ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal
www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2024, Vol. 40, No.(4):
Pg. 987-996

New Synthesis, Solvatochromism, Halochromism and Dying Applications of Azo Compound 4-hydroxy-3-((3-nitrophenyl) diazenyl)benzaldehyde

MYASAR KH. IBRAHIM[1]* and SHIREEN R. MOHAMMED[2]

[1]Department of Basic Science, College of Agricultural Engineering Sciences,
University of Duhok, KIR-IRAQ, Iraq.
[2]Department of Chemistry, College of Science, University of Zakho, KIR-IRAQ, Iraq.
*Corresponding author E-mail: myasar.khalil@uod.ac

http://dx.doi.org/10.13005/ojc/400409

(Received: June 24, 2024; Accepted: July 31, 2024)

ABSTRACT

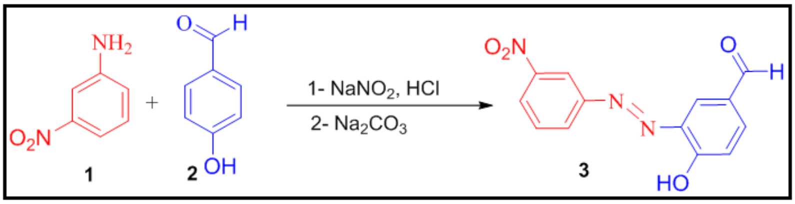
This work includes synthesis of the novel azo compound, which consists of diazotization of 3-nitroaniline followed by reaction with 4-hydroxybenzaldehyde in presence of sodium carbonate. The syanthesized azo compound was confirmed by characterization, using FT-IR, ^{1}HNMR, ^{13}CNMR and GC-MS spectra. The azo compound was screened for solvatochromism, Halochromism using UV-Vis spectrophotometer, and found that the azo compound exhibited low solvatochromic and good Halochromic properties. While the dying study (Dye-doped Polymer Films), Poly ethylene was found the best polymer dyed by azo compound and showed good absorbance in the UV region. All fabrics were dyed with a yellow color except the cotton exhibiting a light brown color.

Keywords: Azo dyes synthesis, Coupling reactions, Solvatochromism, Halochromism, Dye-doped polymer.

INTRODUCTION

Azo compounds contain significant functional groups; therefore, they are widely used in industrial[1], pharmaceuticals[2] and they have biological activity[3,4] like anticancer[5], antimicrobial, antioxidant[6,7].Various compounds have demonstrated pesticide properties due to the presence of an azo moiety[8,9], azo-imine[10], azo-pyrazoline derivatives[11] and pyrimidine derivatives[12]. In organic chemistry, azo derivative compounds with the functional group (-N=N-), have two isomers, trans and cis; the trans isomer is more common[13]. Different modifications and routes were made to obtain azo dyes with desired properties[3,14,15,16]. The most common synthesis method for preparing azo compounds is diazotization of amine, which was reported first by the German organic chemist Peter Griess in 1858[4].Moreover, azo compounds were used as dyes in over 50% of all commercial colorants[17]. Solvatochromic dyes are a broad class of polarity-responsive environmental probes that exhibit color changes. They are typically push-pull dyes that transfer charges within molecules. In more polar solvents, the red shift in emission of their highly polarized excited state occurs. Azo dyes show different colors as pH changes. This is due to the change in the conjugation of π-bonds. This phenomenon is called Halochromic, which is defined as the compound that changes color with changing the pH. Therefore, they are used as indicators[18].

Hence, because of these reasons, much attention is being paid to the synthesis and the industrial significance of azo dye, our present work is an extension of our ongoing efforts toward design, synthesis and identification of azo dye through main processes of reaction between 3-nitroaniline 1 with 4-hydroxybenzaldehyde 2 in basic conditions under coupling reaction step to obtain new azo dye product 3 (Scheme 1).



Scheme 1. Synthetic route and strategy of azo compound 3

EXPERIMENTAL

MATERIALS AND METHODS

Without any additional purification, the chemicals and solvents used during this work were purchased from Scharlau, Merck, and Fluka Companies. Melting points were measured with an uncorrected the measuring device of melting point (melting point type: Electrothermal 12372).NMR spectra were recorded by Bruker NMR spectrometer, operating at 400 MHz with internal standard; tetramethylsilane, all NMR spectrum were measured at the department of chemistry/college of education/ university of Basra. Fourier transform infrared spectra were recorded using Thermo Scientific Nicolet iS 20 FT-IR Spectrometer station (4000-400) cm^{-1} used for Attenuated Total Reflectance (ATR) vibration measurements with 4 cm^{-1} resolution. The software Omnic 9.2.86, Firmware version 1.02 by Thermo Fisher Scientific was used for data collection, drawing and interpretation of FT-IR (ATR) spectra. Preparative TLC silica gel 60, F254 Glass used for clean-up compounds.

Synthesis

Preparation of 4-hydroxy-3-((3-nitrophenyl) diazenyl)benzaldehyde(3)

Azo compound (3) synthesized according to patent[19] with some development as shown: In a 100 mL flask, 3-Nitroaniline1 (1.38 g, 10 mmol, 1.0 eq.) was dissolved in 4 mL of DW and 4 mL of conc. HCl, the solution was cooled down to 0-5°C in an ice-bath with stirring. The cold solution of sodium nitrate (0.828 g, 12mmol, 1.2 eq.) in 2.5 mL of DW, was added drop by drop to the content of the flask, stirring for 1 h while keeping the same temp. The basic phenolic solution [Sodium carbonate (3.71 g, 35mmol, 3.5 eq.) and 4-hydroxybenzaldehyde 2(1.342 g, 11mmol, 1.1 eq.) were dissolved in DW 40 mL], was added to the above flask drop wise with stirring in ice bath for 4 hours. All reactions were monitored using TLC with eluents (toluene/ethyl acetate (EtOAc) 3:1).The cold mixture was filtered under vacuum, and the precipitant was washed with DW and acidified with (2N, HCl) and filtered, then washed with boiling DW twice and followed by purification using preparative TLC to give the expected product 3.

Solvatochromism study

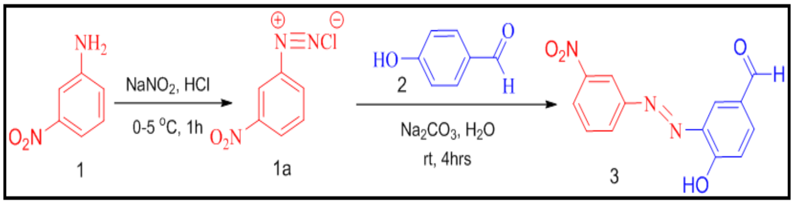
A solvatochromism study of the synthetized compound 3 carried out using UV-Vis spectrophotometer and a quartz cuvette with a range of wave length at (200-800)nm.The solution of compound 3 was prepared in eight different organic solvents and λ_{max} was determined for compound 3 in each solvent. Furthermore, the λ_{max} of each polar solvent was determined in a different medium; acid, neutral and basic,(1drop of 2N HCl added to the neutral tested solution for preparing the acidic medium, and 2 drops of 20% NaOH to prepare the basic medium). Furthermore, the absorption coefficient (ε) of each solvent was calculated from a calibration curve by preparation of different concentrations of each solution of different solvents. Finally, Subtraction of neutral from acid or base was used to find the color change when changing pH. The differences between neutral and acidic medium, neutral and basic medium were calculated by subtracting absorbance (Abs) of neutral from absorbance of acidic to produce acidic subtraction and so on for basic subtraction[20].

Dyeing study

All dyeing processes were carried out using a local market fabric and transparent polymer film samples. The dyeing process of the synthetized azo compound 3 was done according to the procedure of Kurda[21] and with some modifications. Briefly, for dyeing fabric; (10 mg) of compound 3 was dissolved in (20 mL) of (20% Na_2CO_3) using heating until boiling, pieces of the multi-fiber (Chiffon, Satin, Cotton and polyester) strips were immersed in the solution for 20 minute. The strips were removed and rinsed with tap water, then left to dry at room temperature. The fastness properties were tested according to studies[22,23,24,25,21] by dividing each type of fiber into five parts: the first was used as a reference, the second was tested by Perspiration fastness acid test; dyed fabric was immersed in hypochlorite solution for 1 h, and the third (Perspiration fastness basic) was immersed in 1% NaOH solution for 30 minute. The fourth was tested (light fastness test) by immersed in detergent overnight, rinsed with a water tap and irradiated with sunlight for 24 hours. The fourth (wash fastness) was washed with detergents and soaps, then sandwiching a piece of the dyed fabric between un-dyed cotton fabric pieces and immerse it in 60°C water for 30 minutes. Polymer dyeing was done using the same concentration of dye solution. The solution of synthetized dye was heated to 80-90°C, then the pieces of polymers were immersed in the solution for 1 min, then the mixture were transferred to a dark place to cool down slowly. After 24 h, the dyed polymer pieces were removed from the solution, washed with a water tap and left in the dark to dry.

RESULTS AND DISCUSSION

Our protocol of the synthesis consists of preparation of a new azo compound 3 through diazotization reaction at low temperature, of 3-nitroaniline with nitrous acid to produce diazonium salts, followed by one-pot coupling the diazonium salt with 4-hydroxybenzaldehyde in basic solution of Na_2CO_3 as shown in (Scheme 2). The final expected products were easily purified through chromatography silica gel to give the expected product compound 3 as orange color solid (2.547 g, 94%). m. p.=166-171°C. $R_f = 0.65$ (toluene/EtOAc 3:1). FTIR (ATR) ν_{max} (cm^{-1}) = 1745(C-H aldehyde), 1680(C=O), 1523(NO_2), 1452(N=N), 1417(N=N), 1389(N=N), 1346(NO_2) 1270(C-N). ^1H NMR (400 MHz, $CDCl_3$) δ(ppm) 13.00 (s, 1H, OH), 10.02 (s, 1H, HC=O), 8.76 (t, $J = 2.1$ Hz, 1H, CH_{ar}), 8.55 (d, J = 2.1 Hz, 1H, CH_{ar}), 8.40 (dd, $J =$ 8.4 and 1.8 Hz, 1H, CH_{ar}), 8.25 (dd, $J = 10$ and 1.2 Hz, 1H, CH_{ar}), 8.00 (dd, $J = 8.6$ and 2.1 Hz, 1H, CH_{ar}), 7.78 (t, $J = 8.1$ Hz, 1H, CH_{ar}), 7.21 (d, $J = 8.6$ Hz, 1H, CH_{ar}). ^{13}CNMR (100.2 MHz, $CDCl_3$) δ (ppm) 189.85(HC=O), 158.12(C_{-OH}), 150.87(C_{ar}), 149.37(C_{ar}), 137.24(Car), 134.37(C_{ar}), 130.69(C_{ar}), 130.01(C_{ar}), 128.96(C_{ar}), 128.63(C_{ar}), 125.92(C_{ar}), 119.87(C_{ar}), 116.98(C_{ar}). GS-MS (EI, 70 eV) m/z; $C_{13}H_9N_3O_4$ $[M-H]^+$ 270.05 found 270.2.



Scheme 2. Synthesis of azo compound 3 from 3-nitroaniline 1

The disappearance of –OH broad peak due to two reasons: first, Compound 3 can undergo enol-imine/keto-amine tautomerization or (azo and hydrazone) by H-atom transfer from the hydroxyl oxygen to the imine nitrogen probably via intramolecular hydrogen bonding (Scheme 3). Secondly, ATR technique was used instead of FTIR (KBr) to analyzed compound 3.

To give more evidence of producing compound 3, we use the ATR overly spectrums (Fig. 1) of reactant against product to show the disappearing NH_2 peak from 3-Nitroaniline 1 (reactant), and the appearing of N=N and C-N peaks belong to compound 3 (product).

The –OH group shifts in NMR spectra to a less down field caused by the tautomerizm as mansion before.

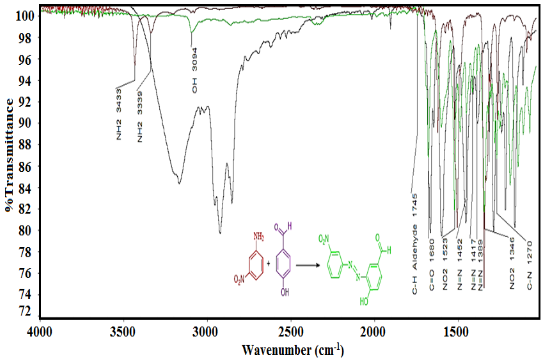


Fig. 1. The overlay of ATR spectrums of 3-nitroaniline 1, product 3 and FTIR (KBr) spectrum of 4-hydroxybenzaldehyde 2

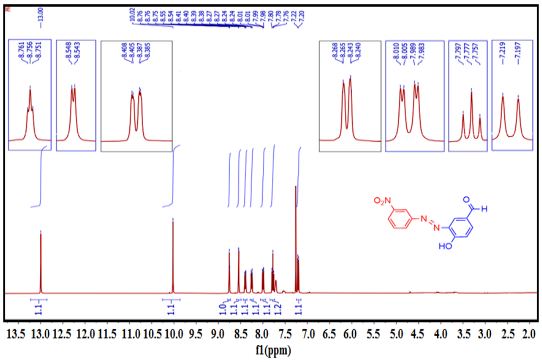


Fig. 2. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of synthesis azo compound 3

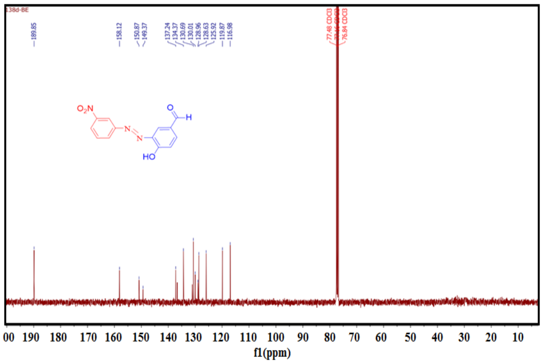
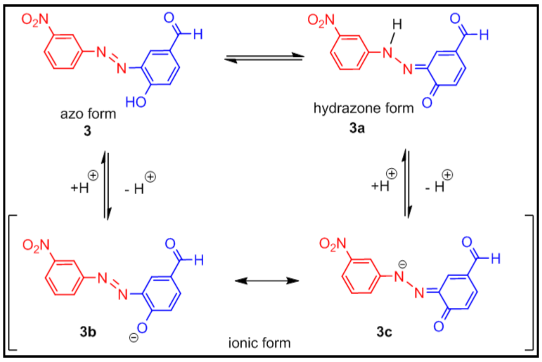


Fig. 3. ^{13}C NMR (100.2 MHz, $CDCl_3$) spectrum of synthesis azo compound 3

Solvatochromism

The effect of solvents on azo compound 3 shown in Scheme 3 has four tautomeric forms; azo form 3, hydrazone form 3a (Ketohydrazo form) and ionic form (3b-3c). Obviously, the azo compound structure is affected by the acid-base equilibrium as shown in Scheme 3, in addition to the relative positions of UV-Vis maximum of anionic and hydrazone forms. Azo compounds can readily dissociate in dipolar proton-accepting solvents and anion form can produce. The same can be done by the addition of a base. However, in solvents that donate protons, like HCl, the hydrazone form 3a is preferred. Therefore, the concentrated HCl and NaOH solution (10%) were added in drops to the acetone (ACT), EtOH and ACN solutions of azo compound in order to find the position of hydrazone and anion forms[26,27,28].



Scheme 3. Possible tautomeric forms of the synthetized azo compound 3

The azo compound 3 exhibits an intense absorption band centered around 260–560nm. The absorption spectra of azo compound 3 were measured in selected solvents as representative examples Fig. 4. Azo compound 3 absorbs light in two main regions of wave length, which appears two mean peaks, each peak having different λmax in different solvents.

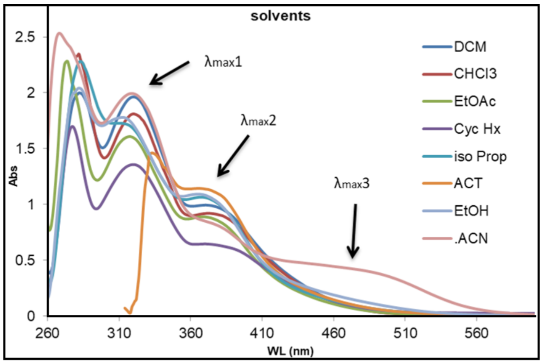


Fig. 4. The UV-Vis absorbance spectra of azo compound 3 in different solvents

In this study, the concentration $0.138x10^{-3}$ M of azo compound 3 was prepared in different organic solvents. The lower λ_{max1} 306nm (blue shift) observed in isopropanol solvent, while the higher λ_{max1} 333nm (red shift) observed in acetone. While the second peak λ_{max2} appears at (365-390)nm for the visible region which belongs to hydrazone form 3a[26], also the lower λ_{max2} (blue shift) observed in ACT and the higher λ_{max2} (red shift) observed in ACN. Furthermore, in cyclohexane (CycHx) had the lower absorbance value (1.357 and 0.646) in the two regions λ_{max1} 320nm and λ_{max2} 370nm respectively, comparing with all other solvent due to very low solubility of the compound in it (Table 1). While in ACN appears higher absorbance value1.993 at λ_{max1}, and very low absorbance value 0.721 at λ_{max2}, which refer to the very good solubility of compound 3 in ACN and containing a higher concentration of azo form 3 than other solvents. All bands showed very weak red shift (close values of λ_{max2}) with decreasing solvent polarity in the visible region except ACN; therefore, the color of the azo compound was yellow in different solvents, and dark yellow in ACN. Moreover, only in ACN solvent appears peak at λ_{max3} 470nm with absorbance 0.430, which refers to containing an ionic form (3b-3c) in neutral medium.

Furthermore, the Molar Absorptivity or Extinction Coefficient (ε) was calculated for λ_{max1} and λ_{max2} in each organic solvent by using the calibration curves (Fig. 5) and supplementary (Fig. 9). The ε can be determined from the linear equation of the calibration curve which plots using absorption of azo compound 3vs. concentration in the indicated solvents at specific λ_{max} Table 1.

Table 1: Spectrometric calculated values for studded azo compound BE solvatochromism using conc. 0.0001385 M

Solvent	DCM	$CHCl_3$	EtOAc	CycHx	Iso Prop	ACT	EtOH	ACN
$\lambda_1$nm	320	320	318	320	309	333	313	319
Abs	1.9635	1.8117	1.6075	1.3571	1.7271	1.4617	1.7795	1.9937
ε	164428	14689	13498	9318.5	11616	10473	12611	14072
B	-0.3201	0.0829	0.0607	0.0509	0.1194	0.0124	0.0266	0.0578
R^2	0.9996	0.999	0.9976	0.9982	0.9995	0.9997	0.9987	0.9997
$\lambda_2$nm	371	373	368	370	367	365	365	390
Abs	0.9944	0.9206	0.8894	0.6462	1.0653	1.1435	1.0924	0.7215
ε		6714.4	7437.1	4379.4	7287	8158.17	8246	6008.1
b		0.0663	0.0306	0.0329	0.0669	0.0225	-0.0608	-0.0181
R^2		0.9932	0.9983	0.9985	0.9989	0.9994	0.998	0.9999

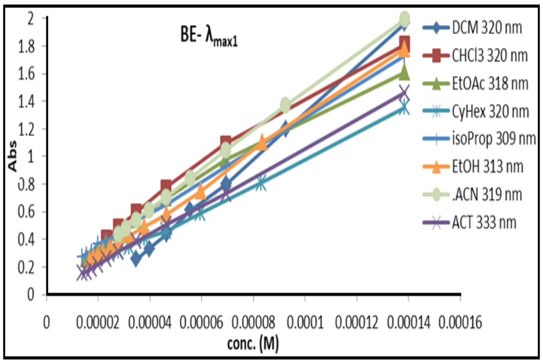


Fig. 5. Calibration curves; plot of absorption of azo compound 3 vs. concentration in the indcated solvents at λ_{max1}

Calculation of ε is very important to calculate the unknown concentration solution of the azo compound using beer-Lambert law. In λ_{max1}, the higher ε was 164428 $M^{-1}cm^{-1}$ in DCM while the lower was 9318 $M^{-1}cm^{-1}$ in cyclohexane. In λ_{max1}, the ε values order of compounds in different solvents can be arranged as follows:

DCM<$CHCl_3$<ACN<EtOAc<EtOH<isoProp<ACT<CycHex

Likewise, the order of ε values at λ_{max2} is are arranged as follows:

EtOH<ACT<EtOAc<isoProp<$CHCl_3$< ACN<CycHex

Finally, an example of spectrum used for calculating ε for organic solvents in different concentrations is illustrated in the supplementary (Fig. 10) which supports the linearity of calibration curve for a series of concentration prepared in indicated solvents.

Halochromism study

In general, the color of azo compound 3 in neutral and acidic medium is yellow, while it is red in basic medium. To study halochromism application for the synthesized compound 3, three solvents (ACN, EtOH and ACN) have been used. Furthermore, λmax for the azo compound 3 in acidic medium was close to the value λmax in neutral medium (Table 2), which presents azo form 3 and hydrazone form 3a.

In the acidic medium, the λ_{max1} was higher in ACT 335nm (more red shift) than in EtOH 312nm and ACN 315nm. Also, the maximum absorbance was in ACN solvent 1.786 at λ_{max1} 316nm, while the minimum absorbance1.315 at λ_{max1} 335nm was in ACN. Therefore, the solvent ACN contains more concentration of azo form 3, while acetone contains more conc. of Hydrazone form. While at λ_{max2} there is no high difference observed between solvents, but absorbance of ACT 1.12 was the highest one. Furthermore, the concentration of hydrazone increased when adding HCl to the ACN solvent only, because the absorbance of the neutral solutions was found 0.721 at λ_{max2} (Table 1), while in acidic medium was 1.036 Table 2, while for ACT and ACN very small change observed.

In general, the basic medium causes a bathochromic shift (red shift). The λ_{max3} for compound 3 in acetone was the higher red shift recorded at 468nm with a higher absorbance value of 1.361. While in EtOH, compound 3 showed the lower red shift recorded at 454nm with a lower absorbance value of 1.067 than ACN and ACT Figure 6.

Table 2: Spectrometric calculated values for studded azo compound 3 Halochromism for acidic and basic medium

Solvent	ACT	EtOH	ACN
A λ_{max1}nm	335	312	316
Abs	1.3159	1.52503	1.7862
Aλ_{max1}nm	362	364	364
A Abs	1.1205	0.99595	1.036
Bλ_{max1}nm		324	315
B Abs		1.65397	1.8978
ε		10290	8660
b		0.2457	0.4261
R^2		0.9966	0.996
Bλ_{max3}nm	468	454	466
B Abs	1.36158	1.06769	1.27846
ε	10254	7397.6	8456.9
b	-0.0668	0.0471	0.0916
R^2	0.9993	0.9988	0.9985
Sub Bλ_{max3}nm	480	471	473
Sub Abs B	-1.26284	-0.88714	-0.8477
Diff Abs A-B	1.26886	0.957	1.2

The ε maximum value was observed in neutral ethanol (8246 $M^{-1}cm^{-1}$) at λ_{max2} 390nm Table 1, while in the basic medium the maximum value was observed also in EtOH (10290 $M^{-1}cm^{-1}$) Table 2 at λ_{max2} 324nm. Moreover, in the basic medium for the third peak, the ε maximum value (10254 $M^{-1}cm^{-1}$) was observed in acetone at λ_{max3} 468nm with a higher absorbance value of 1.36. While the lower value ε (7397 $M^{-1}cm^{-1}$) was observed in EtOH at λ_{max3} 324nm with a lower absorbance value of 1.067.

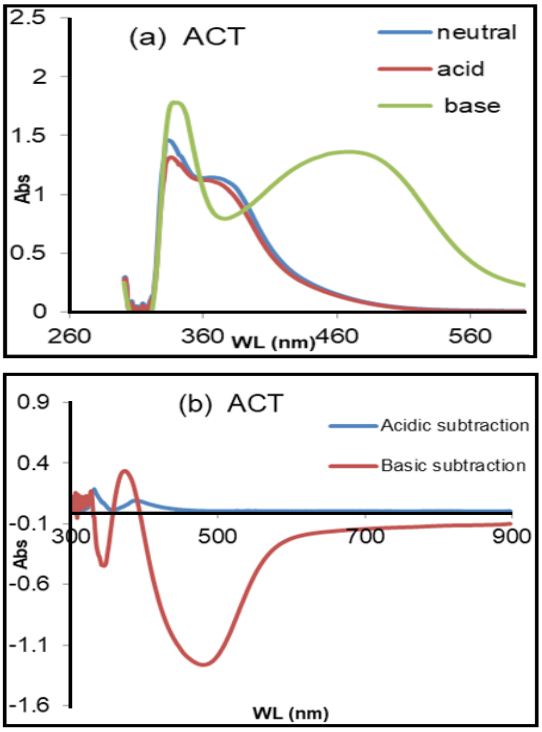


Fig. 6. Absorption spectra for azo compound 3 in (a); acidic, neutral and basic media in ACT solvent. (b); subtraction spectra for the acidc subtraction and basic subtraction

The compound 3 in the basic medium of three different solvents shown in Fig. 6 showed the maximum observed value of 1.268 for A-B (summation of absorbance for acidic and basic subtractions at indicated λ_{max}) in ACT at λ_{max} 480. We can propose that the ACT solvent is stabilized an ionic form (3b-3c) (phenoxide) more than ethanol and ACN Scheme 3. Therefore, the ACT solvent is the best solvent for compound 3 when used as an indicator, which has good Halochromic properties.

Dying Fabrics

The dying results were shown in Fig. 7, the best dyed fabric was cotton, which exhibited a light brown color after dying. Furthermore, the color of dyed cotton was stable after applying all the fastness tests that are mentioned above, except Perspiration basic fastness, which converts the color of cotton from light brown to a red-brown color. Moreover, if the basic cotton is washed with water and dried, it will return to light brown color again. This conversion is very useful in dying fabric application, by using dyed cotton with azo compound 3 as an indicator of the human skin, to distinguish between basic or acidic skin sweating. Satin fabric is dyed with a yellow color, and is also stable against all fastness tests except the base, which is converted to a light red color like dyed cotton. Likewise, polyester is dyed golden-shiny yellow and stable against all fastness tests. Finally, Chiffon was also dyed with a yellow color, and it was stable against all fastness tests.

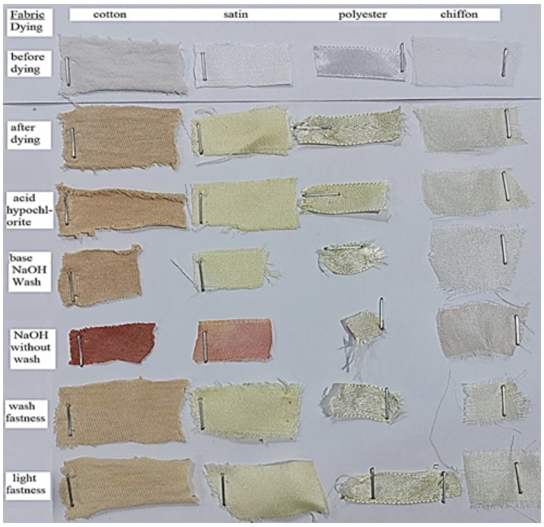


Fig. 7. Fastness test of dyed fabric; before and after dying and fastness tests

Dye-doped Polymer Films

Azo compound 3 shows distinct properties when dyeing polyethylene (PE). In particular, the dyed PE with the compound 3 showed increasing the absorbance in the UV region at λ (350-550)nm and the peak appears at λ_{max} 324nm with absorbance 0.675. The three spectra Fig. 7 for PE before dying, PE after dying and the substrate between them show the maximum absorbance when PE is dyed compared with other polymers. Polypropylene (PP) showed very low spectrum absorbance from UV to Vis region when dyed with compound 3. In other words, compound 3 was an unsuitable dye for PP due to the stability of PP against chemical reactions, and it is chemically inert and resistant to most commonly found organic and inorganic chemicals[29]. On the other hand, polyvinyl chloride (PVC) was better than PP for dyeing, and showed an increase in absorbance with decreasing wave length, especially in the UV region.

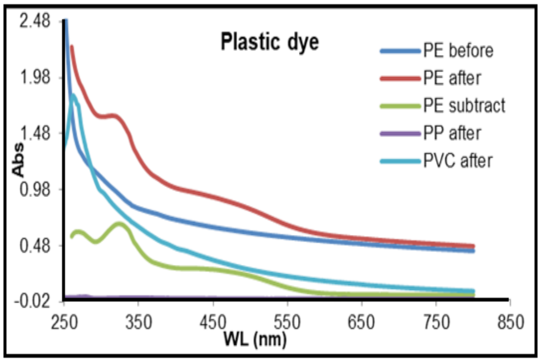


Fig. 8. Absorption spectrums of dyed polymers PE, PP and PVC by azo compound 3

It is worth to mansion that azo compound 3 is a good dye for PE and PVC. Furthermore, they absorb UV light, which makes them a good polymer for protecting against UV light. Therefore, it is a useful application for protecting humans from UV light by using them on the glasses of cars, monitors, house windows and sun screens. Also, these compounds can be used as greenhouses to protect some plants that are affected by UV light.

The chemical reaction between dye and polymer proposed to be chemisorption binding process, according to Fleischmann[30]. He stated that adsorption measurements were performed at pH 8 for basic dyes, and proved that electrostatic interactions between the carboxylate moieties and the cationic dyes contribute to a chemisorption binding process. The evidence for attraction between PE and compound 3 from the (–OH) group can be shown in Fig. 8 for the ATR spectra overly between PE before and after dying. The appearance of the absorption band at (3388 cm^{-1}) after PE dying, which belongs to the hydroxyl group[31,32,33], the lower intesity of this peak confirms the attraction of the hydroxyl group to the carbon chain of PE. Furthermore, dyed PE has a clear absorbance at (2914, 2847, 1471 and 718) cm^{-1}, which belong to the aliphatic CH group of the PE structure. Moreover, the drop down of absorbance from (1680 to 1577) cm^{-1}, which belongs to (C=O) group, and the drop down of absorbance from (1523 to 1540) cm^{-1}, which belongs to NO_2, gave the evidence of binding as chemisorption process between the C=O and NO_2 with aliphatic CH in the PE structure.

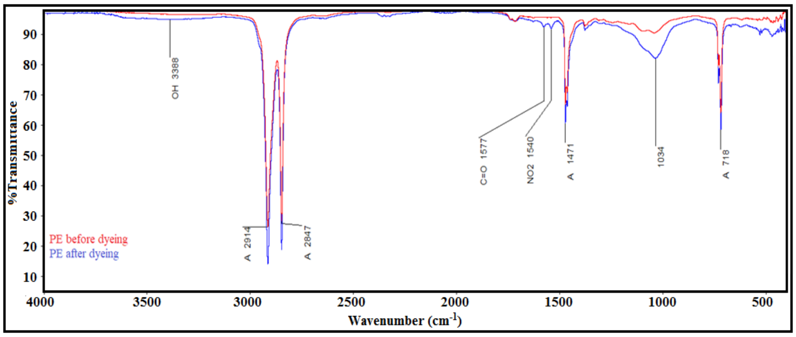


Fig. 9. ATR overlay spectrums for the PE before and after dying

CONCLUSION

The synthesis of the novel azo compound 3 was performed. The synthesized compound was completely identified by FTIR, MS and NMR. The Solvatochromism study showed that the range of λ_{max1} was (309-333nm). The Halochromism study showed highly difference between absorbance in acidic media at λ_{max1} 335nm and basic media at λ_{max3} 468nm in ACT, which was the best solvent for Halochromism. The fabric dying study showed the best dyed fabric was cotton, which exhibited a light brown color after dying. The color of the dyed cotton was stable after applying most of the fastness tests. Finally, the application of dye-doped polymer films showed that PE and PVC were better than PP for dying, and they absorb UV light, which makes them a good polymer for protecting against UV light.

ACKNOWLEDGMENT

We offer our appreciation and affection to Barcopharma Co. (agent of Thermo fisher Co.), for many providing facilities and support, that made this work easy and possible.

Conflict of interest

The author declare that we have no conflict of interest.

REFERENCES

1. Vollheim, T., *Survey of Industrial Chemistry. Adv. Mater.,* **1993**, *5*(5), 400–400. https://doi.org/10.1002/adma.19930050520.
2. Mezgebe, K.; Mulugeta, E. Synthesis and Pharmacological Activities of Azo Dye Derivatives Incorporating Heterocyclic Scaffolds., *A Review. RSC Adv.*, **2022**, *12*(40), 25932–25946. https://doi.org/10.1039/d2ra04934a.
3. Abbas Sh Al-Hamdani, A. L. I.; Shaker, S. A. Synthesis, Characterization, Structural Studies and Biological Activity of a New Schiff Base-Azo Ligand and Its Complexation with Selected Metal Ions., *Orient. J. Chem.*, **2011**, *27*(3), 835–845.
4. Yates, E.; Yates, A. Johann Peter Griess FRS (1829-88): Victorian Brewer and Synthetic Dye Chemist., *Notes Rec.*, **2016**, *70*(1), 65–81.https://doi.org/10.1098/rsnr.2015.0020.
5. Kofie, W.; Dzidzoramengor, C.; Adosraku, R. K. Synthesis and Evaluation of Antimicrobial Properties of AZO Dyes., *Int. J. Pharm. Pharm. Sci.*, **2015**, *7*(4), 398–401.
6. Okolo, E. N.; Ugwu, D. I.; Ezema, B. E.; Ndefo, J. C.; Eze, F. U.; Ezema, C. G.; Ezugwu, J. A.; Ujam, O. T. New Chalcone Derivatives as Potential Antimicrobial and Antioxidant Agent., *Sci. Rep.*, **2021**, *11*(1), 1–13. https://doi.org/10.1038/s41598-021-01292-5.
7. Rohini, R. M.; Devi, K.; Devi, S. Synthesis of Novel Phenyl Azo Chalcone Derivatives for Antitubercular, Antiinflammatory and Antioxidant Activity., *Der Pharma Chem.*, **2015**, *7*(1), 77–83.
8. Katritzky, A. R.; Chen, Q. Y.; Tala, S. R. Convenient and Efficient Preparations of Azodye-Labeled Peptides., *Chem. Biol. Drug Des.*, **2009**, *73*(6), 611–617. https://doi.org/10.1111/j.1747-0285.2009.00813.x.
9. Rojin, B.; Maher, K.; Shireen, M. Synthesis of Some New Bis-4-Thiazolidinones Derived from 2-Hydroxy-1-Naphthaldehyde., *Indian J. Heterocycl. Chem.*, **2022**, *32*(3), 357–362.

10. Hussein, A. J.; Aziz, H. J. Synthesis and Spectroscopic Characterization of Some New Azo-Thiazolidinone Derivatives. *In pelagia Research Library*., **2011**, *6*, 22–26.
11. Haji, R.B.; Ali, M.K.; Mohammed, S.R. Synthesis and Spectroscopy Characterizations of Some New Bis 1,3-Thiazolidin-4-Ones Derived from 4-Hydroxybenzaldehyde Substrate., *Orient. J. Chem*., **2023**, *39*(5), 1156–1163. https://doi.org/10.13005/ojc/390508.
12. Mohammed, S.; Maher, K. A Facile Entry to Fused Dipyrimidines : Preparation of Imidazo [1, 2-a : 3, 4-a'] A Facile Entry to Fused Dipyrimidines : Preparation of Imidazo [1, 2-a: 3,4-a’]., *Indian J. Heterocycl. Chem*., **2017**, *27*(3), 289–294.
13. Mitchell, G. R.; King, N. R. Optimisation of Photo-Induced Geometric Isomerisation of Azobenzene Derivatives in Dye-Doped Polymer Films for Enhanced Photo-Induced Poling., *Macromol. Symp*., **1999**, *137*(1 999), 155–165. https://doi.org/10.1002/masy.19991370116.
14. Kadhium, A. J.; Mohammed, M. S.; Baper, S. H. Design, Preparation Some Transition Metal Complexes of Chalcone-Azo with Paracetamol Ligand and Evaluation Anti-Biological Activity of Some Complexes., *J. Kufa Chem. Sci*., **2023**, *3*(1), 55–67. https://doi.org/10.36329/jkcm/2023/v3.i1.13523.
15. ALKazmi, A. A.; Hawais, F. E.; Alasadi, Y. K. Synthesis and Characterization of Some Pyrazoline Derivatives from Chalcones Containing Azo and Ether Groups., *Tikrit J. Pure Sci*., **2023**, *22*(9), 69–75. https://doi.org/10.25130/tjps.v22i9.877.
16. Baper, S. H.; Mohammd, M. S. Synthesis, Characterization and Study Anticancer Activity of New Azo–Chalcone with Mix Ligand of Some Divalent Metal Chelate Complexes., *J. Kufa Chem. Sci*., **2023**, *2*(9), 390–408. https://doi.org/10.36329/jkcm/2022/v2.i9.13312.
17. Benkhaya, S.; M’rabet, S.; El Harfi, A. Classifications, Properties, Recent Synthesis and Applications of Azo Dyes., *Heliyon.,* **2020**, *6*(1). https://doi.org/10.1016/j.heliyon.2020.e03271.
18. Mckee, S. Azo Dyes as Ionochromic Anion Indicators and the Synthesis of 1,2-Diphenylethane-1,2-Dione, **2018**. https://core.ac.uk/reader/159595447.
19. Botros, R.; CreeK, B. Azomethine Dyes Derived From An O-Hydroxy Aromaticaldehyde And A 2-Amnopyrone., **1977**.
20. Sucre-Rosales, E.; Fernández-Terán, R.; Urdaneta, N.; Hernández, F. E.; Echevarria, L. Solvatochromism and Intramolecular Charge Transfer in Dialkylamino-Substituted Halogenated Thienyl Chalcone Analogues., *Chem. Phys*., **2020**, *537*, 110854. https://doi.org/10.1016/j.chemphys.2020.110854.
21. Kurda, D.; Raheem, D.; Samad, M. K. ZANCO Journal of Pure and Applied Sciences Synthesis, Characterization and Dying Performance Studies of Some Azo Dyes Derived from m-Phenylenediamine., **2017**, No. January.
22. Aftan, M. M.; Toma, M. A.; Dalaf, A. H.; Abdullah, E. Q.; Salih, H. K. Synthesis and Characterization of New Azo Dyes Based on Thiazole and Assess the Biological and Laser Efficacy for Them and Study Their Dyeing Application., *Egypt. J. Chem*., **2021**, *64*(6), 2903–2911. https://doi.org/10.21608/ejchem.2021.55296.3163.
23. Rekaby, M. M.; Shaban, E.; Salama, H. S.; Quhal, G. A.; Qaisy, A. A. One-Pot Synthesis, Characterization, and Antibacterial Activity of Mono Azo-Disperse Dyes Bearing Bis-λ-Aminophosphonates Moiety, and Their Application in Polyester Printing., *Egypt. J. Chem*., **2022**, *65*(13), 331–338. https://doi.org/10.21608/EJCHEM.2022.125556.5581.
24. Characterization, DFT Calculations and Dyeing Performance on Polyester Fabrics of Some Azo Disperse Dyes Containing Pyrazole Ring., *J. Saudi Chem. Soc*., **2023**, *27*(101594).
25. Omar, A. Z.; Mahmoud, M. N.; El-Sadany, S. K.; Hamed, E. A.; El-atawy, M. A. A Combined Experimental and DFT Investigation of Mono Azo Thiobarbituric Acid Based Chalcone Disperse Dyes., *Dye. Pigment*., **2021**, *185* (PA), 1088870. https://doi.org/10.1016/j.dyepig.2020.108887.

26. Wang, J.; Liu, H. B.; Ha, C. S. Zinc-Supported Azobenzene Derivative-Based Colorimetric Fluorescent “turn-on” Sensing of Bovine Serum Albumin., *Tetrahedron.,* **2009**, *65*(47), 9686–9689. https://doi.org/10.1016/j.tet.2009.09.102.
27. Ener, N.; Gür, M.; Çavuλ, M. S.; Zurnaci, M.; ener., Synthesis, Characterization, and Theoretical Calculation of New Azo Dyes Derived from [1,5-a]Pyrimidine-5-One Having Solvatochromic Properties., *J. Heterocycl. Chem*., **2019**, *56*(3), 1101–1110. https://doi.org/10.1002/jhet.3497.
28. Mijin, D.; Božiλ Nedeljkoviλ, B. B.; Božiλ, B.; Kovrlija, I.; Ladareviλ, J.; Ušλumliλ, G. Synthesis, Solvatochromism, and Biological Activity of Novel Azo Dyes Bearing 2-Pyridone and Benzimidazole Moieties., *Turkish J. Chem*., **2018**, *42*(3), 896–907. https://doi.org/10.3906/kim-1711-97.
29. Cruz-Romero, M. C.; Kerry, J. P. 26 - Packaging of Cooked Meats and Muscle-Based, Convenience-Style Processed Foods. In Woodhead Publishing Series in Food Science, Technology and Nutrition; Kerry, J. P., Kerry, J. F. B. T.-P. M., Eds.; Woodhead Publishing., **2011**, 666–705. https://doi.org/https://doi.org/10.1533/9780857092946.3.666.
30. Fleischmann, C.; Lievenbrück, M.; Ritter, H. Polymers and Dyes: Developments and Applications., *Polymers (Basel)*., **2015**, *7*(4), 717–746. https://doi.org/10.3390/polym7040717.
31. Clayden, J.; Greeves, N.; Warren, S., *Organic Chemistry*., **1995**, *270*. https://doi.org/10.1126/science.270.5234.227.b.
32. Mayo, D. W.; Miller, F. A.; Hannah, R. W. Course notes on the interpretation of infrared and raman spectra; Jone Wiley., **2003**.
33. Pavia, D. L. Introduction to Spectroscopy Fifth Edition; **2017**. https://doi.org/10.1201/b21879-2.