

Article



Synthesis and Crystal Structures of Two Novel O, N-Containing Spiro Compounds

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Abstract: Two novel *O*, *N*-containing spiro compounds, $C_{16}H_{16}CINO_4$ (1) and $C_{16}H_{16}N_2O_6$ (2), were prepared by reactions of monosubstituted benzenamine (substituent = $-NO_2$, -CI) and 1,5-dioxaspiro[5.5]undecane-2,4-dione in ethanol solution of trimethoxymethane. Their structures were characterized by elemental analysis, IR, UV-Vis and single-crystal X-ray diffraction. Compound **1** is triclinic with space group P-1 and cell constants: a = 5.9448(12), b = 9.782(2), c = 13.480(3) Å, $\alpha = 100.28(3)^\circ$, $\beta = 100.66(3)^\circ$, $\gamma = 97.83(3)^\circ$, Mr = 321.75, V = 746.3(3) Å³, Z = 2, Dc = 1.432 g/cm³, F(000) = 336, μ (MoKa) = 0.274 mm⁻¹, the final R = 0.0544 and wR = 0.1538. Compound **2** is monoclinic with space group P21/c and cell constants: a = 12.472(3), b = 11.856(2), c = 10.643(2) Å, $\beta = 99.83(3)^\circ$, Mr = 332.31, V = 1550.7(5) Å³, Z = 4, Dc = 1.423 g/cm³, F(000) = 696, μ (MoKa) = 0.110 mm⁻¹, the final R = 0.0444 and wR = 0.1187. In **1**, there exist some intra- and inter-molecular hydrogen bonds and C-H… π supramolecular interactions, while there are still π … π stacking interactions except for some intra- and intermolecular hydrogen bonds in **2**. Two compounds both form a three-dimensional network structure via above intermolecular interactions.

Keywords: synthesis; crystal structure; spiro compounds

1. Introduction

Spiro compounds with special structures and functions have been reported to possess diverse biological and pharmaceutical properties, such as antiplasmodias [1], antibacterial [2,3], antiviral [4], anxiolytic [5], estrogen potentiating [6], anticancer [7,8] antihistamic [9] and antiproliferative [10] agents. Application of spiro compounds in industry [11,12], catalysis [13] and hole-transporting materials [14] has been triggered great interest in recent years. For these reasons, our group has developed a new simple strategy to synthesize various spiro compounds [15–17]. However, to the best of our knowledge, among so many reported spiro-compounds, *O*, *N*-Containing spiro compounds derived from 1,5-dioxaspiro[5.5]undecane-2,4-dione are very rare. In this paper, we synthesize two novel compounds: 3-((4-chlorophenylamino)methylene)-1,5-dioxaspiro [5.5]undecane-2,4-dione **2**. Their structures are also characterized by elemental analysis, IR, UV-Vis and single-crystal X-ray diffraction.

2. Results and Discussion

2.1. Crystal Structures

The selected bond distances and bond angles of **1** and **2** are listed in Table 1. The molecular structures of **1** and **2** are shown in Figure 1. Packing arrangement in the unit cell of **1** and **2** are illustrated in Figure 2, respectively.



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



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

Selected Bond Lengths for 1		Selected Bond Lengths for 2		
C(11)–N(1)	1.422(6)	N(2)–C(7)	1.3248(18)	
N(1)-C(10)	1.308(7)	N(2)–C(1)	1.4023(18)	
C(10)–C(8)	1.371(7)	C(9)–C(7)	1.366(2)	
C(8)–C(9)	1.437(8)	C(8)–C(9)	1.445(2)	
C(8)–C(7)	1.448(6)	C(9)–C(10)	1.456(2)	
Cl(1)–C(14)	1.735(5)	C(2)–N(1)	1.4634(19)	
Selected Bond Angles for 1		Selected Bond Angles for 2		
C(10)–N(1)–C(11)	124.4(4)	C(7)–N(2)–C(1)	125.57(12)	
N(1)-C(10)-C(8)	127.0(5)	N(2)-C(7)-C(9)	125.05(14)	
C(16)-C(11)-C(12)	119.3(5)	C(7)-C(9)-C(10)	117.25(14)	
C(16)–C(11)–N(1)	119.3(4)	C(8)-C(9)-C(10)	120.39(14)	
C(10)–C(8)–C(9)	116.7(4)	C(6)-C(1)-C(2)	116.79(13)	
C(10)–C(8)–C(7)	122.4(5)	C(6)–C(1)–N(2)	121.34(13)	
C(9)–C(8)–C(7)	119.6(5)	C(2)–C(1)–N(2)	121.87(12)	

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1 and 2.

As can be seen from the crystal structures (Figure 1), the central C(10) (C(7) for 2) atom is linked by 1,5-dioxaspiro[5.5]undecane-2,4-dione group and phenylamino ring, forming the N(1)–C(10)–C(8) bond angle of 127.0(5)° (1), (N(2)–C(7)–C(9), 125.05(14)° (2). The double bond length C10–C8 (1.371(7) Å) in (1), (C7–C9) (1.366(2) Å) (2), is likewise in agreement with those described earlier reported (1.3454(2) Å, 1.336(2) Å) [15]. The double bond C10–N1 in (1) (1.308(7) Å), C7–N2 (2) (1.3248(18) Å) is typical C–N single bond. The 1,3-dioxane rings of the two compounds are both in a distorted screw-boat conformation. While the cyclohexane rings of the two compounds both exhibit a chair-like configuration, with puckering parameters [18] for compound 1: Q = 0.552(6) Å, q2 = 0.018(6) Å, q3 = 0.552(6) Å, ϑ = 0.4(6)°, φ = 157(19)°; compound **2**: Q = 0.551(2) Å, q2 = 0.014(2) Å, q3 = -0.550(2) Å, ϑ = 178.2(2)°, φ = 295(9)°, respectively.

In the crystal, weak N–H···O and C–H···O intra- and intermolecular interactions are observed in the two compounds (Table 2). In addition, one type of C–H··· π supramolecular interactions in 1 are also present. The π ··· π stacking interactions in 2 are observed between nearby phenyl rings (Cg2···Cg2). In these two crystal lattices, all of the above intermolecular interactions in both compounds form a three-dimensional network structure.

D-H…A	Symmetry	D–H (Å)	H…A (Å)	D…A (Å)	∠ D – H ···A (°)
N(1)–H(1A)…O(2) 1	intra	0.86	2.168	2.783(6)	128.3
N(1)–H(1A)····O(2) 1	-2-x, 1-y, 1-z	0.86	2.539	3.311(7)	149.8
C(10)–H(10A)…O(1) 1	intra	0.93	2.420	2.767(7)	102.0
C(10)–H(10A)…O(1) 1	-1-x, -y, 1-z	0.93	2.550	3.469(7)	169.7
C(12)–H(12A)…O(1) 1	-1-x, -y, 1-z	0.93	2.346	3.188(7)	150.4
C(16)–H(16A)…O(2) 1	-2-x, $1-y$, $1-z$	0.93	2.463	3.291(7)	148.3
C(5)–H(5B)····Cg(3) ^{<i>a</i>} 1	-2-x, -y, 1-z	0.97	3.254	3.790	116.6
N(2)–H(2A)····O(2) 2	intra	0.86	2.041	2.6809(19)	130.6
N(2)–H(2A)····O(4) 2	intra	0.86	2.103	2.7429(17)	130.8
N(2)–H(2A)····N(1) 2	intra	0.86	2.582	2.911(2)	125.2
C(2)–H(7A)····O(3) 2	intra	0.93	2.462	2.798(2)	101.4
C(4)–H(4A)····O(1) 2	x, 5/2 - y, -1/2 + z	0.93	2.589	3.368(2)	141.7
C(14)–H(4A)…O(3) 2	1-x, 1-y, -z	0.97	2.562	3.465(3)	154.9
Ring	Symmetry	Dihedral angels (°)	$\pi \cdots \pi$ (Å)	Centroid to c	entroid distances (Å)
Cg(2)…Cg(2) ^b 2	2-x, -y, -z	0	3.701	3	3.465

Table 2. Intra- and intermolecular interaction distances and aromatic-aromatic interactions in 1 and 2.

^{*a*} Cg(3) ring denotes phenyl ring of compound **1**: C(11)–C(16), ^{*b*} Cg(2) ring denotes phenyl ring of compound **2**: C(1)–C(6).

2.2. Spectroscopic Properties

The IR spectra of the two compounds show a little difference. The broad bands at 3231 cm^{-1} **1** and at 3208 cm^{-1} **2** are assigned to the N–H stretching vibration. The strong bands at 1732 cm^{-1} **1** and 1736 cm^{-1} **2** are due to the C=O stretching vibration of the 1,3-dioxane ring. For the compounds **1** and **2**, the C–O stretching vibration of the 1,3-dioxane ring is observed at 1248 cm⁻¹, 1095 cm^{-1} and at 1259 cm⁻¹, 1158 cm⁻¹. Meanwhile, a similar band at 1617 cm⁻¹ and 1597 cm⁻¹ was observed in the IR spectra of **1** and **2**, respectively, indicting C=C stretching vibration by 1,5-dioxaspiro[5.5]undecane-2,4-dione group connected with central C(10) **1** (C(7) **2**) atom. These facts are consistent with the X-ray diffraction results.

For the two compounds, UV-Vis spectra are measured in EtOH solution at room temperature (Figure 3). The strong absorption bands at about 226 nm, 328 nm and 218 nm, 312 nm are observed in **1** and **2**, respectively. The former may be associated with K band of the phenyl group, and the latter may attribute to R band of the C=O group [19].



Figure 3. UV-Vis spectra of 1 and 2.

3. Experimental Section

3.1. Materials and Methods

All the reagents and solvents from commercial sources were used without further purification. Germany). IR spectra were recorded as KBr pellets with a Nicolet FT-IR 510P Spectrometer. The analyses of C, H, and N were made on an Elementar Vario EL III elemental analyzer (Elementar, Hanau, Germany). 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. The X-ray single-crystal data collection for the compounds **1** and **2** were performed on a Bruker Smart-1000 CCD diffractometer.

3.2. Preparation of Two Spiro Compounds

The synthetic route is shown in Scheme 1.



Scheme 1. Synthesis of two spiro compounds.

The intermediate compound (1,5-dioxaspiro[5.5]undecane-2,4-dione) was prepared according to our earlier report [16]. The synthesis of two title compounds are described below.

Trimethoxymethane (1.27 g, 0.012 mol) and 1,5-dioxaspiro[5.5]undecane-2,4-dione (1.84 g, 0.01 mol) were dissolved in 30 mL of 95% ethanol, the 3-chlorobenzenamine (1.27 g, 0.01 mol) was added. The mixture was stirred for 2 h and finally refluxed for another 6 h. Then, the solution was filtered. Yield 16.2%. m.p.: 167.9~168.5 °C. Anal. Calcd. for $C_{16}H_{16}CINO_4$: C, 59.73; H, 5.05; N, 4.35. Found: C, 59.82; H, 4.98; N, 4.55. The yellow crystals for X-ray analysis were grown by slow evaporation of a solution in petroleum ether and ethyl acetate (2:1 = v/v).

The synthesis procedure of **2** was similar to that of **1** except that 3-chlorobenzenamine (1.27 g, 0.01 mol) was replaced by 2-nitrobenzenamine (1.38 g, 0.01 mol). Yield 52.7%. m.p.: 175.3~175.8 °C. Anal. Calcd. for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.73; H, 4.78; N, 8.58. The yellow crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in petroleum ether and ethyl acetate (3:1 = v/v).

3.3. Crystallography

The structure of the two compounds were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXS-97 and SHELXL-97 programs [20]. The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were placed in calculated positions and refined as a riding (C–H = 0.93–0.97 Å in **1** and **2**, Uiso(H) = 1.2Ueq(C)). The contributions of hydrogen atoms were included in the structure-factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography [21]. The final cycle of refinement gave $R_1 = 0.0544$ and $wR_2 = 0.1538$ ($R_1 = 0.0444$ and $wR_2 = 0.1187$ for **2**) with $w = 1/(\sigma^2(F_0^2) + (0.1284P)^2 + 0.000P)$ ($w = 1/(\sigma^2(F_0^2) + (0.0665P)^2 + 0.1456P)$ for **2**) where $P = (F_0^2 + 2F_c^2)/3$. Crystallographic data are summarized in Table 3. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-888961 and CCDC-888962. 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).

Compounds	1	2		
Empirical formula	C ₁₆ H ₁₆ ClNO ₄	C ₁₆ H ₁₆ N ₂ O ₆		
Color/shape	yellow/block	yellow/block		
Formula weight	321.75	332.31		
Crystal system	triclinic	monoclinic		
Space group	P-1	P21/c		
Unit cell dimensions	$\begin{array}{l} a = 5.9448(12) ~ {\rm \AA} ~ \alpha = 100.28(3)^{\circ} \\ b = 9.782(2) ~ {\rm \AA} ~ \beta = 100.66(3)^{\circ} \\ c = 13.480(3) ~ {\rm \AA} ~ \gamma = 97.83(3)^{\circ} \end{array}$	$\begin{array}{l} a = 12.472(3) ~ {\rm \AA} ~ \alpha = 90^{\circ} \\ b = 11.856(2) ~ {\rm \AA} ~ \beta = 99.83(3)^{\circ} \\ c = 10.643(2) ~ {\rm \AA} ~ \gamma = 90^{\circ} \end{array}$		
Volume	746.3(3) Å ³	1550.7(5) Å ³		
Z	2	4		
Density (calculated)	$1.432 \text{ g} \cdot \text{cm}^{-3}$	$1.423 { m g} \cdot { m cm}^{-3}$		
Absorption coefficient	0.274 mm^{-1}	$0.110 \ { m mm}^{-1}$		
F(000)	336	696		
Crystal size	$0.15\times0.10\times0.08~mm^3$	$0.25\times0.22\times0.12~\text{mm}^3$		
Theta range for data collection	3.15°–25.25°	3.25°–27.48°		
Limiting indices	$-6 \leqslant h \leqslant 7, -11 \leqslant k \leqslant 11, -16 \leqslant l \leqslant 1$	$-16 \leqslant h \leqslant 16, -15 \leqslant k \leqslant 15, -13 \leqslant l \leqslant 13$		
Reflections collected	6027	14428		
Independent reflections (R _{int})	2701 (0.0497)	3552 (0.0379)		
Reflections observed (I > $2\sigma(I)$)	1007	2471		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2		
Data/restraints/parameters	2701/0/199	3552/0/217		
Goodness-of-fit on F ²	1.041	1.059		
$\frac{R_1/wR_2 \text{ (I} > 2\sigma(\text{I}))}{R_1/wR_2 \text{ (all data)}}$	0.0544 / 0.1538 0.1661 / 0.2587	0.0444 / 0.1187 0.0677 / 0.1345		
Largest diff. peak and hole	$0.421 \text{ and } -0.359 \text{ e} \mathrm{\AA}^{-3}$	0.273 and $-0.227 \text{ e} \text{ Å}^{-3}$		

Table 3. Selected crystal data and details of the structure determination for the two compounds.

4. Conclusions

Two novel *O*, *N*-Containing spiro compounds, 3-((4-chlorophenylamino)methylene)-1, 5-dioxaspiro[5.5]undecane-2,4-dione **1** and 3-((2-nitrophenylamino)methylene)-1,5-dioxaspiro[5.5] undecane-2,4-dione **2**, have been synthesized and characterized by elemental analysis, IR, UV-Vis and single-crystal X-ray diffraction. In **1**, there exist some intra- and intermolecular hydrogen bonds and C–H··· π supramolecular interactions; while there are still π ··· π stacking interactions except for some intra- and intermolecular hydrogen bonds in **2**. Two compounds both form a three-dimensional network structure via above intermolecular interactions.

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Author Contributions: Jinhe Jiang synthesized compound 1 and compound 2. Wulan Zeng conceived and designed the experiments and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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