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ORIGINAL PAPER

Supramolecular Architecture of Two 4-(Methylsulfonyl) Benzaldehyde Schiff Bases

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Abstract Two crystalline forms of 1,4-dimethyl-2-(4-(methyl-sulfonyl) styryl)benzene (**1**) and 1,3-diisopropyl-2-(4-(methyl-sulfonyl)styryl) benzene (**2**) were obtained and their structures were determined by X-ray diffraction technique. Both compound **1** and **2** crystallized in a triclinic space group *P*-1 with cell parameters $a = 5.375(2)$ Å, $b = 18.402(7)$ Å, $c = 23.109(9)$ Å, $\alpha = 95.838(4)$, $\beta = 94.579(4)^\circ$, $\gamma = 91.407(4)^\circ$, $V = 2265.3(15)$ Å^3, $Dc = 1.264$ g/cm^3, $Z = 6$, and $a = 9.332(7)$ Å, $b = 11.028(8)$ Å, $c = 11.574(9)$ Å, $\alpha = 111.795(6)^\circ$, $\beta = 94.162(8)^\circ$, $\gamma = 92.177(7)^\circ$, $V = 1100.3(14)$ Å^3, $Dc = 1.161$ g/cm^3, $Z = 2$, respectively. Both of them display a trans-configuration with respect to the C=N double bond. Their crystal packings are stabilized by weak C–H···O hydrogen bonds and van der Waals interactions.

Keywords 4-(Methylsulfonyl)benzaldehyde · Schiff base · Crystal structure

Introduction

4-(Methylsulfonyl)benzaldehyde is an important precursor for the synthesis of amino alcohol with applications to the synthesis of antibiotics thiamphenicol, which is well acknowledged to possess a wide spectrum of antibacterial bioactivities. In addition, the 4-(methylsulfonyl)benzaldehyde may be condensed with organic amines to prepare kinds of Schiff bases. Not only have Schiff base compounds attracted attention for the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1], but also they have been of great of interest owing to their wide range of biological activities. They have been found to possess pharmacological activities such as antimalarial [2], anticancer [3], antibacterial [4], antifungal, antitubercular, antiinflammatory, antimicrobial and antiviral [5]. In view of above biological importance of Schiff bases, we have synthesized and studied a few crystal structures of 4-(methylsulfonyl)benzaldehyde's Schiff bases [6–8], and attempt to investigate their biological activities and synthesize more these Schiff bases. Herein, the crystal structures of 1,4-dimethyl-2-(4-(methylsulfonyl)styryl)benzene and 1,3-diisopropyl-2-(4-(methylsulfonyl)styryl)benzene were reported.

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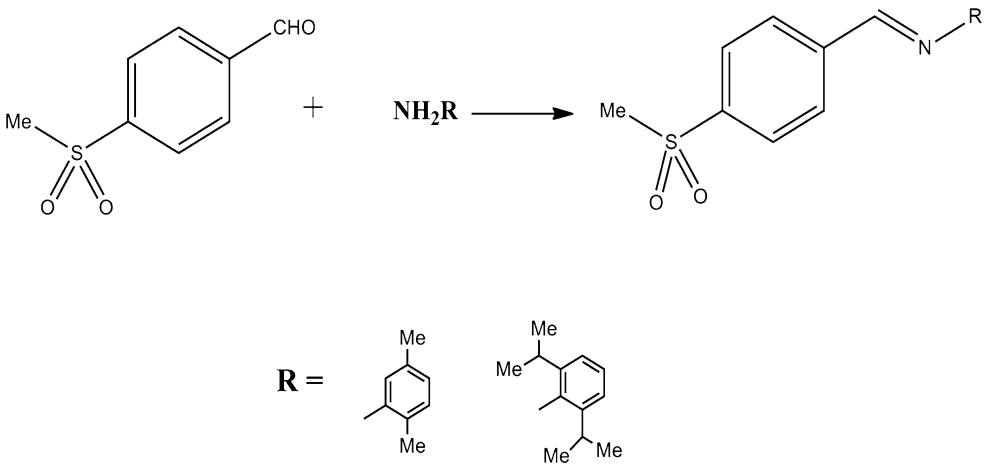
Experimental

All reagents, unless otherwise stated, were purchased as AR grade and used without further purification. The melting point was determined by an XT-4 microscopic melting apparatus and uncorrected. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer using KBr disks with wave numbers in cm^{-1}. ^{1}HNMR spectra were recorded on a Bruker AV-300 instrument at 300 MHz in $CDCl_3$. Crystal data were obtained on a Bruker APEX-II CCD diffractometer. The synthesis route of the title compounds is shown in Scheme 1.

1,4-Dimethyl-2-(4-(methylsulfonyl)styryl)benzene (**1**)

4-(Methylsulfonyl)benzaldehyde (0.184 g) and 2,5-dimethylaniline (0.121 g) were dissolved in acetonitrile

Scheme 1 The synthesis route of two Schiff bases



(20 mL). The mixture was stirred at room temperature for 10 min to give a clear yellow solution. After keeping the solution in air for 7 days, yellow block-shaped crystals were obtained at the bottom of the vessel. Yield 78%; m.p. 147.6–148.7 °C. IR (KBr): 3435.8, 1653.0, 3000.2, 1628.4,1569.4, 1499.9, 1309.0, 1291.8, 1148.6, 1120.0, 1088.3 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz)δ ppm: 8.64(1H, s, H-C7), 8.11 (2H, d, H-C1, H-C5), 8.01 (2H, d, H-C2, H-C4), 7.05–7.25 (3H, m, H-C10, H-C11, H-C13), 3.32(3H, s, H-C16), 2.35(6H, s, H-C14, H-C15).

2,6-Diisopropyl-N-(4-(methylsulfonyl) benzylidene)aniline (**2**)

4-(Methylsulfonyl)benzaldehyde (0.184 g) and 2,6-diisopropylaniline (0.177 g) were dissolved in acetonitrile (20 mL). The mixture was stirred at room temperature for 10 min to give a clear yellow solution. After keeping the solution in air for 7 days, yellow block-shaped single crystals of **2** suitable for X-ray diffraction (XRD) analysis were obtained at the bottom of the vessel, Yield 81%; m.p. 153.4–154.6 °C.

IR (KBr): 3436.7, 2960.9, 1640.0, 1572.1, 1458.5, 1310.8, 1292.6, 1144.0, 1086.1, 968.1 cm^{-1}; ^1H NMR($CDCl_3$, 300 MHz) δ ppm: 8.66(1H, s, H-C7), 8.11 (2H, d, H-C4, H-C5), 8.02 (2H, d, H-C2, H-C6), 7.12–7.51 (3H, m, H-C10, H-C11, H-C12), 3.32(3H, s, H-C20), 2.87(2H, m, H-C14, H-C17), 1.2 (12H, d, H-C15, H-C15, H-C16, H-C18, H-C19).

X-Ray Crystal Structure Determination

The two title compounds gave yellow block crystals. The single crystals with approximate dimensions of 0.23 × 0.20 × 0.16 mm^3 (**1**) and 0.23 × 0.22 × 0.20 mm^3 (**2**) were used to respectively perform for XRD studies. The data were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo Kα radiation (k = 0.071073 nm) using x − 2 h scan technique. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares with the Bruker's SHELXL-97 program [9]. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. Experimental details for X-ray data collection of **1** and **2** are presented in Table 1, and the molecular structure and the atomic numbering Scheme of **1** and **2** are shown in Fig. 1, respectively.

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

Compound	**1**	**2**
Empirical formula	$C_{16}H_{17}NO_2S$	$C_{20}H_{25}NO_2S$, C_2H_3N
Formula weight	287.38	384.52
T (K)	296	296
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	5.375(2)	9.332(7)
b (Å)	18.402(7)	11.028(8)
c (Å)	23.109(9)	11.574(9)
α (°)	95.838(4)	111.795(6)
β (°)	94.579(4)	94.162(8)
γ (°)	91.407(4)	92.177(7)
V ($Å^3$)	2265.3(15)	1100.3(14)
Z	6	2
θ range (°)	2.19–25.3	2.77–25.3
μ (/mm)	0.215	0.165
F (000)	912	412
Dc (g/cm^3)	1.264	1.161
Goodness-of-fit on F^2 (e/$Å^3$)	0.966	1.08
No. data collected	15,101	6,402
No. unique data	8,103	3,901
R_{int}	0.0597	0.04
R_1, wR_2 [$I > 2\sigma(I)$]	0.0663, 0.0861	0.0714, 0.1478
R_1, wR_2 (all data)	0.1560, 0.1053	0.1016, 0.1634
Largest diff. peak and hole (e/$Å^3$)	0.28, −0.25	0.96, −0.48.

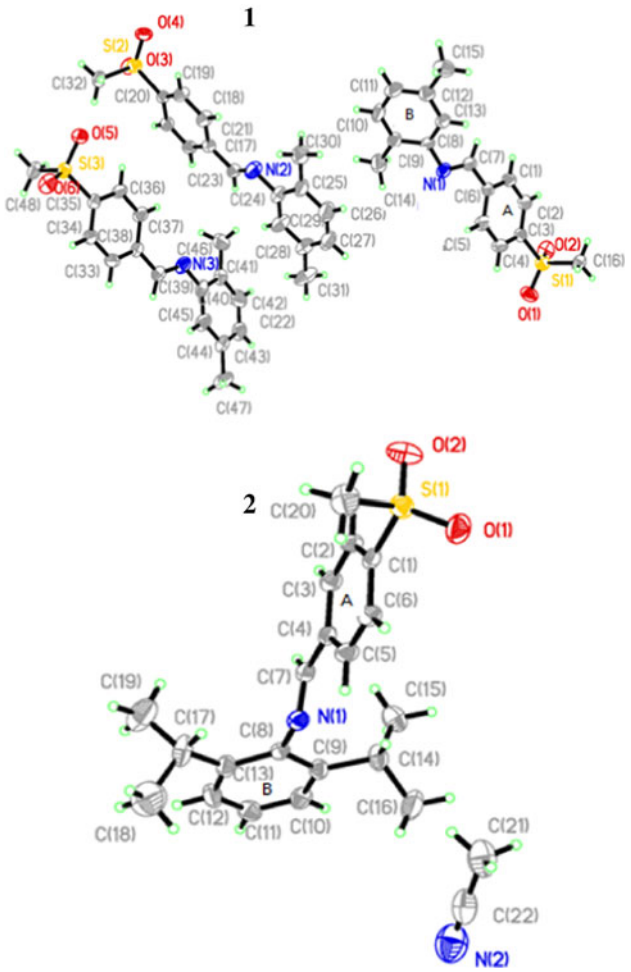


Fig. 1 The molecular configuration and atom numbering scheme for **1** and **2**, atoms are shown as 30% probability ellipsoids

Results and Discussion

Compound **1** contains three molecules in the asymmetric unit, meanwhile the crystal unit of compound **2** is composed of **2** and an acetonitrile molecule, which is linked to the oxygen atom in methylsulfonyl of **2** via C21–H21B···O2 hydrogen bond. Both of compound **1** and **2** display a trans-configuration with respect to the C=N double bond. Their crystal packings are stabilized by weak C–H···O hydrogen bonds, C–H···π interactions and van der Waals interactions.

All the bond lengths of **1** are very close to those of **2**, and comparable to the values observed in similar compounds [6–8]. However, there are significant differences in the dihedral angle between the aromatic ring A plane and the aromatic ring B plane in **1** and **2**. The dihedral angle is 67.95(19) in **1**, but it is 87.64(19) in **2**. Although the chemical compositions of aromatic ring A in **1** is the same as that in **2**, but the torsion angles are very different for two compounds. The torsion angles in **1** are C2–C3–S1–C16 = −26.0(3) and C4–C3–S1–C16 = −175.7(3), in contrast, the corresponding torsion angles in **2** are 109.3(3) for C2–C1–S1–C20 and −71.2(3) for C6–C1–S1–C20.

There are both intramolecular and intermolecular hydrogen bonds in the crystal structure of **1**. Methylsulfonyl carbon atom C16 in the molecule acts as hydrogen-bond donor to sulfonyl atom O1and O2 in the molecule at $(-x, 2 - y, 2 - z)$ and $(1 + x, y, z)$ respectively, forming the intramolecular hydrogen bonds. And the intermolecular hydrogen bonds include: (1) methylsulfonyl oxygen atom O5 in a molecule as a hydrogen-bond acceptor to carbon atom C18 in aromatic ring A in another molecule at $(-1 + x, y, z)$ to form hydrogen bond C18–H18···O5 with C···O distance of 3.311(5) Å, and (2) methylsulfonyl carbon atom C48 as a donor to methylsulfonyl oxygen atom O4 in another molecule at $(1 - x, 1 - y, -z)$ to form hydrogen bond C48–H48···O4 with C···O distance of 3.351(4) Å (as shown in Table 2).

Dissimilar to **1**, the carbon atom C2 in the aromatic ring A of compound **2**, rather than methylsulfonyl carbon atom in compound **1**, acts as hydrogen-bond donor to sulfonyl

Table 2 Hydrogen-bonding geometry (Å and °) for **1** and **2**

Bond	Symmetry code	D–H	H···A	D(D_A)	Angle
1					
C(16)–H(16A)···O(1)	$-x, 2 - y, 2 - z$	0.96	2.57	3.525(4)	174
C(16)–H(16B)···O(2)	$1 + x, y, z$	0.96	2.42	3.287(4)	150
C(18)–H(18)···O(5)	$-1 + x, y, z$	0.93	2.53	3.311(5)	141
C(32)–H(32B)···O(3)	$1 + x, y, z$	0.96	2.48	3.357(4)	152
C(48)–H(48B)···O(6)	$-1 + x, y, z$	0.96	2.46	3.317(4)	148
C(48)–H(48C)···O(4)	$1 - x, 1 - y, -z$	0.96	2.40	3.351(4)	171
2					
C(2)–H(2)···O(2)		0.93	2.54	2.915(5)	105
C(14)–H(14)···N(1)		0.98	2.41	2.878(6)	109
C(17)–H(17)···N(1)		0.98	2.39	2.878(7)	110
C(21)–H(21B)···O(2)	$-x, -y, 1 - z$	0.96	2.53	3.453(8)	161

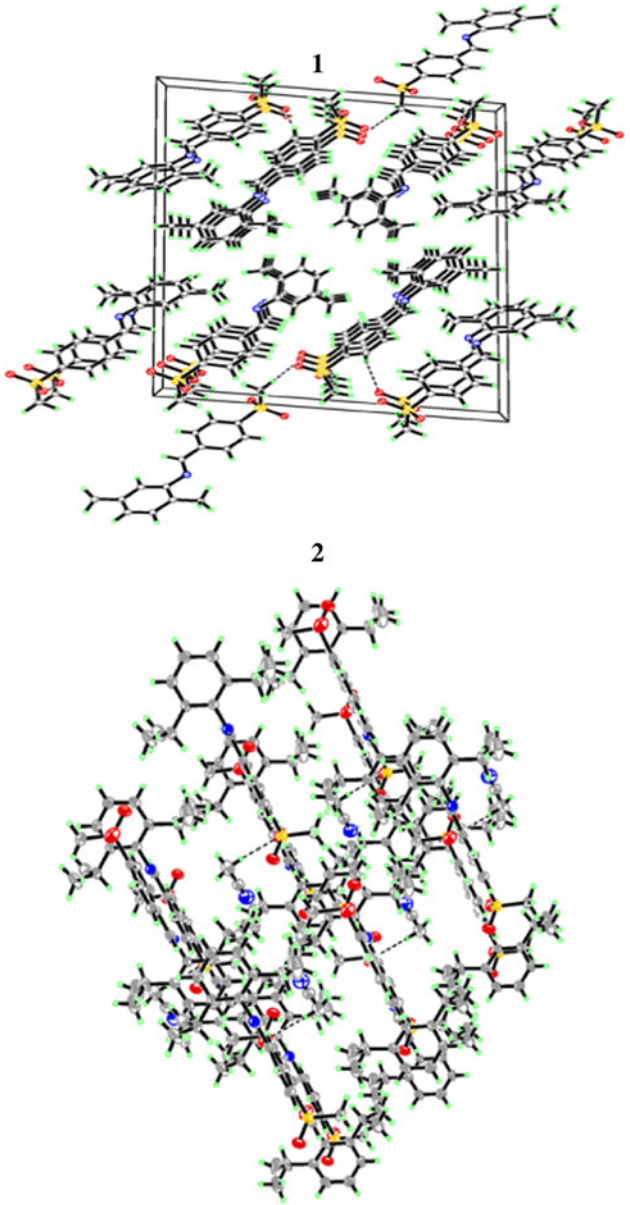


Fig. 2 The packing diagram for **1** and **2**, hydrogen-bonding interactions are represented by *dashed lines*

atom O2 in the molecule, forming intramolecular hydrogen bond.

Carbon atom C21 of acetonitrile solvent molecule takes part in the formation of intermolecular hydrogen bond C21–H21B···O2 (symmetry code: $-x$, $-y$, $1 - z$), which plays an important role in stabilizing crystal packing structure of **2**. Besides, the nitrogen atoms of the Schiff bases also participate in the formation of the weak intramolecular hydrogen C–H···N in the crystal structure of **1** and **2**.

In addition, there are C–H···π interactions in the both compounds. The C15–H15C → Cg interactions with 2.92 Å of distance of C15···Cg (2) exists in compound **1** and the C6-H6 → Cg (2) interactions with 2.83 Å of distance of C6···Cg (2) for compound **2**.

These hydrogen bonds and C–H···π interactions mentioned above not only play crucial roles in the formation, the stability and the crystallization of compound 1 and compound 2, but also these hydrogen bonding, C–H···π interactions and van der Waals interactions lead to the moieties into a three-dimensional network structure (Fig. 2).

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