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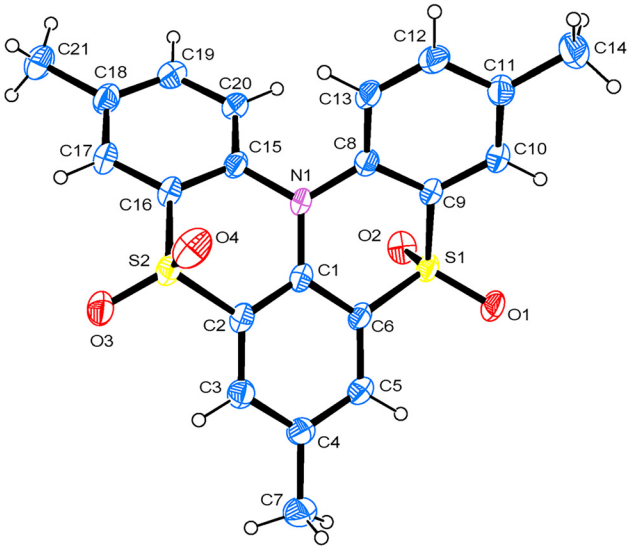
The crystal structure of 3,7,11-trimethylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine 5,5,9,9-tetraoxide, $C_{21}H_{17}NO_4S_2$



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Abstract

$C_{21}H_{17}NO_4S_2$, orthorhombic, *Pna*2$_1$ (no. 33), a = 15.028(3) Å, b = 14.045(3) Å, c = 8.9625(16) Å, V = 1891.7(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0359, w$R_{ref}(F^2)$ = 0.0870, T = 296 (2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.24 × 0.22 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.31 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	25.1°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9522, 3242, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2821
$N(param)_{refined}$:	256
Programs:	Bruker,[1] SHELX,[2,3] WinGX[4]

1 Source of material

All chemicals were purchased from commercial sources and used as received without further purification. First, a mixture of ammonium iodide (730 mg, 5 mmol), sodium iodide (90 mg, 0.6 mmol), and elemental sulfur (512 mg, 2 mmol) was added to an oven-dried reaction vessel (10 mL). The reaction vessel was purged with oxygen gas three times and was then filled with 4-methylcyclohexan-1-one (780 µL, 6 mmol), dimethyl sulfoxide (280 µL, 4 mmol), and ethyl acetate (2 mL) by syringe. The reaction vessel was stirred at 150 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the 3,7,11-trimethylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine product as a yellow solid (423 mg, 61 % yield). Subsequently, a mixture of 3,7,11-trimethylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (347 mg, 1 mmol), 3-chloroperbenzoic acid (1.032 g, 6 mmol), and CH_2Cl_2 (5 mL) was added to an oven-dried reaction vessel (20 mL). The reaction vessel was stirred at room temperature for 24 h. After the reaction finished, it was diluted with ethyl acetate (20 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 2:1) to yield the desired product as a white solid (403 mg, 98 % yield). Finally, dissolve 0.4 g of the target compound in 20 ml of

dichloromethane, heat reflux until the solid is completely dissolved, and filter. The title crystal was precipitated by controlling solvent volatilization.

2 Experimental details

All H-atoms bonded to C atoms were placed geometrically and refined using a riding model with common isotropic displacement factors U_{iso}(H) = 1.2 or 1.5 U_{eq} (parent C-atom).

3 Comment

Bis-phenothiazines as thiabridged triarylamine heterohelicenes with an aryl ring and a nitrogen atom in common are forced into a helical-shaped structure by four long carbon–sulfur bonds. These compounds have found extensive utility as redox-driven molecular switches, organic dyes for dye-sensitized solar cells (DSSCs), and ultralong room-temperature phosphorescence (URTP) materials, due to their unique structural, unusual properties.[5–9] However, structural characterization remains scarce for bis-phenothiazine sulfides featuring double sulfur-atom sulfonated moieties. Consequently, the synthesis and crystal structure determination of the title compound are essential for exploring its potential applications.

Single-crystal structure analysis revealed that the title compound crystallized in the orthorhombic space group $Pna2_1$. The ORTEP diagram is presented in the Figure. The bond lengths of S1–O1, S1–O2, S2–O3, S2–O4 in the title molecule are 1.429(3) Å, 1.430(3) Å, 1.425(3) Å, 1.423(3) Å, respectively. They are similar to reported values in the literature.[10,11]

Weak intermolecular hydrogen bonding exists in the crystal structure of the title compound. The carbon atom C13, for example, provides one intermolecular hydrogen bond to O1′ of another molecule (C13···O1′ = 3.207(4) Å; ′ = x–1/2, –y+1/2, z).

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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Conflict of interest: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. Saint, Apex2 and Sadabs; Bruker AXS Inc.: Madison, WI, USA, 2012.
2. Sheldrick, G. M. Shelxtl – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.
3. Sheldrick, G. M. Crystal Structure Refinement with Shelxl. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Farrugia, L. J. WinGX and Ortep for Windows: An Update. *J. Appl. Cryst.* **2012**, *45*, 849–854.
5. Kim, C.; Choi, H.; Paek, S.; Kim, J.-J.; Song, K.; Kang, M.-S.; Ko, J. Molecular Engineering of Thia-Bridged Triphenylamine Heterohelicenes as Novel Organic Dyes for Dye-Sensitized Solar Cells. *J. Photochem. Photobiol., A* **2011**, *225*, 17–25.
6. Menichetti, S.; Cecchi, S.; Procacci, P.; Innocenti, M.; Becucci, L.; Franco, L.; Viglianisi, C. Thia-Bridged Triarylamine Heterohelicene Radical Cations as Redox-Driven Molecular Switches. *Chem. Commun.* **2015**, *51*, 11452–11454.
7. Gliemann, B. D.; Petrovic, A. G.; Zolnhofer, E. M.; Dral, P. O.; Hampel, F.; Breitenbruch, G.; Schulze, P.; Raghavan, V.; Meyer, K.; Polavarapu, P. L.; Berova, N.; Kivala, M. Configurationally Stable Chiral Dithia-Bridged Hetero[4]helicene Radical Cation: Electronic Structure and Absolute Configuration. *Chem. – Asian J.* **2017**, *12*, 31–35.
8. Lupi, M.; Menichetti, S.; Stagnaro, P.; Utzeri, R.; Viglianisi, C. Thia-Bridged Triarylamine[4]helicene-Functionalized Polynorbornenes as Redox-Active pH-Sensitive Polymers. *Synthesis* **2021**, *53*, 2602–2611.
9. Ma, Z.; Yang, Z.; Mu, L.; Deng, L.; Chen, L.; Wang, B.; Qiao, X.; Hu, D.; Yang, B.; Ma, D.; Peng, J.; Ma, Y. Converting Molecular Luminescence to Ultralong Room-Temperature Phosphorescence via the Excited State Modulation of Sulfone-Containing Heteroaromatics. *Chem. Sci.* **2021**, *12*, 14808–14814.
10. Ning, W.; Wang, H.; Gong, S.; Zhong, C.; Yang, C. Simple Sulfone-Bridged Heterohelicene Structure Realizes Ultraviolet Narrowband Thermally Activated Delayed Fluorescence, Circularly Polarized Luminescence, and Room Temperature Phosphorescence. *Sci. China Chem.* **2022**, *65*, 1715–1719.
11. Ma, Z.; Yang, Z.; Mu, L.; Deng, L.; Chen, L.; Wang, B.; Qiao, X.; Hu, D.; Yang, B.; Ma, D.; Peng, J.; Ma, Y. Converting Molecular Luminescence to Ultralong Room-Temperature Phosphorescence via the Excited State Modulation of Sulfone-Containing Heteroaromatics. *Chem. Sci.* **2021**, *12*, 14808–14814.