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SPECTROFLUORIMETRIC INVESTIGATION OF 2-BENZOPYRYLIUM PERCHLORATES

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Abstract

1,3-Dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**1**) and its 1-substituted- vinyl, 1-styryl, 1-substituted-styryl derivatives were prepared. The fluorescence properties of fifteen compounds were investigated by spectrofluorimetric method. The **1** and the 1-(substituted-vinyl) derivatives fluoresce intensely. The 1-(3-indolybvinyl)-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**14**) shows the most intense fluorescence.

The 1-styryl-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**4**) fluoresces very weakly. The position of the substituent on the benzene ring and the quality of the substituent have an important influence on the fluorescence. Some investigated derivatives show intensive flourescence in the IR-region. Spectrofluorimetric methods were developed for the determination of eight compounds.

Keywords: 2-benzopyrylium perchlorates, spectrofluorimetry, IR fluorescence.

Introduction

The investigation of the pyrylium salts has become an interesting field of research and the possibilities of their applications have increased [1–10]. They can be used as starting materials in different syntheses, and due to their fluorescence properties in the dye industry [2–3]. Some of them can be used as colouring materials or paint precursors absorbing and emitting in IR [2–3]. They find further application in laser technology [4] as Q-switchers [5].

Pyrylium salts can be transformed into pyrydium salts by primary amines in organic solvents [6]. This transformation can be effected also in aqueous medium with water-soluble pyrylium salts [7]. The selectivity of the transformation of the pyrylium cation into pyrydium as well as the almost quantitative yield give the opportunity to use them in identifying primary amines and as covalent indicators in organic and aqueous systems [8]. The phosphorescence quantum yield of the singlet molecular ($^1\Delta_g$) oxygen was determined by pyrylium dyes emitting in IR [9].

Table 1
Results of spectrofluorimetric investigation of 2-benzopyrylium perchlorates

Nr.	Conc. of $HClO_4$ [M/L]	Solvent: Ethanol containing $HClO_4$ Ex. [nm]	Em. [nm]	Rel. Int. $c=10^{-6}$ M/L (arbitr. units)	Int. of **14** = 100%	Solvent: DMSO Ex. [nm]	Em. [nm]	Rel. Int. $c=10^{-6}$ M/L (arbitr. units)	Int. of **14** in ethanol = 100%
1	1.0	340	455	530	11.1				
2	1.0	345	470	361	7.6				
3	0.01	470	490	107	2.2	470	490	105	2.2
4	0.1	470	570	36	0.8				
5	0.1	495	585	662	13.9				
6	0.1	470	570	53	1.1				
7	0.1	470	550	7	0.2				
8	0.01	485	570	236	5.0	480	580	478	10.0
9	0.1	470	560	31	0.7	470	560	19	0.4
10	0.1	470	580	27	0.6				
11	0.1	470	600	60	1.3				
12	0.5	490	605	425	8.9	490	620	581	12.2
13	0.5	485	620	490	10.3	485	640	615	12.9
14	1.0	595	615	4766	100.0	590	625	4659	97.8
15	0.1	550	630	295	6.2	570	640	1095	23.0

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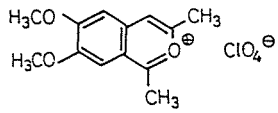
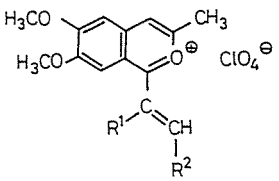
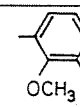




No	R^1	R^2
2	H	$-OC_2H_5$
3	H	$-N(CH_3)_2$
4	H	
5	H	
6	H	
7	H	
8	H	
9	H	
10	H	

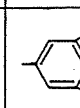
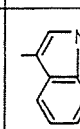
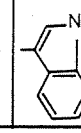
No	R^1	R^2
11	H	
12	H	
13	H	
14	H	
15		

Fig. 1. Investigated 2-benzopyrylium perchlorate compounds.

Table 2
Some parameters of the spectrofluorimetric determination of 2-benzopyryliumperchlorates.
Solvent: Ethanol containing perchloric acid

Number of compound	Excitation wavelength (Ex) [nm]	Emission wavelength (Em) [nm]	Conc. of $HClO_4$ [M/L]	Range of linearity [M/L]	ppb	Rel. stand. deviation at $c = 10^{-6}$ M/L σ [%]	$\frac{\sigma}{\sqrt{n}}$ [%]
1	340	455	1.0	$5 \cdot 10^{-8} - 5 \cdot 10^{-6}$	16 – 1600	± 2.64	±1.18
2	345	470	1.0	$10^{-8} - 5 \cdot 10^{-6}$	4 – 2000	± 2.33	±0.96
3	470	490	0.01	$2 \cdot 10^{-7} - 10^{-6}$	8 – 374	± 5.34	±2.18
5	495	585	0.1	$4 \cdot 10^{-8} - 10^{-5}$	16 – 4000	± 8.66	±3.53
8	485	570	0.01	$4 \cdot 10^{-8} - 5 \cdot 10^{-6}$	20 – 2400	±10.6	±4.3
12	490	605	0.5	$3 \cdot 10^{-8} - 10^{-5}$	10 – 4600	± 4.0	±1.63
13	485	620	0.5	$5 \cdot 10^{-8} - 2 \cdot 10^{-6}$	25 – 1000	± 2.83	±1.16
14	595	615	1.0	$5 \cdot 10^{-9} - 10^{-6}$	3 – 550	± 3.68	±1.50

Another group of pyrylium compounds, e. g. the flavium salts, are natural substances.

Blocking of the pyrylium molecule results in significant enchancement of fluorescence intensity and the Stokes shift is considerable.

The Stokes shift can be partly suppressed by decreasing the temperature [10]. DELIGEORGIEV et al. [11] reported the synthesis of pyrylium compounds with high fluorescence quantum yield, the investigation of the relations between the spectral behaviour and the molecular structure of those compounds and the quantum-chemical interpretation of these relations.

In this paper the spectrofluorimetric study of fifteen 2-benzopyrylium perchlorates is reported.

Experimental

Compounds Studied and Apparatus Used

1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**1**) was prepared by DOROFEENKO et al. [12]. Using it as starting material they prepared mainly 1-styryl-2- benzopyrylium perchlorates with aldehydes, mostly aromatic aldehydes, taking advantage of the loose protons of the methyl group in position 1 [12–15]. The perchlorate salts have some advantages, they can be produced in high purity, they crystallize well and they are relatively stable.

Their disadvantage is their very low solubility in common solvents. Generally they are soluble in dimethyl formamide (DMF) and dimethylsulfoxide (DMSO). The compounds mentioned above and similar compounds were synthesized also in the Institute for Drug Research, Budapest (Hungary).

1-styryl-2-benzopyrylium percholates prepared are E-isomers, the protons of the olefinic part are in trans-position, in the ^{1}H–NMR-spectrum: $J \simeq 16$ Hz. The results of the spectrofluorimetric investigation of fifteen compounds listed in *Fig. 1* are discussed below. Some of the perchlorate-salts were not stable in diluted alcoholic solution therefore the measurements were done in ethanolic containing perchloric acid in optimal concentration, where the examined compounds were stable even at a very low concentration. Some of the compounds were unstable also in DMSO but in this case perchloric acid cannot be used.

Fluorescence spectra and spectrofluorimetric measurements made obtained with a Hitachi Model MPF–2A fluorescence spectrophotometer. The spectra are uncorrected.

Results and Discussion

The results of the spectrofluorimetric investigation are summarized in *Table. 1.* Compounds **4**, **6**, **7**, **9**, **10**, **11** and **15** have not even weak fluorescence in alcoholic solution, so the spectrofluorimetric determinations were carried only with the other eight compounds. Additional three compounds (**1**, **2**, **5**) could not be examined in DMSO because of their instability in that solvent.

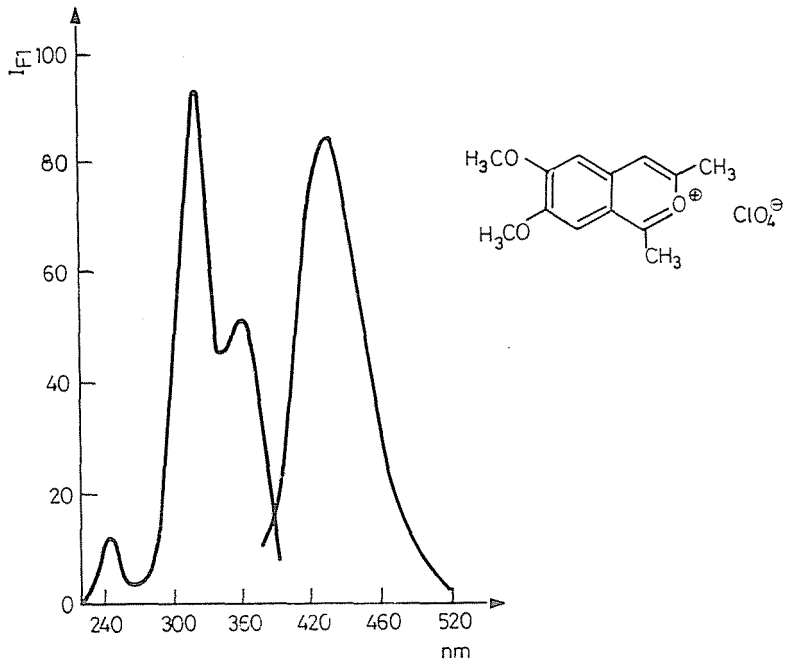


Fig. 2. Fluorescence excitation and emission spectra of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**1**)
Solvent: ethanol ($HClO_4$ conc.: 1 mol/l) Ex.: 340 nm; Em.: 455 nm; $c = 10^{-6}$ mol/l

Figures 2–9 show the excitation and emission spectra of the compounds **1**, **2**, **3**, **5**, **8**, **12**, **13** and **14** in ethanol containing perchloric acid. *Figs. 4, 6, 8* and *9* show also the same spectra in DMSO.

The parameters of the spectrofluorimetric determinations in ethanol containing perchloric acid are summarized in *Table 2*, and those in DMSO in *Table 3.*

Compound **1** shows relatively intensive fluorescence and considerable Stokes shift (*Fig. 2*). Introduction of ethoxy-vinyl and dimethyl-

Table 3
Some parameters of the spectrofluorimetric determination of 2-benzopyryliumperchlorates.
Solvent: dimethylsulfoxide

Number of compound	Excitation wavelength (Ex) [nm]	Emission wavelength (Em) [nm]	Range of linearity [M/L]	Range of linearity ppb	Rel. stand. dev. at $c = 10^{-6}$ M/L σ [%]	Rel. stand. dev. at $c = 10^{-6}$ M/L $\frac{\sigma}{\sqrt{n}}$ [%]
3	470	490	$10^{-8} - 5 \cdot 10^{-6}$	4 – 2000	± 2.71	±1.10
8	480	580	$10^{-8} - 5 \cdot 10^{-6}$	5 – 2400	±10.60	±4.30
12	490	620	$10^{-7} - 5 \cdot 10^{-6}$	46 – 2300	± 2.31	±0.95
13	485	640	$5 \cdot 10^{-8} - 2 \cdot 10^{-6}$	25 – 1000	± 3.86	±1.57
14	585	620	$5 \cdot 10^{-9} - 10^{-6}$	25 – 1000	± 3.85	±1.57

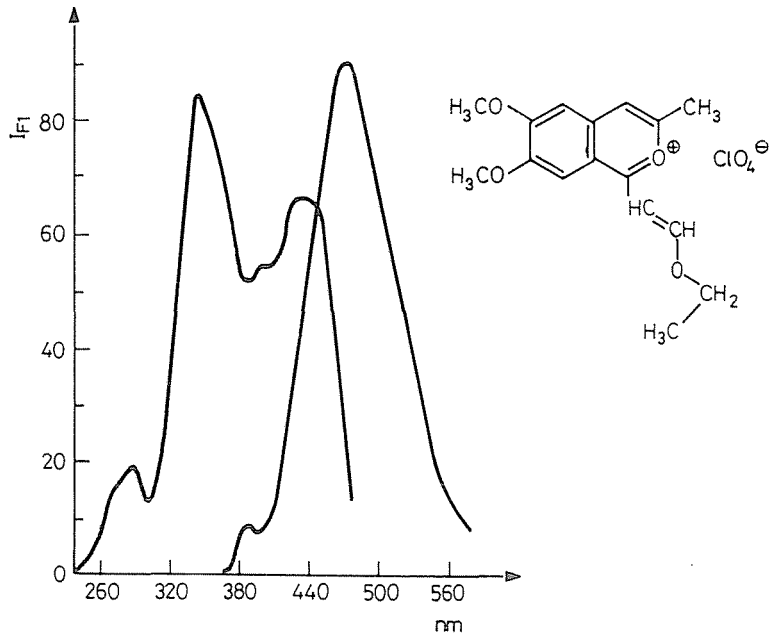


Fig. 3. Fluorescence excitation and emission spectra of 1-ethoxy-vinyl-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**2**)
Solvent: ethanol ($HClO_4$ conc.: 1 mol/l) Ex.: 345 nm; Em.: 470 nm; $c = 10^{-6}$ mol/l

amino-vinyl groups in position 1 reduces the intensity of fluorescence, shifts the spectra towards longer wavelengths and simultaneously decreases the Stokes shift (*Figs. 3* and *4*). In the case of 1-(3-indolyl-vinyl)-derivate (**14**)

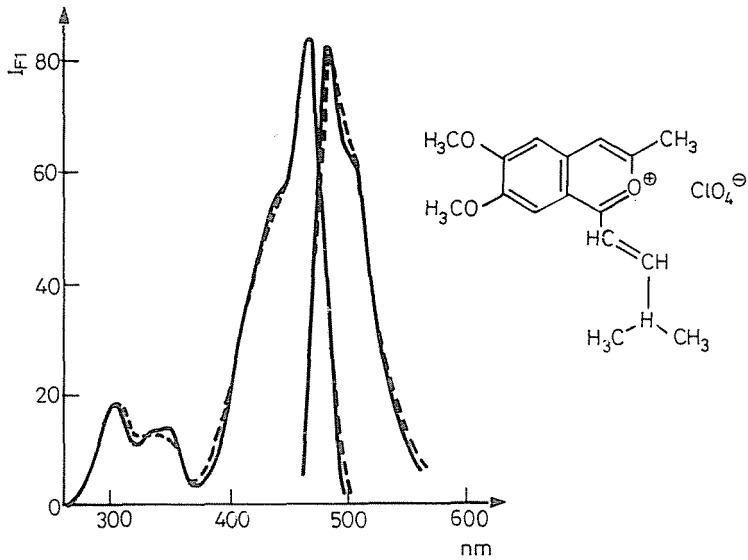


Fig. 4. Fluorescence excitation and emission spectra of 1-dimethylaminovinyl-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**3**)
Solvents: ethanol ($HClO_4$ conc.: 10^{-2} mol/l): ——— dimethylsulfoxide: – – –
Ex.: 470 nm; Em.: 490 nm; $c = 10^{-6}$ mol/l

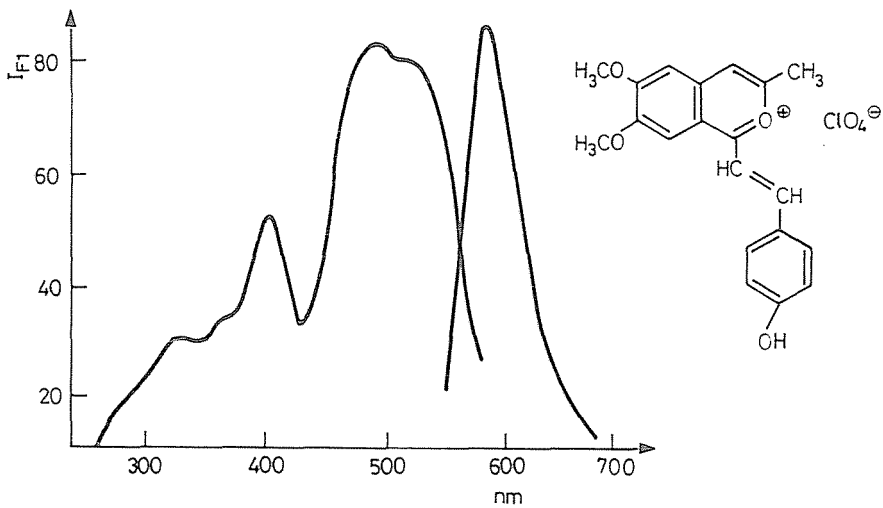


Fig. 5. Fluorescence excitation and emission spectra of 1(E)-(4-hydroxystyryl)-3,6,7-dimethoxy-2-benzopyrylium perchlorate (**5**)
Solvent: ethanol ($HClO_4$ conc.: 10^{-1} mol/l) Ex.: 495 nm; Em.: 600 nm; $c = 10^{-6}$ mol/l

the fluorescence intensity significantly increases the maximum of the emission spectrum shifts towards a relatively long wavelength (615 nm; *Table 1*) and a decrease in the Stokes shift also appears (*Fig. 9*).

Introduction of the styryl group into position 1 resulted in a shift of the maxima of the spectra towards longer wavelengths but surprisingly the unsubstituted styryl compound (**4**) has very low fluorescence intensity (*Table 1*).

Styryl derivatives substituted with hydroxyl group in the 4'-position (**5**) have broad excitation spectra (*Fig. 5*) and relatively intense fluorescence. 4'-nitro (**6**) and 4'-dimethylamino (**7**) substitution hardly changes the shapes of the spectra, but significantly decreases the fluorescence intensity and the fluorescence ability is extremely diminished.

Among the disubstituted styryl derivatives only the 3'-chloro-4'-methoxy (**8**) and the 3',4'-dimethoxy-styryl (**12**) compounds have intensive fluorescence. They have broad excitation spectra and relatively large Stokes shift (*Figs. 6* and *7*).

The 2',4'-dichloro (**9**), 2',3'-dimethoxy (**10**) and the 3',4'-dihydroxy-styryl (**11**) compounds have extremely low fluorescence intensity. On introducing one more methoxy group in 12 (resulted in compound 13: 3',4',5'-trimethoxy- styryl derivative) the shape of the spectra and the fluorescence yield did not change essentially; but the Stokes shift increased and the maximum of the emission spectrum shifted towards longer wavelength by about 15 nm.

Compounds **5**, **7**, **8**, **12**, **13** and **14** show intense IR emission, this feature related to other pyrylium compounds has been already published [2, 3, 9]. This makes them useful in areas where IR emission is necessary.

The **1**, **2**, **3**, **5**, **8**, **12**, **13** and **14** compounds can be determined quantitatively with high sensitivity in ethanolic solution containing perchloric acid. The calibration graph is linear in the range 10^{-6}–10^{-9} g/cm^3 (ppm-ppb).

The relative standard deviation varied between ±2–10 % for different compounds (*Table 2*).

The linear range and the relative standard deviation in DMSO solvent for five examined compounds (**3**, **8**, **12**, **13**, **14**) (*Table 3*) are similar to that found in ethanol.

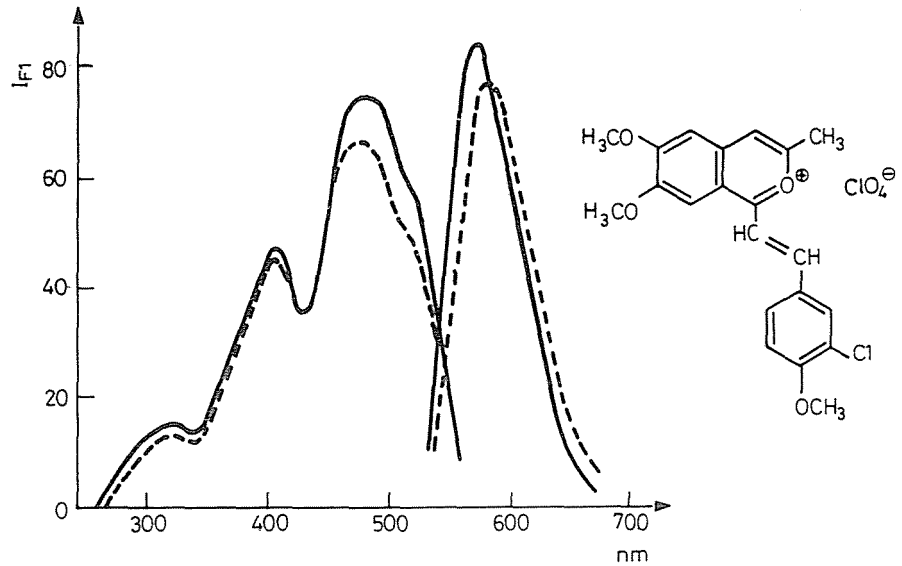


Fig. 6. Fluorescence excitation and emission spectra of 1(E)-(3-chlor, 4-methoxystyryl)-3-methyl-6,7-dimethoxy-2- benzopyrylium perchlorate (**8**)
Solvents: ethanol ($HClO_4$ conc.: 10^{-2} mol/l): ——— dimethylsulfoxide: - - -
Ex.: 485 nm; Em.: 570 nm; $c = 10^{-6}$ mol/l

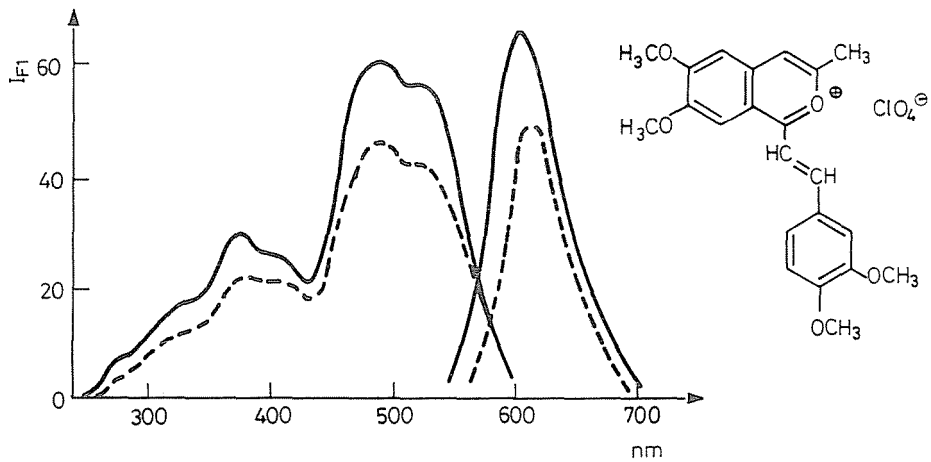


Fig. 7. Fluorescence excitation and emission spectra of 1(E)-(3,4-dimethoxystyryl)-3-mentyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**12**)
Solvents: ethanol ($HClO_4$ conc.: $5 \cdot 10^{-1}$ mol/l): ——— dimethylsulfoxide: - - -
Ex.: 490 nm; Em.: 605 nm; $c = 10^{-6}$ mol/l

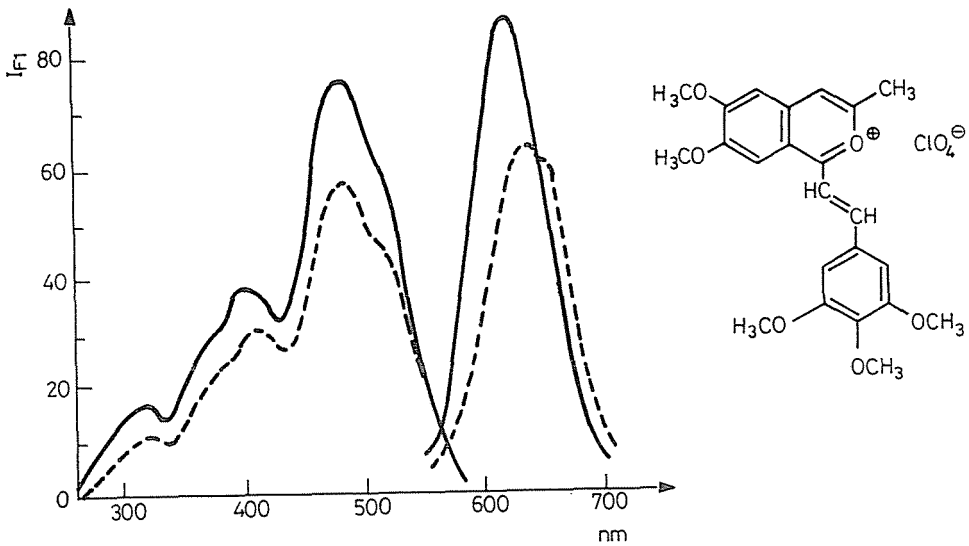


Fig. 8. Fluorescence excitation and emission spectra of 1(E)-(3,4,5-trimethoxystyryl)-3-menthyl-6,7-dimethoxy-2- benzopyrylium perchlorate (**13**)
Solvents: ethanol ($HClO_4$ conc.: $5 \cdot 10^{-1}$ mol/l) ——— dimethylsulfoxide: – – –
Ex.: 485 nm; Em.: 620 nm; $c = 10^{-6}$ mol/l

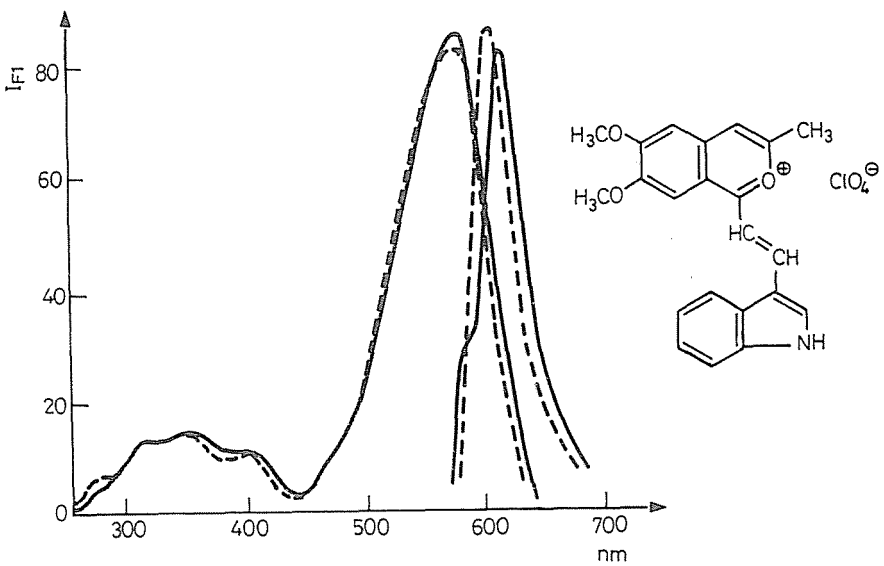


Fig. 9. Fluorescence excitation and emission spectra of 1(E)-(3-indolylvinyl)-3-mentyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**14**)
Solvents: ethanol ($HClO_4$ conc.: 1 mol/l) ——— dimethylsulfoxide: – – – Ex.: 540 nm; Em.: 620 nm; $c = 10^{-6}$ mol/l

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