

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1-Benzhydryl-4-(4-chlorophenyl)sulfonylpiperazine

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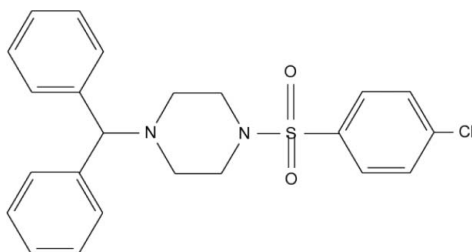
Received 10 December 2007; accepted 20 December 2007

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.051; wR factor = 0.147; data-to-parameter ratio = 14.5.

The title compound, $\text{C}_{23}\text{H}_{23}\text{ClN}_2\text{O}_2\text{S}$, was synthesized by the nucleophilic substitution of 1-benzhydrylpiperazine with 4-chlorophenylsulfonyl chloride. The piperazine ring is in a chair conformation. The geometry around the S atom is that of a distorted tetrahedron. There is a large range of bond angles around the piperazine N atoms. The dihedral angle between the least-squares plane (p1) defined by the four coplanar C atoms of the piperazine ring and the benzene ring is 81.6 (1)°. The dihedral angles between p1 and the phenyl rings are 76.2 (1) and 72.9 (2)°. The two phenyl rings make a dihedral angle of 65.9 (1)°. Intramolecular C—H...O hydrogen bonds are present.

Related literature

For related literature, see: Bassindale (1984); Berkheij *et al.* (2005); Campbell *et al.* (1973); Cremer & Pople (1975); Dinsmore & Beshore (2002); Humle & Cherrier (1999); Katzung (1995).



Experimental

Crystal data

$\text{C}_{23}\text{H}_{23}\text{ClN}_2\text{O}_2\text{S}$
 $M_r = 426.94$
 Monoclinic, $P2_1/c$

$a = 9.392$ (7) Å
 $b = 13.114$ (10) Å
 $c = 19.225$ (11) Å

$\beta = 113.645$ (3)°
 $V = 2169$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.29$ mm⁻¹
 $T = 295$ (2) K
 $0.25 \times 0.20 \times 0.20$ mm

Data collection

MacScience DIPLabo 32001 diffractometer
 Absorption correction: none
 7255 measured reflections

3818 independent reflections
 2917 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.147$
 $S = 1.08$
 3818 reflections

263 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------|-------|-------------|-------------|---------------|
| C2—H2A...O8 | 0.97 | 2.49 | 2.890 (3) | 105 |
| C6—H6B...O9 | 0.97 | 2.56 | 2.965 (3) | 105 |
| C11—H11...O9 | 0.93 | 2.53 | 2.905 (3) | 104 |

Data collection: *XPRESS* (MacScience, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *PLATON*.

The authors are grateful to DST/CSIR, New Delhi, for financial support under the projects SP/I2/FOO/93 and 01(1904)/03/EMR-II 2004. The authors also acknowledge DST-FIST and UGC-SAP (phase I) for support with the collection of CHNS and IR data.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2365).

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Acta Cryst. (2008). E64, o358 [doi:10.1107/S1600536807067888]

1-Benzhydryl-4-(4-chlorophenylsulfonyl)piperazine

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Comment

Piperazines are among the most important building blocks in today's drug discovery. The piperazine nucleus is capable of binding to multiple receptors with high affinity and therefore piperazine has been classified as a privileged structure (Dinsmore *et al.*, 2002). They are found in biologically active compounds across a number of different therapeutic areas (Berkheij *et al.*, 2005) such as antifungal, antibacterial, antimalarial, antipsychotic, antidepressant and antitumour activity against colon, prostate, breast, lung and leukemia tumors (Humble & Cherrier, 1999). 1-Benzylpiperazine was originally synthesized as a potential antihelminthic (Campbell *et al.*, 1973) and these derivatives were found to possess excellent pharmacological activities such as vasodilator, hypotensive, antiviral activity and cerebral blood flow increasing actions, broad pharmacological action on central nervous system (CNS), especially on dopaminergic neurotransmission. Sulfonamides are among the most widely used antibacterial agents (Katzung *et al.*, 1995). Piperazine sulfonamides exhibit diverse therapeutic activity such as antibacterial activity, MMP-3 inhibition and carbonic anhydrase inhibition. Encouraged by the above information, the title compound was synthesized and herein we report its crystal structure.

A perspective view of the title compound is shown in Fig. 1. A study of torsion angles, asymmetry parameters and least-squares plane calculations reveal that the piperazine ring in the structure is in a chair conformation. This has been confirmed by the puckering parameters $q_2=0.0291$ (24) Å, $q_3=0.5969$ (26) Å, $Q_T=0.5977$ (26) Å, $\theta=3.07$ (23)° and $\varphi=198$ (5)° (Cremer & Pople, 1975). The conformation of the attachment of the diphenylmethyl and the sulfonyl groups to the piperazine ring are best described by the torsion angle values of 166.6 (2)° and -177.4 (2)° for S7—N1—C2—C3 and C17—N4—C5—C6, respectively; *i.e.* they adopt +antiperiplanar and -antiperiplanar conformations, respectively. The bonds N1—S7 and N4—C17 connecting the sulfonyl and the diphenyl groups make angles of 86.00 (11)° and 72.92 (14)°, respectively, with the Cremer and Pople plane of the piperazine ring and thus are in the equatorial plane of the piperazine ring.

The bond angles about the S atom shows significant deviation from that of a regular tetrahedron, with the largest deviations being observed for O9—S7—O8 [119.92 (12)°] and O9—S7—C10 [107.88 (12)°]. The widening of O8—S7—O9 is due to the repulsive interactions between the S=O bonds and the non-bonded interactions involving the two S=O bonds and the varied steric hindrance of the substituents. The structure thus has less steric interference. The reduction of the N1—S7—C10 angle from the ideal tetrahedral value is attributed to the Thorpe-Ingold effect (Bassindale, 1984). The sulfonyl O atoms, O8 and O9, are oriented in -synclinal and +synclinal conformations, respectively, as indicated by the torsion angle values of -42.1 (2)° and 53.96 (19)° for C2—N1—S7—O8 and C6—N1—S7—O9, respectively.

Experimental

A solution of 1-benzhydryl-piperazine (0.5 g, 1.98 mmol) in dry dichloromethane was taken, and cooled to 0–5° C in an ice bath. Then triethylamine (0.601 g, 5.94 mmol) was added to the cold reaction mixture and stirred for 10 minutes. Then 4-chloro-benzenesulfonyl chloride (0.417 g, 1.98 mmol) was added. The reaction mixture was stirred at room temperature for 5 hrs. The reaction mixture was monitored by TLC. On completion of the reaction, the solvent was removed under reduced pressure and the residue was taken in water and extracted with ethyl acetate. Finally water wash was given to organic

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layer and dried with anhydrous sodium sulfate. The solvent was evaporated to get crude product, which was purified by column chromatography over silica gel using hexane: ethyl acetate (8:2) as an eluent. Pure white crystals were obtained due to the slow evaporation of the solvent with a yield of 90%. *M.p.* 428.1 K.

$^1\text{H NMR}$ (DMSO, 400 MHz): δ 7.7–7.8 (m, 4H, Ar—H), 7.4 (d, 4H, Ar—H), 7.25 (t, 4H, Ar—H), 7.16 (t, 2H, Ar—H), 4.32 (s, 1H, —CH), 3.32 (dd, 4H, —CH₂), 2.41 (dd, 4H, —CH₂).

MS (ESI + ion): $m/z = 427.9$

IR (KBr, cm^{-1}): 2961, 2889, 1350, 1279, 707.

Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{ClN}_2\text{O}_2\text{S}$ (in %): C-59.87, H-4.81, N-6.07, S-6.95. Found C-59.82, H-4.78, N-6.04, S-6.90%.

Refinement

H atoms were placed at idealized positions and allowed to ride on their parent atoms with C—H distances in the range 0.92–0.97 Å and O—H = 0.82 Å; $U_{\text{iso}}(\text{H})$ values were set equal to $1.2U_{\text{eq}}(\text{carrier atom})$.

Figures

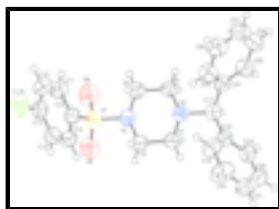


Fig. 1. The molecular structure, with atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radius.

1-Benzhydryl-4-(4-chlorophenylsulfonyl)piperazine

Crystal data

$\text{C}_{23}\text{H}_{23}\text{ClN}_2\text{O}_2\text{S}$

$M_r = 426.94$

Monoclinic, $P2_1/c$

Hall symbol: -P 2 ybc

$a = 9.392$ (7) Å

$b = 13.114$ (10) Å

$c = 19.225$ (11) Å

$\beta = 113.645$ (3)°

$V = 2169$ (3) Å³

$Z = 4$

$F_{000} = 896$

$D_x = 1.307$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 7255 reflections

$\theta = 2.3$ – 25.0 °

$\mu = 0.29$ mm⁻¹

$T = 295$ (2) K

Block, white

$0.25 \times 0.20 \times 0.20$ mm

Data collection

MacScience DIPLabo 32001

2917 reflections with $I > 2\sigma(I)$

diffractometer
 Radiation source: fine-focus sealed tube $R_{\text{int}} = 0.024$
 Monochromator: graphite $\theta_{\text{max}} = 25.0^\circ$
 $T = 295(2)$ K $\theta_{\text{min}} = 2.3^\circ$
 ω scans $h = -11 \rightarrow 11$
 Absorption correction: none $k = -15 \rightarrow 15$
 7255 measured reflections $l = -22 \rightarrow 22$
 3818 independent reflections

Refinement

Refinement on F^2 Hydrogen site location: inferred from neighbouring sites
 Least-squares matrix: full H-atom parameters constrained
 $R[F^2 > 2\sigma(F^2)] = 0.051$ $w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 0.4503P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.147$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.08$ $\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$
 3818 reflections $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
 263 parameters Extinction correction: SHELXL97 (Sheldrick, 1997),
 $FC^* = KFC[1 + 0.001XFC^2\Lambda^3/\text{SIN}(2\Theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.065 (4)
 Secondary atom site location: difference Fourier map

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All e.s.d.'s are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R -factors wR and all goodnesses 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 observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating $-R$ -factor-obs *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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|---------------|--------------|----------------------------------|
| Cl16 | 0.45997 (9) | 0.44356 (6) | 0.31602 (5) | 0.0932 (3) |
| S7 | 0.02536 (7) | 0.06459 (5) | 0.20336 (3) | 0.0673 (2) |
| O8 | -0.12416 (19) | 0.08971 (15) | 0.20131 (11) | 0.0815 (7) |
| O9 | 0.0391 (2) | 0.02536 (16) | 0.13714 (9) | 0.0878 (7) |
| N1 | 0.1012 (2) | -0.02030 (15) | 0.27063 (10) | 0.0592 (6) |
| N4 | 0.28463 (19) | -0.12983 (14) | 0.40601 (10) | 0.0540 (6) |
| C2 | 0.0814 (3) | -0.00363 (19) | 0.34202 (13) | 0.0639 (8) |
| C3 | 0.1236 (3) | -0.09986 (19) | 0.38885 (13) | 0.0602 (8) |
| C5 | 0.2974 (3) | -0.14861 (19) | 0.33344 (12) | 0.0611 (8) |

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| | | | | |
|-----|------------|---------------|--------------|-------------|
| C6 | 0.2608 (3) | -0.05271 (19) | 0.28593 (13) | 0.0631 (8) |
| C10 | 0.1441 (3) | 0.17362 (19) | 0.23278 (12) | 0.0601 (8) |
| C11 | 0.2522 (3) | 0.1935 (2) | 0.20299 (16) | 0.0773 (10) |
| C12 | 0.3485 (4) | 0.2768 (2) | 0.22841 (18) | 0.0847 (12) |
| C13 | 0.3378 (3) | 0.3395 (2) | 0.28381 (14) | 0.0670 (8) |
| C14 | 0.2302 (3) | 0.3203 (2) | 0.31371 (13) | 0.0652 (8) |
| C15 | 0.1327 (3) | 0.23722 (19) | 0.28775 (13) | 0.0631 (8) |
| C17 | 0.3273 (2) | -0.22232 (17) | 0.45406 (12) | 0.0563 (7) |
| C18 | 0.3073 (3) | -0.20476 (18) | 0.52750 (12) | 0.0569 (7) |
| C19 | 0.3666 (3) | -0.1188 (2) | 0.57137 (15) | 0.0762 (10) |
| C20 | 0.3439 (4) | -0.1023 (3) | 0.63736 (15) | 0.0896 (11) |
| C21 | 0.2629 (3) | -0.1724 (3) | 0.66053 (16) | 0.0884 (13) |
| C22 | 0.2052 (3) | -0.2577 (3) | 0.61814 (18) | 0.0877 (11) |
| C23 | 0.2268 (3) | -0.2744 (2) | 0.55178 (16) | 0.0725 (9) |
| C24 | 0.4921 (2) | -0.25730 (17) | 0.46936 (12) | 0.0556 (7) |
| C25 | 0.5204 (3) | -0.3596 (2) | 0.46298 (15) | 0.0710 (9) |
| C26 | 0.6693 (4) | -0.3932 (2) | 0.47724 (17) | 0.0849 (11) |
| C27 | 0.7892 (3) | -0.3270 (3) | 0.49653 (15) | 0.0819 (13) |
| C28 | 0.7633 (3) | -0.2248 (3) | 0.50267 (15) | 0.0785 (10) |
| C29 | 0.6157 (3) | -0.1903 (2) | 0.48981 (14) | 0.0700 (8) |
| H2A | -0.02550 | 0.01470 | 0.33090 | 0.0770* |
| H2B | 0.14780 | 0.05190 | 0.37020 | 0.0770* |
| H3A | 0.11070 | -0.08900 | 0.43590 | 0.0720* |
| H3B | 0.05410 | -0.15440 | 0.36130 | 0.0720* |
| H5A | 0.22580 | -0.20230 | 0.30600 | 0.0730* |
| H5B | 0.40200 | -0.17110 | 0.34290 | 0.0730* |
| H6A | 0.33330 | 0.00080 | 0.31280 | 0.0760* |
| H6B | 0.27090 | -0.06560 | 0.23850 | 0.0760* |
| H11 | 0.26010 | 0.15100 | 0.16600 | 0.0930* |
| H12 | 0.42120 | 0.29090 | 0.20820 | 0.1020* |
| H14 | 0.22290 | 0.36260 | 0.35100 | 0.0780* |
| H15 | 0.05880 | 0.22390 | 0.30740 | 0.0760* |
| H17 | 0.25590 | -0.27700 | 0.42630 | 0.0680* |
| H19 | 0.42240 | -0.07150 | 0.55640 | 0.0910* |
| H20 | 0.38330 | -0.04380 | 0.66600 | 0.1080* |
| H21 | 0.24770 | -0.16160 | 0.70490 | 0.1060* |
| H22 | 0.15070 | -0.30520 | 0.63380 | 0.1050* |
| H23 | 0.18670 | -0.33290 | 0.52340 | 0.0870* |
| H25 | 0.43890 | -0.40610 | 0.44900 | 0.0850* |
| H26 | 0.68700 | -0.46240 | 0.47350 | 0.1020* |
| H27 | 0.88860 | -0.35040 | 0.50560 | 0.0980* |
| H28 | 0.84530 | -0.17880 | 0.51550 | 0.0940* |
| H29 | 0.59950 | -0.12130 | 0.49500 | 0.0840* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|------------|------------|------------|-------------|------------|------------|
| Cl16 | 0.0815 (5) | 0.0828 (5) | 0.1088 (6) | -0.0121 (4) | 0.0313 (4) | 0.0117 (4) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| S7 | 0.0656 (4) | 0.0731 (4) | 0.0505 (4) | 0.0021 (3) | 0.0100 (3) | 0.0025 (3) |
| O8 | 0.0547 (10) | 0.0906 (13) | 0.0809 (12) | 0.0060 (9) | 0.0079 (8) | 0.0115 (10) |
| O9 | 0.1093 (14) | 0.0931 (13) | 0.0481 (9) | 0.0001 (12) | 0.0181 (9) | -0.0040 (10) |
| N1 | 0.0570 (11) | 0.0656 (11) | 0.0507 (10) | 0.0035 (9) | 0.0170 (8) | 0.0024 (9) |
| N4 | 0.0527 (10) | 0.0602 (11) | 0.0488 (9) | 0.0038 (8) | 0.0199 (8) | 0.0002 (8) |
| C2 | 0.0625 (13) | 0.0731 (15) | 0.0598 (13) | 0.0111 (11) | 0.0283 (11) | 0.0045 (12) |
| C3 | 0.0561 (13) | 0.0687 (14) | 0.0586 (13) | 0.0073 (11) | 0.0258 (10) | 0.0003 (12) |
| C5 | 0.0633 (14) | 0.0705 (14) | 0.0511 (12) | 0.0099 (11) | 0.0247 (10) | -0.0015 (11) |
| C6 | 0.0602 (14) | 0.0752 (16) | 0.0552 (13) | 0.0064 (11) | 0.0246 (10) | 0.0004 (12) |
| C10 | 0.0624 (13) | 0.0664 (14) | 0.0488 (12) | 0.0087 (11) | 0.0196 (10) | 0.0103 (11) |
| C11 | 0.0962 (19) | 0.0804 (18) | 0.0711 (16) | 0.0040 (15) | 0.0502 (15) | 0.0042 (15) |
| C12 | 0.091 (2) | 0.089 (2) | 0.096 (2) | -0.0023 (16) | 0.0603 (17) | 0.0113 (18) |
| C13 | 0.0623 (14) | 0.0679 (15) | 0.0674 (15) | 0.0039 (12) | 0.0226 (12) | 0.0163 (13) |
| C14 | 0.0719 (15) | 0.0680 (15) | 0.0563 (13) | 0.0042 (12) | 0.0264 (11) | 0.0023 (12) |
| C15 | 0.0621 (14) | 0.0718 (15) | 0.0606 (13) | 0.0049 (12) | 0.0299 (11) | 0.0057 (12) |
| C17 | 0.0547 (12) | 0.0559 (12) | 0.0539 (12) | -0.0037 (10) | 0.0171 (9) | -0.0030 (10) |
| C18 | 0.0503 (12) | 0.0650 (14) | 0.0533 (12) | 0.0016 (10) | 0.0186 (9) | 0.0083 (11) |
| C19 | 0.0865 (18) | 0.0880 (18) | 0.0602 (14) | -0.0231 (15) | 0.0359 (13) | -0.0095 (14) |
| C20 | 0.093 (2) | 0.118 (2) | 0.0596 (15) | -0.0119 (18) | 0.0325 (14) | -0.0179 (17) |
| C21 | 0.0703 (17) | 0.139 (3) | 0.0609 (15) | 0.0153 (18) | 0.0315 (13) | 0.0205 (19) |
| C22 | 0.0742 (18) | 0.112 (2) | 0.090 (2) | 0.0156 (17) | 0.0467 (16) | 0.040 (2) |
| C23 | 0.0617 (14) | 0.0716 (16) | 0.0852 (18) | 0.0061 (12) | 0.0305 (13) | 0.0190 (14) |
| C24 | 0.0558 (12) | 0.0585 (13) | 0.0482 (11) | 0.0026 (10) | 0.0164 (9) | 0.0009 (10) |
| C25 | 0.0751 (16) | 0.0623 (14) | 0.0759 (16) | 0.0023 (12) | 0.0306 (13) | -0.0057 (13) |
| C26 | 0.087 (2) | 0.0782 (18) | 0.090 (2) | 0.0235 (16) | 0.0360 (16) | -0.0004 (16) |
| C27 | 0.0639 (16) | 0.113 (3) | 0.0660 (16) | 0.0199 (16) | 0.0230 (13) | -0.0014 (16) |
| C28 | 0.0571 (15) | 0.101 (2) | 0.0690 (16) | -0.0054 (14) | 0.0166 (12) | -0.0045 (15) |
| C29 | 0.0605 (14) | 0.0712 (15) | 0.0726 (15) | -0.0041 (12) | 0.0207 (12) | -0.0055 (13) |

Geometric parameters (Å, °)

| | | | |
|----------|-------------|---------|-----------|
| C116—C13 | 1.730 (3) | C25—C26 | 1.385 (5) |
| S7—O8 | 1.427 (2) | C26—C27 | 1.351 (5) |
| S7—O9 | 1.4261 (18) | C27—C28 | 1.376 (6) |
| S7—N1 | 1.637 (2) | C28—C29 | 1.383 (4) |
| S7—C10 | 1.761 (3) | C2—H2A | 0.9692 |
| N1—C2 | 1.473 (3) | C2—H2B | 0.9704 |
| N1—C6 | 1.470 (4) | C3—H3A | 0.9701 |
| N4—C3 | 1.466 (4) | C3—H3B | 0.9700 |
| N4—C5 | 1.468 (3) | C5—H5A | 0.9704 |
| N4—C17 | 1.479 (3) | C5—H5B | 0.9705 |
| C2—C3 | 1.508 (3) | C6—H6A | 0.9699 |
| C5—C6 | 1.511 (3) | C6—H6B | 0.9687 |
| C10—C11 | 1.376 (4) | C11—H11 | 0.9296 |
| C10—C15 | 1.384 (3) | C12—H12 | 0.9296 |
| C11—C12 | 1.377 (4) | C14—H14 | 0.9305 |
| C12—C13 | 1.381 (4) | C15—H15 | 0.9302 |
| C13—C14 | 1.372 (4) | C17—H17 | 0.9806 |
| C14—C15 | 1.381 (4) | C19—H19 | 0.9291 |

supplementary materials

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|-------------------------|-----------|------------------------|--------|
| C17—C18 | 1.515 (3) | C20—H20 | 0.9302 |
| C17—C24 | 1.526 (3) | C21—H21 | 0.9305 |
| C18—C19 | 1.384 (4) | C22—H22 | 0.9297 |
| C18—C23 | 1.381 (4) | C23—H23 | 0.9291 |
| C19—C20 | 1.385 (4) | C25—H25 | 0.9300 |
| C20—C21 | 1.376 (5) | C26—H26 | 0.9306 |
| C21—C22 | 1.362 (5) | C27—H27 | 0.9303 |
| C22—C23 | 1.387 (4) | C28—H28 | 0.9303 |
| C24—C25 | 1.383 (3) | C29—H29 | 0.9296 |
| C24—C29 | 1.381 (4) | | |
| C116…C26 ⁱ | 3.629 (3) | H2B…H6A | 2.4989 |
| C116…H6B ⁱⁱ | 3.1028 | H2B…H15 | 2.5367 |
| C116…H20 ⁱⁱⁱ | 2.9831 | H3A…C18 | 2.4914 |
| O8…H2A | 2.4862 | H3A…C19 | 2.7733 |
| O8…H15 | 2.7200 | H3B…H5A | 2.3453 |
| O8…H5A ^{iv} | 2.8746 | H3B…H17 | 2.4164 |
| O8…H17 ^{iv} | 2.8583 | H3B…C10 ^x | 3.0203 |
| O8…H21 ^v | 2.6767 | H3B…C15 ^x | 3.0457 |
| O9…H6B | 2.5606 | H5A…H3B | 2.3453 |
| O9…H11 | 2.5312 | H5A…H17 | 2.4216 |
| N1…N4 | 2.865 (3) | H5A…O8 ^x | 2.8746 |
| N4…N1 | 2.865 (3) | H5B…C24 | 2.5009 |
| N4…H19 | 2.7600 | H5B…C29 | 2.7426 |
| N4…H29 | 2.7616 | H5B…H12 ^{ix} | 2.2977 |
| C2…C15 | 3.421 (4) | H6A…C10 | 2.9100 |
| C3…C19 | 3.341 (4) | H6A…H2B | 2.4989 |
| C5…C29 | 3.326 (4) | H6A…C20 ^{vii} | 3.0905 |
| C6…C11 | 3.588 (4) | H6A…H20 ^{vii} | 2.5882 |
| C11…C6 | 3.588 (4) | H6B…O9 | 2.5606 |
| C15…C2 | 3.421 (4) | H6B…C116 ^{ix} | 3.1028 |
| C19…C29 | 3.428 (4) | H6B…H22 ^{xi} | 2.5247 |
| C19…C3 | 3.341 (4) | H11…O9 | 2.5312 |
| C26…C116 ^{vi} | 3.629 (3) | H11…C27 ⁱⁱ | 2.9834 |
| C29…C19 | 3.428 (4) | H12…H5B ⁱⁱ | 2.2977 |
| C29…C5 | 3.326 (4) | H14…C26 ^{vii} | 3.0673 |
| C2…H15 | 3.0460 | H14…C27 ^{vii} | 3.0150 |
| C10…H2B | 3.0749 | H15…O8 | 2.7200 |
| C10…H6A | 2.9100 | H15…C2 | 3.0460 |
| C10…H3B ^{iv} | 3.0203 | H15…H2B | 2.5367 |
| C15…H3B ^{iv} | 3.0457 | H17…H3B | 2.4164 |
| C15…H2B | 2.8738 | H17…H5A | 2.4216 |
| C18…H3A | 2.4914 | H17…H23 | 2.3276 |
| C19…H29 | 3.0851 | H17…H25 | 2.3258 |
| C19…H3A | 2.7733 | H17…O8 ^x | 2.8583 |
| C20…H6A ^{vii} | 3.0905 | H19…N4 | 2.7600 |

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|---------------------------|-------------|---------------------------|--------|
| C21...H2A ^v | 3.0936 | H19...C29 | 3.0375 |
| C23...H27 ^{viii} | 3.0998 | H19...H29 | 2.4822 |
| C24...H5B | 2.5009 | H20...H6A ^{vii} | 2.5882 |
| C26...H14 ^{vii} | 3.0673 | H20...C116 ^{xii} | 2.9831 |
| C27...H14 ^{vii} | 3.0150 | H21...O8 ^v | 2.6767 |
| C27...H11 ^{ix} | 2.9834 | H22...H6B ^{xiii} | 2.5247 |
| C29...H5B | 2.7426 | H23...H17 | 2.3276 |
| C29...H19 | 3.0375 | H25...H17 | 2.3258 |
| H2A...O8 | 2.4862 | H27...C23 ^{xiv} | 3.0998 |
| H2A...C21 ^v | 3.0936 | H29...N4 | 2.7616 |
| H2B...C10 | 3.0749 | H29...C19 | 3.0851 |
| H2B...C15 | 2.8738 | H29...H19 | 2.4822 |
| O8—S7—O9 | 119.92 (12) | C3—C2—H2B | 109.79 |
| O8—S7—N1 | 106.87 (11) | H2A—C2—H2B | 108.30 |
| O8—S7—C10 | 108.10 (13) | N4—C3—H3A | 109.44 |
| O9—S7—N1 | 107.06 (11) | N4—C3—H3B | 109.43 |
| O9—S7—C10 | 107.89 (12) | C2—C3—H3A | 109.43 |
| N1—S7—C10 | 106.23 (11) | C2—C3—H3B | 109.45 |
| S7—N1—C2 | 117.23 (16) | H3A—C3—H3B | 108.00 |
| S7—N1—C6 | 116.13 (16) | N4—C5—H5A | 109.60 |
| C2—N1—C6 | 110.86 (18) | N4—C5—H5B | 109.59 |
| C3—N4—C5 | 107.52 (18) | C6—C5—H5A | 109.59 |
| C3—N4—C17 | 110.91 (18) | C6—C5—H5B | 109.52 |
| C5—N4—C17 | 110.54 (17) | H5A—C5—H5B | 108.06 |
| N1—C2—C3 | 109.3 (2) | N1—C6—H6A | 109.82 |
| N4—C3—C2 | 111.0 (2) | N1—C6—H6B | 109.82 |
| N4—C5—C6 | 110.4 (2) | C5—C6—H6A | 109.84 |
| N1—C6—C5 | 109.2 (2) | C5—C6—H6B | 109.84 |
| S7—C10—C11 | 119.87 (19) | H6A—C6—H6B | 108.34 |
| S7—C10—C15 | 120.1 (2) | C10—C11—H11 | 120.23 |
| C11—C10—C15 | 120.0 (2) | C12—C11—H11 | 120.31 |
| C10—C11—C12 | 119.5 (3) | C11—C12—H12 | 119.84 |
| C11—C12—C13 | 120.4 (3) | C13—C12—H12 | 119.79 |
| C116—C13—C12 | 120.2 (2) | C13—C14—H14 | 120.52 |
| C116—C13—C14 | 119.3 (2) | C15—C14—H14 | 120.37 |
| C12—C13—C14 | 120.5 (3) | C10—C15—H15 | 119.73 |
| C13—C14—C15 | 119.1 (2) | C14—C15—H15 | 119.73 |
| C10—C15—C14 | 120.5 (3) | N4—C17—H17 | 107.75 |
| N4—C17—C18 | 110.71 (18) | C18—C17—H17 | 107.76 |
| N4—C17—C24 | 111.52 (17) | C24—C17—H17 | 107.73 |
| C18—C17—C24 | 111.19 (18) | C18—C19—H19 | 119.61 |
| C17—C18—C19 | 121.5 (2) | C20—C19—H19 | 119.51 |
| C17—C18—C23 | 120.3 (2) | C19—C20—H20 | 120.01 |
| C19—C18—C23 | 118.3 (2) | C21—C20—H20 | 119.98 |
| C18—C19—C20 | 120.9 (3) | C20—C21—H21 | 120.20 |
| C19—C20—C21 | 120.0 (3) | C22—C21—H21 | 120.20 |
| C20—C21—C22 | 119.6 (3) | C21—C22—H22 | 119.68 |

supplementary materials

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| C21—C22—C23 | 120.7 (3) | C23—C22—H22 | 119.65 |
| C18—C23—C22 | 120.6 (3) | C18—C23—H23 | 119.71 |
| C17—C24—C25 | 119.4 (2) | C22—C23—H23 | 119.74 |
| C17—C24—C29 | 122.4 (2) | C24—C25—H25 | 119.78 |
| C25—C24—C29 | 118.2 (2) | C26—C25—H25 | 119.83 |
| C24—C25—C26 | 120.4 (2) | C25—C26—H26 | 119.51 |
| C25—C26—C27 | 121.0 (3) | C27—C26—H26 | 119.53 |
| C26—C27—C28 | 119.5 (3) | C26—C27—H27 | 120.19 |
| C27—C28—C29 | 120.2 (3) | C28—C27—H27 | 120.26 |
| C24—C29—C28 | 120.7 (3) | C27—C28—H28 | 119.90 |
| N1—C2—H2A | 109.75 | C29—C28—H28 | 119.94 |
| N1—C2—H2B | 109.78 | C24—C29—H29 | 119.65 |
| C3—C2—H2A | 109.89 | C28—C29—H29 | 119.65 |
| O8—S7—N1—C2 | -42.1 (2) | C10—C11—C12—C13 | 0.5 (4) |
| O9—S7—N1—C2 | -171.75 (18) | C11—C12—C13—C14 | -0.7 (4) |
| C10—S7—N1—C2 | 73.2 (2) | C11—C12—C13—C16 | 179.6 (2) |
| O8—S7—N1—C6 | -176.37 (16) | C16—C13—C14—C15 | 179.9 (2) |
| O9—S7—N1—C6 | 53.96 (19) | C12—C13—C14—C15 | 0.1 (4) |
| C10—S7—N1—C6 | -61.13 (19) | C13—C14—C15—C10 | 0.5 (4) |
| O9—S7—C10—C11 | -13.5 (2) | N4—C17—C18—C19 | -48.4 (3) |
| N1—S7—C10—C11 | 101.0 (2) | C24—C17—C18—C23 | -104.7 (3) |
| O8—S7—C10—C15 | 37.7 (2) | N4—C17—C24—C25 | -135.1 (2) |
| O9—S7—C10—C15 | 168.8 (2) | N4—C17—C24—C29 | 45.2 (3) |
| N1—S7—C10—C15 | -76.7 (2) | C18—C17—C24—C25 | 100.8 (2) |
| O8—S7—C10—C11 | -144.6 (2) | C18—C17—C24—C29 | -78.9 (3) |
| S7—N1—C2—C3 | 166.58 (18) | N4—C17—C18—C23 | 130.7 (2) |
| C6—N1—C2—C3 | -56.9 (3) | C24—C17—C18—C19 | 76.1 (3) |
| C2—N1—C6—C5 | 57.6 (2) | C19—C18—C23—C22 | 0.6 (4) |
| S7—N1—C6—C5 | -165.36 (15) | C17—C18—C23—C22 | -178.6 (3) |
| C3—N4—C5—C6 | 61.4 (3) | C17—C18—C19—C20 | 178.2 (3) |
| C17—N4—C3—C2 | 178.14 (18) | C23—C18—C19—C20 | -0.9 (4) |
| C5—N4—C3—C2 | -60.9 (2) | C18—C19—C20—C21 | 0.7 (5) |
| C3—N4—C17—C24 | 177.36 (17) | C19—C20—C21—C22 | -0.1 (5) |
| C17—N4—C5—C6 | -177.4 (2) | C20—C21—C22—C23 | -0.2 (5) |
| C3—N4—C17—C18 | -58.3 (2) | C21—C22—C23—C18 | 0.0 (5) |
| C5—N4—C17—C18 | -177.4 (2) | C17—C24—C25—C26 | -179.4 (2) |
| C5—N4—C17—C24 | 58.2 (2) | C25—C24—C29—C28 | 0.7 (4) |
| N1—C2—C3—N4 | 59.0 (3) | C29—C24—C25—C26 | 0.3 (4) |
| N4—C5—C6—N1 | -60.3 (3) | C17—C24—C29—C28 | -179.5 (2) |
| S7—C10—C11—C12 | -177.6 (2) | C24—C25—C26—C27 | -1.0 (4) |
| C15—C10—C11—C12 | 0.1 (4) | C25—C26—C27—C28 | 0.5 (4) |
| S7—C10—C15—C14 | 177.0 (2) | C26—C27—C28—C29 | 0.6 (4) |
| C11—C10—C15—C14 | -0.6 (4) | C27—C28—C29—C24 | -1.2 (4) |

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, y+1/2, -z+1/2$; (iii) $x, -y+1/2, z-1/2$; (iv) $-x, y+1/2, -z+1/2$; (v) $-x, -y, -z+1$; (vi) $x, y-1, z$; (vii) $-x+1, -y, -z+1$; (viii) $x-1, y, z$; (ix) $-x+1, y-1/2, -z+1/2$; (x) $-x, y-1/2, -z+1/2$; (xi) $x, -y-1/2, z-1/2$; (xii) $x, -y+1/2, z+1/2$; (xiii) $x, -y-1/2, z+1/2$; (xiv) $x+1, y, z$.

Hydrogen-bond geometry (Å, °)

| <i>D—H···A</i> | <i>D—H</i> | <i>H···A</i> | <i>D···A</i> | <i>D—H···A</i> |
|----------------|------------|--------------|--------------|----------------|
| C2—H2A···O8 | 0.97 | 2.49 | 2.890 (3) | 105 |
| C6—H6B···O9 | 0.97 | 2.56 | 2.965 (3) | 105 |
| C11—H11···O9 | 0.93 | 2.53 | 2.905 (3) | 104 |

Fig. 1

