Investigation of 8-mercaptoquinoline (thiooxine) and its derivatives 115. Spectral and acid-base properties of phenyl derivatives of 8-mercaptoquinoline

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Two new derivatives of 8-mercaptoquinoline have been synthesized: 5-phenyl- and 6-phenyl-8-mercaptoquinoline. Their electronic absorption spectra have been studied and ionization as well as distribution constants have been determined.

At ionic strength $I = 0.1$ mol dm^{-3} and temperature $\theta = 20\,°C$ for 5-phenyl-8-mercaptoquinoline the values $pK_1 = 1.97$ and $pK_2 = 8.41$ have been found, for 6-phenyl-8-mercaptoquinoline $pK_1 = 2.01$ and $pK_2 = 8.19$ (the values found previously for 2-phenyl- and 4-phenyl-8-mercaptoquinoline were $pK_1 = 1.41$, $pK_2 = 8.00$ and $pK_1 = 2.10$, $pK_2 = 8.49$, respectively). In the system chloroform—water at ionic strength $I = 0.1$ mol dm^{-3} and temperature $\theta = 20\,°C$ the following distribution constants have been determined: for 5-phenyl-8-mercaptoquinoline 60 000 and for 6-phenyl-8-mercaptoquinoline 70 800 (the previously found values for 2-phenyl- and 4-phenyl-8-mercapto-quinoline were· 470 000 and 78 000 respectively).

The comparison with the previously investigated 8-mercaptoquinoline, 2-phenyl-, and 4-phenyl-8-mercaptoquinoline is drawn. It is shown that phenyl group in the 4th and 5th position to a large extent affects the p band of $\pi \rightarrow \pi^*$ electron transition while in the 2nd and 6th position it affects the β band of $\pi \rightarrow \pi^*$ electron transition causing the bathochromic and hyperchromic shift. Phenyl group in the 5th and 6th position in the molecule of 8-mercapto-quinoline decreases to some degree the basic properties of nitrogen atom and increases acidic properties of mercapto group, but in the 4th position it slightly increases basic properties of nitrogen atom and decreases acidic properties of mercapto group. In the 2nd position phenyl group considerably decreases basic properties of nitrogen atom and slightly decreases acidic properties of mercap-to group; the latter fact can be explained by steric effects of this group.

Синтезированы два новых производных 8-меркаптохинолина — 5-фенил- и 6-фенил-8-меркаптохинолин. Изучены их электронные спектры поглощения и определены константы ионизации и константы распределения.

При ионной силе $I = 0{,}1$ моль дм$^{-3}$ и $\theta = 20$ °C для 5-фенил-8-меркаптохинолина найдено p$K_1 = 1{,}97$ и p$K_2 = 8{,}41$, для 6-фенил-8-меркаптохинолина p$K_1 = 2{,}01$ и p$K_2 = 8{,}19$ (для 2-фенил- и 4-фенил-8-меркаптохинолинов получены p$K_1 = 1{,}41$, p$K_2 = 8{,}00$ и p$K_1 = 2{,}10$, p$K_2 = 8{,}49$, соответственно). В системе хлороформ—вода при ионной силе $I = 0{,}1$ моль дм$^{-3}$ и $\theta = 20$ °C найдены константы распределения 60 000 для 5-фенил-8-меркаптохинолина и 70 800 для 6-фенил-8-меркаптохинолина (для 2-фенил- и 4-фенил-8-меркаптохинолинов ранее было получено 470 000 и 78 000, соответственно).

Проведено сравнение свойств реагентов с ранее изученным 8-меркаптохинолином, 2-фенил- и 4-фенил-8-меркаптохинолином. Показано, что фенильная группа в положении 4 и 5 больше влияет на p полосу $\pi \to \pi^*$ электронного перехода а в положении 2 и 6 влияет на β полосу $\pi \to \pi^*$ электронного перехода, вызывая ее батохромный и гиперхромный сдвиг. Фенильная группа в положении 5 и 6 в молекуле 8-меркаптохинолина несколько понижает основные свойства атома азота и увеличивает кислотные свойства меркаптогруппы, а в положении 4 несколько увеличивает основные свойства атома азота и понижает кислотные свойства меркаптогруппы. В положении 2 фенильная группа значительно понижает основные свойства атома азота и немного кислотные свойства меркаптогруппы, что можно объяснить пространственными эффектами этой группы.

Phenyl derivatives of 8-mercaptoquinoline are of interest from the view-point of elucidation of the effect of phenyl groups on physicochemical properties of these reagents and their inner complex compounds. The conjugation of phenyl groups with quinoline ring may bring about bathochromic and hyperchromic shifts of absorption maxima of the reagents as well as of their inner complex compounds. This must result in improvement of analytical properties of the reagents.

2-Phenyl-8-mercaptoquinoline [1] and 4-phenyl-8-mercaptoquinoline [2] were synthesized and their physicochemical properties were described previously [3].

In continuation of our studies on this type of metal complexes we now report on the synthesis, spectral properties, and ionization constants of 5-phenyl- and 6-phenyl-8-mercaptoquinoline. Comparing the properties of these reagents to those of the previously investigated 8-mercaptoquinoline, 2-phenyl-, and 4-phenyl-8-mercaptoquinoline, the effects of the position of the phenyl group upon spectral and acid-base properties of the reagent is elucidated.

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Experimental

Absorption spectra of the reagents were recorded on a Specord UV VIS spectrophotometer. Measurements of absorbance of solutions in connection with the determination of molar absorption coefficients and ionization constants were performed on a spectrophotometer SF-16.

Free reagents were used for taking of absorption spectra in organic solvents. For taking of absorption spectra in aqueous solutions and for determination of ionization constants sodium salts of the reagents were used. The required amount of sodium salts of reagents was dissolved on heating in the mixture of 2 cm³ of ethanol, 1 cm³ of water, and 0.1 cm³ of 1 mol dm⁻³ sodium hydroxide and then the solution was diluted to 20 cm³ with distilled water. In order to prepare working solution 1 cm³ of the starting solution was diluted with buffer solution to 100 cm³ and 10^{-4} mol dm⁻³ solution of the reagent was obtained, containing 0.1 % of ethanol.

For preparation of aqueous solutions of methylthio derivatives of the reagents, the substances were dissolved in a small amount of 1 mol dm⁻³ hydrochloric acid and subsequently diluted with buffer solution to the required concentration.

The concentration of hydrogen ions in aqueous solutions was measured using the pH meter of the type M-25 (Radiometer).

Organic solvents were distilled before use, methanol and ethanol were dehydrated and distilled. The other applied reagents were of highly purity or analytical reagent grade quality.

Synthesis of reagents

5-Phenyl- and 6-phenyl-8-mercaptoquinoline were synthesized from the corresponding aminoquinolines (Scheme 1). Aminoquinolines (I) were diazotized, by the action of thiourea on diazonium salts (II) isothiourea derivatives (III) were obtained, which by way of alkaline hydrolysis were transformed into sodium salts of the reagents (IV), from them free reagents (V) were separated with acetic acid. When treating the sodium salts of the reagents with methyl iodide methylthio derivatives were obtained (VI), while the treatment with hydrogen peroxide yielded the corresponding disulfides (VII).

Sodium 5-phenyl-8-mercaptoquinolinate (IV)

To the solution of 3 g of 5-phenyl-8-aminoquinoline [4] in 30 cm³ of dimethylformamide 15 cm³ of 48 % hydrobromic acid are added and cooled in an ice bath to 2 °C. 1 g of sodium nitrite is added and shaken for 15 min with external cooling in the bath. The obtained solution of diazonium salt is added slowly with stirring to 50 cm³ of 10 % solution of thiourea and heated to 60 °C. The stirring is continued till nitrogen evolution ceases (approx. 10 min). The obtained solution is poured with constant stirring into the mixture of 70 g of ice and 30 cm³ of 20 % solution of sodium hydroxide. Orange precipitate of impure sodium salt of 5-phenyl-8-mercaptoquinoline is formed, filtered off and dissolved on heating in the
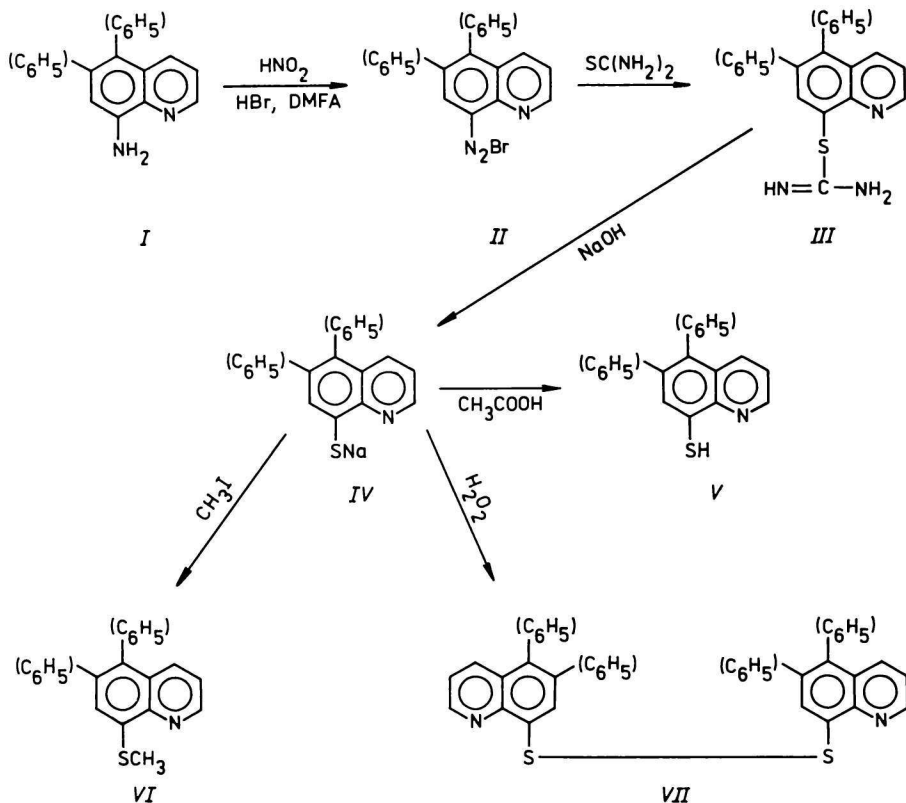
Scheme 1

mixture of 150 cm³ of ethanol and 3 cm³ of glacial acetic acid. 300 cm³ of water are added to ethanol solution and the precipitated emulsion of 5-phenyl-8-mercaptoquinoline is extracted with 300 cm³ of hexane. The extract is filtered off through cotton wool and hexane is distilled off in the vacuum of the water-jet pump, the distilling flask being heated on a water bath. 2.3 g of impure 5-phenyl-8-mercaptoquinoline in the form of yellowish-brown oil are obtained. The obtained oil is dissolved on heating in 50 cm³ of ethanol, the solution is filtered off through cotton wool and 10 % solution of sodium hydroxide is added till the red colour changes to yellow. After cooling to room temperature the formed orange crystalline precipitate is filtered off and washed with 10 cm³ of ethanol and 50 cm³ of chloroform. Yield of the product = 1.7 g (43 %).

For $C_{15}H_{10}NSNa \cdot 1.5H_2O$

w_i(found)/%: C 61.48; H 4.72; N 4.91; S 10.84; H_2O 8.93.

w_i(calc.)/%: C 62.88; H 4.58; N 4.89; S 11.19; H_2O 9.42.

5-Phenyl-8-mercaptoquinoline (V)

0.3 g of *IV* are dissolved on heating in 50 cm³ of ethanol, then 0.3 cm³ of glacial acetic acid and 200 cm³ of water are added and the precipitated 5-phenyl-8-mercaptoquinoline is extracted with 100 cm³ of hexane. The extract is filtered off through cotton wool and hexane is distilled off in the vacuum of a water-jet pump, the distilling flask being heated on a water bath. 0.2 g (80 %) of yellowish oil are obtained, which after rubbing with a glass stick crystallizes into pale yellow crystalline substance (m.p. = 72 °C). Solubility in water $S = 1.5 \times 10^{-4}$ mol dm⁻³.

For $C_{15}H_{11}NS$
w_i(found)/% : C 76.23; H 4.48; N 5.76; S 13.82.
w_i(calc.)/% : C 75.91; H 4.68; N 5.90; S 13.51.

5-Phenyl-8-methylthioquinoline (VI)

0.3 g of *IV* are dissolved on heating in a mixture of 30 cm³ of ethanol, 10 cm³ of water, and 1 cm³ of 1 % solution of sodium hydroxide. 0.1 cm³ of methyl iodide is added and after discolouring of the solution 30 cm³ of water are added and the solution is left to stand at room temperature for 2 h. The colourless crystalline precipitate *VI* is filtered off, washed with water and dried in air. Yield of the product = 0.23 g (87 %), m.p. = 151 °C. Solubility in water $S = 0.1 \times 10^{-4}$ mol dm⁻³

For $C_{16}H_{13}NS$
w_i(found)/% : C 76.82; H 5.38; N 5.70; S 12.50.
w_i(calc.)/% : C 76.45; H 5.22; N 5.57; S 12.76.

5,5'-Diphenyl-8,8'-diquinolyl disulfide (VII)

0.3 g of *IV* are dissolved on heating in a mixture of 30 cm³ of ethanol and 10 cm³ of water. 30 % solution of hydrogen peroxide is added dropwise under stirring till the yellow colour disappears and subsequently 10 cm³ of saturated sodium acetate solution are added. The colourless precipitate is filtered off, washed with water and dried in air. 0.21 g of *VII* (85 %) are obtained, m.p. = 296 °C (after recrystallization from chloroform).

For $C_{30}H_{20}N_2S_2$
w_i(found)/% : C 76.14; H 4.13; N 5.53; S 13.87.
w_i(calc.)/% : C 76.24; H 4.27; N 5.92; S 13.57.

6-Phenyl-8-mercaptoquinoline

15 cm³ of 48 % hydrobromic acid are added to the solution of 3 g of 6-phenyl-8-amino-quinoline [4] in 30 cm³ of dimethylformamide and cooled in an ice bath to 2 °C. 1 g of

sodium nitrite is added and shaken for 15 min with external cooling in an ice bath. The obtained solution of diazonium salt is added slowly with stirring to 50 cm³ of 10 % thiourea solution heated previously to 60 °C. The solution is stirred till evolution of nitrogen ceases (about 10 min). The obtained solution is poured into a mixture of 50 g of ice, 50 cm³ of 20 % sodium hydroxide solution, 400 cm³ of water and filtered off. 20 cm³ of glacial acetic acid are added to the filtrate and the precipitated oil is extracted with 250 cm³ of hexane. The extract is filtered off through cotton wool and hexane is distilled off in the vacuum of water-jet pump, heating the distillation flask on a water bath. 2 g (62 %) of 6-phenyl-8-mercaptoquinoline are obtained in the form of blue oil which, when rubbed with a glass stick, crystallizes into a pale yellow crystalline substance with m.p. = 87 °C. Solubility in water $S = 0.8 \times 10^{-4}$ mol dm⁻³

For $C_{15}H_{11}NS$
w_i(found)/%: C 74.38; H 4.71; N 5.72; S 13.50.
w_i(calc.)/%: C 75.91; H 4.68; N 5.90; S 13.51.

Sodium 6-phenyl-8-mercaptoquinolinate (IV)

2 g of V are dissolved on heating in 25 cm³ of ethanol, 20 % solution of sodium hydroxide is added till the colour of the solution changes from red to yellow, 30 cm³ of diethyl ether are added and the solution is cooled in an ice bath. The formed yellow crystalline substance is filtered off, washed with 10 cm³ of ether and 20 cm³ of chloroform. Yield of the product = 1.7 g (68 %).

For $C_{15}H_{10}NSNa \cdot 2H_2O$
w_i(found)/%: C 60.15; H 4.95; N 4.48; S 10.52; H_2O 12.00.
w_i(calc.)/%: C 61.00; H 4.79; N 4.74; S 10.86; H_2O 12.20.

6-Phenyl-8-methylthioquinoline (VI)

0.3 g of IV are dissolved in a mixture of 20 cm³ of ethanol, 5 cm³ of water, and 1 cm³ of 1 % solution of sodium hydroxide. 0.1 g of methyl iodide is added and after disappearance of the yellow colour of the solution 80 cm³ of water are added and left to stand for 2 h in a refrigerator. The colourless crystalline precipitate is filtered off, washed with water and dried in air. 0.21 g (82 %) of VI are obtained, m.p. = 98 °C. Solubility in water $S = 0.1 \times 10^{-4}$ mol dm⁻³

For $C_{16}H_{13}NS$
w_i(found)/%: C 75.72; H 5.30; N 5.09; S 13.10.
w_i(calc.)/%: C 76.45; H 5.22; N 5.57; S 12.76.

6,6'-Diphenyl-8,8'-diquinolyl disulfide (VII)

0.3 g of IV are dissolved in 50 cm³ of water and 30 % solution of hydrogen peroxide is added dropwise till the yellow colour disappears and then 10 cm³ of saturated solution of

sodium acetate are added. The colourless precipitate is filtered off, washed with water and dried in air. 0.2 g (83 %) of *VII* are obtained, m.p. = 224 °C (after recrystallization from the mixture of chloroform and ethanol with the mole ratio 1:4).

For $C_{30}H_{20}N_2S_2$

w_i(found)/% : C 75.48; H 4.12; N 5.56; S 13.80.

w_i(calc.)/% : C 76.24; H 4.27; N 5.92; S 13.57.

Results and discussion

Electronic absorption spectra

There is a number of papers where it has been shown that naphthalene [5—7], anthracene [8—12], quinoline and its perchlorate [13] absorb only that part of light which is polarized on the plane of molecule. There are two possible directions of light absorption: along the long axis x and along the short axis y (*VIII*).
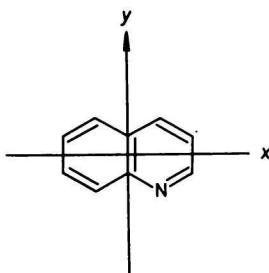
VIII

In the above-mentioned communications it is shown that on interaction of electric vector of light with the molecule in the direction of x axis, there appear in electronic spectrum bands of $\pi \rightarrow \pi^*$ electron transition which according to *Clar's* classification [14] are denoted as α and β bands, but on interaction of electric vector of light with the molecule in the direction of y axis, there appear bands of $\pi \rightarrow \pi^*$ electron transition which are denoted as p and β' bands. There have also been identified $\pi \rightarrow \pi^*$ electron transition bands of 8-mercaptoquinoline [15, 16] and 5-sulfo-8-mercaptoquinoline [15].

In the present communication we report on the absorption spectra of 5-phenyl- and 6-phenyl-8-mercaptoquinoline in aqueous solutions and in organic solvents (Tables 1 and 2, Figs. 1—4). In Table 1 data of the previously investigated 8-mercaptoquinoline and its 2-phenyl and 4-phenyl derivatives are listed for comparison. It can be seen from Table 1 that in the thiolic form of reagent phenyl group in the 2nd and 6th position in the molecule of 8-mercaptoquinoline shifts the β band towards longer wavelengths region of the spectrum and increases its

Table 1

Absorption maxima and molar absorption coefficients of 8-mercaptoquinoline (RSH) [17], 2-phenyl- (2-Ph) [3], 4-phenyl- (4-Ph) [3], 5-phenyl-(5-Ph), and 6-phenyl-8-mercaptoquinolines (6-Ph) and their methylthio derivatives in chloroform[a] and water[b]

Compound	β'		β		$\alpha + p$		α		p	
	λ_{max} / nm	ε_{max} / dm³ mol⁻¹ cm⁻¹	λ_{max} / nm	ε_{max} / dm³ mol⁻¹ cm⁻¹	λ_{max} / nm	ε_{max} / dm³ mol⁻¹ cm⁻¹	λ_{max} / nm	ε_{max} / dm³ mol⁻¹ cm⁻¹	λ_{max} / nm	ε_{max} / dm³ mol⁻¹ cm⁻¹
RSH			250	22 500	324	4 400				
2-PhRSH			277	40 700	333	6 600				
4-PhRSH			253	29 500	338	6 600				
5-PhRSH			254	27 600	341	7 300				
6-PhRSH			269	37 500	328	5 120				
RSH⁺			240	20 900			315	5 300	350 sh	1 500
4-PhRSH₂⁺			245	21 500			318	9 600	380 sh	6 500
5-PhRSH₂⁺			252	24 300			320	4 150	363	4 300
6-PhRSH₂⁺			267	29 500	336	5 650				
RS⁻			260	22 300					367	4 300
2-PhRS⁻	231	23 100	287	31 700					384	3 500
4-PhRS⁻			265	25 700					380	5 500
5-PhRS⁻			266	23 000					382	7 300
6-PhRS⁻	237	28 700	282	28 800					374	4 500
RSH⁺⁻	251	17 400	277	21 700					446	2 000
2-PhRSH⁺⁻	236	16 200	270	14 200					470	2 200
4-PhRSH⁺⁻			280	27 400					460	2 760
5-PhRSH⁺⁻			281	29 200					466	2 840
6-PhRSH⁺⁻	248	32 000	288	19 700					446	2 050
2-PhRSCH₃			276	33 800	331	6 000				
4-PhRSCH₃			253	32 800	342	5 900				
5-PhRSCH₃			255	27 400	345	7 700				
6-PhRSCH₃	227	19 000	269	33 800	335	3 880				

Table 1 (Continued)

Compound	β'		β		α + p		α		p	
	λ_{max} nm	ε_{max} dm³ mol⁻¹ cm⁻¹	λ_{max} nm	ε_{max} dm³ mol⁻¹ cm⁻¹	λ_{max} nm	ε_{max} dm³ mol⁻¹ cm⁻¹	λ_{max} nm	ε_{max} dm³ mol⁻¹ cm⁻¹	λ_{max} nm	ε_{max} dm³ mol⁻¹ cm⁻¹
4-PhRSCH₃H⁺	244	15 000	262	12 500			319	9 200		
5-PhRSCH₃H⁺			259	23 000			320	3 700	360 sh	4 000
6-PhRSCH₃H⁺	252	24 400	273	28 600	339	4 960			371	3 490

a) Thiolic form of the reagents (RSH).

b) Protonated (RSH₂⁺), ionized (RS⁻), zwitterionic form (RSH⁺⁻) of the reagents. Neutral (RSCH₃) and protonated (RSCH₃H⁺) form of methyl derivatives of the reagents.

Table 2

Absorption maxima and molar absorption coefficients of the thiolic form of 5-phenyl- and 6-phenyl-8-mercaptoquinolines and their methylthio derivatives[a] and disulfides[b] in organic solvents

| Organic solvent | 5-Phenyl-8-mercaptoquinoline 6-Phenyl-8-mercaptoquinoline | | | |
| | β | | $\alpha + p$ | |
	λ_{max} nm	ε_{max} $dm^3\ mol^{-1}\ cm^{-1}$	λ_{max} nm	ε_{max} $dm^3\ mol^{-1}\ cm^{-1}$
Chloroform	254	27 600	341	7 300
	269	37 500	328	5 120
Benzene			344	7 260
			331	5 200
Heptane	256	27 000	345	7 100
	270	37 600	333	4 560
Methanol	253	25 900	340	6 700
	267	37 200	323	5 250
Ethanol	254	26 600	340	7 100
	268	35 800	325	5 100
Propanol	254	27 000	340	6 900
	268	37 200	328	4 900
Butanol	254	27 900	341	7 100
	269	36 700	329	4 900
Pentanol	254	26 800	343	6 950
	269	35 600	331	4 770
Chloroform[a]	259	26 700	350	8 380
	274	33 900	345	5 050
Chloroform[b]	253	58 000	342	18 200
	267	64 000	333	12 000

intensity, while in the 4th and 5th position it affects the position of β band only slightly and increases its intensity only to a smaller degree if compared to 8-mercaptoquinoline. In the region of 330—340 nm there exists a less intense absorption band, which can be assigned to the overlapping of α and p bands. Phenyl group in the 4th and 5th position affects $\alpha + p$ band a little more (if compared to 8-mercaptoquinoline and 6-phenyl-8-mercaptoquinoline), this is evidently due to the effect of phenyl group on p component of this band. Molar absorption coefficient of 2-phenyl-8-mercaptoquinoline on $\alpha + p$ band is unexpectedly high — 6600 (identical to that of 4-phenyl-8-mercaptoquinoline), this is possibly connected with considerable influence exerted by phenyl group on α component of this band. In the zwitterionic form and in the ion of 2-phenyl-8-
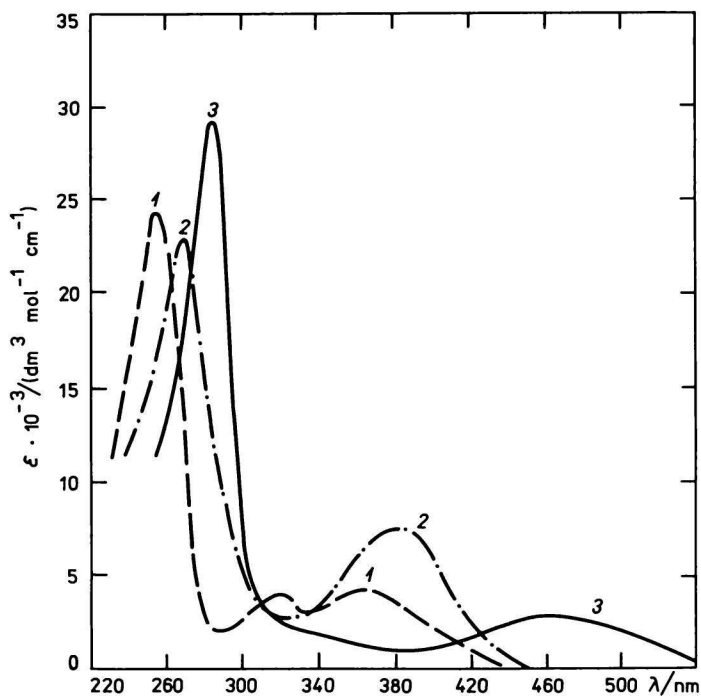
Fig. 1. Absorption spectra of various forms of 5-phenyl-8-mercaptoquinoline in aqueous solution:
1. 5-phenyl-8-mercaptoquinolinium cation (3 M-HCl); *2.* 5-phenyl-8-mercaptoquinolinate anion
(pH = 13.0); *3.* zwitterionic form of 5-phenyl-8-mercaptoquinoline (pH = 5.0).

-mercaptoquinolinate molar absorption coefficients of *p* band, however, are smaller than those of 4-phenyl- and 5-phenyl-8-mercaptoquinolines.

In the protonated form of reagents phenyl group in the 6th position in the molecule of 8-mercaptoquinoline also affects the β band (bathochromic shift and increase of intensity) but in the 4th and 5th position its influence is negligible.

In the spectra of protonated forms of 4-phenyl- and 5-phenyl-8-mercapto-quinolines as a result of the bathochromic shift of *p* band, caused by the protonation of heterocyclic nitrogen atom, splitting of α and *p* bands is observed. In the spectrum of 6-phenyl-8-mercaptoquinoline splitting of these bands does not occur.

In the ionized form of the reagents phenyl group in the 2nd and 6th position also affects the β band (bathochromic shift and increase of intensity), but in the 4th and 5th position it practically does not influence this band. In this form of the reagents phenyl group in the 4th and 5th position affects the *p* band, increasing its intensity if compared to 8-mercaptoquinoline and its 2-phenyl and 6-phenyl derivatives.
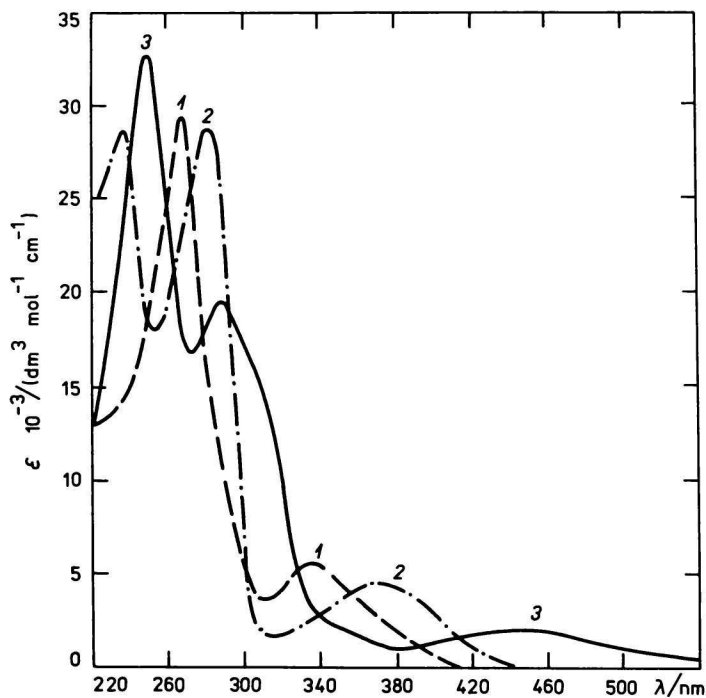
Fig. 2. Absorption spectra of various forms of 6-phenyl-8-mercaptoquinoline in aqueous solution:
1. 6-phenyl-8-mercaptoquinolinium cation (3 M-HCl); 2. 6-phenyl-8-mercaptoquinolinate anion (pH = 13.0); 3. zwitterionic form of 6-phenyl-8-mercaptoquinoline (pH = 5).

Influence of phenyl substituents on β band of zwitterionic form of 8-mercapto-quinoline is incongruous, however, the influence of these substituents on the p band is the same as in other forms of reagents, *i.e.* phenyl groups in the 4th and 5th position increase the intensity of the band but in the 2nd and 6th position practically do not affect its intensity. Effect of phenyl substituents on the absorption spectrum of methylthio derivative of 8-mercaptoquinoline and its protonated form is the same as upon 8-mercaptoquinoline itself and its protonated form. Thus, it is evident that phenyl group in the molecule of 8-mercaptoquinoline in the 2nd and 6th position influences the β band of spectrum to a greater extent, but in the 4th and 5th position it influences the p band of spectrum by shifting it bathochromically and increasing its intensity.

It follows from literature [18] that

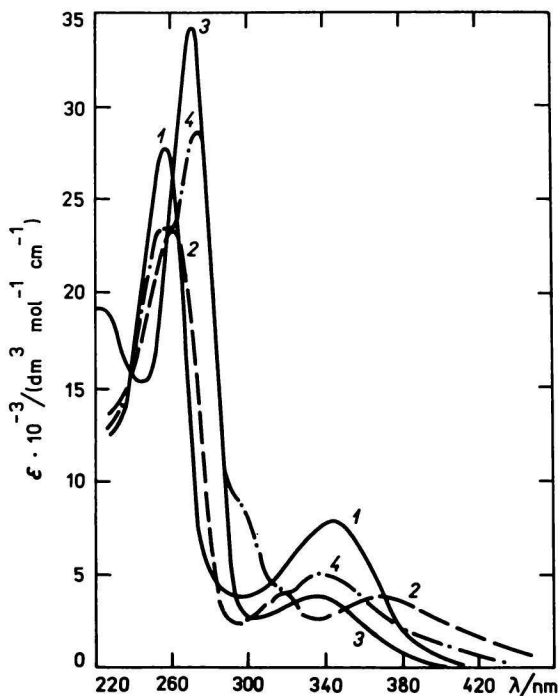$$\varepsilon = 2360 \frac{\bar{\nu} Q^2}{\Delta \bar{\nu}}$$

Fig. 3. Absorption spectra of various forms of methylthio derivatives of 5-phenyl- and 6-phenyl-8--mercaptoquinolines in aqueous solution: *1.* neutral form of 5-phenyl-8-methylthioquinoline (pH=9.0); *2.* 5-phenyl-8-methylthioquinolinium cation (3 M-HCl); *3.* neutral form of 6-phenyl-8-methylthioquinoline (pH = 9.0); *4.* 6-phenyl-8-methylthioquinolinium cation (3 M-HCl).

where $\bar{v}$ — wavenumber in cm^{-1}

$\Delta\bar{v}$ — halfwidth of absorption band in cm^{-1}

Q — length of electron transfer during electron transition in 10^{-1} nm

Phenyl group in the molecule of 8-mercaptoquinoline in the 2nd and 6th position leads to the lengthening of conjugated system in the direction of x axis, thereby increasing the Q value in the same direction, with the resultant bathochromic shift and an increase of intensity of β band which occurs on light absorption in the direction of x axis. (Henceforth under direction of light absorption we shall understand the direction of interaction of the electric vector of light with molecule.) In the 4th and 5th position phenyl group causes lengthening of the conjugated system in the direction of y axis, increasing the Q value in the same direction. This results in a bathochromic shift and an increase of intensity of p band, which occurs when light absorption takes place in the direction of y axis.
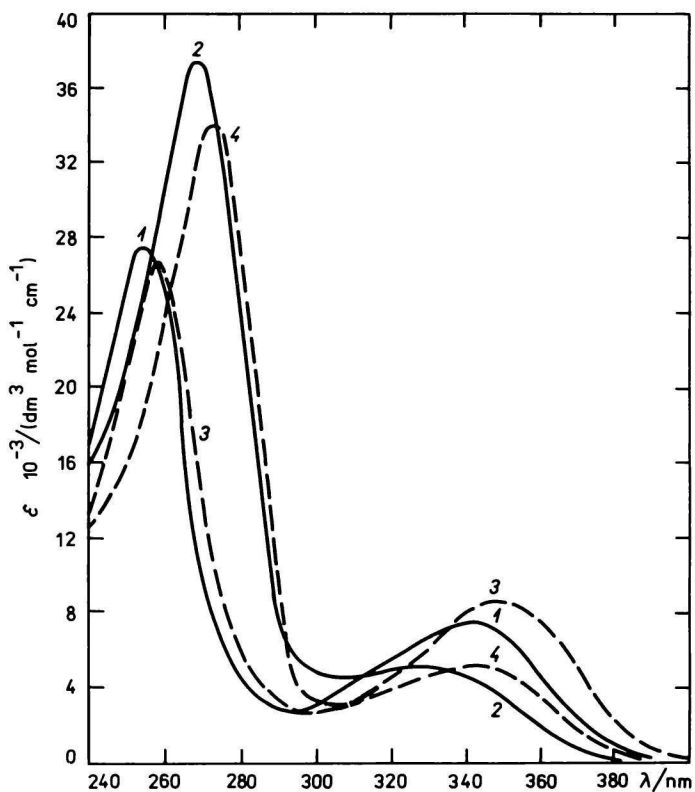
Fig. 4. Absorption spectra of 5-phenyl- and 6-phenyl-8-mercaptoquinolines and their methylthio derivatives in chloroform: *1.* 5-phenyl-8-mercaptoquinoline; *2.* 6-phenyl-8-mercaptoquinoline; *3.* 5-phenyl-8-methylthioquinoline; *4.* 6-phenyl-8-methylthioquinoline.

The considerable bathochromic shift of p band of protonated, ionized and especially of zwitterionic form of the reagent, if compared to the thiolic form, can be accounted for by occurrence of changes in the 1st position (in protonated form), by higher electron density in the 8th position resulting from the presence of negative charge on sulfur atom in ionized form, by occurrence of the charge in the 4th position and higher degree of electron density in the 8th position in zwitterionic form, *i.e.* by occurrence of charges located in the direction of y axis, where light absorption takes place on occurrence of this band. The effect of these charges upon β band is considerably smaller because this band occurs when light absorption takes place in the direction of x axis.

In aqueous solutions at pH_{isoel} phenyl derivatives of 8-mercaptoquinoline exist mainly in zwitterionic form. Zwitterionic form of 2-phenyl-8-mercaptoquinoline
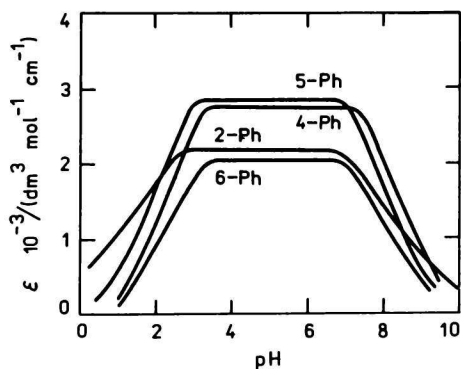
Fig. 5. Dependence of formation of zwitterionic form of phenyl derivatives of 8-mercaptoquinoline (2-Ph, 4-Ph, 5-Ph, 6-Ph) in aqueous solution on hydrogen ion concentration.

has its maximum of formation in pH range 2.7—6.8 [3], of 4-phenyl-8-mercapto-quinoline in pH range 3.5—7.2 [3], of 5-phenyl-8-mercaptoquinoline in pH range 3.2—7.0 and of 6-phenyl-8-mercaptoquinoline in pH range 3.4—7.0 (Fig. 5).

In polar organic solvents the maximum which is characteristic of zwitterionic form appears in the visible region of spectrum only at high reagent concentration (10^{-2}—10^{-1} mol dm^{-3}). Formation of zwitterionic form and its stabilization can be explained by the effects of molecules of the solvent [17]. On the basis of other derivatives of 8-mercaptoquinoline it was previously shown that molar absorption

Table 3

Absorption maxima and concentration of zwitterionic form of 5-phenyl- and 6-phenyl-8-mercapto-quinoline in water and in organic solvents

Solvent	ε_r	5-Phenyl-8-mercapto-quinoline		6-Phenyl-8-mercapto-quinoline	
		$\dfrac{\lambda_{max}}{nm}$	[RH^{+-}]/%	$\dfrac{\lambda_{max}}{nm}$	[RH^{+-}]/%
Water	80.4	466	96.2	446	95.6
Formamide	109.5	508	37.3	495	38.0
Methanol	32.6	507	6.56	493	7.20
Ethanol	24.3	521	2.03	508	2.76
Propanol	20.1	525	1.65	510	1.96
Butanol	17.1	528	1.21	512	1.55
Pentanol	13.9	532	0.93	514	1.27
Chloroform	4.7	558	0.43	547	0.56
Dimethylformamide	37.7	580	1.28	563	1.48

coefficients of zwitterionic form in water and organic solvents are very similar. Therefore using molar absorption coefficient of zwitterionic form in water it is possible to calculate its concentration in organic solvents. The results are presented in Table 3.

In Fig. 6 the dependence of concentration of zwitterionic form of 5-phenyl- and 6-phenyl-8-mercaptoquinolines and also of the previously investigated 2-phenyl- and 4-phenyl-8-mercaptoquinolines [3] on relative permittivity ε_r of normal aliphatic alcohols is shown. It can be seen that with the increase of relative permittivity of alcohol the concentration of zwitterionic form of reagents increases. Relative permittivity of alcohol increases with the increase of the number of molecules of alcohol per volume unit. Since alcohol stabilizes zwitterionic form of the reagents by interaction with its hydroxyl group, concentration of this form increases with the number of hydroxyl groups per volume unit of alcohol. It is evident from Fig. 6 that ability to form zwitterionic form is approximately the same for 4-phenyl-, 5-phenyl-, and 6-phenyl-8-mercaptoquinolines but for 2-phe-
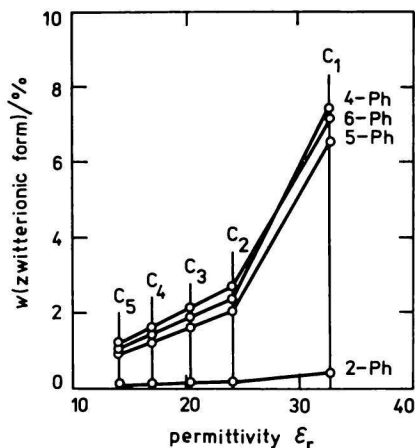

Fig. 6. Dependence of concentration of zwitterionic form of phenyl derivatives of 8-mercaptoquinoline (2-Ph, 4-Ph, 5-Ph, 6-Ph) on relative permittivity ε_r of normal aliphatic alcohols from C_1 to C_5.

nyl-8-mercaptoquinoline it is considerably lower. This can be explained by the fact that phenyl group in the 2nd position hinders the approaching of solvent molecules to nitrogen and sulfur atoms of the reagent molecule, thereby hindering formation of the molecular complex.

Ionization and distribution constants

In aqueous solutions among various forms of phenyl derivatives of 8-mercapto-quinoline there exist equilibria exemplified by Scheme 2.
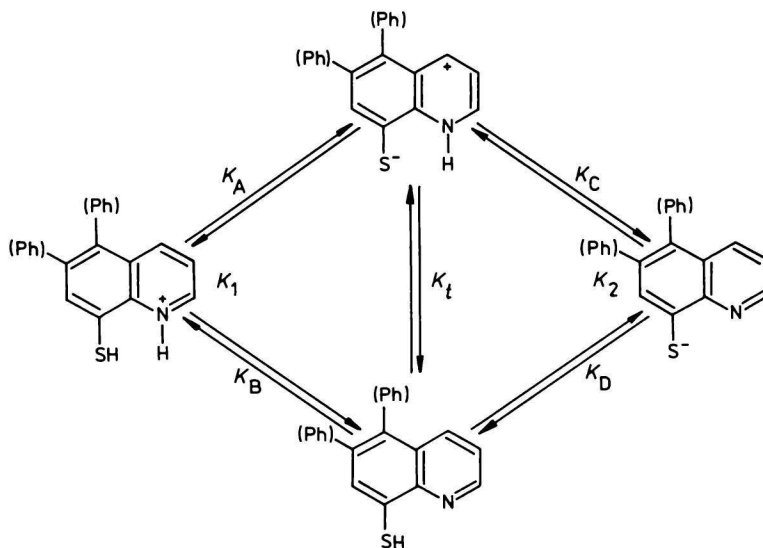
Scheme 2

Ionization constants K_1 and K_2 are of cumulative type and they characterize both equilibria in the right (K_1) and left (K_2) side of the scheme. Constants K_A, K_B, K_C, K_D characterize equilibria between individual forms of reagents. Tautomerization constant K_t characterizes the mole ratio between zwitterionic and thiolic form of reagents.

Ionization constants of reagents and their methylthio derivatives have been determined spectrophotometrically according to the method [19], tautomerization constants have been calculated by *Ebert's* method [20] and individual ionization constants have been calculated as described in [3]. Two-phase ionization (pK_2') and distribution (K_d) constants have been determined spectrophotometrically [17]. The obtained results are presented in Tables 4 and 5. In Table 4 for the sake of comparison there are also presented data about the previously determined ionization and distribution constants of 8-mercaptoquinoline and its 2-phenyl and 4-phenyl derivatives. From Table 4 it is obvious that phenyl group in the 5th and 6th position slightly decreases the basic properties (pK_B) and increases acidic properties (pK_D) of 8-mercaptoquinoline. This can be explained by the weakly negative effect of this group. In the 4th position as a result of the strong ability of

Table 4

Cumulative constants, individual constants, two-phase ionization constants, tautomerization constants, and distribution constants of 8-mercaptoquinoline [17], 2-phenyl- [3], 4-phenyl- [3], 5-phenyl-, and 6-phenyl-8-mercaptoquinolines at ionic strength $I = 0.1$ mol dm^{-3} and $\theta = 20$ °C

Reagent	pK_1	pK_2	pK_A	pK_B	pK_C	pK_D	K_t	$pK_2'^*$	K_d^*
RSH	2.08	8.43	2.10	3.50	8.41	7.01	25.3	10.95	372
2-PhRSH	1.41	8.00	1.49	2.21	7.92	7.20	5.3	13.67	470 000
4-PhRSH	2.10	8.49	2.12	3.56	8.47	7.03	27.8	13.38	78 000
5-PhRSH	1.97	8.41	1.99	3.39	8.39	6.99	25.3	13.19	60 000
6-PhRSH	2.01	8.19	2.03	3.37	8.17	6.83	21.9	13.04	70 800

* Two-phase ionization constants and distribution constants are determined in the system chloroform—water.

Table 5

Two-phase ionization constants and distribution constants between organic solvents and water of 5-phenyl- and 6-phenyl-8-mercaptoquinolines at ionic strength $I = 0.1$ mol dm^{-3} and $\theta = 20$ °C

Solvent	5-Phenyl-8-mercaptoquinoline		6-Phenyl-8-mercaptoquinoline	
	pK_2'	K_d	pK_2'	K_d
Chloroform	13.19	60 000	13.04	70 800
Benzene	12.91	32 000	12.70	32 400
Heptane	11.47	1 150	11.28	1 230

heterocyclic nitrogen atom to attract electrons from carbon atom in the 4th position, phenyl group acts as a weak electron-donating substituent, slightly increasing basic properties (pK_B) and decreasing acidic properties (pK_D) of 8-mercaptoquinoline. Considerable decrease of basic properties ($pK_B = 2.21$) and slight decrease of acidic properties ($pK_D = 7.20$) of 2-phenyl-8-mercaptoquinoline can be explained by steric effect of phenyl group in the 2nd position.

As it follows from tautomerization constants (Table 4) phenyl group in the 4th, 5th, and 6th position practically does not affect the ability of 8-mercaptoquinoline to form zwitterionic form in water, however, in the 2nd position this ability is strongly decreased as a result of hindrance in formation of molecular complex in water.

Distribution constants between organic solvent and water of phenyl derivatives of 8-mercaptoquinoline because of hydrophobic character of phenyl group are considerably higher than those of 8-mercaptoquinoline, and distribution constants of 4-, 5-, and 6-phenyl derivatives of 8-mercaptoquinoline approximately coincide, but the distribution constant of 2-phenyl-8-mercaptoquinoline, due to its smaller

Table 6

Maximum extraction intervals of 5-phenyl- and 6-phenyl-8-mercaptoquinolines with organic solvents

| | Maximum extraction intervals | |
Solvent	5-Phenyl-8-mercaptoquinoline	6-Phenyl-8-mercaptoquinoline
Chloroform	2.5 M-HCl—pH 11.2	2 M-HCl—pH 11.2
Benzene	2.3 M-HCl—pH 11.0	1.5 M-HCl—pH 11.0
Heptane	pH 0.4—pH 10.0	pH 0.8—pH 10.2

degree of hydration in aqueous solution because of steric effects of phenyl group, is considerably greater. Distribution constants of 5- and 6-phenyl derivatives of 8-mercaptoquinoline increase with the organic solvents used as follows: heptane, benzene, chloroform (Table 5).

The intervals of maximum extraction of 5-phenyl- and 6-phenyl-8-mercapto-quinolines also increase according to the order: heptane, benzene, chloroform (Table 6).

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