European Journal of Chemistry 6 (4) (2015) 404-409

European Journal of Chemistry

Journal webpage: www.eurjchem.com

Synthesis, characterization, fluorescence, and thermal studies of a new series of Schiff bases derived from sulfaproxylene

Jabbar Saleh Hadi

Department of Chemistry, College of Education for Pure Sciences, University of Basrah, Basrah, 61004, Iraq

** Corresponding author at: Department of Chemistry, College of Education for Pure Sciences, University of Basrah, Basrah 61004, Iraq. Tel.: +964.771.0822193. Fax: +964.771.0822193. E-mail address: jshalkabi2@gmail.com (J.S. Hadi).*

ARTICLE INFORMATION

DOI: 10.5155/eurjchem.6.4.404-409.1299

Received: 10 July 2015
Received in revised form: 06 August 2015
Accepted: 08 August 2015
Published online: 31 December 2015
Printed: 31 December 2015

KEYWORDS

Sulfa drug
Schiff base
Fluorescence
Coats-Redfern
Sulfaproxylene
Thermal analysis

ABSTRACT

A new series of Schiff bases were synthesized by the condensation of sulfaproxylene with various aldehydes in ethanol. The structures of Schiff bases were characterized by using elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and Mass spectrometry techniques. Thermal stability of the prepared compounds was investigated using TG and DTG. The kinetic and thermodynamic parameters such as activation energy (*E*), enthalpy of activation (ΔH), entropy of activation (ΔS), and Gibbs free energy change of the decomposition (ΔG) were evaluated following Coats-Redfern method. In addition, the compounds were studied for their fluorescence properties, where compound 1 yielded the strongest intensity in 1×10^{-4} M DMSO solution.

Cite this: *Eur. J. Chem.* **2015**, *6(4)*, 404-409

1. Introduction

Schiff bases or imines are compounds that are represented with the general formula $R_1R_2C=NR_3$, where R_1, R_2 and R_3 are substituted by alkyl, aryl, hetero-aryl or hydrogen [1-8]. The Schiff bases derived from sulfa drugs with different R_3 represent a wide variety of sulfa moieties and, in several decades, these vital compounds demonstrate a broad spectrum of activities in industrial, biological, analytical, medicinal, and pharmaceutical applications [9-29]. One of the more interesting applications of Schiff bases derived from sulfa drugs is the possibility to use them as effective antibacterial, antifungal, and anti HIV [30,31]. Schiff bases like Salen-type are fluorescent at low temperature and in solution [25]. In addition, the Schiff bases derived from sulfa drugs has a potential for trace analysis of some transition metals with fluorometric method [32]. Based on thermal stability of Schiff bases, they can be used as stationary phase in gas chromatography [33].

Prompted by these observations, in the present study, a new series of Schiff base have been synthesized and characterized on the basis of spectroscopic methods including IR, ^{1}H and ^{13}C NMR, and mass spectroscopy as well as elemental analysis. Also, the newly synthesized compounds have been utilized by thermogravimetric (TG/DTG) analyses as themostly used techniques and the widely applied Coats-Redfern calculation procedure for the kinetic analysis [34]. The kinetic and thermodynamic parameters (*A*, *E*, ΔH, ΔS and ΔG) have been calculated using Coats-Redfern method based on thermal data analysis. In addition, fluorescence characterization used to verify the proposed assignments.

2. Experimental

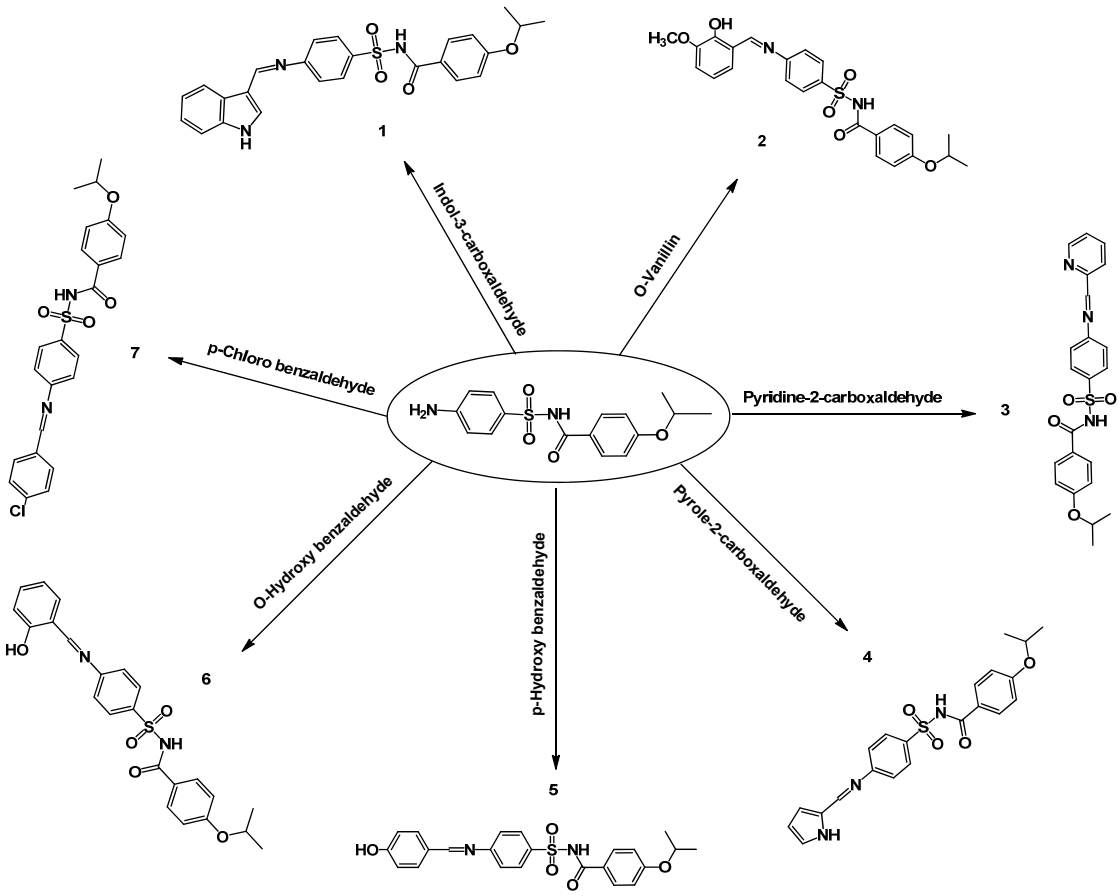
2.1. Materials

All solvents employed in synthesis were extra pure grad and used as received without further purification. Sulfaproxylene was purchased from Himedia, aldehydes were obtained from BDH, Merck, and Fluka and used as received.

2.2. Physical measurement

Melting points were determined in open capillary tube using thermal scientific melting point apparatus. IR spectra were recorded by using Shimadzu FT-IR type affinity spectrophotometer in the region 4000-400 cm^{-1} in KBr pellet. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C).

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.6.4.404-409.1299



Scheme 1

TMS as the internal standard was used as referenced to 0.0 ppm and DMSO-d_6 was used as solvent. The mass spectra were scanned by EI technique at 70 eV with Agilent Technologies 5973C spectrometer. Fluorescence spectra were recorded on Cary Eclipse Florescence spectrophotometer (Agilent technologies). The thermal analyses (TG and DTG) were carried out in dynamic nitrogen atmosphere (20 mL/min) with a heating rate 10 °C/min using Rheumatic Scientific Thermal Analyzer. Elemental analysis was performed in a CHNS-932 LECO apparatus.

2.3. Synthesis methods

2.3.1. Preparation of Schiff bases (1-7)

The Schiff bases (**1**-**7**) were synthesized by the condensation of sulfaproxylene with different aromatic and hetero aldehydes in molar ratio 1:1 either by refluxing in absolute ethanol, direct fusion or microwave irradiation. The reaction proceeded smoothly producing the corresponding Schiff bases in good yield. Also compounds **1**, **4** and **5** were prepared by microwave irradiation assisted method using acidic alumina as a catalyst. The synthesis of Schiff bases were performed in accordance with reaction Scheme 1.

2.3.1.1. Synthesis of N-((4-((2-hydroxy-3-methoxybenzylide ne)amino)phenyl)sulfonyl)-4-isopropoxybenzamide (1)

Compound **1** was prepared by the condensation of 1 mmol of sulfaproxylene and 1 mmol of indol-3-carboxaldehyde in 25 mL of ethanol. The resulting mixture was then refluxed for 2hrs to give a yellow solid. It was cooled down to room temperature then it was filtered, washed with cold ethanol and dried over anhydrous $CaCl_2$. The purity was checked by TLC (ethyl acetate: benzene) (3:7). R_f: 0.67. M.p.: 142-145 °C. Yield: 77%. This compound was also prepared by microwave irradiation (under 100% power for 20 min) in presence of acidic alumina. The solid product dissolved in hot ethanol, filtered to give the yellow solid (Scheme 1). Color: Yellow. Yield: 77%. M.p.: 142-145 °C. FT-IR (KBr, ν, cm^{-1}): 3452(s)(N-H, Indole), 3337 (s) (NH, sulfa), 1654 (s) (C=O), 1631 (s) (C=N), 1343 (s), 1165 (m) (O=S=O), 950 (s) (N-S), 829 (s)(C-S). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 6 Hz, $2CH_3$), 4.72 (m, 1H, CH), 6.59-7.80 (m, 13H, Ar-H), 8.32 (s, 1H, CH=N), 9.93(1H, NH, indole), 11.89 (1H, NH, sulfa). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.5 CH (proxylene), 111.0-137.1 (Ar-C), 153.0 (C-O), 160.0 (C=N), 164.2 (C=O). Anal. calcd. for $C_{25}H_{23}N_3O_4S$: C, 65.06; H, 5.02; N, 9.10. Found: C, 65.13; H, 4.94; N, 9.22%. λ_{Flu} (DMSO, max, nm): 422. λ_{Exc} (DMSO, max, nm): 342.

2.3.1.2. Synthesis of N-(4-(2-hydroxy-3-methoxybenzylidene amino)phenylsulfonyl)-4-isopropoxybenzamide (2)

Compound **2** was prepared by direct condensation of an equimolarratio of *o*-vanillin and sulfaproxylene on water bath at 60-70 °C for 30 min. The obtained orange solid dissolved in acetone and precipitate after addition water, and then the solid filtered and dried (Scheme 1). Color: Orange. Yield: 65%. M.p.: 165-167 °C (Dec.). FT-IR (KBr, ν, cm^{-1}): 3411 (s) (OH), 3257 (s) (NH.-sulpha), 1657 (s) (C=O), 1601 (s) (C=N), 1339

(s), 1165 (m) (O=S=O), 950 (s) (N-S), 833 (s) (C-S). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 6 Hz, 2CH_3), 3.84 (s, 3H, OCH_3), 4.72 (m, 1H, CH), 6.61-8.01 (m, 11H, Ar-H), 8.98 (1H, CH=N), 11.85 (s, 1H, NH), 12.32 (br., 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.5 CH (proxylene), 56.3 (OCH_3), 115-139.1 (Ar-C), 149.2 (C-OCH_3), 151 (C-OH, phenolic), 153 (C-O, proxylene), 162.3 (C=N), 167 (C=O). Anal. calcd. for $C_{24}H_{24}N_2O_6S$: C, 61.52; H, 5.16; N, 5.98. Found: C, 62.03; H, 5.08; N, 6.07%. λ_{Flu} (DMSO, max, nm): 436. λ_{Exc} (DMSO, max, nm): 374.

2.3.1.3. Synthesis of 4-isopropoxy-N-(4-(pyridin-2-yl methyleneamino)phenylsulfonyl)benzamide (3)

Compound **3** was prepared by addition of 1 mmol of pyridine-2-carboxaldehyde in 10 mL of ethanol to a hot solution of 1 mmol of sulfaproxylene in 20 mL of ethanol. The reaction mixture was poured in crash ice, then pink solid filtered and dried (Scheme 1). M.p.: 185-187 °C (Dec.). Yield: 63%. Color: Pink. Yield: 43%. M.p.: 185-187 °C (Dec.). FT-IR (KBr, ν, cm^{-1}): 3263 (s) (NH.-sulpha), 1658 (s) (C=O), 1612 (s) (C=N), 917 (s) (N-S), 839 (s) (C-S). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 6 Hz, 2CH_3), 4.72 (m, 1H, CH), 6.50-7.41 (m, 12H, Ar-H), 8.31 (s, 1H, CH=N), 11.85 (1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.3 CH (proxylene), 111-132 (Ar-C), 151 (OH, phenolic), 153 (C-O, proxylene), 162 (C=N), 164 (C=O). Anal. calcd. for $C_{22}H_{21}N_3O_4S$: C, 62.40; H, 5.00; N, 9.92. Found: C, 61.93; H, 4.97; N, 9.95%. λ_{Flu} (DMSO, max, nm): 436. λ_{Exc} (DMSO, max, nm): 374.

2.3.1.4. Synthesis of N-(4-((1H-pyrrol-2-yl)methyleneamino) phenylsulfonyl)-4-isopropoxybenzamide (4)

Compound **4** was prepared by direct fusion in oil bath of an equimolar ratio of pyrol-2-carboxaldehyde and sulfaproxylene for 30 min. The dark solid dissolved in acetone and re-precipitated from cold water, filtered and washed with water and ether, to give a pink solid (Scheme 1). M.p.: 182-183 °C. Yield: 41%. This compound was also prepared by microwave irradiation (under 80% power for 6 min) in presence of acidic alumina, the solid product dissolved in ethanol and filtered to remove the title compound. It was filtered again and washed with ether to give a pink solid. Color: Dark pink. M.p.: 182-183 °C. Yield: 74%. FT-IR (KBr, ν, cm^{-1}): 3462 (s) (NH, pyrole), 3377 (s) (NH, sulpha), 1654 (s) (C=O), 1627 (s) (C=N), 1317 (s), 1165 (m) (O=S=O), 951 (s) (N-S), 829 (s) (C-S). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 2.2 Hz, 2CH_3), 4.72 (m, 1H, CH), 6.50-8.35 (m, 11H, Ar-H), 8.81 (s, 1H, CH=N), 11.51 (s, 1H, NH pyrrol), 11.81 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.5 CH (proxylene), 112-130 (Ar-C), 153.0 (C-O, proxylene), 162.0 (C=N), 164.2 (C=O). Anal. calcd. for $C_{21}H_{21}N_3O_4S$: C, 61.30; H, 5.14; N, 10.21. Found: C, 61.64; H, 5.01; N, 10.33%. λ_{Flu} (DMSO, max, nm): 438. λ_{Exc} (DMSO, max, nm): 381.

2.3.1.5. Synthesis of N-(4-(4-hydroxybenzylideneamino) phenylsulfonyl)-4-isopropoxybenzamide (5)

Compound **5** was prepared by direct fusion of 4-hydroxybenzaldehyde and sulfaproxylene in oil bath for 30 min. The yellow solid dissolved in acetone and water then kept it in refrigerator overnight. It was filtered, washed with water to give a pale yellow crystal (Scheme 1). M.p.: 183-184 °C. Yield: 52%. This compound was also prepared by microwave irradiation (under 100% power for 16 min) in presence of acidic alumina. The product was purified by the same method of compound **4**. Color: Pale yellow. Yield: 52%. M.p.: 184-186 °C. FT-IR (KBr, ν, cm^{-1}): 3478 (br)(OH), 3282 (s)(NH. sulpha), 1653 (s) (C=O), 1617 (s) (C=N), 1342 (s), 1152 (m) (O=S=O), 949 (s) (N-S), 836 (s) (C-S). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 2.2 Hz, 2CH_3), 4.72 (m, 1H, CH), 6.50-7.82 (m, 12H, Ar-H), 8.31 (1H, CH=N), 11.88 (s, 1H, NH), 12.03 (br., 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.5 CH (proxylene), 114.0-128.1 (Ar-C), 160.0 (C-O, phenolic), 153.0 (C-O, proxylene), 160.0 (C=N), 167.3 (C=O). Anal. calcd. for $C_{23}H_{22}N_2O_5S$: C, 63.00; H, 5.06; N, 6.39. Found: C, 63.21; H, 5.00; N, 6.52%. λ_{Flu} (DMSO, max, nm): 440. λ_{Exc} (DMSO, max, nm): 371.

2.3.1.6. Synthesis of N-(4-(4-chlorobenzylideneamino) phenylsulfonyl)-4-isopropoxybenzamide (6)

Compound **6** was prepared by direct fusion of an equimolar ratio of salicaldehyde and sulfaproxylene in water bath at 50-70 °C for 30 min. The orange solid recrystallized from acetone: water (9:1, *v*:*v*) (Scheme 1). Color: Orange. Yield: 68%. M.p.: 224-226 °C. FT-IR (KBr, ν, cm^{-1}): 3444 (m) (OH), 3250 (s) (NH. sulpha), 1683 (s) (C=O), 1620 (s) (C=N), 1350 (s), 1168 (m) (O=S=O), 962 (s) (N-S), 848 (s) (C-S). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 6 Hz, 2CH_3), 4.72 (hep., 1H, J = 6 Hz, CH), 6.60-7.80 (m, 12H, Ar-H), 8.98 (s, 1H, CH=N), 11.88 (s, 1H, NH), 12.44 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.5 CH (proxylene), 111.0-132.0 (Ar-C), 151.0 (C-OH, phenolic), 153.0 (C-O, proxylene), 162.0 (C=N), 164.4 (C=O). Anal. calcd. for $C_{23}H_{22}N_2O_5S$: C, 63.00; H, 5.06; N, 6.39; S, 7.31. Found: C, 63.16; H, 4.99; N, 6.61; S. 7.11%. λ_{Flu} (DMSO, max, nm): Not observed. λ_{Exc}(DMSO, max, nm): 373.

2.3.1.7. Synthesis of N-(4-(2-hydroxybenzylideneamino) phenylsulfonyl)-4-isopropoxybenzamide (7)

Compound **7** was prepared by refluxing of 1mmol of *p*-chloro benzaldehyde and 1 mmol of sulfaproxylene in 25 mL of ethanol for 4 hrs. The solvent was evaporated and the resulting solid recrystallized from acetone:water (9:1, *v*:*v*) (Scheme 1). Color: Pale yellow. Yield: 71%. M.p.: 166-168 °C. FT-IR (KBr, ν, cm^{-1}): 3252 (br.) (NH. (sulpha), 1658 (s) (C=O), 1627 (s) (C=N), 1354 (s), 1136 (m) (O=S=O), 959 (s) (N-S), 841 (s) (C-S), 615 (s) (C-Cl). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 6H, J = 2.2 Hz, 2CH_3), 4.72 (hep., 1H, J = 6 Hz, CH), 6.60-8.20 (m, 12H, Ar-H), 8.79 (s, 1H, CH=N), 11.88 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 21.6 (CH_3), 69.5 CH (proxylene), 114.0-132.1 (Ar-C), 136.7 (C-Cl), 151.0 (C-O, phenolic), 153.0 (C-O, proxylene), 160.0 (C=N), 167.2 (C=O). Anal. calcd. for $C_{23}H_{21}ClN_2O_5S$: C, 60.46; H, 4.63; N, 6.13. Found: C, 59.57; H, 4.69; N, 6.53%.

3. Result and discussion

The Schiff bases (**1**-**7**) were synthesized by the condensation of sulfaproxylene with different aromatic and hetero aldehydes in molar ratio 1:1 either by refluxing in absolute ethanol, direct fusion or microwave irradiation. The reaction proceeded smoothly producing the corresponding Schiff bases in a good yield. Also compounds **1**, **4** and **5** prepared by microwave irradiation assisted method using acidic alumina as a catalyst. The synthesized compounds are soluble in ethanol, chloroform, ethyl acetate, DMSO and DMF but insoluble in hexane, benzene and ether. All synthesized Schiff bases are stable and non-hydroscopic.

3.1. IR spectra

The IR spectra data of the synthesized Schiff bases (**1**-**7**) exhibited a characteristic band in the range 1601-1631 cm^{-1} assigned to stretching vibration of azomethine group [23,31] thus it clearly shows an evidence for the formation of Schiff bases. All compounds shows a band resulting to ν(NH) of the sulfa moiety in the range 3250-3377 cm^{-1} [35]. In case of compound **1**, the IR spectrum shows two sharp and strong bands including one band at 3452 cm^{-1}is attributed to the

indolemoiety [36] and the other band appears at 3337 cm^{-1} is attributed to the ν(NH) of sulfaproxylene. Also compound **4** shows two sharp bands which are attributed to ν(NH) of sulfaproxylene and pyrrole moiety at 3337 and 3462 cm^{-1}, respectively [36]. Compounds **2** and **6** display a broad band resulting from hydrogen bonds ν(OH) at 3411 (**2**) and 3444 cm^{-1} (**6**). The compound **7**exhibits a strong band at 615 cm^{-1} assigned to ν(C-Cl). All compounds present a strong band attributed to ν(C=O) in the range 1653-1683 cm^{-1}. The two strong bands appear at the range of 1317-1354 and 1136-1181 cm^{-1} are due to asymmetric and symmetric stretching of O=S=O. Similarly all compounds exhibit bands at 937-962 cm^{-1} attributed to stretching of S-N and at 829-848 cm^{-1} attributed to stretching of C-S [36,37].

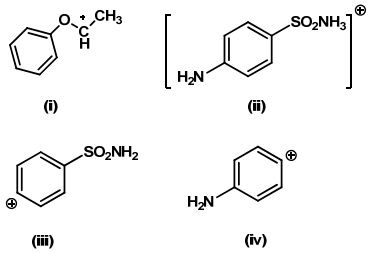
3.2. NMR spectra

^{1}H NMR spectra observed that all compounds spectra shows a doublet signal due to 6 protons of the two methyl groups of sulfaproxylene moiety at δ 1.26 ppm and a multiplet signal due to CH protons at δ 4.72 ppm. Also all compounds display the azomethine proton signal (CH=N) in the range of δ 8.30-8.98 ppm. Compound **1** demonstrates the NH proton of indole moiety at δ 9.93 ppm as a singlet signal [23]. Spectra of compounds **2** and **6** display a broad signal for hydroxyl group proton at δ 12.32 and 12.44 ppm, respectively. It confirms the hydrogen bonding of a nitrogen atom of azomethine group. While a hydroxyl proton of compound **5** appears as a sharp singlet signal at 12.03 ppm. Similarly, compound **4** displays pyrole NH proton as a singlet signal at δ 11.51 ppm, as expected [38].

^{13}C NMR spectra of compounds (**1**-**7**) display the azomethine carbon at δ 160-162 ppm which clearly confirms the formation of Schiff bases. In addition, a signal at 21.6ppm in all compounds spectra is attributed to the two methyl groups' carbon of salfaproxylene, while the CH carbon of proxylene moiety appears at δ 69.3-69.5 ppm. Furthermore, all compounds show a signal of carbonyl at δ 164-167.2 ppm. By details, compounds **2** and **6** spectra show a signal attributed to carbon attached to OH group at δ 151 and 153.1 ppm, respectively. Finally, compound **7** displays a signal at δ 136.7 ppm attributed to carbon attached to Cl.

3.3. Mass spectra analysis

Under the following conditions, direct prop injection program, started at initial temp 50 °C with heating rate 70 °C/min with the final temperature 230 °C, the mass spectra of all synthesized compounds were recorded. The results demonstrate that all compounds display a molecular ion [M^{+}] with low relative abundance 10%. The molecular ion peaks are in a good agreement with proposed formulas. The cleavage of S-N and N-C of sulfaproxylene moiety generates an intense peak represent the base peak in case of compounds **5** and **6**. The mass spectra of a compounds **4** and **7** show the base peak at *m/z* = 121 attributed to ion (i). The common fragments of compounds are shown in Scheme 2.



Scheme 2

All spectra display these peaks at *m/z* = 172, 156 and 92 attributed to the ions (ii, iii, iv), respectively.

3.4. Fluorescence spectra

An additional fluorescence spectra characterization is used as a supplementary study to confirm the validity of the results. The synthesized Schiff bases are subject of fluorescence study based on their structures. Therefore, the absorption and fluorescence spectra of prepared compound in DMSO were analyzed. The fluorescence band position including absorption maximum λ_{abs}, fluorescence λ_{Flu}, and stocks shift data are supplied in the experimental section. The results show that the fluorescence bands of all compounds are broad. Compound **1** shows a high intensity (Figure 1), conversely, compounds **3** and **4** (Figure 2) shows less intensity in comparison with compound **1**. Bands of compounds **2** and **6**, are not observed, this may be attributed to intramolecular hydrogen bonding [39], between the OH group in *ortho*-position and azomethine group in both compounds (Figure 3).

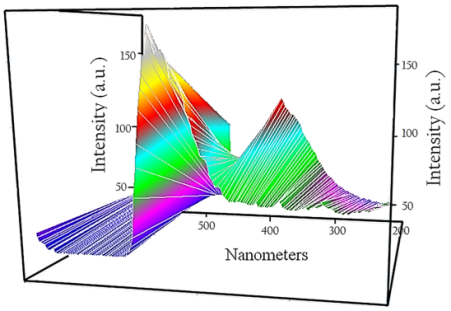


Figure 1. 3D fluorescence spectrum of compound **1** in DMSO.

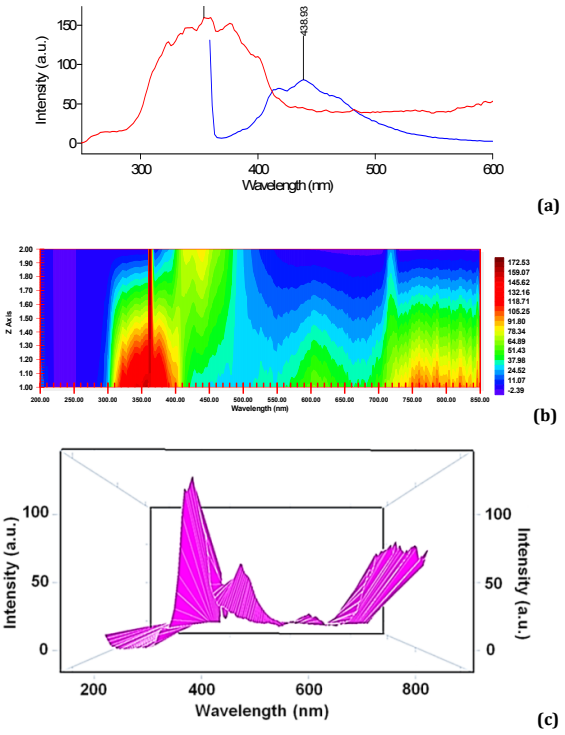


Figure 2. 1D (a), 2D (b) and 3D (c) fluorescence spectra of compound **4** in DMSO.

Table 1. TG data and kinetic parameters of the complexes using the Coats-Redfern equation.

Compound	Temp (°C) [a]	Steps	A (s^{-1})	E (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	r
1	163	1st	2.23×10^{7}	112.167	107.527	-0.109	168.581	0.938
2	224	1st	2.33×10^{3}	61.349	56.777	-0.185	158.803	0.917
		2nd	5.72×10^{2}	68.659	63.563	-0.198	185.005	0.963
3	231	1st	5.89×10^{5}	51.8118	51.3852	0.723	143.208	0.995
		2nd	85.15×10^{2}	36.849	31.586	-0.252	191.422	0.989
4	225	1st	3.31×10^{6}	63.136	61.941	-0.111	113.571	0.997
		2nd	2.89×10^{4}	61.288	59.714	-0.132	82.711	0.991
5	252	1st	1.05×10^{8}	48.254	46.635	-0.106	59.731	0.964
		2nd	2.35×10^{7}	37.822	35.759	-0.124	57.013	0.967
6	227	1st	1.291×10^{9}	61.168	59.321	-0.101	83.162	0.972
		2nd	3.281×10^{10}	73.360	70.664	-0.154	92.229	0.978
7	241	1st	1.297×10^{7}	63.081	60.981	-0.101	78.144	0.983
		2nd	8.391×10^{6}	78.331	75.445	-0.113	101.965	0.986

[a] Initial decomposition temperature.

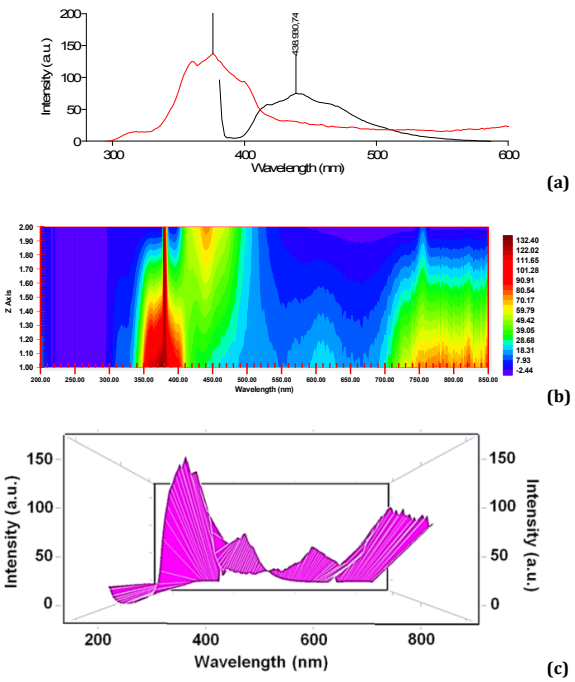


Figure 3. 1D (a), 2D (b) and 3D (c) fluorescence spectra of compound **6** in DMSO.

3.5. Thermal analysis

The thermal analysis (TG and DTG) of the compounds were utilized to get information about the thermal stability of the compounds [34,40-42]. The compounds were subjected to a TG analysis under nitrogen atmosphere up to 800 °C with heating rate 10 °C/min. The initial decomposition temperature is reported in Table 1. As shown in Table 1, most compounds have two steps decomposition process. An investigation of Table 1 illustrates that compound **5** is the most stable compound but compound **1** the least stable compound. A comparison between compounds **2**, **5** and **6** shows that compound **5** is more stable than compound **2** and **6** which all these compounds contain OH group where in compound **5**, it positioned in*para* position but in compound **6**, it placed at *ortho*-position. It clearly indicates that it has no effect on hydrogen bonding in the thermal stability. The compound **2** which contains an additional OCH_3 group is less thermal stability in this comparison with compound **5** and **6** (Figure 4). In general, all compounds indicate a very fast decomposition rate after 300 °C and it continues up to 800 °C. Then, we cannot distinguish the nature of the decomposition product.

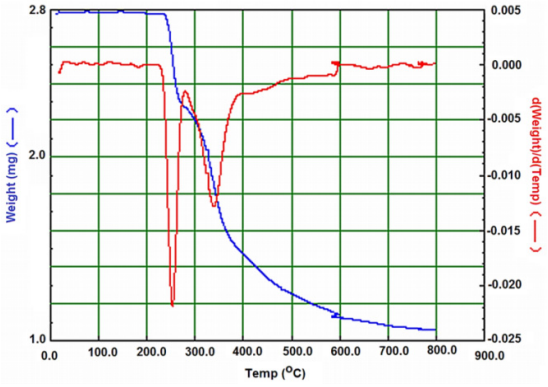


Figure 4. TG/DTG of compound **2**.

3.6. Kinetic and thermodynamic analysis data

The thermal decomposition of the compounds was studied kinetically using the integral method applying the Coats-Redfern method [43-45]. The activation energy (E), frequency factor (A), enthalpy of activation (ΔH), entropy of activation (ΔS) and Gibbs Free energy change (ΔG) have also been evaluated for each step and the results are reported in Table 1. The parameters are evaluated graphically from TG data by employing the Coats-Redfern relation in the following form [43]:

$$log\left[\frac{log\frac{w_f}{w_f-w_t}}{T^2}\right] = \log\left[\frac{AR}{\theta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{2.303RT} \quad (1)$$

Where W_f and W_t are weight loss at end of stage and weight at temperature (t), respectively. Also, E, R, A and θ are the activation energy, the universal gas constant, pre-exponential factor and heating rate (here, 10 °C/min), respectively. The correlation coefficient (r) was calculated using the least square (LSR) method by plotting the left-hand side versus 1000/T. The values of the correlation coefficient are changed in the range of 0.97-0.99 which confirms the validity of results. Activation energy for each step was calculated from slope. It summarized for the first step of decomposition, maximum E obtained from compound **5** and for the second step, maximum E resulted for compound **7**. The frequency factor showsa significant variation in both the first and second steps. Changes in entropy (ΔS) are calculated by using the following equation,

$$A = \left(\frac{k_b T}{h}\right) e^{\frac{\Delta s}{R}} \quad (2)$$

where K_b and hare Boltzmann and Plank constant, respectively. The negative values of ΔS indicate that the

activated compound has a more ordered than the reactants and shows that the decomposition reactions processes occur at very low rate [46]. The positive values of Δ*H* indicate that the decomposition processes are endothermic reactions, as expected. All value of ΔG was calculated from known Gibbs relation:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

The obtained positive value confirms that all steps are non-spontaneous.

4. Conclusion

The reported compounds were synthesized from a general procedure by the condensation of an equimolar ratio of sulfaproxylene with aldehydes either by refluxing in ethanol or direct fusion. In addition, compounds **1**, **4** and **5** were synthesized by microwave irradiation. Spectroscopic techniques including IR, ^{1}H and ^{13}C NMR, fluorescence and mass analysis as well as elemental analysis were used to identify the products. To study the structural properties of studied molecules, complete analyses of thermal decomposition of complexes as well as some kinetic and thermodynamic properties of all complexes was reported. The kinetic and thermodynamic parameters as important values for stability index revealed high chemical reactivity of synthesized compounds in chemical reactions.

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