Research Article

Synthesis and Spectroscopic Studies of Some New Oxazole Derivatives Dyes

Bushra Ahmed Ezze Kateb[1], Manal Ali Elhag[1,2], Abdulkareem Ali Hussein Al-Alie[3], Abdullah M. Asiri[4], M.A. Baseer[1]
[1]P.G. Department of Chemistry, Yeshwant College, S.R.T.M.University, Nanded, India.
[2]Department of Chemistry, Red Sea University, Portsudan, Sudan.
[3]School of chemical sciences, S.R.T.M.University, Nanded, India.
[4]Faculty of Science, Chemistry Department, King Abdul-Aziz University.
***Corresponding author's E-mail:** manalelhag24@gmail.com

Accepted on: 01-04-2014; **Finalized on:** 31-05-2014.

ABSTRACT

The aim of this study is to synthesize new oxazole derivatives dyes and to study their spectral properties, such as UV-Visible, ^{1}HNMR, FT-IR and fluorescence. Most of these compounds showed absorption in the visible region with wave length spreading over wide spectrum of color ranging from brown to violet. The fluorescence of these dyes were measured in ethanol and showed from strong to moderate confirm the dye formation. The solvatochromism of these dyes studied in two solvents with different polarity, namely chloroform and acetonitrile. The photo stability of thin film of PMMA and the rate were monitored and the percentage of degradation upon heating was calculated.

Keywords: Absorption emission spectra, degradation, Oxazole derivatives dyes, Synthesis.

INTRODUCTION

Styryl dyes of the general formula R-Het$^+$-CH =CH-Ar X– can undergo E-Z isomerization, electrocyclization and [2 + 2] cycloaddition photoreactions owing to the presence of ethylene bonds in the dye molecules.[1–5] Styryl dyes are widely used as sensitizers and other additives in the photographic industry.[6-9] Styryl dyes are also of potential interest in the fabrication of nonlinear optical materials due to their large hyperpolarizability.[10] Oxazole or its fused derivatives find extensive use in the industrial purposes and the interest in their chemistry has increased due to the application of such moieties in photosensitization or in valuable optical brighteners[11] and in analytics.[12] Dye organization is also considered to be the key to advanced functional organic materials for electronics and photonics[13-14] some of these dyes are growth inhibitors to bacteria[15] and to the mitosis of fertilized sea urchin eggs.[16] They possess hormonal effects on plant growth[17] and can be used for the determination of the sensitivity of micro-organism to antibiotics.[18] They can also be used as laser dyes[19- 20] and producing offset printing plates.[21-22]

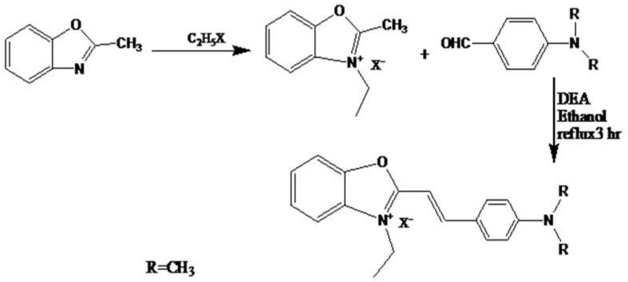
MATERIALS AND METHODS

Physical measurements

The Melting points were determined by using melting point apparatus smp3. The IR spectra were recorded in KBr pellets on a Nicolet 400D spectrometer and ^{1}H NMR spectra were recorded in DMSO with TMS as internal standard on a Bruker spectrometer at 400 MHz. Absorption spectra were recorded on a perkin elmer spectroscopy lambda EZ210 spectrophotometer in various solvents. The thermal stability of all the dyes synthesized in the present study was assessed on a DuPont 951 thermal analyzer in air at a heating rate 80°C min.

General procedure for synthesis of benzoxazole derivatives

Equivalent quantity from 3-ethyl-2-methylbenzo[d]oxazol-3-ium and aldehydes in round bottom, added 0.1 ml diethyl amine to the mixture was heated to reflux in ethanol (10 ml) for 3 h. kept the reaction in the room temperature. The solid was collected washed and recrystallized by ethanol (scheme 1). The derivatives dyes show in (Table 1).



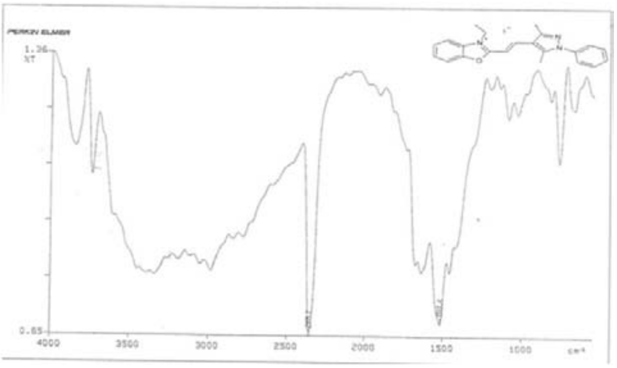


Figure 1: The IR (KBr) spectrum of compound 2.29.

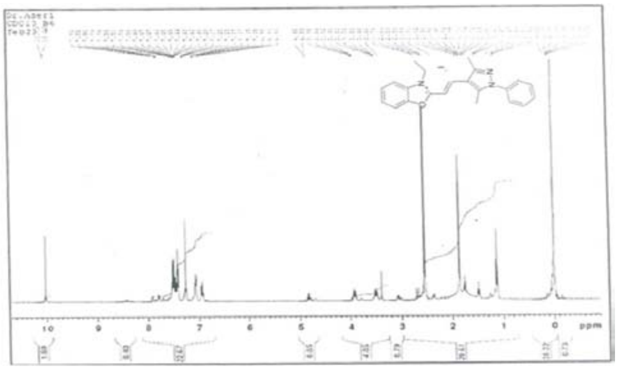


Figure 2: The ^{1}H-NMR (DMSO-d$_6$, TMS, δ-ppm) spectrum of compound 2.29.

Selected spectral data

Compound 2.29: IR (KBr) 1517 (C=N), 1618 (C=C), 3015 (C-H). IH NMR (300 MHz, DMSO-d$_6$ δ ppm) 7.91 (d, 2H), 7.76 (m, 3H), 7.47(m,4H), 7.12(s, 1H), 3.95(s, 6H), 2.71(s, 1H), 1.85(d, 3H).

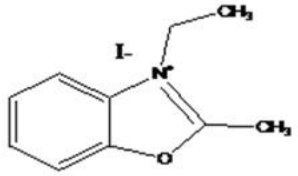
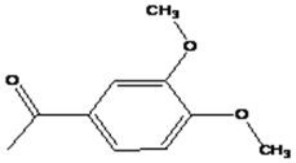
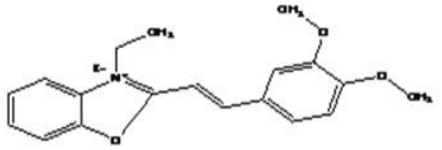
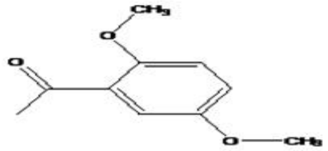
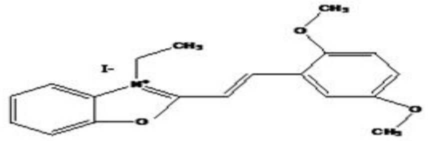
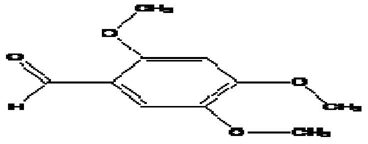
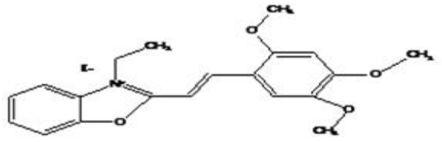
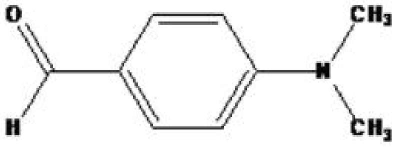
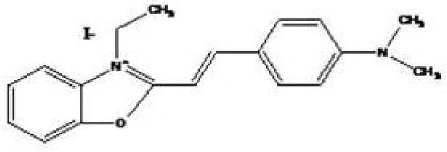
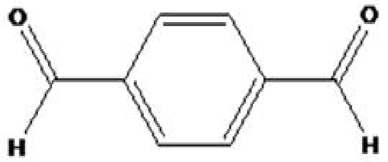
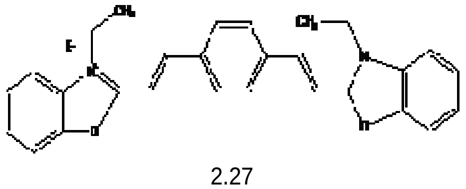
Thermal degradation

The photo stability of thin film of PMMA and the rate were monitored and the percentage of degradation upon heating was calculated, shows in (Table 4)

RESULTS AND DISCUSSION

The structures of newly described compounds were confirmed by FT-IR, ^{1}H-NMR, UV-Vis spectroscopic methods. Physical properties shown in (Table 2). UV-Vis absorption spectra of dyes were recorded in chloroform and acetonitrile. The absorption maxima (ʎ- max) of all dyes was found in range of 355 - 495 nm as shown in (Table 3) It was found that N$^+$ (Atoms with no lone pair electrons but have a partial positive charge) is an electron withdrawing group and auxochrome like I$^-$ and CH$_3$ electron releasing groups, this increases intensity of color .

Table 1: Chemical structures of the starting compounds and styryl dyes

Starting	Starting aldehyde	Styryl dye
 3-ethyl-2-methylbenzo[*d*]oxazol-3-ium iodide	 2.18 1-(3,4-dimethoxyphenyl)ethanone	 2.19 (*E*)-2-(3,4-dimethoxystyryl)-3-ethylbenzo[*d*]oxazol-3-ium iodide
	 2.20 1-(2,5-dimethoxyphenyl)ethanone	 2.21 (*E*)-2-(2,5-dimethoxystyryl)-3-ethylbenzo[*d*]oxazol-3-ium iodide
	 2.22 1-(2,4,5-trimethoxyphenyl)ethanone	 2.23 (*E*)-3-ethyl-2-(2,4,5-trimethoxystyryl)benzo[*d*]oxazol-3-ium iodide
	 2.24 4-(dimethylamino)benzaldehyde	 2.25 (*E*)-2-(4-(dimethylamino)styryl)-3-ethylbenzo[*d*]oxazol-3-ium iodide
	 2.26 terephthalaldehyde	 2.27 3-ethyl-2-((*E*)-4-((*E*)-2-(3-ethyl-2,3-dihydrobenzo[*d*]oxazol-2-yl)vinyl)styryl)benzo[*d*]oxazol-3-ium iodide

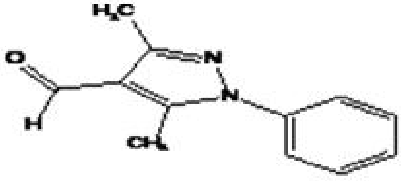
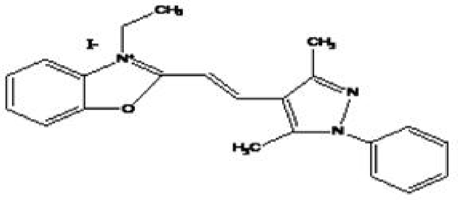
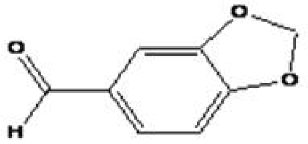
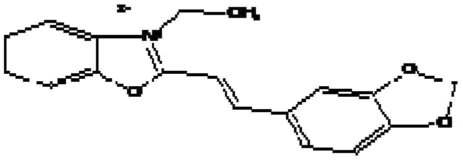
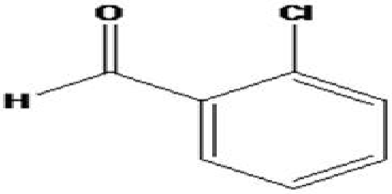
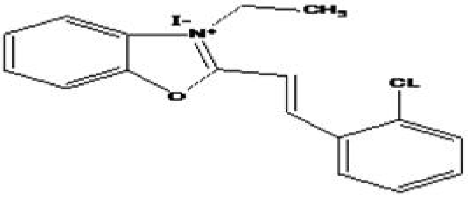
	 2.28 3,5-dimethyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde	 2.29 (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)-3-ethylbenzo[*d*]oxazol-3-ium iodide
	 2.30 Benzo[d][1,3]dioxole-5-carbaldehyde	 2.31 (*E*)-2-(2-(benzo[*d*][1,3]dioxol-5-yl)vinyl)-3-ethylbenzo[*d*]oxazol-3-ium iodide
	 2.32 2-Chlorobenzaldehyde	 2.33 (*E*)-3-ethyl-2-(2-methylstyryl)benzo[*d*]oxazol-3-ium iodide

Table 2: Yield, Melting points and color of styryl dyes

Dye no.	Dye name	Yield%	Melting points °C	Color
2.19	2-[2-(3,4-Dimethoxyphenyl)-vinyl]-3-ethyl-benzooxazol-3-ium;iodide	63.5	Oil	Brown
2.21	2-[2-(2,5-Dimethoxyphenyl)-styryl]-3-ethyl-benzooxazol-3-ium;iodide	50	101	Brown
2.23	3-Ethyl-2-[2-(2,4,5trimethoxyphenyl)-vinyl]-3-ethyl-benzooxazol-3-ium;iodide	77.9	91	Brown
2.25	2-[2-(4-Dimethylaminophenyl)-vinyl]-3-ethyl-benzooxazol-3-ium;iodide	89	76	Violet
2.27	2,2'-(1E,1E')-2,2'-(1,4-phenylene)bis-(ethene-2,1-diyl)Bis-(3-ethylbenzo[d]oxazol-3-ium)iodide	87	Oil	Violet
2.29	2-[2-(3,5-dimethyl-1-phenyl-1H-pyrazol-4-yl))-vinyl]-3-ethyl-benzooxazol-3-ium;iodide	69	Oil	Black
2.31	2-(2-benzo[1,3]dioxol-5-yl-vinyl)-3-ethyl-benzooxazol-3-ium;iodide	56	Oil	Brown
2.33	2-[2-(2-chlorophenyl)-vinyl]3-ethyl-benzooxazol-3-ium;iodide	77	160	Black

When the dyes were dissolved in Chloroform and Acetonitrile, the color of the dye solutions was different. This is the effect of the solvatochromism. The solvatochromic effect happened as a consequence of polarity of the solvent used, influencing ʎ max to shift towards shorter or longer wavelengths depending on types of the interaction between the solvent and the dye molecule in its ground and excited states.(imp) Thus when a given dye was dissolved in Chloroform (less polar), poorer stabilization of the dye's excited electronic state brought about a higher energy gap between the ground and excited states of the dye molecules and a hypsochromic shift was observed, compared with Acetonitrile as show in (Table 3) and Figure 3-4.

Table 3: Photo-physical characteristics of the styryl dyes

Dye no.	ʎmax (nm) (3 (L mol-^{1} cm^{-}1))	
	Chloroform	Acetonitrile
2.19	360	355
2.21	355	350
2.23	470	450
2.25	515	495
2.27	360	355
2.29	370	360
2.31	365	355
2.33	365	355

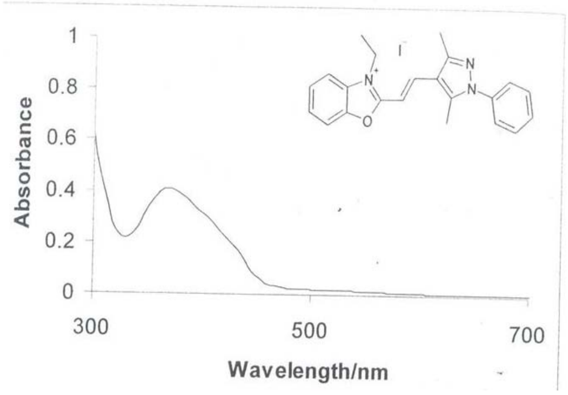


Figure 3: UV-Visible of compound [2.29] in chloroform

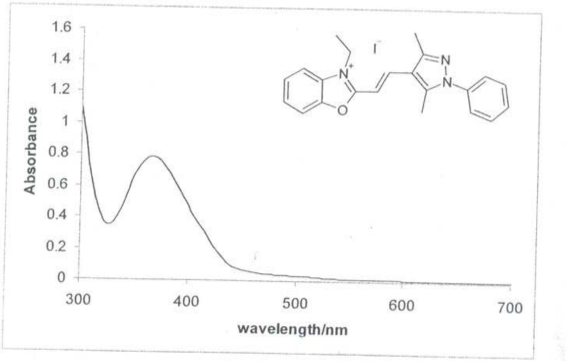


Figure 4: UV-Visible of compound [2.29] in acetonitrile

Thermal analysis plays an important role in the study of the structure and stability of dyes. The applicability of some dyes for special uses and determining the thermal stabilities of them are also very important.[23] The resistance to heat at elevated temperatures is one of the main properties required of dyes used in high temperature processes such as dyeing, printing and photocopying and in high technology areas such as lasers and electro optical devices. [24]

The results of the thermal analysis of these dyes can be used to obtain useful Information about their thermal stability and also to determine the temperature range in which they can be used without changes in their composition, color and properties.[25] From (Table-4) we found that dye [2.29] has less degradation so it is more stable than others because it was found that conjugation of N with alkyl group and another N conjugate with vinyl group in the other side Figure 5.

Table 4: Degradation of dyes at 80°C -Duration 3 hrs

Samples	Percentage of degradation %
2.19	17
2.21	4
2.23	10
2.25	23
2.27	36
2.29	0
2.31	27
2.33	35

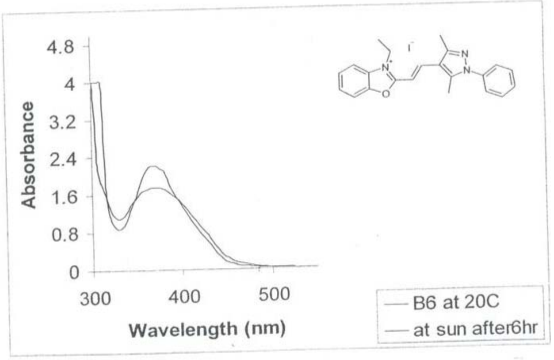


Figure 5: UV-Visible spectra of compound [2.29] in poly methyl methaacrylate film.

CONCLUSION

In this work, eight new oxazole derivatives dyes were synthesized. Characterization and the absorption ability of the dyes were studied. The results showed that the solvent effect on UV-Vis absorption spectra of the investigated oxazole dyes is very complex and strongly depends on the nature of the substituent's. The results on degradation indicate that these compounds have different photochemical and thermal reactivity's. The thermal analysis of oxazole dyes demonstrated that the stability of the dyes depends on the substituted groups and their position in the dye structures.

Acknowledgment: The author is thankful to king abdualziaz university (KSA), for providing research analytical facilities and fellowship, also thankful Hodeidah University (Yemen) for supporting and providing fellowship.

REFERENCES

1. Gromov SP, Alfimov MV, Supramolecular organic photochemistry of crownether-containing stearyl dyes, Russian Chemical Bulletin, 46, 1997, 611–636.
2. Fedorova OA, Fedorov YuV, Andryukhina EN, Gromov SP, Alfimov MV, Lapouyade R,Photochemical electrocyclization of theindolinylphenylethenesin olving a C N bond formation, Organic Letters, 5, 2003, 4533–4535.
3. Alfimov MV, Gromov SP, Stanislavskii OB, Ushakov EN, Fedorova OA ,Crown-containing styryl dyes. 8. Cation-dependent concerted [2 + 2]- autophotocycloaddition of photochromic 15-crown-5 ether betaines, Russian Chemical Bulletin, 42, 1993, 1385–1389.
4. Vedernikov AI, Kuz'mina LG, Sazonov SK, Lobova NA, Loginov PS, Churakov AV, Strelenko YuA, Howard JAK, Alfimov MV, Gromov SP, Styryl dyes.Synthesis and study of the solid state [2 + 2] autophotocycloaddition by NMRspectroscopy and X-ray diffraction, Russian Chemical Bulletin International Edition, 56, 2007, 1860–1883.
5. Gromov SP, Molecular meccano for light-sensitive and light-emitting nanosized systems based on unsaturated and macrocyclic compounds, Russian Chemical Bulletin International Edition, 57, 2008, 1325–1350.
6. Mees CEK, James TH, The theory of the photographic process, part 1[H. Tao Trans.]. Beijing: Science Press, 1979.

7. Hamer FM, The cyanine dyes and related compounds, New York: Interscience Publishers, 1964, 398.

8. Li Q, Lin GL, Peng BX, Li ZX, Synthesis, characterization and photographic Properties of some new styryl cyanine dyes, Dyes Pigments, 38, 1998, 211.

9. Duan X, Konami H, Okada S, Oikawa H, Matsuda H, Nakanishi H, Second-Order Hyperpolarizabilities of Stilbazolium Cations Studied by Semiempirical Calculation, J. Phys. Chem. 100, 1996, 17780.

10. Yeh VSC, Recent advances in the total syntheses of oxazole-containing natural products, Tetrahedron, 60, 2004, 11995–12042.

11. Riego E, Hernández D, Albericio F, Álvarez M, directely linked polyazoles:important moieties in natural product, Synthesis, 2005, 1907–1922.

12. Hughes R A, Moody C J, from amino acids to heteroaromatics--thiopeptide antibiotics, nature's heterocyclic peptides, Angew. Chem. Int. Ed, 46, 2007, 7930-54.

13. Whitesides GM, Matthias JP, Seto CT, Molecular self-assembly and nanochemistry: a chemical strategy for the synthesis of nanostructures, Science, 54, 1991, 1312.

14. Lehn JM, Toward Self-Organization and Complex Matter, Science, 295, 2002, 2400-2403.

15. Ikkala O, ten Brinke G, Functional Materials Based on Self-Assembly of Polymeric Supramolecules, Science, 295, 2002, 2407-2409.

16. Kolev T, Koleva BB, Stoyanov S, Spiteller M, Petkov I, The aggregation of the merocyanine dyes depending of the type of the counterions, Spectrochim. Acta: A, 70, 2008, 1087-96.

17. Abd El-Aal R M, Shindy H A , Koraiem A I M , Synthesis & electronic absorption spectra of some new penta & dimethine cyanine dyes, Heteroatom Chemistry, 8, 1997, 259-266

18. Koraiem A I M, Shindy H A ,Orientation in the synthesis & absorption spectra of 1H-pyrazolo(4,3-d) 1,3-oxazole methine cyanine dyes, Chem. Papers, 52,1998, 762-770.

19. Koraiem A I M, El-Maghraby M A, Khalafalla A K, Shindy H A, Studies on the synthesis & solvatochromic behaviour of mono & trimethine cyanines Dyes Pigments, 11, 1989, 47-63.

20. Masaund MS, Khalil EA, El-Sayed El Shereafy E, El-Enein SA, Thermal and electrical behaviour of nickel (II) and copper (II) complexes of 4-acetamidophenylazo-p-cresol (4-acetylamino-2-hydroxy-5-methyl azobenzene), J. Thermal Anal, 36, 1990, 1033.

21. Egli R, Color Chemistry The Desing and Synthesis of Organic Dyes and Pigments, ed. A.T. Peters, H.S. Freeman, Elsevier, London, 1991.

Source of Support: Nil, **Conflict of Interest:** None.