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# Etoricoxibium picrate

**Jerry P. Jasinski,[a]* Ray J. Butcher,[b] M. S. Siddegowda,[c] H. S. Yathirajan[c] and A. R. Ramesha[d]**

[a]Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA, [b]Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, [c]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and [d]RL Fine Chem., Bangalore 560 064, India, Department of Studies in Chemistry, Mangalore University, Mangalagangotri 574 199, India
Correspondence e-mail: jjasinski@keene.edu

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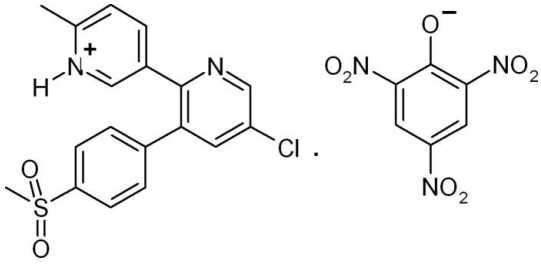
Key indicators: single-crystal X-ray study; $T$ = 123 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.038; $wR$ factor = 0.104; data-to-parameter ratio = 13.6.

In the cation of the title salt (systematic name: 5-{5-chloro-3-[4-(methylsulfonyl)phenyl]-2-pyridyl}-2-methylpyridinium 2,4,6-trinitrophenolate), $C_{18}H_{16}ClN_2O_2S^+\cdot C_6H_2N_3O_7^-$, the mean planes of the two pyridine rings in the bipyridine unit are twisted by 33.9 (2)° with respect to each other. The dihedral angles between the mean planes of the sulfonyl-benzene ring and the chloropyridine and methylpyridine rings are 51.2 (0) and 49.3 (9)°, respectively. The picrate anion interacts with the protonated N atom through a bifurcated N—H···(O,O) hydrogen bond, forming an $R_1^2(6)$ ring motif with the N atom from the methylpyridine group of an adjacent cation. N—H···O hydrogen bonds, weak C—H···O and $\pi$–$\pi$ stacking interactions [centroid–centroid distances = 3.8192 (9)and 3.6749 (9)] occur in the crystal packing, creating a two-dimensional network structure along [110].

## Related literature

For the selective COX-2 inhibitor etoricoxib, see: Patrignani *et al.* (2003). For background to coxibs, traditional non-steroidal anti-inflammatory drugs, see: Rimon *et al.* (2010); Shriner *et al.* (1980); Patrignani *et al.* (2003). For related structures, see: Malathy Sony *et al.* (2005); Vasu Dev *et al.* (1999); Yathirajan *et al.* (2005). For standard bond lengths, see: Allen *et al.* (1987).



## Experimental

### Crystal data

$C_{18}H_{16}ClN_2O_2S^+\cdot C_6H_2N_3O_7^-$
$M_r$ = 587.94
Monoclinic, $P2_1/c$
$a$ = 9.0250 (1) Å
$b$ = 12.7496 (1) Å
$c$ = 21.8011 (3) Å
$\beta$ = 98.114 (1)°
$V$ = 2483.43 (5) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 2.74 mm$^{-1}$
$T$ = 123 K
0.48 × 0.42 × 0.24 mm

### Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
$T_{min}$ = 0.607, $T_{max}$ = 1.000
9467 measured reflections
4932 independent reflections
4454 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.104
$S$ = 1.03
4932 reflections
363 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.38 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2$A$—H2$AB$···O1$B$ | 0.88 | 1.79 | 2.6588 (18) | 172 |
| N2$A$—H2$AB$···O7$B$ | 0.88 | 2.46 | 2.8898 (19) | 111 |
| C2$A$—H2$AA$···O1$A^{i}$ | 0.95 | 2.56 | 3.455 (2) | 156 |
| C9$A$—H9$AA$···O1$B$ | 0.98 | 2.60 | 3.357 (2) | 134 |
| C13$A$—H13$A$···O2$A^{ii}$ | 0.95 | 2.35 | 3.294 (2) | 173 |
| C18$A$—H18$C$···O2$B^{iii}$ | 0.98 | 2.38 | 3.249 (2) | 147 |
| C5$A$—H5$AA$···O6$B^{iv}$ | 0.95 | 2.45 | 3.329 (2) | 153 |
| C7$A$—H7$AA$···O4$B^{v}$ | 0.95 | 2.52 | 3.326 (2) | 143 |

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2336).

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# supporting information

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## Etoricoxibium picrate

**Jerry P. Jasinski, Ray J. Butcher, M. S. Siddegowda, H. S. Yathirajan and A. R. Ramesha**

### S1. Comment

Coxibs are the traditional non-steroidal anti-inflammatory drugs that counter the positive effects of aspirin in preventing blood clots. The research, published in the Proceedings of the National Academy of Sciences (Rimon *et al.*, 2010)), indicates that people who are taking aspirin and coxibs together are in fact inhibiting the aspirin's effectiveness in preventing heart attacks and strokes. Some of the important class of coxib drugs are valdecoxib, celecoxib, rofecoxib, lumiracoxib, etoricoxib *etc*. Etoricoxib (brand name Arcoxia worldwide; also Algix and Tauxib in Italy) is a novel selective COX-2 inhibitor (Patrignani *et al.*, 2003). Like any other COX-2 selective inhibitor, etoricoxib selectively inhibits isoform 2 of the enzyme *cyclo*-oxigenase (COX-2). The crystal structure of valdecoxib, a non-steroidal anti-inflammatory drug (Malathy Sony *et al.*, 2005), a pseudopolymorph of valdecoxib (Yathirajan *et al.*, 2005) and celecoxib, a COX-II inhibitor (Vasu Dev *et al.*, 1999) have been reported. In the view of the importance of etoricoxib, this paper presents the crystal structure of the title compound, etoricoxib picrate.

In the crystal structure of the title compound, $C_{18}H_{16}ClN_2O_2S^+$. $C_6H_2N_3O_7^-$, there is one cation-anion pair in the asymmetric unit (Fig. 1). In the cation, the mean planes of the two pyridine rings in the bipyridine moiety are twisted by 33.9 (2)° against each other. The dihedral angle between the mean planes of the sulfonylbenzene ring and the chloro-pyridine and methylpyridine rings are 51.2 (0)° and 49.3 (9)°, respectively. The picrate anion interacts with the protonated N atom through a bifurcated N—H···O hydrogen bond forming a $R_1^2(6)$ ring motif with the N atom from the methylpyridine group of an adjacent cation.

The dihedral angles between the mean planes of the anion benzene ring and three chloropyridine, methylpyridine and sulfonylbenzene rings of the cation are 53.9 (1)°, 49.3 (9)° and 3.8 (8)°, respectively. The mean planes of the two *o*-$NO_2$ and single *p*-$NO_2$ groups in the picrate anion are twisted by 3.0 (5)°, 30.4 (7)° and 6.5 (9)° with respect to the mean plane of the 6-membered benzene ring. Bond distances and angles are in normal ranges (Allen *et al.*, 1987). N—H···O hydrogen bonds, weak C—H···O (Table 1) and $\pi$–$\pi$ stacking interactions (Table 2) dominate the crystal packing creating an infinite 2-D network structure along the 110 (Fig. 2).

### S2. Experimental

Etoricoxib (3.59 g, 0.01 mmol) and picric acid (2.29 g, 0.01 mmol) in the ratio 1:1 were mixed together in a hot methanol solution. The mixture was warmed to 330 K for few minutes. The resultant precipitate was dried and recrystallized using DMSO. Crystals of the title compound were obtained by the slow evaporation of DMSO solution at room temperature after a few days. (m.p.: 463 – 465 K).

### S3. Refinement

All of the H atoms were placed in their calculated positions and then refined using the riding model with Atom—H lengths of 0.95Å (CH), 0.98Å ($CH_3$) or 0.88Å (NH). Isotropic displacement parameters for these atoms were set to 1.18

times (NH), 1.18–1.22 (CH) or 1.50–1.51 ($CH_3$) times $U_{eq}$ of the parent atom.

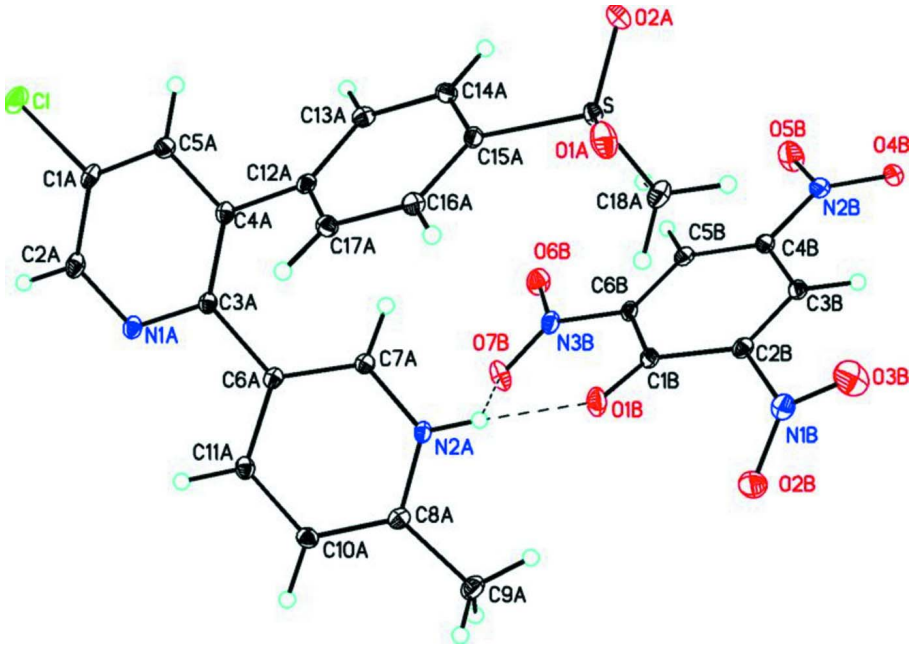


**Figure 1**

Molecular structure of the title compound showing the atom labeling scheme and 50% probability displacement ellipsoids. Dashed lines indicate N—H···O hydrogen bonds between the cation and anion and a $R_1^2(6)$ ring motif.

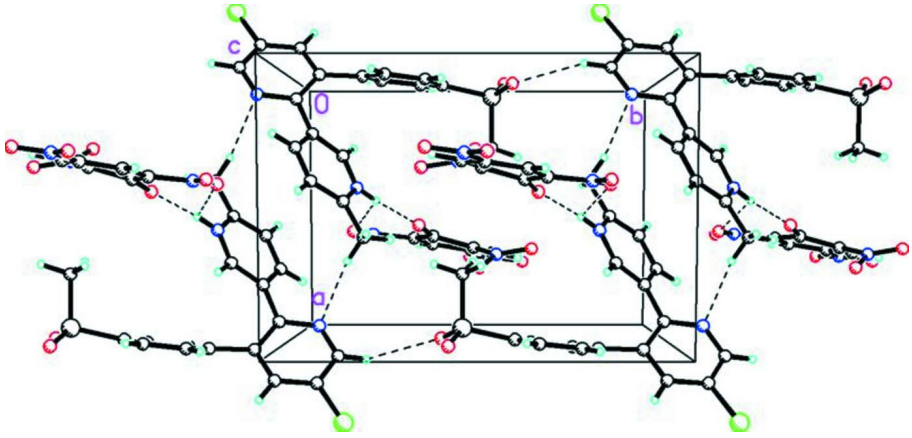


**Figure 2**

Packing diagram of the title compound viewed down the *c* axis. Dashed lines indicate N—H···O hydrogen bonds and weak C—H···O intermolecular interactions creating a 2-D network along the 110.

## 5-{5-Chloro-3-[4-(methylsulfonyl)phenyl]-2-pyridyl}-2-methylpyridinium 2,4,6-trinitrophenolate

*Crystal data*

$C_{18}H_{16}ClN_2O_2S^+·C_6H_2N_3O_7^-$
$M_r$ = 587.94
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 9.0250 (1) Å
$b$ = 12.7496 (1) Å
$c$ = 21.8011 (3) Å
$\beta$ = 98.114 (1)°
$V$ = 2483.43 (5) Å$^3$
$Z$ = 4
$F(000)$ = 1208
$D_x$ = 1.573 Mg m$^{-3}$

Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 6755 reflections
$\theta$ = 5.0–74.0°
$\mu$ = 2.74 mm$^{-1}$
$T$ = 123 K
Prism, pale yellow
0.48 × 0.42 × 0.24 mm

*Data collection*

Oxford Diffraction Xcalibur Ruby Gemini diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 10.5081 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
$T_{min}$ = 0.607, $T_{max}$ = 1.000
9467 measured reflections
4932 independent reflections
4454 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021
$\theta_{max}$ = 74.2°, $\theta_{min}$ = 5.0°
$h$ = −11→9
$k$ = −15→15
$l$ = −26→18

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.104
$S$ = 1.03
4932 reflections
363 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 1.3666P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.38 e Å$^{-3}$

*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 $F^2 > \sigma(F^2)$ 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl | −0.27058 (5) | −0.16223 (3) | 0.30221 (2) | 0.02597 (12) |
| S | 0.06564 (4) | 0.53861 (3) | 0.361812 (19) | 0.01753 (11) |
| O1A | 0.02079 (16) | 0.59365 (10) | 0.41361 (7) | 0.0288 (3) |
| O2A | 0.00758 (15) | 0.57350 (10) | 0.30009 (6) | 0.0287 (3) |
| N1A | 0.06432 (15) | −0.08812 (11) | 0.43234 (6) | 0.0165 (3) |
| N2A | 0.42035 (14) | 0.18006 (10) | 0.47118 (6) | 0.0144 (3) |
| H2AB | 0.4697 | 0.2297 | 0.4547 | 0.017* |
| C1A | −0.13587 (17) | −0.09020 (13) | 0.34908 (8) | 0.0169 (3) |
| C2A | −0.04308 (18) | −0.14008 (13) | 0.39641 (8) | 0.0188 (3) |
| H2AA | −0.0564 | −0.2128 | 0.4034 | 0.023* |
| C3A | 0.08116 (17) | 0.01546 (12) | 0.42314 (7) | 0.0137 (3) |
| C4A | −0.01720 (17) | 0.07282 (13) | 0.37997 (7) | 0.0141 (3) |

| | | | | |
|---|---|---|---|---|
| C5A | −0.12491 (17) | 0.01675 (13) | 0.34070 (7) | 0.0160 (3) |
| H5AA | −0.1893 | 0.0515 | 0.3089 | 0.019* |
| C6A | 0.21601 (17) | 0.06182 (12) | 0.46066 (7) | 0.0137 (3) |
| C7A | 0.29848 (17) | 0.13998 (12) | 0.43700 (7) | 0.0144 (3) |
| H7AA | 0.2683 | 0.1654 | 0.3962 | 0.017* |
| C8A | 0.47188 (17) | 0.14885 (13) | 0.52934 (7) | 0.0150 (3) |
| C9A | 0.60555 (19) | 0.20386 (14) | 0.56235 (9) | 0.0224 (4) |
| H9AA | 0.6164 | 0.2722 | 0.5429 | 0.034* |
| H9AB | 0.6952 | 0.1615 | 0.5600 | 0.034* |
| H9AC | 0.5930 | 0.2140 | 0.6059 | 0.034* |
| C10A | 0.39764 (18) | 0.06695 (13) | 0.55375 (8) | 0.0164 (3) |
| H10A | 0.4335 | 0.0405 | 0.5938 | 0.020* |
| C11A | 0.27134 (18) | 0.02370 (13) | 0.51971 (8) | 0.0156 (3) |
| H11A | 0.2214 | −0.0327 | 0.5366 | 0.019* |
| C12A | −0.01200 (16) | 0.18932 (13) | 0.37508 (7) | 0.0142 (3) |
| C13A | −0.00357 (18) | 0.23552 (13) | 0.31785 (8) | 0.0161 (3) |
| H13A | −0.0098 | 0.1934 | 0.2816 | 0.019* |
| C14A | 0.01398 (18) | 0.34369 (13) | 0.31387 (7) | 0.0160 (3) |
| H14A | 0.0206 | 0.3759 | 0.2751 | 0.019* |
| C15A | 0.02176 (17) | 0.40413 (12) | 0.36752 (8) | 0.0146 (3) |
| C16A | 0.00510 (18) | 0.36004 (13) | 0.42436 (7) | 0.0156 (3) |
| H16A | 0.0063 | 0.4028 | 0.4601 | 0.019* |
| C17A | −0.01336 (18) | 0.25191 (13) | 0.42787 (7) | 0.0159 (3) |
| H17A | −0.0269 | 0.2204 | 0.4662 | 0.019* |
| C18A | 0.2626 (2) | 0.53815 (15) | 0.36775 (9) | 0.0259 (4) |
| H18A | 0.2983 | 0.6096 | 0.3621 | 0.039* |
| H18B | 0.2933 | 0.4923 | 0.3357 | 0.039* |
| H18C | 0.3056 | 0.5123 | 0.4088 | 0.039* |
| O1B | 0.56283 (15) | 0.34250 (10) | 0.43011 (6) | 0.0259 (3) |
| O2B | 0.72286 (18) | 0.50574 (12) | 0.48473 (6) | 0.0361 (4) |
| O3B | 0.6532 (2) | 0.64555 (11) | 0.43287 (7) | 0.0396 (4) |
| O4B | 0.71450 (14) | 0.62738 (10) | 0.21604 (6) | 0.0235 (3) |
| O5B | 0.69640 (18) | 0.47710 (12) | 0.16915 (6) | 0.0342 (3) |
| O6B | 0.60280 (16) | 0.16893 (10) | 0.27056 (6) | 0.0274 (3) |
| O7B | 0.58882 (16) | 0.16083 (10) | 0.36843 (6) | 0.0282 (3) |
| N1B | 0.67468 (17) | 0.55080 (12) | 0.43669 (7) | 0.0214 (3) |
| N2B | 0.69422 (16) | 0.53193 (12) | 0.21568 (7) | 0.0198 (3) |
| N3B | 0.59954 (15) | 0.21143 (11) | 0.32115 (7) | 0.0192 (3) |
| C1B | 0.60694 (17) | 0.37936 (13) | 0.38317 (8) | 0.0162 (3) |
| C2B | 0.65095 (17) | 0.48942 (13) | 0.37955 (8) | 0.0161 (3) |
| C3B | 0.67357 (17) | 0.53950 (13) | 0.32650 (8) | 0.0163 (3) |
| H3BA | 0.6939 | 0.6126 | 0.3266 | 0.020* |
| C4B | 0.66631 (17) | 0.48133 (13) | 0.27202 (8) | 0.0166 (3) |
| C5B | 0.64153 (17) | 0.37444 (13) | 0.27156 (8) | 0.0166 (3) |
| H5BA | 0.6424 | 0.3354 | 0.2345 | 0.020* |
| C6B | 0.61546 (17) | 0.32465 (13) | 0.32535 (8) | 0.0155 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl | 0.0243 (2) | 0.0218 (2) | 0.0298 (2) | −0.00915 (16) | −0.00314 (16) | −0.00647 (16) |
| S | 0.0176 (2) | 0.01094 (19) | 0.0234 (2) | −0.00117 (14) | 0.00049 (15) | 0.00361 (14) |
| O1A | 0.0364 (7) | 0.0128 (6) | 0.0385 (8) | 0.0020 (5) | 0.0102 (6) | −0.0017 (5) |
| O2A | 0.0292 (7) | 0.0219 (6) | 0.0323 (7) | −0.0034 (5) | −0.0053 (5) | 0.0135 (6) |
| N1A | 0.0132 (6) | 0.0127 (6) | 0.0238 (7) | 0.0000 (5) | 0.0027 (5) | 0.0008 (5) |
| N2A | 0.0123 (6) | 0.0124 (6) | 0.0188 (7) | −0.0019 (5) | 0.0033 (5) | 0.0007 (5) |
| C1A | 0.0130 (7) | 0.0158 (8) | 0.0221 (8) | −0.0039 (6) | 0.0030 (6) | −0.0064 (6) |
| C2A | 0.0162 (8) | 0.0114 (7) | 0.0291 (9) | −0.0011 (6) | 0.0038 (7) | −0.0018 (6) |
| C3A | 0.0117 (7) | 0.0131 (7) | 0.0168 (7) | −0.0001 (6) | 0.0039 (6) | −0.0007 (6) |
| C4A | 0.0125 (7) | 0.0129 (7) | 0.0175 (7) | −0.0003 (6) | 0.0045 (6) | −0.0012 (6) |
| C5A | 0.0145 (7) | 0.0163 (8) | 0.0172 (8) | 0.0005 (6) | 0.0018 (6) | −0.0007 (6) |
| C6A | 0.0105 (7) | 0.0123 (7) | 0.0185 (8) | 0.0018 (6) | 0.0030 (6) | −0.0020 (6) |
| C7A | 0.0130 (7) | 0.0150 (7) | 0.0153 (7) | 0.0005 (6) | 0.0027 (6) | −0.0004 (6) |
| C8A | 0.0117 (7) | 0.0152 (7) | 0.0180 (7) | 0.0033 (6) | 0.0017 (6) | −0.0024 (6) |
| C9A | 0.0161 (8) | 0.0206 (8) | 0.0288 (9) | −0.0015 (7) | −0.0033 (7) | −0.0007 (7) |
| C10A | 0.0148 (7) | 0.0176 (8) | 0.0167 (7) | 0.0023 (6) | 0.0019 (6) | 0.0025 (6) |
| C11A | 0.0142 (7) | 0.0136 (7) | 0.0197 (8) | 0.0003 (6) | 0.0046 (6) | 0.0010 (6) |
| C12A | 0.0095 (7) | 0.0129 (7) | 0.0197 (8) | 0.0009 (6) | −0.0001 (6) | −0.0001 (6) |
| C13A | 0.0150 (7) | 0.0163 (8) | 0.0166 (8) | 0.0020 (6) | 0.0009 (6) | −0.0022 (6) |
| C14A | 0.0152 (7) | 0.0176 (8) | 0.0152 (7) | 0.0012 (6) | 0.0014 (6) | 0.0028 (6) |
| C15A | 0.0107 (7) | 0.0105 (7) | 0.0220 (8) | 0.0005 (5) | 0.0003 (6) | 0.0018 (6) |
| C16A | 0.0167 (7) | 0.0133 (7) | 0.0166 (7) | 0.0015 (6) | 0.0019 (6) | −0.0017 (6) |
| C17A | 0.0158 (7) | 0.0158 (8) | 0.0160 (8) | 0.0011 (6) | 0.0023 (6) | 0.0016 (6) |
| C18A | 0.0179 (8) | 0.0285 (10) | 0.0304 (10) | −0.0082 (7) | 0.0004 (7) | 0.0005 (8) |
| O1B | 0.0329 (7) | 0.0235 (6) | 0.0228 (6) | −0.0118 (5) | 0.0096 (5) | 0.0004 (5) |
| O2B | 0.0533 (9) | 0.0336 (8) | 0.0193 (7) | −0.0108 (7) | −0.0028 (6) | 0.0006 (6) |
| O3B | 0.0597 (10) | 0.0230 (7) | 0.0363 (8) | 0.0120 (7) | 0.0073 (7) | −0.0082 (6) |
| O4B | 0.0237 (6) | 0.0217 (6) | 0.0238 (6) | −0.0061 (5) | −0.0010 (5) | 0.0080 (5) |
| O5B | 0.0535 (9) | 0.0311 (8) | 0.0200 (7) | −0.0065 (7) | 0.0119 (6) | −0.0009 (6) |
| O6B | 0.0330 (7) | 0.0204 (6) | 0.0288 (7) | −0.0022 (5) | 0.0043 (6) | −0.0056 (5) |
| O7B | 0.0353 (7) | 0.0176 (6) | 0.0341 (7) | −0.0001 (5) | 0.0136 (6) | 0.0070 (5) |
| N1B | 0.0216 (7) | 0.0219 (7) | 0.0213 (8) | −0.0024 (6) | 0.0052 (6) | −0.0023 (6) |
| N2B | 0.0166 (7) | 0.0219 (7) | 0.0203 (7) | −0.0028 (6) | 0.0004 (5) | 0.0040 (6) |
| N3B | 0.0140 (6) | 0.0153 (7) | 0.0282 (8) | −0.0015 (5) | 0.0029 (6) | 0.0006 (6) |
| C1B | 0.0102 (7) | 0.0176 (8) | 0.0204 (8) | −0.0020 (6) | 0.0009 (6) | 0.0033 (6) |
| C2B | 0.0115 (7) | 0.0171 (8) | 0.0193 (8) | 0.0008 (6) | 0.0004 (6) | −0.0018 (6) |
| C3B | 0.0112 (7) | 0.0146 (8) | 0.0223 (8) | −0.0001 (6) | −0.0001 (6) | 0.0023 (6) |
| C4B | 0.0123 (7) | 0.0190 (8) | 0.0181 (8) | −0.0019 (6) | 0.0011 (6) | 0.0035 (6) |
| C5B | 0.0117 (7) | 0.0190 (8) | 0.0186 (8) | −0.0007 (6) | 0.0002 (6) | −0.0011 (6) |
| C6B | 0.0108 (7) | 0.0134 (7) | 0.0219 (8) | −0.0020 (6) | 0.0005 (6) | 0.0014 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl—C1A | 1.7363 (16) | C12A—C17A | 1.402 (2) |
| S—O1A | 1.4355 (14) | C13A—C14A | 1.392 (2) |

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|---|---|---|---|
| S—O2A | 1.4436 (13) | C13A—H13A | 0.9500 |
| S—C18A | 1.7640 (19) | C14A—C15A | 1.394 (2) |
| S—C15A | 1.7679 (16) | C14A—H14A | 0.9500 |
| N1A—C2A | 1.333 (2) | C15A—C16A | 1.388 (2) |
| N1A—C3A | 1.347 (2) | C16A—C17A | 1.392 (2) |
| N2A—C7A | 1.340 (2) | C16A—H16A | 0.9500 |
| N2A—C8A | 1.348 (2) | C17A—H17A | 0.9500 |
| N2A—H2AB | 0.8800 | C18A—H18A | 0.9800 |
| C1A—C5A | 1.381 (2) | C18A—H18B | 0.9800 |
| C1A—C2A | 1.388 (2) | C18A—H18C | 0.9800 |
| C2A—H2AA | 0.9500 | O1B—C1B | 1.242 (2) |
| C3A—C4A | 1.405 (2) | O2B—N1B | 1.219 (2) |
| C3A—C6A | 1.489 (2) | O3B—N1B | 1.224 (2) |
| C4A—C5A | 1.398 (2) | O4B—N2B | 1.2305 (19) |
| C4A—C12A | 1.490 (2) | O5B—N2B | 1.234 (2) |
| C5A—H5AA | 0.9500 | O6B—N3B | 1.233 (2) |
| C6A—C7A | 1.386 (2) | O7B—N3B | 1.231 (2) |
| C6A—C11A | 1.400 (2) | N1B—C2B | 1.461 (2) |
| C7A—H7AA | 0.9500 | N2B—C4B | 1.441 (2) |
| C8A—C10A | 1.387 (2) | N3B—C6B | 1.452 (2) |
| C8A—C9A | 1.490 (2) | C1B—C6B | 1.452 (2) |
| C9A—H9AA | 0.9800 | C1B—C2B | 1.464 (2) |
| C9A—H9AB | 0.9800 | C2B—C3B | 1.361 (2) |
| C9A—H9AC | 0.9800 | C3B—C4B | 1.394 (2) |
| C10A—C11A | 1.384 (2) | C3B—H3BA | 0.9500 |
| C10A—H10A | 0.9500 | C4B—C5B | 1.381 (2) |
| C11A—H11A | 0.9500 | C5B—C6B | 1.383 (2) |
| C12A—C13A | 1.392 (2) | C5B—H5BA | 0.9500 |

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|---|---|---|---|
| O1A—S—O2A | 118.49 (9) | C12A—C13A—C14A | 119.75 (15) |
| O1A—S—C18A | 109.69 (9) | C12A—C13A—H13A | 120.1 |
| O2A—S—C18A | 107.39 (9) | C14A—C13A—H13A | 120.1 |
| O1A—S—C15A | 109.14 (8) | C13A—C14A—C15A | 119.21 (15) |
| O2A—S—C15A | 108.00 (8) | C13A—C14A—H14A | 120.4 |
| C18A—S—C15A | 103.01 (8) | C15A—C14A—H14A | 120.4 |
| C2A—N1A—C3A | 119.18 (14) | C16A—C15A—C14A | 121.74 (15) |
| C7A—N2A—C8A | 123.92 (14) | C16A—C15A—S | 120.60 (12) |
| C7A—N2A—H2AB | 118.0 | C14A—C15A—S | 117.54 (12) |
| C8A—N2A—H2AB | 118.0 | C15A—C16A—C17A | 118.62 (15) |
| C5A—C1A—C2A | 120.25 (15) | C15A—C16A—H16A | 120.7 |
| C5A—C1A—Cl | 120.11 (13) | C17A—C16A—H16A | 120.7 |
| C2A—C1A—Cl | 119.60 (13) | C16A—C17A—C12A | 120.24 (15) |
| N1A—C2A—C1A | 121.42 (15) | C16A—C17A—H17A | 119.9 |
| N1A—C2A—H2AA | 119.3 | C12A—C17A—H17A | 119.9 |
| C1A—C2A—H2AA | 119.3 | S—C18A—H18A | 109.5 |
| N1A—C3A—C4A | 122.41 (14) | S—C18A—H18B | 109.5 |
| N1A—C3A—C6A | 114.07 (14) | H18A—C18A—H18B | 109.5 |
| C4A—C3A—C6A | 123.47 (14) | S—C18A—H18C | 109.5 |

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|---|---|---|---|
| C5A—C4A—C3A | 117.60 (14) | H18A—C18A—H18C | 109.5 |
| C5A—C4A—C12A | 119.48 (14) | H18B—C18A—H18C | 109.5 |
| C3A—C4A—C12A | 122.92 (14) | O2B—N1B—O3B | 123.86 (16) |
| C1A—C5A—C4A | 118.72 (15) | O2B—N1B—C2B | 118.13 (15) |
| C1A—C5A—H5AA | 120.6 | O3B—N1B—C2B | 117.87 (15) |
| C4A—C5A—H5AA | 120.6 | O4B—N2B—O5B | 123.07 (15) |
| C7A—C6A—C11A | 116.81 (14) | O4B—N2B—C4B | 118.76 (15) |
| C7A—C6A—C3A | 121.39 (14) | O5B—N2B—C4B | 118.16 (14) |
| C11A—C6A—C3A | 121.65 (14) | O7B—N3B—O6B | 122.22 (15) |
| N2A—C7A—C6A | 120.60 (14) | O7B—N3B—C6B | 119.13 (14) |
| N2A—C7A—H7AA | 119.7 | O6B—N3B—C6B | 118.59 (14) |
| C6A—C7A—H7AA | 119.7 | O1B—C1B—C6B | 126.59 (15) |
| N2A—C8A—C10A | 117.52 (14) | O1B—C1B—C2B | 121.90 (15) |
| N2A—C8A—C9A | 117.64 (15) | C6B—C1B—C2B | 111.45 (14) |
| C10A—C8A—C9A | 124.83 (15) | C3B—C2B—N1B | 116.85 (15) |
| C8A—C9A—H9AA | 109.5 | C3B—C2B—C1B | 124.75 (15) |
| C8A—C9A—H9AB | 109.5 | N1B—C2B—C1B | 118.40 (14) |
| H9AA—C9A—H9AB | 109.5 | C2B—C3B—C4B | 118.66 (15) |
| C8A—C9A—H9AC | 109.5 | C2B—C3B—H3BA | 120.7 |
| H9AA—C9A—H9AC | 109.5 | C4B—C3B—H3BA | 120.7 |
| H9AB—C9A—H9AC | 109.5 | C5B—C4B—C3B | 121.29 (15) |
| C11A—C10A—C8A | 120.01 (15) | C5B—C4B—N2B | 118.90 (15) |
| C11A—C10A—H10A | 120.0 | C3B—C4B—N2B | 119.69 (15) |
| C8A—C10A—H10A | 120.0 | C4B—C5B—C6B | 119.59 (16) |
| C10A—C11A—C6A | 120.96 (15) | C4B—C5B—H5BA | 120.2 |
| C10A—C11A—H11A | 119.5 | C6B—C5B—H5BA | 120.2 |
| C6A—C11A—H11A | 119.5 | C5B—C6B—N3B | 115.48 (15) |
| C13A—C12A—C17A | 120.20 (15) | C5B—C6B—C1B | 123.50 (15) |
| C13A—C12A—C4A | 119.49 (14) | N3B—C6B—C1B | 121.01 (14) |
| C17A—C12A—C4A | 120.30 (14) | | |

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|---|---|---|---|
| C3A—N1A—C2A—C1A | 1.2 (2) | C18A—S—C15A—C16A | 93.67 (14) |
| C5A—C1A—C2A—N1A | −4.2 (3) | O1A—S—C15A—C14A | 161.04 (13) |
| Cl—C1A—C2A—N1A | 178.19 (12) | O2A—S—C15A—C14A | 30.96 (15) |
| C2A—N1A—C3A—C4A | 4.7 (2) | C18A—S—C15A—C14A | −82.46 (14) |
| C2A—N1A—C3A—C6A | −172.79 (14) | C14A—C15A—C16A—C17A | 2.8 (2) |
| N1A—C3A—C4A—C5A | −7.5 (2) | S—C15A—C16A—C17A | −173.15 (12) |
| C6A—C3A—C4A—C5A | 169.75 (14) | C15A—C16A—C17A—C12A | 1.3 (2) |
| N1A—C3A—C4A—C12A | 171.79 (15) | C13A—C12A—C17A—C16A | −4.9 (2) |
| C6A—C3A—C4A—C12A | −10.9 (2) | C4A—C12A—C17A—C16A | 174.19 (14) |
| C2A—C1A—C5A—C4A | 1.2 (2) | O2B—N1B—C2B—C3B | −146.94 (17) |
| Cl—C1A—C5A—C4A | 178.77 (12) | O3B—N1B—C2B—C3B | 28.9 (2) |
| C3A—C4A—C5A—C1A | 4.4 (2) | O2B—N1B—C2B—C1B | 32.3 (2) |
| C12A—C4A—C5A—C1A | −174.96 (14) | O3B—N1B—C2B—C1B | −151.84 (16) |
| N1A—C3A—C6A—C7A | 143.34 (15) | O1B—C1B—C2B—C3B | −167.28 (16) |
| C4A—C3A—C6A—C7A | −34.2 (2) | C6B—C1B—C2B—C3B | 10.0 (2) |
| N1A—C3A—C6A—C11A | −32.2 (2) | O1B—C1B—C2B—N1B | 13.6 (2) |
| C4A—C3A—C6A—C11A | 150.31 (15) | C6B—C1B—C2B—N1B | −169.16 (14) |

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|---|---|---|---|
| C8A—N2A—C7A—C6A | 0.2 (2) | N1B—C2B—C3B—C4B | 173.89 (14) |
| C11A—C6A—C7A—N2A | −3.6 (2) | C1B—C2B—C3B—C4B | −5.3 (2) |
| C3A—C6A—C7A—N2A | −179.32 (14) | C2B—C3B—C4B—C5B | −2.1 (2) |
| C7A—N2A—C8A—C10A | 3.2 (2) | C2B—C3B—C4B—N2B | −178.17 (14) |
| C7A—N2A—C8A—C9A | −177.65 (15) | O4B—N2B—C4B—C5B | 179.15 (15) |
| N2A—C8A—C10A—C11A | −3.0 (2) | O5B—N2B—C4B—C5B | −0.7 (2) |
| C9A—C8A—C10A—C11A | 177.88 (16) | O4B—N2B—C4B—C3B | −4.6 (2) |
| C8A—C10A—C11A—C6A | −0.4 (2) | O5B—N2B—C4B—C3B | 175.46 (15) |
| C7A—C6A—C11A—C10A | 3.6 (2) | C3B—C4B—C5B—C6B | 3.5 (2) |
| C3A—C6A—C11A—C10A | 179.36 (14) | N2B—C4B—C5B—C6B | 179.62 (14) |
| C5A—C4A—C12A—C13A | −53.2 (2) | C4B—C5B—C6B—N3B | −176.48 (14) |
| C3A—C4A—C12A—C13A | 127.46 (17) | C4B—C5B—C6B—C1B | 2.3 (2) |
| C5A—C4A—C12A—C17A | 127.70 (16) | O7B—N3B—C6B—C5B | 173.90 (14) |
| C3A—C4A—C12A—C17A | −51.6 (2) | O6B—N3B—C6B—C5B | −3.5 (2) |
| C17A—C12A—C13A—C14A | 4.4 (2) | O7B—N3B—C6B—C1B | −4.9 (2) |
| C4A—C12A—C13A—C14A | −174.62 (14) | O6B—N3B—C6B—C1B | 177.70 (14) |
| C12A—C13A—C14A—C15A | −0.5 (2) | O1B—C1B—C6B—C5B | 168.74 (16) |
| C13A—C14A—C15A—C16A | −3.2 (2) | C2B—C1B—C6B—C5B | −8.4 (2) |
| C13A—C14A—C15A—S | 172.85 (12) | O1B—C1B—C6B—N3B | −12.5 (3) |
| O1A—S—C15A—C16A | −22.84 (15) | C2B—C1B—C6B—N3B | 170.35 (13) |
| O2A—S—C15A—C16A | −152.91 (13) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2*A*—H2*AB*···O1*B* | 0.88 | 1.79 | 2.6588 (18) | 172 |
| N2*A*—H2*AB*···O7*B* | 0.88 | 2.46 | 2.8898 (19) | 111 |
| C2*A*—H2*AA*···O1*A*$^{i}$ | 0.95 | 2.56 | 3.455 (2) | 156 |
| C9*A*—H9*AA*···O1*B* | 0.98 | 2.60 | 3.357 (2) | 134 |
| C13*A*—H13*A*···O2*A*$^{ii}$ | 0.95 | 2.35 | 3.294 (2) | 173 |
| C18*A*—H18*C*···O2*B*$^{iii}$ | 0.98 | 2.38 | 3.249 (2) | 147 |
| C5*A*—H5*AA*···O6*B*$^{iv}$ | 0.95 | 2.45 | 3.329 (2) | 153 |
| C7*A*—H7*AA*···O4*B*$^{v}$ | 0.95 | 2.52 | 3.326 (2) | 143 |

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