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A NEW XANTHENE CHROMOPHORE: SYNTHESIS AND SPECTRAL PROPERTIES

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The reaction of N'-(4-formyl-2,3-dihydro-1H-xanthen-9-yl)-N,N-dimethylimidoformamide with 1-(4-nitrophenyl)butane-1,3-dione under prolonged reflux in acetic anhydride was investigated. The reaction afforded N-acetyl-N-{4-[(1E,4Z)-5-hydroxy-5-(4-nitrophenyl)-3-oxopenta-1,4-dien-1-yl]-2,3-dihydro-1H-xanthen-9-yl}acetamide as the major product. The optical properties of the synthesized compound were evaluated in solvents of different polarity to assess the influence of the solvent environment on its photophysical behavior. The absorption and fluorescence maxima exhibited only a weak dependence on solvent polarity and were located at approximately 500 and 650 nm, respectively. The synthesized dye showed low fluorescence quantum yields in all investigated solvents, indicating limited emissive efficiency. The highest molar absorption coefficient was observed in water, reaching 41500 $M^{-1}\cdot cm^{-1}$, while the optical band gap was the lowest in the same solvent, amounting to 1.98 eV. These results provide new insights into the relationship between molecular structure and photophysical properties of xanthene derivatives and may contribute to the development of fluorescent organic dyes with improved optical characteristics for potential applications in sensing, imaging, and other photonic technologies.

Keywords: xanthene, fluorophore, Stokes shift, Knoevenagel reaction, quantum yield, imide.

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Introduction

The prevailing focus in contemporary organic synthesis is on the development of efficient and selective methodologies for the preparation of functional compounds that exhibit valuable physicochemical and spectral properties. The Knoevenagel reaction is a notable method for the formation of a carbon-carbon bond via the condensation of aldehydes or ketones with compounds containing an active methylene group [1]. The reaction under discussion has been found to be highly efficient, and the execution of the process is relatively simple. Furthermore, a wide range of substrates can be used. These properties have led to the reaction finding widespread application in the synthesis of a variety of heterocyclic and polyfunctional organic compounds [2,3]. One of the promising applications of the Knoevenagel reaction is the synthesis of xanthene dyes – an important class of organic fluorophores characterized by high absorption and fluorescence intensities, good photostability and

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the potential for fine structural modification [4]. Xanthene derivatives are widely used as fluorescent labels [5], sensors [6], components of pH indicators [7], analytical reagents [8], and in biomedical diagnostics and bioimaging [9]. Their unique optical properties are determined by the structural features of the chromophore system, which can be specifically modified by the introduction of various electron-donating and electron-withdrawing substituents [10]. Thus, the Knoevenagel reaction is not only a classical method of organic synthesis, but also an important platform for the preparation of new xanthene dye derivatives with improved photophysical properties and a wide range of practical applications. An examination of the potential of this reaction in the synthesis of xanthene systems is of considerable scientific and applied interest.

Experimental

Unless otherwise stated, all reagents of analytical grade were purchased from commercial suppliers and used without any further purification. ^{1}H and ^{13}C NMR spectra were performed on a Bruker Avance II 400 spectrometer (400.13 MHz and 100.62 MHz for ^{1}H and ^{13}C, respectively) in DMSO-d_6 using residual solvent peak as a reference. The FAB mass spectrum was recorded on a VG7070 spectrometer. Desorption of the ions from the solution of the sample in 3-nitrobenzyl alcohol was realized with a beam of argon atoms with energy 8 keV. ESI-MS spectrum was acquired in positive or negative modes on a Waters Quatro Micro API Mass Spectrometer. Spectrum was recorded at 120^{0}C with energy 3 kV on capillary. Absorption spectra were recorded in 1-cm quartz cells at 25^{0}C using a PerkinElmer Lambda 35 UV–Vis spectrophotometer. Absorption maxima were determined with an accuracy of ±0.5 nm. The spectrophotometer UV-2401 PC (Shimadzu, Japan) was used for other compounds. To measure the extinction coefficients, each dye (7–10 mg) was dissolved in 50 cm^3 of the solvent. The resulting solution was diluted 25–50 times and the absorption spectra were recorded in 5 cm quartz cuvettes. The extinction coefficients were calculated according to the Beer–Lambert law. Measurements were performed three to four times and the obtained data were averaged. The fluorescence measurements for all compounds were performed in 1-cm standard quartz cells at 25^{0}C using a Varian Cary Eclipse spectrofluorometer. The emission spectra were corrected for wavelength-dependent instrument sensitivity. Emission maxima were determined with an accuracy of ±1.0 nm. Quantum yields (Φ_F) were determined using Fluorescein in 0.1 N NaOH [11]. Elemental analysis was performed on a LECO CHN-900 instrument. Melting points were determined using an Electrothermal 9100 Digital Melting Point apparatus and were uncorrected.

Synthesis

N-acetyl-N-{4-[(1E,4Z)-5-hydroxy-5-(4-nitrophenyl)-3-oxopenta-1,4-dien-1-yl]-2,3-dihydro-1H-xanthen-9-yl}acetamide (**2**). 1-(4-Nitrophenyl)butane-1,3-dione (0.37 g, 1.77 mmol) was dissolved in 5 mL acetic anhydride. To the resulting solution, aldehyde **1** (0.5 g, 1.77 mmol) was added and stirred at reflux for 10 h. After cooling, the solvent was then evaporated using a rotary evaporator, and the residue was recrystallized from acetonitrile. Yield 0.74 g (84%), red powder, mp 203–204^{0}C. ^{1}H NMR, δ, ppm (*J, Hz*): 8.35 (2H, d, ^{3}J=8.8, H Ar), 8.22 (2H, d, ^{3}J=8.8, H Ar), 8.12 (1H, d, ^{3}J=15.7, H alkene), 7.38 (1H, t, ^{3}J=8.3, H Ar), 7.27 (1H, d, ^{3}J=7.8, H Ar), 7.09–7.15 (2H, m, H Ar), 6.83 (1H, s, H alkene), 6.33 (1H, d, ^{3}J=15.7, H alkene), 2.42–2.50 (2H, m, CH_2), 2.32–2.40 (2H, m, CH_2), 2.33 (6H, s, $2CH_3$), 1.68–1.75 (2H, m, CH_2). ^{13}C NMR, δ=183.7, 182.2, 171.5, 152.4, 151.0, 149.5, 141.0, 134.8, 131.0, 130.7, 129.3, 128.4, 124.0, 123.9, 122.2, 120.5, 119.5, 115.4, 113.2, 98.8, 25.5, 24.3, 23.7, 19.3. MS (ESI): m/z (I_{rel}, %)= 499 $[M-1]^-$ (100). MS (FAB): m/z (I_{rel}, %)=501 $[M+1]^+$ (100). Found, %: C 67.27; H 4.91; N 5.65. $C_{28}H_{24}N_2O_7$. Calculated, %: C 67.19; H 4.83; N 5.60.

Results and discussion

As demonstrated in previous studies, the reaction of xanthene **1** and analogous compounds with various CH acids in acetic anhydride results in the formation of corresponding dyes. The specific conditions of the reaction influence the outcome, with the amidine fragment being retained at room temperature [12] or replaced by an acetamide group at elevated temperatures [13]. The present paper presents the results of the reaction of xanthene **1** with 1-(4-nitrophenyl)butane-1,3-dione by prolonged boiling in acetic anhydride. The product of this reaction is dye **2** (Scheme). The structure of this compound was determined based on an analysis of ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry data. It is interesting to note that the Knoevenagel reaction proceeds with this CH acid not via the C-2 atom, as expected, but via the C-4 atom, as indicated by the appearance of two signals in the form of doublets at 8.12 ppm and 6.83 ppm. The spin-spin interaction constant of these doublets is ^{3}J=15.7, indicating a trans configuration for this fragment. Due to keto-enolic tautomerism, the C-4 atom in dye **2** undergoes complete enolization under NMR recording conditions. It is the contention of the present study that the subject fragment in DMSO is of a *Z*-configuration. This is due to the fact that, in

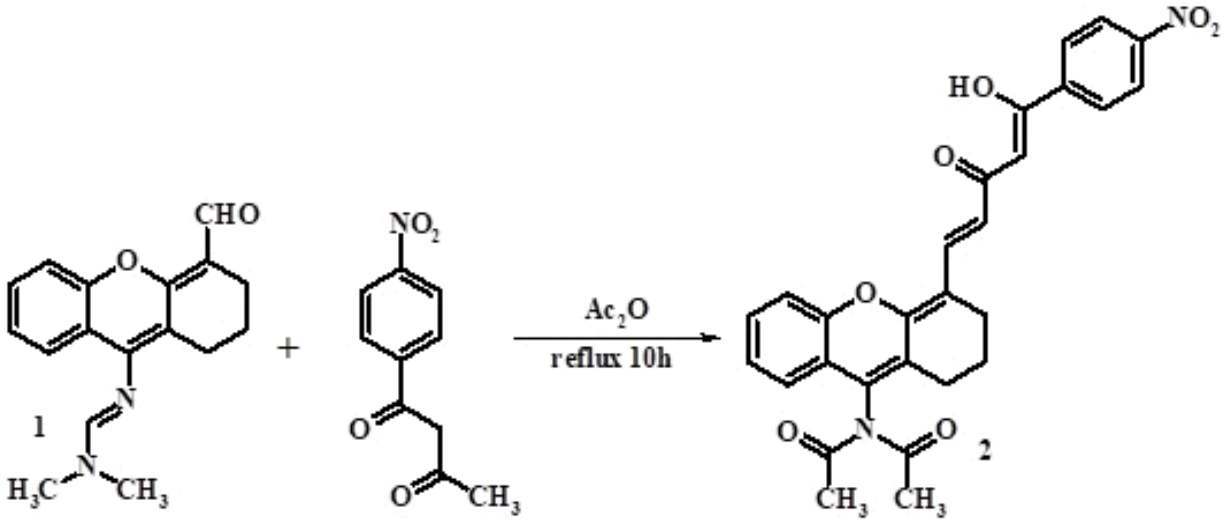
this case, an intramolecular hydrogen bond is able to form, resulting in a six-membered ring. Another unexpected structural feature of dye **2** is the formation of an imide instead of an amide, which had not been previously reported. The molecular weight of the substance under investigation is confirmed by mass spectrometry data obtained using various ionisation methods. According to the ESI-MS data, compound **2** forms a peak at a mass of 499 $[M-1]^-$ with 100% intensity in the negative mode, and does not form a peak at 501 $[M+1]^+$ at all. This is consistent with the acidic properties of this compound. A peak at 501 $[M+1]^+$ was obtained during analysis using FAB ionization.

Spectral properties

Absorption and emission spectra were recorded for the resulting dye **2** in solvents of varying polarity (Table, Figure). The absorption and emission spectra of xanthene **2** are largely independent of solvent polarity and exhibit an absorption maximum at approximately 500 nm and an emission maximum at 650 nm, with low quantum yields in the solvents studied. No fluorescence was detected in acetonitrile and water, likely due to the dye's very low fluorescence intensity in these solvents. Xanthene **2** is distinguished by its notably elevated Stokes shifts, which approximate 150 nm. The extinction coefficient has been observed to have a maximum value of approximately 41500 $M^{-1}\cdot cm^{-1}$ in water, whilst the minimum has been recorded in toluene, with a value of 30300 $M^{-1}\cdot cm^{-1}$. In the other solvents, the value is approximately equivalent, measuring at 38500 $M^{-1}\cdot cm^{-1}$. The smallest energy gap, calculated based on the red band of intrinsic absorption, is observed in water and amounts to 1.98 eV.

Conclusions

Thus, the synthesis of N-acetyl-N-{4-[(1E,4Z)-5-hydroxy-5-(4-nitrophenyl)-3-oxopenta-1,4-dien-1-

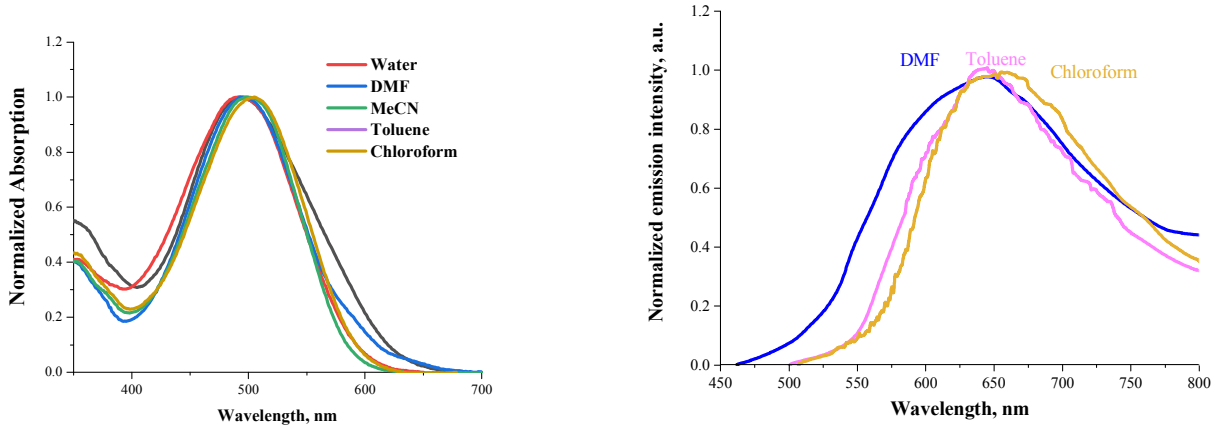


Scheme. Synthesis of dye **2**

The spectral properties[a] of dye 2

Solvent	Solvent polarity, $E_T^{N\,b}$	λ_{max} (Abs), nm	λ_{max} (Em)[c], nm	$\varepsilon_{max}\cdot 10^4$, $M^{-1}\cdot cm^{-1}$	$E_g^{opt\,d}$, eV	Φ_F, %	Stokes shift, nm/cm
PhMe	0.099	500	643	3.03	2.09	1.16	143/4450
$CHCl_3$	0.259	505	655	3.87	2.08	0.64	150/4535
DMF	0.386	492	645	3.85	2.08	0.07	153/4820
MeCN	0.460	496	n.d.	3.85	2.07	–	–
H_2O	1.000	494	n.d.	4.15	1.98	–	–

Notes: [a] – absorption ($\lambda_{Abs\text{-}max}$), emission ($\lambda_{Em\text{-}max}$) maxima and extinction coefficients (ε_{max}) were determined experimentally; [b] – normalized values of solvent polarity were taken from Ref. [14]; [c] – excitation wavelength (λ_{exc}) was 460 nm; [d] – 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].



a b

Normalized absorption (a) and emission (b) spectra of dye **2** in different organic solvents

yl]-2,3-dihydro-1H-xanthen-9-yl}acetamide via the reaction of N'-(4-formyl-2,3-dihydro-1H-xanthen-9-yl)-N,N-dimethylimidoformamide with 1-(4-nitrophenyl)butane-1,3-dione in acetic anhydride was demonstrated. The obtained xanthene derivative exhibits relatively solvent-independent absorption and emission properties, with maxima located in the visible spectral region. The dye is characterized by low fluorescence quantum yields; however, it possesses a high molar absorption coefficient, reaching 41,500 $M^{-1}{\cdot}cm^{-1}$ in water. The lowest optical band gap value (1.98 eV) observed in aqueous solution indicates the influence of the solvent environment on the electronic properties of the dye. The obtained results expand the understanding of the structure–photophysical property relationship in xanthene derivatives and highlight their potential as functional organic chromophores.

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НОВИЙ КСАНТЕНОВИЙ ХРОМОФОР: СИНТЕЗ ТА СПЕКТРАЛЬНІ ВЛАСТИВОСТІ

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Досліджено реакцію N'-(4-форміл-2,3-дигідро-1H-ксантен-9-іл)-N,N-диметилімідоформаміду з 1-(4-нітрофеніл)бутан-1,3-діоном при тривалому кип'ятінні в оцтовому ангідриді. В результаті реакції основним продуктом був N-ацетил-N-{4-[(1E,4Z)-5-гідрокси-5-(4-нітрофеніл)-3-оксопента-1,4-дієн-1-іл]-2,3-дигідро-1H-ксантен-9-іл}ацетамід. Оптичні властивості синтезованої сполуки оцінювали в розчинниках різної полярності для оцінювання впливу середовища розчинника на її фотофізичну поведінку. Максимуми поглинання та флуоресценції демонстрували лише слабку залежність від полярності розчинника та знаходилися приблизно при 500 та 650 нм, відповідно. Синтезований барвник показав низькі квантові виходи флуоресценції у всіх досліджуваних розчинниках, що вказує на обмежену емісійну ефективність. Найвищий молярний коефіцієнт поглинання спостерігався у воді, досягаючи 41500 $M^{-1}{\cdot}см^{-1}$, тоді як оптична ширина забороненої зони була найнижчою в тому ж розчиннику і становила 1,98 еВ. Ці результати дають нове розуміння взаємозв'язку між молекулярною структурою та фотофізичними властивостями похідних ксантену та можуть сприяти розробленню флуоресцентних органічних барвників з покращеними оптичними характеристиками для потенційного застосування в сенсорних, візуалізаційних та інших фотонних технологіях.

Ключові слова: ксантен, флуорофор, Стоксів зсув, реакція Кневенагеля, квантовий вихід, імід.

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