Xia Wang and Wu-Lan Zeng*

Crystal structure of 8-(3,4-dimethylbenzylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione, C₁₇H₁₈O₄

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.35 × 0.32 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	Rigaku Spider Rapid, ω -scans
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14257, 3397, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2604
$N(\text{param})_{\text{refined}}$:	192
Programs:	CrystalClear [1], SHELX [2, 3]

<https://doi.org/10.1515/ncrs-2019-0180>

Received March 11, 2019; accepted April 17, 2019; available online May 17, 2019

Abstract

C₁₇H₁₈O₄, monoclinic, $P2_1/c$ (no. 14), $a = 8.6020(17)$ Å, $b = 14.835(3)$ Å, $c = 11.624(2)$ Å, $\beta = 90.07(3)^\circ$, $V = 1483.3(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0474$, $wR_{\text{ref}}(F^2) = 0.1439$, $T = 293(2)$ K.

CCDC no.: 1910866

The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The spiro title compound was synthesized by the same methods as our earlier report [4]. A 50 mL round-bottomed flask was charged with 3,4-dimethylbenzaldehyde (0.67 g, 5 mmol), 6,10-dioxaspiro[4.5]decane-7,9-dione (0.85 g, 5 mmol), ethanol (15 mL). The solution was refluxed for 3.5 h. The yellow precipitate was obtained by filtration. Yellow block crystals were collected under conditions of petroleum ether and ethyl acetate in volume ratio of 2:1.

*Corresponding author: Wu-Lan Zeng, Department of Chemistry, Chemical Engineering and Environmental Engineering, Weifang University, Weifang, Shandong 261061, P.R. China, e-mail: wulanzeng@163.com

Xia Wang: Department of Chemistry, Chemical Engineering and Environmental Engineering, Weifang University, Weifang, Shandong 261061, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.02720(11)	0.12633(7)	0.70957(8)	0.0486(3)
O2	0.91035(11)	0.10053(6)	0.88774(9)	0.0489(3)
O3	0.91669(15)	0.21068(9)	0.57762(9)	0.0712(4)
O4	0.67584(13)	0.15003(7)	0.92618(10)	0.0610(3)
C1	1.05560(16)	0.11665(9)	0.83027(12)	0.0423(3)
C2	1.15763(18)	0.03398(10)	0.85050(14)	0.0535(4)
H2A	1.099013	−0.013121	0.888758	0.064*
H2B	1.196289	0.010666	0.778003	0.064*
C3	1.2901(2)	0.06508(14)	0.9252(2)	0.0792(6)
H3A	1.384005	0.072405	0.879967	0.095*
H3B	1.310182	0.021909	0.986066	0.095*
C4	1.2386(3)	0.15466(14)	0.97488(18)	0.0758(6)
H4A	1.177030	0.145883	1.043864	0.091*
H4B	1.327393	0.192270	0.993321	0.091*
C5	1.14256(18)	0.19613(10)	0.88065(14)	0.0508(4)
H5A	1.208142	0.224486	0.823267	0.061*
H5B	1.071124	0.240653	0.911251	0.061*
C6	0.91963(17)	0.18759(10)	0.67648(12)	0.0465(3)
C7	0.80677(15)	0.21662(9)	0.76614(11)	0.0407(3)
C8	0.78964(16)	0.15725(9)	0.86743(12)	0.0437(3)
C9	0.71573(16)	0.28764(10)	0.73809(12)	0.0438(3)
H9	0.737710	0.311531	0.665948	0.053*
C10	0.59081(15)	0.33435(9)	0.79717(12)	0.0426(3)
C11	0.56838(17)	0.33617(9)	0.91600(12)	0.0449(3)
H11	0.640715	0.307969	0.963391	0.054*
C12	0.44166(17)	0.37871(9)	0.96559(12)	0.0455(3)
C13	0.33111(17)	0.41998(9)	0.89399(14)	0.0497(4)
C14	0.35636(18)	0.42122(11)	0.77640(14)	0.0540(4)
H14	0.284859	0.450154	0.729028	0.065*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C15	0.48474(18)	0.38070(10)	0.72753(13)	0.0500(4)
H15	0.500723	0.384190	0.648541	0.060*
C16	0.1878(2)	0.46335(13)	0.94420(18)	0.0704(5)
H16A	0.133680	0.420349	0.991099	0.106*
H16B	0.120953	0.483174	0.883054	0.106*
H16C	0.217639	0.514137	0.990413	0.106*
C17	0.4224(2)	0.37862(12)	1.09405(14)	0.0624(4)
H17A	0.415154	0.439588	1.121217	0.094*
H17B	0.510312	0.349669	1.129027	0.094*
H17C	0.329262	0.346557	1.113972	0.094*

Experimental details

The H atoms of CH₂ group and aromatic ring were both refined with riding coordinates, in which the distance of the C—H is 0.97 Å and 0.93 Å, respectively (SHELXL [2, 3]). The H atoms of methyl were refined with rotating group, the C—H distance is 0.96 Å (SHELXL [2, 3]). The $U_{iso}(H)$ values of all CH groups and CH₂ groups were set to 1.2 U_{eq} . The $U_{iso}(H)$ values of CH₃ groups were set to 1.5 U_{eq} .

Discussion

Spiro compounds and their derivatives have been extensively studied due to their diverse biological application in anti-tumor [5], cytotoxic [6] antimicrobial [7], antioxidant [8], antineuroinflammatory [9] and antineoplastic [10]. In recent years, application of spiro compounds in optical fields such as organic semiconductor [11], fluorescent switches [12] and deep-blue emitting materials [13] has also received much attention. A large number of spiro compounds were synthesized for ten years [14–18]. As a continuation of our research, the title compound was obtained.

As shown in the figure, the title compound comprises 3,4-dimethylbenzyl group and 6,10-dioxaspiro[4.5]decane-7,9-dione group. The bond length of C9—C7 1.3525(19) Å, C9—C10 1.4519(19) Å indicates central C(10) atoms linking the above two groups by double and single bond. The eight atoms (C10—C17) are almost co planar, and the maximum deviation is 0.039 Å. The title molecule includes only weak C—H···O intermolecular hydrogen bands. The distances between the donor and acceptor are 3.3075(7) Å.

Acknowledgements: We thank the financial support of the National Natural Science Foundation of China (No. 51541205), and the Natural Science Foundation of Shandong Province (No. ZR2017BEE038).

References

1. Rigaku/MS. CrystalClear. Rigaku/MS Inc., The Woodlands, Texas, USA (2006).

2. Sheldrick, G.-M.: Integrated space-group and crystal structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G.-M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Zeng, W.-L.; Meng, Q.-G.; Guo, H.-M.; Zhang, L.; Jian, F.-F.: Syntheses and crystal structures of two novel spiro compounds containing 1,5-Dioxaspiro[5.5]undecane-2,4-dione. *Chin. J. Struct. Chem.* **29** (2010) 696–699.
5. Ren, W.; Wang, X.-Y.; Li, J.-J.; Tian, M.; Liu, J.; Ouyang, L.; Wang, J.-H.: Efficient construction of biologically important functionalized polycyclic spiro-fused carbocycloindoles *via* an asymmetric organocatalytic quadruple-cascade reaction. *RSC Adv.* **7** (2017) 1863–1868.
6. Berberoglu, I.; Asmafiliz, N.; Kilic, Z.; Hokelek, T.; Koc, L.-Y.; Acik, L.; Türk, M.; Soltanzade, H.; Dal, H.: Phosphorus nitrogen compounds: Part 34. Syntheses, structural investigations, cytotoxic and biological activities of spiro-ansa-spiro and spiro-bino-spiro tetrameric phosphazene derivatives. *Inorg. Chim. Acta.* **446** (2016) 75–86.
7. Lohar, T.; Jadhav, S.; Kumbhar, A.; Mane, A.; Salunkhe, R.: Bis-amino methylation for the synthesis of spiro-fused piperidines using iron(III) trifluoroacetate in aqueous micellar medium. *Res. Chem. Intermediat.* **42** (2016) 5329–5338.
8. Mani, K.-S.; Kaminsky, W.; Rajendran, S.-P.: A facile atom economic one pot multicomponent synthesis of bioactive spiro-indenoquinoxaline pyrrolizines as potent antioxidants and anti-cancer agents. *Chinese Chem. Lett.* **42** (2018) 301–310.
9. Joshi, P.-C.; Samineni, R.; Bhattacharya, D.; Reddy, B.-R.; Veeraval, L.; Das, T.; Swati, M.; Wahul, A.-B.; Karri, S.; Pabbaraja, S.; Mehta, G.; Kumar, A.; Chakravarty, S.: A 2-oxa-spiro[5.4]decane scaffold displays neurotrophic, neurogenic and anti-neuroinflammatory activities with high potential for development as a versatile CNS therapeutic. *Sci. Rep.* **7** (2017) 1492.
10. Abdou, W.-M.; Ganoub, N.-A.; Sabry, E.: Spiro- and substituted thiophenetriazaphospholes and phosphoramidates as potent antineoplastic agents: synthesis, biological evaluation, and SAR studies. *Monatsh. Chem.* **147** (2016) 619–626.
11. Sun, M.-L.; Zhang, F.; Qian, Y.; Ou, C.-J.; Liu, B.; Xie, L.-H.; Wei, Y.; Ren, B.-Y.; Huang, W.: Catalyst-free photocyclization for the synthesis of spirofusedaromatic organic semiconductor based on SFX. *Tetrahedron.* **74** (2018) 2063–2067.
12. Doddi, S.; Narayanaswamy, K.; Ramakrishna, B.; Singh, S.-P.; Banga, P.-R.: Synthesis and spectroscopic investigation of diketopyrrolopyrrole-spiropyran dyad for fluorescent switch application. *J. Fluoresc.* **26** (2016) 1939–1949.
13. Sun, W.; Zhou, N.-L.; Xiao, Y.; Wang, S.-R.; Li, X.-G.: Novel carbazoyl-substituted spiro [acridine-9,9'-fluorene] derivatives as deep-blue emitting materials for OLED applications. *Dyes Pigments.* **154** (2018) 30–37.
14. Zeng, W.-L.: Synthesis and crystal structure of 3-(3,4-Dimethylbenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione. *Asian J. Chem.* **23** (2011) 635–638.
15. Zeng, W.-L.; Wang, X.; Jiang, J. H.: Design and crystal structures of two new compounds fused with 3,4,5-trimethoxybenzyl group and 6,10-dioxaspiro group. *Crystals* **8** (2018) 146.
16. Jiang, J.-H.; Zeng, W.-L.; Yang, Y.-M.: The crystal structure of 3-((phenylamino)methylene)-1,5-dioxaspiro[5.5]undecane-2,4-dione, C₁₆H₁₇N₁O₄. *Z. Kristallogr. NCS* **233** (2018) 677–678.

17. Zeng, W.-L.; Jiang, J.-H.: Synthesis and crystal structure of a new hydrated benzimidazolium salt containing spiro structure. *Crystals* **7** (2017) 303.
18. Zeng, W.-L.; Jiang, J.-H.; Jiang, G.-Y.; Li, Y.-H.: Synthesis, characterization, and fluorescence properties of two new heterocyclic compounds containing 1,5-Dioxaspirogroup. *Crystals* **8** (2018) 269.