1.9 (13H, m, $(CH_2)_5$ and NCH_2CH_3); 2.96 (2H, s, 6-CH_2); 3.86 (2H, q, $J = 7$ Hz, NCH_2CH_3); 7.00-8.20 ppm (9H, m, C_6H_4 and C_6H_5).

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REACTION OF QUINAZOLINE DERIVATIVES WITH QUATERNARY SALTS OF HETEROCYCLIC BASES

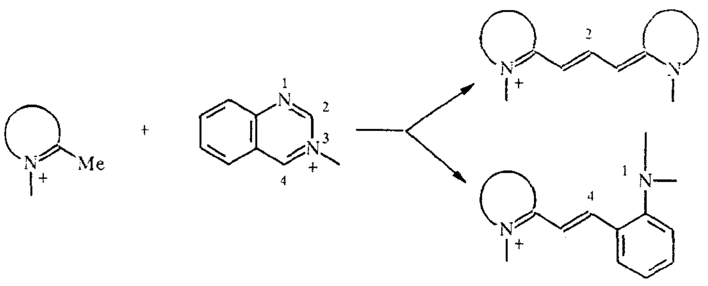
S. P. Gromov and M. A. Razinkin

The formation of carbocyanine and styryl dyes from quinazoline derivatives and quaternary salts of heterocyclic bases was detected. The intermediate compounds were separated and mechanisms of the reactions were proposed.

We proposed opening of the *sym*-triazine ring after addition of a nucleophile according to an electrocyclic mechanism as the basic direction in conversion of *sym*-triazine into pyridine and pyrimidine derivatives by enaminones. This reaction can take place with inclusion of a different number of *sym*-triazine atoms, including one carbon atom [1]. There is also information that trimethinecyanines are formed with extremely high yields in the reactions of quaternary salts of 2-methyl derivatives of heterocyclic bases with *sym*-triazine, which serves as a donor of a central carbon atom in construction of the polymethine chain of the dye [2]. Pentamethine dyes with three atoms in the pyrimidine ring in the polymethine chain are formed in the reaction of pyrimidine derivatives and the quaternary salt of the corresponding methyl derivative of the heterocycle [3].

Quinazoline derivatives can simultaneously be considered as pyrimidine derivatives for which reactions of nucleophilic addition at positions 2 and 4 [4] or cyclotransformation reactions are characteristic [5] and as a condensed diazine system similar to *sym*-triazine derivatives in electron deficiency [6].

It was possible to hypothesize that the diazine ring of the quinazoline nucleus will also be able to act as a donor of one or three carbon atoms in reactions with quaternary salts of heterocyclic bases, respectively forming cyanine and styryl dyes:



N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117977. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 662-670, May, 1992. Original article submitted December 5, 1991.

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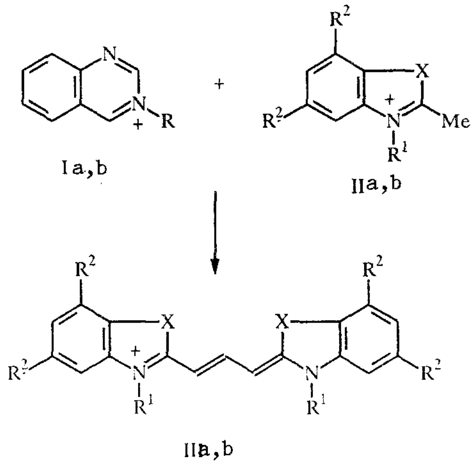
It was actually found that when quinazoline is heated in pyridine with 2-methyl-3-ethylbenzothiazolium iodide (IIa), trimethine dye IIIa is formed, although with a low yield (5%), which could be due to the insufficient electron deficiency of the pyrimidine nucleus of quinazoline.

The N-oxides of heteroaromatic compounds exhibit high reactivity with respect to not only electrophiles but also to nucleophiles [7]. It was previously found that quinazoline N-oxide forms products of cyclotransformation with carbanions [8].

Experiments showed that when quinazoline N-oxides (Ia) are heated in pyridine with the quaternary salt of IIa, trimethine dye IIIa is formed with a yield of 17%.



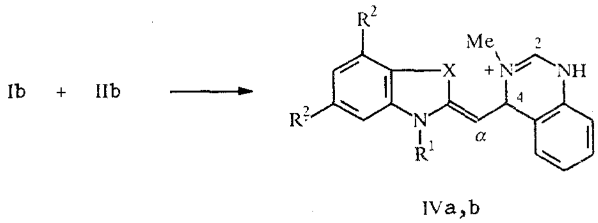
Ia R = O⁻, b R = Me; II, III a R^1 = Et, R^2 = H, X = S; b R^1 = R^2 = Me, X = CMe_2

In other conditions, for example, in acetic anhydride with addition of triethylamine, the cyanine dye is not formed at all from quinazoline or quinazoline N-oxide. That is, incorporation of an even more electron-acceptor substituent in the quinazoline molecule is evidently required for creating the necessary electrophilicity to ensure more efficient nucleophilic attack on the pyrimidine nucleus.

In the quaternary salts of heterocyclic bases, the carbon atoms adjacent to a nitrogen atom are polarized to the greatest degree with respect to the nucleophiles [9]. We hypothesized that use of 3-methylquinazolinium iodide would increase the electrophilicity of the pyrimidine ring in quinazoline to the required level, which would ensure the conditions for effective opening of the heterocyclic ring.

We actually found that when 3-methylquinazoline iodide (Ib) is heated with the quaternary salts of heterocyclic bases IIa, b in acetic anhydride with addition of triethylamine, trimethine dyes IIIa, b are formed with yields of 58 an 66%, respectively.

We attempted to separate the intermediate compounds to study the mechanism of splitting of the quinazoline nucleus of salt Ib in detail. We found that when a mixture of 3-methylquinazoline iodide (Ib) and the quaternary salts of IIa, b are held in acetonitrile in the presence of triethylamine at room temperature, adducts IVa, b are formed at room temperature with a yield of up to 90%:

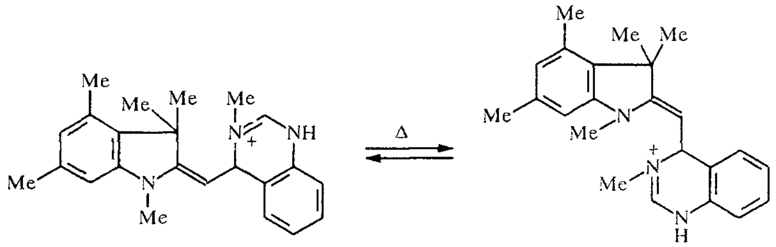


IVa R^1 = Et, R^2 = H, X = S; b R^1 = R^2 = Me, X = CMe_2

Addition of a nucleophile at position 4 in adducts IVa, b was established with the two-dimensional NOESY spectra, in which the protons of the aromatic ring of the quinazoline residue of the adducts and the weak-field singlet hydrogen atom of the dihydropyrimidine ring do not react with each other, indicating their spatial distance. This position of the hydrogen atoms is realized in adducts IVa, b and is impossible for adducts in which the nucleophile is added at position 2 of the quinazoline bicycle. The signal of the carbon atom bound with the singlet hydrogen atom mentioned above is in the weakest field region of the ^{13}C NMR spectra (149.00 ppm for adduct IVa, DMSO-D_6). This also confirms the structure of IVa, b adducts in which this carbon atom is included in the amidinium fragment of the dihydropyrimidine ring. Adducts of quinazoline derivatives with different C- and N-nucleophiles were previously isolated in [10], and addition of nucleophiles at position 4 was proposed for their formation.

The proton signals for the α-H and 4-H system in the ESR spectra of adducts IVa, b were identified with the standard approach with selective suppression of the $^{13}C\{^1H\}$ spin-spin interaction. It was found that the C(α)H olefin carbon of adduct IVa, for example (87.82 ppm in the ^{13}C NMR spectrum, DMSO-D_6), is bound with a proton, giving a doublet in the ESR spectrum in stronger fields (4.86 ppm), and the $C_{(4)}H$ sp^3-hybridized atom (59.87 ppm in the ^{13}C NMR spectrum) is bound with a proton, giving a weaker field doublet at 5.53 ppm.

The analysis of the PMR spectra (at the working frequency of 400 MHz) shows that adduct IVb consists of a pair of E- and Z-isomers whose ratio varies from 10:1 to 2:1 as a function of the conditions (from 25 to 60°C, DMSO-D_6):



E-IVb

Z-IVb

The configuration of the predominant isomer E-IVb was determined with the two-dimensional NOESY spectrum, in which cross peaks between the signals of the 4-H and CMe_2 protons were observed for it.

Adduct IVa does not form spectrally different E- and Z-isomers, perhaps because the rate of their mutual conversion is high at room temperature.

The two-dimensional NOESY spectrum of adduct IVb can also be used to precisely assign the proton signals of the indolenine fragment of the predominant isomer. The analysis of the cross peaks in the spectrum showed that the methyl group at 2.29 ppm ($CDCl_3$) and aromatic protons of the benzene ring (6.30 and 6.44 ppm) are spatially close, while the methyl group at 2.38 ppm only reacts with one of them: the proton at 6.44 ppm. That is, the methyl groups at 2.29 and 2.38 ppm are respectively in positions 6′ and 4′ of the indolenine fragment, and the aromatic protons at 6.30 and 6.44 ppm are in positions 7′ and 5′. The methyl group at the nitrogen atom (3.51 ppm) has cross peaks with the protons in the 3,4-dihydroquinazolinium residue: 2-H and 4-H, while the N-methyl group at 3.00 ppm has cross peaks with the α-H proton. This suggests that the strong-field N-methyl group belongs to the indolenine fragment, while the weaker field group belongs to the 3,4-dihydroquinazolinium residue. This conclusion is also confirmed by a comparison of the spectra of adducts IVa and IVb in DMSO-D_6, where the chemical shifts of the N-methyl group of the 3,4-dihydroquinazolinium residue IVa (3.27 ppm) and the weaker field N-methyl group of E-IVb (3.30 ppm) almost coincide.

The study of conversions of adducts IVa, b in acid media revealed different paths of splitting of the quinazoline nucleus.

When adducts IVa, b are heated in acetic anhydride in the presence of triethylamine, cyanine dyes IIa, b are formed with a yield of the order of 40%:

$$\text{IVa, b} \rightarrow \text{IIIa, b}$$

At the same time, conducting the reaction with addition of an excess of the quaternary salts of IIa, b increases the yield of the dyes to 60-80%.

TABLE 1. Products and Conditions of Conducting Reactions of Quinazoline Derivatives with Quaternary Salts of IIa, b

Expt. No.	Quinazoline derivative; 1 mmole	Quaternar. salt, mmole	Reagents and reaction conditions*	Dye	Yield mmole
1	Ib	II b , 2	A	IIIb	0,53
2	Ib	II b , 3	A	IIIb	0.66
3	IVb	—	A	IIIb	0,19
4	IVb	II b , 1	A	IIIb	0,61
5	IVb	II b , 2	A	IIIb	0,81
6	Ia	II a , 2	B	IIIa	0.34
7	IVa	—	B	IIIa	0,22
8	IVa	II a , 1	B	IIIa	0,44

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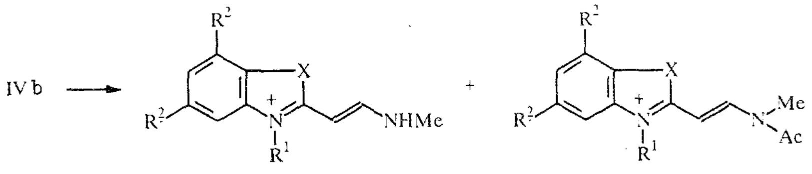
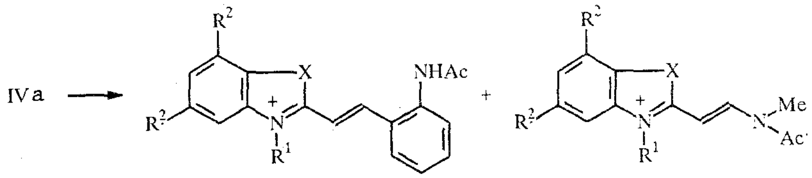
*The starting substances were heated for 1 h at 100°C with 20 ml Ac_2O and 3 ml Et_3N (method A) or 10 ml Ac_2O and 1 ml Et_3N (method B).

Adduct IVb forms a complex mixture of products when held in acetic anhydride without any base, and we chromatographically separated a mixture of azacarbocyanine dyes Vb and VIb from it.

When adduct IVa is heated in acetic anhydride, styryl VIIa and azacarbocyanine VIa dyes are formed with a yield of approximately 15% each:



Vb VIb



VIIa VIa

V—VIIa $R^1 = Et$, $R^2 = H$, $X = S$; b $R^1 = R^2 = Me$, $X = CMe_2$

We also spectrophotometrically identified the formation of styryl and azacarbocyanine dyes in heating 3-methylquinazolinium iodide (Ib) with the quaternary salts of IIa, b in acetic anhydride, but the complex character of the reaction mixture made it impossible to separate these dyes.

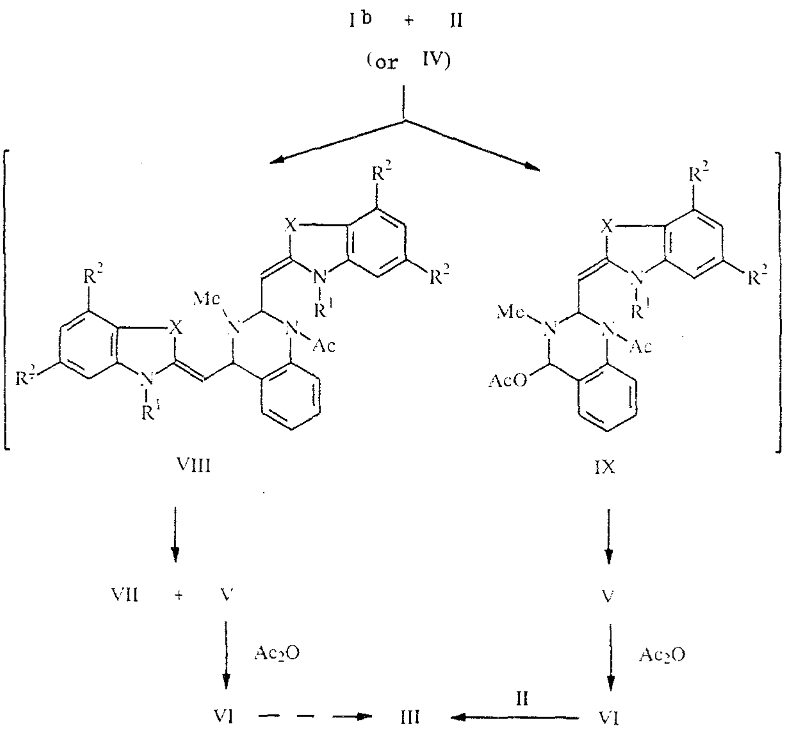
The structure of compounds Vb and VIa, b was established by ESR, and for β-methylaminoethenylindolenine dye Vb also by comparison with the spectral data of its β-aminoethenylindolenine homolog which we investigated previously (a description of the properties of this compound will be published later). The second compound isolated in a mixture with dye Vb produces a similar ESR spectrum, except for an additional methyl group in the 2.40 ppm region, shift of the signals of aromatic and olefin protons to weaker fields, and an increase in the spin-spin coupling constants of olefin protons ^3J from 12.8 to 14.0 Hz. This suggests that compound VIb contains a N-methylacetamide group in the β-position to the heterocyclic residue, formed as a result of acylation of the terminal amino group of compound Vb by acetic anhydride.

According to the ESR data, the compound formed from adduct IVa together with styryl dye VIIa has a benzothiazole nucleus and substituted azadimethine chain similar to VIb, which supports structure VIa. The signal of acetyl group protons is superimposed in the spectrum on the signal of the solvent — DMSO-D_6. The presence of this group is confirmed by the spectrum in deuterochloroform, where its chemical shift is equal to 2.46 ppm.

The high spin-spin coupling constant ^3J = 15.9 Hz for olefin protons in styryl dye VIIa suggests that it exists in the *trans*-form. The SSCC found is characteristic of styryl dyes of the benzothiazole series [11].

The data obtained makes it possible to formulate some hypotheses on the mechanisms of the reactions of cyclotransformation of quinazoline derivatives detected and investigated.

The formation of cyanine IIIa, b and azacarbocyanine Vb, VIa, b dyes from adducts IVa, b alone can hardly be explained if we do not hypothesize the existence of migration of a heterocyclic residue of adducts IVa, b in the reaction conditions from position 4 to position 2 of the quinazoline nucleus with formation of 1,2-dihydroquinazolinium derivatives of different structure.



Addition of one, two, and even three molecules of a nucleophile to an electron-deficient aromatic nucleus is described in [4]. The proposed mechanisms of formation of trimethine dyes from *sym*-triazine [2] and cyclotransformation of quinazoline by C-nucleophiles [12] include the stage of formation of adducts of the heterocycle with several molecules of the nucleophile. For this reason, we hypothesized that conversion of adduct IVa into an approximately equimolar mixture of styryl VIIa and azacarbocyanine VIa dyes in acetic anhydride probably passes through formation of diadduct VIII with its subsequent decomposition according to a [4 + 2] cycloelimination reaction.

The formation of trimethine dyes IIIa, b in acetic anhydride and triethylamine medium from both adduct VIII and from adduct IX can be theoretically represented. However, the experimental data show that only the second path of their formation occurs. We did not detect formation of products with an open pyrimidine ring similar to styryl dye VIIa in these conditions. On the other hand, only a slight increase in the yield of dye IIIb is observed when the ratio of reagents Ib and IIb was changed from 2:1 to 3:1 (Table 1, Expts. 1 and 2) or for IVb and IIb was changed from 1:1 to 2:1 (Expts. 4 and 5). This also corresponds to occurrence of the reaction through an adduct of the type of IX to a greater degree. It is important that the yield of dye IIIb (61%) in experiment 4 (see Table 1) is greater than 50%, which is impossible if the reaction takes place through adduct VIII. We can thus consider it demonstrated that adduct IX is formed in acetic anhydride and triethylamine medium and probably exists in equilibrium with an adduct of the type of IV and azacarbocyanine dye V formed during the reaction of [4 + 2]-cycloelimination. It is most probable that trimethine dyes IIa, b are not directly formed from dye V, but from the product of its acylation VI, which is significantly more reactive to nucleophilic attack by anhydro bases of quaternary salts of heterocyclic bases [13].

Adducts VIII and IX, which we proposed as intermediates, contain N-acetyl and acetate groups. The structure of the final substance VIIa and the ease of addition of acetic anhydride with quinazoline in soft conditions support this possibility [12].

Adducts VIII and IX could not be identified due to their brief lifetime. When the reaction between Ib and IIa was conducted in the presence of triethylamine and acetic anhydride in a deuterated solvent in the ampul of the NMR spectrometer, the spectra indicated the formation of only two compounds: adduct IVa and cyanine dye IIIa.

Strong bases cause quinazoline derivatives to form compounds of a different type than those in the present article. These transformations will be described in future publications.

The reactions found are examples of a previously unknown type of transformation of a quinazoline bicycle and are simultaneously a new method of synthesis of carbocyanine and styryl dyes. Our dual reaction of quinazoline derivatives has not been observed before and can be of theoretical interest as an example of the effect of annelation on the reactivity of the pyrimidine ring.

EXPERIMENTAL

The ESR spectra and two-dimensional NOESY spectra were made on a Bruker WM-400, and the ^{13}C NMR spectra were made with the method of selective suppression of the $^{13}C\{^1H\}$ spin-spin interaction on a Bruker WP-200-SY. TMS was the internal standard. The UV spectra were made on a Shimadzu UV-160A spectrophotometer. The course of the reactions was monitored by TLC on Silufol-UV-254 plates and spectrophotometrically. The products and conditions of conducting some of the reactions of quinazoline derivatives with quaternary salts of IIa, b are reported in Table 1.

The data from elemental analysis for C, H, and N corresponded to the calculations.

Preparation of 1,2,3,3,4,6-hexamethyl-3H-indolium iodide (IIb) is described in [14]. Quinazoline N-oxide was prepared according to [15]. N-methylquinazolinium iodide was prepared similar to the method in [16], but the quaternization reaction time was increased to 1-2 days, which produced a purer substance. The salt obtained is 3-methylquinazolinium iodide (Ib) and is not reactive in reactions of 1-methylquinazolinium iodide with C-nucleophiles [10] in the ratio of 5:1. According to the published data [17], N-methylquinazolinium iodide is used without separation. The yields on conversion to the 3-methylquinazolinium iodide (Ib) used in the reaction are indicated in the methods reported.

3,3′-Diethylthiacarbocyanine iodide (IIIa). A. A mixture of 0.1.3 g (1 mmole) of quinazoline and 0.31 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium iodide (IIa) in 2 ml of pyridine was boiled for 1 h. The solvent was vacuum distilled, and the residue was washed with water and recrystallized from alcohol twice. Mp 264-266°C (decomp., from methanol); according to the data in [18], mp 269°C. Yield of 0.013 g (5%).

B. A mixture of 0.15 g (1 mmole) of quinazoline N-oxide (Ia) and 0.92 g (3 mmole) of compound IIa in 5 ml of pyridine was boiled for 3 h. The reaction mixture was cooled, dry ether was added, and the residue was filtered off and washed with water and acetone. Mp 264-265°C (decomp., from alcohol). Yield of 0.09 g (17%).

C. A mixture of 0.33 g (1.2 mmole) of N-methylquinazolinium iodide and 1.10 g (3.6 mmole) of the quaternary salt of IIa in 20 ml of acetic anhydride with addition of 2 ml of triethylamine was heated for 20 min at 100°C. The reaction mixture was cooled, and the sediment was filtered off, washed with acetone, and recrystallized from methanol, yielding 0.29 g (58%) of compound IIIa, mp 265-267°C (decomp.).

1,1,3,3,3′,3′,4,4′,6,6′-Decamethylindocarbocyanine iodide (IIIb). A mixture of 0.33 g (1.2 mmole) of N-methylquinazolinium iodide and 0.99 g (3 mmole) of 1,2,3,3,4,6-hexamethyl-3H-indolium iodide (IIb) in 20 ml of acetic anhydride with addition of 3 ml of triethylamine was heated for 1 h at 100°C. The reaction mixture was diluted with 110 ml of hot water, cooled, and the sediment was filtered off, dried, and washed with a hot hexane—benzene mixture 3:1. Mp 278-281°C (decomp.). UV spectrum in ethanol, λ_{max} (log ε): 522 (4.87), 554 (5.04). ESR spectrum (DMSO-D_6): 1.72 (12H, s, $2C(CH_3)_2$); 2.34 (6H, s, 6 and 6′-CH_3); 2.45 (6H, s, 4 and 4′-CH_3); 3.61 (6H, s, N and N′—CH_3); 6.36 (2H, d, α and α'-H, $^3J_{trans}$ = 13.6 Hz); 6.87 (2H, s, 5 and 5'-H); 7.11 (2H, s, 7 and 7'-H); 8.34 ppm (1H, t, *meso*-CH, $^3J_{trans}$ = 13.6 Hz). Yield of 0.36 g (66%).

3-Methyl-4-[(3-ethyl-2[3H]-benzothiazolylidene)methyl]-3,4-dihydroquinazolinium iodide (IVa). A mixture of 0.33 g (1.2 mmole) of N-methylquinazolinium iodide, 0.31 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium iodide (IIa), and 0.14 ml (1 mmole) of triethylamine in 2.5 ml of acetonitrile was left for 24 h at ~20°C. The reaction mixture was cooled, and the sediment was filtered off and washed with acetonitrile. Mp 195-198°C (decomp.). ESR spectrum (DMSO-D_6): 1.12 (3H, t, CH_3, $J_{CH_3CH_2}$ = 7.2 Hz); 3.27 (3H, s, N—CH_3); 3.77 (2H, q, CH_2, $J_{CH_3CH_2}$ = 7.2 Hz); 4.86 (1H, d, α-H, $J_{\alpha 4}$ = 9.8 Hz); 5.53 (1H, d, $C_{(4)}H$, $J_{4\alpha}$ = 9.8 Hz); 6.90 (1H, t, 5'-H); 6.94 (1H, d, 7'-H); 7.09 (1H, d, 5-H); 7.17 (1H, d, 8-H); 7.18 (1H, t, 6'-H); 7.24 (1H, t, 7-H); 7.34 (1H, t, 6-H); 7.41 (1H, d, 4'-H); 8.24 (1H, s, NH); 8.39 ppm (1H, s, 2-H). ^{13}C NMR spectrum (DMSO-D_6): 10.78 (CH_3); 39.60 (CH_2 and NCH_3); 59.87 ($C_{(4)}H$); 87.82 ($C_{(\alpha)}H$); 108.34-142.06 (C_{arom}); 146.43 ($C_{(2')}$); 149.00 ppm ($C_{(2)}H$). Yield of 0.41 g (91%).

3-Methyl-4-[(1,3-dihydro-1,3,3,4,6-pentamethyl-2H-indol-2-ylidene)methyl]-3,4-dihydroquinazolinium iodide (IVb). It was prepared similar to compound IVa from N-methylquinazolinium iodide and salt IIb with a yield of 80%. Mp 197-201°C (decomp.). ESR spectrum ($CDCl_3$) for the E-isomer: 1.73 and 1.76 (6H, 2s, $C(CH_3)_2$); 2.29 (3H, s, 6'-CH_3); 2.38 (3H, s, 4'-CH_3); 3.00 (3H, s, 1'-NCH_3); 3.51 (3H, s, 3-NCH_3); 4.32 (1H, d, α-H, $J_{\alpha 4}$ = 11.4 Hz); 5.99 (1H, d, $C_{(4)}H$, $J_{4\alpha}$ = 11.4 Hz); 6.30 (1H, s, 7'-H); 6.44 (1H, s, 5'-H); 7.18-7.49 (4H, m, C_4H_4); 8.53 ppm (1H, s, 2-H). ESR spectrum ($CDCl_3$) for the Z-isomer: 1.35 and 1.43 (6H, 2s, $C(CH_3)_2$); 2.32 and 2.34 (6H, 2s, 4'-CH_3 and 6'-CH_3); 3.43 and 3.46 (6H, 2s, 1'-NCH_3 and 3-NCH_3); 4.23 (1H, d, α-H, $J_{\alpha 4}$ = 11.4 Hz); 6.18 (1H, d, $C_{(4)}H$, $J_{4\alpha}$ = 11.4 Hz); 6.39 and 6.50 (2H, 2s, 5'-H and 7'-H); 7.09-7.46 (4H, m, C_4H_4); 8.49 ppm (1H, s, 2-H).

Reaction of adduct IVb with acetic anhydride. Here 1 mmole of compound IVb was added to 20 ml of acetic anhydride and left at ~20°C for 1 month until the salt was totally dissolved. Then 15 mmole of $NaClO_4$ monohydrate was added to the reaction mixture, the acetic anhydride was distilled off in a vacuum, and the residue was extracted with chloroform. The extracts were combined and evaporated. The product obtained was chromatographed in a column with silica gel L40/100 μ in the benzene—acetonitrile system, 1:1. A mixture of 2-(2-methylaminoethenyl)-1,3,3,4,6-pentamethyl-3H-indolium (Vb) and 2-[2-(N-methylacetamido)-ethenyl]-1,3,3,4,6-pentamethyl-3H-indolium (VIb) perchlorates in the molar ratio of 5:3 was obtained. ESR spectrum (DMSO-D_6) of compound Vb: 1.62 (6H, s, $C(CH_3)_2$); 2.33 and 2.41 (6H, 2s, 4-CH_3 and 6-CH_3); 3.06 (3H, s, $NHCH_3$); 3.57 (3H, s, 1-NCH_3); 5.58 (1H, d, α-H, $^3J_{trans}$ = 12.8 Hz); 6.84 (1H, s, 5-H); 7.09 (1H, s, 7-H); 8.42 ppm (1H, d, β-H, $^3J_{trans}$ = 12.8 Hz). ESR spectrum (DMSO-D_6) of compound VIb: 1.71 (6H, s, $C(CH_3)_2$); 2.32-2.50 (9H, 3s, 4-CH_3, 6-CH_3 and CH_3CO); 3.40 (3H, s, $NAcCH_3$); 3.92 (3H, s, 1-NCH_3); 6.23 (1H, d, α-H, $^3J_{trans}$ = 14.0 Hz); 7.10 and 7.40 (2H, 2s, 5-H and 7-H); 8.64 ppm (1H, d, β-H, $^3J_{trans}$ = 14.0 Hz).

3-Ethyl-2-[2-(2-acetamidophenyl)-ethenyl]benzothiazolium (VIIa) and 3-ethyl-2-[2-(N-methylacetamido)-ethenyl]benzothiazolium (VIa) salts. Here 10 ml of acetic anhydride was added to 0.45 g (1 mmole) of adduct IVa and heated at 95°C for 30 min. The solution was decanted from the undissolved residue, which was again treated with acetic anhydride as previously. The operation was repeated until the sediment had totally dissolved. The solutions obtained were combined, vacuum evaporated to one-third, and cooled for 24 h. The precipitated sediment was filtered off, recrystallized from alcohol, and washed with acetone, yielding 0.03 g (7%) of iodide VIIa, mp 226-228°C (decomp.). ESR spectrum (DMSO-D_6): 1.51 (3H, t, CH_3, $J_{CH_3CH_2}$ = 7.0 Hz); 2.16 (3H, s, $COCH_3$); 5.00 (2H, q, CH_2, $J_{CH_3CH_2}$ = 7.0 Hz); 7.37 (1H, t, 4'-H); 7.54 (1H, d, 6'-H); 7.56 (1H, t, 5'-H); 7.81 (1H, t, 5-H); 7.89 (1H, t, 6-H); 7.95 (1H, d, α-H $^3J_{trans}$ = 15.9 Hz); 8.15 (1H, d, β-H $^3J_{trans}$ = 15.9 Hz); 8.22 (1H, d, 3'-H); 8.31 (1H, d, 7-H); 8.44 (1H, d, 4-H); 9.96 ppm (1H, br. s, NH). After separation of the sediment of VIIa, the filtrate was vacuum evaporated, the residue was dissolved in methanol, and 0.25 ml of 57% perchloric acid was added, yielding 0.11 g of a mixture of perchlorates VIa and VIIa in the molar ratio of 1.7:1. ESR spectrum (DMSO-D_6) of compound VIa: 1.30 (3H, t, CH_3CH_2); 2.50 (3H, s, $COCH_3$); 3.38 (3H, s, NCH_3); 4.79 (2H, q, CH_2); 6.67 (1H, d, α-H, $^3J_{trans}$ = 13.4 Hz); 7.70 (1H, t, 5-H); 7.80 (1H, t, 6-H); 8.15 (1H, d, 7-H); 8.30 (1H, d, 4-H); 8.49 ppm (1H, d, βH, $^3J_{trans}$ = 13.4 Hz).

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