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Synthesis of 5-Substituted 2,9-Dimethyl-1,10-Phenanthroline Dialdehydes and Their Schiff Bases with Sulfur-Containing Amines

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ABSTRACT

Eight new Schiff bases of 5-nitro and 5-bromo-substituted 1,10-phenanthroline-2,9-dicarboxaldehydes with sulfur-containing amines, thiosemicarbazide, S-alkyl/aryl dithiocarbazates and 2-mercaptoaniline have been synthesized and characterized by a variety of spectroscopic methods. The condensation reactions of the dialdehydes with the amines were carried out both in the presence and absence of conc. sulfuric acid. A significant increase in yield of the Schiff bases was observed when the reactions were carried out in the presence of sulfuric acid.

Keywords: 5-Nitro-1,10-Phenanthroline Dialdehyde; 5-Bromo-1,10-Phenanthroline Dialdehyde; Schiff Bases; S-Alkyl/Aryldithiocarbazates; Thiosemicarbazide

1. Introduction

Recently, nitrogen and sulfur-containing organic chelating agents such as the Schiff bases derived from 2,9-dimethyl-1,10-phenanthroline dialdehyde and sulfur-containing amines and their metal complexes have received considerable attention because of their important roles in synthetic and medicinal chemistry[1]. By properly designing this type of compounds and studying their structure-activity relationships, potentially useful antibacterial, antifungal and anticancer agents can also be synthesized [2]. 2,9-Dimethyl-1,10-phenanthroline and its derivatives from which 2,9-dimethyl-1,10-phenanthroline dialdehydes are prepared, are themselves important ligands for complexation with many metal ions [3]. This property has made them important in different areas like self-assembly and catalysis. It has also played a significant role in both analytical and preparative coordination chemistry as well as in the preparation of many mixed-ligand complexes [4].

Although a large number of Schiff bases containing "hard" nitrogen and "soft" sulfur donor atoms have been synthesized using S-alkyl/aryl dithiocarbazates and heterocyclic aldehydes and ketones, which are able to form stable complexes with a variety of metal ions [5], less work has been reported on Schiff bases formed by condensation of 1,10-phenanthroline dialdehydes with sufur-containing amines such as S-alkyl/aryl dithioicarbazates, thiosemi-carbazide and aminobenzenethiol.

In view of the importance of Schiff bases derived from 1,10-phenanthroline dialdehyde and sulfur-containing amines in coordination chemistry and biology, we report here the synthesis and characterization of eight new Schiff bases formed by condensation of 5-nitro-1,10-phenanthroline-2,9-dialdehyde and 5-bromo-1,10-phenanthroline-2,9-dialdehyde with different types of sulfur-containing amines.

2. General Methods and Procedures

HPLC grade solvents were used in all the reactions. The conventional method of synthesis of the Schiff bases involves refluxing the reaction mixture containing the dialdehydes and amines for 1 hour followed by filtration of the solid products using suction filtration.

In all the reactions, 2 - 3 drops of conc. sulfuric acid were used. The solid product that had formed was filtered off using suction filtration. All the NMR data

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were recorded on a 400 MHz Varian NMR Spectrometer. Mass Spectra were obtained on a Varian LC-MS with ESI.

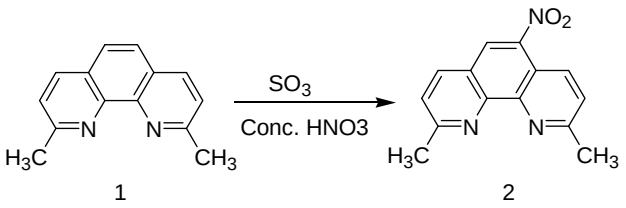
3. Synthesis

We have previously reported the preparation, characterization and X-ray structures of different types of Schiff bases derived from 1,10-phenanthroline [6]. Now we report here the synthesis and characterization of eight new Schiff bases formed by condensation of the 5-bromo- and 5-nitro-substituted phenanthroline dialedhydes with amines containing thione or thiol sulfur donor atoms in their backbones. All the compounds have been structurally characterized by different spectroscopic methods.

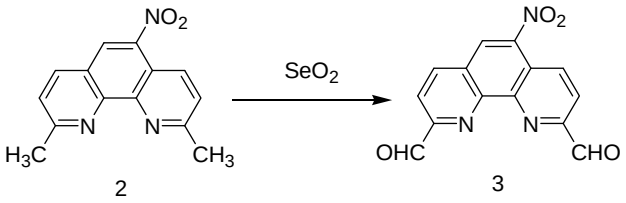
3.1. Synthesis of 5-Nitro-1,10-Phenanthroline-2,9-Dicarboxaldehyde from 5-Nitro 2,9-Dimethyl-1,10-Phenanthroline

5-Nitro-2,9-dimethyl-1,10-phenanthroline (2) was synthesized from 2,9-dimethyl-1,10-phenanthroline hemihydrate (1) following a previously reported procedure (**Scheme 1**) [7,8]. The yield of the compound was found to be the same as reported in the literature. The crude product was purified by chromatography using combi flash (ethyl acetate: dichloromethane) to give the pure compound [Y: 70%].

5-Nitro-1,10-phenanthroline-2,9-dicarboxaldehyde (3) was synthesized from 5-nitro-2,9-dimethyl-1,10-Phenanthroline (2) following a known procedure (**Scheme 2**) [9]. The yield of the compound was found to be the same as that reported in the literature. The crude product was recrystallized from chloroform and dried under vacuum to give the pure compound [Y: 91%].



Scheme 1. Synthesis of 5-Nitro-1,10-phenanthroline.



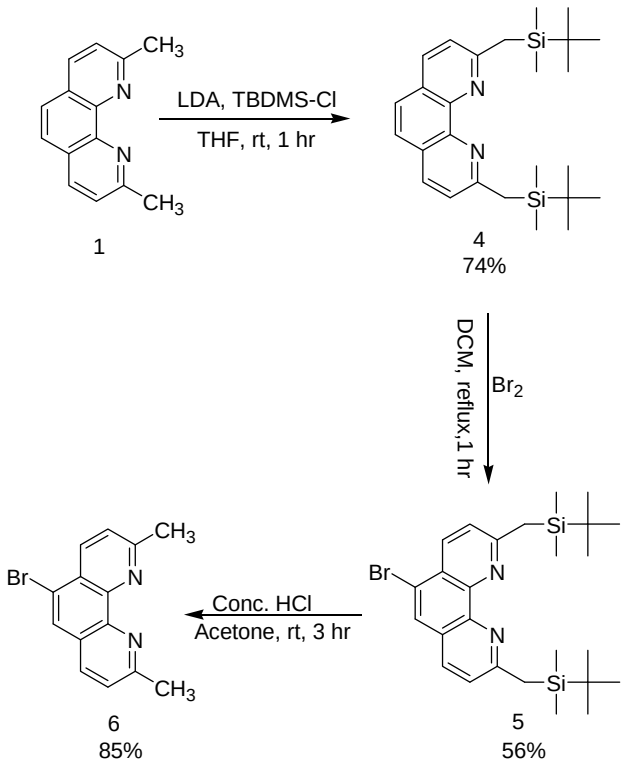
Scheme 2. Synthesis of 5-Nitro-1,10-Phenanthroline-2,9-dialdehyde.

3.2. Synthesis of 5-Bromo-1,10-Phenanthroline-2,9-Dicarboxaldehyde from 5-Bromo-2,9-Dimethyl -1,10-Phenanthroline

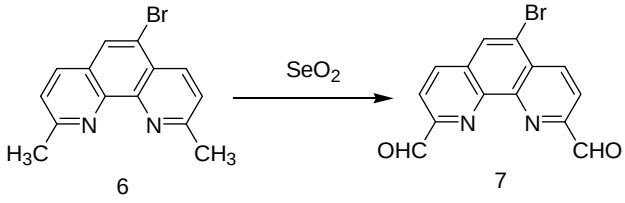
The previously reported procedure [3] involving three steps, was also used here to synthesize 5-bromo-2,9-dimethyl-1,10-phenanthroline (6) from 2,9-dime-thyl-1, 10-phenanthroline (1) (**Scheme 3**).

The yield of the compound was found to be the same as that reported in the literatures procedure. [Y: 85%].

5-Bromo-1, 10-phenanthroline-2,9-dicarboxal dehyde (7) was synthesized from 5-bromo-2,9-dimethyl-1,10-phenanthroline (6) following a known procedure [10] (**Scheme 4**). An increase of reaction time resulted in the increase in the yield of the dialdehyde. The crude product was recrystallized from hot ethanol and dried under vacuum to give the pure compound [Y: 82%]. The reported yield was 62%.



Scheme 3. Synthesis of 5-bromo-1,10-phenanthroline-2,9-dicarboxaldehyde.



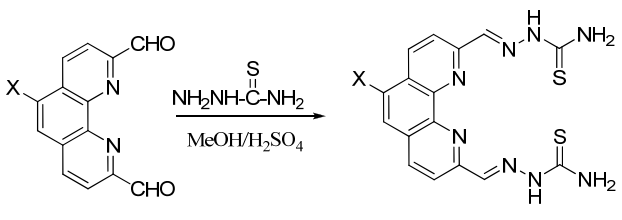
Scheme 4. Synthesis of 5-Bromo-1, 10-Phenanthroline-2,9-dicarboxaldehyde.

3.3. Synthesis of the Schiff Bases with Thiosemicarbazide

Thiosemicarbazide (4 equiv.) was added to a hot solution of 5-nitro- or 5-bromo-1,10-phenanthroline-2,9-dicarboxaldehyde (1 equiv) in methanol (20 mL) containing 2 - 3 drops of conc. sulfuric acid. The solution was refluxed for 1 hr whereupon the reaction mixture was allowed to cool down to room temperature. The product that had formed was filtered off, washed with methanol and dried under vacuum. Recrystallization of the crude product from dichloromethane afforded white crystals (**Scheme 5**). **Table 1** shows different reaction conditions and percent yields for the two starting materials.

(2,2')-2'-(5-Nitro-1,10-Phenanthroline-2,9-diyl) bis (methan-1-yl-1-ylidene)bis-(hydrazinecar-bodithioate) (8): IR: ν (cm^{-1}): 3250 (NH_2), 3154 (C-H), 1589 (C=N), 1522 (N=O), 1115 (C=S). ^{1}H-NMR (DMSO-d_6, ppm): δ_H = 12.05 (s, 1NH), 12.03 (s, 1NH), 9.0 (s, 1H), 8.86 (s, 2H), 8.86 (d, J = 7.44,1H), 8.76 (d, J = 8.56,1H), 8.57 (d, J = 7.44. 1H,), 8.48 (d, J = 8.56, 1H), 7.60 (s, br, $2NH_2$). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 178.61, 178.58, 156.80, 154.60, 146.35, 144.90, 143.78, 141.60, 141.42, 138.63, 132.39, 125.88, 125.70, 121.02, 120.97, 120.49. LC-MS (m/z): 428 ($M+H^+$), 427 (M^+), 426 ($M-H^+$), 411 ($M+H^+-NH_3$), 399 ($M+2H^+-N_2H_2$), 391($M+H^+-2NH_2$), 383 ($M+ 2H^+-NO_2$), 336 ($M+2H^+-CS_2-NH_3$), 254 ($M+4H^+-N_5C_3S_2H_7$).

(2,2')-2'-(5-Bromo-1,10-Phenanthroline-2,9-diyl)bis (methan-1-yl-1-ylidene) bis-(hydrazinecar-bodithioate) (9): IR: ν (cm^{-1}): 3300 (NH_2), 3160 (C-H), 2951(CH aromatic), 1568 (C=N), 1092 (C=S). ^{1}H-NMR (DMSO-d_6, ppm): δ_H = 12.02 (s, 1NH), 12.00 (s, 1NH), 8.84 (d, J = 8.68,1H), 8.76 (d, J = 8.48, 1H), 8.60 (d, J = 8.76,1H), 8.54 (s, 1H),8.52 (s, 2H), 8.45 (d, J = 9.24,1H), 7.56 (s, br, $2NH_2$). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 178.54(2), 154.36, 154.02, 144.94, 143.73, 141.66, 141.43, 136.35, 135.73, 130.19, 128.99, 127.28, 121.02, 120.74, 120.11. LC-MS (m/z): 463/461 ($M+2H^+$), 461/459 (M^+), 446/444 ($M+2H^+-NH_3$), 429/427 ($M+2H^+-2NH_3$), 413/414 (M^+-S-NH_2), 399 (M^+-NH_2CSH), 385/ 383($M+3H^+$-Br). 349/350 ($M^+-CS_2-2NH_3$), 337/335 ($M^+-2C_2S_2H_2-2NH_3$), 281/279 ($M+4H^+-2CS_2-2NH_2$).



3. X = NO_2
7. X = Br

8. X = NO_2
9. X = Br

Scheme 5. Synthesis of Schiff Bases with thiosemicarbazide.

Table 1. Reaction conditions and percent yields for the synthesis of the schiff bases.

Condition	Solvent	Time	Yield %	
			X = NO_2	X = Br
With H_2SO_4	HC_3OH	1 hr	89	81
Without H_2SO_4	CH_3OH	1 hr	60	57

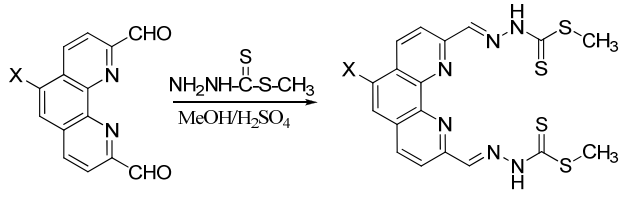
3.4. Synthesis of the Schiff Bases with S-Methyldithiocarbazate (SMDTC):

SMDTC was prepared following the procedure of Taraf-der, *et al.* [11].

SMDTC (3 equiv.) was added to a hot solution of 5-substituted (NO_2, Br) 1,10-phenanthroline-2,9-dicarboxaldehyde (l equiv.) in 20 mL methanol containing 2 - 3 drops of conc. sulfuric acid. The solution was refluxed for 1 hr and then allowed to cool to room temperature. The solid product that had formed was filtered off, washed with methanol and dried under vacuum. The crude product was recrystallized from dimethyl sulfoxide to obtain white crystals (**Scheme 6**). Yields are shown in **Table 2** for various reaction conditions.

(2,2')-Dimethyl 2,2'-(5-Nitro-1,10-Phenanthro-line-2,9-diyl)bis(methan-1-yl-1-ylidene)-bis(hydr-azinecar bodithioate)(10):

IR: ν (cm^{-1}): 3200 (N-H), 2980, 2914 (CH aromatic and aliphatic), 1580 (C=N), 1527(N=O), 1099 (C=S). ^{1}H-NMR (DMSO-d_6, ppm): δ_H = 13.78 (s, 1NH), 13.77 (s, 1NH), 9.02(s, 1H), 8.94(d, J = 8.64,1H), 8.78 (d, J = 7.96, 1H), 8.52 (s,2H), 8.35(d, J = 9.00,1H), 8.32(d, J = 8.36, 1H), 2.61 (s, 6H, CH_3). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 200.13(2), 155.57, 153.53, 146.45, 145.43(2),



3. X = NO_2
7. X = Br

10. X = NO_2
11. X= Br

Scheme 6. Synthesis of the Schiff Bases with S-methyldithiocarbazate (SMDTC).

Table 2. Reaction conditions and percent yields for the synthesis of the schiff bases.

Condition	Solvent	Time	Yield %	
			X = NO_2	X = NO_2
With H_2SO_4	CH_3OH	1 hr	55	54
Without H_2SO_4	CH_3OH	1 hr	35	46

145.27(2), 145.05, 139.35, 133.26, 126.39, 126.16, 121.01, 120.38, 16.95(2). LC-MS (m/z, M^+): 492 ($M+3H^+$), 491 ($M+2H^+$), 490 ($M+H^+$), 489(M^+), 474(M^+-CH_3), 459(M^+-$2CH_3$), 443 (M^+-NO_2), 397 ($M+2H^+$-$2CH_3S$), 384 ($M+H^+$-CH_3SCSNH), 308 ($M+H^+$-$2CH_3SCS$), 307 (M^+-$2CH_3SCS$), 303 (M^+-$2CH_3SH$-$C_2H_2S_2$).

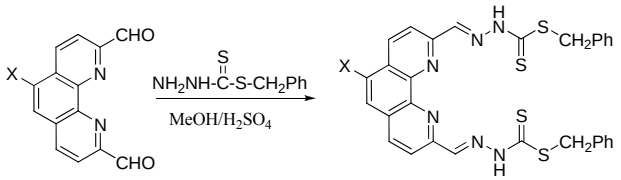
(2,2')-Dimethyl 2,2'-(5-Bromo-1,10-Phenanthro-line-2,9-diyl)bis(methan-1-yl-1-ylidene)-bis(hydr-azinecarbodithioate)(11):

IR: ν (cm^{-1}): 3240 (N-H), 3160, 2915 (CH aromatic and aliphatic), 1567 (C=N), 1056(C=S). ^{1}H-NMR (DMSO-d_6, ppm): δ_H = 13.79 (s, 1NH), 13.76 (s, 1NH), 8.74 (d, J = 8.60, 1H), 8.61 (s, 1H), 8.57 (s, 2H), 8.56 (d, J = 8.56,1H), 8.39 (d, J = 8.84,1H),, 8.29 (d, J = 8.40,1H), 2.61 (s, 3H, CH_3), 2.60 (s, 3H, CH_3). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 199.89, 199.77, 153.30, 153.07, 145.87, 145.46, 144.34, 136.72, 136.68, 130.73, 130.72, 129.37, 127.93, 120.70, 120.31, 119.91, 16.93(2). LC-MS (m/z, M^+): 525/523 ($M+H^+$), 524/522 (M^+), 477/475 (M^+-CH_3S), 450/448 ($M+2H^+$-CS_2), 443/441 (M^+-Br), 429/427 (M^+-$2CH_3S$), 366($M+H^+$-Br-CS_2), 338 (M^+-Br-CH_3S-$2N_2$).

3.5. Synthesis of the Schiff Bases with S-Benzyldithiocarbazate (SBDTC)

SBDTC was prepared using a procedure described by Audrieth *et al*. [12]. SBDTC (3 equiv) was added to a hot solution of 5-substituted (NO_2, Br) 1,10-phenanthroline-2,9-dicarboxaldehyde (1 equiv.) in 20 mL methanol followed by the addition of two drops of acetic acid. The reaction mixture was refluxed for 1 h, then left to cool to room temperature. The product that had formed was filtered off, washed with methanol and dried in vacuum. White crystals of the compound were obtained by recrystallizing the crude product from dimethylsulfoxide (**Scheme 7**). Yields with and without acid are given in **Table 3**.

(2,2')-Benzyl 2,2'-(5-Nitro-1,10-Phenanthroline-2,9-diyl)bis(methan-1-yl-1-ylidene)-bis(hydrazinecarbodithioate)(12): IR: ν (cm^{-1}): 3150 (N-H), 3026 (C-H aromatic), 2920 (C-H aliphatic), 1566 (C=N), 1605,1494 (C=C aromatic),1526 (N=O), 1094(C=S). ^{1}H-NMR (DMSO-d_6, ppm): δ_H = 13.79 (s, 1NH), 13.78 (s, 1NH), 8.99(s, 1H), 8.88(d, J = 8.80,1H), 8.71 (d, J = 8.32, 1H), 8.48(s,1H), 8.47(s,1H), 8.29(d, J = 8.88,1H), 8.25(d, J = 8.44, 1H), 7.48 - 7.31(m, 10H), 4.54 (s, 4H, 2xCH_2). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 198.25, 198.14, 155.51, 153.41, 146.41, 145.62, 139.36, 136.38, 129.32(6), 129.12(8), 128.56(2), 127.38, 126.19, 121.03, 120.39, 37.87(2). LC-MS (m/z): 642 ($M+H^+$), 641 (M^+), 597($M+H^+$-NO_2), 479 ($M+3H^+$-$PhCH_2S$), 393 ($M+2H^+$-$2PhCH_2S$), 356 ($M+4H^+$-$2PhCH_2$-CS_2-S), 303 ($M+2H^+$-$2PhCH_2SCS$), 279 ($M+2H^+$-$2PhCH_2SCSNH$).



3. X = NO_2
7. X = Br

12. X = NO_2
13. X = Br

Scheme 7. Synthesis of the Schiff Bases with S-benzyldithiocarbazate (SBDTC).

Table 3. Reaction Conditions and Percent Yields for the Synthesis of Schiff Bases.

Condition	Solvent	Time	Yield %	
			X = NO_2	X = NO_2
With H_2SO_4	CH_3OH	1 hr	65	96
Without H_2SO_4	CH_3OH	1 hr	60	92

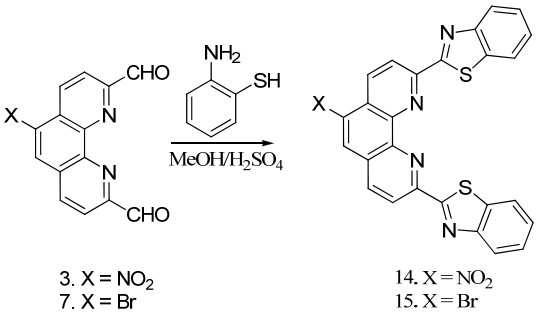
(2,2')-Benzyl 2,2'-(5-Bromo-1,10-Phenanthro line-2,9-diyl)bis(methan-1-yl-1-ylidene)-bis(hydrazinecarbodithioate)(13):

IR: ν (cm^{-1}): 3180 (N-H), 3027 (=CH aromatic), 2925 (C-H aliphatic), 1566 (C=N), 1600, 1479 (C=C aromatic), 1095 (C=S). ^{1}H-NMR (DMSO-d_6, ppm): δ_H = 13.76 (s, 1NH), 13.73 (s, 1NH), 8.58 (d, J = 8.24,1H), 8.51 (s, 1H), 8.49 (s, 1H) ,8.43 (s, 1H), 8.41 (d, J = 8.42, 1H), 8.24 (d, J = 8.36,1H), 8.15 (d, J = 7.96, 1H), 7.48 - 7.27(m, 10 H), 4.54 (s, 4H). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 198.04(2), 153.35, 153.30, 146.28, 145.13, 143.59, 136.74, 136.46, 129.29(6), 129.08(8), 129.56(2), 128.33, 127.37, 120.70, 52.69, 52.79. LC-MS (m/z): 677/675 ($M+H^+$), 676/674 (M^+), 597/595 (M^+-Br), 553/551 (M^+- $PhCH_2S$), 526/524 (M^+-$2CH_3S$-$2N_2$), 403/401 ($M+H^+$- $2PhCH_2S$-N_2), 391 ($M+4H^+$-Br-$2PhCH_2$-N_2).

3.6. Synthesis of the Schiff Bases with 2-Mercaptoaniline

The compound was prepared using the same procedure as described in 3.3, using 2-mercaptoaniline (4 equiv.) and 5-substituted (NO_2, Br) 1,10-phenanthroline-2,9-dicarboxaldehyde (1 equiv.). **Table 4** shows different reaction conditions and percent yields. Cyclized products were obtained in both cases as shown in the equation (**Scheme 8**).

2,9-Di-(benzo[d]thiazol-2-yl)-5-Nitro-1,10-Phenanthroline (14): IR: ν (cm^{-1}): 3062 (CH aromatic), 1610 (C=C aromatic), 1579 (C=N), 1555 (C=C) 1528 (N=O). ^{1}H-NMR (DMSO-d_6,): δ_H = 8.89 (s,1H), 8.83 (d, J = 7.28, 1H), 8.68(d, J = 7.56, 1H), 8.61(2d, app t, J = 8.76, 2H), 8.33 - 8.23 (m, 4H), 7.64(m, 4H). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 168.77, 168.60, 154.89, 154.89, 153.99, 152.07, 149.23, 147.15 145.54, 144.20, 136.36(2), 136.21, 134.30, 126.90(2), 126.72(3), 126.40, 126.33,



3. X = NO_2
7. X = Br

14. X = NO_2
15. X = Br

Scheme 8. Synthesis of Substituted Schiff Bases with 2-Marcaptoaniline

Table 4. Reaction Conditions and Percent Yields of the Schiff Bases.

Condition	Solvent	Time	Yield %	
			X = NO_2	X = NO_2
With H_2SO_4	CH_3OH	1 hr	45	30
Without H_2SO_4	CH_3OH	1 hr	25	25

123.85, 123.67, 122.80.121.89, 121.09. LC-MS (m/z, M^+): 494 ($M+3H^+$), 492 ($M+2H^+$), 491 (M^+), 462($M+H^+$-NO),447 ($M+2H^+$-NO_2), 391 ($M+2H^+$-C_6H_4CN), 392 ($M+3H^+$-C_6H_4CN), 359 ($M+2H^+$-C_6H_4CNS), 283 (M^+-$2C_6H_4CN$), 254($M+3H^+$-$2C_6H_4CS$).

2,9-Di-(benzo[d]thiazol-2-yl)-5-Bromo-1,10-Phenanthroline (15): IR: ν (cm^{-1}): 3053 (CH aromatic), 1602 (C=C aromatic), 1579 (C=N), 1547 (C=C). ^{1}H-NMR (DMSO-d_6,): δ_H = 8.87 (3d,app q, J = 8.4, 3H), 8.75(s, 1H), 8.71(d, J = 7.47, 1H), 8.35 - 8.22 (m, 4H), 7.64 (m, 4H). ^{13}C-NMR (DMSO-d_6, ppm): δ_C = 169.07(2), 153.93(2), 149.67, 137.44(2), 136.19(2), 135.37(2), 131.13(2), 130.98, 126.83(2), 126.53, 123.68, 122.78, 120.33(2), 119.57, 116.43(2), 116.09, 114.79. LC-MS (m/z, M^+): 528/526 ($M+2H^+$), 527/525 ($M+H^+$), 526/524 (M^+), 474/472(M^+-2CN), 452/450 ($M+2H^+$-CS_2), 391 ($M+H^+$-C_6H_4CNS), 279 (M^+-$C_6H_4CH_2S$).

4. Conclusion

Eight new Schiff bases of 5-nitro- and 5-bromo-2,9-dimethyl-1,10-phenanthroline dialdehydes with sufur-containing amines have been successfully synthesized. The addition of conc. H_2SO_4 to the reaction mixtures has a significant effect on the yields of the products. We tried to do the reaction without acid because of the possibility of forming salts by the protonation of nitrogen atoms of the phenanthroline moiety which might cause lower solubility of the Schiff bases. However, it was observed that the yield increased significantly when the reaction was carried out under mild aicidic conditions. This is due to the fact that protonation of the carbonyl group (C=O) enhances the nucleophilic attack by an anion. Also, reaction time was reduced significantly compared to that reported in the previous work, probably because of the presence of the substituted group in the 5-position in the phenanthroline moiety.

5. Acknowledgements

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