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# An amide cyclophane

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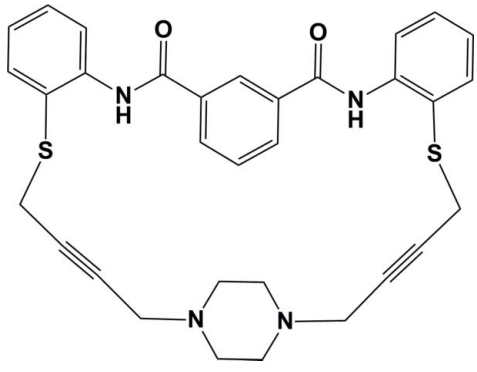
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; disorder in main residue; $R$ factor = 0.042; $wR$ factor = 0.117; data-to-parameter ratio = 19.3.

The title compound, 8,18-dithia-2,6-diaza-13(1,4)-piperidina-1(1,2),4(1,3),7(1,2)-tribenzenaoctadecaphane-10,15-diyne-3,6-dione, $C_{32}H_{30}N_4O_2S_2$, is composed of a relatively planar bis(2-mercaptophenyl)isophthalamide unit linked to a bridging 1,4-di(but-2-yn-1-yl)piperazine unit, forming a macrocycle. The isophthalamide ring is inclined to the outer mercaptophenyl rings by 8.18 (11) and 5.59 (10)°, while these two rings are inclined to one another by 9.10 (12)°. The piperazine ring adopts a chair conformation. There are two intramolecular N—H···S hydrogen bonds generating $S$(5) ring motifs. In the crystal, molecules are linked *via* C—H···S and C—H···O hydrogen bonds, forming slabs lying parallel to (001). An O atom in the isophthalamide group is disordered over two positions with an occupancy ratio of 0.41 (6):0.59 (6).

## Related literature

For the biological activity of piperazine derivatives, see: Fun *et al.* (2011); Kavitha *et al.* (2013). For standard bond lengths, see: Allen *et al.* (1987).




## Experimental

### Crystal data

$C_{32}H_{30}N_4O_2S_2$
$M_r$ = 566.72
Monoclinic, $C2/c$
$a$ = 23.0760 (5) Å
$b$ = 9.9380 (3) Å
$c$ = 27.0341 (7) Å
$\beta$ = 108.428 (2)°
$V$ = 5881.8 (3) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.22 mm$^{-1}$
$T$ = 293 K
0.30 × 0.25 × 0.20 mm

### Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.380, $T_{max}$ = 0.745
27488 measured reflections
7294 independent reflections
4040 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.036

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.117
$S$ = 1.01
7294 reflections
377 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$A$···S1 | 0.83 (2) | 2.46 (2) | 2.9621 (18) | 120 (2) |
| N3—H3$A$···S2 | 0.83 (2) | 2.49 (2) | 2.9905 (19) | 120 (2) |
| C21—H21$B$···O2$A$$^{i}$ | 0.97 | 2.57 | 3.43 (3) | 148 |
| C21—H21$B$···O2$B$$^{i}$ | 0.97 | 2.34 | 3.230 (11) | 152 |
| C24—H24$A$···O1$^{ii}$ | 0.97 | 2.54 | 3.505 (3) | 171 |
| C26—H26$B$···S2$^{ii}$ | 0.97 | 2.85 | 3.632 (2) | 139 |
| C32—H32$B$···O1$^{iii}$ | 0.97 | 2.49 | 3.146 (3) | 125 |

Symmetry codes: (i) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $x, y-1, z$; (iii) $-x+1, y, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors thank the TBI X-ray facility, CAS in Crystallography and Biophysics, University of Madras, India, for the data collection.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2737).

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# supporting information

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## An amide cyclophane

**Vijayan Viswanathan, Ayyavu Thirunarayanan, Perumal Rajakumar and Devadasan Velmurugan**

### S1. Comment

Piperazine derivatives are popular in organic synthesis and for their applications in biology and medicine. They are known to exhibit antibacterial and antimicrobial activities (Fun *et al.*, 2011). They are also amongst the most important building blocks found in biologically active compounds in a number of different therapeutic areas and a review about the current pharmacological and toxicological information for piperazine derivatives is available (Kavitha *et al.*, 2013).

The molecular structure of the title molecule is shown in Fig. 1. It is composed of a relatively planar bis(2-mercaptophenyl)isophthalamide moiety linked to a bridging 1,4-di(but-2-yn-1-yl)piperazine unit forming a macrocycle. The isophthalamide ring (C8-C13) is inclined to the outer mercaptophenyl rings (C1-C6 and C15-C20) by 8.18 (11) and 5.59 (10) °, respectively. The two mercaptophenyl rings (C1-C6 and C15-C20) are inclined to one another by 9.10 (12) °. The S2–C1 and S1–C20 bond lengths are 1.773 (2) Å and 1.777 (2) Å, respectively, similar to the standard value of 1.769 (9) Å (Allen *et al.*, 1987). There are two intramolecular N—H···S hydrogen bonds generating S(5) ring motifs (Fig. 1 and Table 1).

The but-2-yne group is linear and connects the piperazine group to the bis(2-mercaptophenyl)isophthalamide moiety. The piperazine ring (N1/N4/C25-C28) adopts a chair conformation.

In the crystal, molecules are linked via C—H···S and C—H···O hydrogen bonds forming slabs lying parallel to (001); see Table 1 and Fig. 2.

### S2. Experimental

A mixture of precyclophane diyne (0.2 g, 3.98 mmol), piperazine (0.04 g, 3.98 mmol), formaldehyde (0.02 g, 7.96 mmol) from 37-41% formalin solution and CuCl (0.04 g, 3.98 mmol) in dioxane (30 mL) was refluxed at 363 K for 2 h under a nitrogen atmosphere by the Multi Components Reaction (MCR) technique. After the reaction was complete, the solvent was removed under reduced pressure and the residue was extracted with $CHCl_3$ (3 × 100 mL), washed with water (2 × 100 mL), brine (150 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed and the crude product was purified by column chromatography on silica gel using $CHCl_3$/MeOH (24:1) as eluent. After purification the piperazinophane was recrystallised in MeOH by slow evaporation yielding block-like colourless crystals.

### S3. Refinement

N-bound H atoms were refined with distance restraints: N-H = 0.86 (2) Å with $U_{iso}(H) = 1.2U_{eq}(N)$. The C-bound H atoms were positioned geometrically (C–H = 0.93–0.97 Å) and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}$(C-methyl) and $= 1.2U_{eq}(C)$ for other H atoms. In the isophthalamide group atom O2 is disordered over two positions with an occupancy ratio of 0.41 (6):0.59 (6).

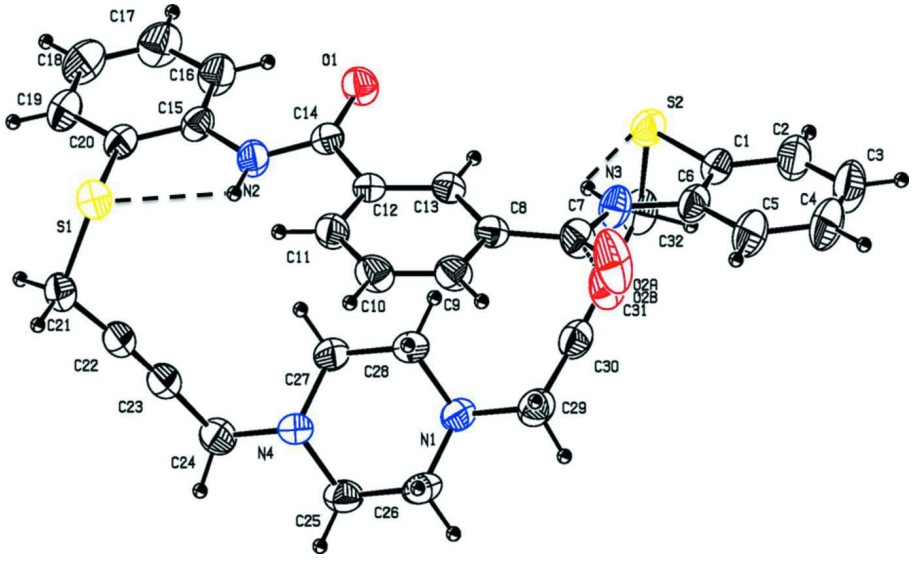


**Figure 1**

The molecular structure of the title molecule, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular N-H···S hydrogen bonds are shown as dashed lines (see Table 1 for details).

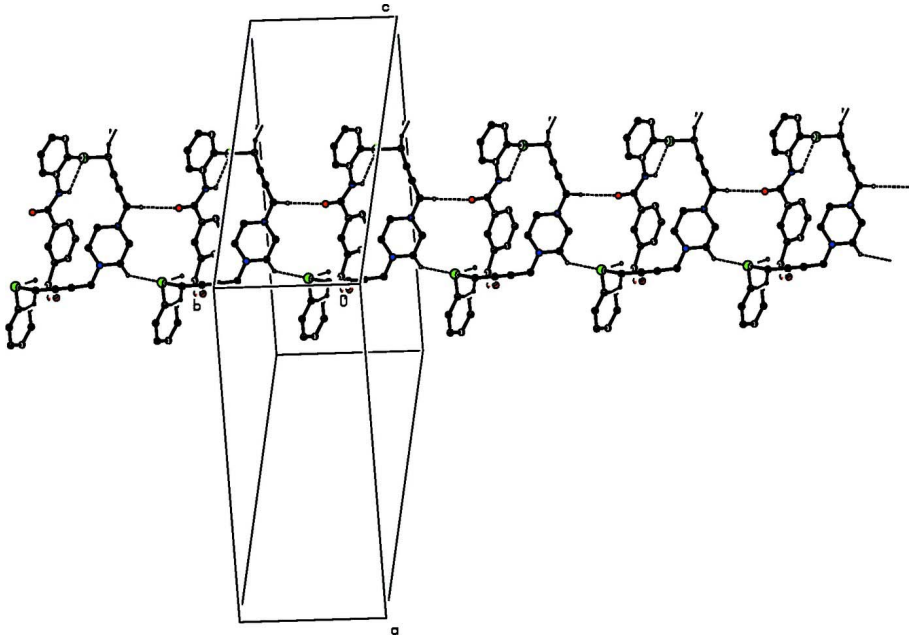


**Figure 2**

A partial view of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines (see Table 1 for details; H-atoms not involved in hydrogen bonding have been omitted for clarity).

### 8,18-Dithia-2,6-diaza-13(1,4)-piperidina-1(1,2),4(1,3),7(1,2)-tribenzenaoctadecaphane-10,15-diyne-3,6-dione

*Crystal data*

$C_{32}H_{30}N_4O_2S_2$
$M_r$ = 566.72
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 23.0760 (5) Å
*b* = 9.9380 (3) Å

$c$ = 27.0341 (7) Å
$\beta$ = 108.428 (2)°
$V$ = 5881.8 (3) Å$^3$
$Z$ = 8
$F$(000) = 2384
$D_x$ = 1.280 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å

Cell parameters from 7294 reflections
$\theta$ = 1.6–28.3°
$\mu$ = 0.22 mm$^{-1}$
$T$ = 293 K
Block, colourless
0.30 × 0.25 × 0.20 mm

*Data collection*

Bruker SMART APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.380, $T_{max}$ = 0.745

27488 measured reflections
7294 independent reflections
4040 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.036
$\theta_{max}$ = 28.3°, $\theta_{min}$ = 1.6°
$h$ = −30→30
$k$ = −13→13
$l$ = −34→35

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.117
$S$ = 1.01
7294 reflections
377 parameters
2 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 2.0132P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 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**. 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| S1 | 0.41059 (2) | 0.21672 (6) | 1.01916 (2) | 0.06329 (16) | |
| S2 | 0.58670 (2) | 0.64936 (6) | 0.76454 (2) | 0.06810 (17) | |
| O1 | 0.47117 (6) | 0.54558 (14) | 0.89655 (5) | 0.0671 (4) | |
| O2A | 0.7513 (7) | 0.440 (3) | 0.9253 (10) | 0.108 (5) | 0.41 (6) |
| O2B | 0.7544 (4) | 0.482 (3) | 0.9314 (5) | 0.115 (4) | 0.59 (6) |
| N1 | 0.57053 (7) | 0.08419 (16) | 0.81521 (6) | 0.0584 (4) | |
| N2 | 0.45152 (7) | 0.37111 (18) | 0.94254 (7) | 0.0634 (5) | |
| H2A | 0.4674 (9) | 0.3112 (19) | 0.9642 (8) | 0.076* | |
| N3 | 0.67548 (7) | 0.5408 (2) | 0.86248 (7) | 0.0650 (5) | |

| | | | | |
|---|---|---|---|---|
| H3A | 0.6377 (7) | 0.544 (2) | 0.8508 (8) | 0.078* |
| N4 | 0.50216 (7) | −0.03836 (15) | 0.87441 (6) | 0.0541 (4) |
| C1 | 0.66745 (9) | 0.6485 (2) | 0.78117 (9) | 0.0625 (5) |
| C2 | 0.69417 (11) | 0.7074 (3) | 0.74746 (11) | 0.0866 (7) |
| H2 | 0.6695 | 0.7458 | 0.7166 | 0.104* |
| C3 | 0.75672 (13) | 0.7100 (3) | 0.75881 (13) | 0.1039 (9) |
| H3 | 0.7744 | 0.7507 | 0.7361 | 0.125* |
| C4 | 0.79235 (11) | 0.6519 (3) | 0.80401 (13) | 0.0995 (9) |
| H4 | 0.8346 | 0.6519 | 0.8115 | 0.119* |
| C5 | 0.76738 (10) | 0.5931 (3) | 0.83875 (10) | 0.0825 (7) |
| H5 | 0.7925 | 0.5540 | 0.8693 | 0.099* |
| C6 | 0.70420 (8) | 0.5926 (2) | 0.82788 (9) | 0.0618 (5) |
| C7 | 0.69931 (9) | 0.4820 (2) | 0.90941 (9) | 0.0660 (6) |
| C8 | 0.65534 (8) | 0.43753 (18) | 0.93660 (8) | 0.0536 (5) |
| C9 | 0.67931 (9) | 0.3618 (2) | 0.98150 (9) | 0.0657 (6) |
| H9 | 0.7211 | 0.3448 | 0.9937 | 0.079* |
| C10 | 0.64258 (10) | 0.3116 (2) | 1.00816 (9) | 0.0709 (6) |
| H10 | 0.6594 | 0.2596 | 1.0379 | 0.085* |
| C11 | 0.58065 (9) | 0.3380 (2) | 0.99107 (8) | 0.0622 (5) |
| H11 | 0.5558 | 0.3034 | 1.0092 | 0.075* |
| C12 | 0.55554 (8) | 0.41599 (17) | 0.94693 (7) | 0.0484 (4) |
| C13 | 0.59316 (8) | 0.46595 (18) | 0.92026 (7) | 0.0497 (4) |
| H13 | 0.5766 | 0.5194 | 0.8909 | 0.060* |
| C14 | 0.48890 (8) | 0.45151 (19) | 0.92630 (7) | 0.0517 (4) |
| C15 | 0.38767 (8) | 0.3776 (2) | 0.93183 (8) | 0.0578 (5) |
| C16 | 0.34978 (10) | 0.4520 (2) | 0.89092 (9) | 0.0770 (7) |
| H16 | 0.3663 | 0.5021 | 0.8696 | 0.092* |
| C17 | 0.28782 (11) | 0.4512 (3) | 0.88210 (11) | 0.0917 (8) |
| H17 | 0.2625 | 0.5006 | 0.8545 | 0.110* |
| C18 | 0.26290 (11) | 0.3792 (3) | 0.91326 (12) | 0.0942 (8) |
| H18 | 0.2209 | 0.3793 | 0.9068 | 0.113* |
| C19 | 0.30033 (10) | 0.3061 (2) | 0.95441 (10) | 0.0763 (6) |
| H19 | 0.2834 | 0.2577 | 0.9759 | 0.092* |
| C20 | 0.36274 (8) | 0.3043 (2) | 0.96403 (8) | 0.0575 (5) |
| C21 | 0.39422 (9) | 0.0419 (2) | 1.00030 (8) | 0.0623 (5) |
| H21A | 0.4140 | −0.0144 | 1.0302 | 0.075* |
| H21B | 0.3505 | 0.0277 | 0.9915 | 0.075* |
| C22 | 0.41344 (9) | −0.0032 (2) | 0.95642 (9) | 0.0573 (5) |
| C23 | 0.42885 (9) | −0.0462 (2) | 0.92174 (9) | 0.0590 (5) |
| C24 | 0.44899 (10) | −0.1063 (2) | 0.88040 (8) | 0.0651 (5) |
| H24A | 0.4587 | −0.2003 | 0.8884 | 0.078* |
| H24B | 0.4158 | −0.1020 | 0.8477 | 0.078* |
| C25 | 0.53008 (10) | −0.1175 (2) | 0.84244 (9) | 0.0685 (6) |
| H25A | 0.5012 | −0.1287 | 0.8077 | 0.082* |
| H25B | 0.5408 | −0.2061 | 0.8577 | 0.082* |
| C26 | 0.58637 (10) | −0.0470 (2) | 0.83922 (9) | 0.0695 (6) |
| H26A | 0.6153 | −0.0366 | 0.8739 | 0.083* |
| H26B | 0.6056 | −0.1007 | 0.8188 | 0.083* |

| | | | | |
|---|---|---|---|---|
| C27 | 0.48647 (9) | 0.0944 (2) | 0.85116 (9) | 0.0638 (5) |
| H27A | 0.4686 | 0.1480 | 0.8726 | 0.077* |
| H27B | 0.4564 | 0.0854 | 0.8169 | 0.077* |
| C28 | 0.54223 (9) | 0.1640 (2) | 0.84643 (9) | 0.0648 (6) |
| H28A | 0.5309 | 0.2514 | 0.8303 | 0.078* |
| H28B | 0.5713 | 0.1779 | 0.8809 | 0.078* |
| C29 | 0.62297 (9) | 0.1516 (2) | 0.80817 (9) | 0.0725 (6) |
| H29A | 0.6431 | 0.0916 | 0.7905 | 0.087* |
| H29B | 0.6518 | 0.1733 | 0.8420 | 0.087* |
| C30 | 0.60525 (10) | 0.2749 (3) | 0.77769 (9) | 0.0668 (6) |
| C31 | 0.58869 (9) | 0.3744 (3) | 0.75342 (9) | 0.0651 (6) |
| C32 | 0.56795 (10) | 0.4989 (2) | 0.72467 (8) | 0.0748 (6) |
| H32A | 0.5240 | 0.4946 | 0.7086 | 0.090* |
| H32B | 0.5861 | 0.5057 | 0.6969 | 0.090* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0621 (3) | 0.0687 (3) | 0.0562 (3) | −0.0058 (3) | 0.0146 (2) | 0.0010 (3) |
| S2 | 0.0538 (3) | 0.0752 (4) | 0.0786 (4) | 0.0148 (3) | 0.0256 (3) | 0.0111 (3) |
| O1 | 0.0593 (8) | 0.0693 (9) | 0.0674 (9) | 0.0087 (7) | 0.0123 (7) | 0.0201 (8) |
| O2A | 0.035 (5) | 0.131 (11) | 0.160 (10) | 0.023 (6) | 0.032 (6) | 0.061 (7) |
| O2B | 0.050 (3) | 0.167 (9) | 0.104 (5) | −0.038 (5) | −0.010 (3) | 0.051 (5) |
| N1 | 0.0518 (9) | 0.0574 (10) | 0.0665 (11) | 0.0045 (8) | 0.0195 (8) | −0.0074 (8) |
| N2 | 0.0491 (9) | 0.0689 (12) | 0.0744 (12) | 0.0115 (8) | 0.0229 (9) | 0.0232 (9) |
| N3 | 0.0378 (8) | 0.0918 (13) | 0.0638 (11) | −0.0020 (9) | 0.0140 (8) | 0.0025 (10) |
| N4 | 0.0568 (9) | 0.0477 (9) | 0.0555 (10) | 0.0057 (7) | 0.0146 (8) | −0.0030 (8) |
| C1 | 0.0536 (11) | 0.0650 (13) | 0.0762 (15) | 0.0019 (10) | 0.0308 (11) | −0.0003 (11) |
| C2 | 0.0780 (16) | 0.1015 (19) | 0.0924 (18) | 0.0038 (14) | 0.0444 (14) | 0.0149 (15) |
| C3 | 0.0777 (18) | 0.134 (3) | 0.118 (2) | −0.0075 (17) | 0.0565 (18) | 0.016 (2) |
| C4 | 0.0535 (14) | 0.137 (3) | 0.119 (2) | −0.0141 (15) | 0.0430 (16) | −0.006 (2) |
| C5 | 0.0482 (12) | 0.114 (2) | 0.0867 (17) | −0.0087 (13) | 0.0239 (12) | −0.0074 (15) |
| C6 | 0.0466 (11) | 0.0719 (13) | 0.0715 (14) | −0.0064 (10) | 0.0250 (10) | −0.0109 (11) |
| C7 | 0.0454 (11) | 0.0712 (14) | 0.0750 (15) | −0.0064 (11) | 0.0098 (11) | 0.0034 (12) |
| C8 | 0.0461 (10) | 0.0476 (10) | 0.0620 (12) | −0.0014 (8) | 0.0101 (9) | −0.0022 (9) |
| C9 | 0.0483 (11) | 0.0615 (13) | 0.0798 (15) | 0.0079 (10) | 0.0094 (10) | 0.0108 (11) |
| C10 | 0.0644 (13) | 0.0672 (14) | 0.0718 (15) | 0.0120 (11) | 0.0082 (11) | 0.0211 (11) |
| C11 | 0.0606 (12) | 0.0617 (12) | 0.0640 (13) | 0.0072 (10) | 0.0194 (10) | 0.0130 (10) |
| C12 | 0.0501 (10) | 0.0419 (10) | 0.0515 (11) | 0.0050 (8) | 0.0138 (9) | −0.0006 (8) |
| C13 | 0.0491 (10) | 0.0452 (10) | 0.0500 (11) | −0.0003 (8) | 0.0087 (8) | −0.0014 (8) |
| C14 | 0.0541 (11) | 0.0515 (11) | 0.0490 (11) | 0.0065 (9) | 0.0156 (9) | −0.0003 (9) |
| C15 | 0.0459 (10) | 0.0674 (13) | 0.0605 (12) | 0.0093 (9) | 0.0176 (9) | 0.0024 (10) |
| C16 | 0.0611 (13) | 0.0964 (17) | 0.0723 (15) | 0.0196 (12) | 0.0192 (11) | 0.0208 (13) |
| C17 | 0.0590 (14) | 0.116 (2) | 0.0890 (18) | 0.0270 (14) | 0.0080 (13) | 0.0195 (17) |
| C18 | 0.0475 (13) | 0.118 (2) | 0.112 (2) | 0.0165 (14) | 0.0184 (14) | 0.0008 (18) |
| C19 | 0.0549 (13) | 0.0916 (17) | 0.0885 (17) | 0.0025 (12) | 0.0313 (12) | −0.0010 (14) |
| C20 | 0.0491 (10) | 0.0642 (12) | 0.0596 (12) | 0.0033 (9) | 0.0176 (9) | −0.0051 (10) |
| C21 | 0.0569 (12) | 0.0657 (13) | 0.0643 (13) | −0.0067 (10) | 0.0192 (10) | 0.0061 (11) |

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|---|---|---|---|---|---|---|
| C22 | 0.0478 (11) | 0.0565 (12) | 0.0624 (13) | −0.0020 (9) | 0.0101 (10) | 0.0099 (10) |
| C23 | 0.0534 (11) | 0.0564 (12) | 0.0627 (14) | −0.0017 (9) | 0.0117 (10) | 0.0056 (11) |
| C24 | 0.0688 (13) | 0.0605 (13) | 0.0627 (13) | −0.0048 (11) | 0.0159 (11) | −0.0036 (11) |
| C25 | 0.0812 (15) | 0.0525 (12) | 0.0730 (15) | 0.0038 (11) | 0.0259 (12) | −0.0107 (11) |
| C26 | 0.0676 (13) | 0.0595 (13) | 0.0838 (16) | 0.0143 (11) | 0.0274 (12) | −0.0113 (12) |
| C27 | 0.0598 (12) | 0.0596 (12) | 0.0746 (14) | 0.0140 (10) | 0.0249 (11) | 0.0068 (11) |
| C28 | 0.0679 (13) | 0.0508 (11) | 0.0794 (15) | 0.0084 (10) | 0.0287 (11) | −0.0017 (11) |
| C29 | 0.0562 (12) | 0.0752 (15) | 0.0877 (17) | 0.0028 (11) | 0.0252 (12) | −0.0067 (13) |
| C30 | 0.0542 (12) | 0.0773 (16) | 0.0728 (15) | −0.0072 (12) | 0.0257 (11) | −0.0155 (13) |
| C31 | 0.0503 (12) | 0.0834 (17) | 0.0638 (14) | −0.0069 (12) | 0.0213 (10) | −0.0138 (13) |
| C32 | 0.0618 (13) | 0.1047 (18) | 0.0559 (13) | −0.0025 (12) | 0.0157 (11) | 0.0029 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C20 | 1.777 (2) | C12—C13 | 1.384 (3) |
| S1—C21 | 1.817 (2) | C12—C14 | 1.503 (2) |
| S2—C1 | 1.773 (2) | C13—H13 | 0.9300 |
| S2—C32 | 1.814 (2) | C15—C16 | 1.387 (3) |
| O1—C14 | 1.217 (2) | C15—C20 | 1.391 (3) |
| O2A—C7 | 1.215 (11) | C16—C17 | 1.373 (3) |
| O2B—C7 | 1.222 (9) | C16—H16 | 0.9300 |
| N1—C29 | 1.448 (3) | C17—C18 | 1.363 (4) |
| N1—C26 | 1.451 (3) | C17—H17 | 0.9300 |
| N1—C28 | 1.454 (2) | C18—C19 | 1.380 (3) |
| N2—C14 | 1.347 (2) | C18—H18 | 0.9300 |
| N2—C15 | 1.411 (2) | C19—C20 | 1.380 (3) |
| N2—H2A | 0.833 (15) | C19—H19 | 0.9300 |
| N3—C7 | 1.346 (3) | C21—C22 | 1.462 (3) |
| N3—C6 | 1.404 (3) | C21—H21A | 0.9700 |
| N3—H3A | 0.828 (15) | C21—H21B | 0.9700 |
| N4—C24 | 1.454 (3) | C22—C23 | 1.183 (3) |
| N4—C27 | 1.457 (2) | C23—C24 | 1.466 (3) |
| N4—C25 | 1.461 (2) | C24—H24A | 0.9700 |
| C1—C2 | 1.382 (3) | C24—H24B | 0.9700 |
| C1—C6 | 1.395 (3) | C25—C26 | 1.503 (3) |
| C2—C3 | 1.378 (3) | C25—H25A | 0.9700 |
| C2—H2 | 0.9300 | C25—H25B | 0.9700 |
| C3—C4 | 1.367 (4) | C26—H26A | 0.9700 |
| C3—H3 | 0.9300 | C26—H26B | 0.9700 |
| C4—C5 | 1.378 (4) | C27—C28 | 1.502 (3) |
| C4—H4 | 0.9300 | C27—H27A | 0.9700 |
| C5—C6 | 1.393 (3) | C27—H27B | 0.9700 |
| C5—H5 | 0.9300 | C28—H28A | 0.9700 |
| C7—C8 | 1.496 (3) | C28—H28B | 0.9700 |
| C8—C9 | 1.386 (3) | C29—C30 | 1.461 (3) |
| C8—C13 | 1.390 (2) | C29—H29A | 0.9700 |
| C9—C10 | 1.369 (3) | C29—H29B | 0.9700 |
| C9—H9 | 0.9300 | C30—C31 | 1.181 (3) |

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|---|---|---|---|
| C10—C11 | 1.381 (3) | C31—C32 | 1.459 (3) |
| C10—H10 | 0.9300 | C32—H32A | 0.9700 |
| C11—C12 | 1.387 (3) | C32—H32B | 0.9700 |
| C11—H11 | 0.9300 | | |

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|---|---|---|---|
| C20—S1—C21 | 102.37 (10) | C18—C17—C16 | 121.0 (2) |
| C1—S2—C32 | 100.43 (10) | C18—C17—H17 | 119.5 |
| C29—N1—C26 | 111.83 (16) | C16—C17—H17 | 119.5 |
| C29—N1—C28 | 111.80 (16) | C17—C18—C19 | 119.7 (2) |
| C26—N1—C28 | 109.05 (16) | C17—C18—H18 | 120.1 |
| C14—N2—C15 | 129.86 (17) | C19—C18—H18 | 120.1 |
| C14—N2—H2A | 117.9 (15) | C18—C19—C20 | 120.6 (2) |
| C15—N2—H2A | 112.1 (15) | C18—C19—H19 | 119.7 |
| C7—N3—C6 | 130.45 (17) | C20—C19—H19 | 119.7 |
| C7—N3—H3A | 116.3 (16) | C19—C20—C15 | 119.24 (19) |
| C6—N3—H3A | 113.1 (16) | C19—C20—S1 | 119.93 (17) |
| C24—N4—C27 | 111.41 (15) | C15—C20—S1 | 120.74 (14) |
| C24—N4—C25 | 111.20 (15) | C22—C21—S1 | 115.54 (14) |
| C27—N4—C25 | 109.16 (16) | C22—C21—H21A | 108.4 |
| C2—C1—C6 | 119.7 (2) | S1—C21—H21A | 108.4 |
| C2—C1—S2 | 118.89 (18) | C22—C21—H21B | 108.4 |
| C6—C1—S2 | 121.39 (15) | S1—C21—H21B | 108.4 |
| C3—C2—C1 | 121.1 (3) | H21A—C21—H21B | 107.5 |
| C3—C2—H2 | 119.5 | C23—C22—C21 | 176.6 (2) |
| C1—C2—H2 | 119.5 | C22—C23—C24 | 176.9 (2) |
| C4—C3—C2 | 118.9 (2) | N4—C24—C23 | 112.22 (16) |
| C4—C3—H3 | 120.6 | N4—C24—H24A | 109.2 |
| C2—C3—H3 | 120.6 | C23—C24—H24A | 109.2 |
| C3—C4—C5 | 121.7 (2) | N4—C24—H24B | 109.2 |
| C3—C4—H4 | 119.1 | C23—C24—H24B | 109.2 |
| C5—C4—H4 | 119.1 | H24A—C24—H24B | 107.9 |
| C4—C5—C6 | 119.5 (2) | N4—C25—C26 | 109.52 (16) |
| C4—C5—H5 | 120.2 | N4—C25—H25A | 109.8 |
| C6—C5—H5 | 120.2 | C26—C25—H25A | 109.8 |
| C5—C6—C1 | 119.1 (2) | N4—C25—H25B | 109.8 |
| C5—C6—N3 | 122.9 (2) | C26—C25—H25B | 109.8 |
| C1—C6—N3 | 117.99 (17) | H25A—C25—H25B | 108.2 |
| O2A—C7—N3 | 123.2 (9) | N1—C26—C25 | 110.17 (17) |
| O2B—C7—N3 | 120.8 (7) | N1—C26—H26A | 109.6 |
| O2A—C7—C8 | 118.2 (9) | C25—C26—H26A | 109.6 |
| O2B—C7—C8 | 121.5 (6) | N1—C26—H26B | 109.6 |
| N3—C7—C8 | 116.93 (17) | C25—C26—H26B | 109.6 |
| C9—C8—C13 | 118.33 (18) | H26A—C26—H26B | 108.1 |
| C9—C8—C7 | 116.48 (17) | N4—C27—C28 | 110.57 (16) |
| C13—C8—C7 | 125.19 (18) | N4—C27—H27A | 109.5 |
| C10—C9—C8 | 121.13 (19) | C28—C27—H27A | 109.5 |
| C10—C9—H9 | 119.4 | N4—C27—H27B | 109.5 |
| C8—C9—H9 | 119.4 | C28—C27—H27B | 109.5 |

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| C9—C10—C11 | 120.15 (19) | H27A—C27—H27B | 108.1 |
| C9—C10—H10 | 119.9 | N1—C28—C27 | 110.61 (17) |
| C11—C10—H10 | 119.9 | N1—C28—H28A | 109.5 |
| C10—C11—C12 | 120.04 (19) | C27—C28—H28A | 109.5 |
| C10—C11—H11 | 120.0 | N1—C28—H28B | 109.5 |
| C12—C11—H11 | 120.0 | C27—C28—H28B | 109.5 |
| C13—C12—C11 | 119.24 (17) | H28A—C28—H28B | 108.1 |
| C13—C12—C14 | 117.33 (16) | N1—C29—C30 | 111.46 (17) |
| C11—C12—C14 | 123.43 (17) | N1—C29—H29A | 109.3 |
| C12—C13—C8 | 121.06 (17) | C30—C29—H29A | 109.3 |
| C12—C13—H13 | 119.5 | N1—C29—H29B | 109.3 |
| C8—C13—H13 | 119.5 | C30—C29—H29B | 109.3 |
| O1—C14—N2 | 123.71 (18) | H29A—C29—H29B | 108.0 |
| O1—C14—C12 | 121.12 (18) | C31—C30—C29 | 177.3 (2) |
| N2—C14—C12 | 115.16 (16) | C30—C31—C32 | 178.5 (2) |
| C16—C15—C20 | 119.81 (18) | C31—C32—S2 | 113.96 (15) |
| C16—C15—N2 | 122.85 (19) | C31—C32—H32A | 108.8 |
| C20—C15—N2 | 117.34 (17) | S2—C32—H32A | 108.8 |
| C17—C16—C15 | 119.7 (2) | C31—C32—H32B | 108.8 |
| C17—C16—H16 | 120.2 | S2—C32—H32B | 108.8 |
| C15—C16—H16 | 120.2 | H32A—C32—H32B | 107.7 |

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| C32—S2—C1—C2 | 86.2 (2) | C13—C12—C14—O1 | −18.3 (3) |
| C32—S2—C1—C6 | −95.30 (19) | C11—C12—C14—O1 | 160.92 (19) |
| C6—C1—C2—C3 | 1.0 (4) | C13—C12—C14—N2 | 160.74 (17) |
| S2—C1—C2—C3 | 179.6 (2) | C11—C12—C14—N2 | −20.0 (3) |
| C1—C2—C3—C4 | 0.7 (4) | C14—N2—C15—C16 | 17.0 (3) |
| C2—C3—C4—C5 | −1.2 (5) | C14—N2—C15—C20 | −163.6 (2) |
| C3—C4—C5—C6 | −0.1 (4) | C20—C15—C16—C17 | −0.8 (3) |
| C4—C5—C6—C1 | 1.8 (4) | N2—C15—C16—C17 | 178.5 (2) |
| C4—C5—C6—N3 | −176.7 (2) | C15—C16—C17—C18 | 0.5 (4) |
| C2—C1—C6—C5 | −2.2 (3) | C16—C17—C18—C19 | 0.2 (4) |
| S2—C1—C6—C5 | 179.22 (17) | C17—C18—C19—C20 | −0.6 (4) |
| C2—C1—C6—N3 | 176.3 (2) | C18—C19—C20—C15 | 0.3 (3) |
| S2—C1—C6—N3 | −2.2 (3) | C18—C19—C20—S1 | 176.77 (19) |
| C7—N3—C6—C5 | −1.6 (4) | C16—C15—C20—C19 | 0.4 (3) |
| C7—N3—C6—C1 | 179.9 (2) | N2—C15—C20—C19 | −178.96 (19) |
| C6—N3—C7—O2A | −15 (2) | C16—C15—C20—S1 | −176.02 (17) |
| C6—N3—C7—O2B | 9.3 (15) | N2—C15—C20—S1 | 4.6 (3) |
| C6—N3—C7—C8 | 180.0 (2) | C21—S1—C20—C19 | 72.16 (19) |
| O2A—C7—C8—C9 | 6 (2) | C21—S1—C20—C15 | −111.40 (17) |
| O2B—C7—C8—C9 | −17.5 (15) | C20—S1—C21—C22 | 66.21 (17) |
| N3—C7—C8—C9 | 171.90 (19) | C27—N4—C24—C23 | −71.5 (2) |
| O2A—C7—C8—C13 | −173 (2) | C25—N4—C24—C23 | 166.44 (17) |
| O2B—C7—C8—C13 | 162.6 (15) | C24—N4—C25—C26 | −177.46 (17) |
| N3—C7—C8—C13 | −7.9 (3) | C27—N4—C25—C26 | 59.2 (2) |
| C13—C8—C9—C10 | 2.5 (3) | C29—N1—C26—C25 | −176.08 (18) |
| C7—C8—C9—C10 | −177.4 (2) | C28—N1—C26—C25 | 59.8 (2) |

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| C8—C9—C10—C11 | −1.2 (3) | N4—C25—C26—N1 | −60.9 (2) |
| C9—C10—C11—C12 | −0.3 (3) | C24—N4—C27—C28 | 178.72 (17) |
| C10—C11—C12—C13 | 0.4 (3) | C25—N4—C27—C28 | −58.1 (2) |
| C10—C11—C12—C14 | −178.84 (18) | C29—N1—C28—C27 | 177.58 (17) |
| C11—C12—C13—C8 | 1.0 (3) | C26—N1—C28—C27 | −58.2 (2) |
| C14—C12—C13—C8 | −179.76 (16) | N4—C27—C28—N1 | 58.1 (2) |
| C9—C8—C13—C12 | −2.4 (3) | C26—N1—C29—C30 | 172.24 (18) |
| C7—C8—C13—C12 | 177.49 (18) | C28—N1—C29—C30 | −65.2 (2) |
| C15—N2—C14—O1 | −2.6 (3) | C1—S2—C32—C31 | 66.79 (18) |
| C15—N2—C14—C12 | 178.37 (19) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*A*···S1 | 0.83 (2) | 2.46 (2) | 2.9621 (18) | 120 (2) |
| N3—H3*A*···S2 | 0.83 (2) | 2.49 (2) | 2.9905 (19) | 120 (2) |
| C21—H21*B*···O2*A*$^{i}$ | 0.97 | 2.57 | 3.43 (3) | 148 |
| C21—H21*B*···O2*B*$^{i}$ | 0.97 | 2.34 | 3.230 (11) | 152 |
| C24—H24*A*···O1$^{ii}$ | 0.97 | 2.54 | 3.505 (3) | 171 |
| C26—H26*B*···S2$^{ii}$ | 0.97 | 2.85 | 3.632 (2) | 139 |
| C32—H32*B*···O1$^{iii}$ | 0.97 | 2.49 | 3.146 (3) | 125 |

Symmetry codes: (i) *x*−1/2, *y*−1/2, *z*; (ii) *x*, *y*−1, *z*; (iii) −*x*+1, *y*, −*z*+3/2.