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Molecular logic gates based on 2-styrylquinoline derivatives*

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Various logical operations can be performed by molecular logic gates (MLG) based on 2-styrylquinoline derivatives using irradiation with light and protonation as input signals and absorbance (optical density) as output signal. The MLG operation type ("INH", "OR", "AND") depends on the observation wavelength.

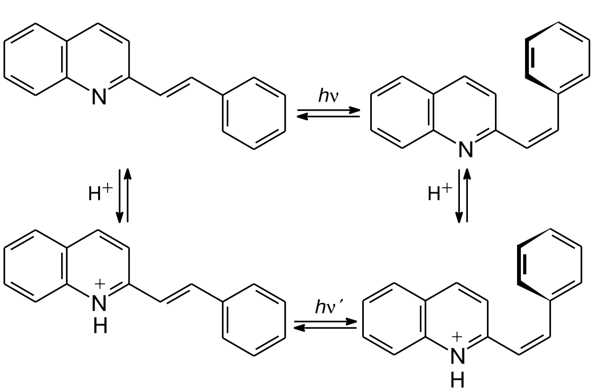
Key words: diarylethylene, photoisomerization, absorption spectrum, molecular logic gate.

Currently, the possibility of performing logical operations on the molecular level in order to design molecular logic gates (MLG) for information technologies has been studied intensively.[2—8] Most often, the role of input signals for MLG is played by some chemical impact or irradiation with light, while the output signal is the optical density or luminescence.

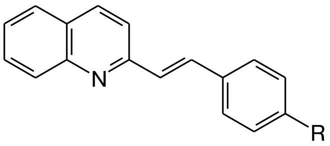
Styrylquinolines represent aza-substituted diarylethylenes (aza-DAE) containing a central double bond and an endocyclic (quinoline) nitrogen atom, which can undergo reversible transformations (photoisomerization and protonation, respectively). This makes aza-DAE convenient systems for studying the principles of the design and operation of MLG including controllable switches, logic gates, *etc*. One can switch between the *cis*- and *trans*-states of aza-DAE using a photoisomerization reaction controlled by protonation of the aza function. Therefore, there are four stable states (forms) in this system including neutral *cis*- and *trans*-isomers and protonated *cis*- and *trans*-isomers. Switching between them occurs in two steps and involves irradiation with light and protonation.

Scheme 1 presents different states of aza-DAE and possible types of transitions between them taking the *s-trans*-conformer of 2-styrylquinoline (**1**) as an example. Compared to other styrylquinolines, both the neutral and protonated forms of **1** are characterized by high quantum yields of *cis—trans*- and *trans—cis*-photoisomerizations; this compound also is not involved in side reactions (with respect to photoisomerization), such as photocyclization and oxidation to fused aromatic compounds.[9,10] Therefore, the cycle of reactions with participation of compound **1** is fully reversible. An important factor is also the thermal stability of all four forms of compound **1** (see Scheme 1).

Scheme 1



In the present work, we studied 2-styrylquinoline (**1**) and its *para*-substituted derivatives **2—5** and showed that these compounds can serve as a basis for various MLG where the role of input signals is played by irradiation with light and protonation while the output signal is the optical density at a specified wavelength. The output signal can take values equal to 0 or 1 depending on whether the optical density is below or above than a particular threshold value. Combining two input signals allows one to produce various output signals and thus perform logical operations.



1—5

R = H (**1**), F (**2**), Cl (**3**), EtO (**4**), NO_2 (**5**)

Experimental

The synthesis of styrylquinolines **1—5** was reported earlier.[10,11] Hydrochlorides were obtained *in situ* by adding HCl solu-

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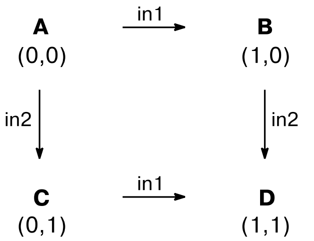
tions to styrylquinoline solutions. Electronic absorption spectra were recorded with a Specord M-40 spectrophotometer in ethanol. The source of UV light was a DRSh-500 mercury lamp; the 313 and 365 nm spectral lines were selected using a set of glass filters. Photochemical studies were carried out in air-saturated solutions at room temperature. The concentration of styrylquinoline in the solutions was $(2-20) \cdot 10^{-5}$ mol L^{-1} and the intensity of incident light was in the range $(5-50) \cdot 10^{-10}$ Einstein cm^{-2} s^{-1} (measured by a PP-1 cavity detector or ferrioxalate actinometer). Quartz cells with an optical path length *l* of 1 cm were used.

Results and Discussion

A logic gate is a switch whose output signal equal to 0 or 1 depends on the input signal, which also can take two values, 0 or 1. A logic gate with two inputs and one output has four states corresponding to four combinations of the input signals, namely, (0,0), (0,1), (1,0), and (1,1). In each case, the value of the output signal (0 or 1) depends on the type of the logic gate and is determined by a truth table in which each combination of input signals (logical variables) is assigned a desired value of the output signal (a logic function in question). Table 1 presents the truth tables for some logic gates whose functions will then be modeled using the derivatives of styrylquinoline **1**.

For clarity, in Scheme 2 four different states (**A**—**D**) of the logic gate occupy the vertices of a square. Transitions between them (responses to some impacts on two inputs, in1 and in2) are shown by arrows aligned to the edges of the square.

Scheme 2



A comparison of the Schemes 1 and 2 shows that each state of the logic gate can be assigned to a particular state (form) of the styrylquinoline molecule. Any form of styrylquinoline can be chosen as the initial state of the logic gate (**A**), because transitions between all forms are possible in all directions due to full reversibility. Now we can formulate the requirements for the properties of particular forms of compound **1**, which should be met to design a MLG. For instance, the operation of a logic gate performing logic multiplication ("AND") requires (see Table 1) that the output signal be equal to 1 only for the (1,1) combination of the input signals and equal to 0 in the other three cases. From a comparison of Schemes 1 and 2 it follows that the properties of a form of compound **1** to be assigned the final state (**D**) of the MLG should differ from the properties of the other three forms treated as the initial and intermediate states (**A**, **B**, and **C**) of the MLG taking into account the possibility for these three states to exhibit identical properties.

Table 1. Truth tables for different logical functions

Input		Output		
in1	in2	AND	INH	OR
0	0	0	0	0
1	0	0	1	1
0	1	0	0	1
1	1	1	0	1

As an example, Fig. 1 presents the absorption spectra of the neutral and protonated forms of *cis*- and *trans*-2-(4-fluorostyryl)quinoline **2**, which correspond to four thermally stable compounds similar to those shown in Scheme 1. Having assigned each compound to a particular state of the MLG, the state (**A**, **B**, **C**, or **D**) of the MLG can be determined with ease because different forms of styrylquinoline exhibit significantly different spectra.

Consider the *cis*-isomer as the initial state of the MLG and irradiation with light and acidification as input signals (in1 and in2, respectively). Then, different states of the MLG, created after the impact of input signals are related to different forms of styrylquinoline as shown in Table 2. The final state (**D**) of the MLG corresponds to the protonated *trans*-isomer. To perform the logical function "AND" (see above), one should distinguish between the state **D** and the other three states. From Fig. 1 it follows that this

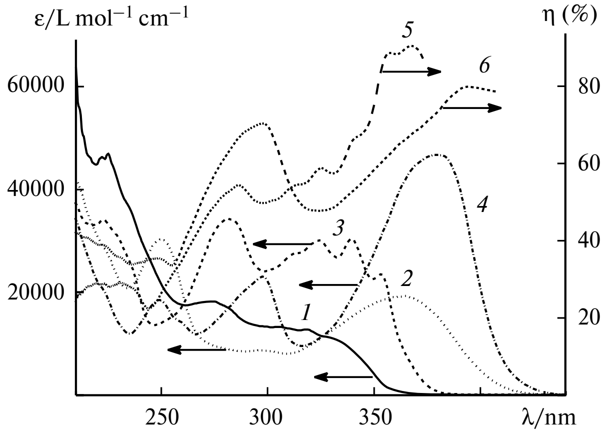


Fig. 1. Absorption spectra of *cis*- (*1*, *2*) and *trans*-isomers (*3*, *4*) of 2-(4-fluorostyryl)quinoline **2** in the neutral (*1*, *3*) and protonated (*2*, *4*) forms and the content of the *cis*-isomer in the photostationary mixture (degree of conversion η) plotted *vs.* irradiation wavelength for the neutral (*5*) and protonated (*6*) forms of **2**.

Table 2. Correspondence between the action on the MLG, its state (see Scheme 2), and the form of 2-(4-fluorostyryl)quinoline **2** corresponding to this state (starting form is the *cis*-isomer)

Action	MLG state	Compound
—	**A**	*cis*-**2**
*h*ν	**B**	*trans*-**2**
HCl	**C**	*cis*-**2** • HCl
*h*ν + HCl	**D**	*trans*-**2** • HCl

can be done with ease using the optical density in the region $\lambda > 380$ nm, where both neutral forms (states **A** and **B**) do not absorb light and the protonated *cis*-isomer (state **C**) absorbs much weaker than the *trans*-isomer.

It should be noted that it is impossible to create "pure" MLG states corresponding to the compounds listed in Table 2, because reversibility of the photoisomerization reaction precludes a 100% conversion of the *cis*-isomer to the *trans*-isomer upon exposure to light and *vice versa*. Actually, irradiation creates a photostationary state PS_λ (a mixture of *cis*- and *trans*-isomers whose composition depends on the irradiation wavelength λ). The composition of the photostationary state can be expressed through the proportion of the *cis*-isomer

$$\eta_\lambda = [cis]_{\mathrm{ps}}/([trans]_{\mathrm{ps}} + [cis]_{\mathrm{ps}}),$$

where $[cis]_{\mathrm{ps}}$ and $[trans]_{\mathrm{ps}}$ are the concentrations of the *cis*- and *trans*-isomers in the mixture, respectively. When using *trans*-isomers formed in the synthesis of styrylquinolines as starting reactants, the parameter η is the degree of conversion. Irradiation of all compounds studied in this work at $\lambda = 313$ and 365 nm produced the photostationary states PS_{313} and PS_{365}, respectively, with the *cis*-isomer content listed in Table 3.

Table 3. Compositions of photostationary states (content of the *cis*-isomer in the mixture η_λ) for neutral and protonated forms of 2-styrylquinoline derivatives as functions of the irradiation wavelength

Compound	η_{313}	η_{365}	$\eta_{\min}$	$\eta_{\max}$	$\lambda_{\min}$	$\lambda_{\max}$
	%				nm	
1	61	93	26	94	245	370
1 • HCl	51	68	31	84	242	394
2	55	90	23	91	244	368
2 • HCl	54	66	34	80	256	397
3	46	87	16	86	247	360
3 • HCl	54	65	31	90	257	423
4	64	86	38	91	237	390
4 • HCl	55	55	25	75	241	440
5	41	82	30	87	246	385
5 • HCl	46	69	25	94	248	393

The absorption spectra of the reaction mixtures in the four photostationary states created upon irradiation of solutions of neutral styrylquinoline **2** and **2** • HCl at $\lambda = 313$ and 365 nm are shown in Fig. 2. Compared to the pure isomers (see Fig. 1), the spectral differences became less pronounced, but they still allow the state of the system to be determined unambiguously. If the initial state of the MLG is the photostationary state PS_{365} enriched with the *cis*-isomer ($\eta_{365} = 90\%$, see Table 3) and the role of the input signals is played by the irradiation at 313 nm and protonation (HCl addition), one gets a fully reversible system, which returns to the initial state after neutralization and irradiation at $\lambda = 365$ nm.

Vertical lines in Fig. 2 show the wavelengths 323, 353, and 373 nm. Signal readout at these wavelengths allows one to obtain three different MLG ("INH" at 323 nm, "OR" at 353 nm, and "AND" at 373 nm), which process the input signals according to Table 2. Using commonly accepted graphic notations of logic elements, the operation of the MLG based on 2-styrylquinoline derivatives is described by Scheme 3.

Since the output signal is the optical density, for each MLG one should set a threshold optical density value, such that if the optical density is below (above) the threshold value, the output signal has a value of 0 (1). Table 4 lists all four combinations of the input signals, the corresponding photostationary states of styrylquinoline **2**, the experimental values of the optical densities at three wavelengths (A_{323}, A_{353}, and A_{373}), and the threshold optical density values; if A_{323}, A_{353}, or A_{373} value exceeds the corresponding threshold, the MLG output signal is equal to 1.

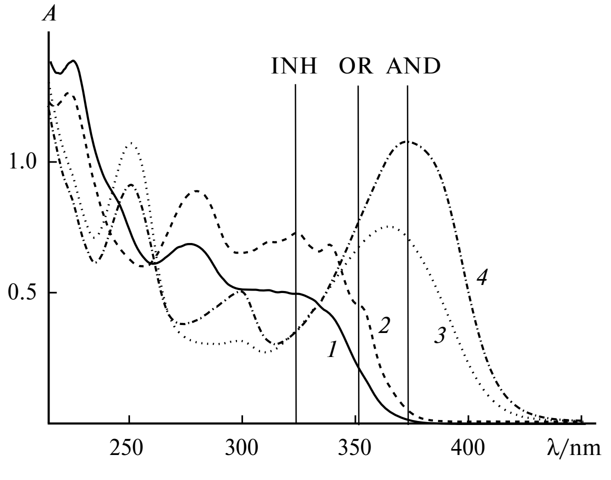
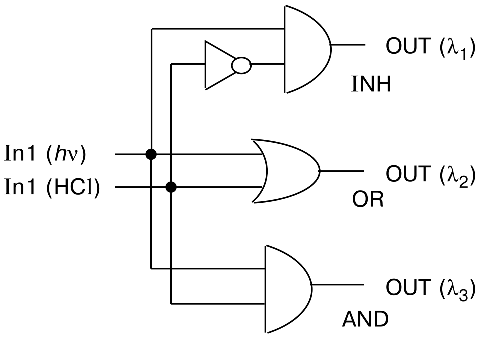


Fig. 2. Absorption spectra of reaction mixtures in the photostationary states of 2-(4-fluorostyryl)quinoline **2** (ethanol, $3.87 \cdot 10^{-5}$ mol L^{-1}): neutral form **2** (*1*, *2*), protonated form **2** • HCl (*3*, *4*), PS_{365} (*1*, *3*), and PS_{313} (*2*, *4*). Vertical lines denote the wavelengths 323, 353, and 373 nm; readout of the optical density at these wavelengths makes it possible to create a corresponding MLG (see text).

Scheme 3



For instance, when the signal is read out at 323 nm, one has $A_{323} = 0.6$ for the threshold optical density. Then, the output signal is 0 at $A_{323} < 0.6$ and 1 at $A_{323} > 0.6$. From Table 4 it follows that in this case the output value equal to 1 is attained only at input1 = 1, input2 = 0 (PS_{313} state), *i.e.* the system operates as the "INH" logic gate (see Table 2). This is clearly seen in Fig. 3, where the optical densities at these wavelengths are shown as diagrams while the threshold optical densities for different logic gates are shown by horizontal lines. At λ = 323 nm (see Fig. 3, *a*), only the optical density in the state PS_{313} is above the threshold line. At λ = 353 nm (see Fig. 3, *b*), the threshold value is $A_{353} = 0.3$, in this case the optical density is above the threshold value for three states (PS_{313}, PS_{365}•HCl, and PS_{313}•HCl) and the system operates as the logic gate "OR" (see Table 2). At λ = 373 nm (see Fig. 3, *c*), the threshold value is $A_{373} = 0.9$, here only the optical density of the state PS_{313}•HCl is above the threshold value and the system operates as the logic gate "AND" (see Table 2).

From Table 3 it follows that the final state of the system corresponding to signals at both inputs (*i.e.* irradiation at λ = 313 nm and protonation) is slightly different depending on the order in which the input signals are applied. If irradiation is followed by acidification of the solution, the content of the *cis*-isomer in the reaction mixture is 55% (in the reverse sequence, 54%). However, this difference does not go beyond the accepted values of the threshold optical densities and agrees with the data in the truth table of the MLG (see Table 4).

Clearly, it is desired that transitions between different states of the system be induced by irradiation at such a wavelength that produces a photostationary mixture with the maximum content of the *trans*- or *cis*-isomer. For irradiation at the wavelength λ, the composition of the PS_λ is given by the following equation:

$$(\varphi_{tc}\varepsilon_t[trans]_{ps})_\lambda = \varphi_{ct}\varepsilon_c[cis]_{ps}, \qquad (1)$$

where φ_{tc} and φ_{ct} are the quantum yields of the *trans—cis*- and *cis—trans*-isomerization reactions, respectively, and ε_c and ε_t are the molar absorption coefficients of the *cis*- and *trans*-isomers, respectively, at the irradiation wavelength λ.

From Eq. (1) one gets the dependence of the content of the *cis*-isomer in the photostationary mixture on the irradiation wavelength

$$\eta_\lambda = [\varphi_{tc}\varepsilon_t/(\varphi_{tc}\varepsilon_t + \varphi_{ct}\varepsilon_c)]_\lambda. \qquad (2)$$

The parameters in Eq. (2) were experimentally measured and used to calculate the dependence of η_λ on the irradiation wavelength for the neutral and protonated forms of styrylquinolines.

Figure 1 (see curves *5* and *6*) presents the plots of η_λ *vs.* irradiation wavelength for the neutral and protonated styrylquinoline **2**. A comparison of the dependence of the degree of conversion on λ with the absorption spectra (see Fig. 1, curves *1—4*) shows that the maximum possible content of the *cis*-isomer in the photostationary mixture (η_{max}) is attained on irradiation at the wavelength (λ_{max}) corresponding to the maximum ratio $(\varepsilon_t/\varepsilon_c)_\lambda$. For the neutral form of styrylquinoline **2**, one has $\eta_{max} = 91\%$ at $\lambda_{max} = 368$ nm. Irradiation at $\lambda_{min} = 244$ nm corresponding to the minimum ratio $(\varepsilon_t/\varepsilon_c)_\lambda$ allows one create a photostationary mixture with the minimum content of the *cis*-isomer ($\eta_{min} = 23\%$) and the maximum content of the *trans*-isomer (77%). The maximum and minimum η_λ val-

Table 4. Truth table for a MLG based on photostationary states of 2-(4-fluorostyryl)quinoline **2***

Input		Photo-stationary state	Output		
in1 hν 313	in2 HCl		INH A_{323} (0.6)	OR A_{353} (0.3)	AND A_{373} (0.9)
0	0	PS_{365}	0 (0.51)	0 (0.18)	0 (0.02)
1	0	PS_{313}	1 (0.73)	1 (0.45)	0 (0.05)
0	1	PS_{365}•HCl	0 (0.35)	1 (0.69)	0 (0.71)
1	1	PS_{313}•HCl	0 (0.34)	1 (0.80)	1 (1.08)

* Listed are the threshold and experimental values of the optical densities at the specified wavelengths and the corresponding values of the output signals.

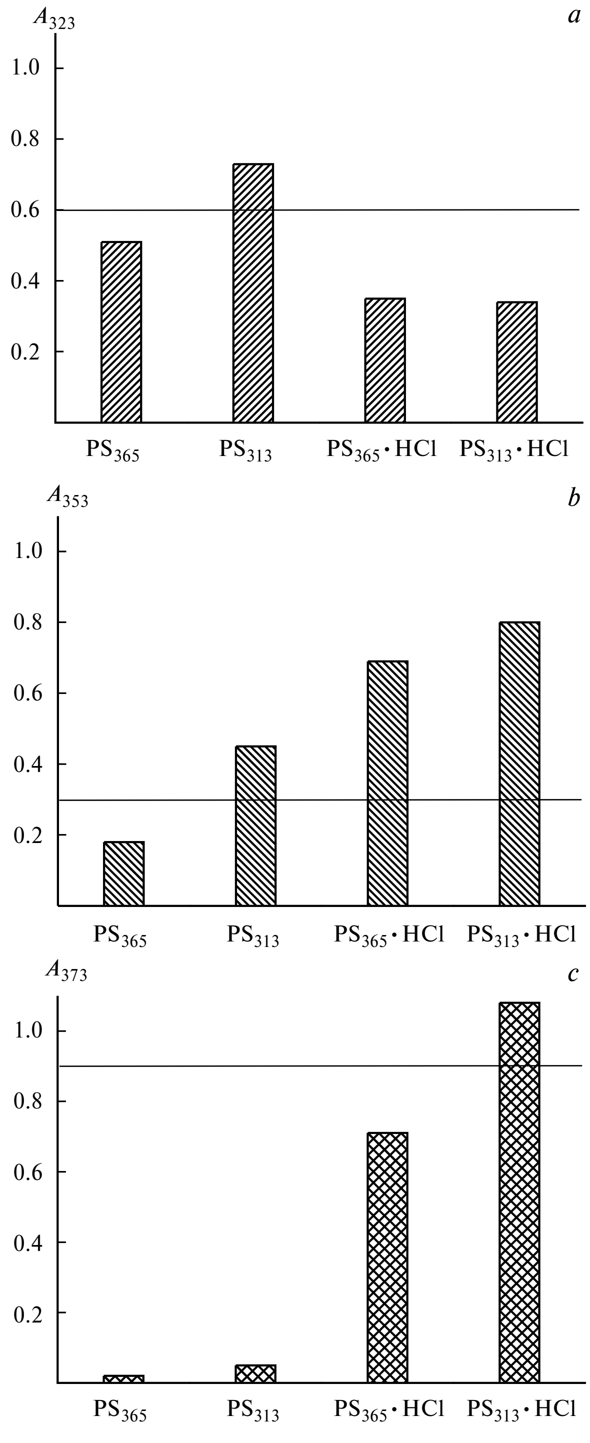


Fig. 3. Optical density diagrams for reaction mixtures in the photostationary states PS_{365} and PS_{313} of neutral 2-(4-fluorostyryl)quinoline **2** and protonated form **2** • HCl at 323 (*a*), 353 (*b*) and 373 nm (*c*); horizontal lines show the threshold optical density values for different logic gates including "INH" (*a*), "OR" (*b*), and "AND" (*c*).

ues for the protonated form of styrylquinoline **2** and the corresponding wavelengths, as well as the corresponding parameters of other compounds under study are listed in Table 3.

Irradiation with long-wavelength light allows one to create photostationary states enriched with the *cis*-isomer (up to 94% for compounds **1** and **5** • HCl). Irradiation in this spectral region can be utilized to return the MLG to the initial state. Irradiation with short-wavelength light in the region ~250 nm is also suitable for the operation of MLG. In this case, the maximum attainable content of *trans*-isomers in the photostationary states is usually at most 70—80%, only for the neutral chloro derivative **3** it reaches 84% (η_{247} = 16%, see Table 3) .

An interesting example is provided by ethoxystyrylquinoline **4**. From Table 3 it follows that the protonated form of this compound is characterized by the same composition of the photostationary state (55%) when irradiated at λ = 313 and 365 nm. This is due to equality of the ratios of the molar absorption coefficients of the *cis*- and *trans*-isomers at these wavelengths (1.46 and 1.44, respectively). Therefore, it is impossible to design a MLG based on the PS_{313} and PS_{365} states. However, the compositions of the photostationary states differ noticeably on irradiation at λ = 237—241 and 390—440 nm (see Table 3). Ethoxystyrylquinoline **4** is a convenient model compound, because its neutral and protonated forms are characterized by high quantum yields of *trans—cis*- and *cis—trans*-photoisomerizations (0.5 and more).[10] In addition, without significant changes in spectral characteristics the ethyl group can be replaced by some other alkyl residue in order to impart specific properties (*e.g.*, the ability to self-assembly) to the new derivative. It is assumed that self-assembly of individual MLG to supramolecular ensembles will be a step in the design of complex nanoscale blocks for molecular nanoelectronics.[12]

Thus, we showed that 2-styrylquinoline is suitable for the design of various MLG using irradiation with light and protonation as input signals; the type of the logical operation ("INH", "OR", or "AND") depends on the observation wavelength.

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