Synthesis and Characterization New Schiff-base Compounds from Thiadiazole Derivative

Shahad M Alsafy[1], Nour Abd Alrazzak[2]
[1]Department of Chemistry, College of Science for women, University of Babylon, Hilla, Iraq
[2]Department of Chemistry, College of Science for women, University of Babylon, Hilla, Iraq
Email: nourchem1983 @gmail.com

Abstract
In this paper Synthesis of new different Schiff-base heterocyclic compounds from azo dye [S1] by the reaction between p-aminobenzoic acid and resorcinol,also [S1] was cyclized by reaction with thiosemicarbazide to form 1,3,4-thiadiazole amine [S2],which reacted with (9-anthraldehyde,terephthaldehyde, N,N-dimethyl amino benzaldehdye,3,5-dichloro salicyaldehyde,3-hydroxybenzaldehdye,2-hydroxy-5-nitro benzal dehyde) in presence of acetic acid to give new Schiff-base compounds, after that these compounds were characterized by the following techniques: FT-IR, 1HNMR,13C-NMR and elemental analysis CHNS.
Keywords: Resorcinol, Azo dyes,1,3,4-thiadiazole amine, aldehydes and Schiff base.

1. Introduction

Azo dyes have a variety of biological uses, including antineoplastic, antidiabetic, cleansing, anti-inflammatory, and other readily available chemotherapeutic agents. Azo compounds are highly colored and have long been used as dyes and pigments; also, Azo colors are extremely important due to their environmental resilience, electrical, and optical properties [1-3].
Heterocyclic compound rings with multiple members have become increasingly important in the pharmacological and industrial fields. 1,3,4-oxadiazoles are important heterocyclic compounds that are used in the production of medicines, polymers, and pigments [4-6].
Thiadiazoles are heterocyclic five-aromatic compounds having two carbon atoms, two nitrogen atoms, and a sulfur atom; that is, thiadiazole derivatives are formed by substituting the oxygen atom in oxadiazole with a sulfur atom [7-11].
Due to their ease of synthesis, different structures with a wide range of color, and high interest in the thermochromic material sector, Schiff bases are currently being explored extensively [12].
The carbonyl group is replaced by an imine or azomethine (C=N) group in Schiff bases, which are condensation products of primary amines and carbonyl compounds. R1HC=NR2 is a typical formula for them, where R1 and R2 are alkyl or aryl groups [13-16].
Schiff bases are a type of organic chemical that has a wide range of uses in a variety of domains, including analytical, biological, and inorganic chemistry. Due to a wide range of biological actions such as anti-inflammatory,Schiff bases have acquired popularity in the medicinal and pharmaceutical fields[17].

2. Experimental section

Apparatus

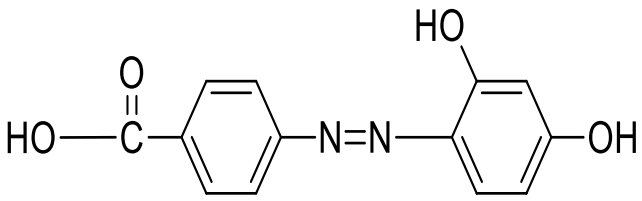
1-Melting points were recorded using hot stage SMP30 melting point apparatus.
2-Infrared spectra were recorded using Fourier Transform infrared SHIMADZU (8400) (FTIR) infrared spectrophotometer, KBr disc or thin film was performed by Babylon University
3- 1H.NMR– Spectra and 13C.NMR - Spectra were recorded on a Bruker (AC 400) NMR spectrometer, operating at (500 MHz) for 1H-NMR and (126 MHz) for 13C- NMR. All chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) as reference (δ=0.0 ppm), CHNS was used for characterization of the prepared compounds.

3. Chemicals

The organic compounds supplied in high purity:Most used chemicals are in the highest available purity (99.98%). All the starting materials used in this paper were take up from CDH and Merk Company.

2.1. Procedures

2.1.1. Synthesis of compounds [S1]

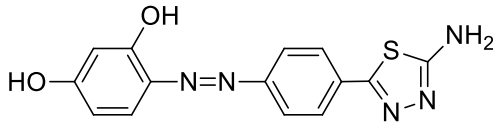


P-Aminobenzoicacid (0.01mole, 1.37g) was dissolved in 17ml distill water and 3ml HCl at a temperature of (0-5)0C. The solution was then dropwise added (0.01 mole, 0.69g) of NaNO2 dissolved in (10 ml) distilled water for (15) minutes. The diazonium salt were add dropwise to the coupling component solution, which is maded using (0.01mole,1.10g) resorcinol in distill water with (1 g) sodium hydroxide in (10ml) distill water. after that, the precipitate was filtered and washed with water,the precipitate was recrystallized by absolute ethanol [18].
IR (v, cm-1): O-H (3267), C-H Ar (3101), C=O carboxylic acid (1683), C=CAr (1602), N=N (1475), C-

doi.org/10.31838/hiv23.01.2 Received: 06.09.22, Revised: 08.10.22, Accepted: 09.11.22

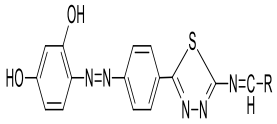
O (1240)
1H-NMR (δ, ppm): (7H, Ar-H): 6.33-8.08.
13C-NMR (δ, ppm): (117-162) for (12C, Ar-C), (169) for C=Ocarboxylic acid.

2.1.2. Synthesis of compounds [S2]:



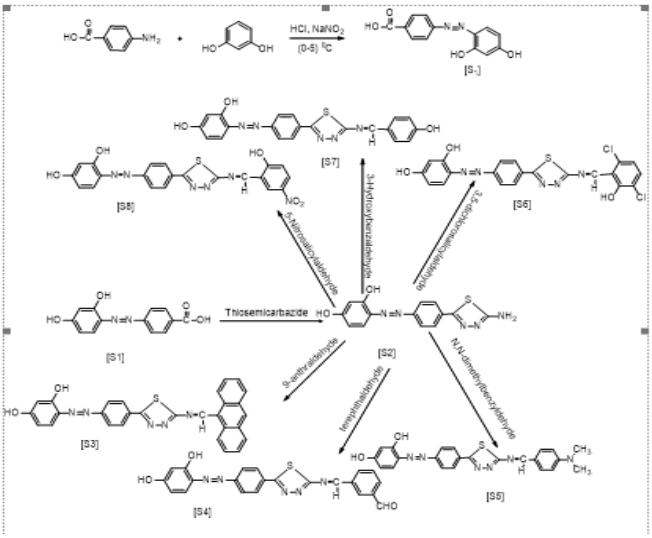
(0.01mole, 2.58g) of compound [S1] and (0.01 mole, 0.91g) thiosemicarbazide were dissolved in (8 ml) POCl3, then was refluxed for (4) hours, after that (40 ml) distilled water was added and refluxed for (4) hours,then added (4 g) potassium hydroxide in (40ml) distilled water. Then filtered and recrystallized by absolute ethanol [19].
IR (v, cm-1): O-H (3406), NH2 (3327,3221), C-HAr (3122), C=N (1608), C=CAr (1577), N=N (1508).
1H-NMR (δ, ppm): (H, NH2) 6.79, (7H, Ar-H) 6.81-8.19.
13C-NMR (δ, ppm): (117-135) for Ar-C,174 for C-S

2.1.3. Synthesis of compounds [S3-S8]:



(R=9-anthraldehyde,terephthaldehyde,N,N-dimethyl amino benzaldehdye,3,5-dichloro salicyaldehyde,3-hydroxy benzaldehdye,2-hydroxy-5-nitrobenzaldehyde)

(0.003mole, 1g) Of compound [S2] was dissolved in (25ml) absolute ethanol, and two drops of glacial acetic acid were added, followed by addition (0.003 mole, 0.618g, 0.402g, 0.44g, 0.573g, 0.36g, 0.50g) of compounds (9-anthraldehyde, terephthaldehyde,N,N-dimethyl amino benzaldehdye,3,5,-dichlorosalicyaldehyde,3- hydroxybenzaldehdye,2-hydroxy-5-nitrobenzal dehyde) respectively the combination was refluxed for 14 hours, after which the solvent was evaporated and the result was collected and recrystallized from absolute ethanol[20].
Compound [S3] IR (v, cm-1): C-HAr (3097), C-Halph (2831), C=N imine (1668), C=CAr , (1600), C=N (1552),N=N (1519) .
1H-NMR (δ, ppm): (H, OH) 4.37, (H,Ar-H) 6.3-8.2,(H,N=CH) :8.9
13C-NMR (δ, ppm) :123-140 for Ar-C,166 for C=N
Compound [S4] IR (v, cm-1): C-HAr (3155), C=Oaldehyde (1697), C=N imine (1602), C=CAr (1570), C=N (1533), N=N (1521).
1H-NMR (δ,ppm): (H,OH)5.86,(H,Ar-H)7.1-8.0,(H,N=CH) 8.12,(H,CHO) :10
Compound [S5] IR (v, cm-1): C-HAr (3134), C-Halph (2885), C=N imine (1653), C=CAr (1533), C=N (1508), N=N (1491).
1H-NMR (δ, ppm) :(6H,2CH3) 2.0-2.8, (H,Ar-H) 6.3-8.0,(H,N=CH) 8.12
Compound [S6] IR (v, cm-1): C-HAr (3074), C-H alph (2928), C=N imine (1681), C=CAr (1600), C=N (1560), N=N (1500), C-Cl (850).
1H-NMR (δ, ppm): (H,Ar-H) 6.4-8.0,(H,N=CH)8.1
13C-NMR (δ, ppm): 118-156 for Ar-C,167 for C=N.
Compound [S7] IR (v, cm-1): C-HAr (3070), C-H alph (2843), C=N imine (1681), C=CAr (1599), C=N (1560), N=N (1539).
1H-NMR (δ, ppm): (H,Ar-H) 6.4 -8.1,(H,N=CH) 8.5
13C-NMR (δ, ppm) :114-158 for Ar-C,167 for C=N
Compound [S8] IR (v, cm-1): C-HAr (3080), C-H alph (2922), C=N imine (1681), C=CAr (1600), C=N (1572), N=N (1492), NO2 (1340).
1H-NMR (δ, ppm): (H,Ar-H) 6.91-8.3,(H,N=CH) 8.4



Scheme 1: preparation of compounds [S1-S8]

4. Results and Discussion

P-amino benzoic acid was react with resorcinol in presence (HCl,NaNO2,NaOH) at (0-5)0C to give azo dye[S1],Azo dye was react with thiosemicarbazide in presence POCl3 to give 1,3,4-thiadiazole [S2],Several Schiff bases [S3-S8] were synthesized from reaction 1,3,4-thiadiazole [S2] with (9-anthraldehyde, terephthaldehyde, N,N-dimethyl aminobenzaldehdye,3,5-dichlorosalicyaldehyde,3-hydroxybenzaldehdye, 2-hydroxy-5-nitrobenzaldehyde) in presence of acetic acid .
The structure of these compounds has been characterized by FT-IR,^{1}H-NMR and ^{13}C-NMR techniques, and elemental analysis. The data of these measurements were presented in table 1 and 2.
[S1] The FTIR spectrum exhibit a new absorption band at (1475) cm^{-1} corresponding to N=N and disappearance absorption band at (3458-3360) cm^{-1} for NH_2.^{1}H-NMR-Spectrum show signals at 6.53 for H of (OH).
[S2] The FTIR spectrum exhibit appearance absorption band of NH_2 at (3221,3327) cm^{-1} and appearance absorption band of C=N at (1608) cm^{-1} and disappearance absorption band of C=O carboxylic acid at (1683) cm^{-1}.^{1}H-NMR (δ, ppm) spectrum exhibits disappearance signal for (H, COOH) and appearance signal for (H, NH_2)
[S3] The FTIR spectrum show disappearance absorption band of NH_2 at (3221, 3327) cm^{-1} and

appearance absorption band of C- H_{aliph} at (2831) cm^{-1} and absorption band at (1552) cm^{-1} for C=N
^{1}H-NMR (δ,ppm) spectrum exhibits disappearance signal for (H, NH_2) and appearance signal for (H, N=CH)
[S4] The FTIR spectrum show disappearance absorption band of NH_2 at (3221, 3327) cm^{-1} and appearance absorption band at (1533) cm^{-1} for C=N
^{1}H-NMR (δ,ppm) spectrum exhibits disappearance signal for (H, NH_2) and appearance signal for (H, N=CH)
[S5] The FTIR spectrum show disappearance absorption band of NH_2 at (3221, 3327) cm^{-1} and appearance absorption band of C- H_{aliph} at (2885) cm^{-1} and absorption band at (1508) cm^{-1} for C=N
^{1}H-NMR (δ,ppm) spectrum exhibits disappearance signal for (H, NH_2) and appearance signal for (H, N=CH) and signal for(H,CH).
[S6] The FTIR spectrum show disappearance absorption band of NH_2 at (3221, 3327) cm^{-1} and appearance absorption band of C- H_{aliph} at (2928) cm^{-1} and absorption band at (1560) cm^{-1} for C=N
^{1}H-NMR (δ,ppm) spectrum exhibits disappearance signal for (H, NH_2) and appearance signal for (H, N=CH)
[S7] The FTIR spectrum show disappearance absorption band of NH_2 at (3221, 3327) cm^{-1} and appearance absorption band of C- H_{aliph} at (2843) cm^{-1} and absorption band at (1560) cm^{-1} for C=N
^{1}H-NMR (δ,ppm) spectrum exhibits disappearance signal for (H, NH_2) and appearance signal for (H, N=CH).
[S8] The FTIR spectrum show disappearance absorption band of NH_2 at (3221, 3327) cm^{-1} and appearance absorption band of C- H_{aliph} at (2922) cm^{-1} and absorption band at (1572) cm^{-1} for C=N
^{1}H-NMR (δ,ppm) spectrum exhibits disappearance signal for (H, NH_2) and appearance signal for (H, N=CH)

Table 1: Physical properties of the synthesized compounds [S1-S8]

Compound Number	M.P (^{0}C)	Yield (%)	Color	Molecular Weight (g\mole)	Molecular formula
[S1]	195-197	93	Orange	258	$C_{13}H_{10}N_2O_4$
[S2]	180-182	78	brown	313	$C_{14}H_{11}N_5O_2S_1$
[S3]	192-194	87	Light brown	501	$C_{29}H_{19}N_5O_2S_1$
[S4]	188-190	82	Light brown	429	$C_{22}H_{15}N_5O_3S_1$
[S5]	180-182	75	Dark brown	444	$C_{23}H_{20}N_6O_2S_1$
[S6]	183-186	86	brown	486	$C_{21}H_{13}Cl_2N_5O_3S_1$
[S7]	190-192	80	black	417	$C_{21}H_{15}N_5O_3S_1$
[S8]	192-194	74	Light brown	462	$C_{21}H_{14}N_6O_5S_1$

Table 2: C.H.N.S data of the prepared compounds [S1-S8]

Comp.NO	C% Calculation	C% Measure	H% Calculation	H% Measure	N% Calculation	N% Measure	S% Calculation	S% Measure
[S1]	54.545	53.22	3.496	3.94	21.70	21.44	-	-
[S2]	53.674	53.00	3.514	3.18	22.364	21.95	10.22	9.69
[S3]	69.46	69.18	3.79	3.65	13.97	14.26	6.38	6.57
[S4]	61.53	61.39	3.49	3.78	16.31	15.94	7.45	7.11
[S5]	62.16	61.85	4.50	4.11	18.91	18.56	7.20	6.89
[S6]	51,85	51.45	3.67	3.48	14.40	14.94	6.58	6.11
[S7]	60.43	60.09	3.59	3.88	16.78	16.32	7.67	7.85
[S8]	54.54	54.81	3.03	2.79	18.18	18.55	6.92	7.43

5. Conclusion

An effective method for the synthesis of azo dye with a high yield that uses water as the solvent, takes a short time, and is performed at a low temperature, several novel Schiff-base heterocyclic compounds were synthesized from 1,3,4-thiadiazole amine with very good yield and confirmed by FTIR, ^{1}HNMR, ^{13}CNMR and CHNS. also, physical properties of these compounds have been investigated.

5. Acknowledgement:
We would want to express our gratitude to the Department of Chemistry at the College of Science for Women University of Babylon for assisting in the completion of this project.

6. References:

[1] Pagariya S.K., Pathade R.M. and Bodkhe P.S. (2015); Synthesis, Characterization and Antimicrobial screening of some Azo compounds derived from Ethyl vanillin, *Res. J of Chem Sci*, 5(7): 20-28.
[2] Mohanad M. K., Nour A. A., Saadoon A. A., and Dr. Nagham M. A. (2021); *Egypt. J. Chem.* Vol. 64, No. 3 pp. 1273 - 1283.
[3] Kate S, and Thakare N.S., (2016): Synthesis and spectral characterisation of some Azo amine Dyes, *journal of Global Biosciences*, 5(1): 3615-3617.
[4] Atyaf Y. A. and Nasreen R., (2016): Synthesis and Characterization A New Thiadiazepine Compounds From New Bis 4-Amino-3-Mercpto-1,2,4-Triazol Derivatives, *International Journal Of Research In Pharmacy And Chemistry*, 6(3), 372-378.
[5] Rama D.K., Rao Patnaik K.S.K., Ashok D., Bathula R., Shobha Rani S., Vasudha B., and Gopagoni S., (2017); Comparison study between convenstional method and mircrowave irradiation method to synthesize oxadiazole derivatives, *Int. J. of Pharmacy*

and Analytical Research, 6(2) 396-404.
[6] Pagariya R. F. and Thakare N.S., (2016): "Synthesis and in vitro antibacterial evaluation of 2, 4- dinitro phenol incorporated azo dyes molecules." *Der Pharma Chemica*, 8(7):130-136.
[7] Nagham Mahmood Aljamali. (2019), Review on (Azo, Formazane, Sulfazane)- Compounds", *International Journal of Innovations in Scientific Engineering.*, Vol. No. 10, Jul-Dec.,19-45
[8] Affeq Jabr Kadhem, Ahmed Adnan Abdul Hussein, Nagham Mahmood Aljamali, Ahmed A A H, Afaq J K. (2020)., Invention of Imidazole & Thiazole-Sulfazane Ligands (Synthesis, Spectral Investigation, Microbial Behavior) for The First Time., *Int. J. Pharm. Res.*, Vol. 12.
[9] Miad Mohamd, Nagham Mahmood Aljamali, Nadheema Abed Abbas.,"Preparation,, (2018); Spectral Investigation, Thermal Analysis, Biochemical Studying of New (Oxadiazole - Five Membered Ring)-Ligands".,*Journal of Global Pharmacy Technology* 10, 1, 20-29.
[10] Miad Mohamd, Nagham Mahmood Aljamali, Wassan Ala Shubber., Sabreen Ali Abdalrahman., (2018):" New Azomethine- Azo Heterocyclic Ligands Via Cyclization of Ester"., *Research J. Pharm. and Tech.* 11,6.
[11] Nagham Mahmood Aljamali., (2019): "The Various Preparation Methods in Synthetic Chemistry".,1 Edt., Evincepub Publishing house, ISBN :978-93-88277-82-2.
[12] Shi,M.et al (2019): Tuning of reversible thermochromic properties of salicylaldehyde Schiff bases through the substitution of methoxy and nitro groups', *Journal of Molecular Structure*, 1182, pp. 72–78. doi: 10.1016/j.molstruc.01.012.
[13] M. M. Abo-Aly, A. M. Salem, A. M. Sayed and A. A. A. Aziz (2015): Molecular and Biomolecular Spectroscopy, 136, 993.
[14] A. A. A. Aziz, A. N. M. Salaem, M. A. Sayed and M. M. Aboaly
2015); *Journal of Molecular structure*, 1010, 130.
[15] A. A. M. Belal, I. M. El-Deen, N. Y, Farid, Z. Rosan and S. R Moamen,(2015): *Journal of Molecular structure*; 2015, 149, 771 ..
[16] C. U. Dueke- Eze, T. M. Fasina and N. Idika (2011); *African Journal of Pure and applied Chemistry*, 5, 2.
[17] Anu Kajal,Suman Bala,Sunil Kamboj,Neha Sharma,and Vipin Saini (2013): Schiff Base :A Versatile Pharmacophore,*Jornal of Catalysts*,dx.doi.org\10.1155
[18] Nour Abd Alrazzak, Suad T. Saad, Hazim Y. Al-gubury, Mohanad M. Kareem and Mawahib M. Assi, (2021) Bull. Chem. Soc. Ethiop., 34(3), 463-469.
[19] Nour Abd Alrazzak, (2018), Synthesis of some New Heterocyclic Derivatives and some of their composites with PVC and Study their PhotoCatalytic Behaviour.
[20] Nour Abd Alrazzak, Suad T. Saad and Nagham Mahmood Aljamali (2019) Asian Journal of Chemistry; Vol. 31, No. 5, 1022-1026.