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# 2′,2′-(2,2′-Dithiodiphenylene)bis(1,1,3,3-tetramethylguanidine)

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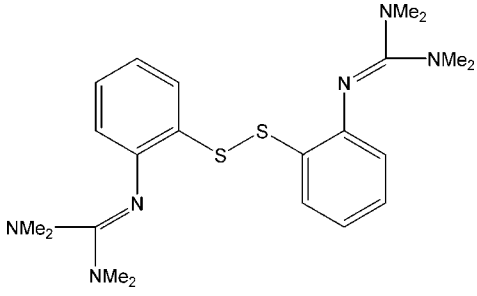
Key indicators: single-crystal X-ray study; $T$ = 153 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.050; $wR$ factor = 0.111; data-to-parameter ratio = 19.9.

The molecular structure of the title compound, $C_{22}H_{32}N_6S_2$, has two guanidyl groups bridged by a 2,2′-dithiodiphenylene linker with localized C=N bonds. The C—S—S—C group has a folded non-planar conformation like that found in $H_2O_2$ or $H_2S_2$, with a torsion angle of 83.80 (9)°. The S—S bond length is 2.0410 (8) Å. The crystal packing shows intermolecular C—H···S hydrogen bonds which link molecules into dimers that are stacked along [100].

## Related literature

For related literature, see: Gomes de Mesquita (1967); Harmjanz (1997); Herres *et al.* (2005); Kaitner & Pavlovic (1997); Lee & Bryant (1970); Neuba, Flörke & Henkel (2007); Neuba, Herres-Pawlis *et al.* (2007); Pohl *et al.* (2000); Schneider (2000); Waden (1999); Wittmann *et al.* (2001).




## Experimental

### Crystal data

$C_{22}H_{32}N_6S_2$
$M_r$ = 444.66
Monoclinic, $P2_1/n$
$a$ = 10.5755 (15) Å
$b$ = 20.287 (3) Å
$c$ = 12.1172 (17) Å
$\beta$ = 115.630 (3)°
$V$ = 2343.9 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.25 mm$^{-1}$
$T$ = 153 (2) K
0.40 × 0.18 × 0.15 mm

### Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min}$ = 0.907, $T_{max}$ = 0.969
20441 measured reflections
5564 independent reflections
4239 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.056

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.111
$S$ = 1.05
5564 reflections
279 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C21—H21$A$···S1$^{i}$ | 0.98 | 2.97 | 3.871 (2) | 154 |

Symmetry code: (i) $-x+1, -y, -z+1$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2590).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, o4661 [ **doi:10.1107/S1600536807056486** ]

# 2',2'-(2,2'-Dithiodiphenylene)bis(1,1,3,3-tetramethylguanidine)

**A. Neuba, U. Flörke and G. Henkel**

## Comment

The synthesis and characterization of molecules containing nitrogen and sulfur as donor functions is important for biomimetic coordination chemistry. The use of these molecules as ligands in the synthesis of copper-complexes as mimics for active centres like the CuA in cytochrome-c-oxidase and $N_2O$-reductase is currently of considerable interest in bioinorganic chemistry. In search of multifunctional ligands we have extended our studies to guanidyl-type systems with N-donor functions. The first derivative, the ligand bis(tetramethyl-guanidino)propylene (btmgp) and its complexes with Cu, Fe, Ni and Mn have earlier been investigated (Harmjanz, 1997; Waden, 1999; Pohl *et al.*, 2000; Schneider, 2000; Wittmann *et al.*, 2001; Herres *et al.*, 2005, Neuba *et al.*, 2007*b*). We have now developed the title compound (I) with disulfide groups as novel ligand with redoxactivity for use in biomimetic copper-sulfur chemistry. Recently, we reported about the molecular structure of *N*,*N*'-bis(1,3-dimethylimidazolidin-2-ylidene)-2,2'-dithiodianiline (II) (Neuba *et al.*, 2007*a*) with a dimethylenthylen-bridge in the guanidyl group. Both molecules, I and II, possess nearly the same arrangement of the phenyl rings and the guanidyl groups. Also the relevant structural characteristics such as the C═N bond lengths (1.300 (2) in I, 1.297 (3) Å in II) as well as the torsion angles C–S1–S2–C' (83.80 (9)° in I, 84.65 (10)° in II) are equal. Analogous to (II) the guanidyl double bonds C═N in I are clearly localized. The S–S atom distances are equal. pπ-dπ interactions between the fully occupied pz orbital on the carbon C atom (part of the aromatic π cloud) with an empty d orbital on the S atom as *e.g.* reported for 2,2'-diaminodiphenyl disulfide (Lee & Bryant, 1970) are neither found in (I) nor in (II).

## Experimental

A solution of tetramethylchloroformamidinium chloride (5.13 g, 30 mmol) in dry MeCN was added dropwise to an ice-cooled solution of 2,2'-dithiodianiline (3.73 g, 15 mmol) and triethylamine (4.18 ml, 3.03 g, 30 mmol) in dry MeCN. After 3 h under reflux, a solution of NaOH (1.2 g, 30 mmol) in water was added. The solvents and $NEt_3$ were then evaporated under vacuum. In order to deprotonate the bis-hydrochloride, 50 wt% KOH (aqueous, 15 ml) was added and the free base was extracted into the THF phase (3 *x* 80 ml). The organic phase was dried with $Na_2SO_4$. After filtration, the solvent was evaporated under reduced pressure. The crude product was recrystallized in THF and the title compound was obtained as a white powder (yield 71.6%, 4.8 g). Crystals suitable for X-ray diffraction were obtained by diffusion of $Et_2O$ into a cold saturated THF solution.

Spectroscopic analysis, $^1$H NMR (500 MHz, $CDCl_3$): δ 2.75 (s, 24H, Me), 6.5 (m, 2H, $CH_{arom}$), 6.75 (m, 2H, $CH_{arom}$), 7.0 (m, 2H, $CH_{arom}$), 7.42 (m, 2H, $CH_{arom}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 39.5 (Me), 120.6 ($CH_{arom}$), 121.1 ($CH_{arom}$), 125.7 ($CH_{arom}$), 126.1 ($CH_{arom}$), 128.3 ($C_{quart}$), 149.4 ($C_{quart}$), 160.0 ($C_{gua}$); IR (KBr, ν, $cm^{-1}$): 3055 (w), 3007 (w), 2917 (*m*), 1552 (*versus*, C═N), 1518 (s, C═N), 1464 (*s*), 1423 (*s*), 1382 (*s*), 1144 (*m*), 1215 (*m*), 743 (*m*); EI—MS: m/*z* (%) 444 (79) [$M^+$], 222 (85), 178 (95), 149 (80), 109 (30), 44 (63), 28 (18); Elemental analysis ($M$ = 444.66 g $mol^{-1}$): calcd. for $C_{22}H_{32}N_6S_2$: C: 59.42; H: 7.25; N: 18.90; found C: 59.0, H: 7.64, N: 18.61.

### Refinement

Hydrogen atoms were refined at idealized positions riding on the carbon atoms with $C_{aromatic}$—H=0.95Å and $C_{methyl}$—H=0.98Å and isotropic displacement parameters $U_{iso}(H) = 1.2U(C_{eq})$ or $1.5U(–CH_3)$. All $CH_3$ hydrogen atoms were allowed to rotate but not to tip.

### Figures

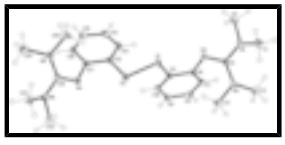

Fig. 1. Molecular structure of I. Displacement ellipsoids are drawn at the 50% probability level.

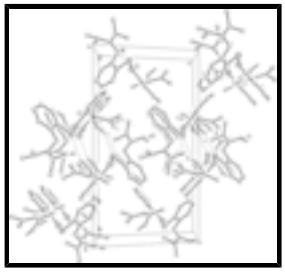

Fig. 2. Crystal packing viewed along [100] with hydrogen bond indicated as dashed lines. H-atoms not involved are omitted.

### 2',2'-(2,2'-Dithiodiphenylene)bis(1,1,3,3-tetramethylguanidine)

*Crystal data*

| | |
|---|---|
| $C_{22}H_{32}N_6S_2$ | $F_{000}$ = 952 |
| $M_r$ = 444.66 | $D_x$ = 1.260 Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2yn | Cell parameters from 943 reflections |
| $a$ = 10.5755 (15) Å | θ = 2.4–26.0º |
| $b$ = 20.287 (3) Å | μ = 0.25 mm$^{-1}$ |
| $c$ = 12.1172 (17) Å | $T$ = 153 (2) K |
| β = 115.630 (3)º | Prism, colourless |
| $V$ = 2343.9 (6) Å$^3$ | 0.40 × 0.18 × 0.15 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX diffractometer | 5564 independent reflections |
| Radiation source: sealed tube | 4239 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.056 |
| $T$ = 153(2) K | $\theta_{max}$ = 27.9º |
| φ and ω scans | $\theta_{min}$ = 2.0º |
| Absorption correction: multi-scan | $h$ = −13→13 |

(SADABS; Bruker, 2002)
$T_{min}$ = 0.907, $T_{max}$ = 0.969
20441 measured reflections
$k$ = −26→24
$l$ = −15→15

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.111
$S$ = 1.05
5564 reflections
279 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.561P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.43 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$
Extinction correction: none

*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 $F^2 > 2$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 | 0.68592 (5) | 0.05490 (2) | 0.32568 (4) | 0.02068 (13) |
| S2 | 0.51780 (5) | 0.09196 (3) | 0.34599 (4) | 0.02214 (13) |
| N1 | 1.01232 (18) | −0.05928 (9) | 0.20495 (15) | 0.0251 (4) |
| N2 | 0.79520 (18) | −0.04220 (8) | 0.04109 (15) | 0.0225 (4) |
| N3 | 0.87386 (17) | 0.02417 (8) | 0.22101 (14) | 0.0200 (4) |
| N4 | 0.36222 (17) | 0.15798 (8) | 0.45061 (14) | 0.0209 (4) |
| N5 | 0.37622 (18) | 0.12855 (8) | 0.64576 (14) | 0.0227 (4) |
| N6 | 0.16183 (17) | 0.14341 (8) | 0.47691 (14) | 0.0186 (4) |
| C1 | 1.0130 (3) | −0.13010 (11) | 0.1837 (2) | 0.0378 (6) |
| H1A | 0.9207 | −0.1437 | 0.1214 | 0.057* |
| H1B | 1.0341 | −0.1538 | 0.2601 | 0.057* |
| H1C | 1.0846 | −0.1403 | 0.1553 | 0.057* |
| C2 | 1.1303 (2) | −0.03492 (12) | 0.31433 (19) | 0.0307 (5) |
| H2A | 1.1362 | 0.0131 | 0.3094 | 0.046* |
| H2B | 1.2174 | −0.0549 | 0.3202 | 0.046* |
| H2C | 1.1167 | −0.0466 | 0.3869 | 0.046* |

| | | | | |
|---|---|---|---|---|
| C3 | 0.8352 (3) | −0.05515 (12) | −0.0568 (2) | 0.0331 (5) |
| H3A | 0.8071 | −0.0179 | −0.1140 | 0.050* |
| H3B | 0.7886 | −0.0954 | −0.1002 | 0.050* |
| H3C | 0.9371 | −0.0609 | −0.0226 | 0.050* |
| C4 | 0.6475 (2) | −0.02957 (11) | 0.00192 (19) | 0.0260 (5) |
| H4A | 0.6287 | −0.0243 | 0.0738 | 0.039* |
| H4B | 0.5928 | −0.0667 | −0.0475 | 0.039* |
| H4C | 0.6209 | 0.0108 | −0.0472 | 0.039* |
| C5 | 0.8917 (2) | −0.02292 (10) | 0.15610 (17) | 0.0194 (4) |
| C6 | 0.78954 (19) | 0.07873 (9) | 0.16245 (16) | 0.0180 (4) |
| C7 | 0.8017 (2) | 0.11356 (10) | 0.06772 (17) | 0.0225 (4) |
| H7A | 0.8628 | 0.0977 | 0.0349 | 0.027* |
| C8 | 0.7259 (2) | 0.17066 (10) | 0.02134 (18) | 0.0247 (5) |
| H8A | 0.7351 | 0.1935 | −0.0433 | 0.030* |
| C9 | 0.6368 (2) | 0.19488 (10) | 0.06818 (19) | 0.0251 (5) |
| H9A | 0.5852 | 0.2342 | 0.0362 | 0.030* |
| C10 | 0.6235 (2) | 0.16119 (10) | 0.16236 (18) | 0.0211 (4) |
| H10A | 0.5630 | 0.1777 | 0.1954 | 0.025* |
| C11 | 0.6983 (2) | 0.10353 (9) | 0.20831 (16) | 0.0176 (4) |
| C12 | 0.5868 (2) | 0.16061 (9) | 0.44668 (17) | 0.0191 (4) |
| C13 | 0.7171 (2) | 0.18895 (10) | 0.47664 (18) | 0.0238 (4) |
| H13A | 0.7743 | 0.1736 | 0.4395 | 0.029* |
| C14 | 0.7631 (2) | 0.24002 (10) | 0.56157 (19) | 0.0261 (5) |
| H14A | 0.8520 | 0.2597 | 0.5824 | 0.031* |
| C15 | 0.6796 (2) | 0.26212 (10) | 0.61570 (19) | 0.0259 (5) |
| H15A | 0.7132 | 0.2956 | 0.6764 | 0.031* |
| C16 | 0.5475 (2) | 0.23565 (10) | 0.58163 (18) | 0.0226 (4) |
| H16A | 0.4895 | 0.2525 | 0.6169 | 0.027* |
| C17 | 0.4975 (2) | 0.18421 (9) | 0.49564 (17) | 0.0191 (4) |
| C18 | 0.3047 (2) | 0.14459 (9) | 0.52355 (17) | 0.0180 (4) |
| C19 | 0.5133 (2) | 0.09729 (11) | 0.6920 (2) | 0.0305 (5) |
| H19A | 0.5245 | 0.0757 | 0.6243 | 0.046* |
| H19B | 0.5213 | 0.0643 | 0.7538 | 0.046* |
| H19C | 0.5866 | 0.1307 | 0.7289 | 0.046* |
| C20 | 0.3339 (3) | 0.15266 (12) | 0.73751 (19) | 0.0337 (6) |
| H20A | 0.2501 | 0.1803 | 0.6981 | 0.051* |
| H20B | 0.4101 | 0.1788 | 0.7984 | 0.051* |
| H20C | 0.3128 | 0.1152 | 0.7779 | 0.051* |
| C21 | 0.0864 (2) | 0.09764 (10) | 0.51975 (19) | 0.0250 (5) |
| H21A | 0.1536 | 0.0692 | 0.5834 | 0.038* |
| H21B | 0.0231 | 0.0705 | 0.4511 | 0.038* |
| H21C | 0.0317 | 0.1225 | 0.5535 | 0.038* |
| C22 | 0.0808 (2) | 0.17019 (10) | 0.35497 (17) | 0.0239 (5) |
| H22A | 0.1271 | 0.2099 | 0.3442 | 0.036* |
| H22B | −0.0136 | 0.1815 | 0.3450 | 0.036* |
| H22C | 0.0743 | 0.1373 | 0.2936 | 0.036* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0213 (3) | 0.0206 (3) | 0.0221 (2) | 0.0033 (2) | 0.0112 (2) | 0.00143 (19) |
| S2 | 0.0185 (3) | 0.0248 (3) | 0.0251 (3) | −0.0038 (2) | 0.0112 (2) | −0.0077 (2) |
| N1 | 0.0198 (10) | 0.0273 (10) | 0.0250 (9) | 0.0080 (8) | 0.0068 (7) | 0.0019 (7) |
| N2 | 0.0180 (9) | 0.0262 (10) | 0.0207 (8) | 0.0019 (7) | 0.0061 (7) | −0.0027 (7) |
| N3 | 0.0170 (9) | 0.0233 (9) | 0.0184 (8) | 0.0045 (7) | 0.0064 (7) | 0.0016 (7) |
| N4 | 0.0166 (9) | 0.0234 (9) | 0.0216 (8) | −0.0016 (7) | 0.0073 (7) | −0.0035 (7) |
| N5 | 0.0192 (9) | 0.0266 (10) | 0.0196 (8) | 0.0010 (7) | 0.0058 (7) | 0.0046 (7) |
| N6 | 0.0153 (9) | 0.0204 (9) | 0.0189 (8) | −0.0003 (7) | 0.0063 (7) | 0.0017 (6) |
| C1 | 0.0435 (15) | 0.0302 (13) | 0.0380 (13) | 0.0186 (11) | 0.0160 (12) | 0.0047 (10) |
| C2 | 0.0184 (11) | 0.0430 (14) | 0.0270 (11) | 0.0099 (10) | 0.0062 (9) | 0.0052 (10) |
| C3 | 0.0355 (14) | 0.0376 (14) | 0.0278 (11) | 0.0018 (11) | 0.0153 (10) | −0.0067 (10) |
| C4 | 0.0163 (11) | 0.0294 (12) | 0.0273 (11) | −0.0019 (9) | 0.0047 (9) | 0.0008 (9) |
| C5 | 0.0156 (10) | 0.0233 (10) | 0.0197 (9) | 0.0012 (8) | 0.0080 (8) | 0.0024 (8) |
| C6 | 0.0130 (10) | 0.0199 (10) | 0.0169 (9) | −0.0008 (8) | 0.0026 (8) | −0.0027 (7) |
| C7 | 0.0173 (11) | 0.0273 (11) | 0.0230 (10) | −0.0011 (9) | 0.0090 (8) | −0.0012 (8) |
| C8 | 0.0238 (12) | 0.0254 (11) | 0.0223 (10) | −0.0038 (9) | 0.0075 (9) | 0.0039 (8) |
| C9 | 0.0252 (12) | 0.0168 (10) | 0.0279 (11) | 0.0014 (9) | 0.0065 (9) | 0.0011 (8) |
| C10 | 0.0170 (10) | 0.0199 (10) | 0.0244 (10) | 0.0009 (8) | 0.0071 (8) | −0.0027 (8) |
| C11 | 0.0164 (10) | 0.0166 (10) | 0.0170 (9) | −0.0018 (8) | 0.0047 (8) | −0.0018 (7) |
| C12 | 0.0182 (10) | 0.0185 (10) | 0.0192 (9) | −0.0016 (8) | 0.0067 (8) | −0.0014 (8) |
| C13 | 0.0191 (11) | 0.0268 (11) | 0.0278 (11) | −0.0011 (9) | 0.0124 (9) | −0.0006 (9) |
| C14 | 0.0190 (11) | 0.0262 (12) | 0.0299 (11) | −0.0051 (9) | 0.0075 (9) | −0.0008 (9) |
| C15 | 0.0290 (12) | 0.0205 (11) | 0.0259 (11) | −0.0047 (9) | 0.0098 (9) | −0.0033 (8) |
| C16 | 0.0240 (12) | 0.0211 (11) | 0.0233 (10) | 0.0015 (9) | 0.0108 (9) | −0.0012 (8) |
| C17 | 0.0174 (10) | 0.0204 (10) | 0.0192 (9) | 0.0010 (8) | 0.0077 (8) | 0.0032 (8) |
| C18 | 0.0183 (10) | 0.0149 (10) | 0.0197 (9) | −0.0006 (8) | 0.0072 (8) | −0.0025 (7) |
| C19 | 0.0202 (12) | 0.0297 (12) | 0.0330 (12) | 0.0018 (9) | 0.0035 (9) | 0.0111 (9) |
| C20 | 0.0364 (14) | 0.0420 (14) | 0.0222 (11) | 0.0000 (11) | 0.0122 (10) | 0.0013 (9) |
| C21 | 0.0198 (11) | 0.0256 (11) | 0.0303 (11) | −0.0007 (9) | 0.0115 (9) | 0.0019 (9) |
| C22 | 0.0195 (11) | 0.0267 (11) | 0.0209 (10) | 0.0000 (9) | 0.0045 (8) | 0.0003 (8) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—C11 | 1.7814 (19) | C6—C7 | 1.400 (3) |
| S1—S2 | 2.0410 (8) | C7—C8 | 1.382 (3) |
| S2—C12 | 1.7862 (19) | C7—H7A | 0.9500 |
| N1—C5 | 1.367 (3) | C8—C9 | 1.383 (3) |
| N1—C2 | 1.458 (3) | C8—H8A | 0.9500 |
| N1—C1 | 1.460 (3) | C9—C10 | 1.389 (3) |
| N2—C5 | 1.381 (2) | C9—H9A | 0.9500 |
| N2—C4 | 1.445 (3) | C10—C11 | 1.387 (3) |
| N2—C3 | 1.446 (3) | C10—H10A | 0.9500 |
| N3—C5 | 1.302 (2) | C12—C13 | 1.388 (3) |
| N3—C6 | 1.406 (2) | C12—C17 | 1.399 (3) |
| N4—C18 | 1.300 (2) | C13—C14 | 1.391 (3) |

| | | | |
|---|---|---|---|
| N4—C17 | 1.398 (3) | C13—H13A | 0.9500 |
| N5—C18 | 1.379 (2) | C14—C15 | 1.382 (3) |
| N5—C20 | 1.451 (3) | C14—H14A | 0.9500 |
| N5—C19 | 1.455 (3) | C15—C16 | 1.383 (3) |
| N6—C18 | 1.366 (2) | C15—H15A | 0.9500 |
| N6—C22 | 1.455 (2) | C16—C17 | 1.406 (3) |
| N6—C21 | 1.458 (2) | C16—H16A | 0.9500 |
| C1—H1A | 0.9800 | C19—H19A | 0.9800 |
| C1—H1B | 0.9800 | C19—H19B | 0.9800 |
| C1—H1C | 0.9800 | C19—H19C | 0.9800 |
| C2—H2A | 0.9800 | C20—H20A | 0.9800 |
| C2—H2B | 0.9800 | C20—H20B | 0.9800 |
| C2—H2C | 0.9800 | C20—H20C | 0.9800 |
| C3—H3A | 0.9800 | C21—H21A | 0.9800 |
| C3—H3B | 0.9800 | C21—H21B | 0.9800 |
| C3—H3C | 0.9800 | C21—H21C | 0.9800 |
| C4—H4A | 0.9800 | C22—H22A | 0.9800 |
| C4—H4B | 0.9800 | C22—H22B | 0.9800 |
| C4—H4C | 0.9800 | C22—H22C | 0.9800 |
| C6—C11 | 1.399 (3) | | |
| C11—S1—S2 | 105.12 (7) | C8—C9—H9A | 120.3 |
| C12—S2—S1 | 104.45 (7) | C10—C9—H9A | 120.3 |
| C5—N1—C2 | 118.82 (17) | C11—C10—C9 | 120.12 (19) |
| C5—N1—C1 | 121.96 (18) | C11—C10—H10A | 119.9 |
| C2—N1—C1 | 115.22 (17) | C9—C10—H10A | 119.9 |
| C5—N2—C4 | 120.20 (17) | C10—C11—C6 | 121.03 (18) |
| C5—N2—C3 | 121.95 (18) | C10—C11—S1 | 124.17 (15) |
| C4—N2—C3 | 114.90 (17) | C6—C11—S1 | 114.79 (14) |
| C5—N3—C6 | 119.92 (16) | C13—C12—C17 | 121.51 (18) |
| C18—N4—C17 | 121.01 (16) | C13—C12—S2 | 124.60 (15) |
| C18—N5—C20 | 122.38 (17) | C17—C12—S2 | 113.89 (15) |
| C18—N5—C19 | 120.56 (17) | C12—C13—C14 | 119.45 (19) |
| C20—N5—C19 | 116.01 (17) | C12—C13—H13A | 120.3 |
| C18—N6—C22 | 118.29 (16) | C14—C13—H13A | 120.3 |
| C18—N6—C21 | 122.81 (16) | C15—C14—C13 | 120.1 (2) |
| C22—N6—C21 | 115.25 (16) | C15—C14—H14A | 119.9 |
| N1—C1—H1A | 109.5 | C13—C14—H14A | 119.9 |
| N1—C1—H1B | 109.5 | C14—C15—C16 | 120.16 (19) |
| H1A—C1—H1B | 109.5 | C14—C15—H15A | 119.9 |
| N1—C1—H1C | 109.5 | C16—C15—H15A | 119.9 |
| H1A—C1—H1C | 109.5 | C15—C16—C17 | 121.10 (19) |
| H1B—C1—H1C | 109.5 | C15—C16—H16A | 119.5 |
| N1—C2—H2A | 109.5 | C17—C16—H16A | 119.5 |
| N1—C2—H2B | 109.5 | N4—C17—C12 | 117.98 (17) |
| H2A—C2—H2B | 109.5 | N4—C17—C16 | 124.39 (18) |
| N1—C2—H2C | 109.5 | C12—C17—C16 | 117.52 (18) |
| H2A—C2—H2C | 109.5 | N4—C18—N6 | 118.79 (17) |
| H2B—C2—H2C | 109.5 | N4—C18—N5 | 125.39 (18) |
| N2—C3—H3A | 109.5 | N6—C18—N5 | 115.77 (17) |

| | | | |
|---|---|---|---|
| N2—C3—H3B | 109.5 | N5—C19—H19A | 109.5 |
| H3A—C3—H3B | 109.5 | N5—C19—H19B | 109.5 |
| N2—C3—H3C | 109.5 | H19A—C19—H19B | 109.5 |
| H3A—C3—H3C | 109.5 | N5—C19—H19C | 109.5 |
| H3B—C3—H3C | 109.5 | H19A—C19—H19C | 109.5 |
| N2—C4—H4A | 109.5 | H19B—C19—H19C | 109.5 |
| N2—C4—H4B | 109.5 | N5—C20—H20A | 109.5 |
| H4A—C4—H4B | 109.5 | N5—C20—H20B | 109.5 |
| N2—C4—H4C | 109.5 | H20A—C20—H20B | 109.5 |
| H4A—C4—H4C | 109.5 | N5—C20—H20C | 109.5 |
| H4B—C4—H4C | 109.5 | H20A—C20—H20C | 109.5 |
| N3—C5—N1 | 119.09 (17) | H20B—C20—H20C | 109.5 |
| N3—C5—N2 | 125.52 (18) | N6—C21—H21A | 109.5 |
| N1—C5—N2 | 115.33 (17) | N6—C21—H21B | 109.5 |
| C11—C6—C7 | 117.88 (18) | H21A—C21—H21B | 109.5 |
| C11—C6—N3 | 118.59 (17) | N6—C21—H21C | 109.5 |
| C7—C6—N3 | 123.24 (18) | H21A—C21—H21C | 109.5 |
| C8—C7—C6 | 120.92 (19) | H21B—C21—H21C | 109.5 |
| C8—C7—H7A | 119.5 | N6—C22—H22A | 109.5 |
| C6—C7—H7A | 119.5 | N6—C22—H22B | 109.5 |
| C7—C8—C9 | 120.58 (19) | H22A—C22—H22B | 109.5 |
| C7—C8—H8A | 119.7 | N6—C22—H22C | 109.5 |
| C9—C8—H8A | 119.7 | H22A—C22—H22C | 109.5 |
| C8—C9—C10 | 119.46 (19) | H22B—C22—H22C | 109.5 |
| C11—S1—S2—C12 | −83.80 (9) | S1—S2—C12—C13 | 13.49 (19) |
| C6—N3—C5—N1 | 152.24 (18) | S1—S2—C12—C17 | −166.00 (13) |
| C6—N3—C5—N2 | −30.7 (3) | C17—C12—C13—C14 | 3.0 (3) |
| C2—N1—C5—N3 | −14.4 (3) | S2—C12—C13—C14 | −176.43 (16) |
| C1—N1—C5—N3 | 142.0 (2) | C12—C13—C14—C15 | 0.1 (3) |
| C2—N1—C5—N2 | 168.24 (18) | C13—C14—C15—C16 | −2.9 (3) |
| C1—N1—C5—N2 | −35.4 (3) | C14—C15—C16—C17 | 2.6 (3) |
| C4—N2—C5—N3 | −24.1 (3) | C18—N4—C17—C12 | 139.44 (19) |
| C3—N2—C5—N3 | 135.4 (2) | C18—N4—C17—C16 | −44.6 (3) |
| C4—N2—C5—N1 | 153.02 (18) | C13—C12—C17—N4 | 172.95 (18) |
| C3—N2—C5—N1 | −47.4 (3) | S2—C12—C17—N4 | −7.5 (2) |
| C5—N3—C6—C11 | 138.50 (19) | C13—C12—C17—C16 | −3.3 (3) |
| C5—N3—C6—C7 | −47.8 (3) | S2—C12—C17—C16 | 176.22 (14) |
| C11—C6—C7—C8 | 0.1 (3) | C15—C16—C17—N4 | −175.52 (18) |
| N3—C6—C7—C8 | −173.61 (18) | C15—C16—C17—C12 | 0.4 (3) |
| C6—C7—C8—C9 | 0.4 (3) | C17—N4—C18—N6 | 155.42 (18) |
| C7—C8—C9—C10 | −0.2 (3) | C17—N4—C18—N5 | −27.3 (3) |
| C8—C9—C10—C11 | −0.4 (3) | C22—N6—C18—N4 | −12.5 (3) |
| C9—C10—C11—C6 | 0.9 (3) | C21—N6—C18—N4 | 144.97 (19) |
| C9—C10—C11—S1 | −178.14 (15) | C22—N6—C18—N5 | 170.00 (17) |
| C7—C6—C11—C10 | −0.8 (3) | C21—N6—C18—N5 | −32.6 (3) |
| N3—C6—C11—C10 | 173.27 (17) | C20—N5—C18—N4 | 140.4 (2) |
| C7—C6—C11—S1 | 178.38 (14) | C19—N5—C18—N4 | −27.4 (3) |
| N3—C6—C11—S1 | −7.6 (2) | C20—N5—C18—N6 | −42.3 (3) |
| S2—S1—C11—C10 | 10.99 (18) | C19—N5—C18—N6 | 149.93 (18) |

| | |
|---|---|
| S2—S1—C11—C6 | −168.11 (13) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C21—H21A···S1$^{i}$ | 0.98 | 2.97 | 3.871 (2) | 154 |

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1.

**Fig. 1**

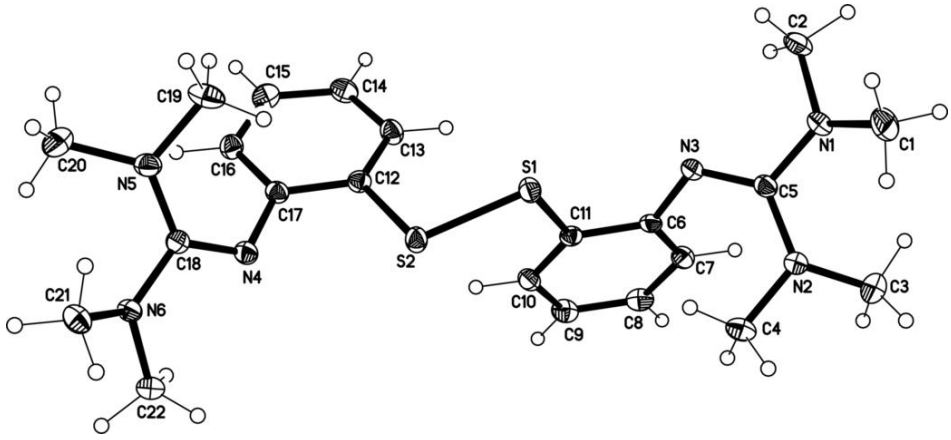
C2
C15
C14
C19
C1
N1
C20
N5
C16
C13
S1
N3
C12
C5
C17
C11
C6
S2
C18
N4
C7
C21
N6
C10
N2
C3
C9
C8
C4
C22

**Fig. 2**