International Journal of Chemistry Studies
www.chemistryjournal.in
ISSN: 2581-348X
Received: 08-09-2025, Accepted: 08-10-2025, Published: 23-10-2025
Volume 9, Issue 2, 2025, Page No. 28-33

Solvent Effects on the UV/ Visible Absorption Spectra of two azobenzothiazole dyes

Orléans Ngomo[1*], Joseph Tsemeugne[2*]
[1] Department of Organic Chemistry, Laboratory of Natural Substances and Environment, University of Yaounde I, P.O. Box Yaounde, Cameroon
[2] Department of Organic Chemistry, Laboratory of Natural Products and Applied Organic Synthesis, Lanapos, University of Yaounde I, P.O. Box, Yaounde, Cameroon

Abstract

The preparation of the two azo dyes, 4 bearing benzothiazole moiety, was undertaken using a known method. The yield of the dyes was moderate. It was established that all the physical, spectroscopic and analytical data of compound 4 were in full agreement with those previously reported. The solvatochromism behaviour of the azo compounds is investigated by studying their spectra in pure organic solvents of different characteristics. The presence of electron donor groups and the delocalization of pi electrons, which establish a long-range conjugation, results in the maximum absorption of compound 4a (2.097 in MeOH) being greater than the maximum absorption of compound 4b (1.243 in EtOH).

Keywords: UV/ Visible Absorption Spectra, azobenzothiazole dyes, coupling, solvatochromism

Introduction

Over the past decade, our research has encompassed the synthesis [1, 2] and medicinal applications [3-6] of azo dyes with diverse heterocycles. Azo dyes, which contain a heterocyclic structure, exhibit a number of advantageous properties. These include excellent brightness and strong adhesion to the fibres of the polymers to which they are applied [7, 9]. Azo dyes are also described in the literature as nonlinear optical materials. It has been demonstrated that azo dyes which contain heterocycles in their structures exhibit superior optical properties in comparison to those derived from aniline [10, 12].

The present study investigates the solvatochromism behaviour of azo compounds that contain a benzothiazole skeleton, a heterocycle, within their structure. This investigation involves the study of the compounds' spectra in four different solvents, each with a distinct polarity. The objective of this study is to evaluate the impact of the nature of the solvent on the degree of absorption of the dyes.

Material and Methods

The azo dye 4 was synthesised in accordance with the literature procedure as published previously [13].

Preparation of the reagents and starting materials

All the reagents mentioned in this work were purchased from Aldrich and Fluka and were used without further purification.

Preparation of diazonium salt solution

As previously described [13], 0.69 g (10 mmol) of dried sodium nitrite was slowly added to 10 mL of concentrated sulphuric acid over a period of 30 minutes, with occasional stirring. The solution was then cooled to 0–5 °C. Compound 1 was dissolved in dimethyl sulfoxide (DMSO) (10 mL) and cooled to 0–5 °C. The nitrosyl sulphuric acid solution was then added to the 1 solution, maintaining the temperature between 0 and 5 °C. The clear diazonium salt solution obtained, consisting of intermediate 2 formed in situ, was used immediately in the coupling reactions.

General procedure for the preparation of the coupling products 4a, b

Acetaminophen (1.51 g, 10 mmol) was dissolved in 10 mL of DMSO and cooled in an ice bath at 0–5 °C. The previously prepared diazonium solution (2) was added dropwise over one hour, after which 15 ml of 10% sodium acetate solution was added to the mixture. The pH of the mixture was in the range 9–11. The solid precipitate was collected by filtration and crystallised from methanol to give the title compound.

N-(2-(6-ethoxy-5-((6-ethoxybenzo[d]thiazol-2-yl)diazenyl)benzo[d]thiazol-2-yl)diazenyl)-3-((6-ethoxy-5-((6-ethoxybenzo[d]thiazol-2-yl)diazenyl)benzo[d]thiazol-2-yl)diazenyl)-5,6-bis((6-ethoxybenzo[d]thiazol-2-yl)diazenyl)-4-hydroxyphenyl)acetamide hexahydrate (4a) Compound 4a was obtained in 47% yield as red powder; m.p. 196 – 199 °C (dec),){Lit. m. p. 197 – 199 °C, [13]}; Anal. Calcd. for $C_{62}H_{63}N_{19}O_{14}S_6$: C, 49.96; H, 4.26; N, 17.85; S, 12.90. Found: C, 49.98; H, 4.28; N, 17.81; S, 12.88. Rf = 0.39.

N-(4-hydroxy-3-((6-methoxybenzo[d]thiazol-2-yl) diazenyl) phenyl) acetamide hexahydrate (4b) Compound 4b was obtained in 51% yield as brown powder; m.p. 196 – 198 °C (dec), {Lit. m. p. 197 – 199 °C, [13]}; Anal. Calcd. for $C_{16}H_{26}N_4O_9S$: C, 42.66; H, 5.82; N, 12.44; S, 7.12. Found: C, 42.63; H, 5.80; N, 12.41; S, 7.10. Rf = 0.30.

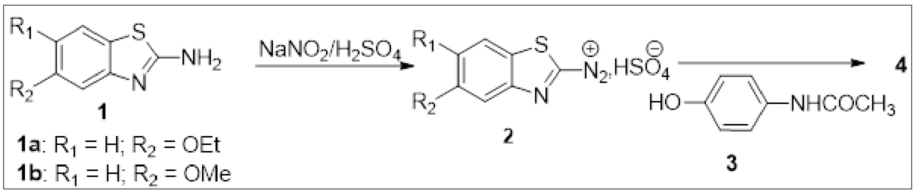
Absorption spectroscopy

Double beam 721G/722G UV–Visible spectrophotometer was used to record the absorption spectra over a wavelength range 338–800 nm which combined with a cell temperature controller. Quartz cuvettes were used for measurements in solution via l = 1 cm.

Results and Discussion

Synthesis of azo dyes 4a, b

The azo dye 4 (Scheme 1, Figure 1) was prepared in excellent yield as previously reported [13]. All the physical, spectroscopic and analytical data of compound 4 were in full agreement with those previously reported [13].



Scheme 1: reactions' sequences to compounds 4

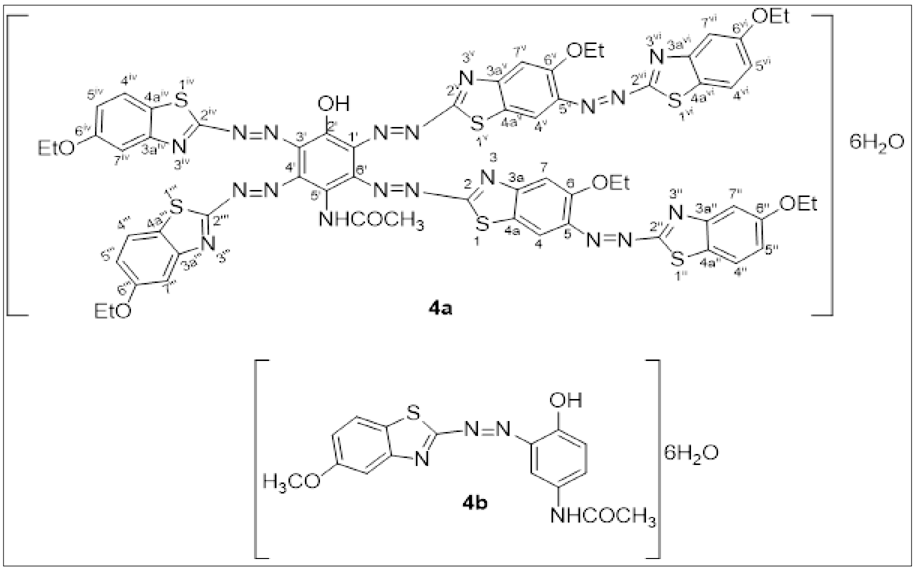


Fig 1: Structures of compounds 4

The solvent effect on the absorption spectra

The absorption spectra of azobenzothiazole dyes 4a and 4b (figure 2) were measured in four organic solvents with different polarities (dichloromethan, ethylacetate, ethanol, methanol) in the wavelength range 338–400 nm at a concentration ~10^{-5} mol·L^{-1}.

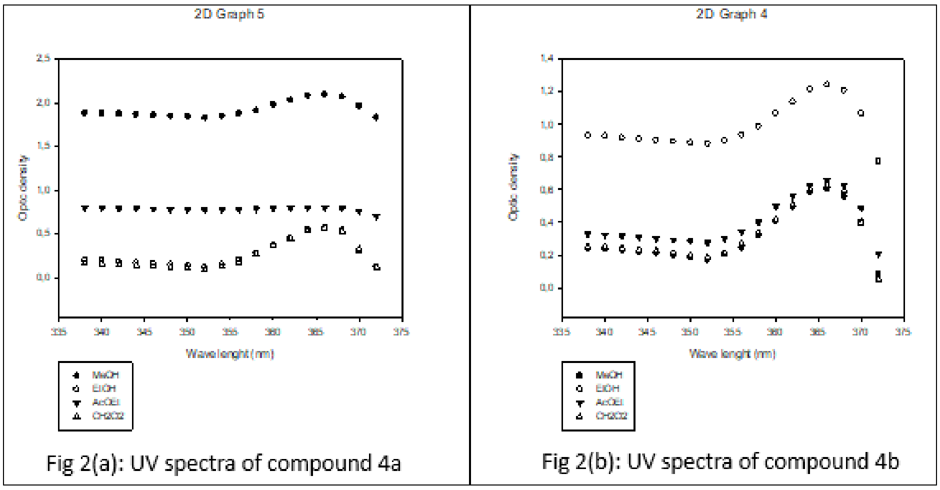


Fig 2(a): UV spectra of compound 4a

Fig 2(b): UV spectra of compound 4b

Fig 2: Electronic spectra of azo dyes 4a in different solvent

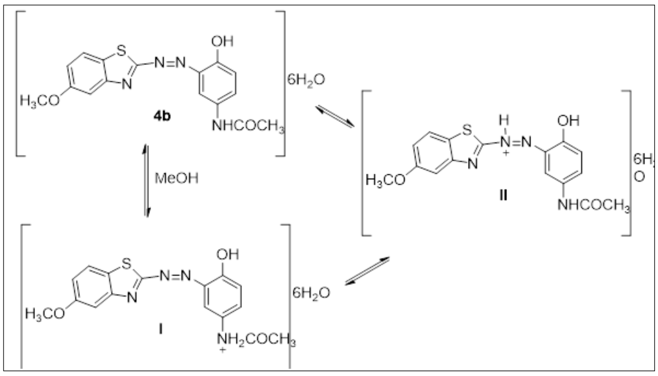
The azo compounds displayed a single band in their electronic absorption spectra in all the organic solvents used. This band was attributed to an electronic transition involving the entire electronic system of the compounds in aromatic and heteroaromatic systems. As can be seen in Figure 2, the electronic absorption spectra of azobenzothiazole dyes 4a and 4b do not show a systematic variation with solvent polarity.

Compound 4a exhibited significant maximum absorption in methanol (MeOH), ethanol (EtOH) and chloroform (CH_2Cl_2), with a maximum absorption wavelength of λ_{max} = 366 nm, but low maximum absorption in acetonitrile (AcOEt). This may be due to the low solubility of compound 4a in AcOEt compared to the other solvents. It is acknowledged that the photophysical behaviour of a dissolved dye depends on its environment. The intensity, shape and maximum absorption wavelength of the dye's absorption band in solution depend strongly on solvent-solute interactions and the nature of the solvent [14]. The absorbance of compound 4a in the polar solvent EtOH (0.576) and the non-polar solvent CH_2Cl_2 (0.572) is very close, suggesting that the solubility of compound 4a is identical in these two solvents, indicating that this dye does not exhibit strong solvent dependence. This finding is consistent with the relevant literature [15]. However, the maximum absorption of compound 4a in EtOH and CH_2Cl_2 is lower than that observed in MeOH. The maximum absorbance is four times greater in MeOH than in EtOH and CH_2Cl_2.

Compound 4b exhibited significant maximum absorption at a wavelength of λ_{max} = 366 nm in all four solvents (methanol, ethanol, acetonitrile and dichloromethane) used in this study. This suggests that the solubility of compound 4b is approximately analogous in these four solvents. However, the maximum absorption is higher in EtOH (1.243) than in AcOEt (0.658), CH_2Cl_2 (0.628) and MeOH (0.606). The maximum absorption of compound 4b in EtOH is almost double the values obtained in the other three solvents.

Overall, comparing the graphs in Figures 2a and 2b shows that the maximum absorption of compound 4a (2.097 in MeOH) is greater than that of compound 4b (1.243 in EtOH). This is due to the presence of electron-donor groups, such as ethoxy and methoxy, which are directly attached to the benzene ring of benzothiazole-based azo dyes. These groups are also associated with the delocalisation of π-electrons, forming long-range conjugation [16].

It also appears that there is better absorbance in the protic solvents MeOH and EtOH. In protic solvents such as methanol or ethanol, azo dye 4 with amino groups in the para position undergoes mono-protonation to give the ammonium (I) and/or azonium (II) tautomers.

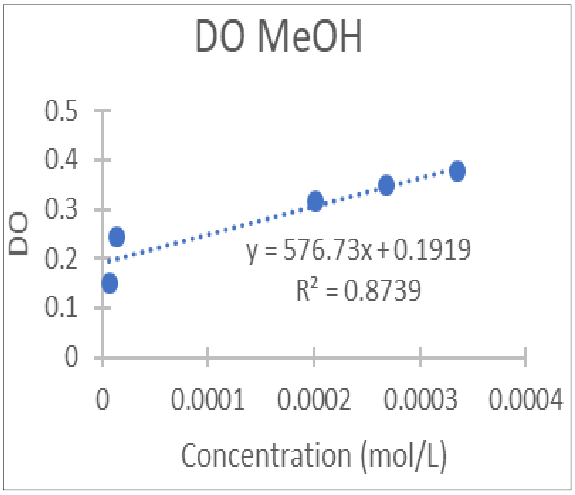


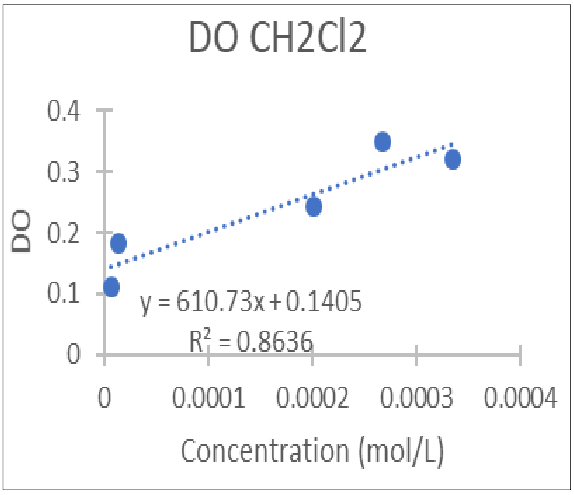
Scheme 2: Tautomeric changes on protonation of aminoazo dye 4b

Effect of concentration on the absorption spectra

Solutions of different concentrations of compounds 4a and 4b were analysed in the same solvent at a wavelength of λ_{max} = 366 nm, and the optical densities were recorded. The effects of the concentrations of compounds 4a and 4b on the optical density were interpreted using the concept of a linear relationship, as shown in Figures 3 and 4. Figures 3 and 4 shows that the optical density increases with the concentration of compound 4 in solution. However, the correlation coefficient R^2 in AcOEt (0.93) is higher than that obtained in EtOH (0.90), MeOH (0.87) and CH_2Cl_2 (0.86) for compound 4a. The correlation coefficient R^2 for compound 4b is generally lower than that for compound 4a. These values range from 0.86 in CH_2Cl_2 to 0.73 in AcOEt. The R^2 correlation coefficients of compounds 4a and 4b in CH_2Cl_2 are equal. Despite the interesting value of R^2 for compound 4a in AcOEt, as observed above, compound 4a exhibits very little absorption in this solvent, probably due to its low solubility in AcOEt. This leads us to conclude that AcOEt is not suitable for measuring the absorption of compound 4a. However, MeOH appears to be the appropriate solvent for determining the maximum absorption of compound 4a, with a correlation coefficient R^2 of 0.87 and a good optical density of 2.097.

Of the four solvents used in this study, chloroform (CH_2Cl_2) with a correlation coefficient (R^2) of 0.86 seems to be the best solvent for analysing compound 4b. However, based on the observations in Figure 4, ethanol (EtOH) remains the best solvent for dye 4b's absorption, with an R^2 close to 1 and an optical density of 1.243.





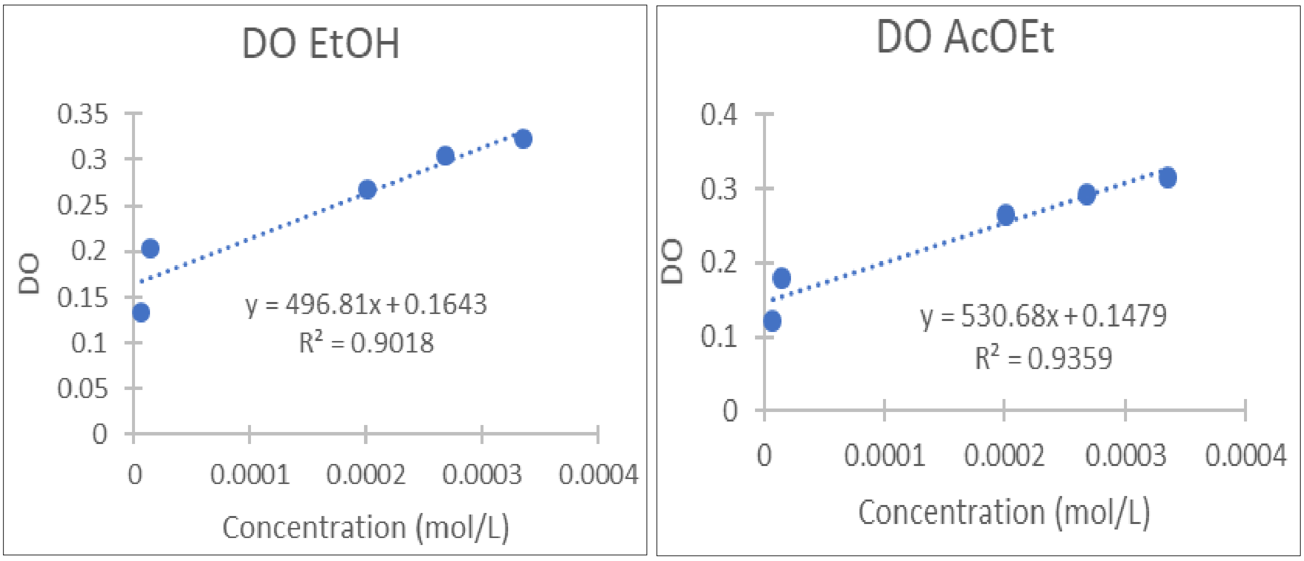


Fig 3: Variation of DO with concentration of compound 4a in different solvent

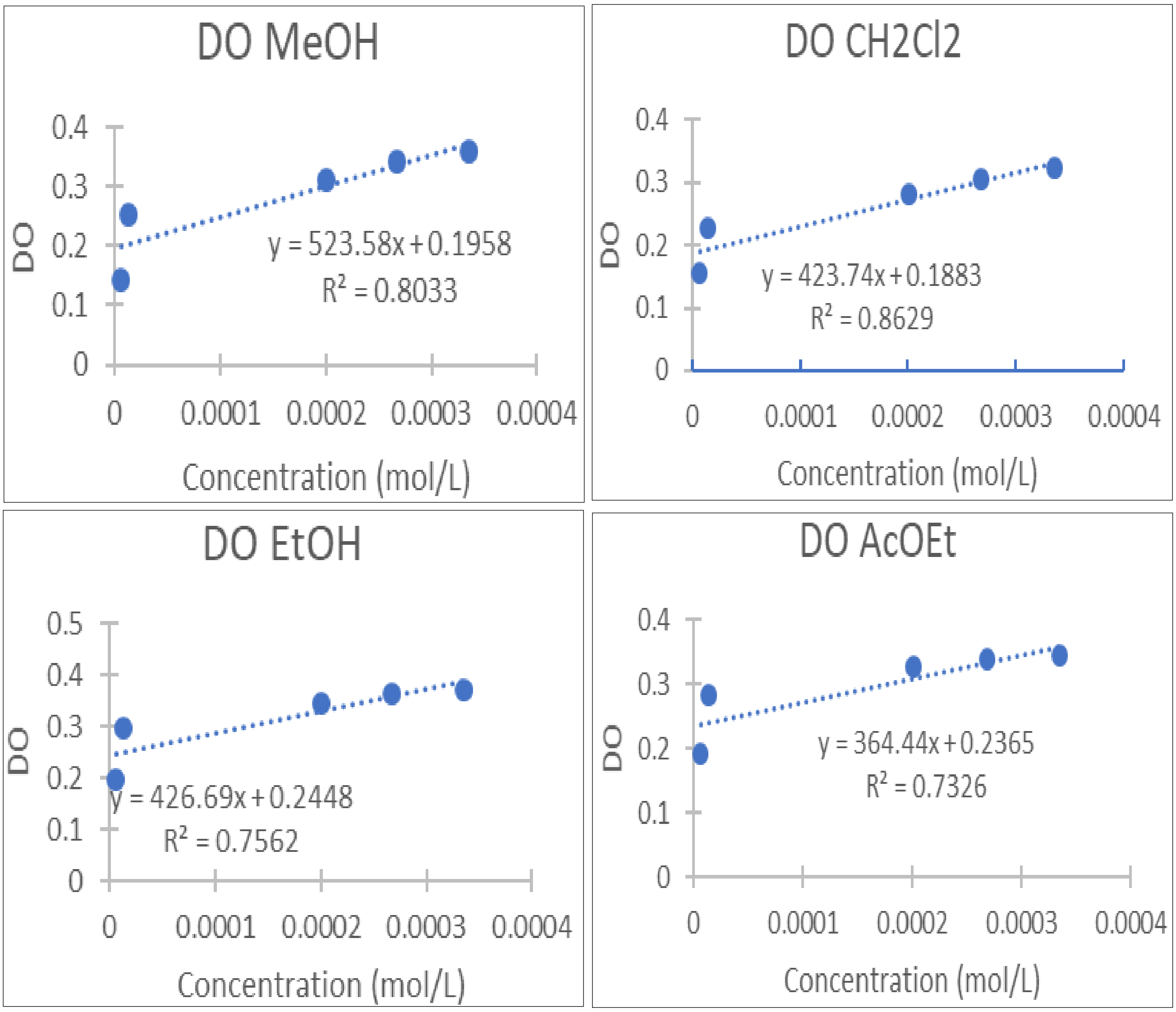


Fig 4: Variation of DO with concentration of compound 4b in different solvent

We also compared the optical density of compounds 4a and 4b in the same solvent at the same concentration (see Figure 6). Figure 6 shows the optical density of compounds 4a and 4b in EtOH, MeOH and CH_2Cl_2 solvents.

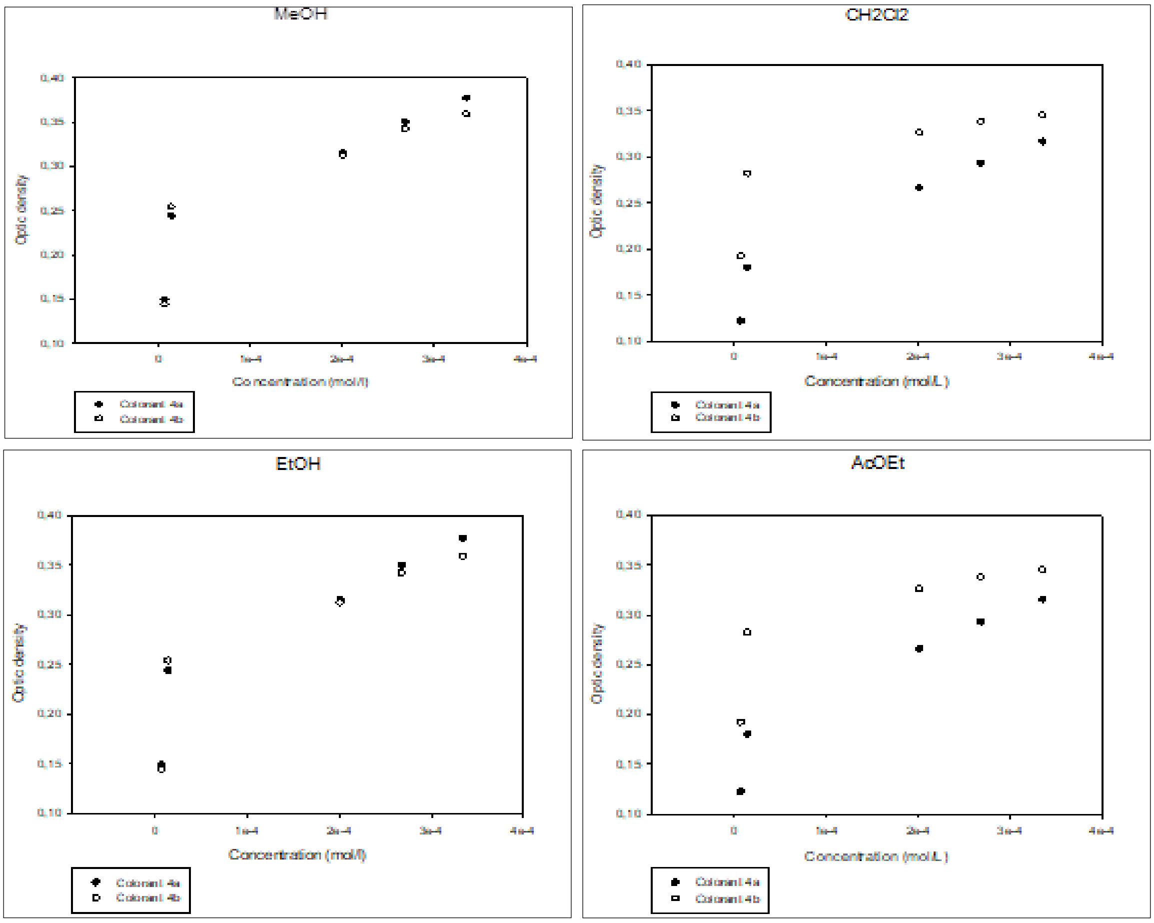


Figure 6: Variation of optical density of compounds 4a and 4b at the same concentration in the same solvent

The optical density of compounds 4a and 4b is comparable in MeOH and EtOH solvents at the same concentrations. However, we also noticed that the optical density of dyes 4a and 4b at the same concentrations is different in AcOEt and CH_2Cl_2 solvents. In these two solvents, the optical density of compound 4b is greater than that of compound 4a.

Conclusion

The absorption maximum of dyes 4a and 4b showed one band in the wavelength range of 338–400 nm in all four of the solvents investigated in this study. Methanol and ethanol are the best solvents for UV-visible analysis of compounds 4a and 4b. The maximum absorption of compound 4a (2.097 in methanol) is greater than that of compound 4b (1.243 in ethanol). This can be attributed to the presence of electron donor groups, which are also linked with the delocalisation of pi electrons, establishing long-range conjugation.

References

1. Fondjo ES, Tsemeugne J, Sondengam BL, Oppenlaender T, Wabo HK, Tane P, *et al*. Coupling of Two Diazotized 3-Aminothieno[3,4-c] coumarins with Aromatic Amines. Journal of Heterocyclic Chemistry,2011:48:1295–1301.
2. Tsemeugne J, Sopbué FE, Djintchui AN, Sabnis RW, Sondengam BL. Coupling of the Diazonium Sulphate of 3-Amino-4H-benzo[f]thieno3,4-c chromen-4-one with Phenol and Naphthol Derivatives in Varied Stoichiometries. Trends in Organic Chemistry,2017:18:55–69.
3. Tamokou J-de-D, Tsemeugne J, Fondjo ES, Sarkar P, Kuiate JR, Djintchui NA, *et al*. Antibacterial and Cytotoxic Activities and SAR of Some Azo Compounds Containing Thiophene Backbone. Pharmacologia,2016:7:182–192.
4. Fondjo ES, Djeukoua DKS, Tamokou J-de-D, Tsemeugne J, Kouamo S, Ngouanet D, *et al*. Synthesis, Characterization, Antimicrobial and Antioxidant Activities of The Homocyclotrimer of 4-Oxo-4H-Thieno[3,4-C] Chromene-3-Diazonium Sulfate. The Open Medicinal Chemistry Journal,2016:10:21–32.
5. Tsemeugne J, Fondjo ES, Tamokou J-de-D, Tonle I, Kengne IC, Ngongang AD, *et al*. Electrochemical Behavior and In-Vitro Antimicrobial Screening of Some Thienylazoaryls Dyes. Chemistry Central Journal,2017:11:119.
6. Tsemeugne J, Fondjo ES, Tamokou J-de-D, Taoufik R, Ngongang AD, Kuiate JR, et al. Synthesis, Characterization and Antimicrobial Activity of a Novel Trisazo Dye from 3-Amino-4H-thieno[3,4-c] [1] benzopyran-4-one. International Journal of Medicinal Chemistry,2018:2018:9197821.
7. Abd-El-Aziz AS, Afifi TH. Novel Azo Disperse Dyes Derived from Aminothiophenes: Synthesis and UV-Visible Studies. Dyes and Pigments,2006:70:8–17.
8. Hallas G, Choi J-H. Synthesis and Spectral Properties of Azo Dyes Derived from 2-Aminothiophenes and 2-Aminothiazoles. Dyes and Pigments,1999:42:249–265.
9. Rangnegar D W, Sabnis R W. Novel Substituted 2-Acetamido Thiophene-4-Styryl Disperse Dyes. Journal of Chemical Technology and Biotechnology,1993:56:401–405.
10. Guru Prasad L. Azo Dye Doped Polymer Films for Nonlinear Optical Applications. Chinese Journal of Polymer Science,2014:32(5):650–657.

11. Razus AC, Birzan L, Surugiu NM, Corbu AC, Chiraleu F. Syntheses of Azulen-1-yl-Benzothiazol-2-yl Diazenes. Dyes and Pigments,2007:74:26–33.
12. Matsui M, Kushida M, Funabiki K, Shibata K, Muramatsu H, Hirota K, et al. Second-Order Optical Nonlinearity of Thiazolylazo Chromophores Containing Hydroxyl Groups. Dyes and Pigments,1998:38:283–289.
13. Tsemeugne J, Nangmo PK, Mkounga P, Tamokou J-de-D, Kengne IC, Edwards G, et al. Synthesis, Characteristic Fragmentation Patterns and Antibacterial Activity of New Azo Compounds from the Coupling Reaction of Diazobenzothiazole Ions and Acetaminophen. Heterocyclic Communications,2021:2 7:79–89.
14. Zakerhamidi MS, Ghanadzadeh A, Moghadam M. Solvent Effects on the UV/Visible Absorption Spectra of Some Aminoazobenzene Dyes. Chemical Science Transactions,2012:1(1):1–8.
15. Fox T, Rosch N. The Calculation of Solvatochromic Shifts: The n-π* Transition of Acetone. Chemical Physics Letters,1992:191:33–37.
16. Eskikanbur S, Sayin K, Kose M, Zengin H, McKee V, Kurtoglu M. Synthesis of Two New Azo-Azomethines; Spectral Characterization, Crystal Structures, Computational and Fluorescence Studies. Journal of Molecular Structure,2015:1094:183–194.