

**SPECTRAL PROPERTIES OF DYES ARE ON BASIS OF
HEXAHYDROBICYCLOPENTA[*b*, *e*]PYRIDINES**

Uman Pavlo Tychyna State Pedagogical University, Ukraine

Viktoriia F. Valiuk

Vvalyuk@mail.ru

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Introduction

Derivatives of dicyclopentanopyridines are compounds of condensed structure with a cross-conjugated system of multiple connections, where the pyridine core is a π -acceptor of electron density. Their electronic structure indicates that they can significantly change the parameters of fluorescence depending on the nature of the environment (1). The passage to the excited state should lead to a substantial redistribution of electron density in the molecule increasing its polarity. Given the high mechanical stiffness of the molecules of these derivatives, they should expect a high enough quantum yield of fluorescence in solutions. Meanwhile, by this time spectral and physico-chemical researches in a number dicyclopentano [*b*, *e*] pyridines have not been carried out.

Objects and methods.

The absorption spectra were measured on a spectrophotometer HITACHI U-3210 (Japan). The absorption spectra were also registered on a spectrometer Specord 40 at 20 °C. The spectra and fluorescence quantum outputs (φ_f) defined on a spektrofluorimeter HITACHI F-4010 fluorescein solution in relation to carbonate buffer ($\varphi_f = 0,85$) (2) and solution of hydrosulphate quinine in 0.05 M of sulfuric acid ($\varphi_f = 0.55$). Measurements were carried out in isothermal cell at 20 + 0.1 °C. Fluorescence spectra and fluorescence excitation were recorded under excitation accordingly at maximum absorption or emission bands. Fluorimetric studies were performed in parallel with spectrophotometric ones on a spektrofluorimeter Cary Eclipse (Varian, Australia) or HITACHI F-4010 (Japan) at 20 °C in standard 1 cm quartz cuvette.

Results and discussion.

Absorption and fluorescence properties of compounds 2.1-2.19 were studied in several solvents of different polarity and protonodonor ability: octane, hexane, toluene, acetonitrile, DMF and in methanol. As expected, absorption and emission spectra of the investigated dicyclopentanopyridines were well structured. In the spectra of absorption and emission there was a change of relative intensity of individual vibrational components (Fig. 1.1). According to this, we evaluated position of individual bands in electronic spectra of compounds 2.1-2.19 not by their formal position of the maxima, but by calculating the center of gravity zone. Fig. 1.1 shows absorption and emission spectra of 2.1 compound in hexane with calculated their secondary derivatives (taken with a "minus" for the maximum line of the original and derivative spectra to be preserved). Provisions of the second peak in the spectra usually coincide well with the gravity center of the absorption or emission.

The absorption spectra of the majority of researched compounds are characterized by the stability of the bands with increasing solvent polarity (Fig. 1.2). Thus, maxima in the spectra of compounds 2.1-2.3, 2.6-2.13, 2.15-2.19 barely shift in the transition from non-polar hexane to high-polar methanol, and only dialkylamino derivatives 2.4, 2.5, 2.14 show little positive solvatochromic effects ($580-640 \text{ cm}^{-1}$) during the transition from aprotic solvent DMF to proton-donor methanol, due to the formation of hydrogen bonds with solvent molecules.

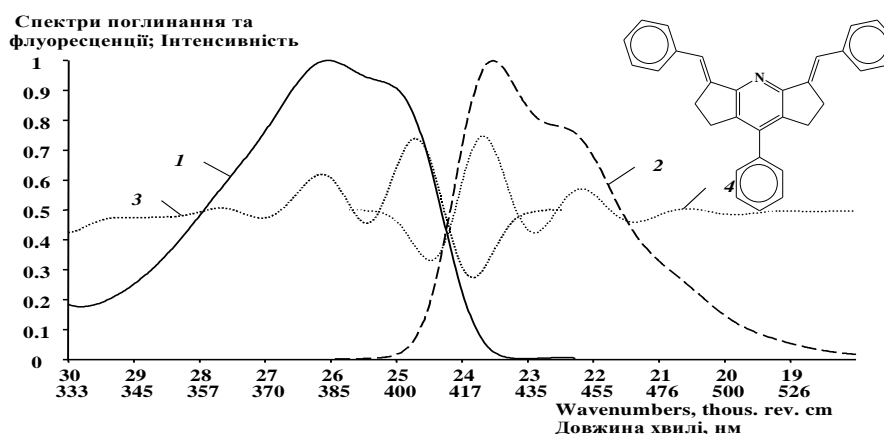


Fig. 1.1. The absorption (1) and fluorescence spectra (2) of 2.1 compound in hexane. Curves (3) and (4) - their secondary derivatives accordingly (taken with the sign "minus").

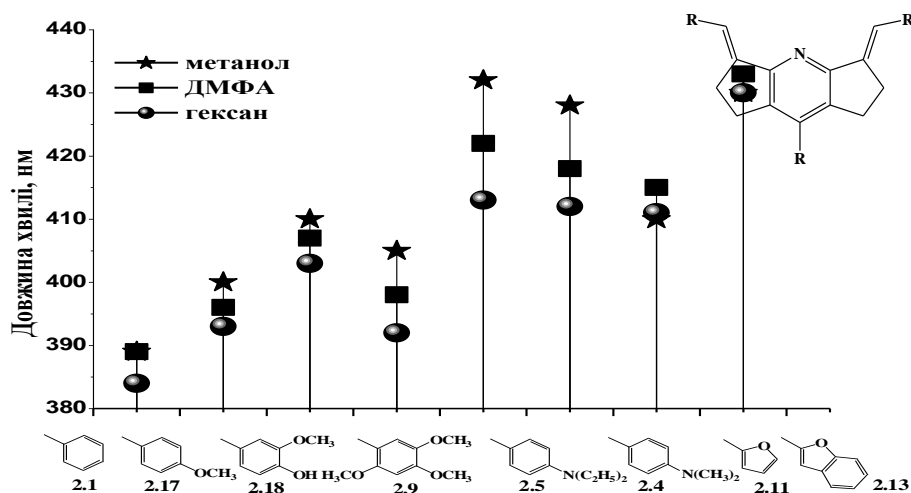


Fig. 1.2. The dependence of the dicyclopentano *[b, e]* pyridines absorption maxima during the solvent polarity change.

A somewhat different situation is observed in fluorescence spectra (Figure 1.3). Here all the compounds 2.1 - 2.19 show positive solvatofluochromism, indicating the increased polarity of the excited state S_1 of the molecules compared to the core.

Major shifts have dialkylamino derivatives of pyridine 2.4, 2.5. At the same time, showing little effect in some aprotic hexane-DMF (960 cm^{-1}) these compounds show high values of solvatofluorohrom shifts in the transition from DMF to methanol (2320 cm^{-1}).

The magnitude of effects in some dicyclopentano pyridine class is close to those that are shown by ketocyanine dyes in the formation of intermolecular hydrogen bonds (3).

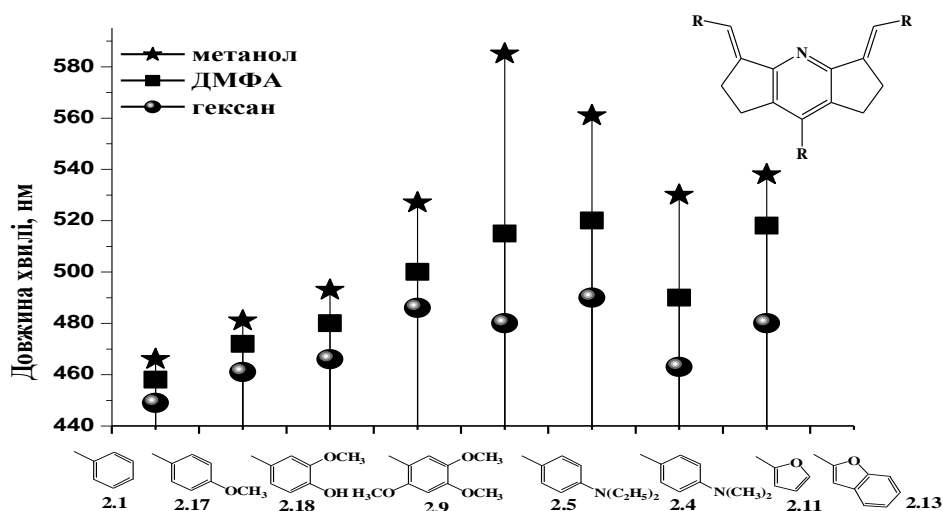


Fig. 1.3. Positive solvatofluochromism of dicyclopentano *[b, e]* pyridines in fluorescence spectra.

Dicyclopentano *[b, e]* pyridines are characterized by the molar absorption coefficient of about 20000-37000 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The highest molar extinction is the characteristic of compounds with the most electro-donor substituents in the side rings – dialkylamino substituted compounds 2.4, 2.5.

The entire range of hexahydrodicyclopentano *[b, e]* pyridines in all investigated solvents is characterized by quite high and similar in size quantum fluorescence output, which varies within 0.4-0.75. Only for dialkylamino derivatives 2.4, 2.5 in methanol the outputs are reduced to 0.05-0.12 (Fig. 1.4).

Quite large indicators of fluorescence decay time (2-4 ns) (4-5) show the ineffectiveness non-radiative deactivation of excited states of researched distirlypyridines (Table 1.1).

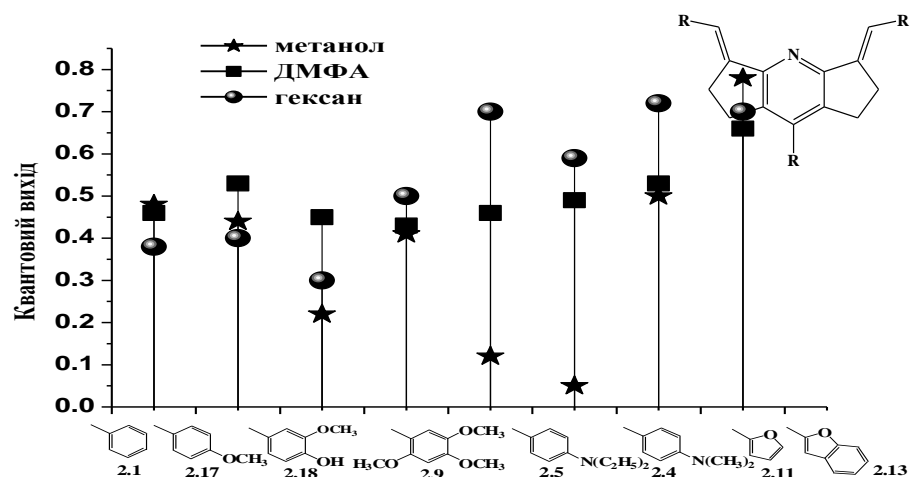
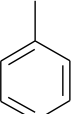
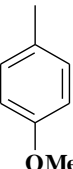
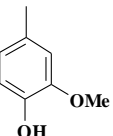
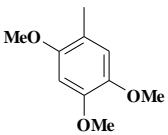
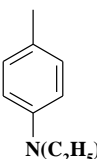
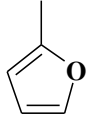
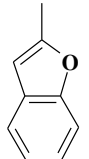


Fig. 1.4. Quantum fluorescence outputs of dicyclopentano [b, e] pyridines. Quantum yield

With the decrease of the quantum yield in methanol of compounds 2.4, 2.5, there is a sharp decrease in the lifetime of the excited state. This shows the inclusion of the channel of fast enough non-radioactive decontamination in this case. According to the analysis of numerous publications on the fluorescent properties of conjugated dialkylamino derivative organic molecules (6-7) it is implied that such a mechanism could be the formation of excited states of twisted intermolecular charge transfer. In our case their formation may contribute to steric interference, causing molecules collapsing and interfragment donor-acceptor interaction raise in the excited molecules under the influence of hydrogen bonds with molecules of solvent. Considerably less, but rather marked decrease in lifetime in methanol is also observed for other compounds with donor substituents - 2.8-2.9, 2.18.

Table 1.1 Data for absorption and fluorescence spectra for individual representatives dicyclopentanopyridines.

Compound (R=)	Solvent	Absorption*			Fluorescence*						
		λ , nm	ν , cm^{-1}	ϵ , $\text{л}\cdot\text{моль}^{-1}\cdot\text{см}^{-1}$	λ , nm	ν , cm^{-1}	$\Delta\nu$, cm^{-1}	ϕ	$\tau \times 10^8$, c	$K_f \times 10^{-8}$, с^{-1}	$K_d \times 10^{-8}$, с^{-1}
2.1 	methanol	389	25720		466	21460	4260	0.48	4.0	1.2	1.3
	acetonitril	386	25880		457	21880	4000	0.48	3.7	1.3	1.4
	DMFA	389	25680	22700	458	21820	3860	0.46	3.6	1.3	1.5
	toluene	389	25720		459	21780	3940	0.35	3.3	1.1	2.0
	octane	386	25920		450	22220	3700	0.31	3.2	0.9	2.1
	hexane	384	26060		449	22260	3800	0.35	3.3	1.1	2.0
2.17  OMe	methanol	405	24720		476	21000	3720	0.40	3.2	1.2	1.9
	acetonitril	396	25280		467	21400	3880	0.45	3.2	1.4	1.7
	DMFA	396	25280	28000	472	21180	4100	0.53	3.4	1.6	1.4
	toluene	397	25160		469	21320	3840	0.35	2.8	1.3	2.4
	octane	389	25720		458	21820	3900	0.29	3.0	1.0	2.4
	hexane	393	25460		461	21700	3760	0.37	2.8	1.3	2.3
2.18  OMe OH	methanol	410	24420		493	20300	4120	0.22	2.1	1.2	1.3
	acetonitril	399	25040		475	21040	4000	0.45	3.3	1.5	1.4
	DMFA	403	24840	29200	489	20460	4380	0.45	3.4	1.6	1.5
	toluene	401	24940		476	21020	3920	0.36	2.9	1.2	1.9
	octane	400	24980		466	21440	3540	0.20	3.2	1.4	2.0
2.9  MeO OMe	methanol	413	24200		527	18980	5220	0.41	2.0	2.1	3.0
	acetonitril	412	24280		493	20300	3980	0.62	3.7	1.7	1.0
	DMFA	414	24180	25300	500	20000	4180	0.43	3.7	1.2	1.6
	toluene	410	24400		491	20380	4020	0.53	2.9	1.8	1.6
	octane	403	24820		479	20880	3940	0.23	2.8	0.8	2.8
	hexane	391	25600		490	20400	5200	0.50	2.7	1.9	1.8

2.4  $N(CH_3)_2$	methanol	430	23240		585	17100	6140	0.12	0.6	1.3	2.7
	acetonitril	434	23060		528	18940	4120	0.71	3.2	1.5	2.4
	DMFA	420	23820	32600	515	19420	4400	0.35	3.3	1.6	1.7
	toluene	422	23680		514	19440	4240	0.66	2.4	2.1	2.0
	octane	414	24140		491	20380	3760	0.75	2.2	2.5	2.1
2.5  $N(C_2H_5)_2$	methanol	438	22840		561	17820	5020	0.05	0.4	1.2	2.6
	acetonitril	425	23520		519	19280	4240	0.47	2.9	1.3	2.3
	DMFA	426	23480	37300	520	19240	4240	0.49	3.2	1.5	1.6
	toluene	424	23560		513	19500	4060	0.51	2.3	2.3	2.2
	octane	414	24160		498	20100	4060	0.54	2.3	2.7	2.2
2.11 	methanol	410	24380		494	20240	4140	0.46	4.5	1.0	1.2
	acetonitril	411	24340		491	20360	3980	0.48	4.1	1.2	1.3
	DMFA	415	24100	20700	499	20060	4040	0.29	4.6	0.6	1.6
	toluene	416	24040		483	20720	3320	0.58	3.5	1.6	1.2
	octane	413	24240		482	20740	3500	0.35	3.8	0.9	1.7
2.13 	methanol	430	23240		538	18600	4640	0.78	4.0	2.0	0.6
	acetonitril	427	23420		516	19380	4040	0.64	3.8	1.7	0.9
	DMFA	433	23100	32000	518	19300	3800	0.46	3.9	1.2	1.4
	toluene	435	23000		515	19400	3600	0.77	3.4	2.3	0.6
	octane	429	23300		472	21200	2100	0.38	3.3	1.2	1.9
	hexane	430	23280		509	19660	3620	0.70	3.3	2.0	0.9

* λ , ν - position of the maxima in the scale of wavelengths and frequencies; $\Delta\nu$ - Stokes shift band; ϕ - quantum yield; τ - true lifetime of the excited state; K_r - rate constant of radiative deactivation; K_d - Rate constant of non-radioactive decontamination speed

Summary

Synthesized hexahydrodicyclopentano [*b, e*] pyridines are stable dyes with bright fluorescence in solutions and high quantum yield. Having a close position of absorption bands, they show significant fluorescence band change when changing electron properties of substituents, and for dialkylamino derivatives by changing the protonodonor solvent properties.

References:

1. Добрецов Г.Е. Флуоресцентные зонды в исследовании биологических мембран. - М.: Наука, 1989. - 278 с.
2. Demas J.N., Crosby G.A. Measurement of photoluminescence quantum yields. Review // J. Phys. Chem. - 1971. - № 75. - P. 991-1025.
3. Barnabas M.V., Liu A., Trifunac A.D., Krongauz V.V., Chang C.T. Solvent effects on the photochemistry of a ketocyanine dye and its functional analogue, Michler's ketone // J. Phys. Chem. - 1992. - №96. - P. 212-217.
4. Валюк В.Ф., Григорович О.В., Дорошенко А.О., Пивоваренко В.Г. 3,5-Диарилдендидициклопентано[*b, e*]пиридини - новий клас флуоресцентних барвників. 2. Синтез і визначення конформації в розчинах. Триазакраун- та гексаамінометилзаміщені похідні // Ukr. Bioorg. Acta. - 2004. - Vol. 1. - P. 79-89.
5. Фрасинюк М.С., Туров А.В., Хиля В.П. Химия гетероаналогов изофлавонов. Реакция Маниха в ряду бензимидазольных и бензтиазольных аналогов изофлавонов // ХГС. - 1998. - №8. - P. 1078-1084.
6. Vollmer F., Rettig W., Birckner E. Photochemical Mechanisms Producing Large Fluorescence Stokes Shifts // J. Fluorescence. - 1994. - Vol. 4, №1. - P. 65-69.
7. Doroshenko A.O., Kyrychenko A.V., Waluk J. Low temperature spectra of the ortho-POPOP molecule: additional arguments of its flattening in the excited state // J. Fluorescence. - 2000. - Vol. 10, №1. - P. 41-48.