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# Spectral properties and complex formation with $Cu^{2+}$ ions of 2- and 4-(*N*-arylimino)-quinolines

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**Abstract**

The spectral-fluorescent properties of substituted 2- and 4-(*N*-arylimino)quinolines have been investigated in solvents of different polarity and proton donating ability, and in immobilized phases of PVC films and sol–gel matrix. The effect of the solvent on spectral characteristics has been estimated. It has been shown that, despite the possibility of quenching process linked with intramolecular motions with great amplitude of the non-fixed azomethine fragment, the low fluorescence quantum yield of the studied compounds in polar solvents and in immobilized phases is caused mainly by the quenching process which is not linked directly with significant changes in molecular geometry.

The complexation process of the studied *ortho*-hydroxyphenols with $Cu^{2+}$ ion caused strong changes in their absorption spectra. Among the studied compounds, 4-chloro-2-[(quinolin-2-yl-methylene)]-amino-phenol has shown better selectivity and sensitivity towards $Cu^{2+}$. This compound could be suggested as a prospective reagent for spectroscopic determination of $Cu^{2+}$ trace amounts ($<10^{-4}$ M), e.g. for copper determination in Al-based alloys.


*Keywords:* Spectral-fluorescence properties; Fluorescence quenching; Complex formation

## 1. Introduction

Scheme 1 shows the structure of the investigated compounds and the corresponding substituents. The practical interest upon 2- and 4-(*N*-arylimino)quinolines is based on their bio-medical application. They have been investigated to their clinical efficacy for use as an analgetic drug [1], but there is no any detailed study of the spectral-fluorescent properties of the investigated compounds, presented in Scheme 1.

It is known that azo compounds (arylazoheterocycles), containing the fragments –N=N–C=N–, –C=N–C–N=N–, –C=N–C=N–C–, –C–N=C–C=N–C–, are very sensitive for $Cu^{2+}$ or $Cu^{+}$ ions and, therefore, are used for spectroscopic copper determination [2–11]. The present compounds also contains these fragments with (azomethine function) pyridinic nitrogen, hence, they (the compounds **1**–**4**) could be considered as possible analytical reagent for spectrophotometric determination of cupric, $Cu^{2+}$ or cuprous, $Cu^{+}$ ions.

The present paper deals with the influence of solvent polarity, solvent hydrogen-bonding ability and viscosity of the media (PVC, sol–gel matrix) on the characteristics of the electronic spectra of 2- and 4-(*N*-arylimino)quinolines of **1**–**4**. Also, we report here the possibility to determine very low concentrations of $Cu^{2+}$ ions using 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol (**1**), by means of UV-Vis spectroscopy.

## 2. Experimental details

### 2.1. Materials

The compounds were synthesized by condensation of quinoline-2-carbaldehyde or quinoline-4-carbaldehyde with aromatic amines [12].

The organic solvents used were all of spectrophotometry grade and were used as supplied from Fluka. The

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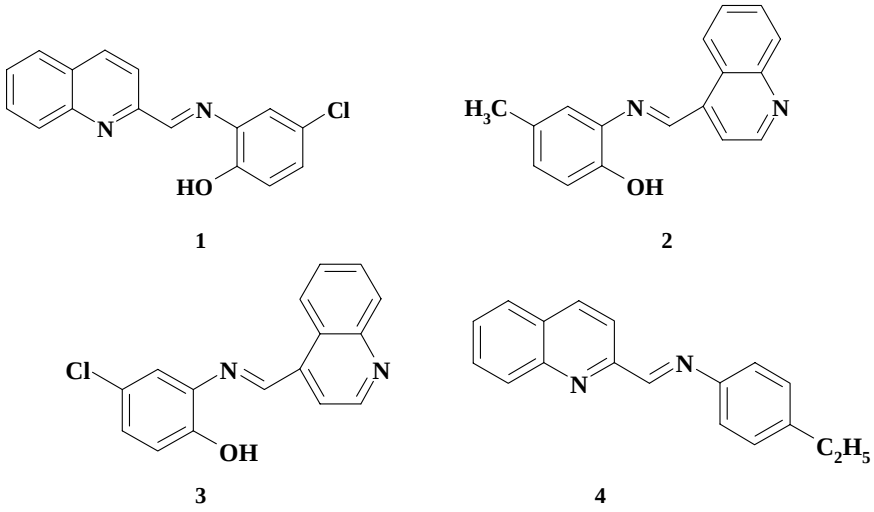



Scheme 1. Structure of the investigated compounds.

copper salt $CuCl_2{\cdot}2H_2O$ and $FeSO_4$, $AlCl_3{\cdot}6H_2O$, $FeCl_3$, $MgCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$ used in complexation experiments was purchased from Merck. Quinine sulfate used as fluorescence standard for quantum yield determination was purchased from Fluka.

### 2.2. Synthesis

A mixture of carbaldehyde (1.0 mmol) and phenolic amine (1.0 mmol) either in absolute ethanol was refluxed until the starting aldehyde completely disappeared (judged by tlc), then cooled, filtered and crystallized from ethanol to give pure compound.

*4-Chloro-2-{[(1E)-quinolin-2-ylmethylene]amino}phenol **(1)***: as yellow needles (77%); mp 159 °C; IR (KBr): 3381, 3080, 3029, 2897, 1612, 1594, 1488, 1364, 1232, 1162, 906, 874, 821 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ (ppm) 6.97–8.31 (m, aromatic and CH, 10H), 8.98 (s, OH, 1H); MS: *m/z* 284 (M + 2), 283 (M + 1), 282 ($M^+$), 281 (M − 1), 265, 253, 221, 155, 129, 109, 101.

*4-Methyl-2-{[(1E)-quinolin-2-ylmethylene]amino}phenol **(2)***: as pale yellow rods (86%); mp 201 °C; IR (KBr): 3375, 3040, 3029, 2927, 2876, 1625, 1574, 1497, 1242, 1191, 808, 757 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ (ppm) 2.38 (s, $CH_3$, 3H), 6.96–9.09 (m, aromatic and CH, 10H), 9.42 (s, OH, 1H); MS: *m/z* 264 (M + 2), 263 (M + 1), 262 ($M^+$), 261 (M − 1), 218, 155, 134, 129, 128, 107.

*4-Chloro-2-{[(1E)-quinolin-4-ylmethylene]amino}phenol **(3)***: as pale yellow cottony crystals (78%); mp 220 °C; IR (KBr): 3380, 3044, 2871, 1626, 1577, 1487, 1279, 1232, 1209, 839, 758 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ (ppm) 7.01–9.06 (m, aromatic and CH, 10H), 9.33 (s, OH, 1H); MS: *m/z* 284 (M + 2), 283 (M + 1), 282 ($M^+$), 281 (M − 1), 218, 154, 129, 128, 127, 101.

*N-(4-Ethylphenyl)-N-[(1E)-quinolin-2-ylmethylene]amine **(4)***: as colorless needles (90%); mp 81 °C; IR (KBr): 3052, 2959, 2924, 2866, 1622, 1593, 1501, 1428, 1361, 1205, 1118, 965, 870, 835, 756, 556 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ (ppm) 1.26 (t, $CH_3$, 3H), 2.67 (q, $CH_2$, 2H), 7.24–8.38 (m, aromatic, 10H), 8.81 (s, CH, 1H); MS: *m/z* 261 (M + 1), 260 ($M^+$), 259 (M − 1), 245, 232, 218, 204, 155, 129, 128, 102.

### 2.3. 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 with reference to the absorption and fluorescence spectra of Quinine sulfate in 0.5 M $H_2SO_4$ solution ($\varphi_f = 0.546$) [13,14]. The calculated relative fluorescence quantum yields were the values corrected for refraction index differences between the measured and standard solutions [15]. The equation, used in calculations of fluorescence quantum yield:

$$\varphi_{fU} = \varphi_{fR} \frac{S_U}{S_R} \frac{(1 - 10^{-A_R})}{(1 - 10^{-A_U})} \frac{n_U^2}{n_R^2} \quad (1)$$

where $\varphi_f$ 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 conducted for dilute solutions in absorbance range of 0.1–0.15 at the excitation wavelength (concentrations $10^{-5}$ to $10^{-6}$ mol $l^{-1}$).

### 2.4. Theoretical calculations

Semi-empirical calculations were performed using the original parameters of the program PM3 [16] based on the restricted Hartree–Fock (RMF). This method is commonly accepted to calculations of nitrogen-containing compounds [17].

Geometries for ground and for excited state were optimized in internal coordinates. The calculations were carried out with full geometry optimization without any assumption of symmetry. Mulliken charges [18] were used to discuss the electron density distributions.

### 2.5. Determination of stoichiometry and stability constant of metal complexes from spectrophotometric titrations

Information on the stoichiometry of the complexes was obtained from the continuous variation method (Job's method) [19].

Let us consider a complex $M_mL_l$ (where ligand denoted L and the metal ion M) formed according to the equation:

$$mM + lL \rightleftharpoons M_mL_l \quad (2)$$

with stability constant $\beta_{ml} = [M_mL_l]/([M]^m[L]^l)$.

The principle of the method as follows: the absorbance (Abs) is measured for a series of solutions containing the ligand and the cation such that the sum of the total concentrations of ligand and cation is constant:

$$C_L + C_M = C = \text{constant} \quad (3)$$

The position of the maximum of absorbance ($Abs_{max}$) is then related to the ratio $m/l$, as shown below. It is convenient to use the following dimensionless quantity (which is analogous to molar fraction but not strictly):

$$X = \frac{C_M}{C_M + C_L} \quad (4)$$

It has been shown [19,20], that

$$\frac{m}{l} = \frac{X_{max}}{1 - X_{max}} \quad (5)$$

where $X_{max}$—correspond to the $Abs_{max}$—maximum of absorbance at an appropriate wavelength (chosen so that the changes of absorbance are as large as possible).

For 1:1 complex, $X_{max} = 1/2$, according to Eq. (4). In this case

$$M + L = ML \quad (6)$$

and stability constant $K_s = [ML]/([M][L])$ could be found from the equation [20]:

$$\frac{Abs - Abs_0}{Abs_{LIM} - Abs} = K_s[M] \quad (7)$$

where Abs is the absorbance of the solution at chosen wavelength after addition of given amount of cation at a concentration [M], $Abs_0$ is the absorbance of the free ligand at given wavelength, before the addition of the cation, $Abs_{LIM}$ is the absorbance at given wavelength in the presence of an excess of cation such that the ligand is fully complexed.

## 3. Results and discussions

### 3.1. Absorption and emission properties of complex-free 2- and 4-(N-arylimino)quinolines

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

Absorption spectra of the studied compounds in the region 200–460 nm consist of five bands of π–π* nature. The conjugated systems of the investigated compounds contain quinoline and azomethine fragments. Hence, the observed absorption bands could be attributed to these chromophoric fragments. In comparison with quinoline and *N*-benzaniline absorption spectra, the absorption spectra of the studied compounds are shifted to the long-wavelength region. Such a bathochromic shift could be explained by the extention of the conjugated system with the addition of azomethine fragment to the quinoline nucleus. Like in the cases of

Table 1
UV-Vis spectroscopic data[a] of complex-free quinolinylazomethines in solvents with different polarities and hydrogen-bonding abilities

| Compound | Solvent | ε | n | $\lambda^1_{abs}$ | $\lambda^2_{abs}$ | $\lambda^3_{abs}$ (shoulder) | $\lambda^4_{abs}$ | $\lambda^5_{abs}$ |
|---|---|---|---|---|---|---|---|---|
| **1** | Toluene | 2.38 | 1.4961 | 376 | 309 | 296 | – | – |
| | Acetonitrile | 36.20 | 1.3441 | 367 | 303 | 266 | 252 | 231 |
| | Methanol | 32.63 | 1.3286 | 371 | 301 | – | 251 | 232 |
| **2** | Toluene | 2.38 | 1.4961 | 390 | 333 | – | – | – |
| | Acetonitrile | 36.20 | 1.3441 | 382 | 330 | 268 | 244 | 230 |
| | Methanol | 32.63 | 1.3286 | 388 | 317 | 269 | 251 | 232 |
| **3** | Toluene | 2.38 | 1.4961 | 384 | 338 | – | – | – |
| | Acetonitrile | 36.20 | 1.3441 | 375 | 334 | – | 248 | 229 |
| | Methanol | 32.63 | 1.3286 | 377 | 302 | – | 246 | 227 |
| **4** | Toluene | 2.38 | 1.4961 | 341 | 302 | – | – | – |
| | Acetonitrile | 36.20 | 1.3441 | 334 | 299 | 258 | 243 | 228 |
| | Methanol | 32.63 | 1.3286 | 340 | 305 | – | 263 | 245 |

[a] ε and *n*—dielectric permeability and refractive index of the solvent; $\lambda^{1-5}_{abs}$—are the positions of the maxima in the absorption spectra (nm).

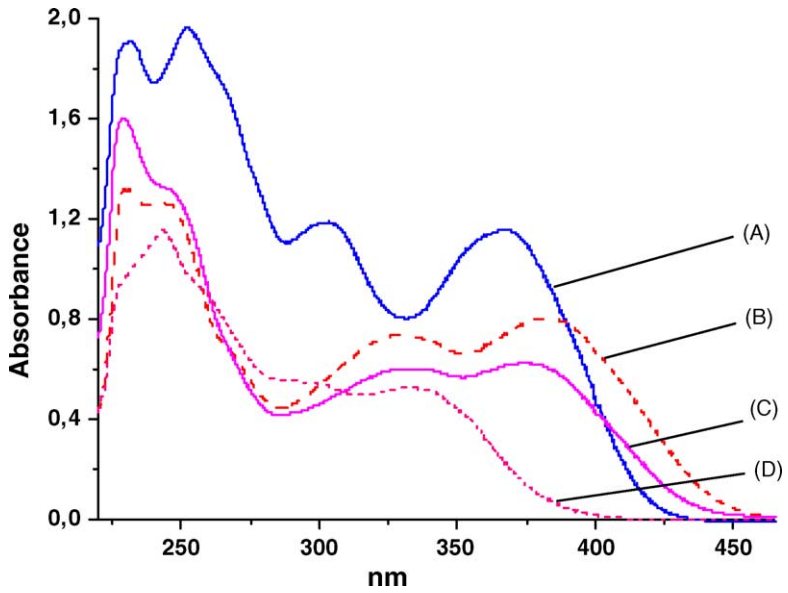



Fig. 1. Absorption spectra of complex-free compounds **1**–**4** in acetonitrile: **1** (A), **2** (B), **3** (C), **4** (D).

quinoline [21] and *N*-benzaniline [22], 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, short-wavelength shifts in the absorption maxima are observed (up to 9 nm, Table 1). This result points out to the fact that the dipole moment of the studied compounds in excited state is lower than the corresponding dipole moment in ground state. Increasing solvent polarity stabilizes the ground state to a greater degree than the electronically excited state and the absorption spectrum tends to shift to shorter wavelength with the increasing solvent polarity [23]. Long-wavelength shift of the absorption spectra is observed in polar proton-donating methanol in comparison with polar non-hydrogen-bonding acetonitrile (see Table 1). Taking into account that according to quantum chemical calculations (see Fig. 2) electronic density redistributes to quinoline and azomethine nitrogens on excitation, one could explain the position of long-wavelength absorption maxima of compounds **1**–**4** in proton donating methanol by interaction of hydrogen-bond donor methanol with unshared valence electron pairs of the nitrogen atoms. The latter are charge acceptor in the excited state.

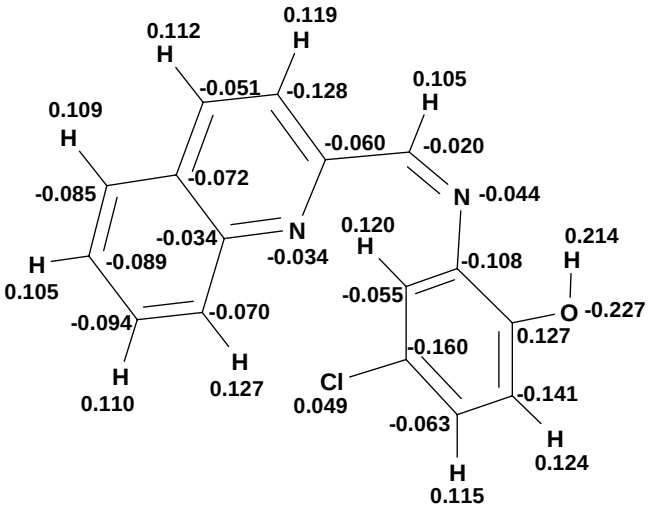
Hydrogen-bonding donor solvent (methanol), interacting with unshared valence electron pairs of functional groups that are charge-transfer acceptors in the excited state (the nitrogen atoms) enhance charge-transfer by introducing a partial positive charge into the functional group (the nitrogen atoms). This interaction stabilizes the charge-transfer excited state relative to the ground state, so that the absorption spectra tend to shift to the lower energies with increasing hydrogen-bond capacity of the solvent [23].

Thus, dipolar and hydrogen-bonding effects both influence electronic spectra, and their combined effects nearly compensate one another. As a result, no significant shift in the position of the absorption of compounds **1**–**4** is observed in methanol solution in comparison with the corresponding position of absorption spectra in low-polar aprotic toluene solution.

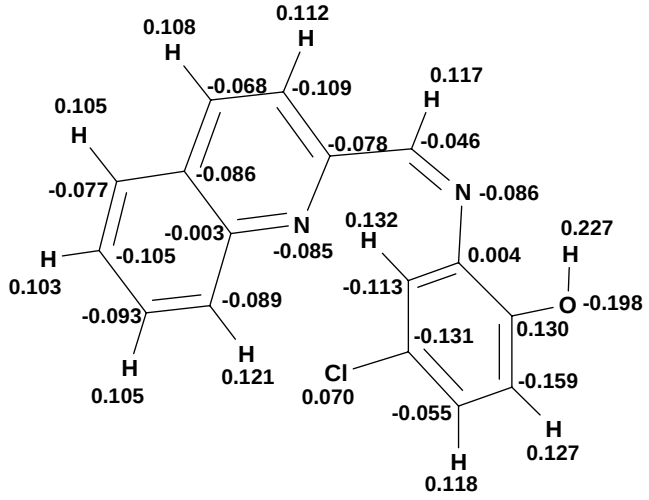
Absorption spectra of 4-quinoline substituted compounds **2** and **3** are observed in more long-wavelength region, than the corresponding spectra of 2-quinoline substituted compounds **1** and **4**. This fact could be explained by the molecular structure of the compounds **1**–**4**.

The quantum-chemical calculations (geometry optimisation, PM3) shows that, the 4-quinoline substituted compounds **2** and **3** are planar, but the 2-quinoline substituted compounds **1** and **4** are non-planar in ground electronic state: dihedral angle between quinoline and phenyl fragments in compounds **1** and **4** is 76°. Such non-planarity in 4-quinoline substituted compounds **1** and **4** results in lack of conjugation between quinoline and phenyl fragments, thus, the absorption spectra of **1** and **4** shifts to higher energies in comparison with the absorption spectra of **2** and **3**. This results in a hypsochromic shift of absorption bands of **1** and **4**. If one compares the absorption spectra of **1** with the corresponding absorption spectra of **4**, and, the absorption spectra of **2** with the corresponding absorption spectra of **3**, one could notice that the electron-donor substituents in the phenyl ring (hydroxy group—for **1**, ethyl group—for **2**) shift the spectra of **1** and **2** to long-wavelength region. On the contrary, the presence of electron-acceptor chlorine in the phenyl ring of compound **3** brings short-wavelength displacement of the absorption spectra with respect to those of compound **2** with electron-donor methyl group in 4′-position of the phenyl ring.

Fluorescence of compounds **1**–**4** is associated with the extended conjugation of the quinoline ring system (Fig. 3). The fluorescence emission spectra of all the studied compounds




(a) Ground State




(b) Excited State

Fig. 2. Calculated charge distribution in $S_0$ (a) and in $S_1$ (b) electronic state of 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol.

consist of only one wide fluorescent band in all the solvents used (see Table 2, Fig. 3).

In contrast to the absorption spectra, the wavelengths of fluorescence bands are not much affected by change in the solvent polarity and/or the hydrogen-bonding ability (Table 2, Fig. 3). This could be explained by the fact that despite the qualitative similarity of solvent polarity influence upon fluorescence and absorption spectra of the solute, the solvent cage relaxation processes occurring subsequent to the absorption and fluorescence, tend to shift the fluorescence to longer wavelength with increasing solvent polarity [23]. As a result, the emission bands of compounds **1**–**4** practically unshifted with the increase of solvent polarity, while the absorption bands clearly shifted to shorter wavelength by the same solvent effect.

As can be seen from the data cited in Table 2, the studied compounds have very low (in comparison with quinoline [21]) fluorescence quantum yields, $\varphi_f = 10^{-4}$, which increases (up to $\varphi_f = 10^{-3}$) with solvent polarity.

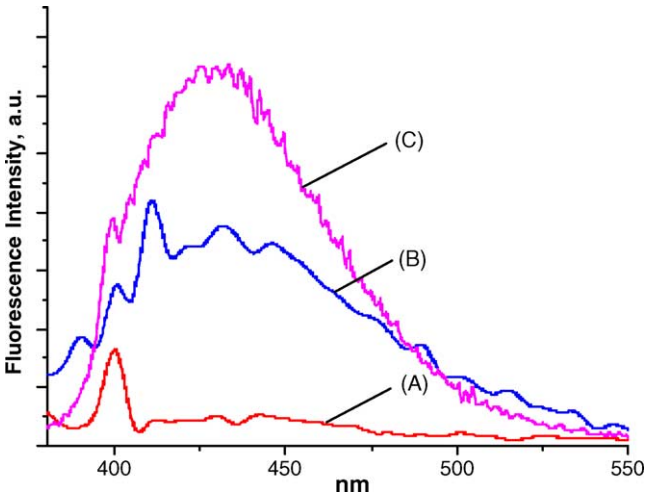



Fig. 3. Fluorescence spectra of complex-free 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol in toluene (A), in acetonitrile (B), and in methanol (C) at $\lambda_{exc} = 360$ nm.

By analogy with quinoline, isoquinoline, phenanthridine, and 5,6-benzoquinoline, such increases of fluorescence quantum yields in solvents of high polarity could be explained by changes in the arrangement of the singlet n–π* and π–π* levels [20] and by the fact that the vibrational spin–orbital interaction between the lowest $S_{\pi\pi^*}$ and the higher $S_{n\pi^*}$ level (with subsequent transition to the triplet level) is less probable in polar or hydroxyl-containing solvents than in hydrocarbon solvents [24].

On the other hand in contrast to quinoline, where fluorescence intensity increases considerably in polar or protic solvents [22], the presence of the azomethine fragment in studied compounds causes the loss of considerable fluorescence intensity in polar or protic solvents (see Table 2).

Table 2
Spectral-luminescent characteristics[a] of complex-free quinolinylazomethines in solvents with different polarities and hydrogen-bonding abilities

| Compound | Solvent | $\lambda_{fl}$ | $\Delta\lambda_{ST}$ | $\varphi_f$ |
|---|---|---|---|---|
| **1** | Toluene | 432 | 56 | $4.5 \times 10^{-4}$ |
| | Acetonitrile | 432 | 65 | $2.3 \times 10^{-3}$ |
| | Methanol | 431 | 60 | $1.4 \times 10^{-3}$ |
| **2** | Toluene | 432 | 42 | $3.3 \times 10^{-4}$ |
| | Acetonitrile | 432 | 50 | $2.1 \times 10^{-3}$ |
| | Methanol | 429 | 41 | $5.3 \times 10^{-3}$ |
| **3** | Toluene | 434 | 50 | $6.2 \times 10^{-4}$ |
| | Acetonitrile | 432 | 57 | $3.1 \times 10^{-3}$ |
| | Methanol | 432 | 55 | $3.4 \times 10^{-3}$ |
| **4** | Toluene | 432 | 91 | $4.3 \times 10^{-4}$ |
| | Acetonitrile | 430 | 96 | $2.6 \times 10^{-3}$ |
| | Methanol | 428 | 88 | $1.1 \times 10^{-3}$ |

[a] $\lambda_{fl}$ and $\Delta\lambda_{ST}$ are the positions of the maxima in the fluorescence spectra (nm), and the Stokes shift of the fluorescence (nm), $\varphi_f$ is the quantum yield of fluorescence, $\lambda_{exc} = 360$ nm.

This fact may be explained by the possibility of two different of quenching process, (i) the quenching process not linked directly with significant change of molecular geometry (intersystem crossing $S_{\pi\pi} \rightarrow T_{n\pi^*}$ caused by introduction of azomethine fragment triplet levels into the system of terms of the studied compounds [24]) and (ii) quenching process linked with intramolecular motions with great amplitude (torsional and deformation vibrations in non-fixed azomethine fragment).

In order to diminish the influence of the latter quenching process, we embedded the studied compounds into PVC and sol–gel matrix, but no noticeable fluorescence intensity increase was detected. This fact means that the contribution of the quenching process not linked directly with significant change of molecular geometry is much more pronounced into fluorescence quenching process of **1**–**4**.

### 3.2. Spectral properties of the complexes with $Cu^{2+}$ ions

According to Hata and Uno [11] *ortho*-hydroxyphenols containing hydroxy group in *ortho*-position of phenyl ring give more intensely colored chelates with different metals ($Fe^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Mn^{2+}$) than the corresponding compounds without the mentioned *ortho*-hydroxy group.

For this reason, we focused our attention on complexation properties of *ortho*-hydroxyphenol derivatives of quinolines, **1**–**3**, and selected to study the compounds **1** and **3**.

Addition of $Cu^{2+}$ ions to methanol solutions of **1** and **3** induced drastic changes in absorption spectra. In the case of compound **1**, the appearance of a new band in 540–550 nm region was observed (see Fig. 4). In the case of compound **3**, a readily detectable long-wavelength shift (up to 70 nm) was detected (see Fig. 5).

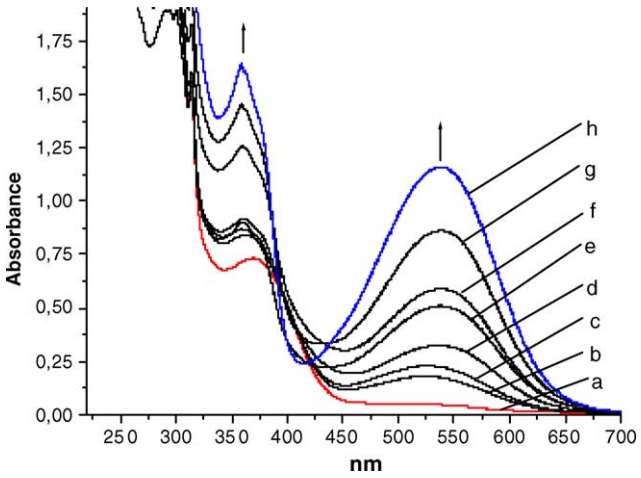



Fig. 4. Changes in the absorption spectra during the complex formation of 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol ($2 \times 10^{-4}$ mol l$^{-1}$), with the $Cu^{2+}$ ions in methanol. Arrows indicate a change in the absorbance with the increase in the concentration of $Cu^{2+}$ (mol l$^{-1}$): 0 (a), $5.7 \times 10^{-6}$ (b), $8.5 \times 10^{-6}$ (c), $2.4 \times 10^{-5}$ (d), $4.2 \times 10^{-5}$ (e), $5.7 \times 10^{-5}$ (f), $8.4 \times 10^{-5}$ (g), $1.5 \times 10^{-4}$ (h).

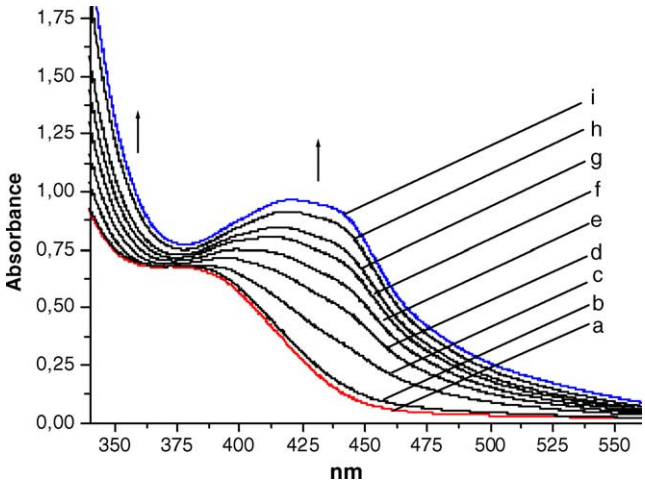



Fig. 5. Changes in the absorption spectra during the complex formation of 4-chloro-2-{[(1*E*)-quinolin-4-ylmethylene]amino}phenol ($2 \times 10^{-4}$ mol l$^{-1}$), with the $Cu^{2+}$ ions in methanol. Arrows indicate a change in the absorbance with the increase in the concentration of $Cu^{2+}$ (mol l$^{-1}$): 0 (a), $5.7 \times 10^{-5}$ (b), $5.6 \times 10^{-4}$ (c), $1.7 \times 10^{-3}$ (d), $2.3 \times 10^{-3}$ (e), $3.3 \times 10^{-3}$ (f), $3.9 \times 10^{-3}$ (g), $5.4 \times 10^{-3}$ (h), $6.4 \times 10^{-3}$ (i).

The observed changes in absorption spectra of compounds **1** and **3** can be attributed to the formation of donor–acceptor complexes of $Cu^{2+}$ ion with the participation of lone electron pairs of the quinoline and the azomethine nitrogen atoms (in case of compound **1**) or of the quinoline nitrogen atom (in case of compound **3**). A strong hyperchromic effect was observed for all the bands of the ligands **1** and **3**.

The delocalisation of the negative charge over the conjugated system during the $Cu^{2+}$ complex formation resulted in a strong red-shift of the absorption long-wavelength bands together with a hyperchromic effect (see Figs. 4 and 5).

No fluorescence emission was detected on addition of $Cu^{2+}$ ions to methanol solutions of **1** and **3**. This result may be explained by the fact that, $Cu^{2+}$ ions usually introduce easily accessible low energy levels which could give rise to energy- and electron-transfer processes [25,26], and capable to quench the fluorescent excited states of the studied compounds.

### 3.3. Structure and stability of the complexes with $Cu^{2+}$ ions

Complex formation was studied at the same concentration of compounds **1** and **3** ($2 \times 10^{-4}$ mol l$^{-1}$) and in a wide range of $Cu^{2+}$ concentrations ($7 \times 10^{-7}$ to $6 \times 10^{-3}$ mol l$^{-1}$). A low and unchanged concentration of the electroneutral organic ligand allowed us to exclude from consideration the theoretically possible formation of biligand complexes (according to the equilibrium $2L + M^{2+} \rightleftharpoons (ML_2)^{2+}$), whose detection, under our experimental conditions, requires the complex formation constant to be higher than $10^7$–$10^9$ mol l$^{-1}$.

Information on the stoichiometry of the metal–ligand complexes of compounds **1** and **3** was obtained from the continuous variation method [19]. Job's plot [19] for compound **1** is presented on Fig. 6.

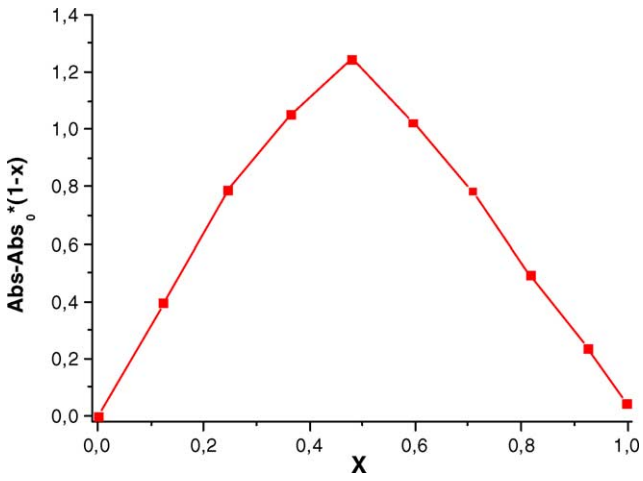



Fig. 6. Job's plot for complex formation of 4-chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol, with $Cu^{2+}$ in methanol ($\lambda_{abs}$ = 540 nm, $C^{sum} = 4 \times 10^{-4}$ M; Abs, $Abs_0$, *X*—defined in Section 2.5).

It was found from the Job's plots for compounds **1** and **3** that $X_{max} = 1/2$ for both compounds, hence, the stoichiometry of the metal–ligand complexes of compounds **1** and **3** was found to be 1:1 at used concentration of the ligands ($2 \times 10^{-4}$ mol l$^{-1}$).

On the base of spectrophotometric titration curves (i.e. plots of $(Abs - Abs_0)/(Abs_{LIM} - Abs)$ versus $[Cu^{2+}]$) the stability constants were calculated (presented in Table 3). The stability constants for chelating complexes of **1** are two orders of magnitude higher than the corresponding stability constants for chelating complexes of **3** (see Table 3). This fact could be explained by taking into consideration the differences of the structures between the compounds **1** and **3**. In contrast to **3**, two nitrogen atoms of **1** are situated close to each other, thus, both of them take part in complex formation with $Cu^{2+}$ ion.

In general, the calculated values of stability constants for **1** and **3** (see Table 3) are compatible with those obtained by photometric methods for binding of calcium and magnesium ions with crown ethers ($K_s \sim 10^4$–$10^3$ [27,28]), which are widely used as building blocks in chromo- and fluoro-ionophore design since they are considered to be highly efficient for alkali and alkaline earth ion binding [20,28].

None of the following ions affected the direct determination of $1 \times 10^{-5}$ mol l$^{-1}$ of $Cu^{2+}$: $Al^{3+}$ ($3 \times 10^{-2}$ mol l$^{-1}$), $Mg^{2+}$ ($10^{-1}$ mol l$^{-1}$), $Mn^{2+}$ ($7 \times 10^{-4}$ mol l$^{-1}$), $Fe^{2+}$ ($5 \times 10^{-4}$ mol l$^{-1}$). The ions were considered as non-interfering when they caused a change in the absorbance of the $Cu^{2+}$–compound **1** complex (Abs = 0.22) less than 5%.

Probably, the selectivity to $Cu^{2+}$ ions could be explained by such factors as: (i) spatial structure of the cation–receptor fits the diameter of $Cu^{2+}$ ion (1.35 Å) and (ii) by appropriate basicity of quinoline and azomethine nitrogen atoms (i.e. "soft" ligand–"soft" copper cation).

The detection limits for compounds **1** and **3** were found to be $2.1 \times 10^{-6}$ and $5.6 \times 10^{-5}$ mol l$^{-1}$, correspondingly.

In general, significant spectroscopic effects of **1** on $Cu^{2+}$ ion binding suggest that this compound is sensitive spectroscopic probe for $Cu^{2+}$ ion, so it has prospects for use as reagent for copper determination in Al-based alloys (e.g. BCS No. 216/1-262: Cu-0.026%, Mg-10.57%, Fe-0.19%, Mn-0.06% [29]).

Table 3
Complex formation of compounds **1** and **3** with the $Cu^{2+}$ ions in methanol

| Compound | $\lambda_{max}$ | $\varepsilon_{abs\,(max)}$ | Log $K_s$ |
|---|---|---|---|
| **1** | 540 | 5560 | 4.19 ± 0.01 |
| **3** | 435 | 4590 | 2.78 ± 0.04 |

$\lambda_{max}$ and $\varepsilon_{abs\,(max)}$ are the position (nm) and molar extinction coefficient (l mol$^{-1}$ cm$^{-1}$) of the long-wavelength maximum in the absorption spectra of $Cu^{2+}$ complex. Log $K_s$ is the logarithm of the stability constant of the $Cu^{2+}$ complex.

## 4. Conclusion

The experimental results for the luminescence characteristics of 2- and 4-(*N*-arylimino)quinolines in solutions and in immobilized phases (PVC, sol–gel matrix) at room temperature indicate that the low fluorescence quantum yield of these structures is connected mainly with the quenching process which is not linked directly with significant change of molecular geometry (intersystem crossing ($S_{n\pi^*} \rightarrow S_{\pi\pi^*}$) caused by introduction of azomethine fragment triplet levels [22]). The contribution of the quenching process linked with intramolecular motions with great amplitude (intramolecular librations of azomethine moiety) is much less pronounced.

4-Chloro-2-{[(1*E*)-quinolin-2-ylmethylene]amino}phenol, have shown in methanol good properties as colorimetric chemosensor. Indeed, **1** form complexes with $Cu^{2+}$ having a 1:1 (ligand:metal) stoichiometry with rather high association constant (log $K_s$ = 4.19). The association causes changes in the absorption properties, i.e. the appearance of the long-wavelength absorption band (540 nm) of $Cu^{2+}$ complex. Taking into account rather good selectivity, high affinity and sensitivity of **1** for $Cu^{2+}$ ions, the studied compound **1** could be proposed as reagent for spectroscopic determination of trace amounts of $Cu^{2+}$ ($<10^{-4}$ mol l$^{-1}$, detection limit: $2.1 \times 10^{-6}$ mol l$^{-1}$), for instance—in Al-based alloys.

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