

# Structurally Rigid 2,6-Distyrylpyridines—A New Class of Fluorescent Dyes. 1. Synthesis, Steric Constitution and Spectral Properties

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Received July 2, 2003; revised September 17, 2003; accepted September 17, 2003

A group of structurally rigid analogues of 2,6-distyrylpyridine was synthesised. Molecular geometry of the synthesised dyes in solutions was studied by <sup>1</sup>H-NMR, electronic absorption and fluorescence spectrometry. The spectral data testify all the compounds exist in E-configuration of their styryl residues. The most planar molecular conformation is typical for the compounds with five-membered side aromatic moieties. In the case of pyridines with six-membered aromatic residues steric hindrance results in turning the above mentioned cyclic groups out of the plane of the central pyridine moiety. The violation of planarity in this case is not significant and saves the possibility of  $\pi$ -electronic conjugation in the molecules. The synthesised compounds are characterized by high fluorescence quantum yields in solutions. The electronic absorption spectra of titled pyridines demonstrate low sensitivity to the nature of the substituents introduced into the side aromatic rings. In contrast to this, the fluorescence bands considerably change their position under the influence of electron donor substituents. The fluorescence spectra display substantial positive solvatochromism only in the cases of the dialkylamino-derivatives, especially on going from aprotic solvents to proton donor ones. Generally, the synthesised structurally rigid distyrylpyridine derivatives have prospects for their application as multi-purposes fluorescent probes.

**KEY WORDS:** 2,6-Distyrylpyridines; electronic absorption; fluorescence and NMR spectra; chemical synthesis; fluorescence probes.

## INTRODUCTION

Only a few classes of fluorescent organic dyes have found their successful application in science and technology. The best known among them are xanthenes, coumarins, naphthalimides, cyanines, various aryl-azoles, acridines, and phenoxazines [1–4]. By their chemical structure, most of these dyes are condensed heterocyclic compounds with extended conjugated  $\pi$ -electronic systems. Mechanical rigidity of such compounds leads to

reduction of the quantity of vibrational and rotational degrees of freedom and to the lowering the non-radiative losses of excitation energy. The latter results in the substantial increase of their fluorescence quantum yields. The presence of heteroatoms (nitrogen, oxygen or sulphur) in the above mentioned molecules usually does not reduce the brightness of their fluorescence, but brings considerable effect onto other optical characteristics: for example, molar extinction and band positions in the absorption and fluorescence spectra. These changes in optical properties of the organic molecules upon their chemical modification can be foreseen by quantum-chemical simulations. However, fluorescence quantum yield is a poorly predicted parameter for most organic molecules. For this reason, the experimental discovery of new classes of highly fluorescent compounds retains its importance up to the present.

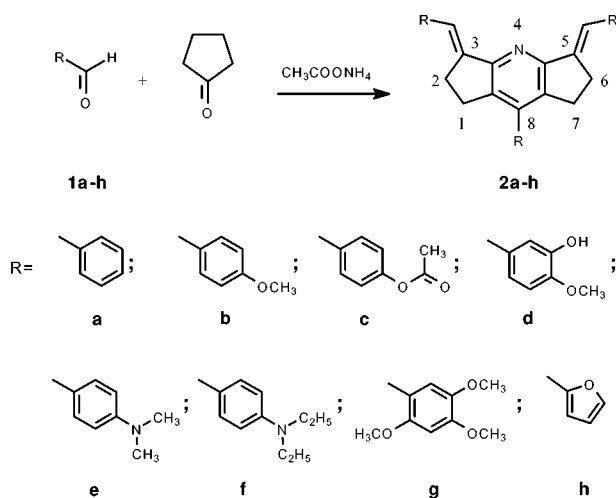
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In our studies of ketocyanine dye synthesis [5–7], taking into account the data published [8–11], we found that similar starting compounds: aromatic aldehydes and cyclopentanone under the conditions of the Chichibabin reaction could give rise to a new class of fluorescent molecules which are pyridine derivatives with structurally fixed styryl moieties. Fluorescent properties of such substances are not discovered yet. Together with our recently studied ketocyanines [5–7] they belong to the wide group of the so-called cross-conjugated molecules, where the pyridine residue serves as an  $\pi$ -electron density acceptor. These kind of dyes having electron donor substituents might possess advanced solvatofluorochromic properties. Structural rigidity of new pyridine compounds allows us to expect for them high fluorescence quantum yields in solutions. Comparatively simple synthesis of this class opens wide possibility for easy modification of their chemical structures in the desired direction. For example, for extending the length of their  $\pi$ -conjugated system, the polycyclic aromatic aldehydes could be used. The application of an aromatic aldehydes with appropriate chelating units might yield the creation of new fluorescent ion indicators. The possible protonation of the highly basic nitrogen atom of pyridine moiety leads to substantial changes in absorption and fluorescence spectra. The last feature could be used in the design of new fluorescent pH sensors. Thus, such distyrylpyridine derivatives have all features required for the design on their skeleton various multipurpose fluorescent sensors for numerous practically important applications.

Our main task in the present work was to synthesise and to study the chemical structure and fluorescence properties of the eight representatives of the structurally rigid distyrylpyridines **2a-h**, that differ by their steric constitution and  $\pi$ -electron donor properties of substituents in the side aromatic moieties.



## EXPERIMENTAL

### Preparation and Structure Elucidation

All the aldehydes and cyclopentanone (Aldrich) of reagent grade purity were used without any additional purification.

Distyrylpyridine **2a-h** synthesis was fulfilled by the improved procedure, initially taken from [8]. For example, 8-(4-diethylaminophenyl)-3,5-di[(E)-1-(4-diethylaminophenyl)methylidene]-1,2,3,5,6,7-hexahydrocyclopenta[b,e]pyridine (**2f**) was prepared in the following steps. A mixture of 4-(diethylamino)benzaldehyde **1f** (1.6 g, 10 mmol), cyclopentanone (0.42 g, 5 mmol) and ammonium acetate (3.85 g, 50 mmol) in ethanol (25 mL) with several drops of 30% hydrogen peroxide was boiled during 1 hr and left to stand overnight at 20°C. The precipitate formed was filtered and washed with acetone. The crude material (2 g) was purified by column chromatography on silica gel (Davisil<sup>TM</sup>, grade 643, 200–425 mesh) using chloroform-methanol mixture (98:2, v/v) as the eluent. The precipitate obtained after the solvent evaporation was recrystallized from acetone (quantitative elemental analysis data were the following: found, % N: 9.06; calculated, % N: 8.96). <sup>13</sup>C NMR spectrum (75 MHz, in CDCl<sub>3</sub>) for the compound **2g** (p.p.m.): quaternary carbon atoms: 164.29; 147.29; 146.44; 143.36; 140.33; 138.23; 129.06; 124.19; tertiary carbon atoms: 133.49; 132.54; 121.51; 111.58; 111.16; secondary carbon atoms: 44.35; 44.30; 29.51; 28.18; primary carbon atoms: 12.68.

Compound **2c**, 8-(4-acetoxyphenyl)-3,5-di[(E)-1-(4-acetoxyphenyl)methylidene]-1,2,3,5,6,7-hexahydrocyclopenta[b,e]pyridine, was prepared from 4-hydroxybenzaldehyde in a similar way, with additional boiling of crude material (about 2 g), collected after completion of the first step, during 20 min with mixture of pyridine (15 mL) and acetic anhydride (15 mL). Then the reaction mixture was cooled and poured into water (100 mL). The precipitate formed was filtered off and washed with acetone. Finally, the compound **2c** was purified by column chromatography and recrystallized from acetone according to the general procedure.


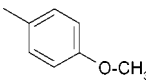
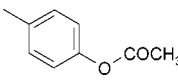
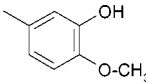
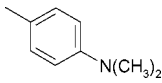
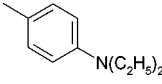
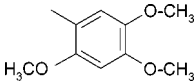

The main physico-chemical data for the compounds **2a-h** are collected in the Tables I and II. The results of quantitative elemental analysis for the investigated compounds (generally not presented here) were in agreement with the proposed empirical formula. All the samples obtained were homogeneous according to thin-layer chromatography (TLC) on silica gel 60, F-254, 5 × 20 cm (Selecto Scientific, USA) with chloroform-methanol mixtures (98:2, 9:1, 85:15, v/v) used as eluents.

Table I. Characteristics of Distyrylpyridines 2a-h

Compound	Yield, %	Empiric formula	Molecular mass	M <sup>+</sup> -ion position <sup>a</sup>	Melting point, °C	Positions of signals in <sup>1</sup> H-NMR spectrum, δ, ppm <sup>a</sup> and coupling constants, J, Hz		
						Substituents in the positions 2 and 6	Substituent in the position 4	
<b>2a</b>	20	C <sub>31</sub> H <sub>25</sub> N	411.55	411.0	231	7.68–7.72m 2H(H-olefin); 7.59d, J = 8, 4H(H-2, H-6); 7.34–7.41m 4H(H-3, H-5); 7.26t, J = 8, 2H(H-4)	7.38d, J = 8, 2H(H-2, H-6); 7.34–7.41m 1H(H-4); 7.47t, J = 8, 2H(H-3, H-5)	3.12–3.20m, 4H; 2.90–2.98m, 4H
<b>2b</b>	13	C <sub>34</sub> H <sub>31</sub> NO <sub>3</sub>	501.62	501.0	192	7.61–7.65m 2H(H-olefin); 7.54d, J = 8, 4H(H-2, H-6); 6.96d, J = 8, 4H(H-3, H-5); 3.85c, 6H(OCH <sub>3</sub> )	7.02d, J = 8, 2H(H-2, H-6); 7.32d, J = 8, 2H(H-3, H-5); 3.87c, 3H(OCH <sub>3</sub> )	3.10–3.18m, 4H; 2.92–3.00m, 4H
<b>2c</b>	28	C <sub>37</sub> H <sub>31</sub> NO <sub>6</sub>	585.65	585.0	229	7.65–7.69m 2H(H-olefin); 7.60d, J = 8, 4H(H-2, H-6); 7.14d, J = 8, 4H(H-3, H-5); 2.31c, 6H(CH <sub>3</sub> )	7.38d, J = 8, 2H(H-2, H-6); 7.21d, J = 8, 2H(H-3, H-5); 2.31c, 3H(CH <sub>3</sub> )	3.05–3.13m, 4H; 2.97–3.05m, 4H
<b>2d</b>	25	C <sub>34</sub> H <sub>31</sub> NO <sub>6</sub>	549.62	549.0	247	9.15–9.21s 2H(OH); 7.43–7.47m 2H(H-olefin); 7.18d, J = 2, 2H(H-2); 7.05d, J = 8, 2H(H-6); 6.84d, J = 8, 2H(H-5); 3.84c, 6H(OCH <sub>3</sub> )	9.21–9.27s 1H(OH); 6.90c, 1H(H-2); 7.04d, J = 8, 1H(H-6); 6.90c, 1H(H-5); 3.80c, 3H(OCH <sub>3</sub> )	3.09–3.17m, 4H; 2.95–3.03m, 4H
<b>2e</b>	29	C <sub>37</sub> H <sub>40</sub> N <sub>4</sub>	540.75	—	258	7.57–7.61m 2H(H-olefin); 7.51d, J = 8, 4H(H-2, H-6); 6.76d, J = 8, 4H(H-3, H-5); 2.99s, 12H (NCH <sub>3</sub> )	7.29d, J = 8, 2H(H-2, H-6); 6.80d, J = 8, 2H(H-3, H-5); 3.02s, 6H(NCH <sub>3</sub> )	3.10–3.18m, 4H; 2.97–3.05m, 4H
<b>2f</b>	24	C <sub>43</sub> H <sub>52</sub> N <sub>4</sub>	624.91	—	247	7.34–7.38m 2H(H-olefin); 7.41d, J = 8, 4H(H-2, H-6); 6.72m, 4H(H-3, H-5); 3.36q, 8H; and 1.12t 12H (NC <sub>2</sub> H <sub>5</sub> )	7.29d, J = 8, 2H(H-2, H-6); 6.72m, 2H(H-3, H-5); 3.36q, 4H; and 1.12t 6H (NC <sub>2</sub> H <sub>5</sub> )	2.98–3.06m, 4H; 2.90–2.98m, 4H
<b>2g</b>	19	C <sub>40</sub> H <sub>43</sub> NO <sub>9</sub>	681.78	681.0	191	7.85–7.89m 2H(H-olefin); 7.13s, 2H(H-6); 6.58c, 2H(H-3); 3.93c, 6H; 3.90c, 6H; 3.88c, 6H (OCH <sub>3</sub> )	6.71s, 1H(H-6); 6.63c, 1H(H-3); 3.96c, 3H; 3.84c, 3H; 3.71c, 3H (OCH <sub>3</sub> )	3.06–3.14m, 4H; 2.79–2.87m, 4H
<b>2h</b>	29	C <sub>25</sub> H <sub>19</sub> NO <sub>3</sub>	381.43	381.0	240	7.48s, 2H(H-3); 7.42–7.46m 2H(H-olefin); 6.46–6.50m 2H(H-4); 6.43d, J = 6, (H-5)	7.61s, 1H(H-3); 6.55–6.59m 1H(H-4); 6.78d, J = 6, (H-5)	3.22–3.30m, 4H; 3.14–3.22m, 4H

<sup>a</sup>The spectra of compounds **2d** and **2f** were measured in DMSO-*d*<sub>6</sub> with TMS as internal standard at 25°C.

Table II. Data of Absorption and Fluorescence Spectra of Distyrylpyridines 2a-h

Compound	R	Solvent	Absorption			Fluorescence				
			$\lambda$ , nm	$\nu$ , $\text{cm}^{-1}$	$\epsilon$ , $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	$\lambda$ , nm	$\nu$ , $\text{cm}^{-1}$	$\Delta\nu$ , $\text{cm}^{-1}$	$\phi$	$\tau$ , ns
2a		Methanol	389	25720		466	21460	4260	0.48	4.06
		Acetonitrile	386	25880		457	21880	4000	0.48	3.73
		DMF	389	25680	22700	458	21820	3860	0.46	3.64
		Toluene	389	25720		459	21780	3940	0.35	3.25
		Hexane	384	26060		449	22260	3800	0.35	3.24
2b		Methanol	405	24720		476	21000	3720	0.40	3.23
		Acetonitrile	396	25280		467	21400	3880	0.45	3.22
		DMF	396	25280	28000	472	21180	4100	0.53	3.41
		Toluene	397	25160		469	21320	3840	0.35	2.77
		Hexane	393	25460		461	21700	3760	0.37	2.97
2c		Methanol	391	25560		475	21060	4500	0.39	3.64
		Acetonitrile	388	25780		459	21780	4000	0.29	3.40
		DMF	390	25640	27400	461	21680	3960	0.49	3.40
		Toluene	392	25540		461	21700	3840	0.34	2.95
		Hexane	392	25480		458	21840	3640	0.29	3.07
2d		Methanol	410	24420		493	20300	4120	0.22	2.10
		Acetonitrile	399	25040		475	21040	4000	0.45	3.37
		DMF	403	24840	29200	489	20460	4380	0.45	3.44
		Toluene	401	24940		476	21020	3920	0.36	2.96
		Hexane	400	24980		466	21440	3540	0.20	3.18
2e		Methanol	430	23240		585	17100	6140	0.12	0.59
		Acetonitrile	434	23060		528	18940	4120	0.71	3.19
		DMF	420	23820	32600	515	19420	4400	0.35	3.30
		Toluene	422	23680		514	19440	4240	0.66	2.47
		Hexane	414	24140		491	20380	3760	0.75	2.23
2f		Methanol	438	22840		561	17820	5020	0.05	0.37
		Acetonitrile	425	23520		519	19280	4240	0.47	2.97
		DMF	426	23480	37300	520	19240	4240	0.49	3.15
		Toluene	424	23560		513	19500	4060	0.51	2.25
		Hexane	414	24160		498	20100	4060	0.54	2.32
2g		Methanol	413	24200		527	18980	5220	0.41	1.97
		Acetonitrile	412	24280		493	20300	3980	0.62	3.66
		DMF	414	24180	25300	500	20000	4180	0.43	3.69
		Toluene	410	24400		491	20380	4020	0.53	2.89
		Hexane	391	25600		490	20400	5200	0.50	2.75
2h		Methanol	410	24380		494	20240	4140	0.46	4.53
		Acetonitrile	411	24340		491	20360	3980	0.48	4.13
		DMF	415	24100	20700	499	20060	4040	0.29	4.58
		Toluene	416	24040		483	20720	3320	0.58	3.52
		Hexane	411	24320		491	20360	3960	0.72	3.75

Melting points (uncorrected) were determined on a PHMK melting point apparatus ("VEB Analytik," Dresden). Mass spectra were obtained on Thermabeam Mass Detector (Waters Integrity System, USA).  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR measurements were made on the Varian Mercury-400 spectrometer. Quantum-chemical simulations of the compounds 2a-h molecular geometry were performed by AM1 semiempirical method using the MOPAC 6.0 program [12].

### Absorption and Fluorescence Measurements

All the commercially available solvents for spectrophotometric investigations were additionally purified and dried according to the procedures described in [13]. Electronic absorption spectra were recorded on an Hitachi U3210 spectrophotometer. Spectrofluorimetric studies were conducted on an Hitachi F4010 spectrometer in standard 1 cm quartz cells in a thermostatted cell holder at 25°C. Fluorescence spectra were presented in

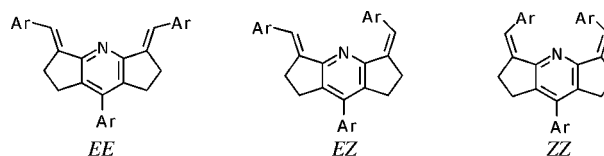
the energy-proportional wavenumber scale (the intensity was expressed as number of quanta per unit wavenumber range). Fluorescence quantum yields ( $\varphi_f$ ) in organic solvents were evaluated with respect to quinine bisulfate in 0.5 M aqueous sulfuric acid ( $\varphi_f = 0.546$  [14],  $\lambda^* = 380$  nm) with introduction of the squared refraction indices correction [15]. Fluorescence kinetic measurements were made on a home-made sub-nanosecond device working in the photon counting mode [16].

## RESULTS AND DISCUSSION

### Synthesis and Structure Confirmation

The condensation of appropriate aldehydes with cyclopentanone was fulfilled in the presence of ammonium acetate and hydrogen peroxide as a mild oxidizing agent. As was expected for the conditions used, formation of 6–8 products was detected by TLC. The titled pyridines were identified easily in such a complex mixture by their bright fluorescence. For all the compounds we obtained the data of mass-,  $^1H$ - and  $^{13}C$ -NMR spectrometry, which were in accord with the chemical structure expected for them (Table I). Stereochemical modelling shows that three types of geometric isomers can exist in this class of distyrylpyridines, that differ by the configuration of substituents at exocyclic C=C double bonds: *EE*-, *EZ*-, and *ZZ*-. Among them *EZ*- and *ZZ*-isomers are sterically hindered compounds with disturbed conjugation in their  $\pi$ -electronic systems, with styryl groups lying out of the plane of the pyridine moiety. The *EE*-isomer seems to be the least sterically hindered. For this reason we supposed the preferable formation of *EE*-isomers in the reaction conditions used. Owing to the increased planarity, *EE*-isomers of **2a-h** must differ from the *EZ*- and *ZZ*-isomers by higher fluorescence quantum yields. This was

indeed observed in the study of their fluorescence properties (Table II).



$^1H$ - and  $^{13}C$ -NMR data testify to the symmetric configuration of the molecules **2a-h**. The signals belonging to the atoms, groups or substituents in the positions 1–7, 2–6 and 3–5 coincide in the experimental spectra (symmetry group  $C_{2v}$ ). This result together with the fluorescence spectroscopy data confirms the *EE*-configuration of the synthesised compounds **2a-h**.

### Conformational Analysis

According to our quantum chemical simulations the spatial structures of compounds **2a-h** have to differ considerably by the planarity of their chromophoric moieties both in the ground (Fig. 1) and in the lowest singlet excited state. By this feature the investigated compounds can be classified in two groups:

- The molecules with the five-membered side aromatic rings: the preferably planar conformation is typical to them. Among all the compounds studied only **2h** belongs to this group.
- In the case of six-membered side aromatic cycles the molecules lose planarity as a result of the increased sterical hindrance. In such cases the aromatic rings at C-4 turn out of the plane of the pyridine moiety by up to  $50^\circ$  (compounds **2a-f**), while as distortions of planarity of their styryl residues were nearly twice lower. In the case of the *ortho*-substituted compound **2g** all three side

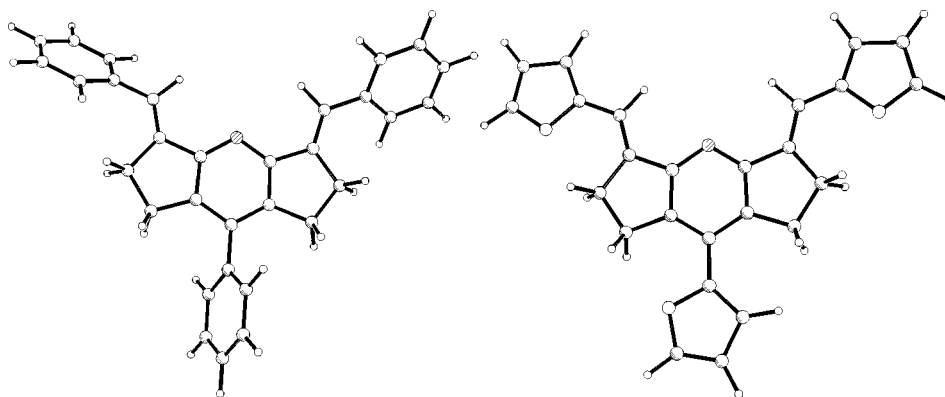
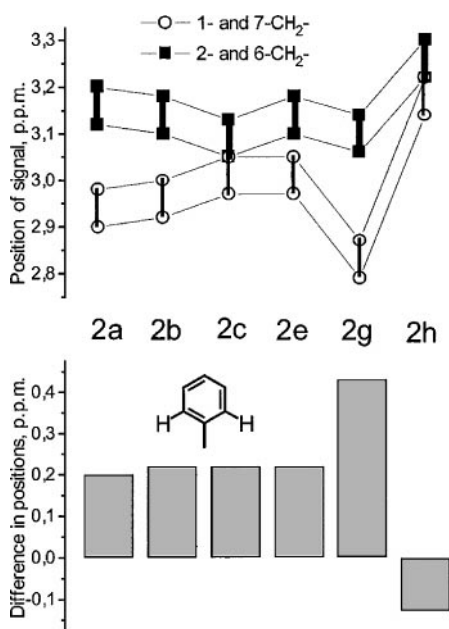


Fig. 1. Geometry of the compounds **2a** and **2h** (optimised by AM1 method).

rings were turned out of the plane of the pyridine nucleus to more substantial angles as a result of additional sterical hindrance.

The above presented geometrical considerations were supported by the data of **2a-h**  $^1H$ -NMR spectra. It is well known that spatial location of a proton out of the plane of the aromatic system causes a high-field shift of its signal in the NMR spectrum [17]. Compounds **2a-h** contain three aromatic rings, which could change their orientation with respect to the protons of neighbouring groups and thus render specific influence onto their NMR signal positions. Comparing the *ortho*-protons of the side aromatic substituents, signal positions for two conformationally different groups of compounds **2a-h** definite regularities can be deduced (Fig. 2). First of all it must be pointed out, that the compound **2h** the signal of *ortho*-proton of the furan moiety at C-8 is located in lower fields (7.61 p.p.m.) than the same signal of furylmethylidene residues at C-3 and C-5 (7.48 p.p.m., see Table III). In contrast to this, for all the other compounds **2a-g**, the signals of the *ortho*-protons of the aromatic cycle at C-8 lie in the higher fields compared with the signals of the same protons in styryl residues (such a behaviour is typical to the solutions both in low-polarity chloroform and in more polar dimethylsulfoxide). This constitutes the verification of the conformational difference of the compound **2h** from



**Fig. 2.** Bottom graph: values of difference in the positions of the signals of aromatic *ortho*-protons  $\delta(H_{\text{styryl}}) - \delta(H_{\text{C8}})$  in  $^1H$ -NMR spectra. Top graph: the positions of multiplets of methylene group protons. All data are taken from the Table III for the solutions in  $CDCl_3$ .

the other ones studied and supports the highest planarity for **2h** in solutions. For the compounds **2a-g** the aromatic moiety at C-8 is turned out of the plane of the pyridine nucleus at a substantial angle. The highest non-planarity was detected for the compound **2g**, where the difference in the positions of signals of *ortho*-protons reaches 0.43 p.p.m.

Additional arguments in favour of the planarity of compound **2h** were obtained from analysis of the positions of methylene groups proton signals (Table III). Depending on their spatial orientation with respect to the nearest aromatic ring, the latter could shield or deshield methylenic protons. The protons of methylenic groups in the positions 1 and 7 in the case of compound **2h** are the most deshielded as a result of their close to in-plane location with the neighbouring furan ring. In contrast, for the compound **2g** these protons are additionally shielded by the effect of "cyclic currents" of the aromatic residue at C-8, which lies out of the plane of the pyridine moiety. Thus, their signals are shifted to the higher field (Table III).

For all the compounds except **2h** it must be noted that the signals of methylene groups in the positions 2 and 6 have quite similar chemical shift values in the NMR spectra measured in  $CDCl_3$ . This fact reflects the existing similarity in torsion angles between pyridinic and styrylic aromatic rings which are located closely in space to the protons of methylene groups and thus have the most significant influence on them. The lowest-field positions of methylene group signals for the compound **2h** reflect once again the planar conformation of this molecule in solution.

### Absorption and Fluorescence Emission Spectra. Hydrogen Bond Formation

Electronic spectra of the synthesised distyrylpyridines were studied in solvents of different polarity and proton donor ability, such as hexane, toluene, acetonitrile and methanol (Table III). Compounds **2a-h** absorb light on the margin between the UV and visible spectral regions with molar extinctions from 20000 to 37000  $L \cdot mol^{-1} \cdot cm^{-1}$ . Their spectra demonstrate well-resolved vibrational structure. Band shape in the absorption and in the fluorescence spectra substantially differ one from another. Thus, in our case the positions of individual bands in the electronic spectra of **2a-h** were evaluated not by their formal maxima, but by the calculated centres of gravity of the spectral bands. The absorption and emission spectra of **2a** in hexane are presented in Fig. 3 together with their second derivatives (the position of the second peak in the derivative spectrum is usually in good correlation with the center of gravity for the structured spectral bands). The highest extinctions in the electronic absorption spectra

Table III.  $^1\text{H}$  NMR Data for Compounds **2a-h** Used to Elucidate Their Conformation

Compound	Solvent	$\delta_{\text{styryl}}^a$	$\delta(\text{C}_8)^a$	$\delta_{\text{styryl}} - \delta(\text{C}_8)$	2- and 6-CH <sub>2</sub> -groups, $\delta(\text{H})$	1- and 7-CH <sub>2</sub> -groups, $\delta(\text{H})$
<b>2a</b>	CDC <sub>3</sub>	7.59	7.39	0.20	3.12–3.20	2.90–2.98
<b>2b</b>	CDC <sub>3</sub>	7.54	7.32	0.22	3.10–3.18	2.92–3.00
<b>2c</b>	CDC <sub>3</sub>	7.60	7.38	0.22	3.05–3.13	2.97–3.05
<b>2d</b>	DMSO	7.05	6.90	0.15	3.09–3.17	2.95–3.03
		7.18	7.04	0.14		
<b>2e</b>	CDC <sub>3</sub>	7.51	7.29	0.22	3.10–3.18	2.97–3.05
	DMSO	7.45	7.32	0.13	2.96–3.04	2.88–2.96
<b>2f</b>	DMSO	7.41	7.29	0.12	2.98–3.06	2.90–2.98
<b>2g</b>	CDC <sub>3</sub>	7.13	6.70	0.43	3.06–3.14	2.79–2.87
<b>2h</b>	CDC <sub>3</sub>	7.48	7.61	–0.13	3.22–3.30	3.14–3.22

<sup>a</sup>Chemical shifts (p.p.m.) for *ortho*-protons of the styryl moieties or of the cycle at C-8 of pyridine moiety.

display the the dialkylamino compounds **2e,f**, which have the strongest electron donor substituents in the side aromatic rings.

Generally, quite low solvatochromism is typical of most of the studied pyridines. Only the dialkylamino derivatives **2e,f** show small positive solvatochromic effects (580–640  $\text{cm}^{-1}$ ) on going from aprotic DMF to proton donating methanol, which is the result of hydrogen bond formation with the protonic solvent molecules.

Another situation is observed in the fluorescence spectra: all the compounds studied **2a-h** display positive solvatofluorochromism. This shows much higher polarity of their excited S<sub>1</sub> states in comparison with the ground ones. The highest solvatofluorochromic shifts were demonstrated by dialkylamino derivatives **2e,f**. Hav-

ing insignificant shifts in the aprotic solvents such as hexane or DMF (960  $\text{cm}^{-1}$ ), these compounds display pronounced bathofluoric effects on going from DMF to methanol (2320  $\text{cm}^{-1}$ ). By their magnitude, the hydrogen bonding effects in the studied pyridine series are close to those shown by the ketocyanine dyes [7,18]. Taking into account the fact, that the observed solvent-induced shifts in fluorescence spectra of compounds **2e,f** are considerably higher with respect to those in absorption spectra, we can point out for them the significant increase in hydrogen bonding ability upon electronic excitation.

It is interesting to note that compounds **2a-h** in all the solvents studied have high and close values of fluorescence quantum yields, from 0.4 to 0.75 (Table II). The rather high fluorescence lifetimes (2–4 ns) testify to

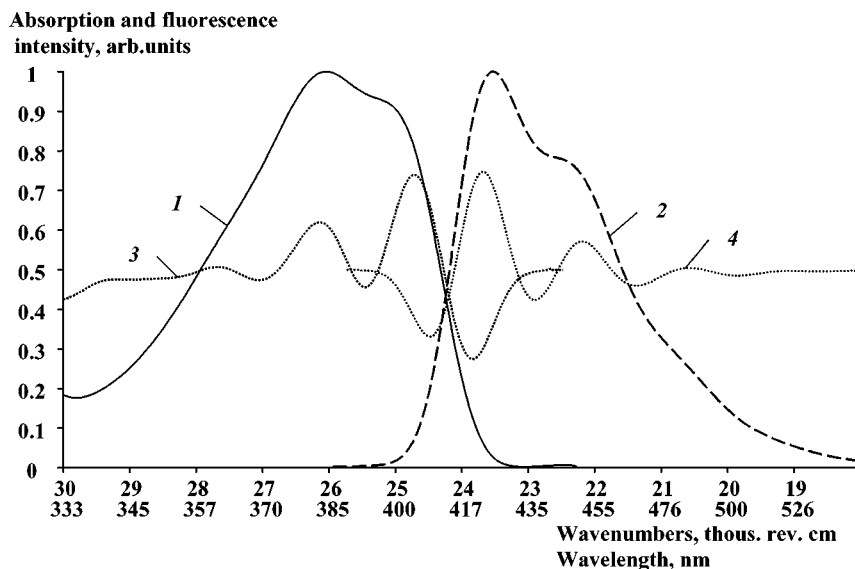


Fig. 3. Absorption (1) and fluorescence (2) spectra of the compound **2a** in hexane. The curves (3) and (4) are correspondingly their second derivatives (taken with negative sign).

the low probability of non-radiative deactivation for the studied compounds in the excited state. The exceptions are seen in the compounds **2e,f**, whose quantum yields in methanol solution falls down to 0.05–0.12. Together with this phenomenon the sharp decrease of fluorescence lifetime is typical to **2e,f** in this solvent. The behaviour described may be the result of appearance of a new channel of effective non-radiative deactivation. Analysing the data published on fluorescence properties of dialkylamino derivatives of conjugated organic compounds [19–23], we could consider the possible formation of low-emitting twisted intramolecular charge transfer states (TICT). An increase of intramolecular donor-acceptor interactions in the excited molecule enforced by hydrogen bond formation with the solvent might make easier the formation of non-radiative TICT states. In general line with this are somewhat lower but quite appreciable decreases of fluorescent lifetime in polar solvents observed for the most sterically hindered compound **2g**.

Finally, we would like to note that the conformational states of the molecules **2a-h** display themselves clearly not only in NMR, but also in the electronic spectra. Here the conformational effects can be highlighted at the comparison of the spectra of the compounds **2b** and **2g** with different electron donor properties of the side aromatic rings, which also differ by intramolecular steric hindrance. The similar positions of absorption bands of **2b** and **2g** in hexane (393 and 392 nm) testify about substantial deviation from planarity of the side rings for the last molecule in the  $S_0$  state. In the other case, the band of **2g** must be shifted towards the long wavelength region. Substantial differences in the absorption band positions of the compounds **2b** and **2h** (393 and 411 nm), especially if to consider higher  $\pi$ -electron donor ability of the anisyl residue in respect to the furyl one, confirms our assumption, that the **2h** molecule really exists in a more planar conformation, whereas in the **2b** molecule at least one cyclic moiety is twisted out of the plane of the pyridine nucleus in  $S_0$  state. This statement is proved additionally by the comparison of fluorescence Stokes shift values for **2b**, **2g** and **2h** in hexane (Table II). As for the majority of another classes of non-planar sterically hindered compounds [23–25], whose molecules become more planar in the excited state, a substantially enlarged Stokes shift was observed for **2g** in respect to the compounds **2b** and **2h**.

Like the compound **2g**, dialkylamino-derivatives **2e,f** are characterized by enhanced fluorescence Stokes shift values, especially in polar solvents. This fact could be explained by the substantial increases of their dipole moments in the excited state due to the high electron donor ability of dialkylamino groups.

## CONCLUSIONS

Owing to the unique chemical structures of distyrylpyridines **2a-h** there is an opportunity to determine their preferred geometry in solutions from the analysis of their  $^1H$ -NMR spectra. The spectral data confirm the planar conformation for the compounds with side five-membered aromatic rings. The steric hindrance appears in the case of six-membered aromatic cycles, which induces definite deviation from planarity of such molecules but only slight distortion of conjugation between their fragments. In the cases when additional steric hindrance exists (*ortho*-substituents in the side rings), the planarity of styryl fragments, and especially—the conjugation of pyridine moiety with the cycle at C-8 decreases substantially.

The intramolecular charge transfer from the side aromatic ring to the central pyridine moiety takes place at excitation of the studied distyrylpyridine molecules. In the excited  $S_1$  state many of them must become more planar as well. The electronic and steric effects of substituents have their clear reflection in the electronic spectra of several representatives of the series studied, demonstrating the increased fluorescence Stokes shifts.

The synthesised compounds are dyes with bright fluorescence in solutions. Having close enough positions of absorption bands they show substantial changes in the fluorescence band positions with the modification of the electron donor properties of side substituents. The titled distyrylpyridines demonstrate substantial positive solvatochromism only for dialkylamino-derivatives on exchange of aprotic solvent to proton donor ones.

The results presented in this paper suggest good prospects for the using the structurally rigid distyrylpyridine derivatives as fluorescence probes for various purposes.

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