Synthesis and photonics of ketocyanine dyes, 2,6-bis(4-dimethylaminoalka-1,3-dienyl)-4*H*-pyran-4-ones and ethoxytridecamethine salts based on them

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The reactions of β-dimethylaminoacrolein aminals with 2,6-dimethyl-γ-pyrone lead to 2,6-bis(4-dimethylaminoalka-1,3-dienyl)-4*H*-pyran-4-ones, whose alkylation affords ethoxytridecamethine salts. The spectral and fluorescence properties of the synthesized compounds were studied. Their absorption spectra are unusual; along with the long-wavelength band in the visible spectral region, they contain a much more intense short-wavelength band in the near UV region. This pattern of the absorption spectra is explained in terms of the model of chromophore interaction, assuming an acute angle between the chromophore "halves" of the polyene chain of the dye molecule. The central pyran ring in the ethoxytridecamethine salts can hamper conjugation in the polymethine chain. Thermochromism of 2,6-bis(4-dimethylaminoalka-1,3-dienyl)-4*H*-pyran-4-ones (the long-wavelength shift of the absorption spectra on cooling of the solutions) is observed; only the long-wavelength absorption band undergoes a pronounced thermochromic shift. The introduction of methyl or phenyl substituents into the polyene chains of substituted 4*H*-pyranones decreases the fluorescence quantum yield.

Key words: 2,6-dimethyl-γ-pyrone, aminals of β-dimethylaminoacroleins, 2,6-bis(4-dimethylaminoalka-1,3-dienyl)-4*H*-pyranones, polymethine salts, absorption and fluorescence spectra, thermochromism, chromophore interaction.

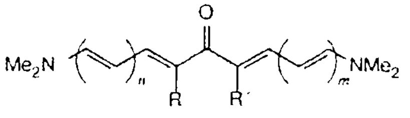
γ-Pyrones combine the properties of aliphatic dienones and aromatic pyrylium betaines. This duality of the nature of γ-pyrones makes these compounds fairly attractive for synthetic purposes. However, the synthetic potential of γ-pyrones have as yet been little studied.

Many properties of γ-pyrone can be explained satisfactorily only when γ-pyrone is regarded as an α,β-unsaturated ketone.[1–3] However, it would be wrong to exclude completely the potential aromatic nature of the heterocycle. The aromatic character of γ-pyrones is manifested, in particular, by the relatively easy formation of oxonium and methoxonium salts from them. Since the carbonyl oxygen atom is highly nucleophilic, treatment with various methylation reagents affords pyrylium derivatives.[4]

Alkyl substituents in positions 2 and 6 of the γ-pyrone ring tend to be readily deprotonated at the α-carbon atom, which is typical not only of pyrylium and pyridinium compounds but also of compounds of the aliphatic series.[3]

We expected that the high mobility of the hydrogen atoms in the Me groups of 2,6-dimethyl-γ-pyrone (**1**) would allow us to convert it into 2,6-bis(4-dimethylaminoalka-1,3-dienyl)-4*H*-pyran-4-ones (BDAP) upon condensation with β-dimethylaminoacrolein aminals (**2a—c**). The possibility of this reaction is also due to the fact that β-dimethylaminoacrolein aminals are highly reactive compounds. It has been shown previously[5] that the reaction involves not only the Me groups located near the carbonyl group but also the Me groups separated from the carbonyl group by one or several double bonds.[5]

The interest in the synthesis of BDAP containing a 4*H*-pyran ring is due to the fact that the conjugated polyene bis(ω,ω'-dimethylamino) ketones (BDAK) prepared previously, which also contain two chromophores interacting through a carbonyl group, possess a number of specific spectral luminescent and chemical



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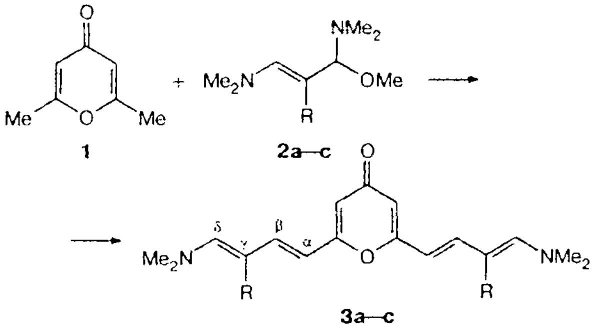
properties.[6—9] We believed that it would be possible to convert the BDAP synthesized into alkoxypolymethine salts, which can be used to prepare cyanine dyes.

When 2,6-dimethyl-γ-pyrone **1** condenses with β-dimethylaminoacrolein aminal acetal **2a** and with aminal acetals of α-substituted β-dimethylaminoacroleins **2b,c** [10] at the molar ratio **1** : **2a—c** = 1 : 2, the formation of BDAP **3a—c** can be observed by UV spectroscopy (Scheme 1).

Scheme 1



R = H (a), Me (b), Ph (c)

However, only ketone **3c** was isolated from the reaction mixture (yield 3%), while ketones **3a,b** were not isolated. Attempts to increase the yield of ketones **3a—c** by changing the reaction temperature and time proved to be unsuccessful. Only the use of excess aminals **2a—c** (**1** : **2a—c** = 1 : 3) increased the yield of BDAP **3a—c** to 40—55%.

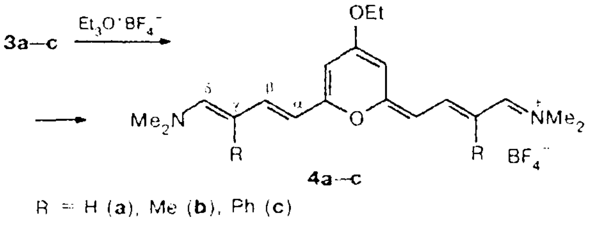
The structures of synthesized ketones **3a—c** were confirmed by ^{1}H and ^{13}C NMR spectra, electronic absorption spectra, the data of elemental analysis, and mass spectra.

^{1}H NMR showed that ketones **3a—c** have *trans*-configuration of protons at the double bonds (J = 12.5—14.7 Hz); ketone **3a** exists mainly as the *s-trans*-conformer at the β-C—γ-C bond (J = 12.5—14.6 Hz).

As noted above, γ-pyrones are readily alkylated at the oxygen atom of the carbonyl group; therefore, it was of interest to attempt to prepare alkoxytridecamethine salts from BDAP **3a—c** containing bulky alkadienyl substituents.

We found that alkylation of BDAP **3a—c** by $Et_3O^+BF_4^-$ affords ethoxytridecamethine salts **4a—c** (Scheme 2).

Scheme 2



R = H (a), Me (b), Ph (c)

It should be noted that, despite the particular interest in higher polymethine salts, no salts with a chain longer than that in alkoxyundecamethine salts could be obtained so far by the alkylation of BDAK.

It has been noted[9,11] that alkoxypolymethine salts containing Me and Ph groups in the polymethine chain are unstable in solutions. However, it was found that salts **4b,c** are rather stable and can be isolated and purified without difficulty.

According to ^{1}H NMR data, tetrafluoroborate **4a** has a *trans*-configuration of protons at the double bonds ($J_{\alpha,\beta}$ = 14.7 Hz; $J_{\gamma,\delta}$ = 12.5 Hz) and exists as the *s-trans*-conformer at the β-C—γ-C bond (J = 12.5 Hz). For salts **4b,c**, the *trans*-configuration of the α-C—β-C bond (J = 12.5—14.6 Hz) was established.

We studied the fluorescence-spectral properties of 4*H*-pyran-4-ones **3a—c** and ethoxytridecamethine salts **4a—c**. The data of the absorption and fluorescence spectra and the fluorescence quantum yields (φ_{fl}) are presented in Table 1.

4*H*-Pyran-4-ones **3a—c** resemble BDAK in a number of photophysical properties,[6—8] in particular, their absorption and fluorescence spectra also undergo a bathochromic shift on going from less polar solvents to more polar ones (positive solvatochromism). Like BDAK, ketones **3a—c** display great Stokes shifts of the fluorescence spectra (more than 100 nm) and the quantum yields of fluorescence in polar (proton-donor) solvents are much higher than those in nonpolar solvents. The fluorescence quantum yields for substituted BDAP **3b,c** (especially, for dimethyl-substituted bisamino ketone **3b**) are much lower than those for unsubstituted ketone **3a**. This can be explained by enhancement of nonradiative deactivation of the excited singlet state due to the vibrational degrees of freedom of the substituents (a similar trend has been identified previously for BDAK having methyl substituents in the polyene chain[7]). Ketones **3a—c**, like BDAK,[7,12] show thermochromism,

Table 1. Absorption and fluorescence spectra and fluorescence quantum yields (φ_{fl}) for compounds **3a—c** and **4a—c**

Compound	λ^{abs}_{max}/nm (ε)			λ^{fl}_{max}/nm (φ_{fl})	
	EtOH	Pr^{i}OH	Toluene	Pr^{i}OH	Toluene
3a	360 (66900), 472 (31000)	356, 461	343, 412	566 (0.031)	483
3b	366 (66500), 472 (35400)	363, 458	351, 415	564 (0.0056)	~492
3c	364 (92300), 475 (51200)	360, 465	351, 418	570 (0.0137)	~491
4a	378 (136800), 615 (42900)	388, 614	—	668	—
4b	398 (104400), 615 (43600)	395, 616	—	~645	—
4c	392 (111200), 625 (53000)	391, 622	—	~655	—

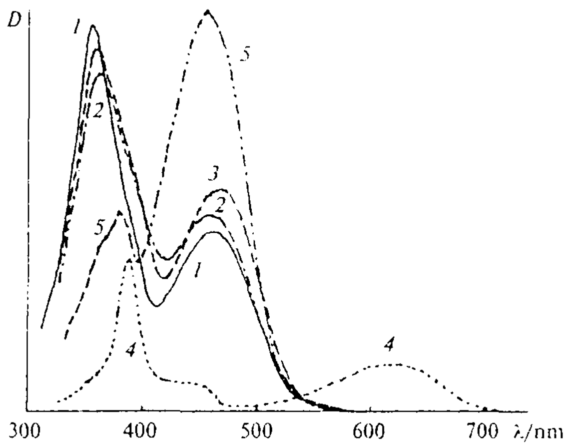


Fig. 1. Absorption spectra (in $\mathrm{Pr^iOH}$) of compounds **3a** (*1*), **3b** (*2*), **3c** (*3*), **4a** (*4*), and **5** (*5*).

i.e., the absorption spectra of solutions shift to longer wavelengths following a decrease in the temperature.

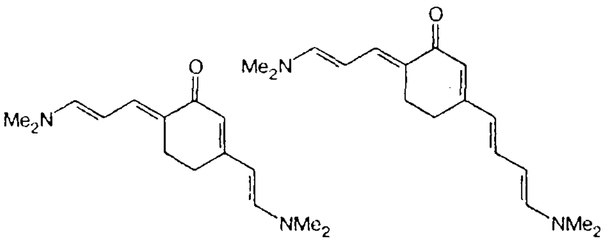
The absorption spectra of BDAP **3a—c** have some peculiar features which sharply distinguish them from the spectra of BDAK: whereas in the case of BDAK, the longest-wavelength absorption band (located in the visible or near-UV region) is the most intense (the extinction coefficient is up to 10^5 mol^{-1} L cm^{-1}),[6,7] the spectra of ketones **3a—c** contain a short-wavelength band (shifted by approximately 100 nm from the long-wavelength band) whose intensity is substantially greater than that of the long-wavelength band (Fig. 1, curves *1—3*).

Such an unusual spectral pattern of compounds **3a—c** can be explained in terms of the theory of chromophore interaction, developed by Kiprianov and Dyadyusha, which is based on dipole—dipole interactions.[13,14] Previously this theory has been used successfully to interpret the absorption spectra and the photochemical behavior of a number of biscyanine dyes,[15] cation—anion polymethine dyes,[16] and ketocyanine dyes (polyene BDAK).[6] In the latter case, each aminopolyenyl group of BDAK (up to the carbonyl group) appears to be a separate chromophore. The chromophores are separated by two formally single bonds in the center of the molecule, which create a barrier to conjugation, and interact *via* the central carbonyl group. The absorption spectra of these compounds are split, in the general case, into two bands, whose intensity is related to the angle between the chromophores θ by the following relation[13]:

$$\cos\theta = (r - 1)/(r + 1), \qquad (1)$$

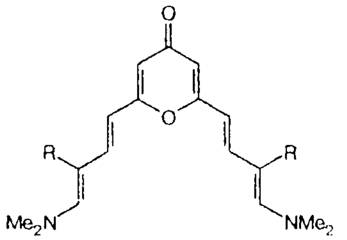
where $r = (\lambda_1\varepsilon_1)/(\lambda_2\varepsilon_2)$; λ_1, ε_1 and λ_2, ε_2 are the wavelength and the extinction coefficient at the maxima of the short- and long-wavelength bands, respectively.

In particular, in the case of linear BDAK[6] ($\theta \approx 180°$), only the long-wavelength absorption band is actually observed, and the intensity of the short-wavelength band is rather low (the short-wave transition is forbidden, $\varepsilon_1 \to 0$ and, hence, $r \to 0$). Meanwhile, the absorption spectra of the ion pairs of cation—anion polymethine dyes, in which the chromophores are parallel to each other ($\theta \approx 0$) and strongly interact, exhibit an intense short-wavelength band, while the long-wavelength band is sharply attenuated[16] (the ε_2 value is small and, hence, $r \to \infty$). For BDAK **5** and **6**, in which the chromophores are arranged at an angle of $\theta \sim 120°$, both bands can be observed and, in conformity with relation (1), the short-wavelength band is less intense[8] ($r \sim 1/3$; see Fig. 1, curve *4*). It should be noted that a more accurate interpretation of the positions of the bands and the ratio of the extinction coefficients should take into account electron tunnelling through the barrier according to the model described previously.[15]



5 **6**

In the case of bisamino ketones **3a—c**, the short-wavelength band is more intense than the long-wavelength band; according to (1), this implies an acute angle between the chromophores. From the absorption spectra shown in Fig. 1 (curves *1—3*) for ketones **3a—c**, we obtain $\varepsilon_1/\varepsilon_2$ = 2.211, 1.703, and 1.640; r = 1.707, 1.350, and 1.270; and θ = 75°, 81°, and 83°, respectively. Taking account of the fact that ketones **3a—c** have *trans*-arranged protons at the double bonds and occur mainly as *s-trans*-conformers, the structure of **3a—c** can be represented as follows.

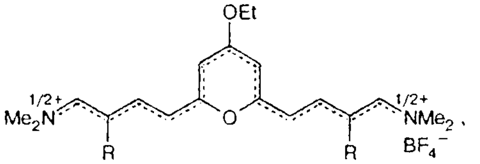


3a—c

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

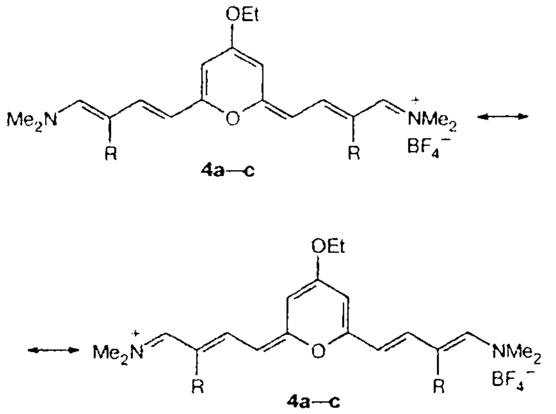
The θ angles are somewhat greater than the angle $\theta \sim 60°$ predicted for structures **3a—c** from geometric considerations, which might be due to the electrostatic repulsion of the terminal amino groups.

The absorption spectra of ethoxytridecamethine salts **4a—c** are also unusual. Salts **4a—c**, like other polymethine salts of this type,[6] contain presumably a symmetrical π-electron structure of a perfect polymethine dye with completely equalized bonds in the polymethine chain



which is the averaged structure over the two canonical forms (Scheme 3).

Scheme 3



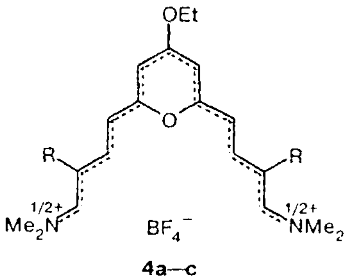
R = H (**a**), Me (**b**), Ph (**c**)

The spectra of salts of this type normally contain a narrow highly intense long-wavelength absorption band ($\varepsilon \sim 10^5$ mol L^{-1} cm^{-1}) and no substantial short-wavelength absorption in the visible or near UV region.[12] However, the short-wavelength band in the absorption spectra of salts **4a—c**, as in the case of ketones **3a—c**, is much more intense (λ_{max} = 378 nm, ε = 136800, **4a**) than the long-wavelength band (λ_{max} = 615 nm, ε = 42900, **4a**; see Fig. 1, curve *4*). These spectral features can be interpreted only in terms of the model of interaction between the chromophores, *viz.*, halves of the polymethine chain in salts **4a—c**. Since the most stable form of polymethine salts is usually that having the *trans*-configuration relative to all polymethine bonds, the structure of salts **4a—c** should be represented as shown in Scheme 4.

In this case, the salt chromophores are arranged at an acute angle to each other, which is consistent with the absorption spectral pattern. In fact, from Fig. 1 we obtain $\varepsilon_1/\varepsilon_2$ = 3.133 and r = 1.98, and relation (1) gives θ = 71°.

The representation of the absorption spectra of salts **4a—c** in terms of the theory of chromophore interaction is justified in the case where the structure contains a barrier to their interaction (otherwise, the whole system of conjugation should be considered as a single chromophore). This barrier is apparently created by the pyran ring. Indeed, the set of canonical structures of salts **4a—c** contains structures **C** and **D** with an aromatic pyrylium fragment, which may act as the obstacle preventing the polymethine moieties from forming a common system of conjugation (Scheme 5).

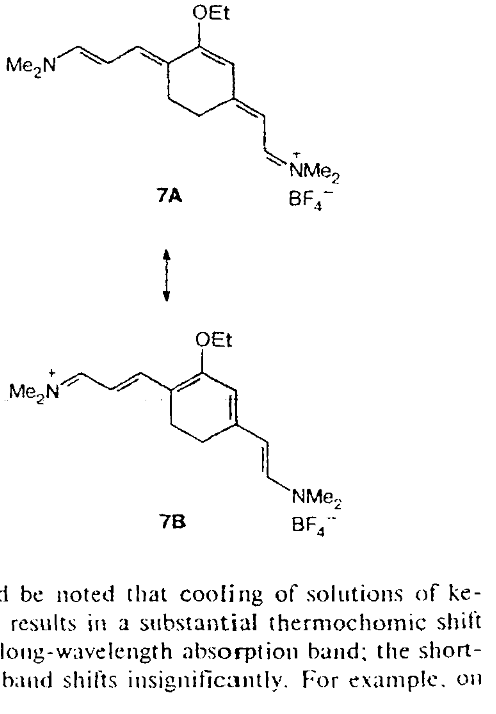
Scheme 4



4a—c

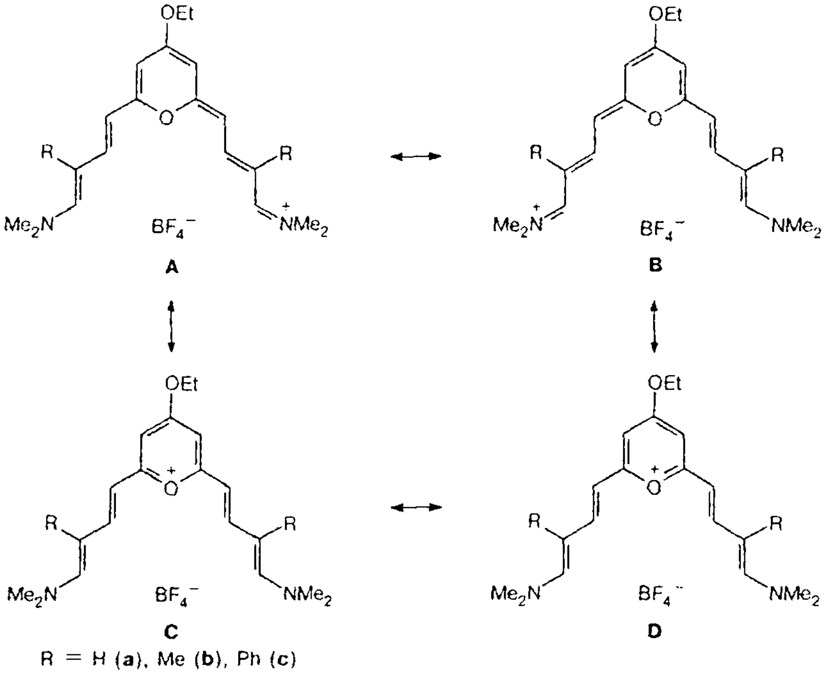
R = H (**a**), Me (**b**), Ph (**c**)

Obviously, no such obstacle is present when there is no central pyran fragment in the salt structure. Thus the absorption spectrum of salt **7** with a dimethylene bridge, prepared from BDAK **5**, has no abnormal features (it does not exhibit a noticeable short-wavelength band in the visible or near UV region),[12] although the halves of the polymethine chain in its structure are arranged at an angle to each other, because the polymethine chain does not have a barrier preventing conjugation.



It should be noted that cooling of solutions of ketones **3a—c** results in a substantial thermochomic shift of only the long-wavelength absorption band; the short-wavelength band shifts insignificantly. For example, on

Scheme 5



cooling of a solution of 3a in propanol from 349 K to 155 K, the long-wavelength absorption band shifts by 2100 cm^{-1}, while the short-wavelength band shifts by only 670 cm^{-1}.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) relative to Me_4Si; the ^{13}C NMR spectrum was run on a Bruker AC-200 spectrometer (50.32 MHz). The mass spectra (EI, m/z (I_{rel} (%)) of compounds **3a,b** were measured on an MS-30 (70 eV) instrument; that of compound **3c** was obtained on a Jeol JMS-D-300 mass spectrometer (70 eV). The absorption spectra of solutions of compounds **3a—c** and **4a—c** were measured on a Specord UV VIS spectrophotometer, and the fluorescence spectra were measured on an Aminco-Bowman spectrofluorimeter with an R136 photomultiplier. The fluorescence spectra were not corrected for the spectral sensitivity of the spectrofluorimeter. The fluorescence quantum yields were determined using Rhodamine B in ethanol (φ_{fl} = 0.65) as the standard.[17] The error in the determination of the fluorescence quantum yields was ~20%.

2,6-Bis(4-dimethylaminobuta-1,3-dienyl)-4*H*-pyran-4-one (3a). 2,6-Dimethyl-γ-pyrone **1** (0.22 g, 1.6 mmol) was added at 20 °C to a solution of aminal **2a** (0.76 g, 4.8 mmol) in 2.5 mL of anhydrous benzene. The reaction mixture was heated for 1 h at 65—70 °C. After cooling to 20 °C, the solvent was removed *in vacuo*. The resulting oil was triturated with anhydrous ether and the precipitate was separated. Then the precipitate was suspended in anhydrous acetone, thoroughly triturated, filtered off, and washed with anhydrous acetone and then with anhydrous ether to give 280 mg (55%) of compound **3a** as red-brown crystals, m.p. 188—192 °C. Found (%): N, 9.61. $C_{17}H_{22}N_2O_2$. Calculated (%): N, 9.78. ^{1}H NMR ($CDCl_3$), δ: 2.86 (s, 12 H, NMe_2); 5.13 (t, 2 H, γ-H, $J_{\beta,\gamma} = J_{\gamma,\delta}$ = 12.5 Hz); 5.71 (d, 2 H, α-H, $J_{\alpha,\beta}$ = 14.7 Hz); 5.79 (s, 2 H, H-3 and H-5); 6.60 (d, 2 H, δ-H, $J_{\gamma,\delta}$ = 12.5 Hz); 7.02 (dd, 2 H, β-H, $J_{\alpha,\beta}$ = 14.7 Hz, $J_{\beta,\gamma}$ = 12.5 Hz). ^{13}C NMR (CD_3OD), δ: 41.22 (NMe_2); 99.45 (γ-C); 107.33 (C-3); 109.59 (α-C); 142.39 (β-C); 152.31 (δ-C); 167.00 (C-2); 182.84 (C=O). The ^{13}C NMR signals were assigned by heteronuclear resonance. MS, m/z: 286 $[M]^+$ (91.6%), 242 $[M - NMe_2]^+$ (100%), 197 $[M - NMe_2 - NHMe_2]^+$ (34.5%).

2,6-Bis(4-dimethylamino-3-methylbuta-1,3-dienyl)-4*H*-pyran-4-one (3b) was prepared similarly to **3a**; yield 39%, m.p. 138—142 °C. ^{1}H NMR (CD_3OD), δ: 2.00 (m, 6 H, Me); 3.09 (s, 12 H, NMe_2); 5.91 (s, 2 H, CH); 5.68 (d, 2 H, α-H, $J_{\alpha,\beta}$ = 14.6 Hz); 6.59 (s, 2 H, δ-H); 7.22 (d, 2 H, β-H, $J_{\alpha,\beta}$ = 14.6 Hz). MS, m/z: 314 $[M]^+$ (17.3%), 269 $[M - Me_2NH]^+$ (92.7%), 254 $[M - Me_2NH - Me]^+$ (20.8%), 225 $[M - Me_2NH - Me_2N]^+$ (100%), 96 [γ-pyrone + H]$^+$ (81.7%).

2,6-Bis(4-dimethylamino-3-phenylbuta-1,3-dienyl)-4*H*-pyran-4-one (3c) was prepared similarly to **3a**. To purify product **3c**, the precipitate obtained after trituration of the reaction mixture in anhydrous ether was suspended in hot anhydrous MeOH, filtered off, and washed with anhydrous MeOH and anhydrous ether; yield 38%, m.p. 191—194 °C. ^{1}H NMR (CD_3OD), δ: 2.64 (s, 12 H, NMe_2); 5.03 (d, 2 H, α-H, $J_{\alpha,\beta}$ = 12.5 Hz); 5.57 (s, 2 H, CH); 6.80 (s, 2 H, δ-H); 7.10—7.40 (m, 12 H, Ph and β-H). MS, m/z: 438 $[M]^+$ (3%), 393 $[M - Me_2NH]^+$ (7%), 348 $[M - 2\ Me_2NH]^+$ (100%), 333 $[M - Ph - CO]^+$ (7%), 320 $[M - 2\ Me_2NH - CO]^+$ (20%), 289 $[M - Ph - CO - Me_2N]^+$ (32%).

(13-Dimethylamino-5,9-epoxy-7-ethoxytrideca-2,4,6,8,10,12-hexaenylidene)dimethylammonium tetrafluoroborate (4a). A solution of $Et_3O^+BF_4^-$ (74 mg, 0.39 mmol) in 1 mL of anhydrous CH_2Cl_2 was added dropwise with stirring to a solution of ketone **3a** (80 mg, 0.28 mmol) in 3 mL of anhydrous CH_2Cl_2 cooled to −10 °C. The reaction mixture was stirred for 1 h at −10 to −5 °C, and the resulting precipitate was filtered off and washed with cold anhydrous CH_2Cl_2 and anhydrous ether to give 70 mg (62%) of compound **4a** as dark crystals; m.p. 212—216 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 1.41 (t, 3 H, CH_3); 3.10 (br.s, 12 H, NMe_2); 4.15 (q, 2 H, CH_2); 5.31 (t, 2 H, γ-H, $J_{\beta,\gamma} = J_{\gamma,\delta}$ = 12.5 Hz); 5.59 (d, 2 H, α-H, $J_{\alpha,\beta}$ = 12.5 Hz); 5.79 (s, 2 H, CH); 7.62 (d, 2 H, δ-H, $J_{\gamma,\delta}$ = 12.5 Hz); 7.82 (t, 2 H, β-H, $J_{\alpha,\beta} = J_{\beta,\gamma}$ = 12.5 Hz).

(13-Dimethylamino-5,9-epoxy-7-ethoxy-2,12-dimethyltrideca-2,4,6,8,10,12-hexaenylidene)dimethylammonium tetrafluoroborate (4b). A solution of $Et_3O^+BF_4^-$ (68 mg, 0.36 mmol) in 1 mL of anhydrous CH_2Cl_2 was added dropwise with stirring to a solution of ketone **3b** (80 mg, 0.26 mmol) in 3 mL of anhydrous CH_2Cl_2 cooled to −10 °C. The reaction mixture was stirred for 70 min at −10 to −5 °C. The solvent was evaporated *in vacuo* (without heating). The solid residue was triturated with anhydrous ether and the precipitate was filtered off. The resulting precipitate was suspended in ~0.5 mL of anhydrous MeOH, thoroughly triturated, filtered off, and washed with an anhydrous ether—anhydrous MeOH mixture (2 : 1) and with anhydrous ether to give 30 mg (27%) of salt **4b** as dark crystals; m.p. 168—172 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 1.42 (t, 3 H, CH_3); 1.98 (s, 6 H, γ-C—Me); 3.21 (s, 12 H, NMe_2); 4.22 (q, 2 H, CH_2); 5.57 (d, 2 H, α-H, $J_{\alpha,\beta}$ = 14.5 Hz); 6.04 (br.s, 2 H, CH); 7.15 (br.s, 2 H, δ-H); 7.59 (d, 2 H, β-H, $J_{\alpha,\beta}$ = 14.5 Hz).

(13-Dimethylamino-5,9-epoxy-7-ethoxy-2,12-diphenyltrideca-2,4,6,8,10,12-hexaenylidene)dimethylammonium tetrafluoroborate (4c) was prepared similarly to **4b**; yield 34%, m.p. 166—168 °C. ^{1}H NMR ($CDCl_3$), δ: 1.32 (t, 3 H, CH_3); 2.82 (s, 12 H, NMe_2); 4.07 (q, 2 H, CH_2); 5.08 (d, 2 H, α-H, $J_{\alpha,\beta}$ = 14.7 Hz); 5.71 (br.s, 2 H, CH); 7.17—7.42 (m, 10 H, Ph); 7.55 (br.s, 2 H, δ-H); 7.94 (d, 2 H, β-H, $J_{\alpha,\beta}$ = 14.7 Hz).

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