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Synthesis, Structure, and Luminescent Properties of 2-[2-(9-Anthryl)vinyl]quinolines

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Abstract—Previously unknown 2-[2-(9-anthryl)vinyl]quinolin-8-ol and 2-[2-(9-anthryl)vinyl]-8-methoxyquinoline were synthesized by condensation of 8-hydroxy(methoxy)-2-methylquinoline with 9-anthraldehyde in acetic anhydride, as well as by the Wittig reaction. The product structure was determined on the basis of their ^{1}H NMR, IR, UV, and mass spectra and quantum-chemical calculations. 2-[2-(9-Anthryl)vinyl]-8-methoxyquinoline showed luminescence with a quantum yield φ of 0.25, which was considerably higher than that of its 8-hydroxy analog (φ = 0.067).

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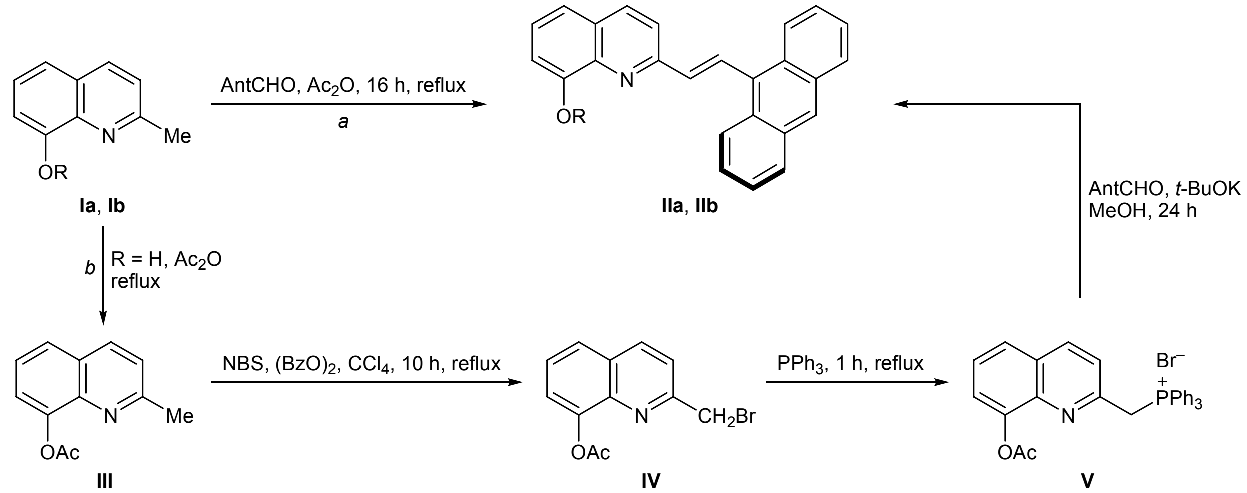
8-Hydroxyquinoline and its derivatives attract considerable interest due to their wide application as chelating ligands for the preparation of various photo- and electroluminescent metal complexes [1, 2] and highly effective fluorescent chemosensors for metal cations [3, 4]; in addition, these compounds exhibit strong biological activity [5]. In particular, 8-hydroxyquinoline aluminum (AlQ_3) due to its good conducting properties and intense yellow–green luminescence in the solid state is one of the main electroluminescent materials in organic light-emitting diodes (OLEDs) [6]. It is known that π–π*-electron transitions in AlQ_3 and analogous metal complexes occur in the chelating 8-hydroxyquinoline ligand and that the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) are localized on the phenol and pyridine fragments, respectively [7]. Electron-donating and electron-withdrawing substituents in the phenol and pyridine rings of the ligand strongly affect the energy gap between the HOMO and LUMO, so that chemical modification of the ligand may be used for fine tuning of optical parameters, as well as of electron and hole transport properties of metal complexes. Furthermore, introduction of substituents, e.g., styryl groups, into the hydroxyquinoline ligand system enhances thermal stability of metal complexes as compared to complexes with unsubstituted quinolines and improves their solubility in organic solvents [8, 9]. The latter factor is very important in the manufacture of light-emitting diodes; it ensures the possibility of using modern high-performance technologies such as spin-coating and ink-jet printing for the preparation of thin amorphous films from such compounds [10].

Taking the above stated into account, we made an attempt to obtain a new 8-hydroxyquinoline ligand system containing a 2-(9-anthryl)vinyl substituent in position *2* of the quinoline ring with a view to synthesize therefrom photo- and electroluminescent metal complexes for light-emitting diodes.

It is known that 2-methylquinolin-8-ol (**Ia**) reacts with 4 equiv of aromatic aldehydes on prolonged heating in boiling acetic anhydride to give the corresponding 2-styrylquinolin-8-ols [5, 11, 12]. By analogous reaction with 9-anthraldehyde we synthesized previously unknown 2-(2-anthrylvinyl)quinolin-8-ol (**IIa**) in moderate yield (29%), and the reaction of the same aldehyde with 8-methoxy-2-methylquinoline (**Ib**) afforded methoxy derivative **IIb** (Scheme 1, path *a*). We also proposed an alternative synthetic route to compound **IIa** via Wittig reaction (Scheme 1, path *b*). The latter path is more advantageous due to higher yield of the target product (68%), simpler procedures for its isolation and purification, and the use of an equimolar amount of the aldehyde component.

The electronic spectra of **IIa** contained a set of strong absorption bands at λ_{max} 213–392 (acetonitrile)

Scheme 1.

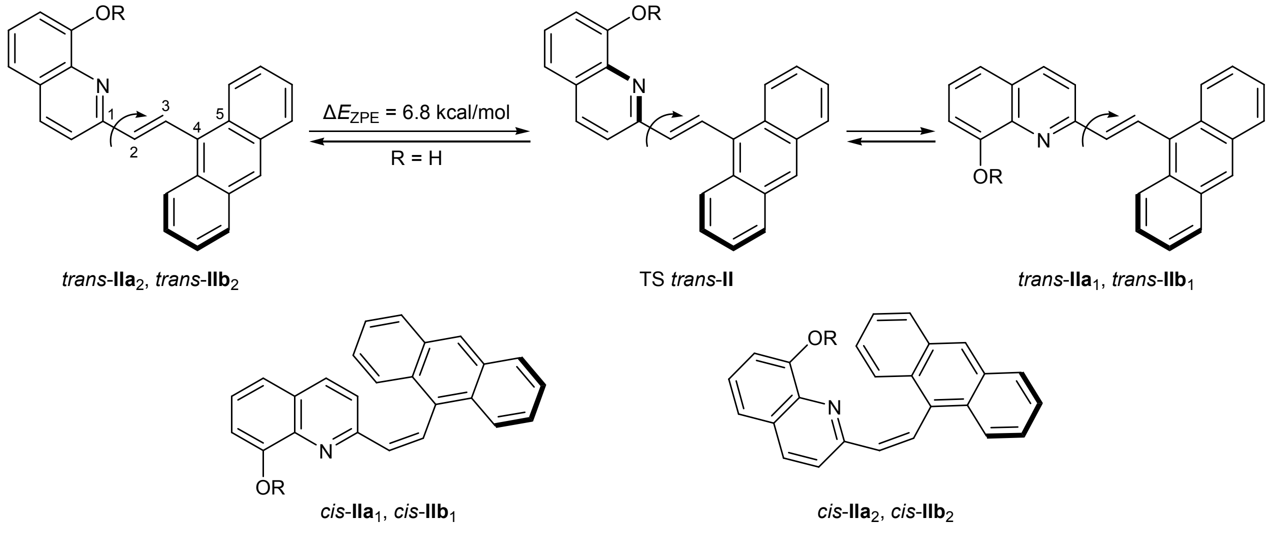


R = H (**a**), Me (**b**); Ant = 9-anthryl.

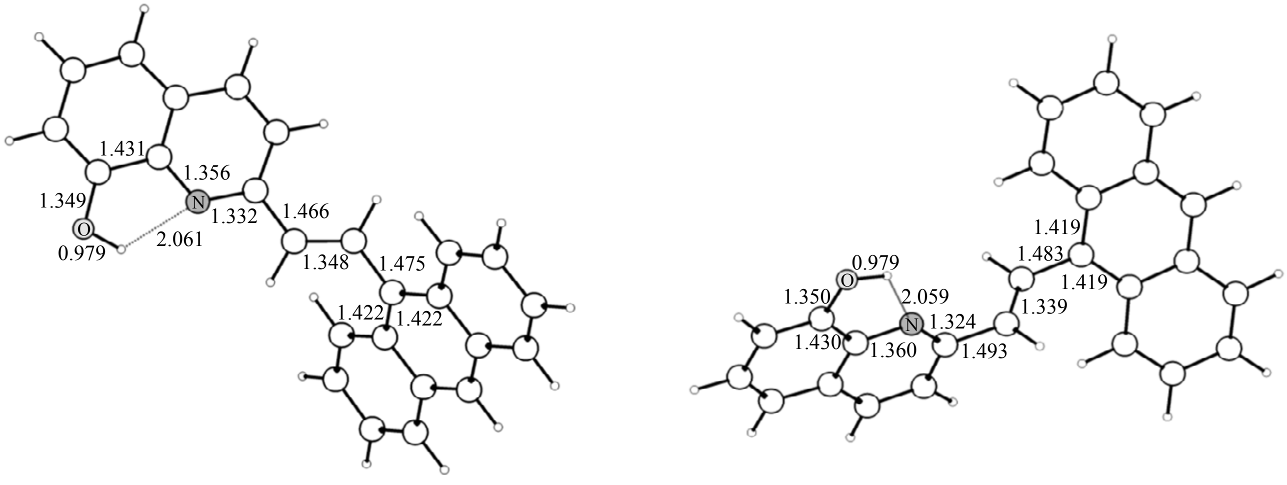
or 333–391 nm (toluene), which were assigned to π–π^* electron transitions in the anthracene and quinoline fragments and in the entire conjugation system of molecule **IIa**. The observed doubling of long-wave maxima may be related to the presence of two forms characterized by fairly similar spectral parameters. Compound **IIa** in acetonitrile displayed a luminescence emission maximum at λ_{fl} 501 nm (φ = 0.005). The low luminescence quantum yield φ of **IIa** may be due to radiationless deactivation of the excited state via photoinitiated intramolecular proton transfer (ESIPT) from the phenolic hydroxy group to the nitrogen atom in the quinoline ring. The ESIPT process is likely to be favored by considerable increase of the acidity of the phenolic hydroxy group and basicity of the pyridine-type nitrogen atom in the 8-hydroxyquinoline system upon excitation [13, 14]. The electronic absorption spectra of methoxyquinoline **IIb** were analogous to the spectra of **IIa**, and their emission maxima in toluene were very similar (λ_{fl} 493 and 496 nm for **IIb** and **IIa**, respectively). However, the luminescence quantum yield of compound **IIb** (φ = 0.25) was considerably higher than that of **IIa** (φ = 0.067) since the former lacks labile proton and ESIPT is impossible.

The electronic and steric structures and relative stabilities of possible *cis* and *trans* isomers and the corresponding conformers of **IIa** and **IIb**) (see table and figure; Scheme 2) were determined by quantum-

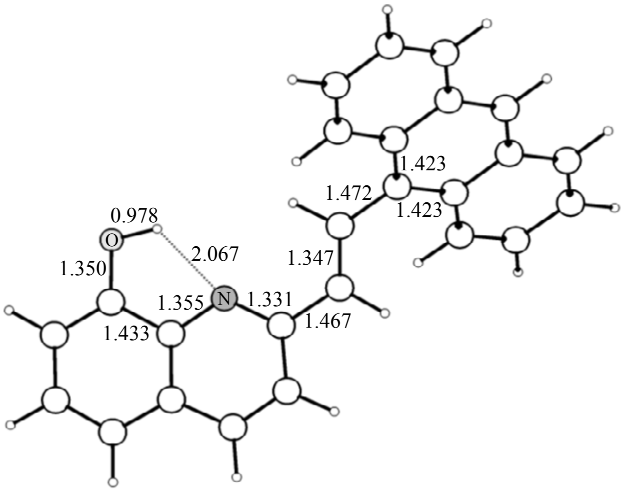
Scheme 2.



R = H (**a**), Me (**b**).



trans-**IIa**$_1$, c_1 TS *trans*-**IIa**, c_1



trans-**IIa**$_2$, c_1

Calculated [B3LYP/6-31G(*d,p*)] structures of conformers *trans*-**IIa**$_1$ and *trans*-**IIa**$_2$ and transition state for their interconversion TS *trans*-**IIa** (bond lengths are given in Å).

chemical calculations in terms of the density functional theory [B3LYP/6-31G(*d,p*)]. Structures *cis*/*trans*-**IIa**$_{1/2}$ and *cis*/*trans*-**IIb**$_{1/2}$ (two conformers for each *cis* and *trans* isomer) occupy minima on the potential energy surfaces. The anthracene fragment in all structures is appreciably turned apart relative to the quinoline ring plane; for example, the dihedral angle $C^2C^3C^4C^5$ in *trans*-**IIa**$_2$ is equal to –131.7°. Both conformers of the *trans* isomer of **IIa** are more stable than *cis* isomers *cis*-**IIa**$_1$ and *cis*-**IIa**$_2$ by ΔE_{ZPE} = 2.4 and 3.7 kcal/mol, and the *trans* isomers of **IIb** (*trans*-**IIb**$_1$ and *trans*-**IIb**$_2$) are more stable than *cis*-**IIb**$_1$ and *cis*-**IIb**$_2$ by ΔE_{ZPE} = 2.5 and 4.9 kcal/mol, respectively. Therefore, compounds **IIa** and **IIb** were found to exist only as *trans* isomers (in keeping with the coupling constants for the vinylic protons in the ^{1}H NMR spectra and X-ray diffraction data for styrylquinolines [8]). Conformers *trans*-**IIa**$_1$ and *trans*-**IIb**$_1$ are similar to *trans*-**IIa**$_2$ and *trans*-**IIb**$_2$ in stability, and the calculated barrier to rotation about the $C^1–C^2$ single bond through transition state TS *trans*-**II** (R = H) is 6.8 kcal/mol (see figure). The presence of two conformers of the *trans* isomers of **IIa** and **IIb** is consistent with the experimental data (doubling of long-wave absorption maxima in the electronic spectra).

EXPERIMENTAL

The IR spectra were recorded on an FSM-1202 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Bruker DPX 250 instrument at 250 MHz from solutions in $CDCl_3$

using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Kratos MS-30 mass spectrometer (ion source temperature 200°C). The electronic absorption spectra were measured on a Varian Cary 100 Scan spectrophotometer. The luminescence spectra were recorded on a Hitachi F-4010 instrument from solutions in acetonitrile and toluene. Quantum-chemical calculations (for isolated molecules) in terms of the density functional theory [15] using B3LYP three-parameter potential and B3LYP/6-31G(*d*,*p*) valence-split basis set were performed with the aid of Gaussian-03 software package. All stationary points on potential energy surfaces were identified by calculating Hessian matrices.

8-Methoxy-2-methylquinoline (**Ib**) [16] and 2-methylquinolin-8-yl acetate (**III**) [17] were synthesized according to known procedures.

2-[2-(9-Anthryl)ethenyl]quinolines IIa and IIb (*general procedure*)**.** A mixture of 10 mmol of 2-methylquinoline **Ia** or **Ib** and 40 mmol of 9-anthraldehyde in 30 ml of acetic anhydride was heated for 16 h under reflux. The solvent was distilled off under reduced pressure, the residue was treated with 6 N sulfuric acid, and the mixture was heated for 3 h at the boiling point. The mixture was then cooled to 0°C and made weakly alkaline by adding 1 N sodium hydroxide. The precipitate was filtered off and recrystallized from benzene–hexane (1 : 1).

2-[2-(9-Anthryl)ethenyl]quinolin-8-ol (IIa). *a*. Yield 1.01 g (29%), yellow crystals, mp 195–196°C (from benzene–hexane, 1 : 1). IR spectrum, ν, cm^{-1}: 3393, 1562, 1511, 1460, 1376, 1331, 1331, 1086, 894. ^{1}H NMR spectrum, δ, ppm: 7.20–7.26 m (3H, CH=, H_arom), 7.33–7.36 m (1H, H_arom), 7.41–7.44 m (1H, H_arom), 7.47–7.52 m (3H, H_arom), 7.76 d (1H, H_arom, J = 8.5 Hz), 8.01–8.05 m (2H, H_arom), 8.20 d (1H, H_arom, J = 8.5 Hz), 8.37–8.45 m (3H, H_arom), 8.57–8.64 d (1H, CH=, J_{trans} = 19.4 Hz). Mass spectrum, *m*/*z* (I_rel, %): 347 (100) $[M]^+$, 346 (96), 203 (37), 202 (64), 173 (68), 164 (22), 163 (20), 159 (15), 158 (18), 145 (29), 117 (27). UV spectrum, λ_max, nm (logε): in acetonitrile: 213 (4.59), 255 (5.00), 370 (3.96), 392 (4.14); λ_fl 501 nm (φ = 0.005); in toluene: 333 (3.82), 371 (4.04), 391 (4.11); λ_fl 496 nm (φ = 0.067). Found, %: C 86.44; H 4.95; N 4.06. $C_{25}H_{17}NO$. Calculated, %: C 86.43; H 4.93; N 4.03.

Total and relative energies of isomers and conformers of the ground state of compounds **IIa** and **IIb** in the gas phase calculated by the B3LYP/6-31G(*d*,*p*) method[a]

Compound no.	E_tot, a.u.	ΔE_ZPE, kcal/mol	ω_1, cm^{-1}
trans-$\mathbf{IIa}_2$	–1092.9248	0	16
trans-$\mathbf{IIa}_1$	–1092.9240	0.6	14
TS *trans*-**IIa**[b]	–1092.9134	6.8	–66[b]
cis-$\mathbf{IIa}_1$	–1092.9201	3.0	11
cis-$\mathbf{IIa}_2$	–1092.9186	3.7	10
trans-$\mathbf{IIb}_2$	–1132.2174	0	15
trans-$\mathbf{IIb}_1$	–1132.2155	1.1	14
cis-$\mathbf{IIb}_1$	–1132.2117	3.6	10
cis-$\mathbf{IIb}_2$	–1132.2091	4.9	10

[a] E_tot is the total energy, 1 a.u. = 627.5095 kcal/mol; ΔE_ZPE is the relative energy with account taken of zero-point harmonic vibration energy; ω_1 is the least harmonic vibration frequency; E_ZPE(*trans*-$\mathbf{IIa}_2$) = –1092.5763 a.u.; E_ZPE(*trans*-$\mathbf{IIb}_2$) = –1131.8411 a.u.

[b] Transition state for the transformation *trans*-$\mathbf{IIa}_2 \rightleftarrows$ *trans*-$\mathbf{IIa}_1$; ω_1 is the only imaginary harmonic vibration frequency.

b. A mixture of 3.14 g (5.8 mmol) of 8-acetoxyquinolin-2-yl(triphenyl)phosphonium bromide (**V**) and 1.19 g (5.8 mmol) of 9-anthraldehyde in 10 ml of methanol was treated with 1.2 g (12.5 mmol) of potassium *tert*-butoxide. The mixture was stirred for 12 h at room temperature, and 50 ml of benzene and 30 ml of water were added. The solution was treated with 30 ml of concentrated hydrochloric acid, the red precipitate was filtered off and dispersed in water, the suspension was treated with excess triethylamine, and the resulting yellow suspension was filtered. The product was dried and recrystallized from benzene–hexane (1 : 1). Yield 1.37 g (68%).

2-[2-(9-Anthryl)ethenyl]-8-methoxyquinoline (IIb). Yield 1.10 g (30%), yellow crystals, mp 174–175°C (from benzene–hexane, 1 : 1). IR spectrum, ν, cm^{-1}: 1557, 1502, 1460, 1376, 1326, 1103, 889. ^{1}H NMR spectrum, δ, ppm: 4.09 s (3H, OMe), 7.06–7.24 m (2H, H_arom), 7.34–7.49 m (7H, CH=, H_arom), 7.92–8.01 m (3H, H_arom), 8.18–8.22 d (1H, H_arom, J = 8.6 Hz), 8.38–8.40 m (4H, CH=, H_arom). Mass spectrum, *m*/*z* (I_rel, %): 361 (100) $[M]^+$, 342 (22), 202 (77), 180 (78), 173 (42), 165 (55), 164 (75), 159 (51), 158 (91), 150 (36), 143 (25), 129 (26), 116 (19). UV spectrum, λ_max, nm (logε): in acetonitrile: 214 (4.61), 256 (5.09), 369 (4.13), 389 (4.17); λ_fl 494 nm (φ = 0.028); in toluene: 332 (3.81), 372 (3.97), 392 (4.08); λ_fl 493 nm (φ = 0.25). Found, %: C 86.42; H 5.33; N 3.86. $C_{26}H_{19}NO$. Calculated, %: C 86.40; H 5.30; N 3.88.

8-Acetoxyquinolin-2-ylmethyl(triphenyl)phosphonium bromide (V). A mixture of 5.03 g (25 mmol) of 2-methylquinolin-8-yl acetate (**III**), 4.45 g (25 mmol) of *N*-bromosuccinimide, and 0.03 g of benzoyl peroxide in 40 ml of carbon tetrachloride was heated for 10 h under reflux. The mixture was filtered from succinimide, the filtrate was carefully evaporated, 20 ml of benzene and 6.55 g (25 mmol) of triphenylphosphine were added to the residue, the mixture was heated for 1 h under reflux, and the precipitate was filtered off. Yield 7.90 g (58%), light brown crystals, mp 294–295°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 1754, 1600, 1463, 1442, 1376, 1205, 1173, 1111, 1074. ^{1}H NMR spectrum, δ, ppm: 1.97 s (3H, MeCO), 5.99–6.09 m (2H, CH_2), 7.24–8.08 m (20H, H_{arom}).

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