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### Synthesis and Characterization of New Schiff Bases 2-(2-(2-(Aryl)Methyleneamino)Phenylthio) Ethylthio)-N-((aryl)Methylene)Benzeneamine

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## SYNTHESIS AND CHARACTERIZATION OF NEW SCHIFF BASES 2-(2-(2-(ARYL)METHYLENEAMINO)PHENYLTHIO)ETHYLTHIO)-N-((ARYL)METHYLENE)BENZENEAMINE

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*A series of Schiff bases containing four to six coordination sites  $N_2S_2$   $X_2$  ( $X = O, N$ ) 2-(2-(2-(aryl)methyleneamino)phenylthio)ethylthio)-N-((aryl)methylene)benzeneamine (2c–f) were prepared from the reaction of 1,2-di(2-aminophenylthio)ethane (1) with aromatic aldehydes. All compounds were characterized by means IR, mass,  $^1H$  and  $^{13}C$  NMR spectroscopy, and elemental analysis, and in the case of 2b with a single crystal X-ray diffraction. The X-ray crystal structure of 2b showed that the resonance occurs between aromatic rings, through the  $C=N$  bonds of the molecule.*

*Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements to view the free supplemental file.*

**Keywords** 2-(2-(2-(Aryl)methyleneamino)phenylthio)ethylthio)-N-((aryl)methylene)benzeneamine; 1,2-di(2-aminophenylthio)ethane; Schiff base; X-ray

## INTRODUCTION

The coordination chemistry of transition metal ions with the  $N_2S_2$  donor sets has received considerable interest in recent years.<sup>1–5</sup> Quadridentate ligands with the donor sets  $N_2S_2$  are very important for nuclear medicine, because their technetium and rhenium complexes are sufficiently stable in vivo to function as effective radioimaging and therapeutic agents.<sup>6,7</sup>

The N, S donor ligand and Pd(II), Pt(II) complexes, used to prepare antiviral, antifungal, antimicrobial, antitumor<sup>8,9</sup> products, and their mechanism of action most probably involves the inhibition of ribonucleotide reductase, converting ribonucleotides to deoxyribonucleotides.<sup>10,11</sup> Recently, new  $N_2S_2$  Schiff bases **2a–b** were prepared from the reaction of 1,2-di(2-amino phenylthio)ethane (**1**) with aromatic aldehydes.<sup>12–14</sup> These Schiff bases are suitable for preparation of coordination polymers and oxidative cleavage of the ligand when it was reacted with transition metal ions, rather than forming a simple complex.<sup>15–17</sup> Considering these properties, we have prepared some new Schiff bases,  $N_4S_2$ ,  $N_2O_4$ ,  $N_2S_4$ ,

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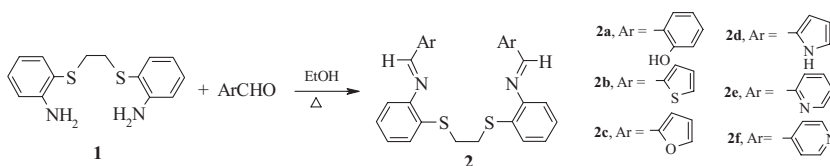
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and  $\text{N}_2\text{O}_2\text{S}_2$ , from the reaction of 1,2-di(2-aminophenylthio)ethane (**1**) with aromatic aldehydes. The Schiff bases **2** contain four to six coordination sites; they are therefore suitable for the preparation of catalysts or coordination polymers.

## RESULTS AND DISCUSSION

The condensation reaction of 1,2-di(2-aminophenylthio)ethane (**1**) with various substituted aromatic aldehydes in absolute ethanol gave the acyclic Schiff base products (Scheme 1). All prepared compounds **2c–f** are air-stable solids and soluble in acetone,  $\text{CDCl}_3$ , and THF. The structure of the prepared compounds **2c–f** was confirmed by means of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, mass spectroscopy, and elemental analysis. The compound **2b** was further characterized by single crystal X-ray crystallography (Figure 1).



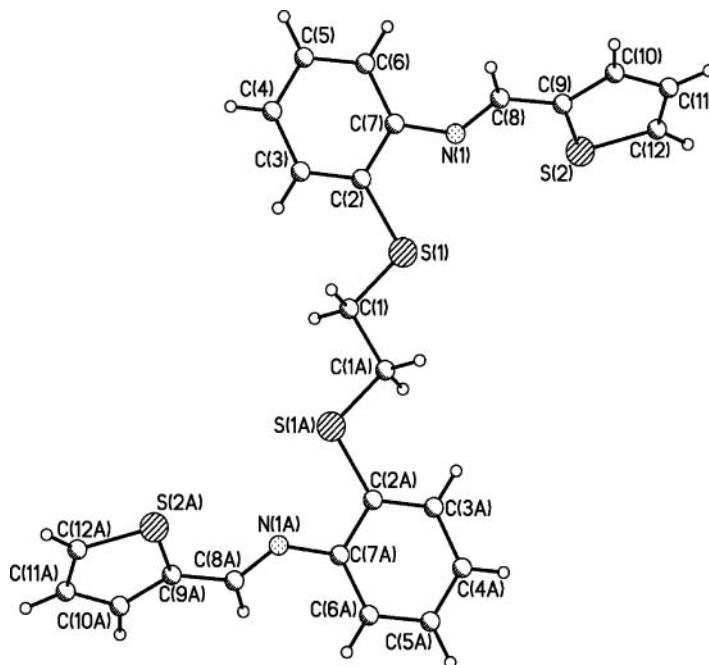
Scheme 1

The infrared spectra of all products, recorded in the region of  $4000\text{--}500\text{ cm}^{-1}$ , similar to the total absence of  $\text{NH}_2$  in the IR spectra of **1**, together with the appearance of new absorption ( $\text{C=N}$ ) in the range of  $1605\text{--}1627\text{ cm}^{-1}$ , clearly indicated that a new Schiff base had formed in each case. A band observed in the spectra of **2c–f** in the region of  $2835\text{--}2923\text{ cm}^{-1}$  can be assigned to the  $\text{CH=N}$  group. The IR spectra of **2c–f** show bands at  $740\text{--}778\text{ cm}^{-1}$  assigned to the C–S stretching mode. The  $^1\text{H}$  NMR spectrum of **2c–f** shows a single  $^1\text{H}$  imine resonance at ca.  $8.18\text{--}8.71\text{ ppm}$ , demonstrating the equivalence of the two imine environments. The absorption signals of aromatic protons appeared in the region of  $6.54\text{--}7.81\text{ ppm}$ , and the  $\text{CH}_2$  group of all Schiff bases appeared in  $3.19\text{--}3.27\text{ ppm}$ . The  $^{13}\text{C}$  NMR spectra include imine and methylene carbons, which appeared at  $152.21\text{--}154.58\text{ ppm}$  and  $31.51\text{--}31.92\text{ ppm}$ , respectively. The molecular structure of **2b**, which is shown in Figure 1, possesses a center of symmetry and exhibits a helical structure.<sup>18</sup>

The bond lengths, angle, and torsion of **2b** show that a resonance occurs between aromatic rings, through the  $\text{C=N}$  bonds of the molecule. The thiophene ring is a rather planar relative to the aminothiophenole ring, and the imine groups have the *anti* conformation in agreement with the NMR spectra. However, the  $\text{C}(1)\text{--C}(1\text{A})$  bond has a single bond characteristic (Table I).

## EXPERIMENTAL

All chemical reagents were obtained from Merck and Fluka and used without further purification. The diamine 1,2-di(2-aminophenylthio)ethane (**1**) was prepared by the method in the literature.<sup>8</sup> Melting points were measured with Electrothermal 9200 apparatus and are uncorrected. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. The FT-IR spectra (potassium bromide) were recorded with a Shimadzu 8400 S spectrometer. Mass spectra were recorded on a Shimadzu QD 5050.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a Bruker DRX-500 Avance Spectrometer in  $\text{CDCl}_3$  as solvent.



**Figure 1** ORTEP drawing of 2-(2-(2-((thiophen-2-yl)methyleneamino)phenylthio) ethylthio)-N-((thiophen-2-yl) methylene)benzenamine (**2b**).

### General Procedure for Preparation of Schiff Base from the Reaction of 2-(2-(2-Amino phenylthio)benzeneamine with Aldehyde

To a stirring solution of 1,2-di(2-aminophenylthio)ethane (**1**) (2.76 g, 10 mmol) in absolute ethanol (25 mL), a solution of aldehyde (20 mmol) was added dropwise for 10 min at room temperature. The mixture was stirred and heated to reflux for 5 h. Then the solvent was evaporated under reduced pressure, and the product was crystallized from acetonitrile.

**2-(2-(2-(Furan-2-yl)methyleneamino)phenylthio)ethylthio)-N-((furan-2-yl)methylene) benzeneamine (**2c**).** Yield: 2.12 g (49%), mp 122–123°C; Color:

**Table I** Selected bond lengths (Å), bond angles (°), and torsion angles (°) for **2b**

Bond lengths	Å	Bond angles	(°)	Torsion angles	(°)
C(1)–C(1)#1	1.524	C(1)#1–C(1)–S(1)	107.55	C(2)–S(1)–C(1)–C(1)#1	–166.07
S(1)–C(1)	1.811	C(2)–S(1)–C(1)	102.36	C(1)–S(1)–C(2)–C(3)	–4.13
S(1)–C(2)	1.763	S(1)–C(1)–H(1A)	110.20	C(1)–S(1)–C(2)–C(7)	174.52
C(2)–C(7)	1.412	C(7)–C(2)–S(1)	115.42	C(8)–N(1)–C(7)–C(6)	53.92
N(1)–C(7)	1.411	C(3)–C(2)–S(1)	125.63	S(1)–C(2)–C(7)–N(1)	2.73
N(1)–C(8)	1.282	N(1)–C(7)–C(2)	117.03	C(8)–N(1)–C(7)–C(2)	–130.73
C(8)–C(9)	1.439	C(8)–N(1)–C(7)	118.94	C(7)–N(1)–C(8)–C(9)	–177.31
S(2)–C(9)	1.726	N(1)–C(8)–C(9)	121.68	N(1)–C(8)–C(9)–C(10)	–174.31
C(9)–C(10)	1.3757	N(1)–C(8)–H(8A)	119.20	N(1)–C(8)–C(9)–S(2)	8.43
C(8)–H(8A)	0.9500	C(8)–C(9)–S(2)	121.50	C(8)–C(9)–C(10)–C(11)	–177.69
C(1)–H(1A)	0.9900	C(12)–S(2)–C(9)	91.53	S(2)–C(9)–C(10)–C(11)	–0.20

yellow; FT-IR: 3124–3095 (Ar–H), 2923, 2880 (CH=N), 1623 (C=N), 1571–1436 (C=C), 1022 (C–O), 783 (C–S), 744 (C–S)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  = 8.18 (s, 2H, CH=N), 7.62 (d, 2H, Ar–H,  $J$  = 3.7 Hz), 7.29 (d, 2H, Ar–H,  $J$  = 3.4 Hz), 7.20–7.18 (d, 2H, Ph–H,  $J$  = 5.2 Hz), 7.15–7.12 (t, 2H, Ar–H), 7.00–6.95 (m, 4H, Ph–H), 6.55–6.54 (d, 2H, Ph–H,  $J$  = 4.7 Hz), 3.19 (s, 4H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR:  $\delta$  152.21, 150.73, 145.88, 130.59, 128.11, 126.72, 126.38, 118.46, 118.26, 118.14, 116.20, 112.24, 31.51. The EI-MS:  $m/z$  432( $\text{M}^+$ ), 429, 355, 271; Anal. Calcd. For  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$ : C, 66.64; H, 4.66; N, 6.48; S, 14.83. Found: C, 66.47; H, 4.53; N, 6.34; S, 14.03.

**2-(2-(2-(1H-Pyrrol-2-yl)methylene)-2-(2-(1H-pyrrol-2-yl)methyleneamino)phenylthio)ethylthio)benzeneamine (2d).** Yield: 2.2 g (51%), FT-IR: 3329 (N–H), 3132–3095 (Ar–H), 2912, 2877 (CH=N), 1650 (C=N), 1606–1477 (C=C), 748 (C–S)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.17 (s, 2H, CH=N), 7.44 (d, 2H, Ar–H,  $J$  = 4.1 Hz), 7.38 (d, 2H, Ar–H,  $J$  = 3.3 Hz), 7.23 (d, 2H, Ph–H,  $J$  = 5.4 Hz), 7.17–7.14 (t, 2H, Ar–H), 7.03 (d, 2H, Ph–H,  $J$  = 4.9 Hz), 6.76–6.71 (m, 4H, Ph–H), 6.30 (bs, 2H, NH), 3.18 (s, 4H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR:  $\delta$  150.73, 150.18, 136.17, 130.48, 129.91, 126.83, 126.30, 118.49, 117.02, 116.26, 114.88, 31.50. The EI-MS:  $m/z$  430( $\text{M}^+$ ), 429( $\text{M}-1$ ) $^+$ , 271; Anal. Calcd. For  $\text{C}_{24}\text{H}_{22}\text{N}_4\text{S}_2$ : C, 66.94; H, 5.15; N, 13.01; S, 14.89. Found: C, 66.62; H, 4.91; N, 12.89; S, 15.02.

**2-(2-(2-(Pyridin-2-yl)methyleneamino)phenylthio)ethylthio)-N-((pyridin-2-yl)methyl ene)benzeneamine (2e).** Yield: 2.22 g (51%), mp 127–128°C, Color: red; FT-IR: 3153–3062 (Ar–H), 2975, 2877 (N=CH), 1627 (C=N), 1588–1471 (C=C), 777 (C–S), 740 (C–S)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.53 (s, 2H, CH=N), 8.70 (d, 2H, Py–H,  $J$  = 5.3 Hz), 8.28 (d, 2H, Py–H,  $J$  = 4.9 Hz), 7.81–7.77 (t, 2H, Py–H,  $J$  = 2.8 Hz), 7.38–7.35 (t, 2H, Py–H,  $J$  = 3.05 Hz), 7.31–7.19 (m, 8H, Ar–H), 3.23 (s, 4H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR:  $\delta$  160.73, 154.58, 149.87, 149.62, 136.69, 130.97, 128.25, 127.06, 126.96, 125.27, 122.00, 118.21, 31.53; The EI-MS:  $m/z$  454( $\text{M}^+$ ), 452( $\text{M}-2$ ) $^+$  431, 429, 355, 271. Anal. Calcd. For  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{S}_2$ : C, 68.69; H, 4.88; N, 12.32; S, 14.11. Found: C, 68.84; H, 4.71; N, 12.14; S, 14.38.

**2-(2-(2-(Pyridin-4-yl)methyleneamino)phenylthio)ethylthio)-N-((pyridin-4-yl)methyl ene)benzeneamine (2f).** Yield: 2.80 g (60%), mp 162–162.5°C, Color: yellow; FT-IR: 3058–3018 (Ar–H), 2993, 2887 (CH=N), 1623 (C=N), 1596–1460 (C=C), 817 (C–S), 746 (C–S)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  8.37 (s, 2H, N=CH), 8.76 (d, 2H, Py–H,  $J$  = 5.6 Hz), 7.77, 7.75 (d, 2H, Py–H,  $J$  = 5.6 Hz), 7.32–7.01 (m, 8H, Ar–H), 3.21 (s, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR:  $\delta$  158.07, 150.65, 149.74, 142.48, 130.93, 128.12, 127.36, 126.90, 122.39, 118.06, 31.25. The EI-MS:  $m/z$  454( $\text{M}^+$ ), 452( $\text{M}-2$ ) $^+$  431, 429, 355, 271. Anal. Calcd. For  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{S}_2$ : C, 68.69; H, 4.88; N, 12.32; S, 14.11. Found: C, 68.41; H, 4.68; N, 12.11; S, 14.29.

### X-Ray Structure Analysis of 2-(2-(2-((Thiophen-2-yl)methyleneamino)phenylthio)ethylthio)-N-((thiophen-2-yl)ethylene)benzenamine (2b)

The clear colorless crystal with dimension  $0.30 \times 0.20 \times 0.15 \text{ mm}^3$  crystallized from MeCN/MeOH was used for data collection on a Bruker SMART 1000 CCD diffractometer with graphite monochromated  $\text{MoK}\alpha$  ( $\lambda$  = 0.71073 Å).  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{S}_4$ , FW = 464.66. Monoclinic crystals in a P 21/c Space group,  $a$  = 11.179(5) Å,  $b$  = 7.730(4) Å,  $c$  = 12.608(6) Å,  $\alpha$  = 90°,  $\beta$  = 91.899(12)°,  $\gamma$  = 90°,  $V$  = 1088.9(9) Å $^3$ .  $Z$  = 2,  $D_{\text{calc}}$  = 1.417 g/cm $^3$ .  $\mu$  = 0.451 mm $^{-1}$ ,  $F(000)$  = 484,  $T$  = 100 (2) K. Of the 12,880 total reflections, 2899 were unique ( $[R(\text{int}) = 0.0294]$ ). The structure was solved by direct methods (SHELXTL) $^{19}$  and refined by full-matrix least-squares on  $F^2$  (isotropic refinement of the

molecule and location of remaining non-hydrogen atoms from a difference Fourier map and subsequent anisotropy refinement on all atoms; H atoms were found after high-angle refinement in a difference Fourier map and their positions included in the final stages of refinement), factors of  $R = 0.0288$ ,  $wR2 = 0.0751$  for 2569 reflections with  $I < 2\sigma(I)$ . No significant features, only ripples from 0.337 to  $-0.257 \text{ e } \text{\AA}^{-3}$ , were observed in the final difference map. The nonhydrogen atoms were refined anisotropically.

Complete bond lengths and angles, coordinates, and displacement parameters have been deposited at Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK on request, quoting the deposition numbers 730627 for 2-(2-(-2-((thiophen-2-yl)methyleneamino)phenylthio)ethylthio)-N-((thiophen-2-yl)methylene)benzenamine (K5).

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