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ORIGINAL PAPER

Syntheses and Crystal Structures of 1,5-Dioxaspiro[5.5]undecane-2,4-dione Derivatives

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Abstract The 3-(2,3,4-trimethoxybenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione **1** and 3-(3,4,5-trimethoxybenzylidene)-1,5-dioxaspiro[5.5]undecane-2,4-dione **2** have been synthesized and characterized by X-ray single-crystal diffraction, IR and UV–Vis. Compound **1** belongs to the orthorhombic system, space group Pna21 with $a = 10.182(2)$ Å, $b = 11.828(2)$ Å, $c = 14.356(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1{,}729.0(6)$ Å^3, $Z = 4$. Compound **2** is of Triclinic system, space group P-1 with $a = 8.7807(18)$ Å, $b = 9.4383(19)$ Å, $c = 11.450(2)$ Å, $\alpha = 98.64(3)°$, $\beta = 103.28(3)°$, $\gamma = 99.44(3)°$, $V = 893.4(3)$ Å^3, $Z = 2$. It is very interesting that there are only C–H···O and C–H···π intermolecular interaction in the **1,** while there are still π···π stacking interactions except for C–H···O and C–H···π intermolecular interaction in the structure of **2**.

Keywords Synthesis · Crystal structure · 1,5-Dioxaspiro[5.5]undecane-2,4-dione · Spiro compound

Introduction

Spiro compounds with special structures and functions have wide application in various fields such as medicine [1–3], catalysis [4] and optical material [5, 6]. Also it has been found that selectivities and activities of spiro compounds will be stronger by inducting oxygen atom. Numerous oxaspirocyclic compounds have been attracting considerable attention due to their biological activities such as antifungal [7, 8], insecticidal [9], antitumor [10], herbicides with low toxicity to microorganisms [11], etc. Therefore, many compounds containing oxaspirocyclic skeleton have been reported over the past decades [12–14]. For these reasons, our group began to design and synthesize various oxaspirocyclic compounds derived from 1,5-dioxaspiro[5.5]undecane-2,4-dione [15, 16]. In this paper, we report the crystal structures and the characterization of 3-(2,3,4-trimethoxybenzylidene)-1,5-dioxaspiro[5.5] undecane-2,4-dione **1** and 3-(3,4,5-trimethoxybenzylidene)-1,5-dioxaspiro[5.5] undecane-2,4-dione **2**.

Experimental

Materials and Methods

All the reagents and solvents from commercial sources were used without further purification. IR spectra (400–4,000 cm^{-1}) were recorded on a Nicolet FT-IR 510P Spectrometer. UV–Vis absorption spectra were recorded on a Shimadzu UV3100 spectrometer in EtOH solution. Melting points were measured by using a melting point apparatus made in Shanghai Instrument Limited Company. X-ray diffraction was performed on a SMART CCD area detector diffractometer.

Syntheses of **1** and **2**

A mixture of 2,3,4-trimethoxybenzaldehyde (1.96 g, 0.01 mol) and 1,5-dioxaspiro[5.5]undecane-2,4-dione (1.84 g, 0.01 mol) was stirred in ethanol (20 mL) for 2.5 h at reflux temperature. After cooling to room temperature, the precipitate was filtered off and dried. Yield 46 %, m.p.:

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Table 1 Crystal and experimental data for **1** and **2**

Compounds	**1**	**2**
Empirical formula	$C_{19}H_{22}O_7$	$C_{19}H_{22}O_7$
Color/shape	Yellow/block	Yellow/block
Formula weight	362.37	362.37
Crystal system	Orthorhombic	Triclinic
Space group	Pna21	P-1
Unit cell dimensions	a = 10.182(2) Å α = 90° b = 11.828(2) Å β = 90° c = 14.356(3) Å γ = 90°	a = 8.7807(18)Å α = 98.64(2)° b = 9.4383(19)Å β = 103.28(3)° c = 11.450(2)Å γ = 99.44(3)°
Volume	1,729.0(6) Å^3	893.4(3) Å^3
Z	4	2
Density(calculated)	1.392 g cm^{-3}	1.347 g cm^{-3}
Absorption coefficient	0.106 mm^{-1}	0.103 mm^{-1}
F(000)	768	608
Crystal size	0.15 × 0.11 × 0.09 mm^3	0.34 × 0.30 × 0.28 mm^3
Theta range for data collection	3.00°–27.48°	3.18–25.02°
Limiting indices	$-11 \leq h \leq 13, -15 \leq k \leq 15, -18 \leq l \leq 18$	$-10 \leq h \leq 11, -11 \leq k \leq 11, -13 \leq l \leq 13$
Reflections collected	16,023	6,981
Independent reflections	3,939 [R(int) = 0.0420]	3,148 [R(int) = 0.0273]
Reflections observed(I > 2\σ(I))	2,973	2,104
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3,939/1/235	3,148/1/247
Goodness-of-fit on F^2	1.141	1.113
Final R indices [I > 2σ(I)]	$R_1 = 0.0356$, $wR_2 = 0.0817$	$R_1 = 0.0463$, $wR_2 = 0.1344$
R indices (all data)	$R_1 = 0.0588$, $wR_2 = 0.1101$	$R_1 = 0.0726$, $wR_2 = 0.1666$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2$	$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 0.0395P$
Largest diff. peak and hole	0.181 and −0.239e Å^{-3}	0.260 and −0.279e Å^{-3}

Table 2 Selected bond lengths (Å) and bond angles (°) for **1** and **2**

Selected bond lengths for **1**				Selected bond lengths for **2**			
C(9)–C(8)	1.399(3)	O(7)–C(13)	1.351(2)	C(9)–C(4)	1.408(3)	O(7)–C(14)	1.362(3)
C(9)–C(4)	1.419(3)	O(7)–C(14)	1.437(2)	C(10)–C(4)	1.454(3)	O(7)–C(11)	1.435(3)
C(9)–C(10)	1.445(3)	O(6)–C(11)	1.355(2)	C(4)–C(5)	1.395(3)	O(6)–C(12)	1.356(3)
C(12)–C(10)	1.353(3)	O(6)–C(14)	1.438(2)	C(10)–C(13)	1.363(3)	O(6)–C(11)	1.430(3)
Selected bond angles for **1**				Selected bond angles for **2**			
C(12)–C(10)–C(9)	136.78(18)	C(10)–C(12)–C(11)	115.34(17)	C(13)–C(10)–C(4)	136.5(2)	C(10)–C(13)–C(12)	128.1(2)
C(8)–C(9)–C(10)	125.98(17)	C(10)–C(12)–C(13)	128.11(17)	C(5)–C(4)–C(9)	119.0(2)	C(10)–C(13)–C(14)	114.95(19)
C(4)–C(9)–C(10)	116.91(17)	C(11)–C(12)–C(13)	116.53(17)	C(5)–C(4)–C(10)	125.9(2)	C(12)–C(13)–C(14)	116.90(19)

141.8 ~ 142.5 °C. The yellow single crystal of **1** were obtained by evaporation for petroleum ether and ethyl acetate (4:1 = v/v) after a few days.

The yellow single crystals of **2** were obtained by the same method used for the synthesis of **1** by replacing 2,3,4-trimethoxybenzaldehyde with 3,4,5-trimethoxybenzaldehyde at a yield of 48 %, m.p.: 152.0–153.5 °C.

Results and Discussion

A summary of the crystallographic data was given in Table 1. The selected bond distances and bond angles of **1** and **2** are listed in Table 2. The structures of **1** and **2**, packing arrangement in a unit cell of **1** and **2** are shown in Figs. 1 and 2, respectively. The structures of two compounds

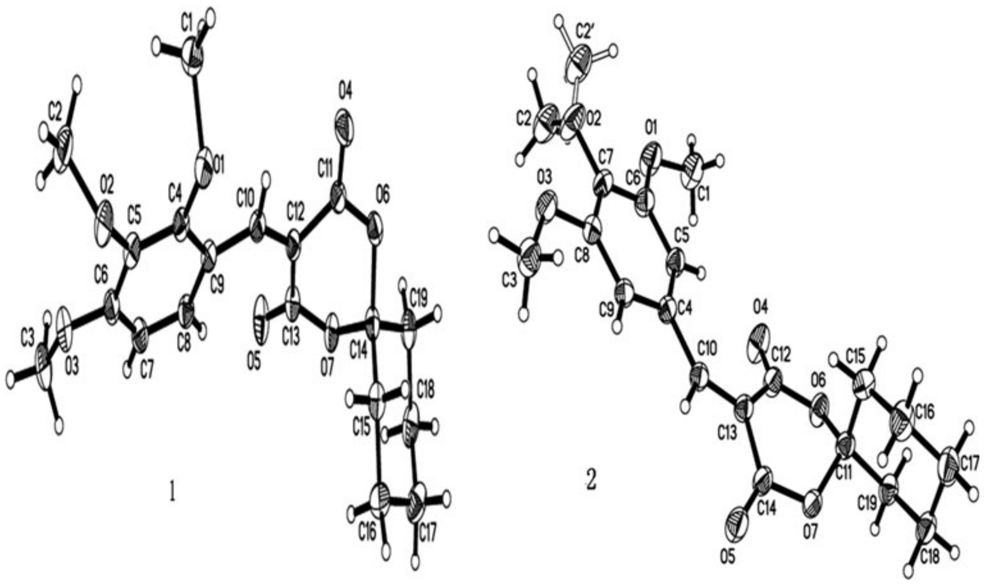

Fig. 1 The molecular structures of **1** and **2** with atomic numbering scheme

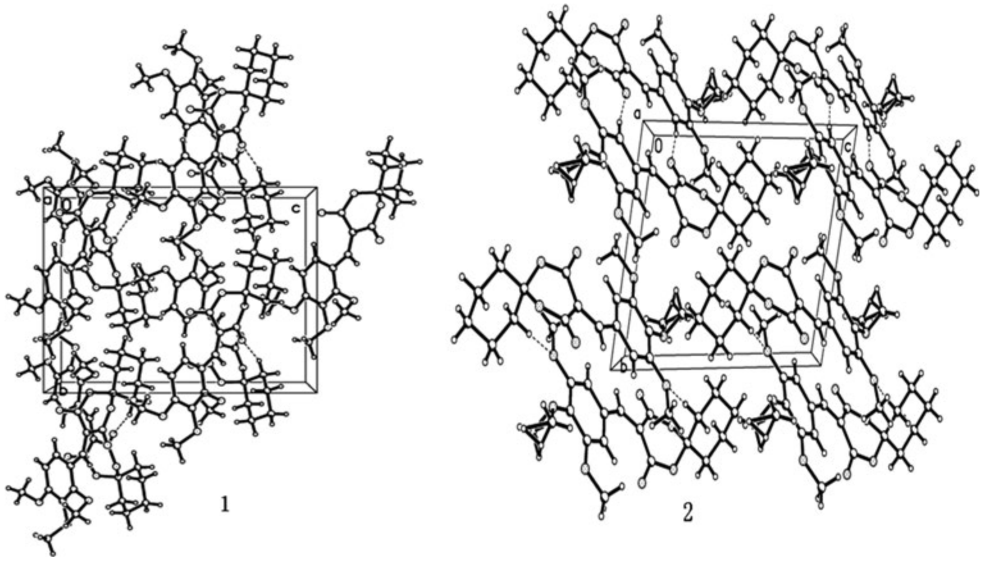

Fig. 2 The packing arrangement in a unit cell of **1** and **2**

Table 3 Intermolecula hydrogen bonds and C–H···π supramolecular interactions in **1** and **2**

D–H···A	Symmetry	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
C(15)–H(15A)···O(4) **(1)**	1/2 + x, 3/2 − y, z	0.97	2.550	3.392(3)	144.9
C(9)–H(9A)···O(8) (2)	1 − x, 2 − y, 2 − z	0.93	2.384	3.294(3)	165.8
C(15)–H(15A)···O(3) **(2)**	−x, 2 − y, 2 − z	0.97	2.565	3.399(3)	144.1
C(15)–H(15B)···phenyl ring **(1)**	1/−x,1/2 + y,1/2 + z	0.97	3.326	4.199	150.65
C(17)–H(17A)···phenyl ring **(2)**	x, y, −1 + z	0.97	3.266	3.978	131.72

were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXS-97 and SHELXL-97 programs [17]. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography [18].

As can be seen from the crystal structure (Fig. 1), the central C(10) atom is linked by 1,5-dioxaspiro[5.5]undecane-2,4-dione group and phenyl ring in **1** and **2**, forming the C(9)–C(10)–C(12) bond angle of 136.78(18)° (C(13)–C(10)–C(4), 136.5(2)° for **2**). The C10–C12 (C10–C13 for

Table 4 Hydrogen bond lengths (Å) and bond angles (°) of compound **2**

Ring	Symmetry	Distance between ring centroids (Å)	Perpendicular distance of Cg(I) on ring J(Å)	Perpendicular distance of Cg(J) on ring I(Å)
Phenyl ring···phenyl ring	−x, 2 − y, 2 − z	3.906	3.418	3.418

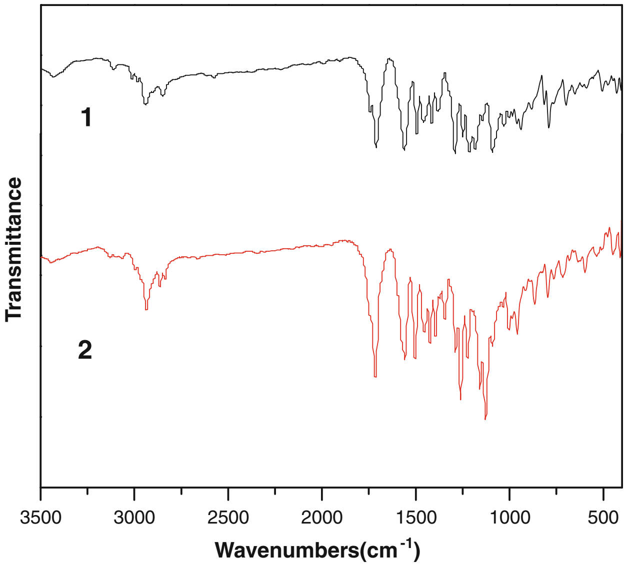

Fig. 3 IR spectra of **1** and **2**

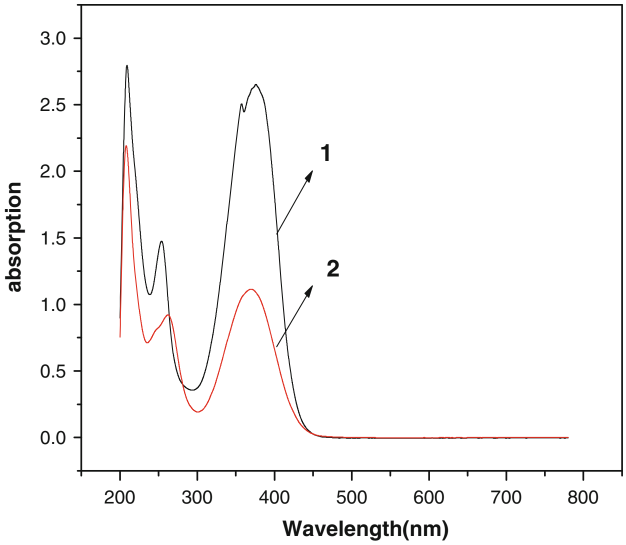

Fig. 4 UV–Vis spectra of **1** and **2**

2) bond length of 1.353(3) Å (1.363(3) Å) is indicative of the considerable double-bond character, while C10–C9 (C10–C4 for **2**) bond length of 1.445(3) Å (1.454(3) Å) is typical C–C single bond. The 1,3-dioxane ring is in a distorted envelope conformation with atom C(14) (C(11) for **2**) common to the cyclohexane ring forming the flap. It is noteworthy that the cyclohexane rings of two title compounds both exhibit a chair-like configuration, with puckering parameters [19] for Q = 0.543(3) Å (0.554(3) Å), q2 = 0.005(2) Å (0.028(3) Å), q3 = 0.543(3) Å (0.553(3) Å), ϑ = 1.7(2)° (3.3(3)°), φ = 259(32)° (187(6)°).

The salient feature in two crystal packings is that they both form strong intermolecular hydrogen bonding networks. In the compound **1**, there are one classical C–H···O intermolecular hydrogen bonds, one type of C–H···π supramolecular interactions. However, in the compound **2**, there are two classical C–H···O intermolecular hydrogen bonds, one type of C–H···π supramolecular interactions and one type of π···π stacking interactions (Tables 3 and 4). In these two crystal lattices, all above hydrogen bonds and intermolecular interactions play a significant role in stabilizing the crystal structures.

The two compounds have a similar feature in the IR spectra. As can be seen from Fig. 3, **1** and **2** show an intense band at 1,710 and 1,715 cm^{-1}, respectively, due to the C=O stretching vibration of the 1,3-dioxane ring. The broad absorptions at 1,287, 1,090 cm^{-1} for **1** and at 1,260, 1,127 cm^{-1} for **2** are assigned to the C–O stretching vibration of the 1,3-dioxane ring. Meanwhile, a similar band at 1,556 and 1,561 cm^{-1} was observed in the IR spectra of **1** and **2**, respectively, confirming that the 1,5-dioxaspiro[5.5]undecane-2,4-dione group connects central C(10) atom by C=C. These facts are consistent with the X-ray diffraction results.

The UV–Vis spectra of **1** and **2** were measured in EtOH solution at room temperature (Fig. 4). They both show three broad bands around 211, 255, 377 nm for **1** and 209, 264, 370 nm for **2**, respectively. The former two absorption band are ascribed to n→π* electron transition of the C=O group, while the latter absorption band is associated with π→π* transition of the phenyl group.

Supporting Information

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-879130 and CCDC-858992. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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