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1,5-DIARYL-3-BENZIMIDAZOLYL-2-PYRAZOLINES AND PYRAZOLES – NOVEL FLUORESCENT DYES OF PYRAZOLINE FAMILY

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A series of novel aryl derivatives of 2-pyrazoline bearing 2-benzimidazolyl moiety was synthesized via condensation of corresponding chalcones with phenyl hydrazine. Pyrazoles on their background were obtained by the optimized oxidation procedure with manganese dioxide in benzene. Fluorescent characteristics of the title compounds were determined for their solutions in acetonitrile. Quantum-chemical modeling of molecular structure, UV/Vis spectra, electron density redistribution and structural relaxation at electronic excitation resulting in high fluorescence Stokes shifts were conducted as well.

Keywords: pyrazoline, pyrazole, benzimidazole, organic synthesis, fluorescence, quantum-chemical modeling, ESSA.

Introduction

Derivatives of 2-pyrazoline with aryl radicals in positions 1, 3 and 5 are known from the middle 50-th as blue-to-green fluorescent dyes, possessing relatively high quantum yields [1,2]. During decades of their history, fluorescent pyrazolines had found wide practical application as optical brightening agents [3,4], spectra shifters in scintillation techniques [5,6], components of electroluminescent devices [7-9], fluorescent ligands for metals cations [10-14], intracellular pH probes [15,16], etc. They were extensively studied in the crystalline state [17], polymer matrices [9,18], in Langmuir-Blodgett films [19] and in donor-acceptor molecular complexes with electron-deficient compounds [20,21]. Several representatives of this class demonstrated physiological activity and were tested as potential medical drugs, see for example [22,23].

1,3,5-triaryl substituted pyrazoles being oxidation products of the parent pyrazolines were considered earlier to fluoresce at shorter wavelengths with lower quantum yields [24]. Interest to 1,3,5-triaryl substituted pyrazoles was reasoned also by the fact, that they are potential products of chemical and/or photochemical oxidative processes [25], which often take place at practical application of parent pyrazolines.

Another heterocyclic unit of the title compounds, benzimidazole bicycle, is widely used for constructing fluorescent materials. SCOPUS database reports more than 1400 references on this request, its biological applications are much wider …

Quite unexpected to us is the limited number of publications devoted to aryl pyrazolines with benzimidazole moiety [26-30]. Most of these papers are focused on their synthesis, and only a few ones – on the investigation of luminescent properties [31,32] and their application as fluorescent sensing compounds [33]. No examples of the synthesis of benzimidazolic pyrazoles by direct oxidative procedure were reported, however, a few compounds of this family were obtained by alternative synthetic procedure [34].

Thus, the main purpose of this communication is to synthesize a series of new fluorescent benzimidazloic pyrazolines, then – to convert them into pyrazoles (via oxidative aromatization of the main heterocycle) with the aim to study spectral properties of both sub-series of the dyes.

In 1,3,5-triarylpyrazoline system synthesis on the basis of isomeric benzimidazolic chalcones [35,36], the benzimidazole unit may appear in positions 3- or 5- of pyrazoline cycle. Here we do not consider the last possibility, because in such a case 5-aryl moiety is out of conjugation with the main chromophoric fragment of the molecule, 1,3-diaryl-2-pyrazoline. In most cases substituents in position 5 of pyrazoline cycle have no effect on fluorescent characteristics at all, however, several publications reported dramatic decreasing of fluorescence quantum yields in case of introducing into position 5 electron-withdrawing groups or polycyclic aromatic moieties like anthracene [37-40].

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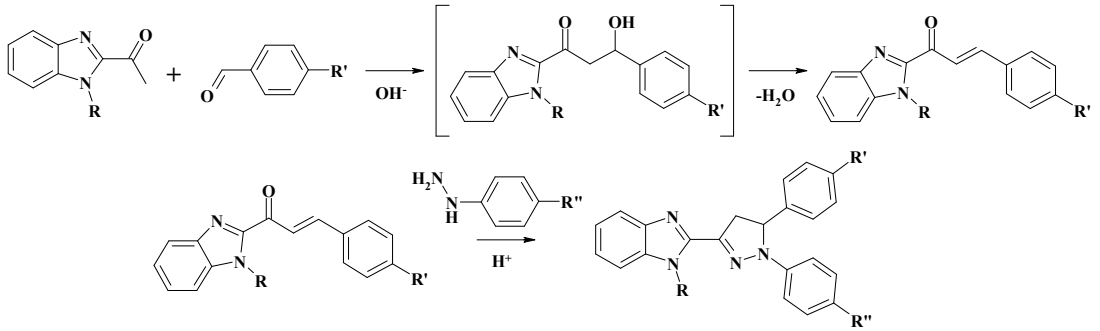
Experimental

The required chemicals were purchased from Aldrich local representatives in Ukraine. Commercially available acetonitrile was additionally purified by distillation before spectra measurement.

The 1,5-diaryl-3-benzimidazolyl-2-pyrazolines were synthesized from corresponding chalcones (products of condensation of 2-acetylbenzimidazole with aromatic aldehydes) and phenylhydrazine under acidic catalysis:



The final cyclization could be conducted in the presence of base catalyst as well. However, this leads to lower yields of target products.

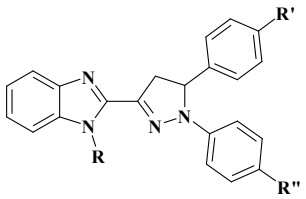
Synthesis of benzimidazolic chalcones. 50% aqueous NaOH was added dropwise to saturated solution of 2-acetylbenzimidazole 10 mmol (1.6 g) and an appropriate aldehyde (10 mmol) in ethanol until appearance of yellow color. The reaction mixture allowed staying overnight, and then neutralized by 5% aqueous acetic acid. The precipitate was filtered off, dried on air and crystallized from ethyl alcohol or acetic acid.

In several cases the base-catalyzed Claisen-Schmidt condensation yielded intermediate products of aldol-type (see the above scheme, in square brackets), which conversion to corresponding chalcones was conducted by boiling in acetic acid under periodic TLC control.

Cyclization of benzimidazolic chalcones to pyrazolines. 20 mmol of substituted 1-(2-benzimidazolyl)-3-aryl-propenone was dissolved in boiling ethyl alcohol and then 20 mmol of arylhydrazine and several drops of concentrated HCl was added. The reaction mixture was heated until the beginning of precipitation, than kept overnight at room temperature. The precipitate was filtered off, dried on air and crystallized from ethyl alcohol.

The molecular formulae and physico-chemical characteristics of the synthesized benzimidazolic pyrazolines are presented in Table 1. The evidence for their successive synthesis is the appearance of fluorescence and characteristic ABC signals system of pyrazoline cycle in ^{1}H NMR spectra.

Table 1. The main physico-chemical characteristics of the synthesized 1,5-diphenyl-3-(2-benzimidazolyl)-pyrazolines.



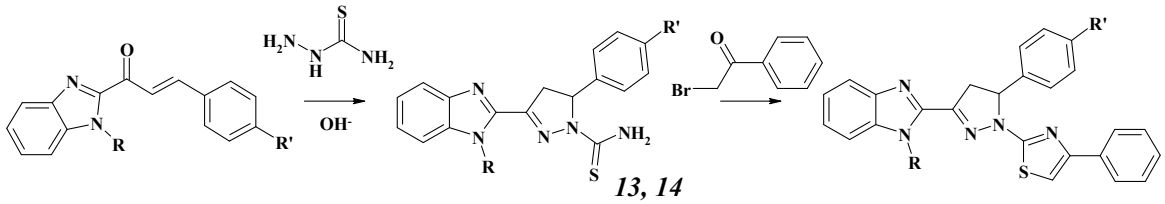
Compound	R	R’	R”	M.P. °C	Yield, %	Element composition	Found, N% / Calc., N%	^{1}H NMR data
1	H	H	H	250°	55	$C_{22}H_{18}N_4$	16.59/ 16.56	3.43 (1H, dd, J=6.4, 11.0 Hz); 4.23 (1H, dd, J=4.2, 13.4 Hz); 5.80 (1H, dd, J=6.4, 6.4 Hz); 6.82-7.77 (14H, m); 12.8 (1H, s, NH)
2	CH_3	H	H	170°	50	$C_{23}H_{20}N_4$	15.93/ 15.90	3.48 (1H, dd, J= 6.4, 11.1 Hz); 3.90 (3H, s,NCH3); 4.25 (1H, dd, J=4.2, 13.4 Hz); 5.81 (1H, dd, J=6.4, 6.4 Hz); 6.93-7.88 (14H, m)

Continuation of table 1.

Com-pound	R	R'	R"	M.P. °C	Yield, %	Element composition	Found, N% / Calc., N%	^{1}H NMR data
3	H	CH_3O	H	265°	55	$C_{23}H_{20}N_4O$	15.20/ 15.21	3.45 (1H, dd, J=6.7, 11.1 Hz); 3.75 (1H, s, OCH3); 4.30 (1H, dd, J=4.2, 13.6 Hz); 5.67 (1H, dd, J=6.4, J=6.6); 6.93-7.88 (13H, m); 12.89 (1H, s, NH)
4	CH_3	CH_3O	H	165°	49	$C_{24}H_{22}N_4O$	14.67/ 14.65	3.77 (3H, s, NCH3); 3.89 (1H, s, OCH3); 4.35 (1H, dd, J=6.4, 11.4 Hz); 5.30 (1H, dd, J=4.2, 13.4 Hz); 5.95 (1H, dd, J=6.4, 6.4 Hz); 6.51-7.56 (13H, m)
5	H	$(CH_3)_2N$	H	240°	52	$C_{24}H_{23}N_5$	18.38/ 18.36	2.52 (6H, s, N(CH3)2); 3.40 (1H, dd, J=6.4, 11.1 Hz); 4.21 (1H, dd, J=4.2, 13.6 Hz); 5.80 (1H, dd, J=6.4, 6.4 Hz); 6.75-7.67 (13H, m); 12.8 (1H, s, NH)
6	CH_3	$(CH_3)_2N$	H	194°	50	$C_{25}H_{25}N_5$	17.70/ 17.71	2.52 (6H, s,N(CH3)2); 3.91 (3H, s, NCH3); 4.30 (1H, dd, J=6.4, 11 Hz); 5.26 (1H, dd, J=4.2, 13.4 Hz); 5.88 (1H, dd, J=6.3, 6.4 Hz); 6.69-7.71(13H, m)
7	H	F	H	235°	50	$C_{22}H_{17}FN_4$	15.75/ 15.72	3.45 (1H, dd, J=6.4, 11.1 Hz); 4.25 (1H, dd, J=4.4, 13.4 Hz); 5.79 (1H, dd, J=6.4, 6.4 Hz); 6.79-7.81 (13H, m); 13.0 (1H, s, NH)
8	H	Cl	H	243°	55	$C_{22}H_{17}ClN_4$	15.01/ 15.03	3.44 (1H, dd, J=6.4, 11.1 Hz); 4.23 (1H, dd, J=4.2, 13.4 Hz); 5.80 (1H, dd, J=6.4, 6.4 Hz); 6.80-7.69 (13H, m); 13.0 (1H, s, NH)
9	H	Br	H	250°	52	$C_{22}H_{17}BrN_4$	13.45/ 13.43	3.44 (1H, dd, J=6.6, 11 Hz); 4.22 (1H, dd, J=4.2, 13.6 Hz); 5.80 (1H, dd, J=6.4, 6.3 Hz); 6.81-7.69 (13H, m); 13.0 (1H, s, NH)
10	CH_3	Br	H	258°	48	$C_{23}H_{19}BrN_4$	13.00/ 12.99	3.45 (1H, dd, J=6.4, 11.2 Hz); 3.88 (3H, s, NCH3); 4.23 (1H, dd, J=4.2, 13.4 Hz); 5.81 (1H, dd, J=6.4, 6.4 Hz); 6.69-7.69 (13H, m)
11	H	H	Cl	199°	55	$C_{22}H_{17}ClN_4$	15.02/ 15.03	3.44 (1H, dd, J=6.4, 11 Hz); 4.23 (1H, dd, J=4.2, 13.4 Hz); 5.81 (1H, dd, J=6.4, 6.4 Hz); 6.80-7.69 (13H, m) 13.0 (1H, s, NH)
12	H	H	Br	205°	50	$C_{22}H_{17}BrN_4$	13.44/ 13.43	3.44 (1H, dd, J=6.4, 11 Hz); 4.22 (1H, dd, J=4.2, 13.6 Hz); 5.80 (1H, dd, J=6.4, 6.4 Hz); 6.81-7.69 (13H, m); 13.0 (1H, s, NH)

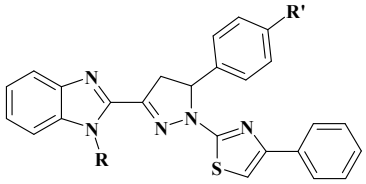
Replacing phenylhydrazine by thiosemicarbazide and boiling the reaction mixture during 6 hours with addition of 1 ml of 10% aqueous NaOH resulted in obtaining of 3,5-diaryl-1-thiocarboxamido-2-pyrazolins (***13***, ***14***). The latter are considered as semi-products only and thus were not characterized spectrally.

Their interaction with α-bromo-acetophenone at 2 hours boiling in ethanol solution leads to 3,5-diaryl-1-(3-phenyl-thiazol-2-yl)-2-pyrazolines (***15***, ***16***, Table 2).



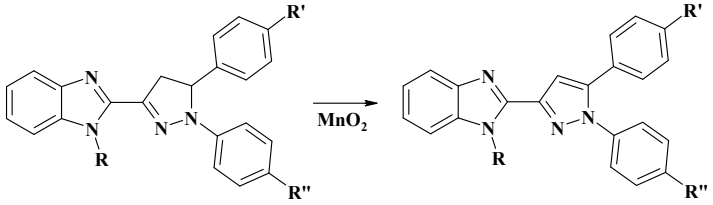
13, 14

Table 2. The main physico-chemical characteristics of the synthesized 3,5-diaryl-1-(3-phenyl-thiazol-2-yl)-2-pyrazolines.



Com-pound	R	R'	M.P. °C	Yield, %	Element composition	Found, N% / Calc., N%	^{1}H NMR data
15	H	H	240°	75	$C_{25}H_{19}N_5S$	16.60/ 16.61	3.63(1H, dd, J=7.1, 11.0 Hz); 4.34 (1H, dd, J=5.4, 12.7 Hz); 5.93 (1H, dd, J=5.6, 7.1 Hz); 7.17-7.82(15H, m); 12.9 (1H, s, NH)
16	H	CH_3O	215°	75	$C_{26}H_{21}N_5OS$	15.50/ 15.51	3.44 (1H, dd, J=6.4, 11.2 Hz); 3.71(1H, s, OCH3); 4.16 (1H, dd, J=5.6, 12.2 Hz); 5.81(1H, dd, J=5.6, 6.4 Hz); 6.91-7.76(14H, m); 12.9(1H, s, NH)

Oxidation of pyrazolines into pyrazoles. Solutions of 10 mmol of corresponding pyrazoline in toluene were boiled with 2 g of activated MnO_2 during 2-5 hours under the periodic TLC control. Then, solid inorganic components were filtered off, the toluene solution was evaporated to dryness under reduced pressure. The precipitate, obtained by solidification of resulting amorphous mass by addition of small amount of isopropyl alcohol, was filtered off and crystallized from ethanol.



The main physico-chemical characteristics of pyrazoles, synthesized in such a way are presented in Table 3. The characteristic feature in their ^{1}H NMR spectra is the disappearance of pyrazoline cycle ABC signals system and appearance of a low-field singlet at 8.1-8.3 ppm, which we attribute to pyrazole ring proton in position 4.

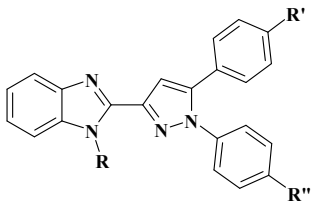
Let us note that we failed to oxidize pyrazolines with N,N-dimethylamino group in phenyl-5: all starting compounds returned unchanged. Thus we concluded that strong electron donor groups in this moiety prevent oxidation of pyrazoline cycle. Analogous observations were reported earlier [41].

UV-Vis absorption spectra were measured on Hitachi U-3210 spectrophotometer, fluorescence spectra and quantum yields - on Hitachi F-4010 spectrofluorimeter in rectangular 1 cm quartz cells. Absolute fluorescence quantum yields of the title compounds (φ_X) were estimated by relative method using *quinine sulfate* as quantum yield standard and the following equation, where φ_0 – absolute quantum yield of quinine in aqueous 0.5 M sulfuric acid (0.546 [42]); $I_F(\nu)$ – fluorescence intensity in wavenumber scale; A_X, A_0 – absorbencies of the sample and reference solutions on the excitation wavelength; n_X, n_0 – refraction indices of the above solutions. The refraction indices squared correction was introduced owing to significant difference in refractions of the sample and reference solutions [43,44].

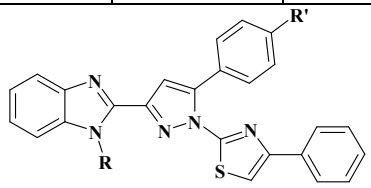
$$\varphi_X = \varphi_0 \frac{\int I_F^X(\nu)d\nu}{\int I_F^0(\nu)d\nu} \cdot \frac{(1-10^{-A_0})}{(1-10^{-A_X})} \cdot \frac{n_X^2}{n_0^2}$$

Molecular structure and electronic spectra of target compounds were modeled by quantum-chemical calculations in *b3lyp/cc-pvdz* scheme [45, 46]. The following program packages were used: Gaussian-09 (B.01) [47] (for optimization of molecular structure in the ground and in the excited states) and NWChem (5.1) [48] (upgraded by the special module for ESSA, "*excited state structural analysis*" [49, 50] – for calculation of electronic absorption spectra and analysis of the electron density redistribution at electronic excitation).

Table 3. The main physico-chemical characteristics of 1,5-diphenyl-3-(2-benzimidazolyl)-pyrazoles, synthesized via oxidation of corresponding pyrazolines.



Com-pound	R	R'	R"	M.P. °C	Yield, %	Element composition	Found, N% / Calc., N%	^{1}H NMR data
17	H	H	H	119°	50	$C_{22}H_{16}N_4$	16.67/ 16.65	7.14-7.69 (14H, m); 12.93 (1H, s, NH)
18	CH_3	H	H	101°	52	$C_{23}H_{18}N_4$	16.01/ 15.99	3.93 (1H, s, NCH_3); 7.05-7.63 (14H, m)
19	H	CH_3O	H	105°	56	$C_{23}H_{18}N_4O$	15.31/ 15.29	3.71 (3H, s, OCH_3); 7.14-7.71 (13H, m); 12.98 (1H, s, NH)
20	CH_3	CH_3O	H	155°	55	$C_{24}H_{20}N_4O$	14.72/ 14.73	3.75 (3H, s, OCH_3); 4.01 (3H, s, NCH_3); 7.03-7.89 (13H, m)
21	H	F	H	130°	50	$C_{22}H_{15}FN_4$	15.83/ 15.81	7.10-8.01 (14H, m); 12.95 (1H, s, NH)
22	H	Cl	H	108°	50	$C_{22}H_{15}ClN_4$	15.13/ 15.11	7.11-7.99 (14H, m); 12.95 (1H, s, NH)
23	H	Br	H	115°	45	$C_{22}H_{15}BrN_4$	13.52/ 13.49	7.15-7.87 (14H, m); 12.90 (1H, s, NH)



Continuation of table 3.

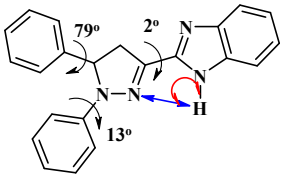
Com-pound	R	R'	M.P. °C	Yield, %	Element composition	Found, N% / Calc., N%	^{1}H NMR data
24	H	H	275°	58	$C_{25}H_{17}N_5S$	16.71/ 16.69	7.12-7.60 (15H, m); 12.63 (1H, s, NH)
25	H	CH_3O	278°	60	$C_{26}H_{19}N_5OS$	15.60/ 15.58	3.83 (3H, c, OCH_3); 7.05-8.03 (15H, m); 13.06 (1H, s, NH)

Results and discussion

3.1. Quantum-chemical modeling

According to our quantum-chemical calculations, molecules of unsubstituted compounds of both pyrazoline (***1*** and ***15***) and pyrazole (***17*** and ***24***) sub-series are substantially unplanar. Typical angles

between the mean planes of their heterocyclic moieties and benzene rings are presented on the following scheme:



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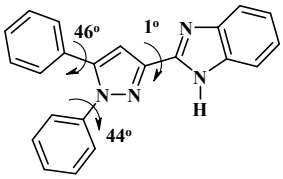


17

As expected, side phenyl residue in position 5 of pyrazoline cycle, which is not included into the main π-conjugated chromophoric system of this molecule (***1***), is practically orthogonal to the mean plane of pyrazoline cycle. Substantial pyramidalization is typical to the nitrogen atom in position 1, which manifests itself in 2-3° deviation of the sum of its valence angles from the value expected for ideal sp^2 hybrid state (360°). Another indication of pyramidalization is the distance from N1 atom to the plane drawn through its three neighboring atoms (~0.12 Å). Benzimidazole and pyrazoline moieties lie practically in the same plane with the angle between their mean planes within 1-2°.

First, we have to check the existence of intramolecular hydrogen bond between the benzimidazole N-H group and pyrazoline nitrogen atom in position 2. The distance between these acidic and basic centers was estimated as 2.6-2.7 Å, this retains just theoretical possibility for existence of weak hydrogen bonding. However, the N-H···N angles for the modeled compounds is near 91-93°, this contradicts with one of the general criteria for H-bond formation [51, 52]. Finally the existence or absence of intramolecular hydrogen bonding was elucidated with the application of R.F.W. Bader AIM (atoms in molecules) theory [53, 54]. The H-bond critical point (-3,1) was not detected in space between the corresponding N and H centers, thus we had to exclude the possibility of existence of H-bonding. From another point of view, the purely electrostatic interaction between these oppositely charged atoms could be among the factors, which favor space arrangement of the pyrazoline and benzimidazole moieties in the common plane.

Concerning the thiazolic derivative ***15***, its side benzene ring, connected to thiazole cycle position 4', is not included in direct conjugation with pyrazoline unit of this molecule, thus we do not expect its significant influence on the spectral properties of the main chromophore of ***15***.

Oxidation of pyrazoline heterocycle to pyrazole one does not result in formation of fully-conjugated system, because of significant steric repulsion between the cyclic subunits in positions 1 and 5 of pyrazole moiety. In case of compound ***17***, the discussed 1- and 5- benzene rings form angles of 44-46° with the pyrazole cycle. In case of 1-thiazolic derivative ***24***, thiazole and pyrazole rings are almost coplanar (with the angle between their planes of 7-8°), however, phenyl-5 in this case rotates around its single bond to pyrazole cycle on 52°, indicating significant violation of conjugation.

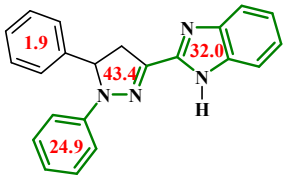
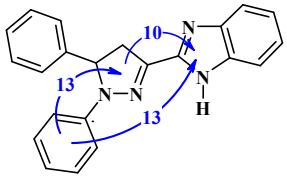
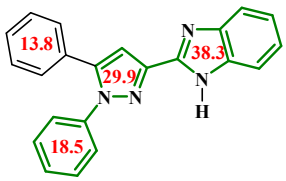
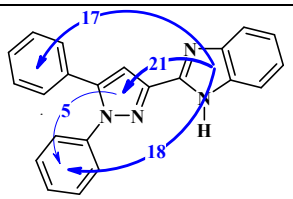
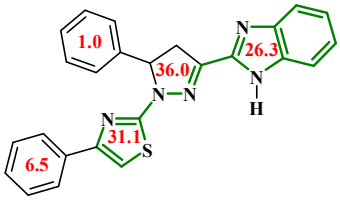
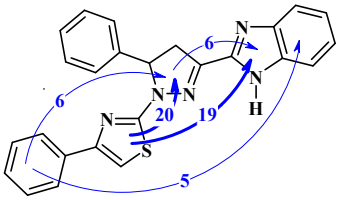
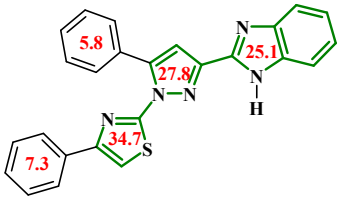
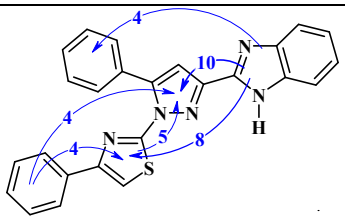
Resuming the molecular structure simulations, one can conclude, that the main chromophoric unit of compounds of pyrazoline series includes benzimidazole bicycle, π-conjugated C=N-N part of pyrazoline cycle and aromatic moiety (phenyl or thiazolyl) in position 1. In case of the most of investigated pyrazoles, their chromophoric system includes benzimidazole and pyrazole subunits with the special situation of compound ***24*** and ***25***, when it extends to thiazole ring as well. Other aromatic moieties of the title compounds fall out of their chromophoric system and have minor influence on their optical characteristics.

Electronic spectra and electron density redistribution at electronic excitation were modeled with ESSA approach [49, 50], which requires calculation and analysis of several special quantum-chemical indices: 1) the electronic excitation numbers (L_i) reflect the participation of distinct atoms and more complicated moieties in formation of a given electronic transition (in %); the charge transfer indices (l_{ij}) reflect the redistribution of electron density in a molecule at electronic excitation to a given excited state (% of the elementary electric charge). The latter indices are much more informative compared to traditional *net charge changes*, calculated by the most of quantum-chemical software, because they show also the directions of charge transfer between the distinct atoms and moieties of the excited molecule. The ESSA is the generalization of the earlier π-electronic approach [55] to the contemporary TDDFT calculation schemes. The ESSA data for several most typical compounds of the investigated series are presented in Table 4.

Higher electronic excitation indices (L_i) help to define the chromophoric systems of the title molecules (see Table 4, in which data for long-wavelength electronic transitions are shown). Thus, for pyrazolines ***1*** and ***15***, the main chromophore includes the central heterocycle and (hetero)aromatic moieties in its positions 1 and 3. Participation in electronic excitation is miserable for phenyl-5 and quite low for "thiazolic" side benzene ring. First of them is not conjugated with the main π-system of the discussed molecules, while second one is not in *direct polar conjugation* (i.e., connected to analog of *meta*-position in benzene ring). However, definite interaction of the above mentioned side phenyls with the main chromophoric unit of their molecules still remains in case of thiazole-substituted compounds ***15*** and ***24***: the long-wavelength electronic transitions demonstrate substantial bathochromic shift.

As it follows from the data of Table 4, benzimidazole bicycle plays a role of electron withdrawing center in respect to pyrazoline moiety at the electronic transition of compound ***1*** to its lowest singlet excited state. Increase of electron density on the benzimidazole moiety reduces the S_1 state acidity of benzimidazolic N-H group, thus no photochemical activity connected with its possible excited state dissociation is expected.

Table 4. Energy, localization and electron density redistribution of the long-wavelength transitions S_0-S_1 in the electronic spectra of several model benzimidazolic pyrazolines and pyrazoles in ESSA approach.

Compound	Electronic transition S_0-S_1	Electronic excitation localization numbers (L_i)	Charge transfer indices (l_{ij})
1	26860 cm^{-1} 372 nm f = 0.83 Δμ = 10 D		
17	31900 cm^{-1} 314 nm f = 0.32 Δμ = 21 D		
15	25360 cm^{-1} 394 nm f = 0.57 Δμ = 18 D		
24	28700 cm^{-1} 348 nm f = 0.48 Δμ = 4 D		

Here: f – electronic transition oscillator strength, Δμ – vector difference of the ground and excited state dipole moments (directly reflecting the direction and amount of redistributed electron density). The main chromophoric fragments of compounds ***1***, ***17***, ***15***, ***24***, localization of electronic transitions on which is close or exceeds "*all-molecule average value*", are highlighted in green color.

Aromatization of pyrazoline ring to pyrazole one principally changes the directions of the excited state electron density redistribution (compare compounds ***1*** with ***17***, ***15*** with ***24***). The benzimidazole moiety becomes an electron donor in respect to the pyrazole one.

The excited state intramolecular donor-acceptor interaction intensifies at replacing of phenyl-1 by thiazolyl-phenyl subunit. This reflects itself in nearly doubling of the ground-to-excited state dipole

moments vector difference, Δμ, for the long-wavelength electronic transition of ***15*** compared to ***1***. This circumstance allows expecting strong solvatochromic and solvatofluorochromic effects for the compounds of this sub-series.

The obvious exception is the case of compound ***24***, which Δμ value is quite low owing to the specific excited state electron density redistribution from the periphery to the central part of this molecule.

The excited state geometry of the investigated molecules was modeled in TD-DFT scheme. Generally, enlarged fluorescence Stokes shifts are typical to 1,3,5-triphenyl-substituted pyrazolines and pyrazoles (see section 3.2). Definite excited state structural relaxation processes could be among the reasons of such behavior, which make the initially unplanar unexcited molecule more planar and more conjugated in its fluorescent S_1-state [56-59]. This results in additional decrease of the energy of structurally relaxed excited state and corresponding Stokes shift enlargement.

The calculated ground and excited state molecular geometry of compounds ***1*** and ***17*** are compared in Figure 1.

For the benzimidazolic pyrazoline ***1***, the most important S_1 state geometry changes occur around the nitrogen atom in position 1 of the main heterocycle. Being slightly pyramidal in the ground state, it completely looses this feature at the electronic excitation: the sum of its valence angles become 359.9°, while as deviation from the plane of three neighboring atoms does not exceed 0.03 Å. All these reflect N1 atom hybrid state approaching to sp^2. At the same time, nearly planar in the ground state pyrazoline cycle of ***1*** demonstrates substantially nonplanar conformation in the excited state of the "*open envelope*" type with maximal displacement of its carbon-5. Thus, pyrazole cycle bents around the axis, which passes through its atoms N1 and C4, approximately to 24°. Evidently, the above mentioned changes in the spatial shape of pyrazoline cycle were predetermined by the excited state de-pyramidalization of its N1 atom.

Structural relaxation does not change substantially the electronic excitation localization – deviations in L_i indices, calculated for the excited state molecular geometry of compound ***1***, do not exceed a few % for benzimidazole and phenyl-1 and were negligible for two benzene rings in positions 1 and 5.

At the same time, calculated for compound ***1*** excited state energy lowering related to the structural relaxation is rather significant, ~6900 cm^{-1} in wavenumber scale, and this should be the main contribution to the enlarged fluorescence Stokes shift of ***1*** (even if the structurally relaxed excited state energy is slightly overestimated in our calculations, as it was sometimes happened when applying *b3lyp* functional to the systems with significant charge redistribution [60,61]).

The driving force of the excited state structural relaxation of pyrazolic compound ***17*** is the increase of conjugation of its phenyl radicals in positions 1 and 5 with the central heterocycle. The angles between the planes of pyrazole ring and phenyl-1 decreases from 44° in the ground state to 30° in S_1-state, while as corresponding parameter for phenyl-5 changes from 46° to 29°. The pyrazole and benzimidazole moieties remain coplanar in S_1 state as they were in S_0. To minimize steric repulsion, which increases as a result of 1 and 5 benzene rings rotation, the torsion angle, formed by two single bonds in positions 1, 5 and atoms N1 and C5 of pyrazole ring, increases to 21°. This circumstance does not affect conjugation of the side phenyls with pyrazole moiety, thus the excited molecule of compound ***17*** should be also considered as more conjugated, than in its ground state.

Partial planarization decreases the energy of the structurally relaxed excited states, resulting in bathochromic shift of the long-wavelength electronic transition of ***17*** to 25800 cm^{-1} compared with 31900 cm^{-1} calculated for the ground state geometry. First value corresponds to position of fluorescence spectrum, second one – to position of the long-wavelength absorption band, thus "theoretic" Stokes shift should be near 6100 cm^{-1}. Experimental Stokes shift of compound ***17*** in acetonitrile is higher, than that of compound ***1***. However, in case of ***17*** the contribution of solvent relaxation processes into Δ_{ST} value should be higher as well: the ground-to-excited state change in dipole moment is more significant for pyrazole ***17*** (Δμ~21 D), than that for pyrazoline ***1*** (Δμ~10 D).

The NH···N distance in the excited molecule ***17*** decreases to 2.42 Å from 2.59 Å in the ground state, however the angle NHN remains near 97°, this does not allow to consider appearance of intramolecular hydrogen bonding in the S_1-state. The AIM analysis does not confirm such possibility as well: the critical bond point of (-3,1) type in the space between the discussed H and N atoms was not observed for the excited molecule ***17***. Thus, there is no reason to interpret higher Stokes shifts of the investigated pyrazols as a result of the excited state intramolecular proton transfer reaction.

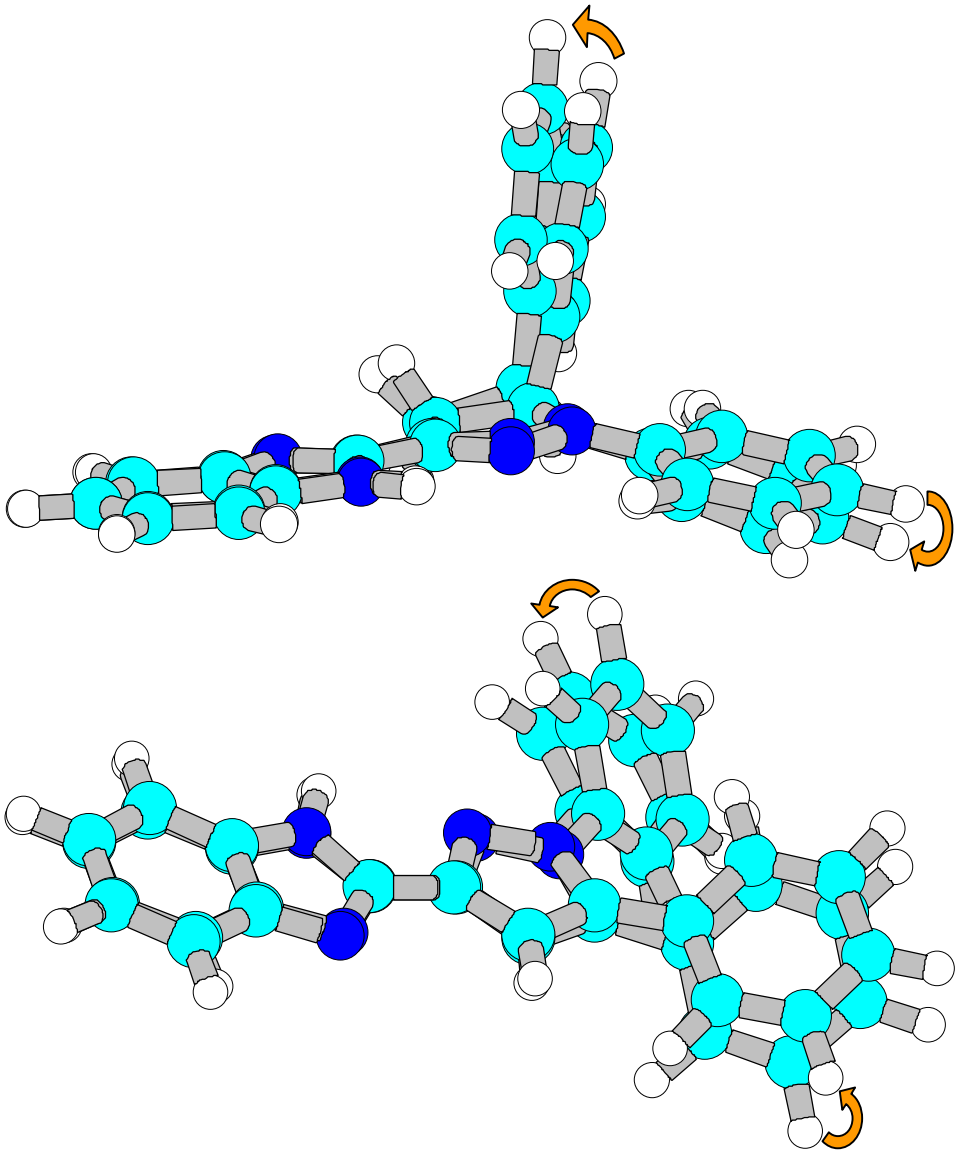


Figure 1. Lowest singlet excited states molecular geometries of benzimidazolic pyrazoline ***1*** (above) and pyrazole ***17*** (below) compared to those in the ground states - quantum-chemical modeling in (TD) DFT schemes. Carbons are shown in cyan, nitrogens – in blue, hydrogens – in white color. Yellow arrows indicate conformational changes on going from S_0 to S_1* state.

3.2. Experimental fluorescent properties

The experimental spectral data for the studied benzimidazolic pyrazolines and pyrazoles in acetonitrile solutions are presented in Tables 5 and 6. The choice of this solvent was reasoned by its wide transparency in UV spectral range and good solubility of all the title dyes in it. Benzimidazolic pyrazolines dissolved in polar aprotic solvents emit fluorescence in bluish-green spectral region with moderate quantum yields, usually do not exceeding 0.5. In solvents of lower polarity they are generally higher.

Experimental absorption and fluorescence spectra of unsubstituted representatives of benzimidazolic pyrazolines and pyrazoles series are shown in Figure 2 as an example.

Fluorescence Stokes shifts of benzimidazolic pyrazolines are slightly enlarged (~6000 cm^{-1}), reflecting realization of the already discussed structural and solvent relaxation processes (section 3.1). The "theoretically estimated" $\Delta\nu_{ST}$ values are nearly of the same order of magnitude with the experimental ones.

Let us note that spectral parameters of compounds with N-methylated benzimidazolic moiety are close to those of their N-H analogs. This fact is in favor of our conclusion about the lack of the in-

tramolecular hydrogen bond of N-H···N type and connected to this fact absence of the excited state intramolecular proton transfer reaction in the discussed series.

Substituents in aryl-5, which are not conjugated with the main chromophoric system of the molecule, seem to have no significant effect on positions of the long-wavelength absorption and fluorescence bands in the electronic spectra. However, definite variations in fluorescence quantum yields were observed. Groups with low-to-moderate positive mesomeric effect (+M) like methoxy, bromine, fluorine increase fluorescence quantum yield. Chlorine in aryl-5 does not change quantum yield compared to unsubstituted compound. The expected *heavy atom effect* of bromine did not manifest itself at all: fluorescence quantum yields of compounds ***9*** and ***10*** are the highest among those presented in Table 5.

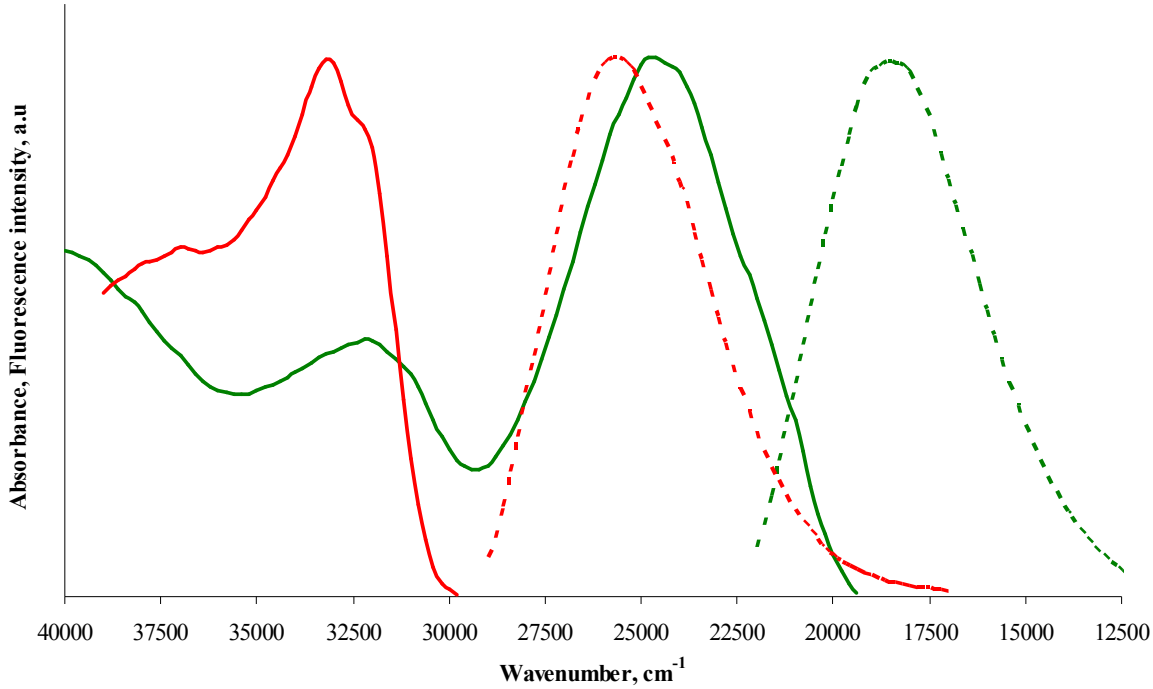
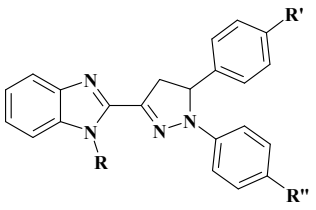


Figure 2. Electronic absorption (solid lines) and fluorescence spectra (dashed lines) of compounds ***1*** (**green**) and ***17*** (**red**) in acetonitrile.

Strong electron donor in aryl-5 (N,N-dimethylamino group) decreases fluorescence efficiency. The analogous behavior was reported previously [62] and was attributed to the quenching by electron transfer from the $N(CH_3)_2$-group nitrogen atom lone electron pair to the excited chromophore of the molecule, taking into account, that it should increase its electron affinity in the first singlet excited state. The applied polar solvent favors the realization of such process.

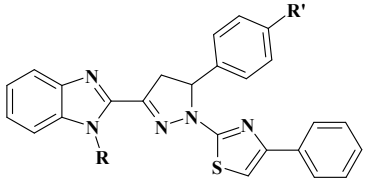
Thyazolic derivatives ***15*** and ***16*** have low and hardly measurable quantum yields, which are generally typical to compounds with significant excited state electron density redistribution in polar solvents [63,64]. Such a behavior could be clarified not only by the excited state twisting, the main focus of the above-cited reviews. Another entirely photophysical mechanism of S_1-S_0 internal conversion could be responsible for such behavior as well [65,66].

Table 5. Absorption and fluorescence spectral and photophysical data for benzimidazolic pyrazolines in acetonitrile solutions.



Continuation of table 5.

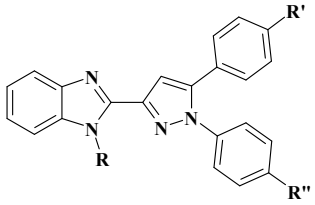
Com-pound	R	R'	R"	Absorption	Fluorescence		
				ν_a, cm^{-1}	ν_f, cm^{-1}	Stokes shift $\Delta\nu_{ST}$, cm^{-1}	Quantum yield, φ
1	H	H	H	24700	18500	6200	0.27
2	CH_3	H	H	24100	18400	5700	0.24
3	H	CH_3O	H	24200	18400	5800	0.36
4	CH_3	CH_3O	H	24400	18200	6200	0.34
5	H	$(CH_3)_2N$	H	26800	20700	6100	0.13
6	CH_3	$(CH_3)_2N$	H	27500	20700	6800	0.13
7	H	F	H	26900	20900	6000	0.37
8	H	Cl	H	27500	20800	5700	0.26
9	H	Br	H	27300	21100	6200	0.46
10	CH_3	Br	H	27900	21100	6800	0.42



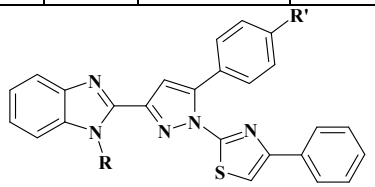
Com-pound	R	R'	Absorption	Fluorescence		
			ν_a, cm^{-1}	ν_f, cm^{-1}	Stokes shift $\Delta\nu_{ST}$, cm^{-1}	Quantum yield, φ
15	H	H	26800	17900	8900	*low*
16	H	CH_3O	25900	17800	8100	*low*

Benzimidazolic pyrazoles absorption and emission spectra lie in shorter-wavelength region in respect to parent pyrazolines. This could be attributed to the lower planarity of their molecules, which causes violation of conjugation between their cyclic subunits. Such behavior of 1,3,5-triaryl-pyrazols was reported in the early 80-th [24]. The main feature of benzimidazolic pyrazoles series is significantly higher quantum yields in comparison with corresponding pyrazolines.

Table 6. Absorption and fluorescence spectral and photophysical data for benzimidazolic pyrazoles in acetonitrile solutions.



Com-pound	R	R'	R"	Absorption	Fluorescence		
				ν_a, cm^{-1}	ν_f, cm^{-1}	Stokes shift $\Delta\nu_{ST}$, cm^{-1}	Quantum yield, φ
17	H	H	H	33100	25600	7500	0.91
18	CH_3	H	H	32700	25500	7200	0.80
19	H	CH_3O	H	32500	25300	7200	0.78
20	CH_3	CH_3O	H	32500	25300	7200	0.65
21	H	F	H	33400	25500	7900	0.70
22	H	Cl	H	33500	25700	7800	0.45
23	H	Br	H	33200	25600	7600	0.49



Continuation of table 6.

Compound	R	R'	Absorption	Fluorescence		
			ν_a, cm^{-1}	ν_f, cm^{-1}	Stokes shift $\Delta\nu_{ST}$, cm^{-1}	Quantum yield, φ
24	H	H	29500	(~24000)	(~5500)	*low*
25	H	CH_3O	30900	24400	6500	0.07

According to our quantum-chemical modeling of compound ***17***, the excited state redistribution of electron density is directed from the benzimidazole to the pyrazole moieties, thus benzimidazolic N-H should become more acidic, while as pyrazolic nitrogen atom – more nucleophilic, than they were in the ground state. All these could be the prerequisites of the excited state proton transfer reaction, usually resulting in significant Stokes shift increase. However, like it was already discussed for the pyrazoline series, the spectral properties of pyrazoles with N-methylated benzimidazole moiety are practically the same as for the corresponding derivatives without methyl group, clearly indicating again the absence of intramolecular proton transfer reaction is S_1* state.

Introduction of methyl group into benzimidazole moiety had another effect – systematic decrease of fluorescence quantum yields. This is probably due to the steric effects: further violation of planarity of N-methylated compounds (Table 6).

Substituents with positive mesomeric effects in aryl-5 decrease the fluorescence quantum yields of benzimidazolic pyrazoles.

Thiazole-containing benzimidazolic pyrazoles are practically non-fluorescent, like their parent pyrazolines. However, in this case the fluorescence quenching could not be attributed to the enforced excited state charge redistribution. Our quantum-chemical modeling reveals that it is rather weak and has no preferential direction (Table 4). It seems, that appearance of thiazole moiety launches a new radiationless process of undefined nature, which identification would be, probably, the subject of out further investigations.

Conclusions

Series of benzimidazolic pyrazoline and pyrazole fluorescent dyes were synthesized and characterized by their UV-Vis absorption and emission spectra. The synthetic procedure for mild oxidation of pyrazoline ring to pyrazole one was optimized for obtaining higher chemical yields of target compounds. It was revealed, that strong electron donor substituents in pyrazoline aryl-5 prevent oxidative aromatization of this heterocycle.

Compounds of both investigated sub-series demonstrate enlarged fluorescence Stokes shifts of the order of 6000-8000 cm^{-1}, which was attributed to the excited state structural relaxation processes, making the investigated molecules chromophoric units more planar, and, correspondently,- more conjugated in S_1-state.

Contrary to widespread insights, benzimidazolic pyrazoles are characterized by substantially higher fluorescence quantum yields with respect to the parent pyrazolines.

Introduction of thiazole moiety in position 1 of pyrazoline or pyrazole cycles leads to nearly complete disappearance of fluorescence.

Acknowledgements

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В.Н. Котляр, В.Д. Орлов, А.В. Григорович, А.О. Коломойцев, Д.В. Николаевский, А.О. Дорошенко. 1,5-диарил-3-бензимидазолил-2-пиразолины и пиразолы – новые флуоресцентные красители пиразолинового ряда.

Ряд новых арильных производных 2-пиразолина с 2-бензимидазольным бициклом в положении 3 были синтезированы конденсацией соответствующих халконов с фенилгидразином. Пиразолы на их основе были получены оптимизированной процедурой окисления диоксидом марганца в бензоле. Флуоресцентные характеристики исследуемых соединений были определены для растворов в ацетонитриле. Проведено квантово-химическое моделирование молекулярной структуры, электронных спектров поглощения, перераспределения электронной плотности и структурной релаксации в электронно-возбужденном состоянии, приводящей к высоким Стоксовым сдвигам флуоресценции.

Ключевые слова: пиразолин, пиразол, бензимидазол, органический синтез, флуоресценция, квантово-химическое моделирование, ESSA.

В.М. Котляр, В.Д. Орлов, О.В. Григорович, О.О. Коломойцев, Д.В. Ніколаєвський, А.О. Дорошенко. 1,5-диарил-3-бензімідазоліл-2-піразоліни і піразоли – нові флуоресцентні барвники піразолінової серії.

Ряд нових арильних похідних 2-піразоліну з 2-бензімідазольним біциклом в положенні 3 були синтезовані конденсацією відповідних халконів з фенілгідразином. Піразоли на їх основі були отримані оптимізованою процедурою окислення діоксидом мангану в бензолі. Флуоресцентні характеристики досліджуваних сполук були визначені для розчинів в ацетонітрилі. Проведено квантово-хімічне моделювання молекулярної будови, електронних спектрів поглинання, перерозподілу електронної густини і структурної релаксації в електронно-збудженому стані, яка приводить до високих Стоксових зсувів флуоресценції.

Ключові слова: піразолін, піразол, бензімідазол, органічний синтез, флуоресценція, квантово-хімічне моделювання, ESSA.

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