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## Structure Reports

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## 4,6-Bis[4-(benzylsulfanyl)styryl]-2-(methylsulfanyl)pyrimidine

Min Wang, Le-Hua Cheng,\* Xian-Ping Chu and Shi-You Xu

Department of Chemistry, Chaohu College, Chaohu 238000, People's Republic of China

Correspondence e-mail: chlehua@sohu.com

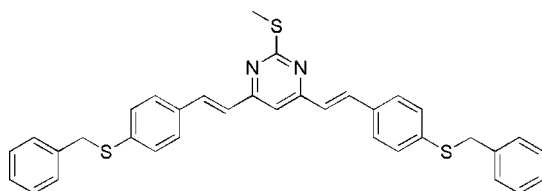
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.046;  $wR$  factor = 0.129; data-to-parameter ratio = 14.4.

The title compound,  $\text{C}_{35}\text{H}_{30}\text{N}_2\text{S}_3$ , has been synthesized by a solvent-free reaction. The molecule exhibits an *E,E* configuration, the benzene rings and pyrimidine rings being located on the opposite sides of the  $\text{C}=\text{C}$  bonds. The centroid-centroid separation of 3.5808 (17) Å indicates the existence of  $\pi$ - $\pi$  stacking between nearly parallel pyrimidine and benzene rings of adjacent molecules.

## Related literature

For details of the applications of conjugated organic molecules, see: Frederiksen *et al.* (2001); Zhao *et al.* (1995). For heterocycle-based two-photon absorbing chromophores exhibiting large TPA cross-sections, see: Huang *et al.* (2003).



## Experimental

## Crystal data

$\text{C}_{35}\text{H}_{30}\text{N}_2\text{S}_3$	$\gamma = 81.129$ (2)°
$M_r = 574.79$	$V = 1493.8$ (3) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.199$ (1) Å	Mo $K\alpha$ radiation
$b = 10.1694$ (15) Å	$\mu = 0.28$ mm <sup>-1</sup>
$c = 21.161$ (2) Å	$T = 298$ (2) K
$\alpha = 77.412$ (1)°	$0.50 \times 0.38 \times 0.31$ mm
$\beta = 88.425$ (3)°	

## Data collection

Bruker SMART CCD area detector diffractometer	7820 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5185 independent reflections
$T_{\min} = 0.875$ , $T_{\max} = 0.920$	3229 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	361 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.22$ e Å <sup>-3</sup>
5185 reflections	$\Delta\rho_{\text{min}} = -0.21$ e Å <sup>-3</sup>

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2372).

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**supplementary materials**

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## 4,6-Bis[4-(benzylsulfanyl)styryl]-2-(methylsulfanyl)pyrimidine

M. Wang, L.-H. Cheng, X.-P. Chu and S.-Y. Xu

### Comment

Two-photon absorption (TPA) processes in conjugated organic molecules have aroused considerable attention due to their potential applications in optical data storage, three-dimension fluorescence imaging, photodynamic therapy, two-photon upconversion lasing and three-dimension lithographic microfabrication (Frederiksen *et al.*, 2001; Zhao *et al.*, 1995). A sustained level of fundamental research over the past ten years has left organic nonlinear optical (NLO) well positioned to make a technological impact in a variety of disciplines. Some studies showed that the heterocycle-based two-photon absorbing chromophores exhibit large TPA cross-sections (Huang *et al.*, 2003). As part of our ongoing investigation on heterocycle-based two-photon absorbing chromophores, the title compound has been prepared and its crystal structure is presented here.

The molecule structure is shown in Fig. 1. Bond lengths and angles are normal. The C7-containing and C22-containing benzene rings are nearly coplanar with the pyrimidine ring, dihedral angles being 8.59 (2)° and 8.40 (2)°, respectively. In the crystal structure,  $\pi$ - $\pi$  stacking is observed between nearly parallel pyrimidine and C10<sup>i</sup>-containing benzene rings as shown in Fig. 2 [symmetry code: (i) 1 + *x,y,z*]; the dihedral angle and centroid-to-centroid separation being 8.69 (13)° and 3.5808 (17) Å, respectively.

### Experimental

At room temperature, t-BuOK (5.6 g, 50 mmol) was placed into a dry mortar and milled to very small, then 2-thiomethyl-4,6-dimethylpyrimidine (1.54 g, 10 mmol) and 4-benzylthiobenzaldehyde (4.56 g, 20 mmol) were added and mixed. The mixture was milled vigorously for about 20 min. The mixture became sticky and then continuously milled for 10 min. After completion of the reaction (monitored by TLC), the mixture was dispersed in 100 ml methanol. The residual solid was filtered and recrystallized from anhydrous dichloromethane/methanol solution, to give microcrystals (2.87 g, yield 50%). Single crystals suitable for X-ray analysis were obtained by slow evaporation from a dichloromethane/2-propanol (3:1) solution.

### Refinement

The H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 or 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C})$ .

### Figures

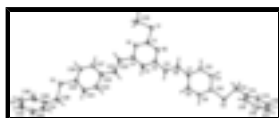


Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids for non-H atoms.

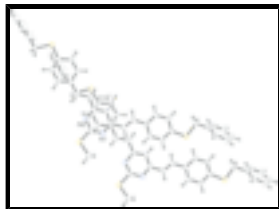


Fig. 2. A diagram showing  $\pi$ - $\pi$  stacking [symmetry code: (i)  $1 + x, y, z$ ].

## 4,6-Bis[4-(benzylsulfanyl)styryl]-2-(methylsulfanyl)pyrimidine

### Crystal data

$C_{35}H_{30}N_2S_3$	$Z = 2$
$M_r = 574.79$	$F_{000} = 604$
Triclinic, $P\bar{1}$	$D_x = 1.278 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 7.199 (1) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 10.1694 (15) \text{ \AA}$	Cell parameters from 2350 reflections
$c = 21.161 (2) \text{ \AA}$	$\theta = 2.5\text{--}25.8^\circ$
$\alpha = 77.412 (1)^\circ$	$\mu = 0.28 \text{ mm}^{-1}$
$\beta = 88.425 (3)^\circ$	$T = 298 (2) \text{ K}$
$\gamma = 81.129 (2)^\circ$	Block, red
$V = 1493.8 (3) \text{ \AA}^3$	$0.50 \times 0.38 \times 0.31 \text{ mm}$

### Data collection

Bruker SMART CCD area detector diffractometer	5185 independent reflections
Radiation source: fine-focus sealed tube	3229 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.026$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.875, T_{\text{max}} = 0.920$	$k = -12 \rightarrow 9$
7820 measured reflections	$l = -25 \rightarrow 25$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.129$	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.0894P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
5185 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$

361 parameters

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.57325 (12)	0.40771 (8)	0.15862 (4)	0.0709 (3)
S2	-0.76178 (11)	1.09386 (8)	0.14193 (4)	0.0630 (3)
S3	1.42863 (10)	0.70995 (8)	0.54464 (4)	0.0593 (2)
N1	0.6566 (3)	0.5069 (2)	0.25966 (10)	0.0453 (5)
N2	0.3517 (3)	0.5797 (2)	0.21019 (10)	0.0477 (6)
C1	0.5236 (4)	0.5089 (3)	0.21646 (12)	0.0461 (7)
C2	0.3081 (4)	0.6646 (3)	0.25115 (12)	0.0437 (6)
C3	0.4379 (4)	0.6735 (3)	0.29656 (12)	0.0472 (7)
H3	0.4085	0.7335	0.3241	0.057*
C4	0.6107 (4)	0.5926 (3)	0.30053 (12)	0.0435 (6)
C5	0.1233 (4)	0.7484 (3)	0.24433 (13)	0.0525 (7)
H5	0.0955	0.8108	0.2708	0.063*
C6	-0.0066 (4)	0.7414 (3)	0.20317 (13)	0.0487 (7)
H6	0.0239	0.6759	0.1785	0.058*
C7	-0.1931 (4)	0.8236 (3)	0.19117 (12)	0.0449 (7)
C8	-0.2598 (4)	0.9304 (3)	0.22157 (13)	0.0553 (8)
H8	-0.1856	0.9487	0.2529	0.066*
C9	-0.4317 (4)	1.0091 (3)	0.20649 (13)	0.0535 (8)
H9	-0.4712	1.0804	0.2272	0.064*
C10	-0.5476 (4)	0.9832 (3)	0.16040 (13)	0.0468 (7)
C11	-0.4868 (4)	0.8747 (3)	0.13147 (13)	0.0496 (7)
H11	-0.5639	0.8539	0.1016	0.060*
C12	-0.3126 (4)	0.7972 (3)	0.14656 (12)	0.0487 (7)
H12	-0.2740	0.7252	0.1263	0.058*
C13	-0.8416 (4)	1.0492 (3)	0.06998 (14)	0.0627 (9)
H13A	-0.7393	1.0448	0.0393	0.075*
H13B	-0.8820	0.9604	0.0813	0.075*
C14	-1.0021 (4)	1.1548 (3)	0.03979 (13)	0.0518 (7)
C15	-1.1850 (4)	1.1341 (3)	0.05280 (14)	0.0610 (8)
H15	-1.2083	1.0543	0.0808	0.073*

## supplementary materials

C16	-1.3336 (5)	1.2288 (4)	0.02532 (19)	0.0816 (11)
H16	-1.4562	1.2134	0.0352	0.098*
C17	-1.3021 (7)	1.3434 (5)	-0.01566 (19)	0.0933 (14)
H17	-1.4033	1.4061	-0.0351	0.112*
C18	-1.1220 (8)	1.3695 (4)	-0.02939 (19)	0.1124 (15)
H18	-1.1011	1.4499	-0.0574	0.135*
C19	-0.9702 (5)	1.2737 (4)	-0.00067 (17)	0.0872 (11)
H19	-0.8477	1.2910	-0.0091	0.105*
C20	0.7619 (4)	0.5923 (3)	0.34563 (12)	0.0481 (7)
H20	0.8696	0.5292	0.3446	0.058*
C21	0.7625 (4)	0.6709 (3)	0.38730 (12)	0.0486 (7)
H21	0.6516	0.7290	0.3911	0.058*
C22	0.9207 (4)	0.6763 (3)	0.42844 (12)	0.0442 (6)
C23	0.8985 (4)	0.7586 (3)	0.47332 (13)	0.0556 (8)
H23	0.7807	0.8077	0.4779	0.067*
C24	1.0456 (4)	0.7700 (3)	0.51137 (13)	0.0553 (8)
H24	1.0254	0.8246	0.5416	0.066*
C25	1.2236 (4)	0.6999 (3)	0.50432 (12)	0.0437 (6)
C26	1.2470 (4)	0.6161 (3)	0.45996 (12)	0.0502 (7)
H26	1.3648	0.5673	0.4549	0.060*
C27	1.0977 (4)	0.6045 (3)	0.42341 (13)	0.0505 (7)
H27	1.1165	0.5468	0.3945	0.061*
C28	1.3614 (4)	0.8283 (3)	0.59547 (16)	0.0743 (10)
H28A	1.2957	0.9133	0.5703	0.089*
H28B	1.2786	0.7914	0.6295	0.089*
C29	1.5394 (4)	0.8521 (3)	0.62436 (14)	0.0545 (8)
C30	1.6381 (5)	0.7501 (4)	0.66976 (15)	0.0777 (10)
H30	1.5944	0.6669	0.6825	0.093*
C31	1.8009 (6)	0.7694 (4)	0.69664 (17)	0.0919 (12)
H31	1.8660	0.6999	0.7278	0.110*
C32	1.8670 (5)	0.8905 (4)	0.67762 (17)	0.0742 (10)
H32	1.9762	0.9038	0.6962	0.089*
C33	1.7747 (5)	0.9907 (3)	0.63203 (16)	0.0704 (9)
H33	1.8214	1.0726	0.6186	0.085*
C34	1.6106 (5)	0.9720 (3)	0.60510 (15)	0.0682 (9)
H34	1.5477	1.0417	0.5735	0.082*
C35	0.8140 (5)	0.3378 (4)	0.17513 (18)	0.0965 (13)
H35A	0.8879	0.4104	0.1698	0.145*
H35B	0.8570	0.2800	0.1457	0.145*
H35C	0.8268	0.2855	0.2188	0.145*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0735 (6)	0.0698 (6)	0.0726 (6)	0.0162 (4)	-0.0277 (5)	-0.0374 (4)
S2	0.0491 (5)	0.0758 (6)	0.0681 (5)	0.0111 (4)	-0.0168 (4)	-0.0363 (4)
S3	0.0447 (4)	0.0671 (5)	0.0722 (5)	-0.0031 (4)	-0.0138 (4)	-0.0303 (4)
N1	0.0461 (14)	0.0443 (13)	0.0459 (13)	-0.0042 (11)	-0.0087 (11)	-0.0113 (10)

N2	0.0471 (14)	0.0467 (13)	0.0490 (13)	-0.0035 (11)	-0.0109 (11)	-0.0110 (11)
C1	0.0542 (18)	0.0397 (15)	0.0435 (15)	-0.0052 (13)	-0.0100 (14)	-0.0072 (12)
C2	0.0426 (16)	0.0443 (16)	0.0426 (15)	-0.0047 (13)	-0.0023 (13)	-0.0070 (13)
C3	0.0478 (17)	0.0544 (17)	0.0422 (15)	-0.0073 (14)	-0.0027 (13)	-0.0166 (13)
C4	0.0466 (17)	0.0442 (16)	0.0394 (14)	-0.0096 (13)	-0.0053 (13)	-0.0057 (12)
C5	0.0501 (18)	0.0574 (18)	0.0514 (17)	-0.0041 (14)	-0.0055 (14)	-0.0166 (14)
C6	0.0493 (17)	0.0429 (16)	0.0535 (17)	-0.0063 (13)	-0.0037 (14)	-0.0098 (13)
C7	0.0419 (16)	0.0429 (16)	0.0487 (16)	-0.0062 (13)	-0.0044 (13)	-0.0072 (13)
C8	0.0550 (19)	0.0578 (18)	0.0567 (18)	-0.0080 (15)	-0.0181 (15)	-0.0182 (15)
C9	0.0514 (18)	0.0501 (17)	0.0628 (19)	0.0007 (14)	-0.0109 (15)	-0.0250 (14)
C10	0.0417 (16)	0.0492 (16)	0.0503 (16)	-0.0036 (13)	-0.0047 (13)	-0.0141 (13)
C11	0.0428 (17)	0.0546 (17)	0.0551 (17)	-0.0064 (14)	-0.0102 (13)	-0.0189 (14)
C12	0.0518 (18)	0.0462 (16)	0.0519 (17)	-0.0067 (14)	-0.0030 (14)	-0.0192 (13)
C13	0.0527 (19)	0.074 (2)	0.066 (2)	0.0063 (16)	-0.0156 (15)	-0.0344 (17)
C14	0.0540 (19)	0.062 (2)	0.0413 (16)	0.0007 (15)	-0.0049 (14)	-0.0207 (15)
C15	0.054 (2)	0.069 (2)	0.0616 (19)	-0.0117 (17)	-0.0106 (16)	-0.0160 (16)
C16	0.056 (2)	0.106 (3)	0.084 (3)	0.006 (2)	-0.019 (2)	-0.034 (2)
C17	0.110 (4)	0.091 (3)	0.066 (3)	0.033 (3)	-0.032 (3)	-0.020 (2)
C18	0.153 (5)	0.090 (3)	0.074 (3)	-0.005 (3)	0.002 (3)	0.015 (2)
C19	0.083 (3)	0.102 (3)	0.070 (2)	-0.015 (2)	0.012 (2)	-0.006 (2)
C20	0.0444 (17)	0.0530 (17)	0.0465 (16)	-0.0057 (13)	-0.0058 (13)	-0.0099 (13)
C21	0.0403 (16)	0.0590 (18)	0.0472 (16)	-0.0062 (14)	-0.0029 (13)	-0.0138 (14)
C22	0.0383 (15)	0.0511 (16)	0.0454 (16)	-0.0102 (13)	-0.0017 (12)	-0.0122 (13)
C23	0.0405 (17)	0.071 (2)	0.0616 (18)	-0.0047 (15)	-0.0001 (14)	-0.0299 (16)
C24	0.0461 (18)	0.071 (2)	0.0581 (18)	-0.0081 (15)	0.0002 (14)	-0.0339 (15)
C25	0.0427 (16)	0.0449 (16)	0.0439 (15)	-0.0073 (13)	-0.0057 (12)	-0.0094 (13)
C26	0.0423 (16)	0.0544 (17)	0.0535 (17)	0.0021 (14)	-0.0070 (13)	-0.0167 (14)
C27	0.0536 (18)	0.0534 (18)	0.0495 (16)	-0.0038 (14)	-0.0067 (14)	-0.0238 (14)
C28	0.055 (2)	0.094 (3)	0.088 (2)	-0.0027 (18)	-0.0088 (18)	-0.053 (2)
C29	0.0501 (18)	0.068 (2)	0.0533 (18)	-0.0103 (16)	-0.0037 (14)	-0.0294 (16)
C30	0.100 (3)	0.076 (2)	0.063 (2)	-0.042 (2)	-0.020 (2)	-0.0031 (18)
C31	0.110 (3)	0.091 (3)	0.074 (2)	-0.029 (3)	-0.044 (2)	-0.001 (2)
C32	0.066 (2)	0.094 (3)	0.075 (2)	-0.024 (2)	-0.0118 (19)	-0.036 (2)
C33	0.085 (3)	0.065 (2)	0.074 (2)	-0.034 (2)	0.005 (2)	-0.0270 (19)
C34	0.085 (3)	0.0491 (19)	0.073 (2)	-0.0029 (18)	-0.0146 (19)	-0.0211 (16)
C35	0.080 (3)	0.110 (3)	0.106 (3)	0.032 (2)	-0.030 (2)	-0.066 (2)

*Geometric parameters (Å, °)*

S1—C1	1.760 (3)	C16—H16	0.9300
S1—C35	1.782 (3)	C17—C18	1.374 (6)
S2—C10	1.761 (3)	C17—H17	0.9300
S2—C13	1.812 (3)	C18—C19	1.401 (5)
S3—C25	1.753 (3)	C18—H18	0.9300
S3—C28	1.788 (3)	C19—H19	0.9300
N1—C1	1.336 (3)	C20—C21	1.314 (3)
N1—C4	1.357 (3)	C20—H20	0.9300
N2—C1	1.327 (3)	C21—C22	1.467 (3)
N2—C2	1.350 (3)	C21—H21	0.9300

## supplementary materials

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C2—C3	1.385 (3)	C22—C27	1.381 (3)
C2—C5	1.457 (3)	C22—C23	1.387 (3)
C3—C4	1.376 (3)	C23—C24	1.381 (3)
C3—H3	0.9300	C23—H23	0.9300
C4—C20	1.466 (3)	C24—C25	1.388 (3)
C5—C6	1.316 (3)	C24—H24	0.9300
C5—H5	0.9300	C25—C26	1.390 (3)
C6—C7	1.465 (3)	C26—C27	1.375 (3)
C6—H6	0.9300	C26—H26	0.9300
C7—C12	1.389 (3)	C27—H27	0.9300
C7—C8	1.397 (3)	C28—C29	1.509 (4)
C8—C9	1.370 (4)	C28—H28A	0.9700
C8—H8	0.9300	C28—H28B	0.9700
C9—C10	1.394 (3)	C29—C30	1.371 (4)
C9—H9	0.9300	C29—C34	1.371 (4)
C10—C11	1.383 (3)	C30—C31	1.376 (4)
C11—C12	1.380 (3)	C30—H30	0.9300
C11—H11	0.9300	C31—C32	1.363 (5)
C12—H12	0.9300	C31—H31	0.9300
C13—C14	1.502 (4)	C32—C33	1.345 (4)
C13—H13A	0.9700	C32—H32	0.9300
C13—H13B	0.9700	C33—C34	1.382 (4)
C14—C19	1.369 (4)	C33—H33	0.9300
C14—C15	1.376 (4)	C34—H34	0.9300
C15—C16	1.372 (4)	C35—H35A	0.9600
C15—H15	0.9300	C35—H35B	0.9600
C16—C17	1.339 (5)	C35—H35C	0.9600
C1—S1—C35	102.24 (14)	C17—C18—H18	120.3
C10—S2—C13	102.92 (12)	C19—C18—H18	120.3
C25—S3—C28	106.17 (13)	C14—C19—C18	120.0 (4)
C1—N1—C4	115.2 (2)	C14—C19—H19	120.0
C1—N2—C2	115.8 (2)	C18—C19—H19	120.0
N2—C1—N1	128.4 (2)	C21—C20—C4	127.4 (3)
N2—C1—S1	112.86 (18)	C21—C20—H20	116.3
N1—C1—S1	118.8 (2)	C4—C20—H20	116.3
N2—C2—C3	120.5 (2)	C20—C21—C22	126.5 (3)
N2—C2—C5	117.6 (2)	C20—C21—H21	116.7
C3—C2—C5	121.8 (2)	C22—C21—H21	116.7
C4—C3—C2	119.3 (2)	C27—C22—C23	117.0 (2)
C4—C3—H3	120.3	C27—C22—C21	122.5 (2)
C2—C3—H3	120.3	C23—C22—C21	120.5 (2)
N1—C4—C3	120.8 (2)	C24—C23—C22	122.2 (3)
N1—C4—C20	114.0 (2)	C24—C23—H23	118.9
C3—C4—C20	125.2 (2)	C22—C23—H23	118.9
C6—C5—C2	124.2 (2)	C23—C24—C25	119.9 (2)
C6—C5—H5	117.9	C23—C24—H24	120.1
C2—C5—H5	117.9	C25—C24—H24	120.1
C5—C6—C7	128.3 (3)	C24—C25—C26	118.4 (2)
C5—C6—H6	115.8	C24—C25—S3	126.20 (19)



C7—C6—H6	115.8	C26—C25—S3	115.4 (2)
C12—C7—C8	116.8 (2)	C27—C26—C25	120.7 (2)
C12—C7—C6	119.4 (2)	C27—C26—H26	119.7
C8—C7—C6	123.9 (2)	C25—C26—H26	119.7
C9—C8—C7	121.9 (2)	C26—C27—C22	121.8 (2)
C9—C8—H8	119.1	C26—C27—H27	119.1
C7—C8—H8	119.1	C22—C27—H27	119.1
C8—C9—C10	120.5 (2)	C29—C28—S3	107.2 (2)
C8—C9—H9	119.8	C29—C28—H28A	110.3
C10—C9—H9	119.8	S3—C28—H28A	110.3
C11—C10—C9	118.5 (2)	C29—C28—H28B	110.3
C11—C10—S2	124.3 (2)	S3—C28—H28B	110.3
C9—C10—S2	117.21 (19)	H28A—C28—H28B	108.5
C12—C11—C10	120.5 (2)	C30—C29—C34	118.2 (3)
C12—C11—H11	119.8	C30—C29—C28	119.7 (3)
C10—C11—H11	119.8	C34—C29—C28	122.1 (3)
C11—C12—C7	121.9 (2)	C29—C30—C31	120.8 (3)
C11—C12—H12	119.0	C29—C30—H30	119.6
C7—C12—H12	119.0	C31—C30—H30	119.6
C14—C13—S2	109.33 (18)	C32—C31—C30	120.0 (3)
C14—C13—H13A	109.8	C32—C31—H31	120.0
S2—C13—H13A	109.8	C30—C31—H31	120.0
C14—C13—H13B	109.8	C33—C32—C31	120.2 (3)
S2—C13—H13B	109.8	C33—C32—H32	119.9
H13A—C13—H13B	108.3	C31—C32—H32	119.9
C19—C14—C15	118.6 (3)	C32—C33—C34	120.0 (3)
C19—C14—C13	120.9 (3)	C32—C33—H33	120.0
C15—C14—C13	120.5 (3)	C34—C33—H33	120.0
C16—C15—C14	121.4 (3)	C29—C34—C33	120.8 (3)
C16—C15—H15	119.3	C29—C34—H34	119.6
C14—C15—H15	119.3	C33—C34—H34	119.6
C17—C16—C15	120.0 (4)	S1—C35—H35A	109.5
C17—C16—H16	120.0	S1—C35—H35B	109.5
C15—C16—H16	120.0	H35A—C35—H35B	109.5
C16—C17—C18	120.8 (4)	S1—C35—H35C	109.5
C16—C17—H17	119.6	H35A—C35—H35C	109.5
C18—C17—H17	119.6	H35B—C35—H35C	109.5
C17—C18—C19	119.3 (4)		
C2—N2—C1—N1	2.8 (4)	C13—C14—C15—C16	-179.5 (2)
C2—N2—C1—S1	-176.85 (19)	C14—C15—C16—C17	0.8 (5)
C4—N1—C1—N2	-2.8 (4)	C15—C16—C17—C18	-1.8 (6)
C4—N1—C1—S1	176.89 (19)	C16—C17—C18—C19	0.9 (6)
C35—S1—C1—N2	175.6 (2)	C15—C14—C19—C18	-1.9 (5)
C35—S1—C1—N1	-4.1 (3)	C13—C14—C19—C18	178.6 (3)
C1—N2—C2—C3	-0.5 (4)	C17—C18—C19—C14	1.0 (6)
C1—N2—C2—C5	177.7 (2)	N1—C4—C20—C21	175.0 (3)
N2—C2—C3—C4	-1.4 (4)	C3—C4—C20—C21	-3.0 (5)
C5—C2—C3—C4	-179.5 (2)	C4—C20—C21—C22	-174.9 (2)
C1—N1—C4—C3	0.4 (4)	C20—C21—C22—C27	5.9 (5)

## supplementary materials

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C1—N1—C4—C20	-177.7 (2)	C20—C21—C22—C23	-176.1 (3)
C2—C3—C4—N1	1.4 (4)	C27—C22—C23—C24	0.4 (4)
C2—C3—C4—C20	179.3 (2)	C21—C22—C23—C24	-177.7 (3)
N2—C2—C5—C6	3.6 (4)	C22—C23—C24—C25	1.4 (5)
C3—C2—C5—C6	-178.2 (3)	C23—C24—C25—C26	-1.9 (4)
C2—C5—C6—C7	-177.8 (3)	C23—C24—C25—S3	175.9 (2)
C5—C6—C7—C12	-178.0 (3)	C28—S3—C25—C24	-0.3 (3)
C5—C6—C7—C8	2.8 (5)	C28—S3—C25—C26	177.6 (2)
C12—C7—C8—C9	-2.5 (4)	C24—C25—C26—C27	0.8 (4)
C6—C7—C8—C9	176.7 (3)	S3—C25—C26—C27	-177.3 (2)
C7—C8—C9—C10	1.0 (5)	C25—C26—C27—C22	0.9 (4)
C8—C9—C10—C11	1.3 (4)	C23—C22—C27—C26	-1.5 (4)
C8—C9—C10—S2	-177.6 (2)	C21—C22—C27—C26	176.6 (3)
C13—S2—C10—C11	-10.8 (3)	C25—S3—C28—C29	-173.1 (2)
C13—S2—C10—C9	168.1 (2)	S3—C28—C29—C30	-70.1 (3)
C9—C10—C11—C12	-2.1 (4)	S3—C28—C29—C34	107.6 (3)
S2—C10—C11—C12	176.7 (2)	C34—C29—C30—C31	2.0 (5)
C10—C11—C12—C7	0.5 (4)	C28—C29—C30—C31	179.8 (3)
C8—C7—C12—C11	1.7 (4)	C29—C30—C31—C32	-0.8 (6)
C6—C7—C12—C11	-177.5 (2)	C30—C31—C32—C33	-0.8 (6)
C10—S2—C13—C14	-168.0 (2)	C31—C32—C33—C34	1.1 (5)
S2—C13—C14—C19	83.3 (3)	C30—C29—C34—C33	-1.7 (5)
S2—C13—C14—C15	-96.2 (3)	C28—C29—C34—C33	-179.5 (3)
C19—C14—C15—C16	1.1 (4)	C32—C33—C34—C29	0.2 (5)

Fig. 1

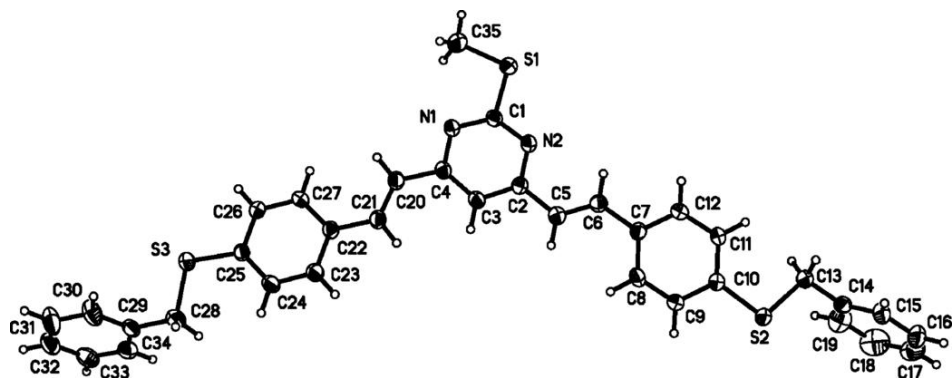


Fig. 2

