Benzo[a][1,4]benzothiazino[3,2-c]phenothiazine

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The title compound, $C_{22}H_{12}N_2S_2$, crystallizes in space group $P2_1/c$ with four molecules in the asymmetric unit. The heterocyclic molecule is quasi-planar with a dihedral angle between the phenyl rings on the periphery of the molecule of 1.73 (19)°. Short H···S (2.92 Å) and C—H···π [2.836 (3) Å] contacts are observed in the crystal with shorted π–π stacking distances of 3.438 (3) Å along the b axis. Surprisingly, and unlike a closely related material, this molecule readily forms large crystals by sublimation and by slow evaporation from dichloromethane. The maximum absorbance in the UV-Vis spectrum is at 533 nm. Emission was measured upon excitation at 533 nm with a fluorescence λ_{max} of 658 nm and cutoff of 900 nm.

3D view
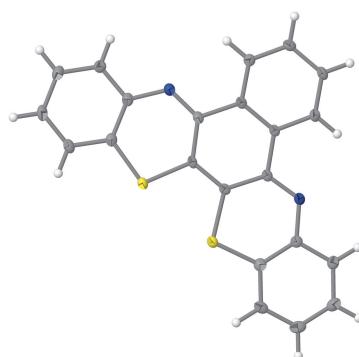

Chemical scheme
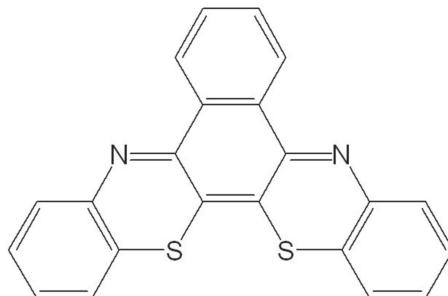
Structure description

Fused heterocyclic aromatic compounds are of interest as an alternative to oligoacenes (Spangler *et al.*, 1989; McLean *et al.*, 1989, 1990; Pham *et al.*, 2008). Surprisingly, despite this intensely researched area, structural studies of these materials are scarce. Sulfur-containing fused heterocyclic compounds, such as phenothiazine ladder polymers and oligomers are particularly interesting. Phenothiazine systems can be obtained readily by reaction of halo-*p*-benzoquinones and amino thiophenols (Agarwal & Schaefer, 1980; Okafor *et al.*, 1988). The title compound was prepared as part of our work in crystalline organic semiconductors and was used in the construction of a single-crystal field effect transistor (Pham *et al.*, 2008).

The molecule is quasi-planar (Fig. 1) with a dihedral angle between the C11–C16 and C17–C22 phenyl rings on the periphery of the molecule of 1.73 (19)°. Individual molecules stack along the b axis with π–π distances of 3.438 (3) Å between symmetry-related C3–C8 rings. The shortest interactions are H15···S1($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$) = 2.92 Å and C—H···$\pi$ [H13···C13($2 - x, \frac{1}{2} + z, \frac{1}{2} - z$)] of 2.84 Å. The packing of molecules is shown in Fig. 2.
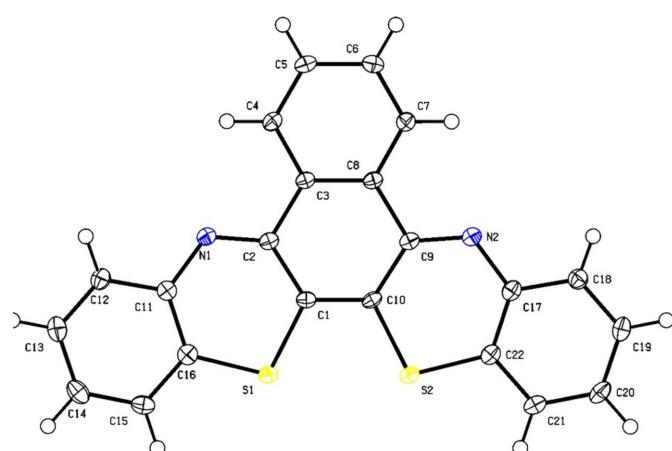
Figure 1
Structure of title compound with 50% probability ellipsoids.
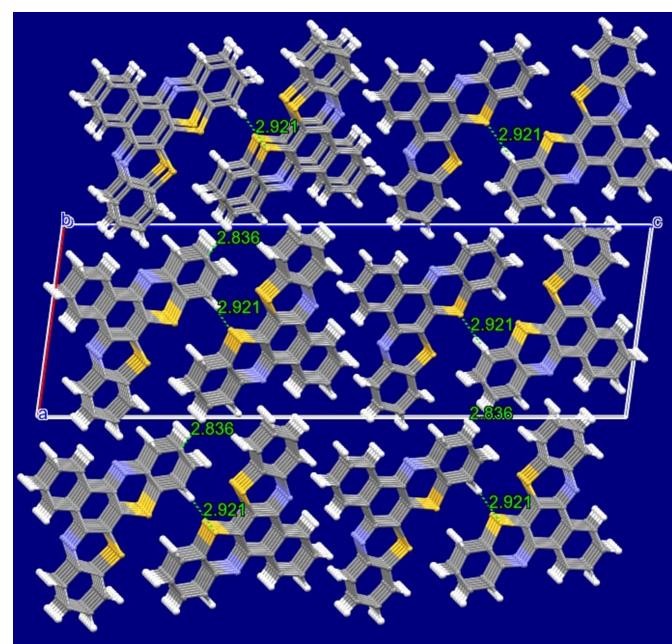
Figure 2
Packing of molecules governed by π-stacking and C—H$\cdots\pi$ contacts (H13$\cdots$C13).

Table 1
Experimental details.

|	
Crystal data	
Chemical formula	$C_{22}H_{12}N_2S_2$
M_r	368.46
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	11.7365 (5), 3.8149 (2), 35.7260 (15)
β (°)	97.669 (2)
V (Å^3)	1585.27 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.34
Crystal size (mm)	$0.25 \times 0.06 \times 0.01$
Data collection	
Diffractometer	Bruker PHOTON-III CPAD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.642, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13015, 3927, 3341
R_{int}	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.116, 1.06
No. of reflections	3927
No. of parameters	235
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.52, −0.56

Computer programs: *APEX4* and *SAINT* (Bruker, 2014), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

A survey of the Cambridge Structural Database (Groom *et al.*, 2016) on March 28, 2024 revealed no hits for this compound or any closely related structures.

This class of compounds have unique optical and electrical properties (Spangler *et al.*, 1989; Pham *et al.*, 2008; McLean *et al.*, 1990). The uv–vis spectra and florescence spectra are shown in Figs. 3 and 4. We note that the fluorescence cutoff spectra extend to 900 nm, which might be of interest for non-linear optical and biological applications.

Figure 3
Uv–vis spectrum of the title compound in DMF.
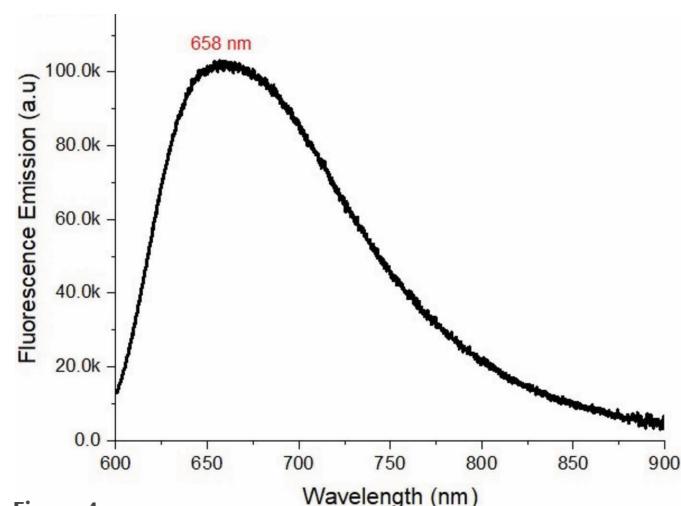
Figure 4
Emission spectrum of the title compound excited at 533 nm in DMF.

Synthesis and crystallization

The title compound was prepared followed published procedures (Feister *et al.*, 2023; Okafor, 1988). In a typical experiment, 2,3-dichloro-1,4-naphthoquinone (1 mmol, 1.0693 g) was dissolved in 10 ml DMF. 2-Aminothiophenol (2 mmol, 1 ml) was added to the solution. The reaction was then left stirring for 10 h, and the product was vacuum filtered. The product was then dried for 10 h in a vacuum oven, and then recrystallized from a dichloromethane solution, resulting in a dark-purple solid (0.7974 g, yield 46%), m.p. 280°C. Suitable crystals were grown either by sublimation or by slow evaporation from dichloromethane.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

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full crystallographic data

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Crystal data

$C_{22}H_{12}N_2S_2$	$F(000) = 760$
$M_r = 368.46$	$D_x = 1.544$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.7365$ (5) Å	Cell parameters from 2950 reflections
$b = 3.8149$ (2) Å	$\theta = 2.3$–28.3°
$c = 35.7260$ (15) Å	$\mu = 0.34$ mm^{-1}
$\beta = 97.669$ (2)°	$T = 100$ K
$V = 1585.27$ (13) Å^3	Plate, brown
$Z = 4$	$0.25 \times 0.06 \times 0.01$ mm

Data collection

Bruker PHOTON-III CPAD diffractometer	3927 independent reflections
Radiation source: micro-focus	3341 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.035$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.0°$
	$h = -15\rightarrow15$
$T_{min} = 0.642$, $T_{max} = 0.746$	$k = -3\rightarrow5$
13015 measured reflections	$l = -47\rightarrow43$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.047$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 2.0952P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
3927 reflections	$(\Delta/\sigma)_{max} = 0.001$
235 parameters	$\Delta\rho_{max} = 0.52$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.56$ e Å^{-3}

Special details

Experimental. Prof. M. Bader/ Prof. D. Alvacado / A. Bradley

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.54183 (4)	0.21127 (14)	0.30740 (2)	0.01608 (13)
S2	0.33242 (4)	0.20563 (14)	0.34472 (2)	0.01608 (13)
C1	0.55313 (16)	0.3928 (5)	0.35287 (5)	0.0133 (4)
C2	0.66054 (16)	0.5414 (5)	0.37063 (5)	0.0136 (4)
C3	0.66375 (16)	0.6660 (5)	0.40993 (5)	0.0130 (4)
C4	0.76638 (17)	0.7994 (6)	0.42939 (6)	0.0161 (4)
H4	0.833194	0.811698	0.417086	0.019*
C5	0.77115 (17)	0.9132 (6)	0.46631 (6)	0.0173 (4)
H5	0.841216	1.001428	0.479273	0.021*
C6	0.67283 (17)	0.8986 (6)	0.48468 (6)	0.0171 (4)
H6	0.676060	0.977146	0.510033	0.021*
C7	0.57106 (17)	0.7691 (5)	0.46564 (6)	0.0158 (4)
H7	0.504467	0.759988	0.478081	0.019*
C8	0.56486 (16)	0.6513 (5)	0.42822 (5)	0.0139 (4)
C9	0.45459 (16)	0.5176 (5)	0.40854 (5)	0.0136 (4)
C10	0.45630 (16)	0.3844 (5)	0.37040 (5)	0.0131 (4)
N1	0.75471 (14)	0.5822 (5)	0.35518 (5)	0.0152 (3)
C11	0.76197 (17)	0.4805 (5)	0.31800 (6)	0.0149 (4)
C12	0.86667 (17)	0.5499 (6)	0.30445 (6)	0.0174 (4)
H12	0.926848	0.662186	0.320482	0.021*
C13	0.88363 (19)	0.4577 (6)	0.26821 (6)	0.0204 (4)
H13	0.955212	0.505662	0.259611	0.025*
C14	0.79652 (19)	0.2954 (6)	0.24432 (6)	0.0215 (5)
H14	0.808693	0.231235	0.219467	0.026*
C15	0.69185 (19)	0.2267 (6)	0.25667 (6)	0.0186 (4)
H15	0.632088	0.117180	0.240201	0.022*
C16	0.67390 (17)	0.3185 (5)	0.29338 (6)	0.0158 (4)
N2	0.36590 (14)	0.5329 (5)	0.42687 (5)	0.0157 (4)
C17	0.25691 (17)	0.4184 (6)	0.41125 (6)	0.0160 (4)
C18	0.16828 (17)	0.4541 (6)	0.43387 (6)	0.0178 (4)
H18	0.185008	0.553665	0.458358	0.021*
C19	0.05728 (17)	0.3472 (6)	0.42117 (6)	0.0197 (4)
H19	−0.001115	0.371277	0.437018	0.024*
C20	0.03085 (18)	0.2041 (6)	0.38515 (6)	0.0210 (4)
H20	−0.045527	0.132118	0.376360	0.025*
C21	0.11667 (17)	0.1672 (6)	0.36219 (6)	0.0182 (4)
H21	0.098693	0.071365	0.337562	0.022*
C22	0.22938 (17)	0.2703 (5)	0.37509 (6)	0.0155 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0154 (2)	0.0172 (3)	0.0152 (2)	−0.0022 (2)	0.00051 (17)	−0.00166 (19)
S2	0.0136 (2)	0.0180 (3)	0.0160 (2)	−0.0023 (2)	−0.00017 (17)	−0.00226 (19)
C1	0.0148 (9)	0.0119 (9)	0.0125 (9)	0.0016 (8)	−0.0013 (7)	0.0015 (7)

C2	0.0138 (9)	0.0115 (9)	0.0147 (9)	0.0007 (8)	−0.0007 (7)	0.0013 (7)
C3	0.0130 (8)	0.0111 (9)	0.0140 (9)	0.0009 (7)	−0.0012 (7)	0.0011 (7)
C4	0.0131 (8)	0.0160 (10)	0.0187 (10)	0.0001 (8)	0.0001 (7)	−0.0001 (8)
C5	0.0158 (9)	0.0164 (10)	0.0184 (10)	−0.0021 (8)	−0.0028 (7)	−0.0016 (8)
C6	0.0196 (10)	0.0165 (10)	0.0145 (9)	0.0015 (8)	−0.0003 (7)	−0.0014 (8)
C7	0.0154 (9)	0.0156 (10)	0.0161 (9)	−0.0001 (8)	0.0015 (7)	0.0009 (8)
C8	0.0136 (9)	0.0123 (9)	0.0148 (9)	0.0013 (8)	−0.0012 (7)	0.0006 (7)
C9	0.0139 (9)	0.0110 (9)	0.0150 (9)	0.0000 (8)	−0.0011 (7)	0.0017 (7)
C10	0.0116 (8)	0.0104 (9)	0.0160 (9)	−0.0003 (7)	−0.0025 (7)	0.0014 (7)
N1	0.0137 (8)	0.0155 (8)	0.0160 (8)	−0.0002 (7)	0.0001 (6)	−0.0003 (7)
C11	0.0167 (9)	0.0118 (9)	0.0163 (9)	0.0019 (8)	0.0018 (7)	0.0019 (7)
C12	0.0173 (9)	0.0137 (10)	0.0215 (10)	−0.0024 (8)	0.0035 (8)	0.0015 (8)
C13	0.0223 (10)	0.0167 (10)	0.0239 (11)	0.0020 (9)	0.0089 (8)	0.0024 (9)
C14	0.0299 (11)	0.0182 (10)	0.0175 (10)	0.0045 (9)	0.0068 (8)	0.0023 (8)
C15	0.0231 (10)	0.0153 (10)	0.0162 (10)	0.0016 (9)	−0.0013 (8)	−0.0002 (8)
C16	0.0185 (9)	0.0116 (9)	0.0172 (9)	0.0008 (8)	0.0020 (7)	0.0036 (8)
N2	0.0146 (8)	0.0158 (9)	0.0162 (8)	−0.0006 (7)	0.0006 (6)	0.0002 (7)
C17	0.0139 (9)	0.0148 (10)	0.0189 (10)	0.0014 (8)	0.0007 (7)	0.0031 (8)
C18	0.0168 (9)	0.0182 (10)	0.0182 (10)	0.0006 (8)	0.0022 (7)	0.0001 (8)
C19	0.0149 (9)	0.0196 (11)	0.0254 (11)	0.0016 (8)	0.0052 (8)	0.0032 (9)
C20	0.0130 (9)	0.0235 (11)	0.0252 (11)	−0.0022 (9)	−0.0021 (8)	0.0041 (9)
C21	0.0162 (9)	0.0168 (10)	0.0204 (10)	−0.0020 (8)	−0.0022 (7)	0.0001 (8)
C22	0.0139 (8)	0.0132 (10)	0.0187 (9)	0.0017 (8)	0.0002 (7)	0.0028 (8)

Geometric parameters (Å, º)

S1—C16	1.740 (2)	C11—C12	1.405 (3)
S1—C1	1.755 (2)	C11—C16	1.407 (3)
S2—C22	1.747 (2)	C12—C13	1.382 (3)
S2—C10	1.751 (2)	C12—H12	0.9500
C1—C10	1.369 (3)	C13—C14	1.387 (3)
C1—C2	1.449 (3)	C13—H13	0.9500
C2—N1	1.309 (2)	C14—C15	1.385 (3)
C2—C3	1.478 (3)	C14—H14	0.9500
C3—C4	1.404 (3)	C15—C16	1.400 (3)
C3—C8	1.407 (3)	C15—H15	0.9500
C4—C5	1.382 (3)	N2—C17	1.396 (3)
C4—H4	0.9500	C17—C18	1.406 (3)
C5—C6	1.403 (3)	C17—C22	1.407 (3)
C5—H5	0.9500	C18—C19	1.383 (3)
C6—C7	1.384 (3)	C18—H18	0.9500
C6—H6	0.9500	C19—C20	1.394 (3)
C7—C8	1.403 (3)	C19—H19	0.9500
C7—H7	0.9500	C20—C21	1.389 (3)
C8—C9	1.479 (3)	C20—H20	0.9500
C9—N2	1.303 (2)	C21—C22	1.398 (3)
C9—C10	1.457 (3)	C21—H21	0.9500
N1—C11	1.398 (3)		

C16—S1—C1	102.32 (10)	C12—C11—C16	118.08 (18)
C22—S2—C10	102.41 (10)	C13—C12—C11	121.1 (2)
C10—C1—C2	122.38 (18)	C13—C12—H12	119.4
C10—C1—S1	116.71 (15)	C11—C12—H12	119.4
C2—C1—S1	120.91 (14)	C12—C13—C14	120.25 (19)
N1—C2—C1	126.58 (18)	C12—C13—H13	119.9
N1—C2—C3	116.52 (17)	C14—C13—H13	119.9
C1—C2—C3	116.89 (16)	C15—C14—C13	120.1 (2)
C4—C3—C8	119.40 (18)	C15—C14—H14	120.0
C4—C3—C2	119.92 (17)	C13—C14—H14	120.0
C8—C3—C2	120.68 (17)	C14—C15—C16	120.1 (2)
C5—C4—C3	120.62 (18)	C14—C15—H15	119.9
C5—C4—H4	119.7	C16—C15—H15	119.9
C3—C4—H4	119.7	C15—C16—C11	120.35 (19)
C4—C5—C6	120.19 (19)	C15—C16—S1	117.50 (16)
C4—C5—H5	119.9	C11—C16—S1	122.11 (15)
C6—C5—H5	119.9	C9—N2—C17	122.41 (17)
C7—C6—C5	119.59 (19)	N2—C17—C18	116.65 (18)
C7—C6—H6	120.2	N2—C17—C22	125.35 (18)
C5—C6—H6	120.2	C18—C17—C22	118.00 (18)
C6—C7—C8	120.95 (18)	C19—C18—C17	121.3 (2)
C6—C7—H7	119.5	C19—C18—H18	119.3
C8—C7—H7	119.5	C17—C18—H18	119.3
C7—C8—C3	119.24 (18)	C18—C19—C20	120.15 (19)
C7—C8—C9	119.63 (17)	C18—C19—H19	119.9
C3—C8—C9	121.12 (17)	C20—C19—H19	119.9
N2—C9—C10	126.69 (18)	C21—C20—C19	119.70 (19)
N2—C9—C8	116.92 (17)	C21—C20—H20	120.1
C10—C9—C8	116.40 (16)	C19—C20—H20	120.1
C1—C10—C9	122.38 (17)	C20—C21—C22	120.4 (2)
C1—C10—S2	116.83 (15)	C20—C21—H21	119.8
C9—C10—S2	120.79 (14)	C22—C21—H21	119.8
C2—N1—C11	122.00 (17)	C21—C22—C17	120.46 (18)
N1—C11—C12	116.25 (18)	C21—C22—S2	117.29 (16)
N1—C11—C16	125.67 (18)	C17—C22—S2	122.25 (15)
C16—S1—C1—C10	173.32 (16)	C1—C2—N1—C11	−0.2 (3)
C16—S1—C1—C2	−7.01 (19)	C3—C2—N1—C11	−178.92 (17)
C10—C1—C2—N1	−175.1 (2)	C2—N1—C11—C12	177.87 (19)
S1—C1—C2—N1	5.3 (3)	C2—N1—C11—C16	−1.7 (3)
C10—C1—C2—C3	3.7 (3)	N1—C11—C12—C13	179.44 (19)
S1—C1—C2—C3	−175.95 (14)	C16—C11—C12—C13	−0.9 (3)
N1—C2—C3—C4	−3.8 (3)	C11—C12—C13—C14	0.4 (3)
C1—C2—C3—C4	177.34 (18)	C12—C13—C14—C15	0.4 (3)
N1—C2—C3—C8	176.48 (19)	C13—C14—C15—C16	−0.5 (3)
C1—C2—C3—C8	−2.4 (3)	C14—C15—C16—C11	−0.1 (3)
C8—C3—C4—C5	0.5 (3)	C14—C15—C16—S1	−177.97 (17)

C2—C3—C4—C5	−179.23 (19)	N1—C11—C16—C15	−179.62 (19)
C3—C4—C5—C6	−0.5 (3)	C12—C11—C16—C15	0.8 (3)
C4—C5—C6—C7	0.1 (3)	N1—C11—C16—S1	−1.9 (3)
C5—C6—C7—C8	0.2 (3)	C12—C11—C16—S1	178.56 (16)
C6—C7—C8—C3	−0.1 (3)	C1—S1—C16—C15	−176.64 (16)
C6—C7—C8—C9	−179.42 (19)	C1—S1—C16—C11	5.5 (2)
C4—C3—C8—C7	−0.2 (3)	C10—C9—N2—C17	−0.2 (3)
C2—C3—C8—C7	179.50 (18)	C8—C9—N2—C17	179.35 (18)
C4—C3—C8—C9	179.07 (19)	C9—N2—C17—C18	−179.1 (2)
C2—C3—C8—C9	−1.2 (3)	C9—N2—C17—C22	1.2 (3)
C7—C8—C9—N2	3.3 (3)	N2—C17—C18—C19	−179.7 (2)
C3—C8—C9—N2	−176.02 (19)	C22—C17—C18—C19	0.1 (3)
C7—C8—C9—C10	−177.15 (18)	C17—C18—C19—C20	−0.7 (3)
C3—C8—C9—C10	3.5 (3)	C18—C19—C20—C21	0.4 (3)
C2—C1—C10—C9	−1.3 (3)	C19—C20—C21—C22	0.5 (3)
S1—C1—C10—C9	178.35 (15)	C20—C21—C22—C17	−1.1 (3)
C2—C1—C10—S2	178.49 (15)	C20—C21—C22—S2	178.64 (17)
S1—C1—C10—S2	−1.8 (2)	N2—C17—C22—C21	−179.5 (2)
N2—C9—C10—C1	177.2 (2)	C18—C17—C22—C21	0.8 (3)
C8—C9—C10—C1	−2.3 (3)	N2—C17—C22—S2	0.8 (3)
N2—C9—C10—S2	−2.6 (3)	C18—C17—C22—S2	−178.90 (16)
C8—C9—C10—S2	177.87 (14)	C10—S2—C22—C21	177.42 (17)
C22—S2—C10—C1	−176.21 (16)	C10—S2—C22—C17	−2.8 (2)
C22—S2—C10—C9	3.60 (18)		