CYANINE DYES FROM SEVEN-MEMBERED HETEROCYCLIC SYSTEMS

V. Dyes in the Benzo[b]cyclohexano[f]- and -[e]-1,4-Thiazepine Series*

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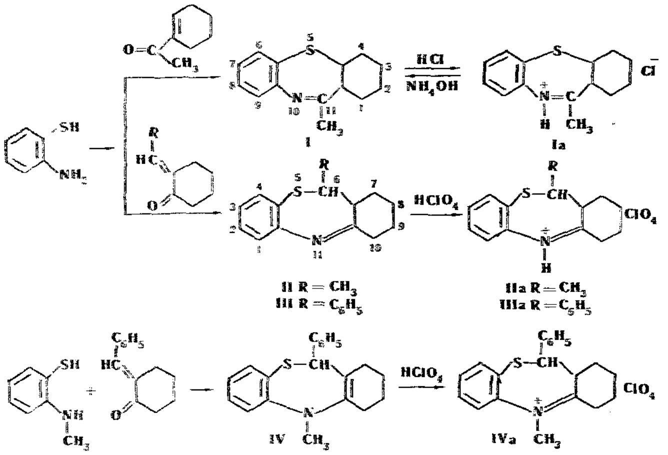
The condensation of o-aminothiophenol with tetrahydroacetophenone, 2-ethylidenecyclohexanone, and 2-benzylidenecyclohexanone and also the condensation of N-methyl-o-aminothiophenol with 2-benzylidenecyclohexanone has given the bases of derivatives of benzo[b]cyclohexano[f]- and -[e]-1,4-thiazepines. From the hydrochlorides, perchlorates, and quaternary salts of these bases, cyanine dyes have been synthesized. The dyes—norcyanines—exhibit solvatochromism, which is explained by the existence of a hydrogen bond between the molecules of the dye and an alcohol.

The condensation of o-aminothiophenol or its N-methyl derivative with α,β-unsaturated cyclic ketones has given seven-membered heterocyclic bases forming derivatives of benzo[b]cyclohexano[f]- and -[e]-1,4-thiazepines (I, II, III, and IV).

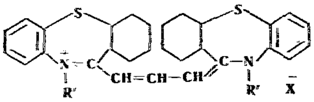


The condensation reaction takes place readily on heating. If the products obtained directly from the reaction consisted of viscous oils (I, II, III), they were converted into the chlorides (Ia) or the perchlorates (IIa, IIIa), which crystallized well from alcohols. The free bases were obtained in the form of crystalline products from the purified salts by treatment with aqueous ammonia.

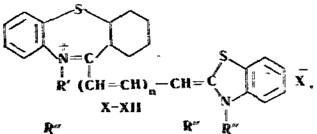
When the perchlorate IIa was treated with aqueous ammonia, the N=C bond underwent cleavage, adding water, and instead of the expected 6-methyl-6,6a-dihydrobenzo[b]cyclohexano[e]-1,4-thiazepine (II) analogous in structure to III, o-aminophenyl α-(cyclohexanon-2-yl)ethyl sulfide (IIb) was formed. The IR spectra of IIa, IIb, and III confirmed this. In the IR spectra of IIb there is a strong absorption band at 1705 cm^{-1} corresponding to the stretching vibrations of the CO group [1], and also two bands at 3345 cm^{-1} and 3450 cm^{-1} corresponding to the NH stretching vibrations, while in the IR spectrum of the initial perchlorate IIa these bands are absent and there is an absorption band at 1650 cm^{-1} which can be ascribed to the stretching vibrations of the C=N bond. The IR spectrum of III also lacks absorption bands corresponding to the stretching vibrations of the CO and NH groups.

In the salts obtained from the base I, the methyl group in position 11 is active, and in the salts of the other bases the methylene group in position 10 is active; consequently they all proved to be capable of condensation reactions leading to the formation of cyanine dyes. It was impossible to obtain the symmetrical monomethinecyanine from the perchlorate IVa. The condensation of the base IV with orthoformic ester in the presence of acetic anhydride with subsequent treatment of the product obtained with perchloric acid led to bis(3-methylbenzothiazole-2)trimethinecyanine perchlorate. The formation of this dye can be explained by the cleavage of the thiazepine ring under the influence of the acetic anhydride and the appearance of a new thiazoline ring. The quaternary salt of 2-methylbenzothiazole formed reacts with the orthoformic ester to form a carbocyanine, which was isolated and identified in the form of the perchlorate. The cleavage of the thiazepine and the formation of a thiazoline ring were confirmed in the following way: the base IV was heated with acetic anhydride for 30 min, the anhydride was driven off in vacuum, and the residue, dissolved in ethanol, was treated with perchloric acid. The crystalline product obtained gave no depression of the melting point with 2,3-dimethylbenzothiazoline perchlorate.

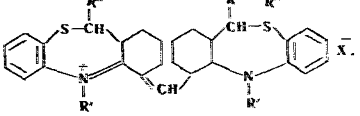
The general formulas of the dyes VIII–XXII synthesized are given below.



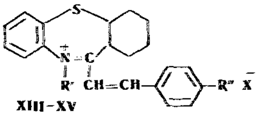
VIII, IX



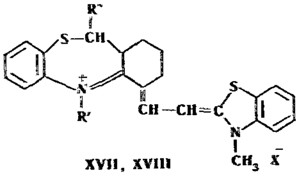
X–XII



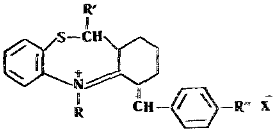
XVI



XIII–XV



XVII, XVIII



XIX–XXII

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*For part IV, see [3].

Absorption Maxima of the Cyanine Dyes

Compound	R′	R″	X	λ_{max}, nm		
				в CH_3OH	в $CHCl_3$	в C_6H_6
VIII	H	—	Cl	535	566	567
IX	CH_3	—	I	496	504	—
X	H	C_2H_5	Cl	544	559	557
XI	CH_3	CH_3	I	523	—	548
XII	H	CH_3	ClO_4	435	428	—
XIII	H	$N(CH_3)_2$	ClO_4	546	—	550
XIV	CH_3	$N(CH_3)_2$	I	546	548	—
XV	H	OH	Cl	433	—	—
XVI	H	C_6H_5	Cl	578	—	622
XVII	H	C_6H_5	Cl	558	574	—
XVIII	CH_3	C_6H_5	ClO_4	560	570	—
XIX	C_6H_5	$N(CH_3)_2$	ClO_4	537	551	550
XX	C_6H_5	$N(CH_3)_2$	ClO_4	500	490	478
XXI	CH_3	$N(CH_3)_2$	ClO_4	528	547	538
XXII	CH_3	OH	ClO_4	420	—	—

Note: In compounds **XIX**, **XXI**, and **XXII**, R = H; in **XX**, R = CH_3; in **X** and **XI**, n = 1; in **XII**, n = 0.

The table gives the absorption maxima of the dyes synthesized in methanol, chloroform, and benzene. When a 2,2-dimethylbenzo[b]thiazepine heterocycle [2] in cyanine dyes is replaced by an 11-methylbenzo [b]-cyclohexano[f]thiazepine residue, there is a deepening of the color for the symmetrical trimethinecyanine by 13 nm and when it is replaced by a 6-phenylbenzo[b]cyclohexano[e]thiazepine residue a deepening by 68 nm.

As for the norcyanines described previously [2–4] the compounds reported in the present paper **VIII**, **X**, **XIII**, **XV**, **XVII**, and **XXI** (see table) give solutions with different colors according to the solvent. In benzene and chloroform they are all colored more deeply than in methanol—a solvent capable of forming hydrogen bonds with the dye molecule. Consequently, at the true absorption maximum of the norcyanines we must take the maximum of the absorption curve of a benzene or chloroform solution. For the symmetrical norcyanines, the hypsochromic shift on passing from benzene to methanol solution is fairly considerable: 32 nm for **VIII** and 44 nm for **XVI**. For the unsymmetrical norcyanines, the hypsochromic shift is considerably less: 13 nm for **X** and 16 nm for **XVII**. For reasons that are not clear to us, the monomethinecyanine **XII** does not obey this rule. The replacement of the hydrogen atom attached to nitrogen in the norcyanine **VIII** by a methyl group (dye **IX**) leads to a hypsochromic shift of 62 nm, in analogy with the results obtained previously.

EXPERIMENTAL

11-Methyl-4a,10,11aH-benzo[b]cyclohexano[f]-1,4-thiazepinium chloride (Ia). When 64.2 g (0.52 mole) of o-aminothiophenol and 64.5 g (0.52 mole) of tetrahydroacetophenone were heated in a sealed tube in the water bath for 5 hr, a condensation product was obtained in the form of a colorless vitreous mass. An ethereal solution of this product was washed with 5% ammonia solution and dried with magnesium sulfate, and a current of dry hydrogen chloride was passed into it. A small amount of dark resin and a crystalline product were formed. When the first crystals appeared, the ethereal solution was separated from the resin by decantation and the passage of hydrogen chloride was continued to saturation. The chloride obtained was dried in a vacuum desiccator over sulfuric acid. Colorless prisms, mp 194–195° C (from ethanol, decomp.). Yield 88 g (64%). Found, %: Cl 13.12, 13.44; S 11.74, 12.01. Calculated for $C_{14}H_{17}NS \cdot HCl$, %: Cl 13.24; S 11.98.

11-Methyl-4a, 11a-dihydrobenzo[b]cyclohexano[f]-1, 4-thiazepine (I). A suspension of 2.42 g (0.009 mole) of Ia in 10% aqueous ammonia was saturated with ether until the base formed had dissolved completely in the ether. The etheral solution was dried with sodium sulfate and evaporated in the air or in vacuum. Colorless rhombs, mp 94.5–95.5° C (from ethanol). Yield 1.1 g(54%). Found, %: S 13.67, 13.77. Calculated for $C_{14}H_{17}NS$, %: S 13.86.

6-Methyl-6,6a,11H-benzo[b]cyclohexano[e]-1,4-thiazepinium perchlorate (IIa). A mixture of 27.7 g (0.22 mole) of 2-ethylidenecyclohexanone and 28 g (0.22 mole) of o-aminophenol was left in a sealed tube at room temperature for a day. The reaction was exothermic. The purification of the viscous yellow oil formed and the preparation of the hydrochloride were similar to the case of **Ia**. Yield 44 g (74%). It was impossible to purify the hydrochloride. The perchlorate crystallized readily from ethanol. Prisms, mp 200–201° C (decomp.). Found, %: Cl 10.54, 10.68; S 9.75, 9.97. Calculated for $C_{14}H_{17}NS \cdot HClO_4$, %: Cl 10.69; S 9.67. When the perchlorate IIa was treated with aqueous ammonia, it was impossible to isolate the base. Hydrolysis took place with the formation of o-aminophenyl α-(cyclohexanon-2-yl)ethyl sulfide (IIb) with a yield of 56%. Colorless prisms, mp 125–126° C (from ethanol). Found, %: S 12.89, 12.90. Calculated for $C_{14}H_{19}NOS$, %: S 12.85.

6-Phenyl-6, 6a, 11H-benzo[b]cyclohexano[e]-1, 4-thiazepinium perchlorate (IIIa). A mixture of 25.3 g (0.14 mole) of 2-benzylidenecyclohexanone and 17 g (0.14 mole) of o-aminophenol was heated in a sealed tube in the water bath for 5 hr. The condensation product was extracted with ether. The ethereal solution was washed with 5% aqueous ammonia and dried with sodium sulfate. The residue after the elimination of the solvent, a viscous yellow oil, 34 g, could not be crystallized. Consequently the base was converted into the perchlorate, and this was purified by boiling the finely ground salt with ether and subsequent crystallization from ethanol. Colorless prisms, mp 203.5–204 ° C. Yield 18 g (40%). Found, %: S 8.09, 8.12. Calculated for $C_{19}H_{19}NS \cdot HClO_4$, %: S 8.14. The unpurified hydrochloride was used to synthesize several cyanine dyes. The free base **III** was obtained in the pure form from 1.52 g (0.004 mole) of the perchlorate IIIa in the same way as I. Colorless prisms, mp 130–131° C (from methanol). Yield 1.02 g (69%). The base contained methanol of crystallization. Found, %: S 9.82, 10.00. Calculated for $C_{19}H_{19}NS \cdot CH_4O$, %: S 9.85. After vacuum sublimation and drying in a Fischer pistol, the melting point remained unchanged. Found, %: N 4.74, 4.78; S 10.95, 11.02. Calculated for $C_{19}H_{19}NS$, %: N 4.77; S 10.92.

11-Methyl-6-phenyl-6H-benzo[b]cyclohexeno[1,2-e]-1,4-thiazepine (IV). A mixture of 9.9 g (0.07 mole) of N-methyl-o-aminothiophenol and 12.6 g (0.07 mole) of 2-benzylidenecyclohexanone was left in an atmosphere of nitrogen at room temperature for 2 days. The reaction mixture crystallized. To complete the reaction, it was heated for another 2 hr 30 min in the water bath. After cooling it formed a uniform crystalline product sparingly soluble in ether and ethanol. For purification, the finely ground base was boiled with ether and was crystallized from n-propanol, mp 134–134.5° C. Yield 18.3 g (88%). Found, %: S 10.30, 10.41. Calculated for $C_{20}H_{21}NS$, %: S 10.42. From 2.2 g (0.007 mole) of IV and 42% of perchloric acid in n-propanol, the perchlorate IVa was obtained. Colorless prisms, mp 204.5–206° C (from propanol). Yield, 1.8 g (62%). Found, %: Cl 8.71, 8.81. Calculated for $C_{20}H_{22}ClNO_4S$, %: S 8.69.

10,11-Dimethyl-4a,11a-dihydrobenzo[b]cyclohexano[f]-1,4-thiazepinium mesosulfate (V) was obtained from 0.35 g (0.002 mole) of I and 0.5 g (0.005 mole) of dimethyl sulfate by heating in 25 ml of ether. The oil isolated crystallized on standing. Yield 0.4 g (70%). The product was not analyzed but was converted into the perchlorate. The perchlorate (VI) was obtained from 0.4 g (0.001 mole) of V and 0.12 g (0.001 mole) of sodium perchlorate. Colorless prisms. Yield 0.27 g (71%), mp 190–191° C (from ethanol). Found, %: Cl 10.01, 10.18; S 9.17, 9.20. Calculated for $C_{15}H_{20}ClNO_4S$, %: Cl 10.24; S 9.27. The iodide (VII) was obtained by heating I with methyl iodide in absolute benzene in the water bath. It liberates iodine in alcoholic and dioxane solutions, particularly in the light and on heating.

Bis(4a,10a,11aH-benzo[b]cyclohexano[f]-1,4-thiazepine-5)trimethinecyanine chloride (VIII). A mixture of 0.6 g (0.002 mole) of Ia and 3 ml (0.018 mole) of orthoformic ester was heated in the water bath in 2 ml of ethanol for 15 min. Red needles, mp 182–183° C (decomp. from ethanol). Yield 0.24 g (18%). Found, %: Cl 6.93, 6.94; S 12.36, 12.39. Calculated for $C_{29}H_{32}N_2S_2 \cdot HCl$, %: Cl 6.96; S 12.59.

Bis(10-methyl-4a,11-dihydrobenzo[b]cyclohexano[f]-1,4-thiazepine-5)-trimethinecyanine iodide (IX). A mixture of 0.83 g (0.002 mole) of VII, 2 ml (0.012 mole) of orthoformic ester, and 1 ml of acetic anhydride was left in a dark place at room temperature for two weeks. The dye, precipitated and washed with ether, was dissolved in a small amount of chloroform and, after the elimination of the solvent, washed with methanol; mp 255–257° C (decomp.). Yield 0.73 g (52%). Found, %: I 20.19, 20.26; S 10.14, 10.26. Calculated for $C_{31}H_{37}IN_2S_2$, %: I 20.18; S 10.20.

(4a,10,11aH-benzo[b]cyclohexano[f]-1,4-thiazepine-5)-(3-ethylbenzothiazole-2)trimethinecyanine chloride (X). A mixture of 1.96 g (0.007 mole) of Ia, 1.6 g (0.013 mole) of 3-ethyl-2-formylmethylenebenzothiazoline, and 15 ml of acetic anhydride was heated in the water bath for 1 hr. The dye was precipitated and washed with ether. mp 215–216° C (decomp., from ethanol). Yield 1.46 g (44%). Found, %: Cl 7.59, 7.61; S 13.88, 14.06. Calculated for $C_{25}H_{26}N_2S_2 \cdot HCl$, %: Cl 7.79; S 14.09. The base of the carbocyanine was obtained by passing gaseous ammonia into a saturated hot ethanolic solution of 0.88 g (0.0002 mole) of X until the reaction was alkaline. The dye base separated on cooling. Red needles, mp 198–199° C (decomp.). Yield 0.75 g (95%). λ_{max}: in methanol 465 nm, in benzene 453 nm. Found, %: S 15.15, 15.39. Calculated for $C_{25}H_{26}N_2S_2$, %: S 15.32.

(10-Methyl-4a,11a-dihydrobenzo[b]cyclohexano[f]-1,4-thiazepine-5)-(3-methylbenzothiazole-2)trimethinecyanine iodide (XI) was obtained from 0.3 g (0.0001 mole) of VII and 0.19 g (0.001 mole) of 3-methyl-2-formylmethylenebenzothiazoline in 4 ml of acetic anhydride under the same conditions as for carbocyanine IX. Mp 224–226° C (decomp.). Yield 0.22 g (50%). Found, %: S 11.82, 11.93. Calculated for $C_{25}H_{27}IN_2S_2$, %: S 11.73.

(4a,10,11aH-Benzo[b]cyclohexano[f]-1,4-thiazepine-5)-(3-methylbenzothiazole-2)monomethinecyanine perchlorate (XII). A mixture of 0.35 g (0.001 mole) of Ia, 0.4 g (0.001 mole) of 3-methyl-2-methylthiobenzothiazolium mesosulfate, 0.1 g anhydrous sodium acetate, and 7 ml of absolute ethanol was heated in the water bath for 2 hr. A solution of the dye in chloroform was chromatographed on alumina and the solvent was evaporated off. The base, obtained in the form of a reddish oil, was converted into the perchlorate. The dye was sparingly soluble in ethanol and was purified by being boiled with ethanol. Dark yellow powder, mp 268–269° C (decomp.). Yield 0.05 g (8%). Found, %: S 13.20, 13.26. Calculated for $C_{22}H_{22}N_2S_2 \cdot HClO_4$, %: S 13.39.

11-(p-Dimethylaminostyryl)-4a,10,11aH-benzo[b]cyclohexano[f]-1,4-thiazepinium chloride (XIII). A mixture of 5.07 g (0.02 mole) of Ia and 2.84 g (0.02 mole) of dimethylaminobenzaldehyde in 50 ml of ethanol was left overnight. Blue-green needles with a metallic luster separated out, mp 148.5–149.5° C (decomp., from ethanol). Yield 7.5 g (64%). Found, %: S 7.80, 7.86. Calculated for $C_{23}H_{26}N_2S \cdot HCl$, %: S 8.04. The perchlorate of the styryl XIII formed blue-violet needles, mp 195.5–196.5° C (decomp., from ethanol). Found, %: S 6.95, 7.00. Calculated for $C_{23}H_{26}N_2S \cdot HClO_4$, %: S 6.98. The base of the dye XIII was obtained in a similar manner to the base of X from 0.2 g (0.001 mole) of XIII and was washed on the filter with hot ethanol saturated with ammonia. Yellow crystalline product, mp 193.5–194° C (decomp.). Yield 0.15 (83%). λ_{max}, nm: in methanol 400, in benzene 393. Found, %: S 8.72, 8.84. Calculated for $C_{23}H_{26}N_2S$, %: S 8.85.

11-(p-Dimethylaminostyryl)-10-methyl-4a,11a-dihydrobenzo[b] cyclohexano[f]-1,4-thiazepinium iodide (XIV). Ethanolic solutions of 0.43 g (0.001 mole) of VII and of 0.17 g (0.001 mole) of p-dimethylaminobenzaldehyde saturated in the cold were mixed and left in a dark place at room temperature for several days. The red-violet prisms that had deposited were recrystallized from ethanol, mp 182–183° C (decomp.). Yield 0.18 (28%). Found, %: S 6.46, 6.59. Calculated for $C_{24}H_{29}IN_2S$, %: S 6.37.

11-(p-Hydroxystyryl)-4a,10,11aH-benzo[b]cyclohexano[f]-1,4-thiazepinium chloride (XV). A mixture of 0.81 g (0.003 mole) of Ia and 0.36 g (0.003 mole) of p-hydroxybenzaldehyde was heated in the boiling water bath in 5 ml of ethanol for 30 min. Orange crystals, mp 200.5–201.5° C (decomp., from ethanol). Yield 0.78 g (70%). Found, %: Cl 9.72, 9.85; S 8.87, 8.92. Calculated for $C_{21}H_{21}NOS \cdot HCl$, %: Cl 9.54, S 8.62.

Bis(6-phenyl-6,6a,11H-benzo[b]cyclohexano[e]-1,4-thiazepine-10)-monomethinecyanine chloride (XVI). A mixture of 0.36 g (0.002 mole) of the hydrochloride of III and 5 ml (0.032 mole) of orthoformic ester was heated in the water bath for 10 min. This time was insufficient for the reaction to take place quantitatively, but longer heating of the reaction mixture leads to the decomposition of the dye formed. The unchanged hydrochloride was filtered off, washed with benzene (the carbocyanine is readily soluble in benzene), and again heated with orthoformic ester. The operation of washing and preparing the dye was repeated several times. The dye was precipitated from the filtrate and washed with ether, dissolved in chloroform, and chromatographed on alumina, after which the chloroform solution was saturated with dry hydrogen chloride. Dark green crystals from methanol, mp 132–133.5° C. Yield 0.1 g (29%). Found, %: Cl 5.20, 5.36; S 10.07, 10.14. Calculated for $C_{39}H_{36}N_2S_2 \cdot HCl$, %: Cl 5.60; S 10.13.

(6-Phenyl-6,6a,11H-benzo[b]cyclohexano[e]-1,4-thiazepine-10)-(3-methylbenzothiazole-2)dimethinecyanine chloride (XVII). We heated 0.42 g (0.001 M) hydrochloride III and 0.24 g (0.001 M) 3-methyl-2-formylmethylenebenzthiazoline in a water bath for 1 hr in 5 ml acetic anhydride. The dye was precipitated with ether: mp 207–208° C (from dimethylformamide). Yield 0.23 g (35%). Found, %: 5.77, 5.80; S 12.43, 12.53%. Calculated for $C_{29}H_{26}N_2S_2$ HCl, %: N 5.57; S 12.75%.

(6-Phenyl-11-methyl-6, 6a-dihydrobenzo[b]cyclohexano[e]-1, 4-thiazepine-10)-(3-methylbenzthiazole-2)dimethynecyanineperchlorate (XVIII). We heated 0.47 g (0.001 m) IVa and 0.27 g (0.001 M) 3-methyl-2-formylmethylenebenzthiazoline in a water bath for 30 min in 2 ml acetic anhydride. When the reaction mixture was allowed to stand, the dye crystallized out, and it was dissolved in a small amount of chloroform. After the elimination of the solvent, it formed dark red crystals with mp 249–250° C (decomp., from ethanol). Yield 0.4 g (60%). Found, %: S 11.28, 11.32. Calculated for $C_{30}H_{29}ClN_2O_4S_2$, %: S 11.06.

10-(p-Dimethylaminobenzylidene)-6-phenyl-6,6a,11H-benzo[b] cyclohexano[e]-1,4-thiazepinium perchlorate (XIX). A mixture of 0.87 g (0.008 mole) of IIIa and 0.33 (0.002 mole) of p-dimethylaminobenzaldehyde in 5 ml of acetic anhydride was heated in the water bath for 20 min. Blue-black needles, mp 200.5–201.5° C (decomp., from ethanol). Yield 0.76 6 (60%). Found, %: S 6.49, 6.53. Calculated for $C_{28}H_{28}N_2S \cdot HClO_4$, %: S 6.75. The base of the dye XIX was obtained from 0.03 g (0.0001 mole) of XIX in a similar manner to the base of X. Yellow needles, mp 197–199° C (decomp., from ethanol). Yield 0.02 g (83%). λ_{max}, nm: in methanol 381, in chloroform 379.

10-6-Dimethylaminobenzylidene)-11-methyl-6-phenyl-6,6a-dihydrobenzo[b]-cyclohexano[e]-1,4-thiazepinium perchlorate (XX). A mixture of 0.51 g (0.001 mole) of IVa and 0.18 g (0.001 mole) of p-dimethylaminobenzaldehyde in 5 ml of acetic anhydride was heated in the water bath for 1 hr. The dye was precipitated and washed with ether and was dissolved in a small amount of chloroform (the perchlorate of IVa is sparingly soluble in chloroform), and then the solvent was eliminated and the product was crystallized from methanol. Dark red crystals with a metallic luster, mp 192–194° C (decomp.). Yield 0.45 g (65%). Found, %: Cl 6.34, 6.35. Calculated for $C_{29}H_{31}ClN_2O_4S$, %: Cl 6.58. The diperchlorate was obtained by the crystallization of 0.71 g (0.001 mole) of XX from a mixture of acetone, methanol, and perchloric acid in a ratio of 1 : 1 : 1. Yellow powder, mp 204–205° C (decomp.). Yield 0.67 (80%). Found, %: Cl 11.11, 11.26; S 5.21, 5.22. Calculated for $C_{29}H_{31}ClN_2O_4S \cdot HClO_4$, %: Cl 11.09: S 5.01.

6-Methyl-10-(p-dimethylaminobenzylidene)benzo[b]cyclohexano[e]-1,4-thiazepinium perchlorate (XXI). A mixture of 1.9 g (0.006 mole) of IIa, 0.85 (0.006 mole) p-dimethylaminobenzaldehyde, and 0.5 ml of acetic anhydride in 10 ml of ethanol was heated in the water bath for 30 min. Green crystals with a metallic luster, mp 163–164° C (decomp., from ethanol). Yield 0.93 g (35%). Found, %: Cl 7.57, 7.64. Calculated for $C_{23}H_{26}N_2S \cdot HClO_4$, %: Cl 7.66. The base of XXI was obtained from 0.31 g (0.007 mole) of XXI in a similar manner to the base of X. To initiate crystallization, a few drops of aqueous ammonia was added to an ethanolic solution of the base of the dye saturated with gaseous ammonia. MP 134.5–135.5° C (from ethanol). Yield 0.14 g (58%). λ_{max}, nm: in methanol 375, in benzene 369. Found, %: S 8.99, 9.09. Calculated for $C_{28}H_{26}N_2S$, %: S 8.85.

10-(p-Hydroxybenzylidene)-6-methyl-6,6a,11H-benzo[b]cyclohexano[e]-1,4-thiazepinium perchlorate (XXII). A mixture of 2.09 g (0.006 mole) of IIa and 0.08 g (0.006 mole) of p-hydroxybenzaldehyde in 10 ml of ethanol was heated in the boiling water bath for 1 hr. The dye was precipitated and washed with ether. Orange needles, mp 214–215.5° C (decomp., from ethanol). Yield 0.38 g (14%). Found, %: S 7.88, 8.05. Calculated for $C_{21}H_{21}NOS \cdot HClO_4$, %: S 8.13.

The IR spectra were recorded on IK-10 double-beam spectrophotometers in the 400–3600 cm^{-1} region with KBr, NaCl, and LiF prisms. The substances were compressed into tablets with KBr. The electronic spectra were recorded on an SF-10 spectrophotometer. The densities of the dye solutions varied considerably with the time, and this circumstance did not permit us to determine the molecular extinctions of the dyes.

The solutions of the sparingly benzene-soluble dyes were prepared by a published procedure [6].

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