoms of a symmetry-related molecule.

Related literature

For related literature, see: Barltrop *et al.* (1954); Claeson *et al.* (1960); Shigeru *et al.* (1982); Smiles & Price (1928); Stepanov *et al.* (1977); Tesmer & Vahrenkamp (2001); Zweig & Hoffman (1965); Ashe *et al.* (1994).



Experimental

Crystal data

$C_{14}H_{11}N_3O_6S_2$
M_r = 381.38
Monoclinic, $C2/c$
a = 19.477 (3) Å
b = 20.754 (4) Å
c = 8.1658 (14) Å
β = 105.909 (3)°
V = 3174.4 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 294 (2) K
0.26 × 0.24 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.876, T_{max} = 0.964
8118 measured reflections
2803 independent reflections
1856 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
S = 1.03
2803 reflections
229 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2089).

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supporting information

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3-*tert*-Butyl-5,6,8-trinitronaphtho[1,8a,8-*cd*][1,2]dithiole

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S1. Comment

Naphthalene-1,8-disulfide is a bright-red crystalline compound (Smiles *et al.*, 1928; Zweig *et al.*, 1965) due to the introduction of S—S group into the naphthalene ring leading to a considerable bathochromic shift of the absorption bands characteristic of disulfides in the electronic spectrum (Barltrop *et al.*, 1954; Claeson *et al.*, 1960). There are only a few reports concerning the nitration of naphthalene-1,8-disulfide (Stepanov *et al.*, 1977; Shigeru *et al.*, 1982). In an attempt to nitrate 2,7-di-*tert*-butyl-naphthalene-1,8-disulfide(BNT) (Tesmer *et al.*, 2001) with fuming nitric acid in an attempted synthesis of 3,8-di-*tert*-butyl-5,6-dinitro-naphtho[1,8-cd][1,2]dithiole, the title compound was obtained unexpectedly. Herein, we present its preparation and single-crystal structure (Fig. 1).

The crystal was obtained by recrystallization from ethyl acetate. The length of the S—S bond is 2.0627 (10) Å, which is consistent with that of analogues reported by Arthur *et al.* (1994). The three rings form a slightly non-perfect plane owing to the asymmetric substitution of nitro and *tert*-butyl groups. The dihedral angles between the rings are: A/B, 3.9 (3) °; A/C, 2.3 (3) °; B/C, 3.0 (3) °. A perspective view of the packing is shown in Figure 2. A slightly wavy tape motif is formed by the head-to-tail weak interactions between S1 and O2 of a molecule related via 0.5+x,0.5-y,0.5+z.

S2. Experimental

To a solution of BNT (3.02 g, 10 mmol) in acetic acid (50 mL), fuming nitric acid (30 mmol) was added. The reaction mixture was stirred for 0.5 h and cooled to room temperature. The precipitate was collected by filtration and recrystallized from ethyl acetate to give the title compound as red crystals, yield 80%.

S3. Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained C-H distances of 0.96 Å (RCH_3) and 0.93 Å ($C_{Ar}H$) with $U_{iso}(H)$ values set to either $1.5U_{eq}$ (RCH_3) or $1.2U_{eq}$ of the attached C atom.

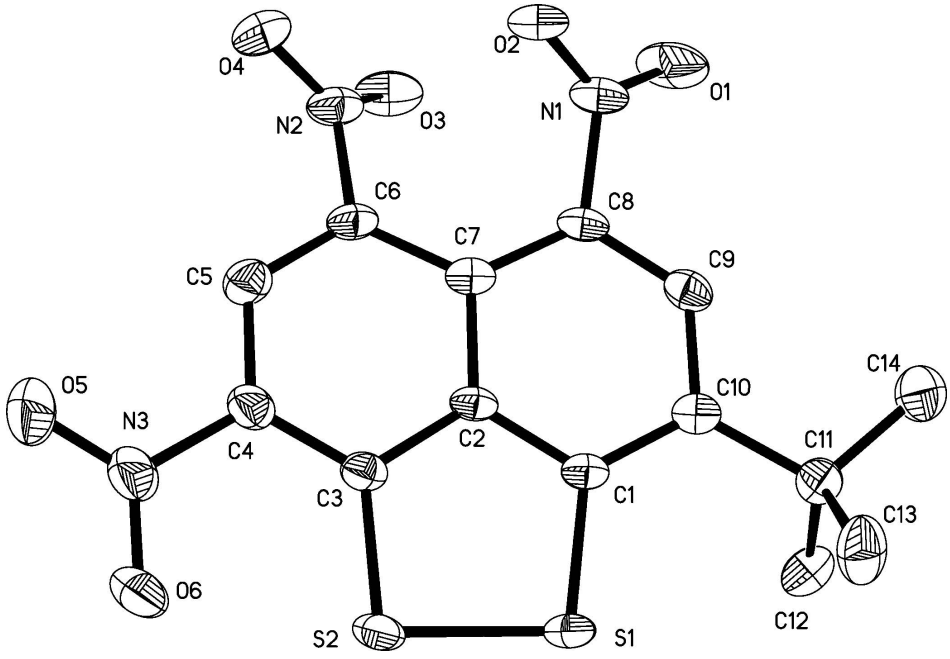

Figure 1

The structure of the title compound showing 30% probability ellipsoids.

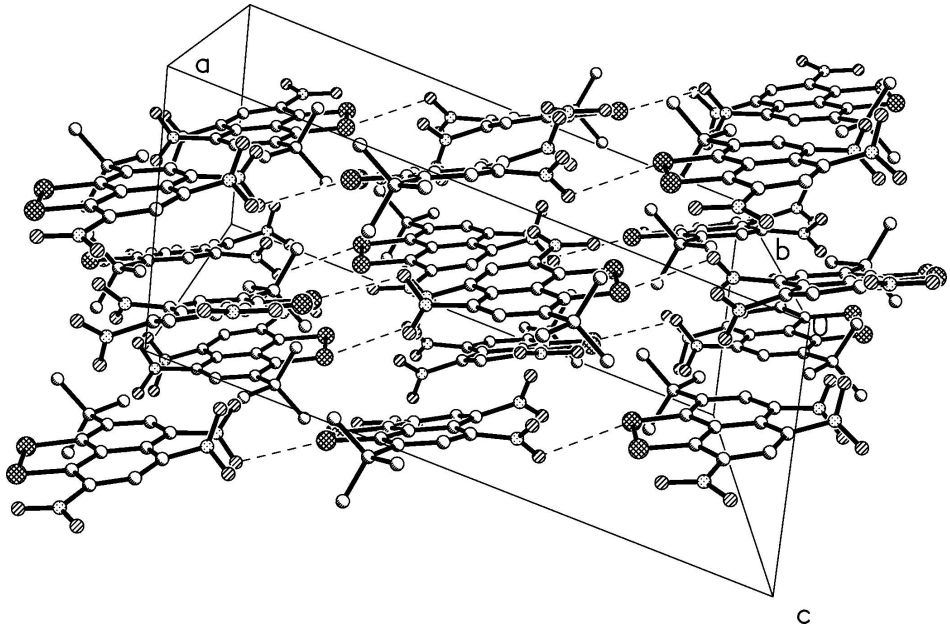

Figure 2

Packing structure of the title compound.

3-*tert*-Butyl-5,6,8-trinitronaphtho[1,8a,8-cd][1,2]dithiole

Crystal data

$C_{14}H_{11}N_3O_6S_2$
M_r = 381.38
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 19.477 (3) Å
b = 20.754 (4) Å

c = 8.1658 (14) Å
β = 105.909 (3)°
V = 3174.4 (10) Å^3
Z = 8
F(000) = 1568
D_x = 1.596 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 2099 reflections
θ = 2.7–25.8°
μ = 0.37 mm^{-1}
T = 294 K
Block, red
0.26 × 0.24 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.876, T_{max} = 0.964

8118 measured reflections
2803 independent reflections
1856 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 25.0°, θ_{min} = 1.5°
h = −19→23
k = −24→22
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
S = 1.03
2803 reflections
229 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
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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}
S1	0.22607 (3)	0.26843 (3)	0.74057 (9)	0.0476 (2)
S2	0.21867 (3)	0.17028 (3)	0.77160 (9)	0.0490 (2)
O1	−0.10572 (11)	0.34597 (11)	0.3300 (3)	0.0838 (7)
O2	−0.12517 (9)	0.26776 (9)	0.4864 (2)	0.0525 (5)
O3	−0.10009 (10)	0.18790 (11)	0.2446 (2)	0.0661 (6)
O4	−0.12944 (10)	0.12220 (10)	0.4212 (3)	0.0665 (6)
O5	0.08457 (13)	0.00261 (10)	0.7190 (3)	0.1019 (9)
O6	0.18753 (12)	0.05183 (10)	0.7857 (3)	0.0809 (7)
N1	−0.08510 (11)	0.30111 (12)	0.4295 (3)	0.0494 (6)
N2	−0.08763 (12)	0.15858 (12)	0.3800 (3)	0.0513 (6)

N3	0.12234 (14)	0.05040 (12)	0.7216 (3)	0.0693 (8)
C1	0.13641 (12)	0.28171 (11)	0.6422 (3)	0.0349 (6)
C2	0.09381 (12)	0.22503 (11)	0.6122 (3)	0.0332 (6)
C3	0.12897 (13)	0.16621 (11)	0.6715 (3)	0.0378 (6)
C4	0.08893 (14)	0.10991 (12)	0.6509 (3)	0.0469 (7)
C5	0.01708 (14)	0.10991 (13)	0.5605 (3)	0.0487 (7)
H5	−0.0084	0.0714	0.5431	0.058*
C6	−0.01603 (12)	0.16565 (12)	0.4978 (3)	0.0402 (6)
C7	0.01938 (12)	0.22687 (11)	0.5293 (3)	0.0349 (6)
C8	−0.00856 (12)	0.28886 (12)	0.4886 (3)	0.0378 (6)
C9	0.03362 (13)	0.34351 (12)	0.5203 (3)	0.0418 (6)
H9	0.0116	0.3831	0.4882	0.050*
C10	0.10644 (13)	0.34324 (12)	0.5964 (3)	0.0388 (6)
C11	0.14946 (14)	0.40632 (12)	0.6359 (3)	0.0445 (7)
C12	0.20882 (15)	0.40735 (14)	0.5453 (4)	0.0603 (8)
H12A	0.2363	0.4462	0.5746	0.090*
H12B	0.1880	0.4058	0.4244	0.090*
H12C	0.2394	0.3707	0.5803	0.090*
C13	0.18252 (17)	0.41303 (14)	0.8288 (3)	0.0655 (9)
H13A	0.2145	0.3777	0.8691	0.098*
H13B	0.1453	0.4127	0.8853	0.098*
H13C	0.2084	0.4529	0.8523	0.098*
C14	0.10141 (16)	0.46540 (13)	0.5768 (4)	0.0678 (9)
H14A	0.1295	0.5040	0.6038	0.102*
H14B	0.0643	0.4661	0.6338	0.102*
H14C	0.0804	0.4631	0.4560	0.102*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0239 (3)	0.0561 (5)	0.0571 (5)	0.0011 (3)	0.0013 (3)	−0.0029 (3)
S2	0.0287 (4)	0.0533 (4)	0.0576 (5)	0.0105 (3)	−0.0008 (3)	−0.0063 (3)
O1	0.0463 (13)	0.1089 (19)	0.0858 (15)	0.0205 (12)	0.0004 (11)	0.0525 (15)
O2	0.0270 (10)	0.0763 (14)	0.0557 (12)	0.0019 (9)	0.0140 (9)	0.0021 (10)
O3	0.0457 (12)	0.1145 (17)	0.0317 (10)	0.0013 (11)	0.0000 (9)	−0.0013 (11)
O4	0.0399 (12)	0.0745 (15)	0.0789 (14)	−0.0160 (11)	0.0057 (11)	−0.0059 (11)
O5	0.0882 (18)	0.0412 (13)	0.155 (3)	−0.0054 (12)	−0.0030 (17)	−0.0026 (14)
O6	0.0535 (14)	0.0582 (13)	0.1134 (19)	0.0205 (11)	−0.0069 (13)	−0.0051 (12)
N1	0.0285 (12)	0.0749 (17)	0.0422 (13)	0.0080 (11)	0.0051 (10)	0.0072 (12)
N2	0.0314 (13)	0.0721 (17)	0.0468 (14)	−0.0024 (12)	0.0050 (11)	−0.0145 (12)
N3	0.0602 (18)	0.0427 (15)	0.093 (2)	0.0105 (14)	0.0005 (16)	−0.0149 (14)
C1	0.0269 (13)	0.0478 (15)	0.0289 (13)	0.0022 (11)	0.0060 (10)	−0.0008 (11)
C2	0.0247 (13)	0.0481 (15)	0.0252 (12)	0.0044 (11)	0.0042 (10)	−0.0027 (10)
C3	0.0315 (13)	0.0438 (15)	0.0352 (13)	0.0043 (11)	0.0041 (11)	−0.0106 (11)
C4	0.0418 (16)	0.0425 (16)	0.0504 (16)	0.0070 (13)	0.0027 (13)	−0.0099 (13)
C5	0.0423 (16)	0.0485 (17)	0.0507 (17)	−0.0061 (13)	0.0053 (13)	−0.0127 (13)
C6	0.0269 (13)	0.0571 (17)	0.0336 (14)	−0.0022 (12)	0.0032 (11)	−0.0081 (12)
C7	0.0292 (13)	0.0541 (16)	0.0219 (12)	0.0015 (11)	0.0079 (10)	−0.0016 (11)

C8	0.0248 (13)	0.0569 (17)	0.0303 (13)	0.0072 (12)	0.0051 (10)	0.0064 (12)
C9	0.0395 (15)	0.0478 (17)	0.0383 (14)	0.0105 (12)	0.0107 (12)	0.0116 (12)
C10	0.0350 (14)	0.0505 (17)	0.0313 (13)	0.0015 (12)	0.0097 (11)	0.0039 (11)
C11	0.0460 (17)	0.0451 (16)	0.0410 (15)	−0.0004 (12)	0.0097 (13)	0.0026 (12)
C12	0.0556 (19)	0.066 (2)	0.0591 (19)	−0.0194 (15)	0.0155 (15)	−0.0042 (14)
C13	0.094 (3)	0.0513 (18)	0.0480 (18)	−0.0007 (16)	0.0145 (17)	−0.0109 (14)
C14	0.068 (2)	0.0496 (18)	0.082 (2)	0.0001 (15)	0.0139 (17)	0.0122 (15)

Geometric parameters (Å, º)

S1—C1	1.733 (2)	C5—H5	0.9300
S1—S2	2.0627 (10)	C6—C7	1.435 (3)
S2—C3	1.716 (2)	C7—C8	1.401 (3)
O1—N1	1.229 (3)	C8—C9	1.383 (3)
O2—N1	1.226 (3)	C9—C10	1.384 (3)
O3—N2	1.227 (3)	C9—H9	0.9300
O4—N2	1.223 (3)	C10—C11	1.540 (3)
O5—N3	1.231 (3)	C11—C12	1.534 (4)
O6—N3	1.234 (3)	C11—C13	1.536 (3)
N1—C8	1.458 (3)	C11—C14	1.538 (4)
N2—C6	1.468 (3)	C12—H12A	0.9600
N3—C4	1.441 (3)	C12—H12B	0.9600
C1—C10	1.411 (3)	C12—H12C	0.9600
C1—C2	1.421 (3)	C13—H13A	0.9600
C2—C3	1.419 (3)	C13—H13B	0.9600
C2—C7	1.422 (3)	C13—H13C	0.9600
C3—C4	1.389 (3)	C14—H14A	0.9600
C4—C5	1.392 (3)	C14—H14B	0.9600
C5—C6	1.355 (3)	C14—H14C	0.9600
C1—S1—S2	96.81 (8)	C9—C8—N1	114.8 (2)
C3—S2—S1	94.96 (9)	C7—C8—N1	122.3 (2)
O2—N1—O1	123.5 (2)	C8—C9—C10	124.3 (2)
O2—N1—C8	118.4 (2)	C8—C9—H9	117.8
O1—N1—C8	118.1 (2)	C10—C9—H9	117.8
O4—N2—O3	124.9 (2)	C9—C10—C1	114.9 (2)
O4—N2—C6	117.8 (2)	C9—C10—C11	121.5 (2)
O3—N2—C6	117.3 (2)	C1—C10—C11	123.5 (2)
O5—N3—O6	124.5 (3)	C12—C11—C13	109.5 (2)
O5—N3—C4	118.8 (3)	C12—C11—C14	108.2 (2)
O6—N3—C4	116.6 (3)	C13—C11—C14	107.3 (2)
C10—C1—C2	121.6 (2)	C12—C11—C10	110.5 (2)
C10—C1—S1	123.91 (18)	C13—C11—C10	110.1 (2)
C2—C1—S1	114.50 (17)	C14—C11—C10	111.3 (2)
C3—C2—C1	116.7 (2)	C11—C12—H12A	109.5
C3—C2—C7	121.3 (2)	C11—C12—H12B	109.5
C1—C2—C7	122.0 (2)	H12A—C12—H12B	109.5
C4—C3—C2	118.7 (2)	C11—C12—H12C	109.5

C4—C3—S2	124.31 (19)	H12A—C12—H12C	109.5
C2—C3—S2	116.97 (18)	H12B—C12—H12C	109.5
C3—C4—C5	120.9 (2)	C11—C13—H13A	109.5
C3—C4—N3	119.7 (2)	C11—C13—H13B	109.5
C5—C4—N3	119.4 (2)	H13A—C13—H13B	109.5
C6—C5—C4	120.4 (2)	C11—C13—H13C	109.5
C6—C5—H5	119.8	H13A—C13—H13C	109.5
C4—C5—H5	119.8	H13B—C13—H13C	109.5
C5—C6—C7	122.2 (2)	C11—C14—H14A	109.5
C5—C6—N2	115.5 (2)	C11—C14—H14B	109.5
C7—C6—N2	122.0 (2)	H14A—C14—H14B	109.5
C8—C7—C2	114.6 (2)	C11—C14—H14C	109.5
C8—C7—C6	129.4 (2)	H14A—C14—H14C	109.5
C2—C7—C6	116.0 (2)	H14B—C14—H14C	109.5
C9—C8—C7	122.5 (2)		

C1—S1—S2—C3	2.27 (11)	C1—C2—C7—C8	−3.2 (3)
S2—S1—C1—C10	176.23 (18)	C3—C2—C7—C6	−4.8 (3)
S2—S1—C1—C2	−2.85 (17)	C1—C2—C7—C6	176.2 (2)
C10—C1—C2—C3	−176.8 (2)	C5—C6—C7—C8	−173.2 (2)
S1—C1—C2—C3	2.3 (3)	N2—C6—C7—C8	13.8 (4)
C10—C1—C2—C7	2.3 (3)	C5—C6—C7—C2	7.6 (3)
S1—C1—C2—C7	−178.63 (16)	N2—C6—C7—C2	−165.4 (2)
C1—C2—C3—C4	177.5 (2)	C2—C7—C8—C9	2.6 (3)
C7—C2—C3—C4	−1.5 (3)	C6—C7—C8—C9	−176.7 (2)
C1—C2—C3—S2	−0.2 (3)	C2—C7—C8—N1	−169.64 (19)
C7—C2—C3—S2	−179.27 (17)	C6—C7—C8—N1	11.1 (4)
S1—S2—C3—C4	−179.1 (2)	O2—N1—C8—C9	−138.7 (2)
S1—S2—C3—C2	−1.51 (19)	O1—N1—C8—C9	38.6 (3)
C2—C3—C4—C5	5.7 (4)	O2—N1—C8—C7	34.1 (3)
S2—C3—C4—C5	−176.7 (2)	O1—N1—C8—C7	−148.6 (3)
C2—C3—C4—N3	−175.3 (2)	C7—C8—C9—C10	−1.0 (4)
S2—C3—C4—N3	2.3 (4)	N1—C8—C9—C10	171.8 (2)
O5—N3—C4—C3	171.9 (3)	C8—C9—C10—C1	−0.2 (4)
O6—N3—C4—C3	−6.0 (4)	C8—C9—C10—C11	−176.9 (2)
O5—N3—C4—C5	−9.0 (4)	C2—C1—C10—C9	−0.5 (3)
O6—N3—C4—C5	173.0 (3)	S1—C1—C10—C9	−179.49 (17)
C3—C4—C5—C6	−3.2 (4)	C2—C1—C10—C11	176.2 (2)
N3—C4—C5—C6	177.8 (2)	S1—C1—C10—C11	−2.8 (3)
C4—C5—C6—C7	−3.7 (4)	C9—C10—C11—C12	−121.4 (3)
C4—C5—C6—N2	169.7 (2)	C1—C10—C11—C12	62.2 (3)
O4—N2—C6—C5	46.7 (3)	C9—C10—C11—C13	117.6 (3)
O3—N2—C6—C5	−130.7 (3)	C1—C10—C11—C13	−58.8 (3)
O4—N2—C6—C7	−139.9 (2)	C9—C10—C11—C14	−1.2 (3)
O3—N2—C6—C7	42.7 (3)	C1—C10—C11—C14	−177.6 (2)
C3—C2—C7—C8	175.8 (2)		