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2,6-DISTYRYLPYRIDINES – SYNTHESIS AND SPECTRAL PROPERTIES

A group of structurally rigid analogues of 2,6-distyrylpyridine have been synthesised. The molecular geometry of the synthesised compounds in solutions was studied by 1H -NMR spectroscopy, electron absorption and fluorescence spectra were measured as well. The spectral data testify all the compounds exist in E-configuration of their styryl residues. The most planar molecular conformation is typical to the compounds with five-membered terminal aromatic moieties. In the case of six-membered terminal groups the steric hindrance appears, which results in turning the above mentioned cyclic groups out of the plane of the molecule. The violation of planarity in this case is not very significant and makes possible remaining of π -electronic conjugation in such molecules.

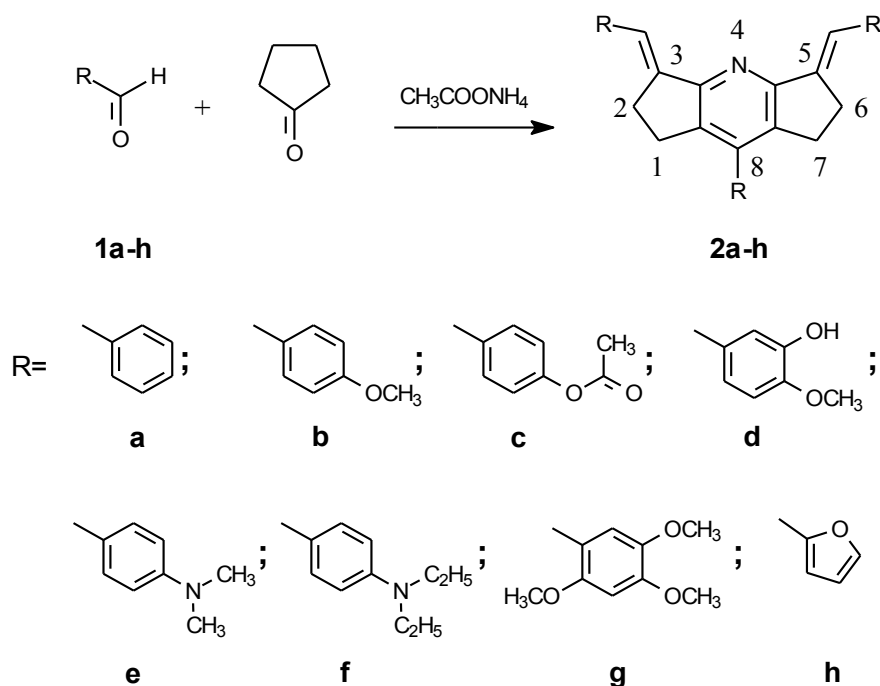
The synthesised compounds are characterized by quite high fluorescence quantum yields in solutions. The electronic absorption spectra of titled pyridines demonstrate low sensitivity to the nature of the substituents introduced into their side aromatic rings. In contrary to this, fluorescence band substantially changes its position under the influence of introduced electron donor substituents. The fluorescence spectra of the studied compounds display substantial positive solvatochromism only in the case of dialkylamino-derivatives, especially on going from aprotic solvents to proton donor ones. Generally, the synthesised structurally rigid distyrylpyridine derivatives have all prospects for their application as multi-purposes fluorescent probes.

Only a few classes of fluorescent organic dyes have been found their successful application in science and technology. The most known among them are xanthenes, coumarins, naphthalimides, cyanines, various aryl-azoles, acridines, phenoxazines, etc [1]. By their chemical structure, most of these dyes are the condensed heterocyclic compounds with the extended conjugated π -electronic system. Mechanic rigidity of such compounds leads to reducing the quantity of vibrational and rotational degrees of freedom and to the lowering the non-radiative losses of the excitation energy. The latter results in the substantial increasing of their fluorescence quantum yields. The presence of heteroatoms (nitrogen, oxygen or sulphur) in the above mentioned molecules usually do not reduce the brightness of their fluorescence, but possess considerable effect onto another optic characteristics, for example, molar extinction or band positions in the absorption and fluorescence spectra. The last mentioned

changes in optical properties of the organic molecules at their chemical modification can be foreseen by the quantum-chemical simulations. However, fluorescence quantum yield is a hardly predicted parameter for the most of organic molecules. On this reason, an experimental discovery of a new classes of highly fluorescent compounds retains its importance last time.

Taking into account the data published, in our studies of ketocyanine dyes synthesis we were forced to conclude that similar starting compounds - aromatic aldehydes and cyclopentanone in the conditions of Chichibabin reaction could give rise a new class of nicely fluorescent molecules which are the pyridine derivatives with structurally fixed styryl moieties. Fluorescent properties of such substances have not been discovered yet. Together with our recently studied ketocyanines they belong to the wide group of the so-called cross-conjugated molecules, where their pyridine residue serves as π -electron density acceptor. The rigidised distyryl pyridines with electron donor substituents might possess advanced solvatofluorochromic properties. Structural rigidity of these 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 structure in the desired directions. For example, for extending the length of their π -conjugated system the polycyclic aromatic aldehydes could be used. The application of aromatic aldehydes with appropriate chelating unit might yield a new fluorescent ion indicators creation. The possible protonation of the highly basic nitrogen atom of pyridine moiety have to lead to substantial changes in absorption and fluorescence spectra. The last feature could be used in the design of a new fluorescent pH sensors. Thus, in such distyrylpyridine derivatives we have observed all prospects for the developing on their skeleton unit various multi-purpose fluorescent sensors for a great amount of the practically important applications.

Our aim in this work was to synthesise and to study the chemical structure and fluorescence properties of the eight simplest representatives of the structurally rigid distyrylpyridines **2a-h** that differ by their steric constitution and π -electron donor properties of substituents in the side aromatic moieties.



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

Distyrylpyridines **2a-h** synthesis was fulfilled by the improved procedure, initially taken from [2]. For example, 8-(4-diethylaminophenyl)-3,5-di[(*E*)-1-(4-diethylaminophenyl)methylidene]-1,2,3,5,6,7-hexahydrodicyclopenta[*b,e*]pyridine (**2f**) was prepared by 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 hour 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™, grade 643, 200-425 mesh) using chloroform-methanol mixture (98:2, v/v) as the elutriator. 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). ¹³C NMR spectrum (75 MHz, in CDCl₃) for compound **2g** (p.p.m.): quaternary carbons: 164.29; 147.29; 146.44; 143.36; 140.33; 138.23; 129.06; 124.19; tertiary carbons: 133.49; 132.54; 121.51; 111.58; 111.16; secondary carbons: 44.35; 44.30; 29.51; 28.18; primary carbons: 12.68.

Compound **2c**, 8-(4-acetoxyphenyl)-3,5-di[(*E*)-1-(4-acetoxyphenyl)methylidene]-1,2,3,5,6,7-hexahydrodicyclopenta[*b,e*]pyridine, was prepared from 4-hydroxybenzaldehyde by the similar way, with additional boiling of crude material (about 2 g), collected after completion of the first stadium, during 20 minutes with mixture of pyridine (15 ml) and acetic anhydride (15 ml). Then the reaction mixture was cooled and poured into water (100 ml). The formed precipitate 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** have been collected in the tables 1 and 2. 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, 5x20 cm (Selecto Scientific, USA) with chloroform-methanol mixtures (98:2, 9:1, 85:15, v/v) used as elutriators.

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

All the commercially available solvents for spectrophotometric investigations were additionally purified and dried according to the procedures described in. Electronic absorption spectra have been recorded on Hitachi U3210 spectrophotometer. Spectrofluorimetric studies have been conducted on Hitachi F4010 spectrometer in the standard 1 cm quartz cells in a temperature-controlled cell

holder at 25°C. Fluorescence spectra were presented in the energy-proportional wavenumber scale (the intensity has been expressed in a number of quanta per unit wavenumber range). Fluorescence quantum yields (ϕ_f) in organic solvents were evaluated in respect to quinine bisulfate in 0.5 M aqueous sulfuric acid ($\phi_f = 0.546$, $\lambda^* = 380$ nm) with introduction of the squared refraction indices correction. Fluorescence kinetics measurements were made on the home-made sub-nanosecond device working in the photon counting mode.

The synthesised compounds are the dyes with rather bright fluorescence in solutions. Having close enough positions of absorption bands they show substantial changes in the fluorescence bands positions at 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 facts presented in this paper testify good prospects for the using of the structurally rigid distyrylpyridine derivatives as fluorescence probes for various purposes.

References

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