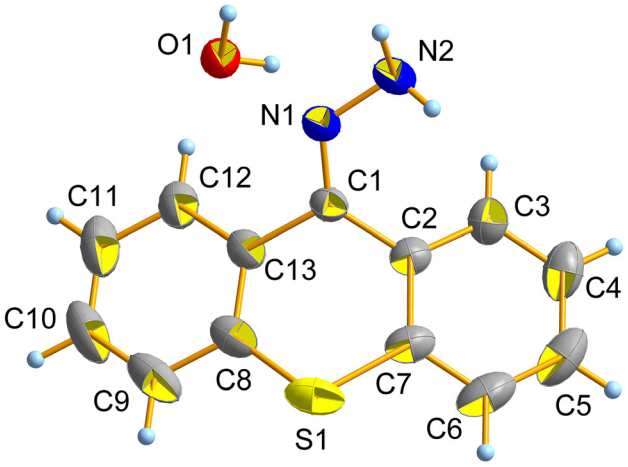
Qi Zhou, Li-Wen Zhai, Jing-Jing Zuo, Zhong-Yan Li* and Lin Yuan*

The crystal structure of (9*H*-thioxanthen-9-ylidene)hydrazine monohydrate, $C_{13}H_{11}N_2SO_{0.5}$



https://doi.org/10.1515/ncrs-2024-0377
Received September 19, 2024; accepted October 18, 2024;
published online October 31, 2024

Abstract

$C_{13}H_{10}N_2S$, orthorhombic, *Pccn* (no. 56), a = 30.55(2) Å, b = 7.760(6) Å, c = 9.622(7) Å, V = 2,281(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0393, $wR_{ref}(F^2)$ = 0.1033, T = 296(2) K.

CCDC no.: 2392066

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

The 9*H*-thioxanthene-9-thione (0.2 g, 0.9 mmol) was dissolved in THF (30 mL). The solution was treated at room temperature with aq. 80 % hydrazine (4 mL, 140.0 mmol). The solution decolorized within several minutes. The solvent and excess hydrazine were removed at reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 10/1) to yield the product as pale yellow solid (0.18 g, 0.79 mmol, 88 %). Single crystals of the product can be obtained by recrystallization from dichloromethane.

Table 1: Data collection and handling.

Crystal:	Block
Size:	0.51 × 0.46 × 0.38 mm
Wavelength:	Mo*K*α radiation (0.71073 Å)
μ:	0.26 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II, φ and ω
θ_{max}, completeness:	27.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22,664, 2,574, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 2,345
$N(param)_{refined}$:	155
Programs:	Bruker,[1] Shelx,[2,3] Olex2[4]

2 Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. The U_{iso} values of all hydrogen atoms were set to 1.2U_{eq}(C).

3 Comment

As a class of sulfur-containing polycyclic aromatic hydrocarbons, thioxanthene often appears in biologically active aromatic heterocyclic compounds and can also be used in solid solutions.[5,6] In addition, because of its good optical properties, thioxanthene is often used as a part of light-driven molecular motors.[7] Because of this, the structure of thioxanthene has always been the focus of researchers.[8,9]

In the crystal structure, the 9*H*-thiaxanthene unit is significantly distorted from planarity, the benzene ring C(2)–C(7) and C(8)–C(13) connects to each other with C(1) and S(1) atom. The dihedral angle between the plane through C(2)–C(7) and the plane through C(8)–C(13) is 34.368(17)°. The bond

***Corresponding authors: Zhong-Yan Li and Lin Yuan**, College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou Hunan 425199, P.R. China,
E-mail: lizhongyandongdong@126.com (Z.-Y. Li), tcyl431102@163.com (L. Yuan). https://orcid.org/0000-0002-6955-0161 (L. Yuan)
Qi Zhou, Li-Wen Zhai and Jing-Jing Zuo, College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou Hunan 425199, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.15131 (5)	−0.01165 (18)	0.33458 (14)	0.0334 (3)
C2	0.10734 (5)	0.01680 (18)	0.27308 (16)	0.0357 (3)
C3	0.10141 (6)	0.1056 (2)	0.14768 (17)	0.0444 (4)
H3	0.1257	0.1474	0.1003	0.053*
C4	0.05996 (6)	0.1322 (2)	0.0930 (2)	0.0591 (5)
H4	0.0566	0.1909	0.0095	0.071*
C5	0.02362 (6)	0.0711 (3)	0.1633 (3)	0.0665 (6)
H5	−0.0041	0.0859	0.1252	0.080*
C6	0.02823 (6)	−0.0116 (2)	0.2893 (2)	0.0601 (5)
H6	0.0036	−0.0498	0.3371	0.072*
C7	0.06989 (5)	−0.0381 (2)	0.34501 (18)	0.0435 (4)
C8	0.12185 (6)	−0.0491 (2)	0.57506 (17)	0.0461 (4)
C9	0.12660 (8)	−0.0380 (3)	0.71979 (19)	0.0644 (6)
H9	0.1041	−0.0744	0.7778	0.077*
C10	0.16472 (9)	0.0268 (3)	0.7759 (2)	0.0736 (7)
H10	0.1679	0.0329	0.8719	0.088*
C11	0.19801 (8)	0.0826 (3)	0.6910 (2)	0.0665 (6)
H11	0.2236	0.1259	0.7298	0.080*
C12	0.19352 (6)	0.0746 (2)	0.54774 (18)	0.0496 (4)
H12	0.2159	0.1150	0.4910	0.059*
C13	0.15558 (5)	0.00633 (19)	0.48765 (15)	0.0382 (3)
N1	0.18700 (4)	−0.05159 (17)	0.26942 (13)	0.0382 (3)
N2	0.18654 (5)	−0.06885 (19)	0.12698 (13)	0.0464 (3)
H2A	0.2078	−0.1354	0.1005	0.056*
H2B	0.1620	−0.1142	0.0996	0.056*
O1	0.2500	0.7500	0.43799 (17)	0.0472 (4)
H1	0.2339 (7)	0.810 (3)	0.382 (2)	0.076 (7)*
S1	0.07357 (2)	−0.14275 (6)	0.50767 (5)	0.05887 (17)

lengths of S(1)–C(7), S(1)–C(8), C(1)–C(2), C(1)–C(13), C(1)–N(1) and N(1)–N(2) are 1.767(2), 1.767(2), 1.485(2), 1.485(2), 1.2953(19) and 1.377(2) Å, respectively. The bond angles of C(7)–S(1)–C(8), C(2)–C(1)–C(13), C(2)–C(1)–N(1), C(13)–C(1)–N(1) and C(1)–N(1)–N(2) are 100.91(8), 117.44(12), 127.18(14), 115.39(13) and 119.77(13)°, respectively, indicating the C(1) atom is in the sp^2 hybridization state. The geometric parameters are all in the expected ranges.[10]

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

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

Research funding: Scientific Research Fund of Hunan Provincial Education Department (21A0518), Yongzhou Guiding Science and Technology Plan Project (2021).

References

1. Bruker: Apex3, Saint–*Plus*, XPREP; Bruker AXS Inc.: Madison, Wisconsin, USA, 2016.
2. Sheldrick, G. M. Shelxt - 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. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.12; Puschmann, H. Olex2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
5. Levy, A.; Cohen, S.; Agranat, I. Overcrowded 1,8-diazafluorenylidene-Chalcoxanthenes. Introducing Nitrogens at the Fjord Regions of Bistricyclic Aromatic Enes. *Org. Biomol. Chem.* **2003**, *1*, 2755–2763.
6. Saršūns, K.; Bērziņš, A.; Rekis, T. Solid Solutions in the Xanthone-Thioxanthone Binary System: How Well Are Similar Molecules Discriminated in the Solid State? *Cryst. Growth Des.* **2020**, *20*, 7997–8004.
7. Faulkner, A.; Van Leeuwen, T.; Feringa, B. L.; Wezenberg, S. J. Allosteric Regulation of the Rotational Speed in a Light-Driven Molecular Motor. *J. Am. Chem. Soc.* **2016**, *138*, 13597–13603.
8. Chopra, D.; Nagarajan, K.; Guru Row, T. N. *N*-[(9*E*)-2–Chloro-9-Thia-9*h*-Xanthen-9-Ylidene]-*N*-(4-Fluorophenyl)amine. *Acta Crystallogr.* **2004**, *E60*, o2408–o2409.
9. Brikci–Nigassa, N. M.; Nauton, L.; Moreau, P.; Mongin, O.; Duval, R.; Picot, L.; Thiéry, V.; Souab, M.; Ruchaud, S.; Bach, S.; Le Guevel, R.; Bentabed-Ababsa, G.; Erb, W.; Roisnel, T.; Dorcet, V.; Mongin, F. Functionalization of 9-thioxanthone at the 1-position: from Arylamino Derivatives to [1]benzo(thio)pyrano[4,3,2-*de*]benzothieno[2,3-*b*] quinolines of Biological Interest. *Bioorg. Chem.* **2020**, *94*, 103347.
10. Deng, S. -W.; Guo, W. -Y.; Yuan, L. The crystal structure of (*R*)-9-(5-methoxy-2-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ylidene)-9*H*-thioxanthene, $C_{28}H_{22}OS$. *Z. Kristallogr. - N. Cryst. Struct.* **2024**, *239*, 189–191.