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Spectral Fluorescent Properties of New 5-R-2-(Quinolin-2-yl)- and 5-R-2-(Quinolin-4-yl)-1,3-Benzoxazoles

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The spectral-fluorescent properties of 5-R-2-(quinolin-2-yl)- and 5-R-2-(quinolin-4-yl)-1,3-benzoxazoles (R = Me and Cl) have been investigated in solvents of different polarity and proton donating ability. The effect of the solvent on spectral characteristics has been estimated. It has been shown that all the studied compounds have low fluorescence quantum yields in non-polar solvent. The experimental data together with the results of *ab initio* calculations indicate that the main quenching channel of the fluorescent S_1 π-π^* excited state in non-polar solvents is intersystem crossing to close-lying n-π^* triplet state. By growth of solvent polarity and solvent hydrogen-bonding ability, long-wavelength shifts in the fluorescence maxima and increase of fluorescence quantum yields are observed for the studied quinolinyl-5-methyl-benzoxazoles, whereas no considerable changes of fluorescence band positions and of quantum yields are observed for the quinolinyl-5-chloro-benzoxazoles in polar and protic solvents. This difference is suggested to be caused by the difference in solvent cage relaxation process, occurring in polar and protic solvents after the absorption, for quinolinyl-5-methyl-benzoxazoles and for quinolinyl-5-chloro-benzoxazoles.

Key Words: Spectral-fluorescent properties, Intersystem crossing, 5-R-2-(Quinolin-2-yl)-, 5-R-2-(Quinolin-4-yl)-1,3-benzoxazoles.

INTRODUCTION

The interest in 5-R-2-(quinolin-2-yl)-1,3-benzoxazoles is due to their application as optical whitening agents[1,2] and as components in dye laser[3]. 5-R-2-(Quinolin-2-yl)-1,3-benzoxazole has been studied as ligand for complex formation with copper(II)[4], palladium(II) and platinum(II) chlorides[5], cobalt(II) and nickel(II) chlorides[6] and group II metal chloride complexes[7].

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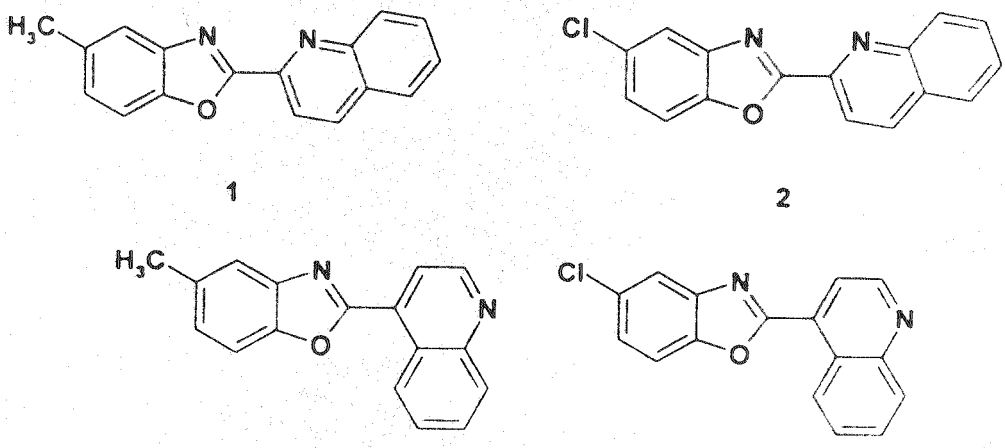
Along with this there is UV/Vis spectroscopic study of quinolinylbenzoxazole derivatives with substituents in quinolinyl fragment [8]. UV/Vis and fluorescence spectral properties of 2-(quinolin-2-yl)benzoxazole have been reported by Klyuev *et al.*[9] and Kurapov *et al.*[10]

Nevertheless, to the best of our knowledge, no spectral data on the quinolinylbenzoxazole derivatives with substituents in phenyl fragment of benzoxazole moiety have been reported.

In the present work we report absorption and fluorescence properties of the newly synthesized 2-(quinolin-2-yl)- and 2-(quinolin-4-yl)-1,3-benzoxazoles with substituents (CH_3 and Cl) in 5-position of benzoxazole ring (compounds **1**–**4**).



Structure of the investigated compounds

EXPERIMENTAL

The organic solvents used for the spectral-fluorescent measurement were all of spectrophotometry grade and were used as supplied from Fluka. Quinine sulfate used as fluorescence standard for quantum yield determination was purchased from Fluka.

In the first step of the synthesis, which was conducted in three steps, the heteroaromatic carboxaldehydes to be used in the reactions were prepared by the oxidation of 2-metylquinoline and 4-methylquinoline by selenium dioxide[11], which is a mild oxidant, in a medium containing dioxane. In the second step, both of these aldehydes were reacted with 2-amino-4-methylphenol and 2-amino-4-chlorophenol, producing 4 imine compounds[12], which are also known to be used as intermediate products especially in the preparation of pharmaceutical chemicals, insecticides and certain plastic materials. In the last step, imine compounds produced in the second step were subjected to oxidative intramolecular cyclization reaction with manganese triacetate, producing some new benzoxazoles[12].

The purity of the synthesized compounds was monitored by TLC.

Synthesis

To a stirred solution of imine compound (1.0 mmol) in dry benzene (20 mL), manganese(III) acetate dihydrate (2.0 mmol) was added and the mixture was

refluxed for 4 h by stirring. After elimination of the residual manganese diacetate by filtration, most of the solvent was distilled out under reduced pressure. The crude product so obtained was purified by recrystallization from the appropriate solvent as reported earlier[12].

5-Methyl-2-(quinolin-2-yl)-1,3-benzoxazole (1): Cream-coloured powder crystals (methanol/water, 1 : 1) (96%); m.p. 146–7°C; IR (KBr, cm^{-1}): 3053, 2918, 2862, 1595, 1547, 1504, 1354, 1267, 1148, 1074, 849, 810, 760; ^1H NMR ($CDCl_3$): δ (ppm) 2.51 (s, CH_3, 3H), 7.22 8.48 (m, aromatic, 9H); MS: m/z 261 (M + 1), 260 (M^+), 259 (M – 1), 236, 154, 128, 111, 106, 101, 97, 83, 69.

5-Chloro-2-(quinolin-2-yl)-1,3-benzoxazole (2): Beige plate crystals (methanol/water, 1 : 1) (78%); m.p. 197–8°C; IR (KBr, cm^{-1}): 3086, 3053, 1545, 1504, 1448, 1354, 1257, 1082, 930, 835, 814, 714; ^1H NMR ($CDCl_3$): δ (ppm) 7.36–8.46 (m, aromatic, 9H); ^{13}C NMR ($CDCl_3$): δ (ppm) 114.15–164.86 (aromatic carbons); MS: m/z 282 (M+2), 281 (M + 1), 280 (M^+), 279 (M – 1), 254, 217, 154, 128, 101, 63.

5-Methyl-2-(quinolin-4-yl)-1,3-benzoxazole (3): Honey-coloured plate crystals (methanol) (61%); m.p. 159–60°C; IR (KBr, cm^{-1}): 3093, 3042, 2918, 2856, 1579, 1533, 1498, 1175, 1082, 978, 851, 793, 770; ^1H NMR ($CDCl_3$): δ (ppm) 2.53 (s, CH_3, 3H), 7.25–9.51 (m, aromatic, 9H); ^{13}C NMR ($CDCl_3$): δ (ppm) 23.50 (CH_3 carbon), 112.16–162.62 (aromatic carbons); MS: m/z 261 (M + 1), 260 (M^+), 259 (M – 1), 154, 132, 128, 127, 106, 101.

5-Chloro-2-(quinolin-4-yl)-1,3-benzoxazole (4): Straw yellow fluffy crystals (methanol) (65%); m.p. 152°C; IR (KBr, cm^{-1}): 3055, 1614, 1545, 1510, 1452, 1140, 1059, 851, 804, 770; ^1H NMR ($CDCl_3$): δ (ppm) 7.40–9.44 (m, aromatic, 9H); ^{13}C NMR ($CDCl_3$) δ (ppm) 113.54–163.88 (aromatic carbons); MS: m/z 282 (M + 2), 281 (M+1), 280 (M^+), 279 (M – 1), 154, 152, 128, 127, 126, 101.

Melting points are uncorrected. The IR spectra were recorded in a Jasco FT-IR-5300 spectrophotometer using KBr pellets. The PMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz NMR spectrophotometer using $CDCl_3$ as solvent and TMS as internal standard and all chemical shifts are in ppm downfield from TMS. Mass spectra were recorded on Shimadzu GC-MS QP 2000A instrument.

Spectroscopic measurements

The electronic absorption spectra were measured using Jasco V-530 UV/Vis spectrophotometer. Fluorescence emission spectra were recorded on PTI-QM1 fluorescence spectrophotometer. Fluorescence quantum yields were referenced to the absorption and fluorescence spectra of quinine sulfate in 0.5 M H_2SO_4 solution ($\phi_f = 0.546$)[13, 14]. The calculated relative fluorescence quantum yields were the values corrected for refractive index differences between the measured and standard solutions[15]. The equation used in calculations of fluorescence quantum yield is

$$\phi_{fu} = \phi_{fr} \frac{S_U(1 - 10^{-A_R})}{S_R(1 - 10^{-A_U})} \frac{n_U^2}{n_R^2} \quad (1)$$

where ϕ_f is the quantum yield, A is the absorbance on the excitation wavelength, S is the integrated emission band area, n is the solvent refractive index, U and R refer to the unknown and reference (standard), respectively. All fluorescence measurements were performed for dilute solutions in absorbance range of 0.1–0.15 at the excitation wavelength (concentrations 10^{-5}–10^{-6} mol L^{-1}).

Theoretical calculations

Ab initio calculations were performed using the GAMESS package[16]. Geometries for ground states were optimized without any assumption of symmetry (*i.e.*, without any constraints) with full geometry optimization in B3LYP/6-31G (d, p), because this method is more appropriate for geometry optimization. Obtained optimized geometries were used as starting points for calculations of Mulliken charges[17] and dipole moments. Single point calculations with RHF/6-31G (d, p) and CIS/6-31G (d, p) levels were performed to calculate ground and excited state characteristics, correspondingly.

RESULTS AND DISCUSSION

Absorption properties

In Table-1, the absorption wavelengths of quinolinylbenzoxazoles in solvents with different polarities and hydrogen bonding abilities are presented. Fig. 1 shows the absorption spectra of compounds **1**–**4** in acetonitrile.

Absorption spectra of the studied compounds in the region 200–380 nm consist of four bands of π-π^* nature. The conjugated systems of the investigated compounds consist of benzoxazole and quinoline fragments. Hence, the observed absorption bands could be attributed to these chromophoric fragments. In comparison with quinoline and benzoxazole absorption spectra[18], the absorption spectra of the studied compounds are shifted to the long-wavelength region. Such a bathochromic shift could be explained by the extension of the conjugated system with the addition of benzoxazole fragment to the quinoline nucleus. Like in the cases of quinoline[19] and N-benzaniline[3], the n-π^* absorption bands of the studied compounds are hidden by the more intense long-wavelength π-π^* band.

By the growth of solvent polarity or hydrogen-bonding ability, no (or negligible) shifts in the absorption maxima are observed. The absence of solvatochromic effects suggests that the ground state solvatation energies of the studied molecules are about the same as the corresponding excited state solvatation energies for all the solvents used.

If one compares the absorption spectra of 2-(quinolin-2-yl)benzoxazole[9,10] with the corresponding absorption spectra of **1** and **2** (Table-1, Fig. 1), one could notice that the nature of the substituent in the 5-position of benzoxazole fragments has practically no influence on the absorption spectra of 5-R-2-(quinolin-2-yl)-1,3-benzoxazoles. The same is true for 5-R-2-(quinolin-4-yl)-1,3-benzoxazoles (**3**, **4**): the absorption spectra of **3** nearly coincide with the corresponding absorption spectra of **4**.

The quantum-chemical calculations (geometry optimization, B3LYP/6-31G (d,p)) show that for each studied compound the geometry search converged to one of the two most stable conformers, designated as I and II (Figs. 2a, 2b), which

differ from each other by mutual orientation of quinolinyl and benzoxazole fragments (Figs. 2a, 2b).

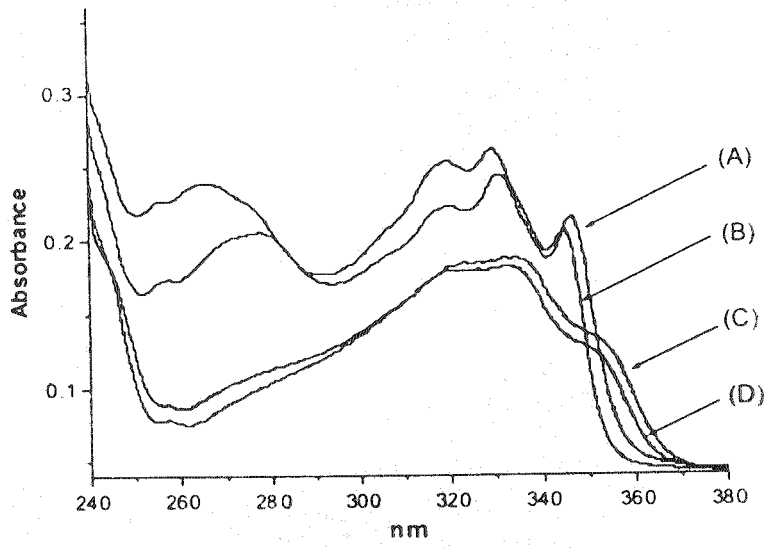


Fig. 1. Absorption spectra of compounds 1–4 in acetonitrile: **1** (A), **2** (B), **3** (C), **4** (D)

TABLE-1
UV-Vis SPECTROSCOPIC DATA* OF QUINOLINYLBENZOXAZOLES IN SOLVENTS WITH DIFFERENT POLARITIES AND HYDROGEN BONDING ABILITIES.

Compd.	Solvent	ε	n	λ^{1}_{abs} (shoulder)	λ^{2}_{abs}	λ^{3}_{abs} (shoulder)	λ^{4}_{abs}	λ^{5}_{abs}	λ^{6}_{abs}
	Toluene	2.38	1.4916	348	333	319	—	—	—
1	Acetonitrile	36.20	1.3441	347	331	319	277	241	211
	Methanol	32.63	1.3286	347	333	320	278	—	—
	Toluene	2.38	1.4916	347	332	319	—	—	—
2	Acetonitrile	36.20	1.3441	345	330	319	265	241	217
	Methanol	32.63	1.3286	345	332	320	266	—	—
	Toluene	2.38	1.4916	357	339	324	—	—	—
3	Acetonitrile	36.20	1.3441	355	336	322	—	238	218
	Methanol	32.63	1.3286	355	336	323	—	—	—
	Toluene	2.38	1.4961	357	339	324	—	—	—
4	Acetonitrile	36.20	1.3441	355	336	321	—	241	218
	Methanol	32.63	1.3286	355	336	322	—	—	—

*Here ε and n-dielectric permeability and refractive index of the solvent; λ^{1-6}_{abs} are the positions of the maxima in the absorption spectra (nm).

All the studied conformers I, II of **1–4** are found to be nearly planar. Dihedral angles between quinolinyl and benzoxazole fragments are found to be: *ca.* 0.007–0.03 degree for conformers I, II of compounds **1, 2** and 4.01 degrees (for conformer I) and 0.007–0.028 degree (for conformer II) in case of **3, 4.**

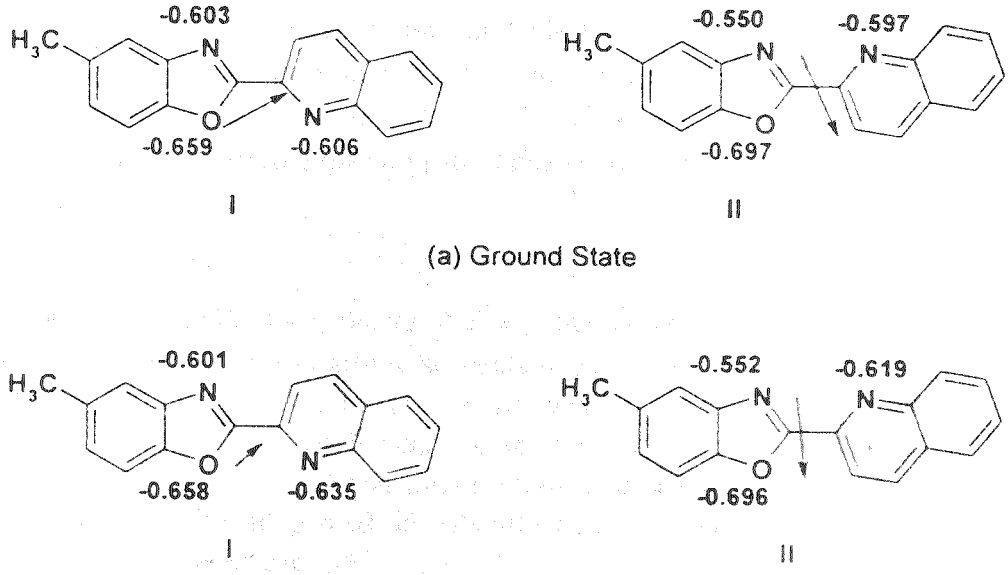


Fig. 2a. Calculated charge distribution on heteroatoms and dipole moment directions in S_0 (a) and in S_1 (b) electronic state of the most stable conformers (I and II) of 5-methyl-2-(quinolin-2-yl)-1,3-benzoxazole (**1**)

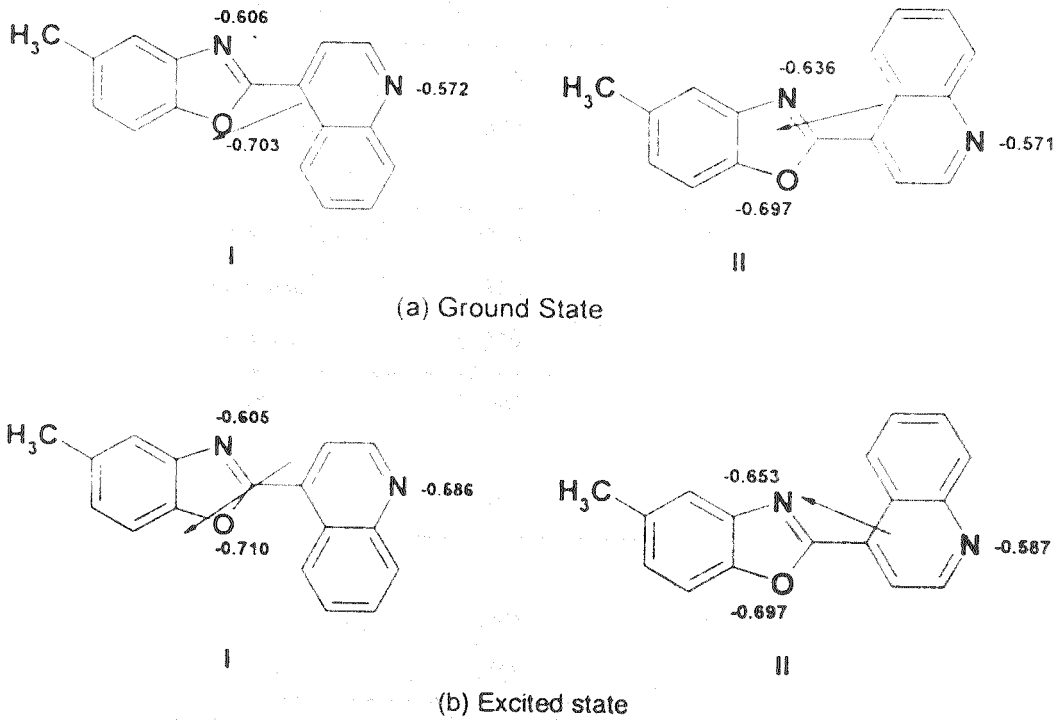


Fig. 2b. Calculated charge distribution on heteroatoms and dipole moment directions in S_0 (a) and in S_1 (b) electronic state of the most stable conformers (I and II) of 5-methyl-2-(quinolin-4-yl)-1,3-benzoxazole (**3**).

Each pair of conformers (I, II), being planar and having identical conjugated systems, must have identical absorption and fluorescence spectra. For this reason, we neglect the existence of different conformers, when the absorption or fluorescence spectra of **1**–**4** are discussed.

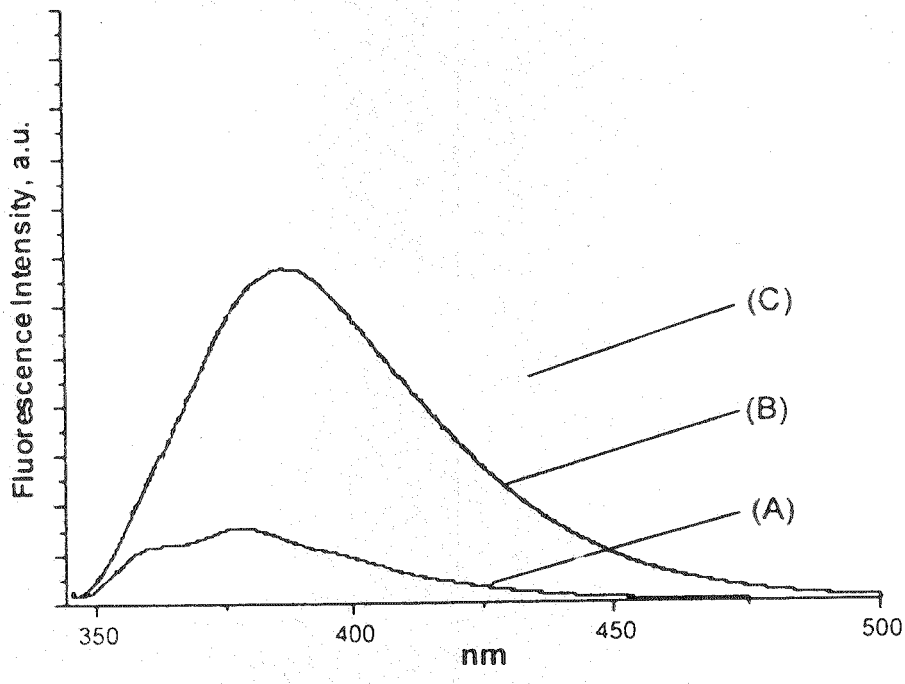


Fig. 3. Fluorescence spectra of 5-methyl-2-(quinolin-2-yl)-1,3-benzoxazole (**1**) in toluene, A, in acetonitrile, B, and in methanol, C at λ_{exc} = 345 nm

Probably, the solvent cage relaxation processes occurring in polar and protic solvents after the absorption are more pronounced for compounds **1**, **3** than for compounds **2**, **4**. Such solvent cage relaxation processes tend to shift the fluorescence to longer wavelength with increasing solvent polarity and hydrogen-bonding ability[20].

The conjugated system of the molecules **1–4** could be considered as: (a) benzoxazole fluorophoric system, containing 2- or 4-quinolinyl substituent in 2-position of benzoxazole ring, or (b) as quinoline fluorophoric system, containing 2-benzoxazole ring in 2- or 4-position of quinoline ring.

The latter consideration seems to be more probable, because, in contrast to 2-arylbenzoxazoles, which are rather fluorescent in non-polar solvents[3] and similarly to the case of quinoline[3, 21], the studied compounds **1–4** have very low fluorescence quantum yields (ϕ_f *ca.* 0.003–0.07) in toluene solutions (see Table-2).

This fact could be explained by the effective quenching processes with the participation of singlet or triplet states of n-π* nature, introduced into the system by the presence of the nitrogen heterocycles.

If the lowest-lying transitions of organic substance are of π-π* type such a substance usually has relatively high fluorescence quantum yield. When a heteroatom is involved in the π-system an nπ* transition may be the lowest-lying transition. This opens the possibility for radiationless deactivation of the lowest singlet excited state *via* the efficient inter-system crossing (ISC) of S(n-π*)-T(π-π*) or S(π-π*)-T(n-π*) type. According to El-Sayed rule[22], the rate of ISC between the singlet and triplet states of the different orbital nature exceeds that for the states of the identical orbital nature up to several orders of magnitude. Owing to this circumstance, the ISC between n-π* and π-π* states successfully competes with the radiative depopulation of S_1^* energetic level.

This explains the low fluorescence quantum yields of many molecules in which the lowest excited state is $n\pi^*$ in nature. This is the case for most of the azo compounds and some compounds containing carbonyl groups and nitrogen heterocycles (with pyridine-type nitrogens)[20, 21].

According to the absorption spectra of **1–4** (Table-1 and Fig. 1), the $S(n-\pi^*)$ levels of **1–4** are found to be higher in energy than the corresponding $S(\pi-\pi^*)$ levels ($(n-\pi^*)$ absorption bands of **1–4** are hidden by the more intense long-wavelength $\pi-\pi^*$ bands). Thus, the quenching of the fluorescence for **1–4** is, probably, caused by $S(\pi-\pi^*)$-$T(n-\pi^*)$ intersystem crossing.

As it was mentioned above, in cases where the lowest excited states of nitrogen-containing heterocyclic compounds are of the $n-\pi^*$ type (usually, such cases are observed in non-polar/non-hydrogen bonding solvents), no fluorescence takes place. However, if $\pi-\pi^*$ states of nitrogen-containing heterocyclic compounds lie only slightly higher than $n-\pi^*$ states, the increase of solvent polarity or hydrogen-bonding ability could change the arrangement of the $n-\pi^*$ and $\pi-\pi^*$ levels and, hence, rather intense fluorescence can be observed in polar or in protic solvents.

The solvent may not only change the arrangement of the singlet $n-\pi^*$ and $\pi-\pi^*$ levels, but also promotes the vibrational spin-orbital interaction between the lowest $S(\pi-\pi^*)$ and the higher $S(n-\pi^*)$ levels with subsequent transition to the triplet level. This vibrational interaction is more probable in hydrocarbon solvents. In polar solvents, such interaction is insignificant and, as a result, the fluorescence intensity is higher[23]. This fact is considered as another reason for the increase of fluorescence quantum yield of the compounds, containing $n-\pi^*$-levels, with increase of solvent polarity[23].

Nevertheless, by analogy with unsubstituted 2-(quinolin-2-yl)benzoxazole[9, 10], in case of compounds **2, 4** the fluorescence emission remains very low even in polar (acetonitrile) and protic (methanol) solvents, though small growth of quantum yields of **2, 4** is observed on passing from toluene to methanol Table-2).

In contrast to the case of compounds **2, 4**, the fluorescence quantum yields of the compounds **1, 3** increases up to ϕ_f *ca.* 0.11–0.30 with the growth of solvent polarity (*i.e.*, on passing from toluene to acetonitrile, Table-2). Additional increase of the fluorescence quantum yields of the compounds **1, 3** (up to ϕ_f *ca.* 0.38–0.52) is observed with growth of solvent hydrogen-bond donor ability, *i.e.*, in case of methanol solutions (Table-2).

By analogy with quinoline, the increase of the fluorescence quantum yields in solvents of high polarity and hydrogen-bonding ability, observed for compounds **1, 3**, could be explained by changes in the arrangement of the triplet $n-\pi^*$ and singlet $\pi-\pi^*$ levels.

Solvent cage relaxation processes, occurring in polar and protic solvents after the absorption of **1, 3** cause the long-wavelength shift of the fluorescence bands of **1, 3** in polar and protic solvents and, thus, the rearrangement of the triplet $n-\pi^*$ and singlet $\pi-\pi^*$ levels occurs.

To elucidate such possibility, the singlet and triplet energy levels of **1–4** in vacuum were calculated by *ab initio* (CIS/6-31G(d,p)) quantum-chemical calculations. The results of the quantum-chemical calculations are presented in Fig. 4.

It could be seen from Fig. 4 that $T_1(n-\pi^*)$ levels of compounds **1, 2, 4** are the lowest-lying. In case of compound **3**, S_1 $(\pi-\pi^*)$ level is the lowest-lying and the energy gap between $S_1(\pi-\pi^*)$ and $T_1(n-\pi^*)$ levels is 142 cm^{-1}. Here, we have to note

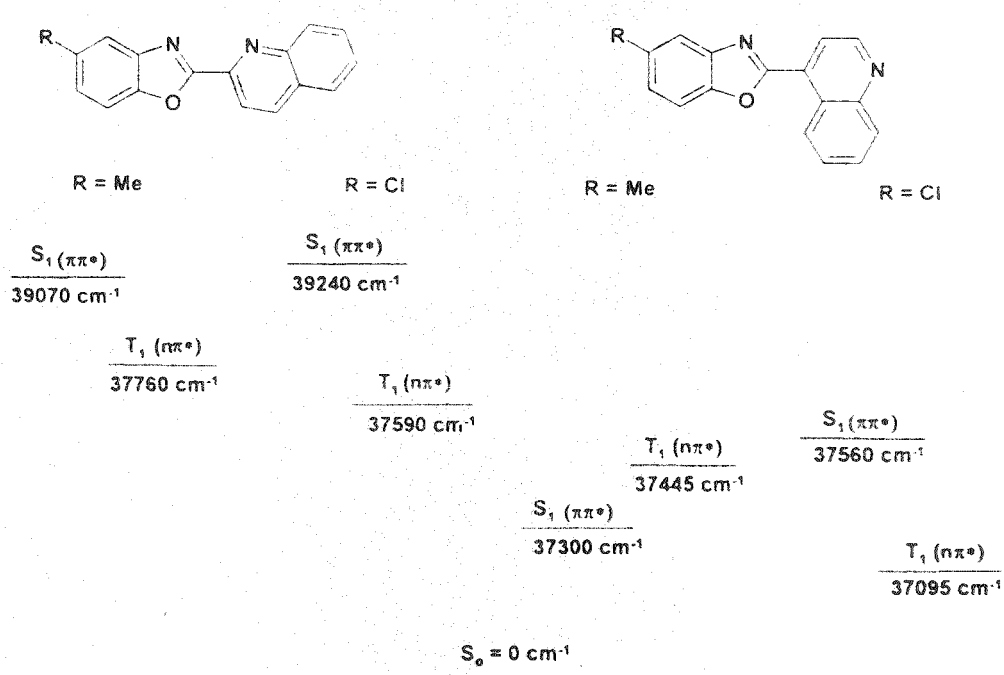


Fig.4. Schematic energy level diagrams of $S_1(\pi\text{-}\pi^*)$ and $T_1(n\text{-}\pi^*)$ states for 1-4 in vacuum.

that if the $S_1(\pi\text{-}\pi^*)$ state is somewhat lower in energy than the $T_1(n\pi\text{-}^*)$ one and energy gap between them is smaller than 600–700 cm^{-1}, a possibility for the temperature-activated ISC still exists; thus, additional low energy shift of the $S_1(\pi\text{-}\pi^*)$-level on approximately 600–700 cm^{-1} (thermal movement energy for the room temperature) is highly desirable in order for intensive fluorescence to occur.

In general, the calculated data on arrangement of $S_1(\pi\text{-}\pi^*)$ and $T_1(n\text{-}\pi^*)$ levels of **1–4** in vacuum are in good agreement with the fluorescence quantum yield data for **1–4** in toluene.

According to data in Table-2, on growth of solvent polarity or proticity, $S_1(\pi\text{-}\pi^*)$ levels of **1, 3** shift to lower energies: $S_1(\pi\text{-}\pi^*)$ level of **1** shifts on 690 cm^{-1} in acetonitrile and on 1020 cm^{-1} in methanol and $S_1(\pi\text{-}\pi^*)$ level of **3** shifts on 950 cm^{-1} in acetonitrile and on 1545 cm^{-1} in methanol.

The calculated energy gap between $S_1(\pi\text{-}\pi^*)$ and $T_1(n\text{-}\pi^*)$ levels of compound **1** is *ca.* 1307 cm^{-1}. This means that, in order to observe the increase of fluorescence intensity of **1**, the shift of $S_1(\pi\text{-}\pi^*)$ level to lower energy on 2000–1900 cm^{-1} is necessary. Nevertheless, according to experimental data (Table-2), the increase of fluorescence intensity of **1** is observed in acetonitrile solution, where $S_1(\pi\text{-}\pi^*)$ level of **1** shifts to lower energies on 690 cm^{-1}. Hence, the calculated energy gap between $S_1(\pi\text{-}\pi^*)$ and $T_1(n\text{-}\pi^*)$ in case of compound **1** is overestimated approximately on *ca.* 1300–1200 cm^{-1}. By contrast, the calculated $S_1(\pi\text{-}\pi^*)$–$T_1(n\text{-}\pi^*)$ energy gap for **3** is in good accordance with the experimentally observed growth of fluorescence quantum yield of **3** in polar and protic solvents.

Solvent cage relaxation processes, occurring in polar and protic solvents after the absorption of **2, 4** do not lead to considerable long-wavelength shift of the fluorescence bands of **1, 3** in polar and protic solvents; thus, the arrangement of the triplet $n\text{-}\pi^*$ and singlet $\pi\text{-}\pi^*$ levels for **2, 4** does not change considerably in polar and protic solvents in comparison to non-polar ones.

The difference in the above-mentioned solvent cage relaxation processes

between **1, 3** and **2, 4** may be caused by a few possibilities[20, 21, 24]: (i) if the changes of dipole moment values on excitation are greater in case of **1, 3** than the corresponding changes in case of **2, 4**; (ii) if the changes of dipole moment values on excitation are not considerable, but the changes in dipole moment orientations on excitation in case of **1, 3** are greater than the corresponding changes in case of **2, 4**.

In order to elucidate which possibility takes place for the studied compounds **1–4**, *ab initio* quantum chemical calculations have been performed. The results of the quantum-chemical calculations are presented in Table-3 (Figs. 2a, 2b).

TABLE-3
DIPOLE MOMENTS AND TOTAL ENERGIES† (ET, kcal/mol), CALCULATED BY *AB INITIO* CALCULATIONS FOR MOST STABLE CONFORMERS (I AND II) OF **1–4** IN VACUUM

Compd.	Conformer	a_0	μ_g	μ_e	$\Delta\mu = \mu_e - \mu_g$	θ	E_T
1	I	5.64	1.26	0.39	–0.87	27.7	–523449.36
	II	5.63	2.69	2.32	–0.37	15.7	–523446.83
2	I	5.31	3.99	4.12	–0.13	5.9	–786792.73
	II	5.36	5.21	5.20	–0.01	4.4	–786790.14
3	I	4.90	3.01	4.09	1.08	12.2	–523444.59
	II	4.90	2.89	3.02	0.13	26.7	–523446.17
4	I	4.79	2.34	3.82	1.48	5.0	–786787.63
	II	4.80	1.41	0.82	–0.59	112.4	–786789.14

*Here, the values of ground state μ_g and of excited state μ_e dipole moments and the vector difference of them $\Delta\mu$ are in Debye; the value of Onsager radius a_0 is in Å; according to Lippert[25], Onsager radius is taken as 40% of long axis of an ellipsoid enclosing the molecule; θ is the angle between ground and excited dipole moment vectors, in degrees.
†Presented only for S_0 states of the conformers I and II.

As could be seen from the Table-3: (a) in general, the changes of dipole moment values on excitation for **1–4** are not considerable (i.e., $\Delta\mu \leq 1.5$ debye); (b) the angles between ground and excited state dipole moment directions for **1–4** are sharp (the only exception is observed for conformer II of compound **4**); (c) the Onsager radii for **1** and **3** are approximately 0.33–0.11 Å greater than the corresponding Onsager radii for **2** and **4**.

The difference in energy of the conformers I and II, calculated for vacuum (Table-3), is rather small for all the studied compounds (*i.e., ca.* 2.5–2.6 kcal/mol for compounds **1, 2** and *ca.* 1.5–1.6 kcal/mol for **3, 4**).

In polar solvents, the energies of conformers I and II, calculated for **1–4** in vacuum (Table-3), will change because of the greater solvent stabilization of the more polar conformers. Hence, conformational equilibria between I and II will be shifted in the direction of conformers II for the case of compounds **1, 2** and in the direction of conformers I for the case of **3, 4**.

The comparison of $\Delta\mu$ and θ values (Table-3) for conformers II of compounds **1** and **2** shows that the absolute value of dipole moment change on excitation [Abs ($\Delta\mu$)] for compound **1** is greater than the corresponding absolute value for

compound **2** and the angle between ground and excited state dipole moments (θ) for compound **1** is greater (or less sharp) than the corresponding angle for compound **2**.

Despite the fact that calculated changes of dipole moment on excitation for conformer I of compound **3** ($\Delta\mu$ *ca.* 1.1 debye) is smaller than the corresponding changes for conformer I of compound **4** ($\Delta\mu$ *ca.* 1.5 debye), the angle between ground and excited state dipole moments for **3** (θ *ca.* 12.2 degrees) is somewhat greater than the corresponding angle for **4** (θ *ca.* 5.0 degrees).

Thus, the results of the *ab initio* calculations show that both the above mentioned possibilities (i) and (ii), which could cause the difference in solvent cage relaxation processes between **1, 3** and **2, 4**, take place.

On the other hand, to take into account the difference in Onsager radii between **1** and **2** and, also, between **3** and **4** (Table-3), another explanation is possible. Perhaps, the greater is the cavity in which the solute resides (*i.e.*, Onsager radius), the greater number of solvent molecules are involved in the solute solvatation and, hence, the greater reorganization of the solvent cage after the absorption occurs in polar or protic solvents, if the solute dipole moment value or the solute dipole moment direction change on excitation. Such extra reorganization of the solvent cage after the absorption, occurring in polar or protic solvents, leads to extra long-wavelength shift of the fluorescence spectra, as observed for **1, 3**.

It should be noted that the greater Onsager radii in case of **1** and **3** are due to the bulkiness of the methyl groups, introduced into 5-position of benzoxazole fragment of **1, 3**. The verification of the hypothesis, which suggests that the introduction of bulky substituents into benzoxazole fragment of the quinolinylbenzoxazoles leads to quantum yield increase in polar and protic solvents, will be the subject of our future study.

Conclusion

The spectral-fluorescent properties of 5-R-2-(quinolin-2-yl)- and 5-R-2-(quinolin-4-yl)-1,3-benzoxazoles (R = Me and Cl) have been investigated in solvents of different polarity and proton donating ability. The effect of the solvent on spectral characteristics has been estimated. It has been shown that all the studied compounds have low fluorescence quantum yields in non-polar solvent.

The experimental data together with the results of *ab initio* calculations indicate that the main quenching channel of the fluorescent $S_1(\pi\text{-}\pi^*)$ excited state in non-polar solvents is intersystem crossing to close-lying $(n\text{-}\pi^*)$ triplet state.

By growth of solvent polarity and solvent hydrogen-bonding ability, long-wavelength shifts in the fluorescence maxima and increase of fluorescence quantum yields are observed for the studied 5-methyl-quinolinylbenzoxazoles, whereas no considerable changes of fluorescence band positions and of quantum yields are observed for the 5-chloro-quinolinylbenzoxazoles in polar and protic solvents. This difference is suggested to be caused by the difference in solvent cage relaxation process, occurring in polar and protic solvents after the absorption, for 5-methyl-quinolinylbenzoxazoles and for 5-chloro-quinolinylbenzoxazoles.

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