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*S.A. Varenichenko, A.V. Kovtun, O.K. Farat***NOVEL XANTHENE-LIKE DYES AS pH INDICATORS IN ACIDIC MEDIA****Ukrainian State University of Science and Technologies, Dnipro, Ukraine**

In this work, a previously unknown aldazine, N'-[4-((E)-{(2Z)-[(12-[(1E)-(dimethylamino)methylene]amino}amino}-2,3-dihydro-1H-benzo[b]xanthene-4-yl)methylene]hydrazono)methyl]-2,3-dihydro-1H-benzo[b]xanthene-12-yl]-N,N-dimethylimidoforamide was synthesized by reacting the corresponding aldehyde with hydrazine hydrate. The spectral characteristics of the two azomethine dyes were studied: N,N-dimethyl-N'-{4-[(E)-(phenylimino)methyl]-2,3-dihydro-1H-xanthen-9-yl}imidoforamide and N'-[4-((E)-{(2Z)-[(12-[(1E)-(dimethylamino)methylene]amino}-2,3-dihydro-1H-benzo[b]xanthen-4-yl)methylene]hydrazono)methyl]-2,3-dihydro-1H-benzo[b]xanthen-12-yl]-N,N-dimethylimidoforamide. Both dyes exhibit a bathochromic shift in their absorption maxima at lower pH levels. The observed deepening of the color can be attributed to the protonation of the azomethine nitrogen atom and the change in the hybridization of the orbital that carries the unpaired electron pair of the azomethine nitrogen atom, switching from the sp² orbital to the unhybridized p-orbital, which is capable of conjugation with the xanthene fragment. The color of N,N-dimethyl-N'-{4-[(E)-(phenylimino)methyl]-2,3-dihydro-1H-xanthen-9-yl}imidoforamide changes from yellow to red as the pH decreases, while the color of N'-[4-((E)-{(2Z)-[(12-[(1E)-(dimethylamino)methylene]amino}-2,3-dihydro-1H-benzo[b]xanthen-4-yl)methylene]hydrazono)methyl]-2,3-dihydro-1H-benzo[b]xanthen-12-yl]-N,N-dimethylimidoforamide shifts from red to blue. The synthesized dyes have potential as pH indicators in acidic environments. These dyes demonstrate a color change not only in response to pH reduction but also in the presence of transition metal salts.

Keywords: xanthene-like dyes, pH indicator, azomethine, azine, acidic media.**DOI:** 10.32434/0321-4095-2024-155-4-4-9**Introduction**

Xanthene-like dyes are employed in a multitude of scientific and industrial applications [1–3], including as dyes [4,5], fluorophores [6], photonic [7], optic sensors [8], and so forth. In all the aforementioned xanthene dyes, the 9-position remains either unsubstituted or substituted with a non-functionalized group, which restricts the potential for further transformations. Previously, we devised a novel methodology for synthesizing a xanthene backbone by rearranging the 1,3-benz(naphth)oxazine and 1,3-benzodioxine cycles in the presence of the Vilsmeier-Haack reagent [9,10]. The newly developed reactions facilitate the synthesis of xanthene dyes in

satisfactory yields, with the additional benefit of enabling the introduction of functional groups at the 9-position, thereby markedly enhancing their chemical and optical properties. This provided a significant impetus for the development of a multitude of distinct dyes based on synthesized xanthene building-blocks [11–13]. In this work, we present the synthesis and study of the optical properties of xanthene-like dyes with amidine fragment that can be utilized as pH indicators in acidic environments.

Experimental

Unless otherwise stated, all reagents of analytical grade were purchased from commercial suppliers and used without any further purification. The ¹H NMR

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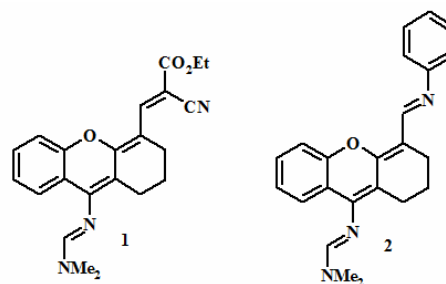
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and ^{13}C NMR spectra were performed on a Bruker Avance II 400 spectrometer (400.13 MHz and 100.62 MHz for ^1H and ^{13}C , respectively) in $\text{DMSO-}d_6/\text{CCl}_4$ using residual solvent peak as internal standard. The UV-vis spectra were measured by a Hitachi U-1900 spectrophotometer using quartz cuvette with optical path length 10 mm, the baseline was corrected relative to the solvent absorption. The FAB mass spectrum was recorded on a VG7070 spectrometer. Desorption of the ions from the solution of the samples in 3-mercapto-1,2-propanediol was realized with a beam of argon atoms with energy 8 keV. Elemental analysis was performed on a LECO CHN-900 instrument. Melting points were carried out using an Electrothermal 9100 Digital Melting Point apparatus and were uncorrected. The control of reactions and the purity of the obtained compounds were monitored by TLC on Merck Silica gel 60 F-254 plates with 10:1, v/v $\text{CHCl}_3/\text{MeOH}$ as eluent. Compound 3 was synthesized according to the literature method [6].

N' - [4 - ((E) - { (2 Z) - [(1 2 - { [(1 E) - (dimethylamino)methylene]amino)-2,3-dihydro-1*H*-benzo[*b*]xanthen-4-yl)methylene]hydrazono}methyl)-2,3-dihydro-1*H*-benzo[*b*]xanthen-12-yl) - N,N -dimethylimidofornamide (4). The aldehyde 3 (0.1 g, 0.15 mmol) was dissolved in boiling *i*-PrOH (5 mL), after cool to room temperature 0.015 mL (0.3 mmol) of hydrazine hydrate were added. The reaction mixture was left off at room temperature for 24 h. The precipitate formed was filtered off and purified by recrystallization from MeCN. Yield 0.08 g (82%), reddish-brown powder, mp. 250–252°C (decomp.). ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6/\text{CCl}_4$), δ , ppm: 8.80 (2H, s, 2CH), 8.00 (2H, s, 2CH), 7.87 (2H, d, $^3J=8.1$ Hz, Ar), 7.75 (2H, d, $^3J=8.0$ Hz, Ar), 7.55 (2H, s, Ar), 7.45 (2H, s, Ar), 7.37 (2H, t, $^3J=7.1$ Hz, Ar), 7.30 (2H, t, $^3J=7.1$ Hz, Ar), 3.15 (6H, s, 2Me), 3.08 (6H, s, 2Me), 2.51 (4H, t, $^3J=6.1$ Hz, 2CH₂), 2.37 (4H, t, $^3J=5.9$ Hz, 2CH₂), 1.56–1.65 (4H, m, 2CH₂). ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6/\text{CCl}_4$), δ , ppm: 161.2, 158.1, 152.2, 148.1, 145.6, 133.9, 132.2, 131.5, 128.4, 126.4, 124.4, 121.5, 120.3, 118.0, 117.0, 107.2, 36.1, 33.2, 31.2, 27.0, 18.3. Mass spectrum (FAB), m/z (I_{rel} , %): 661 [$\text{M}+\text{H}$]⁺ (100). Found, %: C 76.47; H 6.16; N 12.83. $\text{C}_{42}\text{H}_{40}\text{N}_6\text{O}_2$. Calculated, %: C 76.34; H 6.10; N 12.72

Results and discussion

In previous studies [11, 12], we synthesized dyes 1 and 2 (Scheme 1) based on the xanthene framework. When the pH of the solution of compound 1 is reduced, a gypsochrome shift of the absorption maximum from 531 nm to 478 nm occurs [14].



Scheme 1

The reaction of compound 2 to protonic acids was found to be the opposite. Consequently, when compound 2 is treated with trifluoroacetic acid in MeCN, a bathochromic shift of the absorption maximum is observed, from 431 nm to 504 nm. This is accompanied by a color change from yellow to red (Figs. 1 and 2).

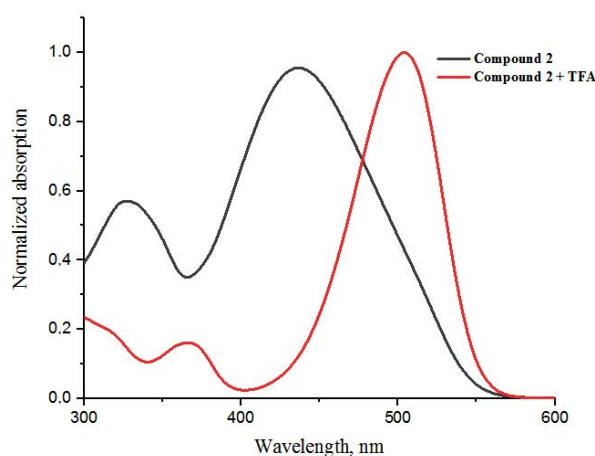


Fig. 1. The absorption spectra of compound 2 in neutral and acidic media

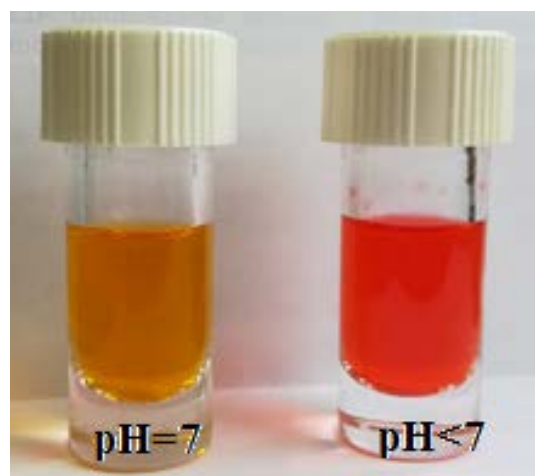


Fig. 2. The photograph depicts solutions of compound 2 in MeCN with and without $\text{CF}_3\text{CO}_2\text{H}$

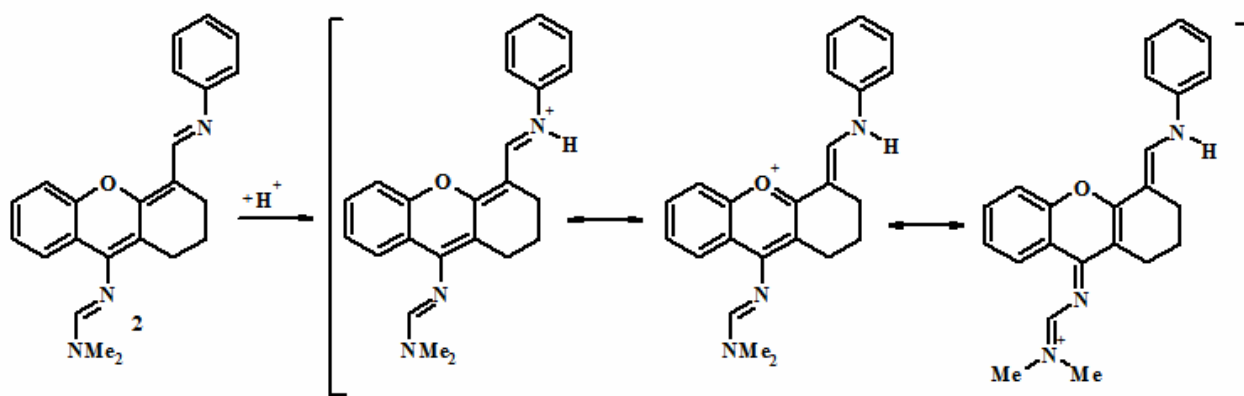
In the case of compound 1, it was found that the protonation reaction occurs at the dimethylamidine fragment. In the case of the Schiff bases, protonation is likely to occur at the nitrogen atom of the azomethine group, since only protonation at this atom can lead to absorption in the longer-wavelength region of the spectrum. This phenomenon can be attributed to the potential for a protonation reaction on the unpaired electron pair of the azomethine nitrogen atom, resulting in charge transfer to the oxygen atom and the amidine fragment (Scheme 2). This reaction is more favorable than protonation on the amidine fragment.

The intensification of the color of compound 2 upon the addition of acid is attributed to the protonation of the unshared pair of electrons of the azomethine nitrogen atom, which results in the transfer of a positive charge to the oxygen atom. This process leads to a transformation in the hybridization of the orbital

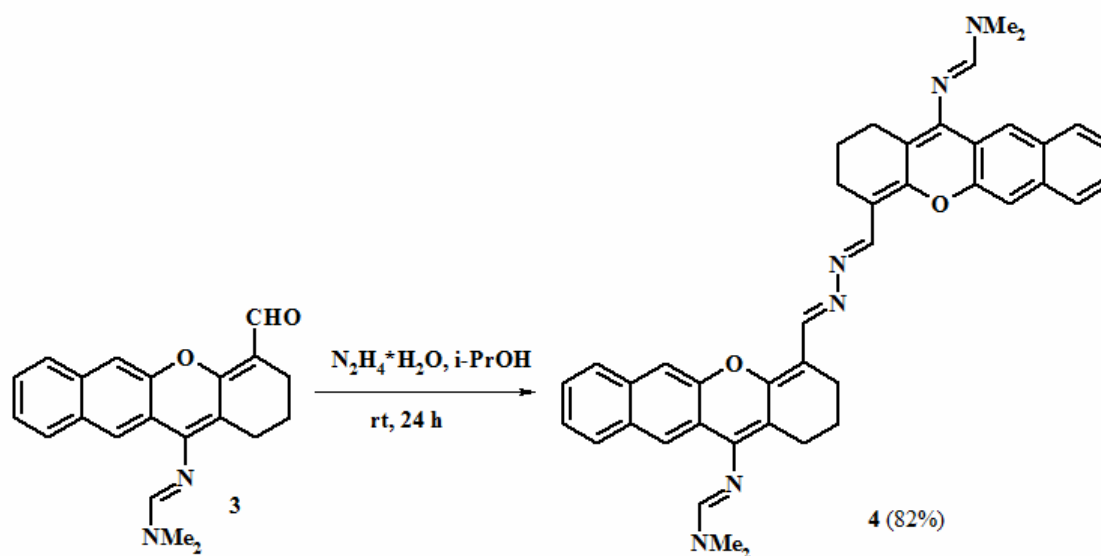
carrying the unshared pair of electrons, shifting from the sp^2 orbital to the unhybridized p -orbital. This latter orbital is capable of conjugation with the xanthene fragment. The change in the hybridization of the orbital on which the unshared pair of electrons of the azomethine atom of the nitrogen atom is located is responsible for the bathochromic shift of the absorption maximum upon acidification of compound 2 (Scheme 2).

Continuing our investigation, we proceeded to synthesize aldazine 4 by reacting aldehyde 3 with hydrazine hydrate (Scheme 3).

Additionally, compound 4 demonstrated sensitivity to changes in pH. Absorption spectra for compound 4 were recorded in acetonitrile solution with a concentration of $5 \cdot 10^{-6}$ mol/L. The absorbance maximum for compound 4 was observed at 508 nm. The addition of one equivalent of TFA ($\text{CF}_3\text{CO}_2\text{H}$)



Scheme 2



Scheme 3

resulted in a bathochromic shift of the absorbance maximum to 615 nm. The addition of a second equivalent of TFA shifts the absorption maximum to shorter wavelengths, up to 570 nm (Figs. 3 and 4). The color subsequently undergoes a transformation, transitioning from red to blue. Further addition of acid has almost no effect on the maximum absorption of compound 4. Neutralizing the acidic solution of compound 4 to pH 8 with Et_3N restores the absorption spectrum of the neutral molecule. In addition to determining the absorption maxima of compound 4 in relation to the acidity of the medium, the absorption coefficients and the optical energy gap of the HOMO-LUMO transition were also determined. The optical properties of compound 4, as a function of the amount of TFA, are summarized in Table.

The change in the maximum absorption of compound 4 upon addition of one equivalent of TFA is caused by protonation of the nitrogen atom of the azomethine group with delocalization of the positive charge to the pyran cycle, as observed in the case of compound 2. The addition of the second equivalent of TFA results in a shift of the absorption maximum to 570 nm, which is associated with the protonation of the second nitrogen atom of the azomethine group and the conditional separation of two symmetric chromoform systems.

Conclusions

It was shown that *N,N*-dimethyl-*N'*-{4-[(*E*)-(phenylimino)methyl]-2,3-dihydro-1*H*-xanthen-9-yl}imidoforamide and *N'*-[4-((*E*)-{(2*Z*)-[(1*E*)-(dimethylamino)methylene]amino}-2,3-dihydro-1*H*-benzo[*b*]xanthen-4-yl)methylene]hydrazono}methyl]-2,3-dihydro-1*H*-benzo[*b*]xanthen-12-yl]-*N,N*-dimethylimidoforamide bathochromically shift the absorbance maxima at lower pH. The observed intensification of color can be attributed to the protonation of the azomethine nitrogen atom and a change in the hybridization of the orbital carrying the unpaired electron pair of the azomethine nitrogen atom, which transitions from the sp^2 orbital to the

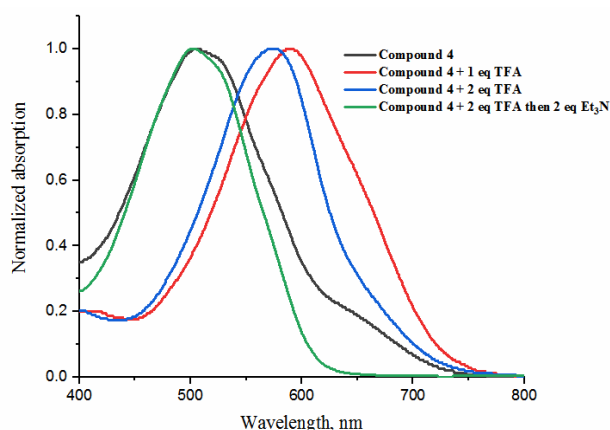


Fig. 3. The absorption spectra of compound 4 in neutral and acidic media



Fig. 4. The photograph depicts solutions of compound 4 in MeCN with and without $\text{CF}_3\text{CO}_2\text{H}$

unhybridized *p*-orbital. This latter orbital is capable of conjugation with the xanthen fragment. The synthesized dyes have potential utility as pH indicators for acidic media.

Acknowledgments and funding

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Spectral characteristics* of compound 4 in MeCN solution with the addition of TFA

TFA equivalent, eq.	$\lambda_{\text{Abs-max}}$, nm	$\lambda_{\text{onset}}^{\text{abs}}$, nm**	E_g^{opt} , eV***	$\epsilon_{\text{max}} \cdot 10^4$, $\text{M}^{-1} \cdot \text{cm}^{-1}$
0	508	615	2.02	3.68
1	615	732	1.72	4.12
2	570	630	1.97	4.20
2+2 eq. Et_3N	508	—	—	—

Notes: * – absorption maxima ($\lambda_{\text{Abs-max}}$) and extinction coefficients (ϵ_{max}) were determined experimentally; ** – the red line of self-absorption; *** – E_g^{opt} is the optical energy gap of the HOMO-LUMO transition calculated on the basis of the wavelength of the red limit of intrinsic absorption [15].

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НОВІ КСАНТЕНОПОДІБНІ БАРВНИКИ ЯК рН-ІНДИКАТОРИ НА КИСЛЕ СЕРЕДОВИЩЕ

С.А. Варениченко, А.В. Ковтун, О.К. Фарат

У цій роботі раніше невідомий альдазин, N'-[4-((E)-{(2Z)-[(12-[(1E)-(диметиламіно)метил]аміно]-2,3-дигідро-1H-бензо[b]ксантен-4-іл)метил]гідразоно)метил]-2,3-дигідро-1H-бензо[b]ксантен-12-іл]-N,N-диметилімідоформамід, одержано реакцією відповідного альдегіду з гідрозин гідратом. Досліджено спектральні характеристики двох азометинових барвників: N,N-диметил-N'-{4-[(E)-(феніліміно)метил]-2,3-дигідро-1H-ксантен-9-іл}імідоформаміду і N'-[4-((E)-{(2Z)-[(12-[(1E)-(диметиламіно)метил]аміно]-2,3-дигідро-1H-бензо[b]ксантен-4-іл)метил]гідразоно)метил]-2,3-дигідро-1H-бензо[b]ксантен-12-іл]-N,N-диметилімідоформаміду. Обидва барвники батохромно змінюють максимуми поглинання при зниженні рН. Поглиблення забарвлення, яке спостерігається, можна пояснити протонуванням азометинового атома азоту зі зміною гібридизації орбіталі з неспареною парою електронів азометинового атома нітрогену з sp² на негібридизовану р-орбіталь, яка здатна до кон'югації з ксантеновим фрагментом. Колір N,N-диметил-N'-{4-[(E)-(феніліміно)метил]-2,3-дигідро-1H-ксантен-9-іл}імідоформаміду змінюється з жовтого на червоний при зниженні рН розчину, а N'-[4-((E)-{(2Z)-[(12-[(1E)-(диметиламіно)метил]аміно]-2,3-дигідро-1H-бензо[b]ксантен-4-іл)метил]гідразоно)метил]-2,3-дигідро-1H-бензо[b]ксантен-12-іл]-N,N-диметилімідоформамід в аналогічних умовах змінює колір розчину з червоного на синій. Згадані барвники потенційно перспективні як рН-індикатори на кисле середовище. Вони також змінюють колір не лише при зниженні рН розчину, але й при додаванні солей перехідних металів.

Ключові слова: ксантеноподібні барвники, рН-індикатор, амідин, азометин, азин, кисле середовище.

NOVEL XANTHENE-LIKE DYES AS pH INDICATORS IN ACIDIC MEDIA

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