Synthesis and spectroscopic properties of cross-conjugated ketones and *meso*-substituted tridecamethine salts containing the pyran or pyridone fragment

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The reactions of substituted 4*H*-pyrones and *N*-methyl-2,6-dimethylpyridone with dimethylformamide acetal and aminal acetals of conjugated ω-dimethylaminoaldehydes were studied. Cross-conjugated ketones and *meso*-ethoxy(dialkylamino)tridecamethine salts containing the pyran or pyridone fragment were synthesized and their spectroscopic properties were investigated. The replacement of the bridging O atom by the NMe group precludes an interaction between chromophores in cross-conjugated ketone and the related tridecamethine salt. In addition, the insertion of a *meso*-amino substituent into the polymethine chain of the salts containing the central pyrylium fragment leads to a sharp weakening of the chromophore interaction. In spite of the dramatic differences in the UV spectra of ketocyanines containing the bridging O or NMe fragments, these dyes have similar ^{13}C NMR spectra.

Key words: polyenic bis-aminoketone, pyran and pyridone fragments, aminal acetals, tridecamethine salts, protonation, prototropic equilibrium, chromophore interaction.

Ketocyanine dyes, ω,ω´-bis(aminopolyenyl) ketones, belong to bichromophoric cross-conjugated polyenes containing two polymethine chains. Due to simple structures, these compounds appeared to be convenient for modeling various photophysical and photochemical processes. Recently, we have developed a procedure for the synthesis of a new type of ketocyanine dyes (Scheme 1), *viz.*, 2,6-bis(4-dimethylaminoalka-1,3-dienyl)-4*H*-pyran-4-ones **3a—d*** and related ethoxytridecamethine salts **4a—c****.[1]

Studies of the photonics of these dyes revealed that they exhibit unusual absorption features. Thus, the spectra of these compounds have a long-wavelength absorption band in the visible region along with a much more intense short-wavelength band in the near-UV region. We explained such absorption spectrum patterns based on a model of the chromophore interaction assuming an acute angle between these chromophores.[1,2] The aim of the present study was to synthesize compounds structurally similar to bis-polyenic ketones **3** for the purpose of investigating the effect of their structures on the spectral luminescence properties. Another goal of our investigation is to examine the possibility of using these compounds for the preparation of new cyanine dyes containing the pyran fragment in the polymethine chain.

It was of interest to prepare symmetrical ketones, which differ from ketones **3** by the length of polyenic chains, unsymmetrical ketones containing different chromophores at positions 2 and 6, and ketones containing only one chromophore.

We studied condensation of 2,6-dimethyl-γ-pyrone (**1**) with aminal acetal **5** [3] and dimethylformamide acetal (Scheme 2) with the aim of synthesizing bis-dimethylaminopyranones **6** and **8**. We failed to prepare polyenic ketones **6** and **8** by varying the reaction conditions (temperature, solvent, reagent ratio). The reaction with aminal acetal **5** afforded only resinous products, whereas the reaction with dimethylformamide acetal gave rise only to 2-dimethylaminoethenyl-6-methyl-4*H*-pyran-4-one (**7**) in low yield (5%).

An attempt to prepare compound **9** containing one polyenic chromophore also failed. The reaction of equimolar amounts of 2,6-dimethyl-γ-pyrone (**1**) and β-dimethylaminoacrolein aminal acetal **2a** afforded only bis-aminoketone **3a** in low yield (see Scheme 2).

* Compound **3d** was prepared in the present study.

** Compounds **4** can be represented by limit structures **A** (ethoxytridecamethine salts) and **B** (pyrylium salts).[1] For convenience of discussion, we use mesomeric structure **4B**.

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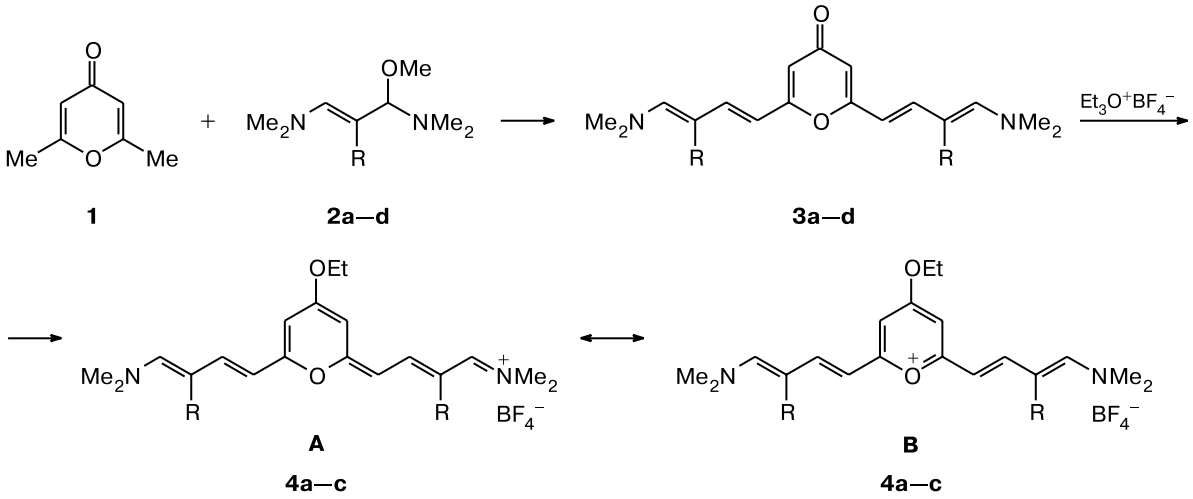
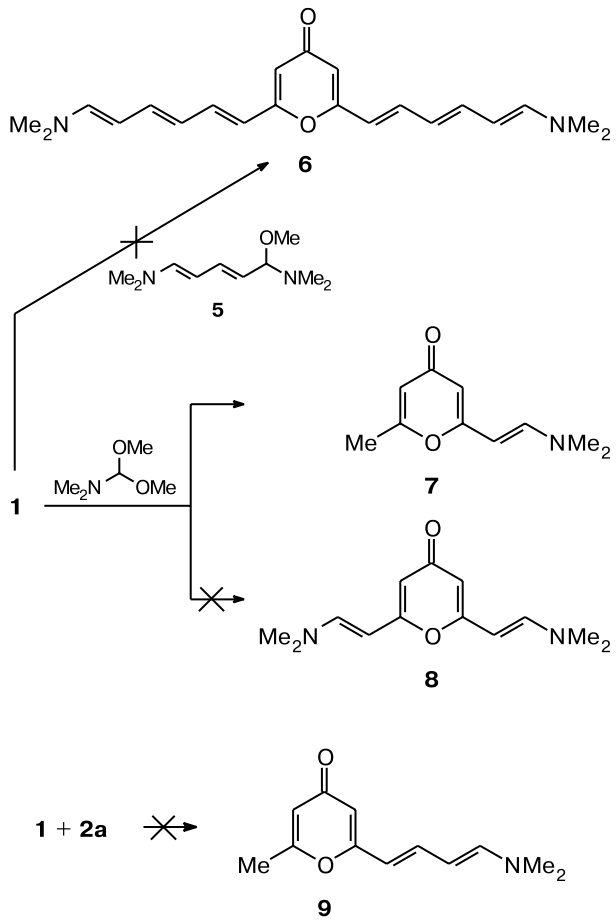
Scheme 1



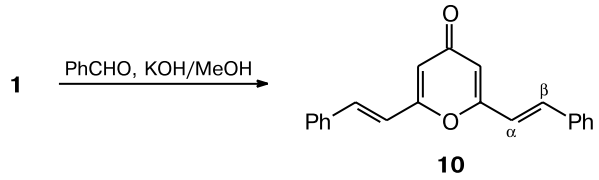
R = H (**a**), Me (**b**), Ph (**c**), OEt (**d**)

Scheme 2



We chose 6-methyl-2-styryl-4*H*-pyran-4-one as the starting compound for the synthesis of compounds containing different chromophores at positions 2 and 6, because we expected that the synthesis of this compound would present no problems. However, the use of a simple procedure proposed for the preparation of this vinyl ketone[4] gave rise to 2,6-distyryl-4*H*-pyran-4-one (**10**) (Scheme 3).

Scheme 3



The two-step synthesis of 6-methyl-2-styryl-4*H*-pyran-4-one (**13**) from dehydroacetic acid **11** [5—7] (Scheme 4) proved to be more successful.

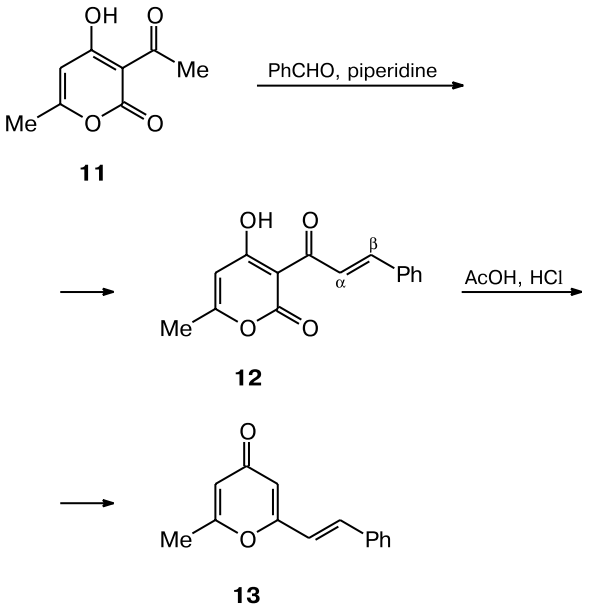
Condensation of ketone **13** with β-dimethylaminoacrolein aminal acetal **2a** under mild conditions (25 min, 70—75 °C) afforded unsymmetrical polyenic ketone **14** (Scheme 5) in good yield (63%).

It was of interest to compare the physicochemical properties of polyenic compounds containing the γ-pyrone fragment with the properties of compounds containing the pyridone fragment. For this purpose, we prepared polyenic pyridone **16** in 33% yield by condensation of *N*-methyl-2,6-dimethylpyridin-4-one[8,9] (**15**) with aminal acetal **2a** (Scheme 6).

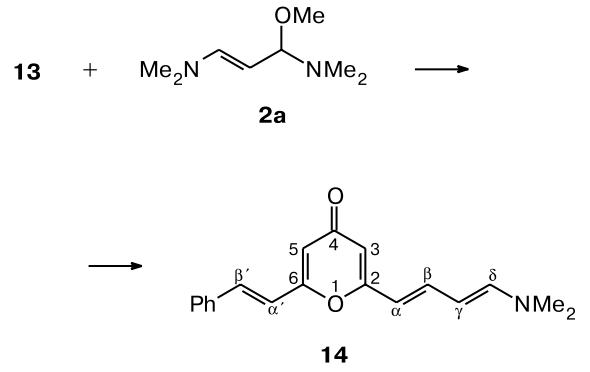
The structures of the resulting ketones were confirmed by ^{1}H and ^{13}C NMR, electronic, and mass spectra.

According to the ^{1}H NMR spectroscopic data, the methine protons in ketones **7**, **14**, and **16** have a *trans*

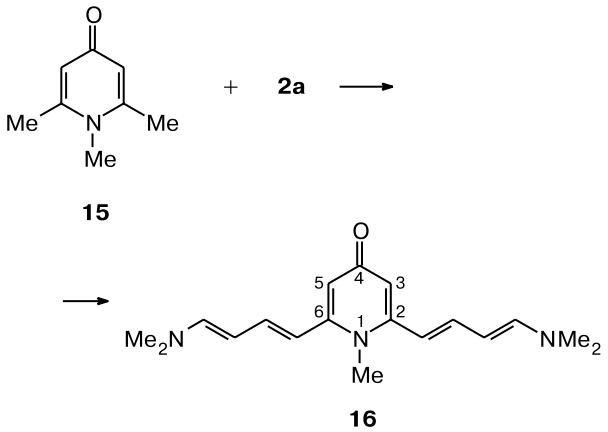
Scheme 4



Scheme 5



Scheme 6

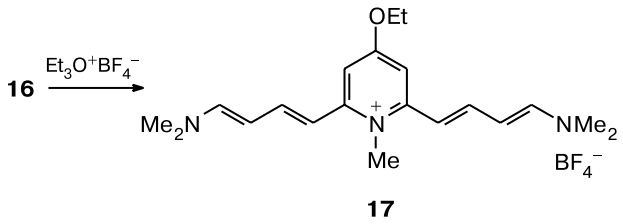


configuration and these ketones exist predominantly as the *s-trans* conformers (J = 11.1—15.1 Hz).

A comparison of the ^{1}H NMR spectra of compounds **3a** and **16** shows that the signals for the corresponding protons are located virtually in the same regions. In going from pyrone **3a** to pyridone **16**, a substantial change is observed only for the signals of the H(3) and H(5) protons. The spectrum of compound **3a** has a signal for the H(3) and H(5) protons at δ 5.87, whereas the corresponding signal in the spectrum of compound **16** is observed at δ 6.52. The ^{13}C NMR spectrum of ketone **3a** is also very similar to that of ketone **16**. The only essential difference is that the signals for the C(2) and C(3) atoms in the spectrum of pyridone **16** are shifted upfield (δ 151.9) compared to those in the spectrum of pyrone **3a** (δ 167.0).

Alkylation of ketone **16** with triethyloxonium tetrafluoroborate under mild conditions (0 °C, 1 h) afforded salt **17** (Scheme 7). According to the ^{1}H NMR spectroscopic data, salt **17** contained up to 10% of unidentified impurities. Attempts to purify product **17** were unsuccessful.

Scheme 7

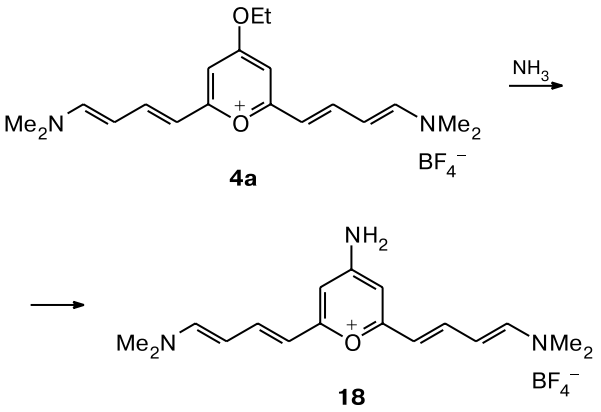


According to the data published in the literature, pyrylium and alkoxypyrylium salts are readily subjected to recyclization in reactions with ammonia and primary amines to form pyridine derivatives. Recyclization of alkoxypyrylium salts is accompanied by the replacement of the alkoxy group by the amino group.[10—12] In this connection, it was of interest to examine the possibility of preparing polyenic pyridinium salts from alkoxypolymethine salts **4** and to study the influence of long aminopolyenic substituents at positions 2 and 6 on the properties of pyrylium salts.

We investigated the behavior of alkoxypolymethine salt **4a** in the reactions with ammonia and primary amines (methylamine and benzylamine). It appeared that neither the reaction of salt **4a** with ammonia nor the reactions with primary amines led to recyclization giving rise to a new heterocyclic system. For example, the reaction of salt **4a** with aqueous ammonia produced aminopyrylium salt **18** in good yield (72%) (Scheme 8).

The reactions of salt **4a** with methylamine and benzylamine afforded complex mixtures of products. In these reactions, individual compounds were not isolated. How-

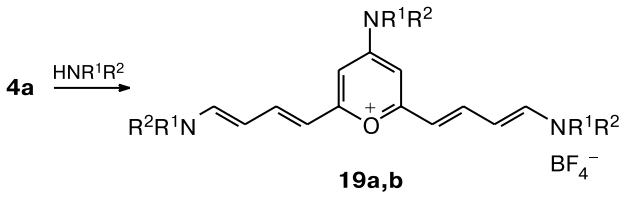
Scheme 8



ever, it can be said with assurance that recyclization giving rise to *N*-substituted pyridinium salts did not occur, because the ^{1}H NMR spectra of the mixtures prepared by both reactions have no signals at δ 3.90—4.15 characteristic of *N*-substituted pyridinium salts.[13,14] Therefore, salt **4a** reacted with primary amines with retention of the pyrylium ring. This can be associated with the lower electrophilicity of salt **4a** with respect to nitrogen-containing nucleophiles compared to structurally simple pyrylium salts. Presumably, a decrease in the electrophilicity of salt **4a** is favored by a higher degree of delocalization of the positive charge of the mesomeric cation compared to that observed in pyrylium salts devoid of long aminopolyenic substituents.

The retention of the pyrylium structure is typical of the reactions of structurally simple 2- and 4-alkoxypyrylium salts with secondary amines.[10,15] The reactions of salt **4a** with dimethylamine and piperidine afforded aminopyrylium salts **19a,b** (Scheme 9). In the reaction of salt **4a** with piperidine, the replacement of the alkoxy group by the amino group was accompanied by transamination of the terminal amino groups. Complete transamination of the NMe_2 groups to form salt **19b** was achieved only with the use of a tenfold molar excess of piperidine and the reaction time of 3 days.

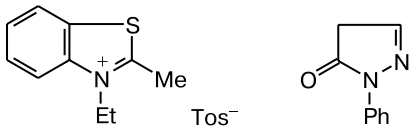
Scheme 9



$R^1 = R^2 = Me$ (**a**), $R^1 + R^2 = (CH_2)_5$ (**b**)

It should be noted that the replacement of the ethoxy group by the amino group is not typical of alkoxypolymethine salts derived from bis-dimethylaminopolyenic ketones, which we have studied earlier.[16,17]

We attempted to prepare cyanine dyes containing the γ-pyrone fragment based on salt **4a**. However, in spite of the use of different conditions of condensation, pyrylium salt **4a** did not react with *N*-ethylbenzooxazolium tosylate (**20**) and 5-methyl-*N*-phenylpyrazolone (**21**).



20 **21**

The photophysical study of the newly synthesized bichromophoric compounds revealed a series of interesting features, whose investigation will serve to the further development of the theory of chromophore interactions. As mentioned above, the S—S absorption spectra of dyes **3a—d** consist of two bands, *viz.*, an intense short-wavelength band and a much less intense long-wavelength band. The positions of these bands, their intensity ratio, and the energy splitting (Δν) between the S_1 and S_2 levels were explained based on this theory. The chromophores composing the dye (halves of dye **3a** from the NMe_2 fragment to the carbonyl group) are oriented at an acute angle with respect to each other.[1,2] We found that the replacement of the O atom in the pyran ring of ketocyanine **3a** by the NMe group (dye **16**) led to a radical change in the absorption spectrum of the dye (Fig. 1). Unlike compound **3a**, the absorption spectrum of ketocyanine **16** has only one band (λ_{max} = 395 nm) located between two

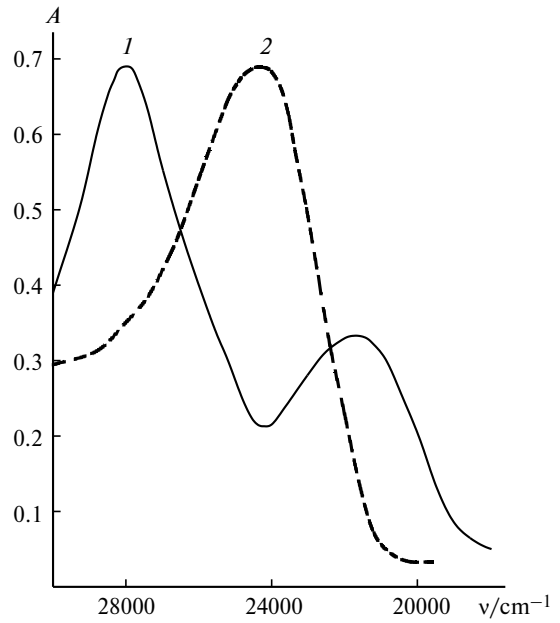


Fig. 1. Absorption spectra of compounds **3a** (*1*) and **16** (*2*) in Pr^iOH.

absorption bands of dye **3a**, *i.e.*, the chromophore interaction is not manifested (the fluorescence excitation spectrum of ketone **16** also consists of one band, like the absorption spectrum). Therefore, the presence of the NMe group in the pyridone fragment, apparently, precludes the chromophore interaction in compound **16**. Since the absorption band of dye **16** is bathochromically shifted on going from toluene to chloroform and Pr^{i}OH (λ_{max} = 385, 389, and 395 nm, respectively), it is, apparently, a charge-transfer band. The carbonyl group acts as an electron acceptor and the amino groups serve as electron donors (the long-wavelength absorption band of ketocyanine **3a** [1] is analogous in character). The addition of trace amounts of acid ($C_{HCl} \approx 10^{-6}$ mol L^{-1}) to a solution of dye **16** led to a sharp change in its absorption spectrum. Thus, the intensity of the initial band (λ_{max} = 395 nm in Pr^{i}OH) decreased and a new band at λ_{max} = 468 nm with a shoulder at λ_{max} = 390 nm appeared. Apparently, the latter band corresponds to the protonated form (PF) of dye **16** (PF-**16**). An isosbestic point, which was observed in the absorption spectra in the course of titration of ketocyanine **16** with acid, indicates that there is a simple equilibrium between the starting and protonated forms (Fig. 2). The addition of small amounts of diethylamine restored the initial spectral pattern, which is evidence for the reversibility of the prototropic equilibrium Dye + H^+ $\rightleftharpoons$ DyeH^+(Fig. 3).

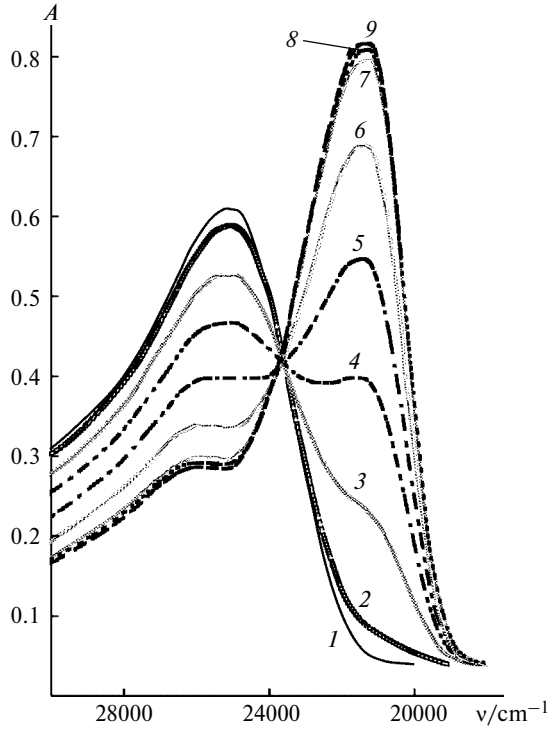


Fig. 2. Changes in the absorption spectrum of ketocyanine **16** in the course of titration with hydrochloric acid in Pr^{i}OH: C_{HCl} = 0 (*1*), $3.84 \cdot 10^{-6}$ (*2*), $7.70 \cdot 10^{-6}$ (*3*), $1.15 \cdot 10^{-5}$ (*4*), $1.54 \cdot 10^{-5}$ (*5*), $1.92 \cdot 10^{-5}$ (*6*), $2.31 \cdot 10^{-5}$ (*7*), $2.69 \cdot 10^{-5}$ (*8*), $4.69 \cdot 10^{-5}$ mol L^{-1} (*9*).

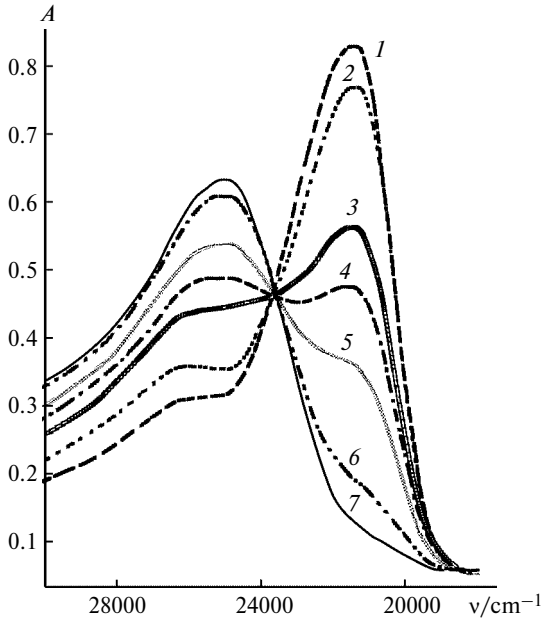


Fig. 3. Changes in the absorption spectrum of PF-**16** in the course of titration with diethylamine (DEA) in Pr^{i}OH (C_{HCl} = $2.3 \cdot 10^{-5}$ mol L^{-1}): C_{DEA} = 0 (*1*), $2.23 \cdot 10^{-5}$ (*2*), $3.01 \cdot 10^{-5}$ (*3*), $3.74 \cdot 10^{-5}$ (*4*), $4.47 \cdot 10^{-5}$ (*5*), $5.24 \cdot 10^{-5}$ (*6*), $6.70 \cdot 10^{-5}$ mol L^{-1} (*7*).

The absorption spectrum of PF-**16** is similar to that of polymethine salt **17** (Fig. 4). A slight bathochromic shift in the spectrum of salt **17** compared to the spectrum of PF-**16** is, apparently, associated with the electron-releasing effect of the Et group at the O atom. This indicates

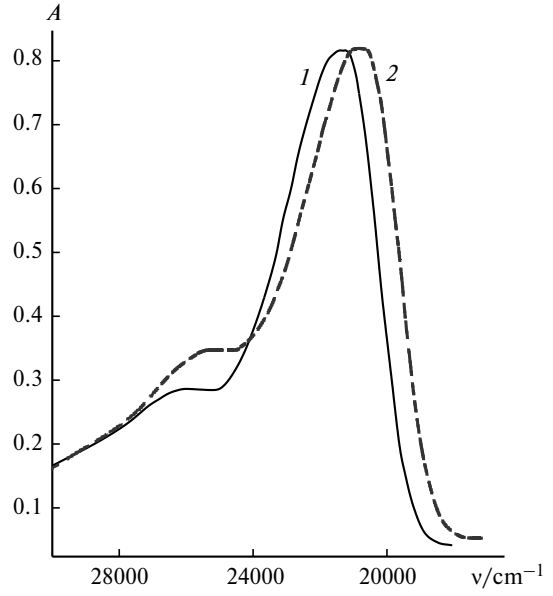


Fig. 4. Absorption spectra of salts PF-**16** (*1*) and **17** (*2*) in Pr^{i}OH.

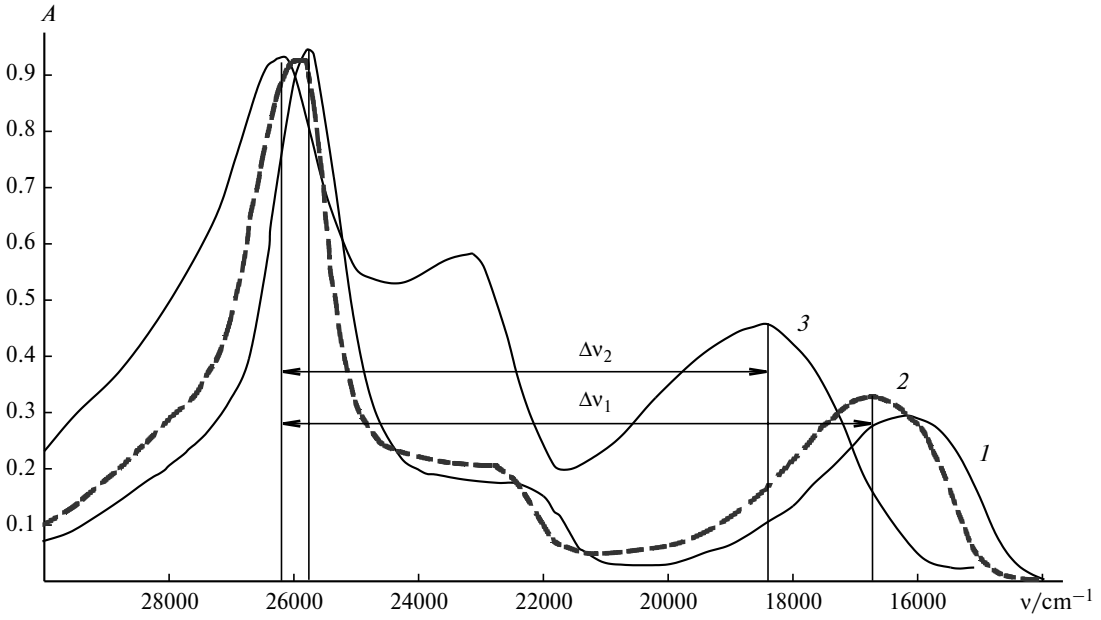
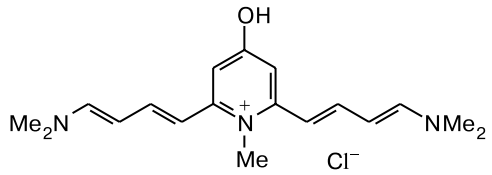


Fig. 5. Absorption spectra of salts **4a** (*1*), PF-**3a** (*2*), and **19a** (*3*) in Pr^{i}OH (for $\Delta\nu_1$ and $\Delta\nu_2$, see comments in the text).

that ketocyanine **16** is protonated at the carbonyl group of the dye to form the corresponding polymethine salt (protonation of simple pyrones proceeds analogously[18]).



PF-**16**

Alkylation of ketocyanines **3a—c** proceeded in a similar way to produce polymethine salts **4a—c** (see above).

The absorption spectra of PF-**16** and salt **17** differ sharply from the spectrum of analogous polymethine salt **4a** containing the central pyrylium fragment, which has been described earlier.[1,2] Two bands in the spectrum of salt **4a** were attributed to the interaction between the chromophores (halves of the molecule) oriented at an acute angle. The absorption bands of PF-**16** and salt **17** are substantially shifted toward the short-wavelength region with respect to the long-wavelength band of salt **4a**. Besides, the second (more intense) short-wavelength band observed in the spectrum of salt **4a** is weakly manifested in the spectra of PF-**16** and salt **17** (Fig. 5). The latter spectra have only a short-wavelength shoulder at λ_{max} = 380 nm and an intense band at 480 nm. Since the shift of the bands (spectrum-line splitting $\Delta\nu$) caused by the chromophore interaction depends on the energy of this interaction, it can be concluded that this interaction in PF-**16** and salt **17** is much weaker than that in salt **4a**, *i.e.*, the chromophore interaction is sharply weakened by the central NMe group, like in the case of ketocyanine **16**.

The addition of larger amounts of acid to ketocyanine **16** led to a decrease in the intensity and a small hypsochromic shift of the absorption band (the short-wavelength shoulder disappeared). In this case, the spectral changes were irreversible (Fig. 6). An analogous situation was ob-

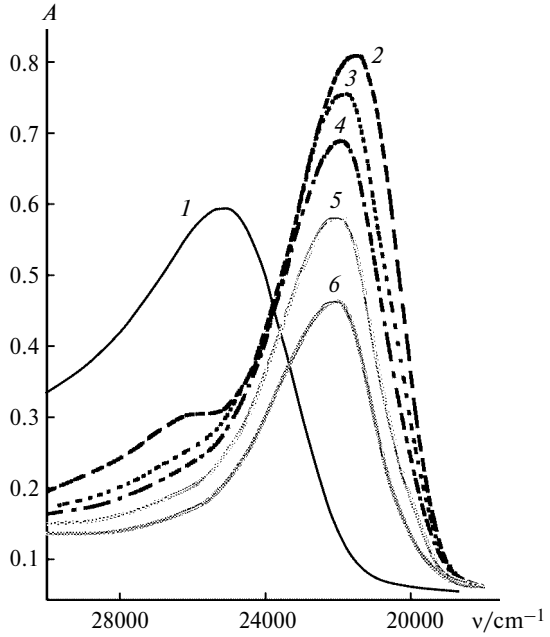
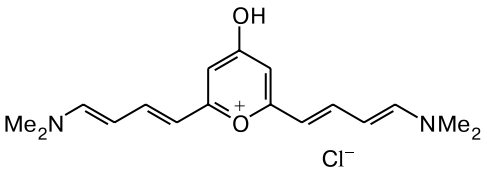


Fig. 6. Absorption spectra of ketocyanine **16** in Pr^{i}OH upon the addition of acid in high concentrations: C_{HCl} = 0 (*1*), $2.30\cdot10^{-4}$ (*2*), $4.30\cdot10^{-3}$ (*3*), $6.20\cdot10^{-3}$ (*4*), $1.06\cdot10^{-2}$ (*5*), $1.70\cdot10^{-2}$ mol L^{-1} (*6*).

served upon the addition of acid to salt **17**. Apparently, this is associated with further protonation of these compounds accompanied by secondary irreversible reactions.

In spite of the fact that the absorption spectrum of ketocyanine **3a** differs substantially from that of **16** (see Fig. 1), their ^{13}C NMR spectra are similar (see the Experimental section). The absorption spectra of bichromophoric ketocyanines are determined by the chromophore interaction (which influences the positions of the S_1 and S_2 levels), whereas the ^{13}C NMR spectra reflect the electron density distribution within the polymethine chains of both chromophores. Therefore, one would hardly expect that a change in this interaction upon the replacement of the bridging O atom outside the chromophores by the NMe group would radically change the electron density distribution on the C atoms of the polymethine chains inside the chromophores, because the chromophore interaction *via* conjugation through the carbonyl group is much weaker than the π-electron conjugation within each chromophore. This is reflected in similar values of the chemical shifts in the ^{13}C NMR spectra of dyes **3a** and **16**.

It was of interest to compare the absorption spectra of salt **4a**, the salt prepared by protonation of ketocyanine **3a** (PF-**3a**), and newly synthesized salt **19a** (see Fig. 5).



PF-**3a**

The spectrum of salt **4a** is similar to that of PF-**3a** (a small bathochromic shift of the bands in the spectrum of **4a** is, apparently, attributed to the electron-releasing effect of the central Et group), whereas the spectrum of salt **19a** much more substantially differs from the spectra of **4a** and PF-**3a**. First, the line splitting $\Delta\nu_2$ in the spectrum of salt **19a** is much smaller than that observed in the spectra of **4a** ($\Delta\nu_1$) and PF-**3a**, which is indicative of weakening of the chromophore interaction in **19a**. Apparently, this is a consequence of the perturbing electronic effect of the *meso*-amino group on the polymethine chromophore of the salt. An analogous phenomenon was also observed for *meso*-amino-substituted thiacarbocyanines. Thus, the insertion of the *meso*-amino group leads to broadening and a hypsochromic shift in the absorption spectrum of the dye.[19] An analogous perturbing effect of the amino group resposible for a sharp weakening of the chromophore interaction, was also observed in salts **17** and PF-**16**. The elimination of the chromophore interaction in ketocyanine **16** is, apparently, explained analogously.

The absorption spectra of polymethine salts **4a**, **19a**, and PF-**3a** have bands at ~380 and 500—600 nm along with an additional band at ~430 nm, which is observed as a small plateau in the spectra of salts **4a** and PF-**3a** and is much more pronounced in the spectrum of salt **19a**. This band is, apparently, attributed to excitation localized on the central pyrylium fragment, because the long-wavelength absorption band of the triphenylpyrylium cation is located in this region. The presence of the amino group in salt **19a** increases the intensity of this band.

The absorption spectra of ketones **7** and **14** containing the terminal amino group are characterized by a long-wavelength charge-transfer band, which is shifted bathochromically in alcohols compared to that in toluene. Titration of these compounds with hydrochloric acid afforded protonated forms, which are characterized by absorption in the longer-wavelength region compared to the spectrum of the starting compound. The absorption spectra show isosbestic points. The initial absorption spectrum was restored upon the addition of diethylamine to the reaction solution, which indicates that protonation is reversible.

Experimental

The ^1H NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (300.13 MHz) instruments with respect to Me_4Si. The ^{13}C NMR spectra were measured on a Bruker AC-200 spectrometer (50.32 MHz). The mass spectra (EI, 70 eV, direct inlet of the sample) were obtained on an MS-30 instrument. The absorption spectra of the dyes were measured on a Specord UV—VIS spectrophotometer. The fluorescence and fluorescence excitation spectra of the dyes were studied on an Aminco—Bowman spectrofluorometer equipped with an R136 photomultiplier.

2,6-Bis(4-dimethylamino-3-ethoxybuta-1,3-dienyl)-4*H*-pyran-4-one (3d) was prepared from 2,6-dimethyl-γ-pyrone (**1**) and β-dimethylamino-α-ethoxyacrolein aminal acetal **2d** [20] in 38% yield analogously to ketones **3a—c** [1], m.p. 163—165 °C. UV (EtOH), λ_{max}/nm (ε): 370 (44900), 480 (20500). ^1H NMR (CD_3OD), δ: 1.32 (t, 6 H, Me, J = 7.5 Hz); 3.07 (s, 12 H, NMe_2); 3.76 (q, 4 H, CH_2, J = 7.5 Hz); 5.77 (d, 2 H, α-H, J = 14.5 Hz); 5.88 (s, 2 H, CH); 6.19 (s, 2 H, δ-H); 6.90 (d, 2 H, β-H, J = 14.5 Hz). MS, m/z (I_{rel} (%)): 374 $[M]^+$ (7), 329 $[M - OEt]^+$ (43), 300 $[M - OH - NMe_2]^+$ (96), 284 $[M - 2\ OEt]^+$ (85), 272 $[M - OEt - Me_2NCH_2]^+$ (8), 255 $[M - OH - Me_2NCH_2 - Me_2NH]^+$ (46), 243 $[M - OH - 2\ Me_2NCH_2]^+$ (21), 228 $[M - OEt - Me_2NCH_2 - Me_2N]^+$ (100), 200 $[M - OEt - Me_2NCH_2 - CO]^+$ (16).

(13-Dimethylamino-5,9-epoxy-7-ethoxytrideca-2,4,6,8,10,12-hexaenylidene)dimethylammonium tetrafluoroborate (4a). The synthesis of compound **4a** has been described in our earlier study.[1] ^{13}C NMR (DMSO-d_6), δ: 14.0 ($OCH_2\underline{Me}$); 65.5 ($O\underline{C}H_2Me$); 96.6 (γ-C); 99.7 (C(3), C(5)); 104.1 (α-C); 146.3 (β-C); 156.3 (δ-C); 167.0 (C(2), C(6)); 169.4 (C(4)). The signals of the dimethylamino groups overlap with the residual signal of DMSO-d_6.

2-Dimethylaminoethenyl-6-methyl-4*H*-pyran-4-one (7). A mixture of 2,6-dimethyl-γ-pyrone (**1**) (0.2 g, 1.6 mmol) and dimethylformamide acetal (0.58 g, 4.8 mmol) was heated at

110—120 °C for 2 h. Then the reaction mixture was cooled, anhydrous diethyl ether was added, and the precipitate that formed was separated. After recrystallization from anhydrous ether, compound **7** was obtained in a yield of 15 mg (5%) as pale-yellow crystals, m.p. 106—108 °C. UV (EtOH), λ_{max}/nm (ε): 364 (38600). ^{1}H NMR ($CDCl_3$), δ: 2.20 (s, 3 H, Me); 2.90 (s, 6 H, NMe_2); 4.72 (d, 1 H, α-H, J = 12.5 Hz); 5.76 and 5.91 (both s, 1 H each, CH); 7.10 (d, 1 H, β-H, J = 12.5 Hz). MS, m/z (I_{rel} (%)): 179 $[M]^+$ (100), 164 $[M - Me]^+$ (3), 151 $[M - CO]^+$ (10), 136 $[M - Me - CO]^+$ (13), 121 $[M - CH_2NMe_2]^+$ (5), 109 $[M - C_2H_2NMe_2]^+$ (24), 95 [γ-pyrone − H]$^+$ (81).

2,6-Distyryl-4*H*-pyran-4-one (10). Ketone **10** was prepared in 14% yield from compound **13** using the procedure described earlier.[4] The physicochemical data are identical with those published in the literature.[6] ^{1}H NMR (CD_3OD), δ: 6.41 (s, 1 H, CH); 7.02 (d, 2 H, α-H, J = 12.0 Hz); 7.30—7.48 and 7.62—7.76 (both m, 12 H, 2 Ph + 2 β-H).

3-Cinnamoyl-4-hydroxy-6-methyl-2*H*-pyran-2-one (12) was prepared according to a procedure described earlier.[5] ^{1}H NMR ($CDCl_3$), δ: 2.68 (s, 3 H, Me); 5.98 (s, 1 H, CH); 7.45 (br.s, 3 H, Ph); 7.70 (t, 2 H, Ph, J = 2.0 Hz); 7.91 (d, 1 H, α-H, J = 14.5 Hz); 8.42 (d, 1 H, β-H, J = 14.5 Hz); 17.86 (s, 1 H, OH).

6-Methyl-2-styryl-4*H*-pyran-4-one (13) was prepared according to known procedures.[6,7] ^{1}H NMR ($CDCl_3$), δ: 2.36 (s, 3 H, Me); 6.11 and 6.21 (both s, 1 H each, CH); 6.68 (d, 1 H, α-H, J = 17.5 Hz); 7.30—7.42 (m, 4 H, Ph, β-H); 7.59—7.47 (m, 2 H, Ph).

2-(4-Dimethylaminobuta-1,3-dienyl)-6-styryl-4*H*-pyran-4-one (14). A mixture of 6-methyl-2-styryl-4*H*-pyran-4-one (**13**) (150 mg, 0.71 mmol) and β-dimethylaminoacrolein aminal acetal **2a** (110 mg, 0.71 mmol) was heated at 70—75 °C for 25 min. After cooling to 20 °C, anhydrous diethyl ether was added to a glassy mixture, the mixture was triturated, and the precipitate that formed was separated. Compound **14** was prepared in a yield of 130 mg (63%) as dirty-orange crystals, m.p. 138—142 °C (decomp.). UV (EtOH), λ_{max}/nm (ε): 328 (42500), 455 (23800). ^{1}H NMR ($CDCl_3$), δ: 2.91 (s, 6 H, NMe_2); 5.19 (t, 1 H, γ-H, J = 11.2 Hz); 5.77 (d, 1 H, α-H, J = 15.1 Hz); 5.97 and 6.16 (both d, 1 H each, CH, J = 2.0 Hz); 6.66—6.72 (m, 2 H, α′-H, δ-H); 7.13 (dd, 1 H, β-H, J = 15.1 Hz, J = 11.2 Hz); 7.30—7.60 (m, 6 H, Ph, β′-H). ^{13}C NMR ($CDCl_3$), δ: 40.5 (NMe_2); 97.4 (γ-C); 108.6 (C(3)); 109.1 (α-C); 113.6 (C(5)); 120.3 (β′-C); 127.3 (*o*-C_{Ph}); 128.8 (*m*-C_{Ph}); 129.3 (*p*-C_{Ph}); 134.5 (α′-C); 135.1 (*i*-C_{Ph}); 139.0 (β-C); 149.4 (δ-C); 160.1 (C(6)); 164.1 (C(2)); 180.1 (C=O). MS, m/z (I_{rel} (%)): 293 $[M]^+$ (78), 265 $[M - CO]^+$ (22), 249 $[M - Me_2N]^+$ (68), 231 $[M - Me_2N - H_2O]^+$ (11), 221 $[M - Me_2N - CO]^+$ (11), 216 $[M - Ph]^+$ (9), 196 $[M - CO - Me_2NC_2H_2 + H]^+$ (23), 191 $[M - PhC_2H_2 + H]^+$ (27), 173 $[M - Me_2N - Ph + H]^+$ (28), 162 $[M - PhC_2H_2 - CO]^+$ (62), 155 $[M - Me_2N - CO - Ph + H]^+$ (56), 148 $[M - C_3H_5O - H_2O - Me_2NC_2H_2]^+$ (74), 141 $[M - C_3H_5O - H_2O - Ph]$ (31), 131 $[M - C_3H_5O - CO - Ph]$ (75), 121 $[M - Ph - Me_2NC_4H_3]^+$ (100), 115 $[M - Ph - Me_2NH - 2\ CO]^+$ (55), 103 $[PhC_2H_2]^+$ (57).

2,6-Di(4-dimethylaminobuta-1,3-dienyl)-1-methyl-1*H*-pyridin-4-one (16). A mixture of pyridone **15** (130 mg, 0.09 mmol) and aminal acetal **2a** (450 mg, 2.9 mmol) was heated at 105—110 °C for 1 h. After cooling to 20 °C, the reaction mixture was dissolved in anhydrous CH_2Cl_2 (12 mL) and then SiO_2 (L 40/100; 200 mg) was added. After one day, SiO_2 was filtered off and washed with CH_2Cl_2. The filtrate was concentrated. Anhydrous acetone was added to the semicrystalline residue. The precipitate that formed was filtered off and washed first with anhydrous acetone and then with anhydrous diethyl ether. Product **16** was obtained in a yield of 90 mg (33%) as red-orange crystals, m.p. 187—190 °C. UV (EtOH), λ_{max}/nm (ε): 412 (37700). ^{1}H NMR ($CDCl_3$), δ: 2.84 (s, 12 H, NMe_2); 3.51 (s, 3 H, Me); 5.13 (dd, 2 H, γ-H, J = 11.1 Hz, J = 13.1 Hz); 5.84 (d, 2 H, α-H, J = 14.4 Hz); 6.30 (d, 2 H, δ-H, J = 13.1 Hz); 6.52 (s, 2 H, CH); 6.78 (dd, 2 H, β-H, J = 14.4 Hz, J = 11.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 36.6 (NMe); 40.3 (NMe_2); 97.6 (γ-C); 110.0 (C(3), C(5)); 111.4 (α-C); 139.0 (β-C); 147.7 (δ-C); 151.9 (C(2), C(6)); 177.4 (C=O). MS, m/z (I_{rel} (%)): 299 $[M]^+$ (11), 258 $[M - MeCN]^+$ (4), 254 $[M - Me_2NH]^+$ (72), 239 $[M - Me_2NH - Me]^+$ (13), 237 $[M - Me_2NH - OH]^+$ (44), 210 $[M - Me_2NH - Me_2N]^+$ (100), 196 $[M - Me_2NH - OH - MeCN]^+$ (18), 181 $[M - 2\ Me_2NH - CO]^+$ (35), 168 $[M - 2\ Me_2NH - MeCN]^+$ (20), 166 $[M - 2\ Me_2NH - CO - Me]^+$ (16).

2,6-Di(4-dimethylaminobuta-1,3-dienyl)-4-ethoxy-1-methylpyridinium tetrafluoroborate (17). A solution of $Et_3O^+BF_4^-$ (74 mg, 0.24 mmol) in anhydrous CH_2Cl_2 (1 mL) was added dropwise with stirring to a solution of ketone **16** (50 mg, 0.17 mmol) in CH_2Cl_2 (2 mL) cooled to 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The solvent was removed *in vacuo* (without heating). The resulting viscous mixture was triturated with an anhydrous ether—anhydrous MeOH mixture (20 : 1) and the solvent was removed by decantation. The precipitate that formed was filtered off, washed with anhydrous ether, suspended in refluxing anhydrous MeOH, thoroughly triturated, and filtered off. Compound **17** was prepared in a yield of 55 mg as red crystals. According to the ^{1}H NMR spectroscopic data, the product contained up to 10% of unidentified impurities. ^{1}H NMR ($CDCl_3$), δ: 1.41 (t, 3 H, Me); 2.83 (s, 6 H, NMe_2); 3.82 (s, 3 H, NMe); 4.32 (q, 2 H, CH_2); 5.45 (t, 2 H, γ-H); 6.17 (d, 2 H, α-H); 7.00 (s, 2 H, CH); 7.03 (d, 2 H, δ-H); 7.45 (dd, 2 H, β-H). The signals at δ 3.08, 3.31, 3.23, 3.54, and 3.90 were not identified.

4-Amino-2,6-bis(4-dimethylaminobuta-1,3-dienyl)pyrylium tetrafluoroborate (18). A solution of ethoxypyrylium salt **4a** (150 mg, 0.37 mmol) in DMF (5 mL) was added to a concentrated aqueous ammonia solution (7 mL) heated to 30—35 °C. The reaction mixture was stirred at 30—35 °C for 30 min and then kept at ~20 °C for one day. The solvent was evaporated *in vacuo* and distilled water was added to the crystalline residue. The precipitate that formed was separated and intensely washed with an anhydrous ether—EtOH mixture (1 : 1). Compound **17** was obtained in a yield of 100 mg (72%) as a dark-claret precipitate, m.p. 203—205 °C (decomp.). Found (%): C, 55.41; H, 6.46. $C_{17}H_{24}BF_4N_3O$. Calculated (%): C, 54.71; H, 6.48. UV (EtOH), λ_{max}/nm: 383, 429, 543. UV (Pr^iOH), λ_{max}/nm: 380, 430, 536. Low solubility of aminopyrylium salt **18** did not allow us to determine ε. ^{1}H NMR (DMSO-d_6), δ: 2.95 (br.s, 12 H, NMe_2); 3.15 (br.s, 2 H, NH_2); 5.31 (t, 2 H, γ-H, J = 12.2 Hz); 5.78 (d, 2 H, α-H, J = 14.0 Hz); 6.28 (s, 2 H, CH); 7.23 (d, 2 H, δ-H, J = 12.2 Hz); 7.44 (dd, 2 H, β-H, J = 14.5 Hz, J = 12.2 Hz).

4-Dimethylamino-2,6-bis(4-dimethylaminobuta-1,3-dienyl)pyrylium tetrafluoroborate (19a). A 1 : 1 solution of Me_2NH in benzene (2 mL) was added to a solution of ethoxypyrylium salt **4a** (150 mg, 0.37 mmol) in a mixture of anhydrous MeOH (5 mL) and anhydrous DMF (3 mL) cooled to −5 °C. The reaction mixture was stirred at ~20 °C for 1 h. The solvent

was removed *in vacuo*, anhydrous diethyl ether was added to the residue, and the precipitate that formed was separated. Compound **19a** was obtained in a yield of 50 mg (33%) as dark crystals, m.p. 235—237 °C. UV (EtOH), λ_{max}/nm (ε): 380 (47200), 432 (31500), 544 (21700). ^{1}H NMR (DMSO-d_6), δ: 2.95 (br.s, 12 H, NMe_2); 3.16 (br.s, 6 H, NMe_2); 5.31 (t, 2 H, γ-H, J = 12.0 Hz); 5.78 (d, 2 H, α-H, J = 14.6 Hz); 6.28 (s, 2 H, CH); 7.22 (d, 2 H, δ-H, J = 12.0 Hz); 7.43 (dd, 2 H, β-H, J = 14.8 Hz, J = 12.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 94.4 (C(3)); 97.5 (γ-C); 105.5 (α-C); 143.2 (β-C); 153.4 (C(4)); 156.3 (δ-C); 163.5 (C(2)). The signals of the dimethylamino groups overlap with the residual signal of DMSO-d_6.

4-Piperidino-2,6-bis(4-piperidinobuta-1,3-dienyl)pyrylium tetrafluoroborate (19b). Freshly distilled piperidine (0.5 mL, 5.1 mmol) was added to a solution of salt **4a** (65 mg, 0.16 mmol) in dry DMF (5 mL) at ~20 °C. The reaction mixture was kept at ~20 °C for 3 days. Then the solvent was removed *in vacuo*. The residue was successively triturated with diethyl ether and water and then filtered off. After washing with water and diethyl ether, product **19b** was obtained in a yield of 80 mg (95%) as a dark-claret precipitate, m.p. 138—141 °C. UV (EtOH), λ_{max}/nm (ε): 385 (72000), 435 (48000), 550 (29000). ^{1}H NMR ($CDCl_3$), δ: 1.65 (br.s, 18 H, CH_2); 3.35 (br.s, 8 H, N—CH_2); 3.54 (br.s, 4 H, N—CH_2); 5.34 (t, 2 H, γ-H, J = 11.8 Hz); 5.63 (d, 2 H, α-H, J = 13.8 Hz); 5.90 (s, 2 H, CH); 7.25 (d, 2 H, δ-H); 7.57 (dd, 2 H, β-H, J = 14.0 Hz, J = 11.8 Hz). The signal for H partially overlaps with the residual signal of $CDCl_3$.

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