

2,2'-[2,3,5,6-Tetramethyl-*p*-phenylene-bis(methylenethio)]bis(pyridine *N*-oxide)

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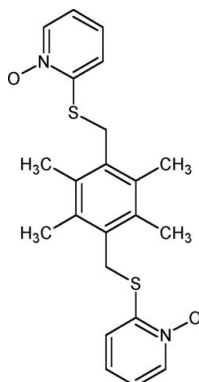
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Key indicators: single-crystal X-ray study; $T = 193$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.057; wR factor = 0.170; data-to-parameter ratio = 14.1.

Molecules of the title compound, $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2\text{S}_2$, lie across centres of inversion. The two thiopyridine *N*-oxide groups adopt a stepped *trans* configuration with respect to the benzene ring, by virtue of the symmetry. The oxopyridinium ring forms a dihedral angle of $79.9(2)^\circ$ with the benzene ring. The crystal structure is stabilized by a strong π - π interaction between the pyridinium rings of adjacent molecules [ring centroid-centroid distance = $3.464(3)$ Å].

Related literature

For bond-length data, see: Allen *et al.* (1987). For biological activities of *N*-oxide derivatives, see: Bovin *et al.* (1992); Katsuyuki *et al.* (1991); Leonard *et al.* (1955); Lobana & Bhatia (1989); Symons & West (1985). For a related structure, see: Hartung *et al.* (1996).



Experimental

Crystal data

$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2\text{S}_2$

$M_r = 412.55$

Monoclinic, $P2_1/c$

$a = 11.8431(13)$ Å

$b = 9.0108(9)$ Å

$c = 9.7551(10)$ Å

$\beta = 112.611(9)^\circ$

$V = 961.01(17)$ Å³

$Z = 2$

Cu $K\alpha$ radiation

$\mu = 2.68$ mm⁻¹

$T = 193(2)$ K

$0.10 \times 0.10 \times 0.05$ mm

Data collection

Enraf-Nonius CAD-4

diffractometer

Absorption correction: ψ scan

(North *et al.*, 1968)

$T_{\text{min}} = 0.80$, $T_{\text{max}} = 0.87$

1929 measured reflections

1813 independent reflections

1200 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.077$

3 standard reflections

frequency: 60 min

intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.170$

$S = 0.99$

1813 reflections

129 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.42$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2548).

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supplementary materials

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Comment

N-Oxides and their derivatives show a broad spectrum of biological activity, such as antifungal, antibacterial, antimicrobial and antibiotic activities (Lobana & Bhatia, 1989; Symons *et al.*, 1985). These compounds are also found to be involved in DNA strand scission under physiological conditions (Katsuyuki *et al.*, 1991; Bovin *et al.*, 1992). Pyridine N-oxides bearing a sulfur group in position 2 display significant antimicrobial activity (Leonard *et al.*, 1955).

The asymmetric unit of the title compound consists of one half of a centrosymmetric molecule. The two thiopyridine-N-oxide groups adopt a stepped *trans* conformation with respect to the benzene ring, by virtue of the symmetry. The oxopyridinium ring forms a dihedral angle of 79.9 (2)° with the benzene ring. The N—O bond length is in good agreement with the mean value of 1.304 (15) Å reported in the literature for pyridine N-oxides (Allen *et al.*, 1987). As observed in a similar structure (Hartung *et al.*, 1996), the S atom is bent significantly towards the N-oxide O atom [N9—C8—S7 = 111.4 (3)°].

The crystal packing is stabilized by a strong π - π interaction between the pyridinium rings of adjacent molecules at (*x*, *y*, *z*) and ($-x$, $2 - y$, $-z$), with a ring centroid to centroid distance of 3.464 (3) Å.

Experimental

A mixture of 1,4-bis(bromomethyl)durene (0.320, 1 mmol) and 1-hydroxypyridine-2-thione sodium salt (0.298, 2 mmol) in water (30 ml) and methanol (30 ml) was heated at 333 K with stirring for 30 min. The compound formed was filtered off, and dried (0.34 g, 82%). The compound was recrystallized from chloroform-methanol (1:2 *v/v*).

Refinement

C-bound H atoms were placed in calculated positions [C—H = 0.95 Å (aromatic), 0.98 Å (methylene), and 0.99 Å (methyl)] and refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2 - 1.5 U_{\text{eq}}(\text{C})$.

Figures

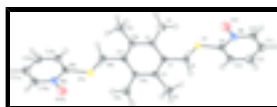


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids. Atoms labelled with the suffix a are generated by the symmetry operations ($1 - x$, $1 - y$, $1 - z$).

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Crystal data

C₂₂H₂₄N₂O₂S₂

$F_{000} = 436$

supplementary materials

$M_r = 412.55$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 11.8431$ (13) Å

$b = 9.0108$ (9) Å

$c = 9.7551$ (10) Å

$\beta = 112.611$ (9)°

$V = 961.01$ (17) Å³

$Z = 2$

$D_x = 1.426$ Mg m⁻³

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 25 reflections

$\theta = 15$ – 29.3 °

$\mu = 2.68$ mm⁻¹

$T = 193$ (2) K

Block, colourless

$0.10 \times 0.10 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.80$, $T_{\max} = 0.87$

1929 measured reflections

1813 independent reflections

1200 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.077$

$\theta_{\max} = 70$ °

$\theta_{\min} = 4.0$ °

$h = -14$ → 13

$k = 0$ → 10

$l = 0$ → 11

3 standard reflections

every 60 min

intensity decay: 3%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.170$

$S = 0.99$

1813 reflections

129 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1008P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.42$ e Å⁻³

$\Delta\rho_{\min} = -0.41$ e Å⁻³

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|------------|------------|------------|----------------------------------|
| C1 | 0.4444 (3) | 0.6186 (4) | 0.4063 (4) | 0.0220 (8) |
| C2 | 0.5351 (3) | 0.6459 (4) | 0.5463 (4) | 0.0234 (8) |

| | | | | |
|-----|-------------|--------------|--------------|-------------|
| C3 | 0.4077 (3) | 0.4715 (4) | 0.3606 (4) | 0.0243 (8) |
| C4 | 0.5706 (4) | 0.8042 (4) | 0.5965 (4) | 0.0305 (9) |
| H4A | 0.5049 | 0.8714 | 0.5374 | 0.046* |
| H4B | 0.646 | 0.8299 | 0.583 | 0.046* |
| H4C | 0.5838 | 0.8136 | 0.7017 | 0.046* |
| C5 | 0.3044 (4) | 0.4452 (4) | 0.2124 (4) | 0.0347 (10) |
| H5A | 0.2428 | 0.5233 | 0.1942 | 0.052* |
| H5B | 0.267 | 0.3484 | 0.2132 | 0.052* |
| H5C | 0.3365 | 0.447 | 0.1336 | 0.052* |
| C6 | 0.3835 (3) | 0.7458 (4) | 0.3017 (4) | 0.0258 (8) |
| H6A | 0.3528 | 0.7114 | 0.1973 | 0.031* |
| H6B | 0.4429 | 0.827 | 0.3138 | 0.031* |
| S7 | 0.25697 (9) | 0.81142 (11) | 0.34802 (10) | 0.0290 (3) |
| C8 | 0.1962 (3) | 0.9526 (4) | 0.2167 (4) | 0.0254 (8) |
| N9 | 0.1042 (3) | 1.0262 (4) | 0.2392 (4) | 0.0293 (7) |
| C10 | 0.0488 (4) | 1.1435 (4) | 0.1524 (5) | 0.0340 (10) |
| H10 | -0.0123 | 1.1969 | 0.1725 | 0.041* |
| C11 | 0.0792 (4) | 1.1863 (4) | 0.0363 (5) | 0.0347 (9) |
| H11 | 0.0394 | 1.2683 | -0.0242 | 0.042* |
| C12 | 0.1688 (4) | 1.1083 (5) | 0.0083 (5) | 0.0358 (10) |
| H12 | 0.1889 | 1.1346 | -0.0739 | 0.043* |
| C13 | 0.2287 (4) | 0.9925 (4) | 0.0998 (4) | 0.0287 (9) |
| H13 | 0.2918 | 0.9405 | 0.0826 | 0.034* |
| O14 | 0.0730 (3) | 0.9825 (4) | 0.3471 (3) | 0.0443 (8) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.032 (2) | 0.0160 (17) | 0.0218 (18) | 0.0012 (15) | 0.0144 (16) | 0.0009 (14) |
| C2 | 0.0280 (19) | 0.0172 (17) | 0.0262 (19) | -0.0026 (14) | 0.0117 (15) | -0.0053 (15) |
| C3 | 0.0294 (19) | 0.0227 (19) | 0.0217 (17) | -0.0043 (15) | 0.0106 (15) | -0.0028 (15) |
| C4 | 0.038 (2) | 0.0189 (19) | 0.033 (2) | -0.0065 (17) | 0.0124 (18) | -0.0023 (17) |
| C5 | 0.044 (2) | 0.025 (2) | 0.031 (2) | -0.0021 (19) | 0.0101 (19) | -0.0028 (18) |
| C6 | 0.0303 (19) | 0.0221 (17) | 0.026 (2) | 0.0011 (16) | 0.0116 (16) | -0.0001 (16) |
| S7 | 0.0373 (5) | 0.0247 (5) | 0.0282 (5) | 0.0039 (4) | 0.0160 (4) | 0.0041 (4) |
| C8 | 0.028 (2) | 0.0183 (18) | 0.0265 (19) | -0.0018 (15) | 0.0065 (16) | -0.0063 (15) |
| N9 | 0.0308 (17) | 0.0260 (17) | 0.0300 (17) | 0.0000 (14) | 0.0102 (14) | -0.0034 (14) |
| C10 | 0.030 (2) | 0.025 (2) | 0.038 (2) | 0.0035 (16) | 0.0031 (18) | -0.0069 (18) |
| C11 | 0.035 (2) | 0.0224 (19) | 0.037 (2) | -0.0048 (18) | 0.0027 (17) | -0.0011 (19) |
| C12 | 0.039 (2) | 0.031 (2) | 0.034 (2) | -0.0059 (18) | 0.0102 (18) | 0.0004 (18) |
| C13 | 0.035 (2) | 0.0233 (19) | 0.0249 (19) | -0.0011 (16) | 0.0086 (17) | 0.0008 (16) |
| O14 | 0.055 (2) | 0.0477 (19) | 0.0421 (18) | 0.0125 (16) | 0.0316 (16) | 0.0064 (15) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------|-----------|---------|-----------|
| C1—C2 | 1.398 (5) | C11—C12 | 1.384 (6) |
| C1—C3 | 1.412 (5) | C12—C13 | 1.379 (6) |
| C1—C6 | 1.520 (5) | C4—H4A | 0.98 |

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| | | | |
|--------------------------|-------------|-----------------|------------|
| C2—C3 ⁱ | 1.389 (5) | C4—H4B | 0.98 |
| C2—C4 | 1.514 (5) | C4—H4C | 0.98 |
| C3—C2 ⁱ | 1.389 (5) | C5—H5A | 0.98 |
| C3—C5 | 1.511 (5) | C5—H5B | 0.98 |
| C6—S7 | 1.822 (4) | C5—H5C | 0.98 |
| S7—C8 | 1.752 (4) | C6—H6A | 0.99 |
| C8—N9 | 1.364 (5) | C6—H6B | 0.99 |
| C8—C13 | 1.384 (5) | C10—H10 | 0.95 |
| N9—O14 | 1.303 (4) | C11—H11 | 0.95 |
| N9—C10 | 1.355 (5) | C12—H12 | 0.95 |
| C10—C11 | 1.369 (6) | C13—H13 | 0.95 |
| C2—C1—C3 | 120.1 (3) | C2—C4—H4C | 109 |
| C2—C1—C6 | 120.8 (3) | H4A—C4—H4B | 109 |
| C3—C1—C6 | 119.2 (3) | H4A—C4—H4C | 109 |
| C3 ⁱ —C2—C1 | 120.2 (3) | H4B—C4—H4C | 109 |
| C3 ⁱ —C2—C4 | 120.1 (3) | C3—C5—H5A | 109 |
| C1—C2—C4 | 119.7 (3) | C3—C5—H5B | 110 |
| C2 ⁱ —C3—C1 | 119.7 (3) | C3—C5—H5C | 109 |
| C2 ⁱ —C3—C5 | 121.2 (3) | H5A—C5—H5B | 109 |
| C1—C3—C5 | 119.1 (3) | H5A—C5—H5C | 109 |
| C1—C6—S7 | 107.5 (2) | H5B—C5—H5C | 110 |
| C8—S7—C6 | 101.51 (18) | S7—C6—H6A | 110 |
| N9—C8—C13 | 119.9 (4) | S7—C6—H6B | 110 |
| N9—C8—S7 | 111.4 (3) | C1—C6—H6A | 110 |
| C13—C8—S7 | 128.7 (3) | C1—C6—H6B | 110 |
| O14—N9—C10 | 121.4 (4) | H6A—C6—H6B | 108 |
| O14—N9—C8 | 118.4 (3) | N9—C10—H10 | 119 |
| C10—N9—C8 | 120.2 (4) | C11—C10—H10 | 119 |
| N9—C10—C11 | 121.2 (4) | C10—C11—H11 | 120 |
| C10—C11—C12 | 119.1 (4) | C12—C11—H11 | 120 |
| C13—C12—C11 | 119.9 (4) | C11—C12—H12 | 120 |
| C12—C13—C8 | 119.6 (4) | C13—C12—H12 | 120 |
| C2—C4—H4A | 109 | C8—C13—H13 | 120 |
| C2—C4—H4B | 109 | C12—C13—H13 | 120 |
| C3—C1—C2—C3 ⁱ | 2.0 (6) | C6—S7—C8—C13 | 5.8 (4) |
| C6—C1—C2—C3 ⁱ | -178.3 (3) | C13—C8—N9—O14 | 177.6 (3) |
| C3—C1—C2—C4 | -177.7 (3) | S7—C8—N9—O14 | -1.6 (4) |
| C6—C1—C2—C4 | 1.9 (5) | C13—C8—N9—C10 | -3.5 (5) |
| C2—C1—C3—C2 ⁱ | -2.0 (6) | S7—C8—N9—C10 | 177.3 (3) |
| C6—C1—C3—C2 ⁱ | 178.3 (3) | O14—N9—C10—C11 | -177.9 (4) |
| C2—C1—C3—C5 | 176.5 (3) | C8—N9—C10—C11 | 3.2 (6) |
| C6—C1—C3—C5 | -3.1 (5) | N9—C10—C11—C12 | -0.4 (6) |
| C2—C1—C6—S7 | -86.0 (4) | C10—C11—C12—C13 | -2.1 (6) |
| C3—C1—C6—S7 | 93.6 (4) | C11—C12—C13—C8 | 1.8 (6) |
| C1—C6—S7—C8 | -178.8 (2) | N9—C8—C13—C12 | 1.0 (6) |
| C6—S7—C8—N9 | -175.2 (3) | S7—C8—C13—C12 | -180.0 (3) |

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

Fig. 1

