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Reviews

Synthesis and photonics of polyfunctional conjugated polyenes

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Methods for the synthesis of various types of polyfunctional conjugated polyenes based on aminals of unsaturated ω-amino aldehydes are surveyed. The influence of the interaction of chromophores on the photophysical properties of polyene bis(amino)-substituted ketones and polymethine salts based on them as well as on the properties of absorption and fluorescence spectra of the cation-anionic polymethine dyes are considered.

Key words: aminals of unsaturated ω-amino aldehydes, conjugated polyenes, photonics, chromophore interaction.

Introduction

The number of studies devoted to the synthesis, photophysics, and photochemistry of polyenes has substantially increased in recent years. This is due to the extensive practical application of these compounds (in particular, in nonlinear optics and medicine) and their use as objects of quantum-chemical calculations and simulation. Many dyes used for practical purposes and in theoretical investigations contain a polyene chain as a chromophore. Due to its simple structure, the polyene chromophore serves as a good model for the study of key photophysical and photochemical processes in organic molecules.

Highly important are studies devoted to polyenes containing electron-releasing and electron-withdrawing substituents within one molecule (push-pull polyenes), in particular, merocyanine dyes.[1] These polyenes possess a series of interesting photophysical and photochemical properties, in particular, solvatochromism, easy photoisomerization, *etc*. However, rather detailed studies have been carried out only for some representatives of this class, for example, for merocyanines, which have found extensive use in photochromic systems (merocyanine $\rightleftharpoons$ spiropyran),[2] in medicine (photodynamic therapy),[3] and in the study of solvation.[4] A systematic photochemical study of a large uniform series of compounds of this class has not yet been carried out due to the lack of convenient methods for their synthesis. It should be noted that the compounds in question usually have complex structures, in particular, they contain terminal

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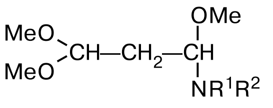
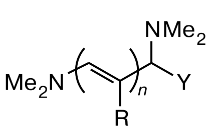
heterocycles; this hampers calculations and simulation of such molecules.

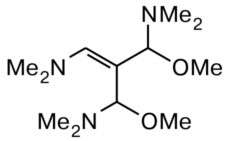
Extensive opportunities for the synthesis of diverse polyfunctional conjugated polyenes, many of which have not been known previously, are provided by derivatives of malonaldehyde and its heteroanalogs or vinylogs, namely, 3-dialkylamino-1,1,3-trimethoxypropanes (DTP),[5,6] aminals and aminal acetals of ω-dimethylamino aldehydes (ADA)*,[7—13] and dimethylaminomethylenemalonaldehyde bis-*N*,*O*-acetal (DMBA)[14,15].



DTP



DMBA



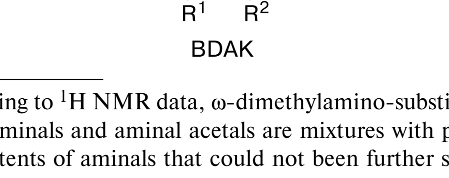
ADA

Y = OMe, NMe$_2$; n = 1—4.

A variety of polyenes have been synthesized by the reactions of aminals of conjugated ω-dimethylamino aldehydes with aliphatic, cyclic, unsaturated, and heterocyclic ketones and diketones, triketones and CH-acids; many of these syntheses have involved unusual chemical transformations of aminals or products prepared from them.

The polyenes belong to different classes of organic compounds including conjugated ω-dimethylamino ketones, ketoesters, diketones, diesters, thioaldehydes, substituted phenols, oxygen-containing analogs of cyanines (oxanine salts), tetracyanopolymethines, *etc.* Some of them are polymethine dyes or intermediates for their synthesis.

Many of the prepared compounds exhibit unusual absorption and luminescence properties. A special place among them is occupied by the newly prepared ω,ω´-bis(dialkylaminopolyenyl) ketones (BDAK) (ketocyanines), which are cross-conjugated bichromophore systems containing two polyene chains connected by a carbonyl group.[16—18] They have electron-releasing substituents (dialkylamino groups) at the ends of the chain, while the carbonyl bridge is the electron-withdrawing group.



BDAK

These BDAK contain chromophores, which interact *via* the carbonyl group; they have an extended π-electron system that absorbs in the visible and near-UV regions with high extinction coefficients. The electronic structure of BDAK stipulates a number of specific properties such as clear-cut solvatochromism,[19,20] pronounced thermochromism,[21] intense fluorescence, generation of laser radiation,[22] exceptionally easy alkylation and protonation at the carbonyl group with a sharp color change,[17,18,23,24] and so on.

On the basis of BDAK, a highly sensitive method for direct determination of free acid in aprotic solvents with a low dielectric constant (DC < 10) has been developed.[25—27]

Due to their simple structure, BDAK proved to be convenient models for the study of various photophysical and photochemical processes, in particular, the interaction of chromophores in excited singlet and triplet states (see below, Section 5).

The use of various methods for the synthesis of BDAK from aminals of conjugated ω-dimethylamino aldehydes has resulted in a broad range of BDAK (differing in the length and the spatial arrangement of the polyene chromophores, the symmetry of the molecule, the substituents in the polyene chains, the presence of various heterocyclic fragments) and BDAK analogs with a single chromophore. This enabled a systematic photochemical and photophysical research, which has revealed a number of highly interesting properties of these compounds.

Aminals of conjugated aldehydes, which are convenient reagents for the introduction of the ω-dimethylaminopolyene fragment, cannot be used to prepare compounds containing more than two aminopolyene chromophores. Compounds of this type have been synthesized using a recently prepared reagent, namely, dimethylaminomethylenemalonaldehyde bis-*N*,*O*-acetal (DMBA), containing three reactive centers.[14,15] In a study of the reactivity of DMBA, diverse reactions involving this compound have been found.

For example, the condensation of DMBA with ketones is accompanied by an unusual intramolecular cyclization, which yields cross-conjugated ketones containing an *N*-methylpyrrole ring in the β- or β- and β´-positions; this is a new pathway to substituted pyrroles.

Study of the condensation of aminals of conjugated ω-dimethylamino aldehydes and DMBA with various β-dicarbonyl compounds and CH-acids showed that in some cases, the reaction can follow two different pathways depending on the conditions. In particular, in addition to the expected route resulting in conjugated α,α-difunctionally substituted ω-aminopolyenes, the reaction can proceed in a different way to give oxanine salts or tetracyanopolymethines, which are anionic dyes. These were used to prepare a series of cation-anionic polymethine dyes of a new type. A photochemical investiga-

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* According to ^{1}H NMR data, ω-dimethylamino-substituted aldehyde aminals and aminal acetals are mixtures with predominant contents of aminals that could not been further separated (below, aminals).

tion of these dyes showed the presence of interaction between the polymethine chromophores of the cation and the anion, transfer of the excitation and electron energy between them (see Section 6), the formation of fluorescing and nonfluorescing aggregates in low-polarity media,[28—30] and other interesting properties.

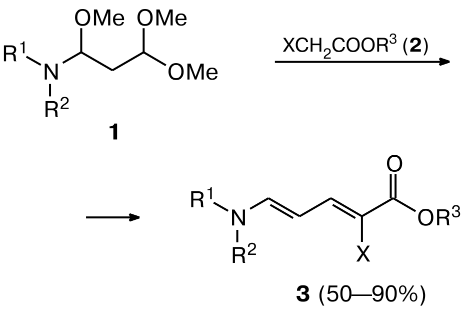
This review considers the main results of authors´ research dealing with the synthesis of polyfunctional conjugated polyenes and study of their photonics.*

1. Synthesis of ω-dimethylaminopolyenones from aminals of β-dimethylaminoacrolein and its vinylogs

1.1. Condensation of 3-dialkylamino-1,1,3-trimethoxypropanes and unsaturated ω-amino aldehydes with CH-acids

The reaction of DTP **1** with esters **2** without a catalyst smoothly leads to δ-amino esters **3**, containing an electron-withdrawing substituent in the α-position (Scheme 1).[5,17]

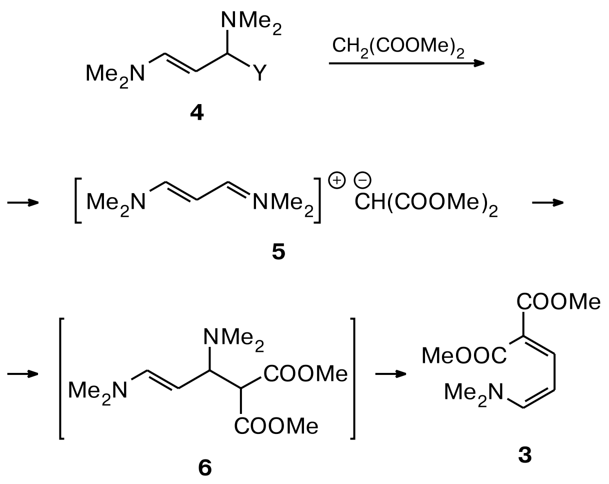
Scheme 1



$R^1 = R^2 = Me$, $R^1 + R^2 = (CH_2)_5$; $R^3 = Me, Et$;
$X = NO_2, CN, COOMe, COOEt, CONH_2$.

Apart from compounds **1**, aminals **4** were used for the synthesis of δ-aminodienes.[9,12] The reaction of **4** with CH-acids gives first dimethylaminopropenylideneammonium salts **5** with the CH-acid anion, some of which were isolated (Scheme 2).[31,32]

Scheme 2

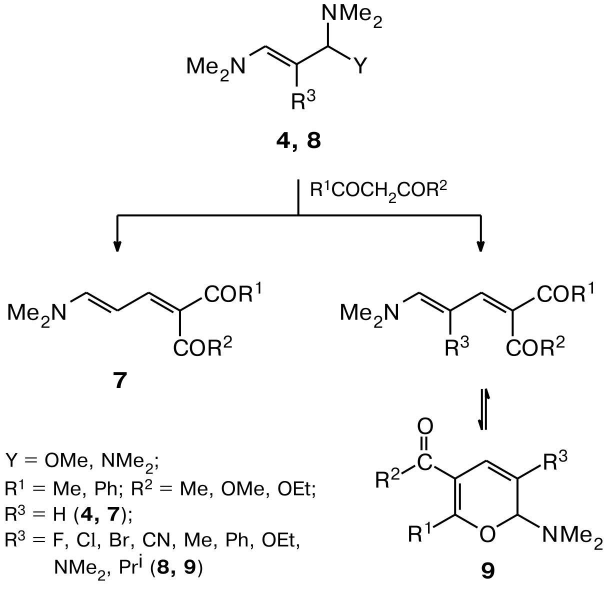


Y = OMe, NMe$_2$.

During the transformation of salt **5** into diene diester **3** (see Scheme 2), diamine **6** is formed as an intermediate product (diamines of this type were isolated in some reactions of aminals **4**).[33] The formation of salts **5** at the first step is due to the fact that aminals **4** tend to be readily protonated.[31] The possibility of isolation of type **5** salts and the capacity of these salts for transformation into δ-aminodienes **3** depends on the p*K* of the initial CH-acid and the nucleophilicity of the anion derived from the acid.[31]

By reactions of aminal **4** with diketones and ketoesters, a series of diene δ-dimethylamino diketones and ketoesters **7**, existing in the open dienone form, have been obtained.[32] When aminals of α-substituted β-dimethylaminoacroleins **8** are used,[10,11,13] the reaction yields δ-dimethylaminocarbonyl compounds **9**, which contain a substituent in the γ-position. These compounds were found to undergo δ-aminodienone $\rightleftharpoons$ 2-amino-2*H*-pyran valence isomerization (Scheme 3), which accounts for their solvato-, thermo-, and photochromism. This isomerization was discovered and studied by ^{1}H NMR, ^{13}C NMR,

Scheme 3



Y = OMe, NMe$_2$;
$R^1 = Me, Ph$; $R^2 = Me, OMe, OEt$;
$R^3 = H$ (**4, 7**);
$R^3 = F, Cl, Br, CN, Me, Ph, OEt, NMe_2, Pr^i$ (**8, 9**)

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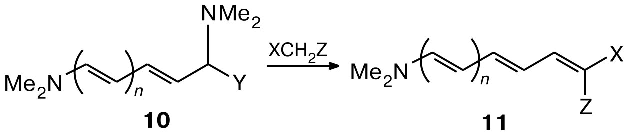
* Proving of the structure of the synthesized polyenes, their stereochemistry, and a number of spectroscopic data presented in the original publications are not included in the review.

UV, and IR spectroscopy and pulse photolysis (see review[34] and references cited therein).

The condensation of ω-dimethylaminopolyenal aminals **10** (n = 1—3)[12] with various CH-acids afforded ω-dimethylamino-substituted polyene carbonyl compounds **11**, containing three to five double bonds, in high yields (Scheme 4).[35]

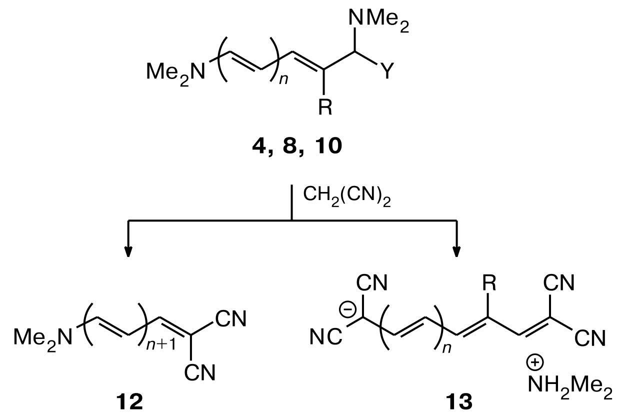
Scheme 4



Y = OMe, NMe$_2$; X, Z = COOMe, COOEt, COMe, CN; n = 1—3.

The condensation of aminals of unsaturated ω-dimethylamino aldehydes with malononitrile gives not only conjugated ω-dimethylamino dinitriles **12**, which are the major products, but also tetracyanopolymethines **13**. When reaction conditions are changed, the latter compounds become the major products and can be isolated in 80—90% yields (Scheme 5).[31,35,36]

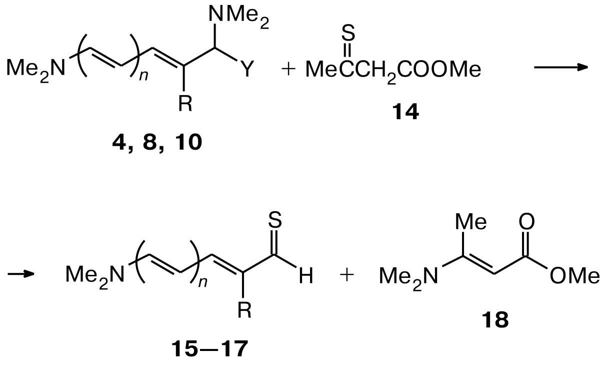
Scheme 5



Y = OMe, NMe$_2$; R = H (**4**, **10**, **12**, **13**);
n = 0 (**4**, **10**, **12**, **13**), 1, 2 (**10**, **12**, **13**)
8, 13: R = H (**a**), Me (**b**), Ph (**c**), Cl (**d**), Br (**e**), F (**f**), OEt (**g**), NMe$_2$ (**h**), Pr^i (**i**), CN (**j**), n = 0.

In order to synthesize diene and triene ω-dimethylamino esters containing a thioaceto group in the α-position, the reactions of aminals **4**, **8**, and **10** with methyl thioacetoacetate **14** were studied. However, instead of the expected esters, the reactions gave previously unknown conjugated thioaldehydes **15—17** in good yields.[37] The role of ester **14** in this reaction is formally to transfer the thiocarbonyl group; thus, it is converted into crotonate **18** (Scheme 6).

Scheme 6

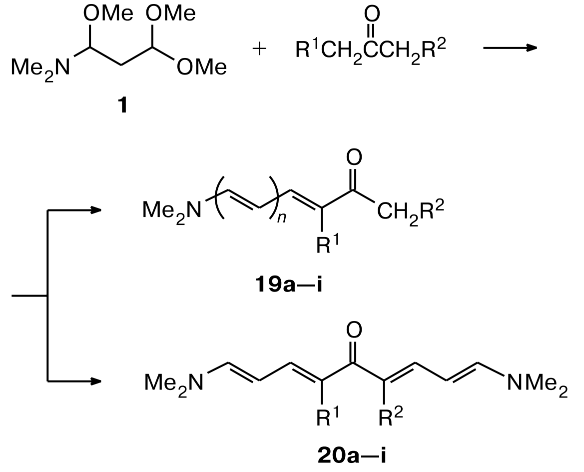


Y = OMe, NMe$_2$;
4, 15: R = H, n = 0;
10, 16: R = H, n = 1;
8, 17: R = Me, n = 0.

1.2. Condensation of 3-dimethylamino-1,1,3-trimethoxypropanes and aminals of unsaturated ω-amino aldehydes with ketones

We developed a simple method for the synthesis of ω-mono(dimethylaminopolyenyl) ketones (MDAK) and ω,ω′-bis(dimethylaminopolyenyl) ketones (BDAK) by condensation of 3-dimethylamino-1,1,3-trimethoxypropane (**1**) with ketones.[16—18] Depending on the conditions, the reaction can be directed either toward MDAK **19a—i**, containing one 3-dimethylaminopropenylidene substituent in the α-position, or toward BDAK **20a—i**, containing two substituents in the α- and α′-positions (Scheme 7).

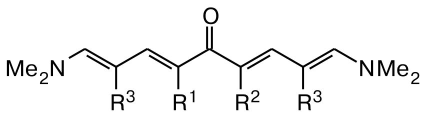
Scheme 7



n = 1, R^1 = R^2 = H (**a**), R^1 + R^2 = (CH$_2$)$_2$ (**b**), (CH$_2$)$_3$ (**c**), (CH$_2$)$_4$ (**d**), (CH$_2$)$_2$CHMe (**e**), CH$_2$CH(Me)CH$_2$ (**f**), CH$_2$CH(Me)CHMe (**g**), CH$_2$OCHMe (**h**); R^1 = H, R^2 = Me (**i**).

Aminals **4** can also be used, instead of 3-dimethylamino-1,1,3-trimethoxypropane (**1**), for the synthesis of ketones **19a—i** and **20a—i**. In both cases, condensation proceeds without a catalyst and gives virtually no side products. An important feature of this method is the possibility of preparing BDAK **20**, which have two aminopolyene chromophores.

Bis(dimethylaminopolyenyl) ketones **21a—g** substituted at the γ,γ′-positions, were prepared by the reaction of α-substituted aminals **8** with acetone,[10,11] cyclopentanone,[38,39] or cyclohexanone.[40]

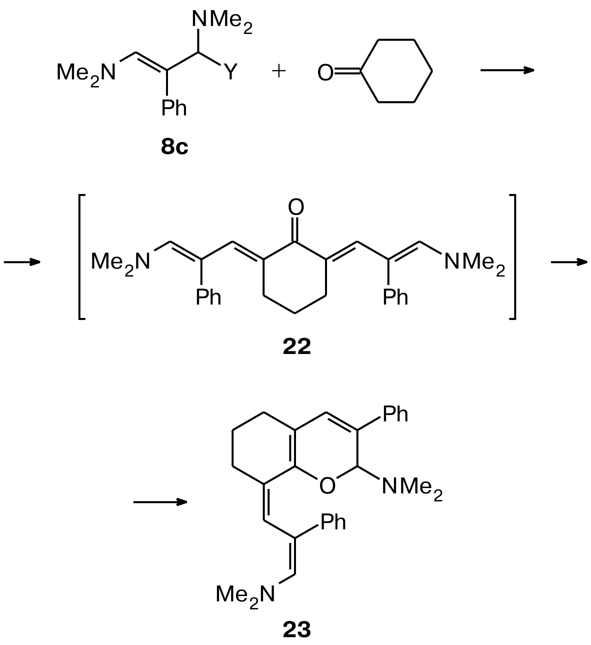


21a—g

$R^1 = R^2 = H$, $R^3 = Me$ (**a**), Ph (**b**);
$R^1 + R^2 = (CH_2)_2$, $R^3 = Me$ (**c**), OEt (**d**), Cl (**e**), F (**f**);
$R^1 + R^2 = (CH_2)_3$, $R^3 = F$ (**g**).

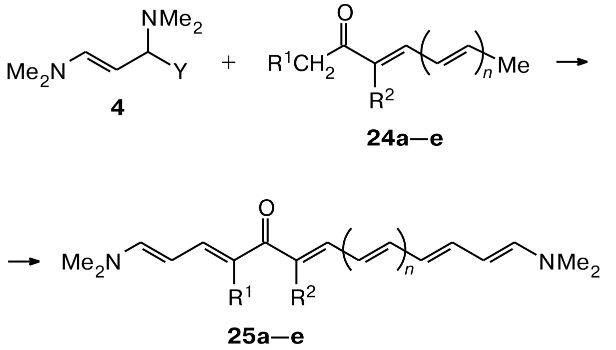
The reaction between aminal **8c** and cyclohexanone affords ketone **22**, which was isolated as a valence isomer, 2*H*-pyran **23** (Scheme 8).[11]

Scheme 8



The reactivity of aminals **4** is so high that they react with cyclic and acyclic α,β-unsaturated ketones **24a,d** and their vinylogs **24b,c,e**, containing not more than three double bonds, with transformation of not only the α-methyl or α-methylene group but also the methyl group separated from the carbonyl function by double bonds or by a heterocycle. This gives rise to bis(dimethylamino)-substituted polyunsaturated ketones **25a—e** (Scheme 9). The reactions with bisethylideneacetone and some cyclic unsaturated ketones resulted in compounds **26**, **27a,b**, and **28a** (Scheme 10).[19]

Scheme 9

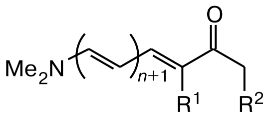


Compounds **24**, **25**	R^1, R^2	R^1+R^2	*n*	Yield of **25** (%)
a	H, H	—	0	54
b	H, H	—	1	40
c	H, H	—	2	27
d	—	$(CH_2)_3$	0	75
e	—	$(CH_2)_3$	1	48

Y = OMe, NMe_2.

This method proved to be efficient for the synthesis of a number of polyene BDAK containing up to seven double bonds. However, it is restricted by the necessity of using unsaturated ketones difficult to obtain as the starting compounds and the possibility of preparing only unsymmetrical BDAK. Hence, the method was successfully supplemented (Scheme 11) by using ω-dimethylamino-substituted polyenal aminals **10** (*n* = 1, 2).[12,20]

When the conditions are changed, the reaction proceeds regioselectively to yield only polyene monodimethylamino-substituted ketones **19k—p**.[35]



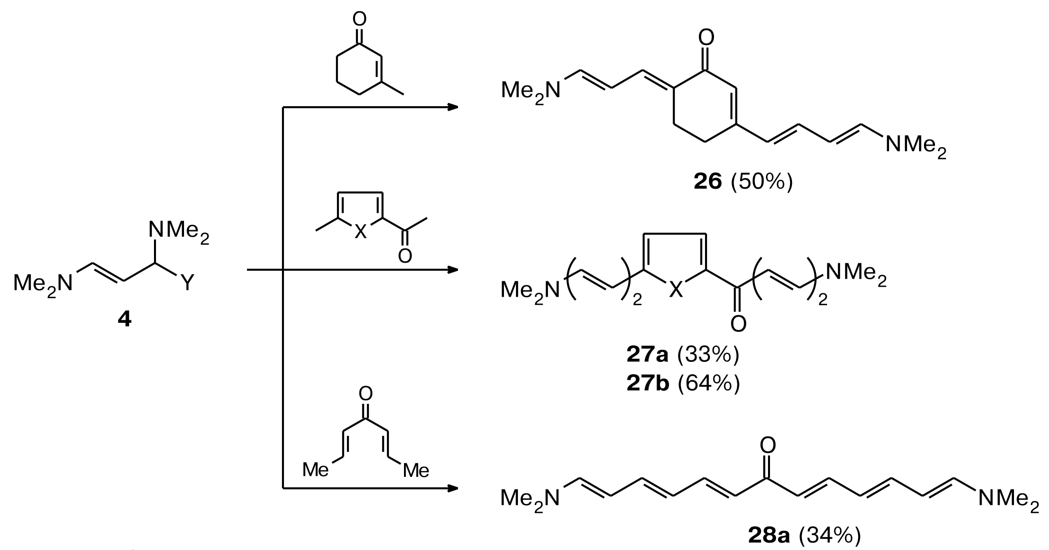
19k—p

$R^1 = R^2 = H$, $n = 1$ (**k**), 2 (**l**);
$R^1 + R^2 = (CH_2)_2$, $n = 1$ (**m**), 2 (**n**);
$R^1 + R^2 = (CH_2)_3$, $n = 1$ (**o**), 2 (**p**).

The condensation of aminals **4** and **10** (*n* = 1) with ene, diene, and triene amino ketones **29—31** provided the synthesis of polyene BDAK **32a,b**, **33**, and **34a,b** (Scheme 12).[18,20,41]

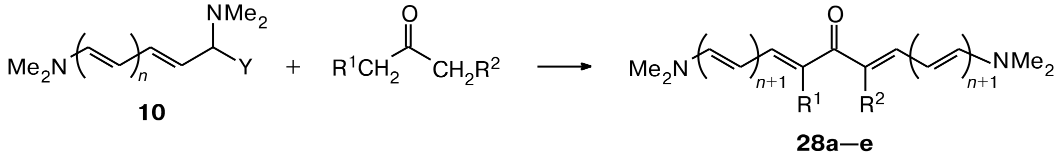
It is noteworthy that the reactivity of aminals **10** (*n* = 1) is rather high, their reaction with 2-ethylidenecyclo-

Scheme 10



X = O (**a**), S (**b**); Y = NMe$_2$, OMe.

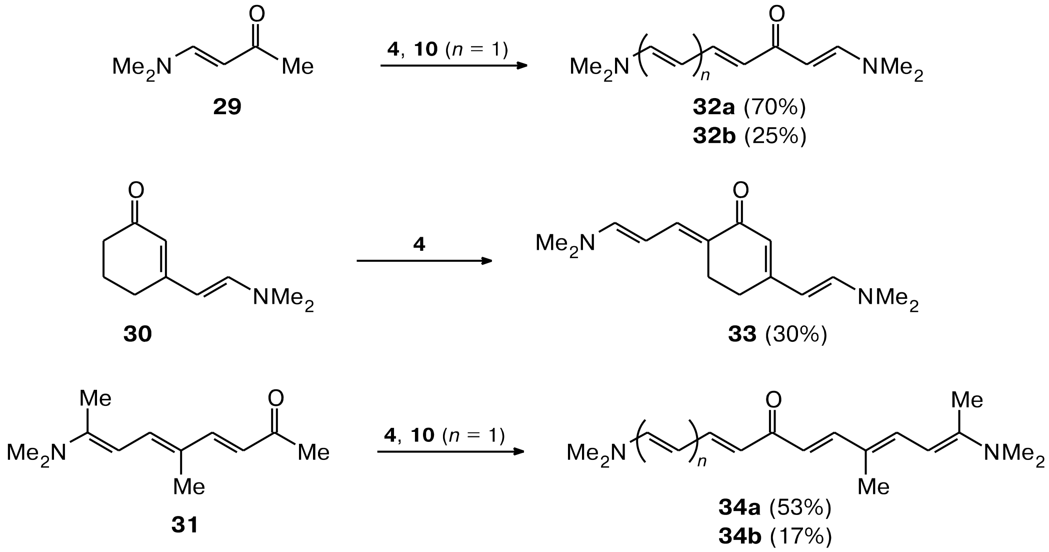
Scheme 11



Compound **28**	R^1, R^2	R^1+R^2	*n*	Yield of **28** (%)
a	H, H	—	1	98
b	—	(CH$_2$)$_2$	1	62
c	—	(CH$_2$)$_3$	1	60
d	H, H	—	2	3
e	—	(CH$_2$)$_2$	2	12

Y = OMe, NMe$_2$; *n* = 1, 2.

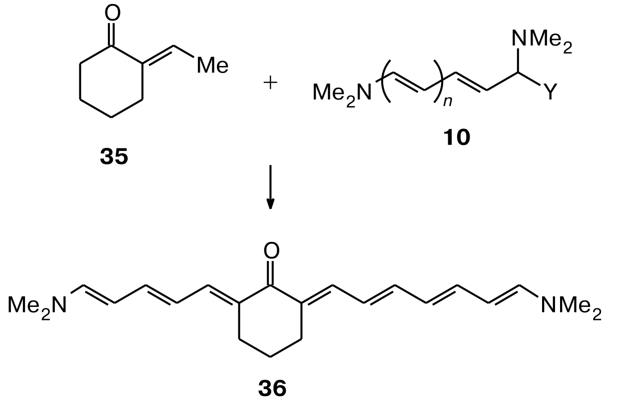
Scheme 12



n = 1 (**a**), 2 (**b**).

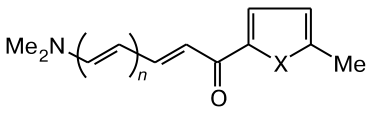
hexanone **35** involving not only the α-methylene but also the methyl group to give BDAK **36** (Scheme 13).

Scheme 13



Y = OMe, NMe$_2$; *n* = 1.

The condensation of heterocyclic compounds having an acetyl or an activated methylene group with aminals **4** or **10** (*n* = 1) furnished δ-aminodienones and ξ-aminotrienones **37—41**, containing a heterocyclic fragment.[19,31,35,42]



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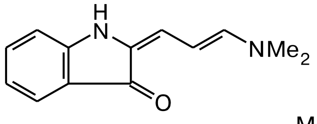

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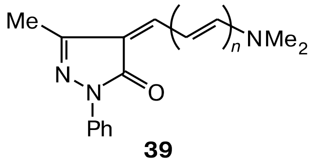

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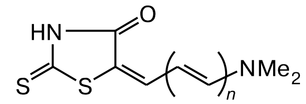

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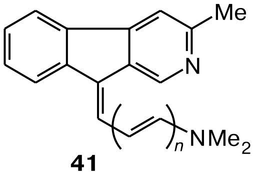
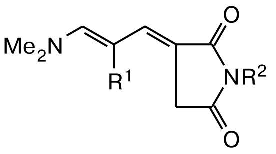


41

X = O, S; *n* = 1, 2.

A number of conjugated mono-ω- (**42**) and bis-ω,ω′-dimethylamino derivatives (**43**) of succinimides were synthesized in good yields by condensation of aminals **4**, **10** (*n* = 1), and **8b** with succinimides.[43]



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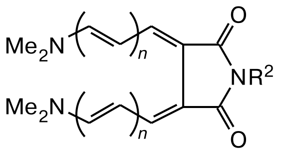


43

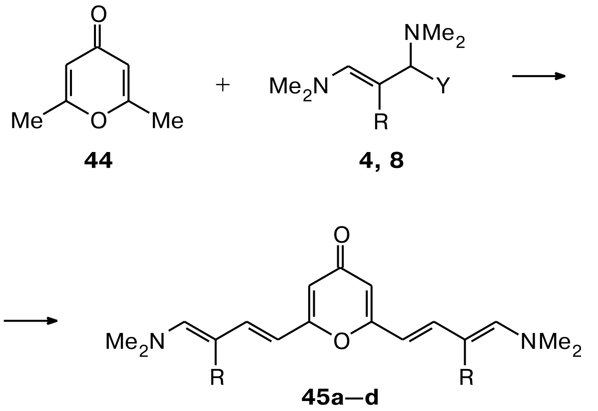
R^1 = H, Me; R^2 = H, Ph; *n* = 1, 2.

The introduction of a succinimide fragment into the polymethine chain is of interest because bisalkylidene derivatives of disuccinimides are used as photochromic materials and in holography.[44]

The combined use of ^{1}H and ^{13}C NMR and X-ray diffraction methods resulted in determination of the spatial structures for the succinimide dimethylamino derivatives synthesized and provided data that have been used to establish the configurations of other cyclic δ-aminodienones.

The condensation of aminals **4** and **8b,c,g** with 2,6-dimethylpyrone **44** affords 2,6-bis(ω,ω′-dimethylaminopolyenyl)pyranones **45a—d** in 40—55% yields (Scheme 14).[15,45]

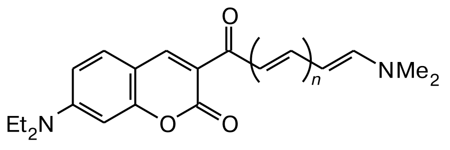
Scheme 14



R = H (**a**), Me (**b**), Ph (**c**), OEt (**d**); Y = OMe, NMe$_2$.

Study of the absorption and fluorescence properties of 4*H*-pyranones **45a—d** showed an unusual pattern of the absorption spectra of these compounds sharply differing from the spectra of BDAK (see Section 5).

A special place belongs to the synthesis of ω-dimethylaminopolyenones containing a coumarin fragment, because coumarin derivatives constitute an important group of organic luminophores and laser dyes. The reactions of aminals **4** and **10** (*n* = 1) with various coumarin derivatives provided the synthesis of coumarins **46—48** containing an aminopolyene chain as a substituent.[15,46]



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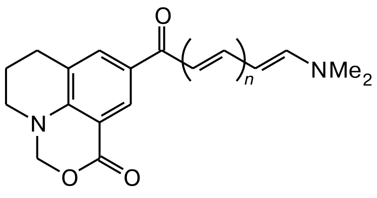
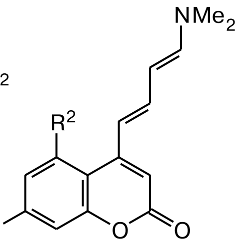


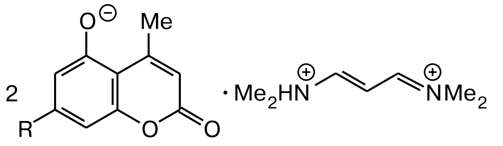
47

$n = 1, 2$



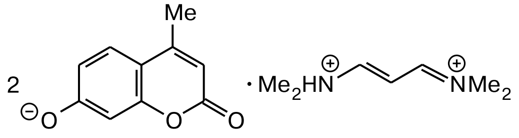
48a: R^1 = Me, R^2 = OMe
48b: R^1 = OH, R^2 = H

The reaction of aminal **4** with alkyl-substituted coumarins having a hydroxy group in position 5 or 7 led to an unexpected result. Trimethine salts **49** and **50** of an unknown type were formed in very high yields. The molecules of these salts contain one double-charged bisammonium cation per two phenolate anions.



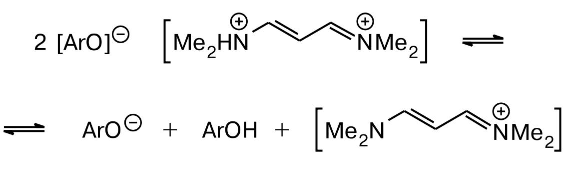
49

R = Me, C_5H_{11}, C_6H_{13}, C_7H_{15}.



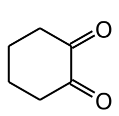
50

Study of the properties of these unusual salts by spectral and luminescence methods showed that in solution, these salts occur as the equilibrium

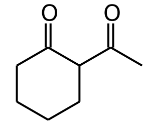


1.3. Reactions of aminals of unsaturated ω-amino aldehydes with diketones

In order to synthesize previously unknown ω,ω′-bis(dimethylaminopolyenyl) diketones (BDADK) in which the aminopolyene chains are separated by two rather than one carbonyl groups, the reactions of aminals **4** and **10** (n = 1) with 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-diketones **51—54** were studied.



51



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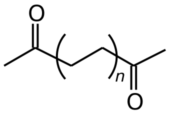
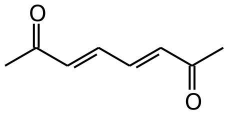


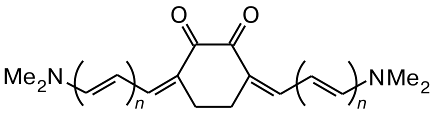
53



54

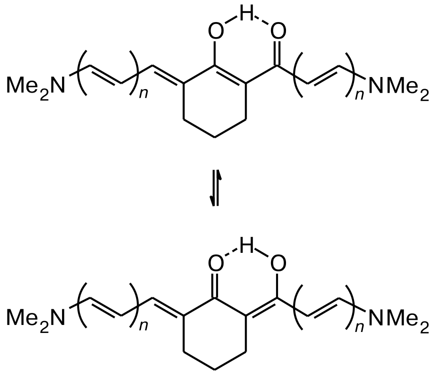
$n = 2, 3$.

This resulted in the synthesis of BDADK **55a,b**, **56a,b**, **57a,b**, and **58**.[32]



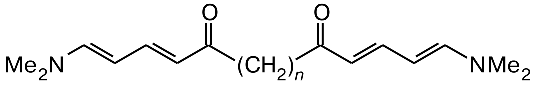
55a (65%)
55b (20%)

n = 1 (**a**), 2 (**b**).



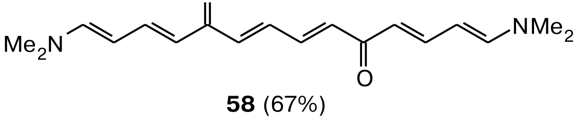
56a (50%)
56b (15%)

n = 1 (**a**), 2 (**b**).



57a (62%)
57b (35%)

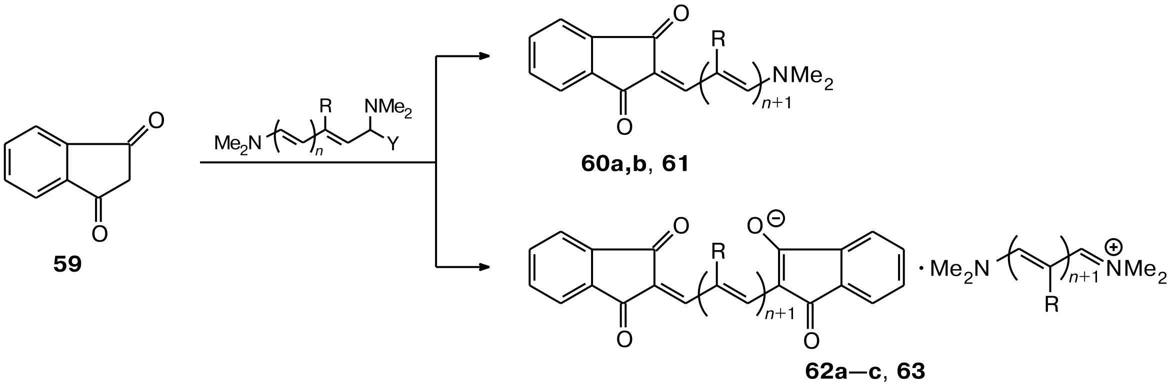
n = 2 (**a**), 3 (**b**).



58 (67%)

Compounds **56a,b** are chelates with an intramolecular hydrogen bond.

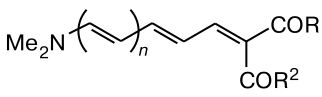
Scheme 15



Y = OMe, NMe$_2$;
60, 62: *n* = 0, R = H (**a**), Me (**b**), F (**62c**);
61, 63: *n* = 1, R = H.

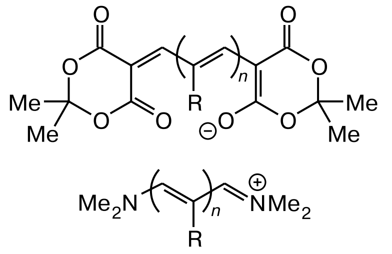
The mutual influence of ω-aminopolyene chromophores separated by two C=O groups was studied using electronic absorption spectroscopy.[32]

Unlike numerous examples of condensation of ω-dimethylamino aldehyde aminals with acyclic β-dicarbonyl compounds, which yield most often a single product



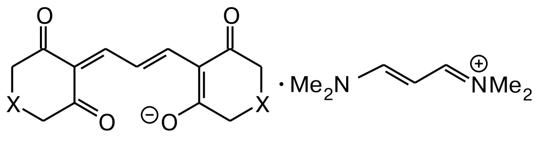
(see Section 1.1), the reaction of aminals with indandione **59** and some other cyclic β-diketones was found to proceed ambiguously. Thus, the reactions of aminals **4**, **8b**, and **10** (*n* = 1) with indandione carried out in benzene at 20 °C without a catalyst give ω-aminodiene- and -trienediones **60a,b** and **61** together with previously unknown trimethine- and pentamethineoxanine salts **62a—c** and **63** (Scheme 15).[47]

The formation of oxanine salts was unexpected; however, the set of data on the reactivity of aminals made it possible to represent the route for their formation.[47] Oxanine salts **64a,b**, **65a,b**, and **66** were prepared by the reactions of aminals **4**, **8**, and **10** with other cyclic β-diketones.[42,48]



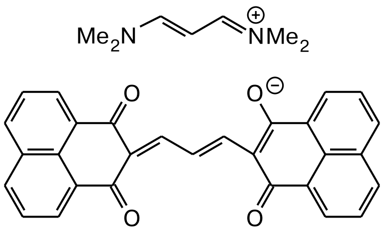
64a,b

R = Me, *n* = 1 (**a**);
R = H, *n* = 2 (**b**).



65a,b

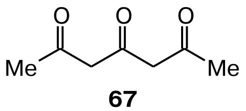
X = CH$_2$ (**a**), CMe$_2$ (**b**).



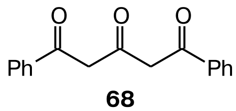
66

1.4. Synthesis of substituted phenols of a new type by the condensation of β-dimethylaminoacrolein aminals with triketones

The reactions of aminals **4** and **8** with triketones **67** and **68** were studied in order to obtain amino-substituted polyene triketones.

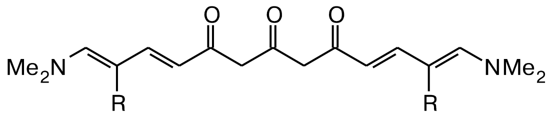


67

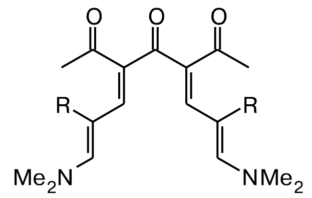


68

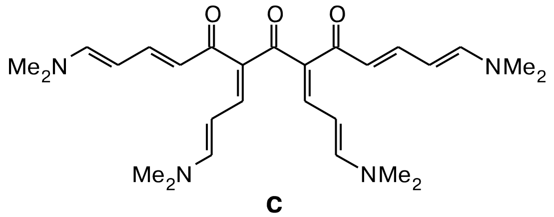
Since triketone **67** contains several reactive sites (two methyl and two methylene groups), one could expect the formation of three types of amino polyene triketones (**A**, **B**, and **C**).



A



B

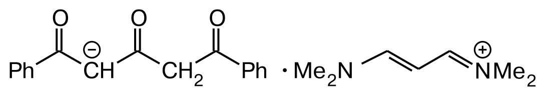


C

However, contrary to expectations, the condensation of aminals **4** and **8** (R = Me, Ph) with triketone **67** under mild conditions (a **4** or **8** to **67** ratio of 3 : 1, 60—70 °C, benzene, 30 min) resulted in a new type of polyfunctionally substituted phenols **69a—c**, stabilized by an intramolecular hydrogen bond,[49] which formed in good yields (Scheme 16).

Probably, the reaction of aminals **4** and **8** with triketone **67** affords initially triketones **70a—c**, which undergo intramolecular cyclization accompanied by 1,6-deamination, being converted into phenols **71a—c**, which react with excess aminals to give phenols **69a—c**. When the **4** or **8** to **67** ratio was 2 : 1, phenols **71a—c** were isolated.

The reaction of diphenyl triketone **68** with aminal **4** gives only the trimethine salt.



2. Synthesis of new polychromophore systems from dimethylaminomethylenemalonaldehyde bis-*N*,*O*-acetal

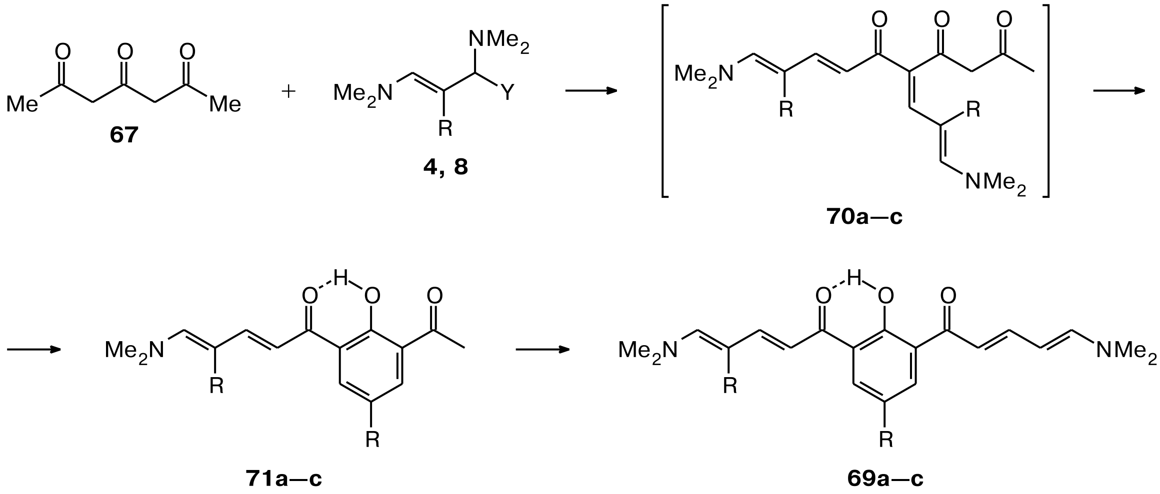
As shown above, aminals of conjugated ω-dimethylamino aldehydes cannot be used to prepare compounds containing more than two aminopolyene chromophores.

We believed that the possibility of preparing various types of polychromophore systems can be embodied with the aid of dimethylamino dialdehyde bis-*N*,*O*-acetals, because the molecules of these compounds incorporate three reactive sites. To this end, we developed a method for the preparation of a previously unknown reagent, dimethylaminomethylenemalonaldehyde bis-*N*,*O*-acetal (DMBA) **72** [14,15] and studied its reactions with various ketones, diketones, and CH-acids.

2.1. Reactions of dimethylaminomethylenemalonaldehyde bis-N,O-acetal with ketones. New route to the pyrrole ring

Study of the condensation of bis-*N*,*O*-acetal **72** with acetone, cyclopentanone, and cyclohexanone showed that the reaction is accompanied by an unusual intramolecular cyclization, which gives previously unknown β,β′-bis(*N*-methylpyrrol-3-yl)divinyl ketones **73a—c**.[15,41,50,51]

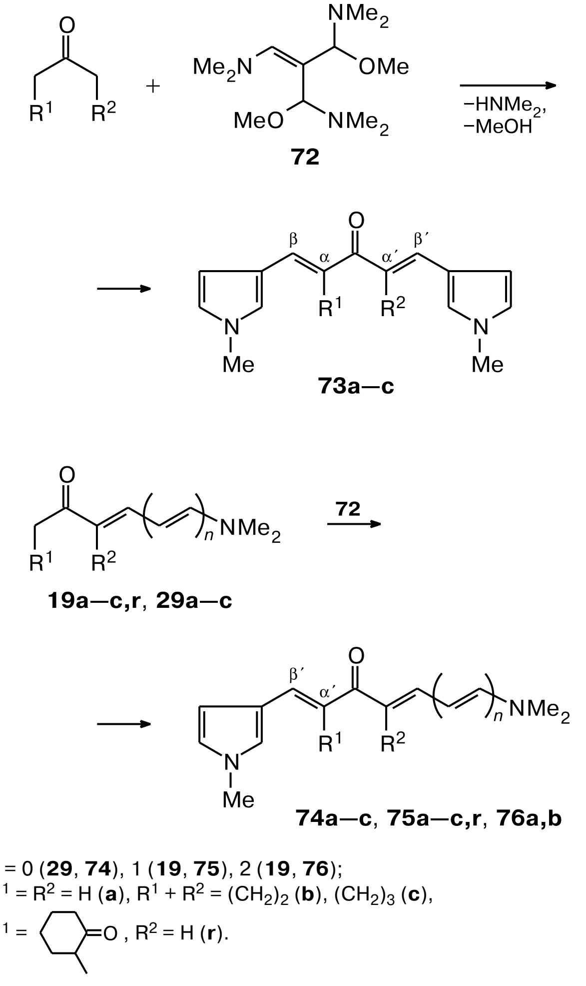
Scheme 16



Y = OMe, NMe_2;
R = H (**a**), Me (**b**), Ph (**c**).

The reaction of bis-*N*,*O*-acetal **72** with unsaturated dimethylamino ketones **29a—c** and **19a—c,r** was also accompanied by intramolecular cyclization. This provided the first synthesis of cyclic and acyclic cross-conjugated ketones containing an *N*-methylpyrrole ring in the β′-position **74a—c**, **75a—c,r**, and **76a,b** (Scheme 17).[41,50,51]

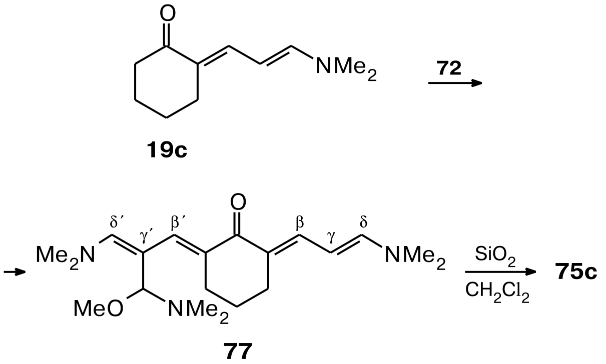
Scheme 17



n = 0 (**29**, **74**), 1 (**19**, **75**), 2 (**19**, **76**);
$R^1 = R^2$ = H (**a**), $R^1 + R^2 = (CH_2)_2$ (**b**), $(CH_2)_3$ (**c**),
R^1 = =O , R^2 = H (**r**).

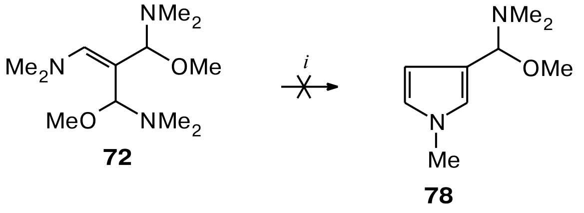
In the case of condensation of bis-*N*,*O*-acetal **72** with δ-dimethylaminodienone **19c**, it was possible to isolate the intermediate crystalline product **77**, which contained an *N*,*O*-acetal group in the γ′-position. On treatment with silica gel in a CH_2Cl_2 solution, this compound was converted into cross-conjugated polyene ketone **75c** in 50% yield (Scheme 18).[51]

Scheme 18



The isolation of the intermediate product **77** may indicate that cyclization giving the *N*-methylpyrrole fragment taking place during the formation of ketones **73a—c**, **74a—c**, **75a—c,r**, and **76a,b** occurs in the products of condensation of DMBA **72** with ketones rather than in the initial DMBA **72**. It was shown in special experiments that heating of bis-*N*,*O*-acetal **72** does not afford *N*-methylpyrrole **78** (Scheme 19).

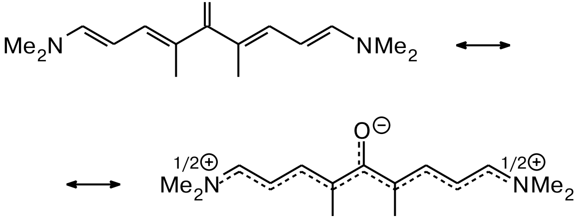
Scheme 19



i. 80—120 °C, 0.5 h.

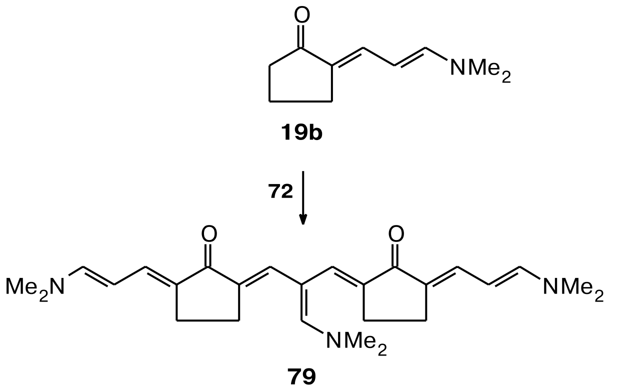
Thus, condensation of bis-*N*,*O*-acetal **72** with ketones is a new route to substituted pyrroles, which is based on the reaction of the *N*,*O*-acetal functional group with one of the methyls in the dimethylamino group, resulting in the formation of the C(2)—C(3) bond of the pyrrole ring. This reaction appears to proceed very easily, because even with an excess of amino ketone in the reaction mixture, the *N*,*O*-acetal group in the intermediate BDAK does not react with a second ketone molecule but is involved in the pyrrole ring construction.

The elimination of two protons from the methyl radical of the NMe_2 group in the intermediate BDAK of type **77** leading to the *N*-mehylpyrrole ring is unusual and can be explained by specific properties of BDAK, caused by a substantial contribution of an ionic structure to the electronic structure of BDAK.



Unlike the synthesis of polyene ketones containing an *N*-methylpyrrole ring, we found only one example where the reaction of bis-*N*,*O*-acetal **72** with ketone **19b** (a **72** : **19b** ratio of 1 : 2) gave unknown polyene tris-dimethylamino diketone **79** (Scheme 20).[51]

Scheme 20



2.2. Reaction of dimethylaminomethylenemalonaldehyde bis-N,O-acetal with 1,3-indandione

It was shown above that condensation of the aminals of conjugated ω-dimethylamino aldehydes with indandione gives rise to conjugated 2-(ω-dimethylamino-alkenylidene)-1,3-indandiones and trimethine- and pentamethineoxanine salts. In view of the high reactivity of DMBA **72**, we studied its reaction with indandione. It was found that bis-*N*,*O*-acetal **72**, containing three reactive sites (two *N*,*O*-acetal functions and one NMe$_2$ group), can react with indandione at one, two, or three sites.[52] Indeed, the reaction of bis-*N*,*O*-acetal **72** with indandione **59** can follow one of three routes, depending on the conditions, most of all, on the reactant ratio, giving rise to previously unknown products, namely, dioxoaldehyde **80**, tetraketone **81**, or oxanine salt **82**, containing three indandione fragments (Scheme 21).

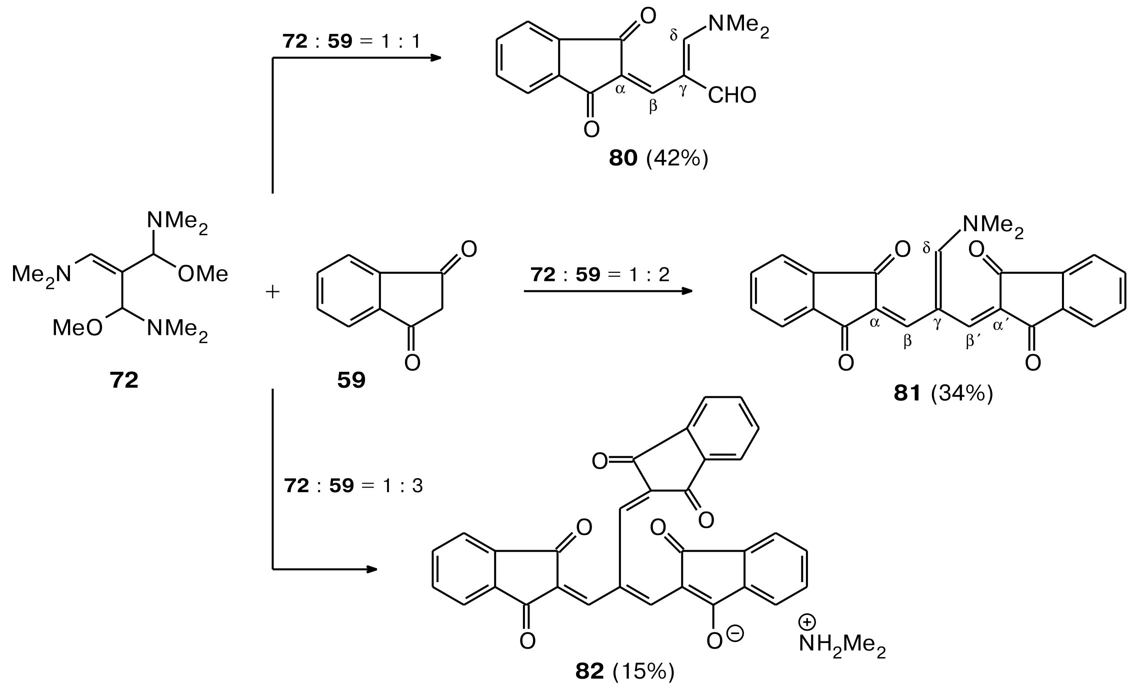
The electronic absorption spectra of these compounds show that the presence of conjugation between four carbonyl groups and the cross-conjugated system consisting of three double bonds in tetraketone **81** results in an appreciable shift of the absorption maximum (Δλ ~ 100 nm) with respect to that for diketone **60a**, containing one indandione fragment.

2.3. Reactions of dimethylaminomethylenemalonaldehyde bis-N,O-acetal with CH-acids

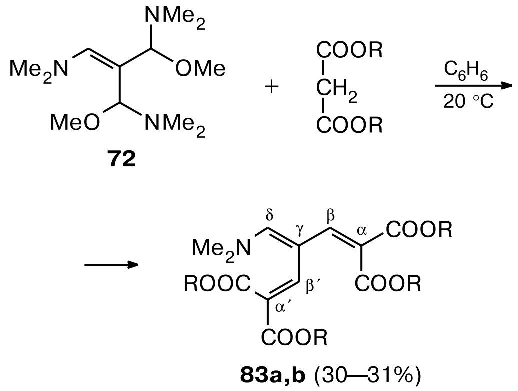
We have studied the reactivity of bis-*N*,*O*-acetal **72** with respect to alkyl malonates, malonodinitrile, and alkyl cyanoacetates. Condensation of bis-*N*,*O*-acetal **72** with two moles of alkyl malonate resulted in the previously unknown trienoic tetraesters **83a,b** (Scheme 22).[14,15]

The reaction of bis-*N*,*O*-acetal **72** with malonodinitrile **84** can follow two pathways that, depending on the conditions, give rise to either triene δ-dimethylamino-substi-

Scheme 21



Scheme 22



R = Me (**a**), Et (**b**).

tuted tetranitrile **85** or cross-conjugated salt **86** containing four nitrile groups[53] (Scheme 23).

The decision between the structures of aldehyde **87** and enol form **86** in favor of the latter was based on NMR data.

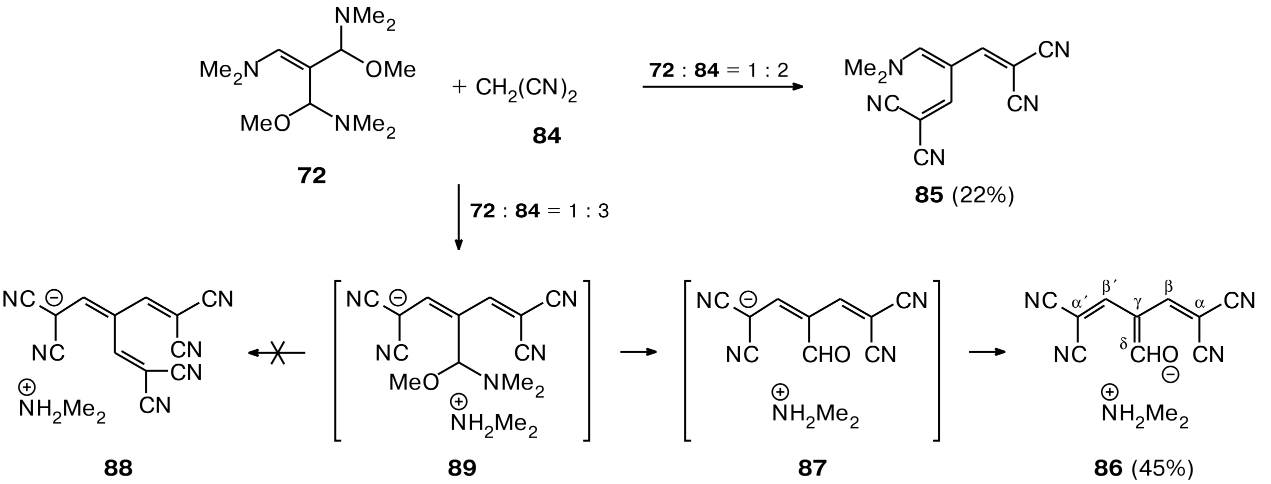
Salt **88** containing six CN groups, whose formation could be expected in the condensation of intermediate **89** with malonodinitrile **84**, was not detected.

The reaction of bis-*N*,*O*-acetal **72** with three alkyl cyanoacetate molecules proceeds very smoothly involving all three reactive functions of DMBA **72** to afford cross-conjugated salts **90**, containing three nitrile groups, in very high yields (84—87%). δ-Dimethylamino-substituted triene nitriloesters **91a,b** were also obtained in moderate yields (10%) (Scheme 24).[53]

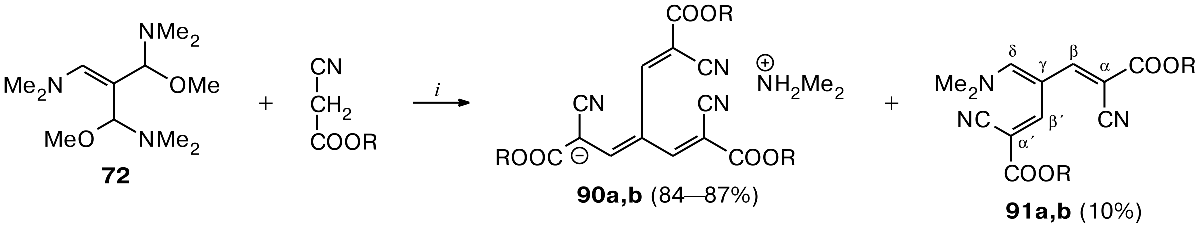
As follows from comparison of the electronic absorption spectra of cross-conjugated triene δ-dimethylamino compounds **85** and **91a,b** with the spectra of the corresponding diene derivatives **12** (*n* = 0) and **3** ($R^1 = R^2$ = Me; R^3 = Me, Et; X = CN) described above, the introduction of the $—CH=C(CN)_2$ or —CH=C(CN)COOMe fragment into the γ-position induces a substantial bathochromic shift (Δλ = 17—19 nm), which is indicative of enhancement of the donor-acceptor interaction between the terminal substituents in the triene derivatives.

Meanwhile, the absorption maxima in the electronic spectra of tetraesters **83a,b** and diesters **3** ($R^1 = R^2$ = Me;

Scheme 23



Scheme 24



R = Me (**a**), Et (**b**).

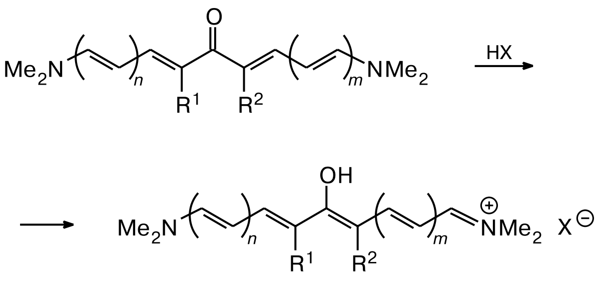
i. C_6H_6 or Et_2O, 20 °C, 5—10 min.

X = COOR^3, R^3 = Me, Et) are almost identical. This can be due to the fact that not all the bulky carbomethoxy groups present in tetraesters **83a,b** occur in the plane of the cross-conjugated system and are involved in conjugation. This assumption was confirmed by X-ray diffraction analysis, which made it possible to determine the geometric parameters and the conformation of tetraester **83a** and demonstrated that only two of the four carbomethoxy groups lie in the plane of the cross-conjugated system, while the other two groups are eliminated from the chain of conjugation.

3. Protonation and alkylation of ω,ω´-bis(dimethylaminopolyenyl) ketones. Synthesis of alkoxypolymethine salts

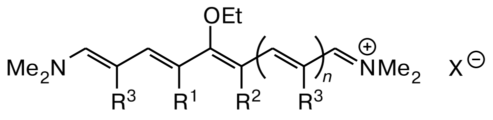
ω,ω´-Bis(dimethylaminopolyenyl) ketones (BDAK) are very easily protonated at the oxygen atom (Scheme 25). Elongation of the conjugation chain results in substantial color deepening, accompanied by a bathochromic shift of the maximum in the electronic absorption spectrum ($\Delta\lambda_{max}$ = 100—105 nm).[17]

Scheme 25



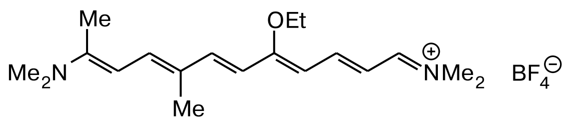
Owing to this feature, inherent in any of the BDAK, they proved to be highly sensitive indicators for the presence of traces of acids in organic solvents or reagents. The content of the acid in the solvent can be roughly estimated based on the solution color. A spectrophotometric procedure is used for more accurate determination of the concentration of free acid (determination limit 10^{-7} mol L^{-1}). This procedure is suitable for determination of the contents of free acid in aprotic solvents with a low dielectric constant (DC < 10) for which direct and highly sensitive methods are missing.[25—27].

Alkylation of BDAK and their analogs with terminal *N*-methylpyrrole rings occurs, like protonation, at the oxygen atom and gives stable crystalline alkoxypolymethine salts **92a—n**, **93**, **94b,c**, **95a—c**, and **96a—c** in high yields[15,23—25] (Table 1). The alkylating reagents used were $Et_3O^+BF_4^-$, RI, and $(RO)_2SO_2$. The reagent used most widely is $Et_3O^+BF_4^-$, which allows alkylation to be carried out under very mild conditions (anhydrous CH_2Cl_2, −10 to −5 °C).

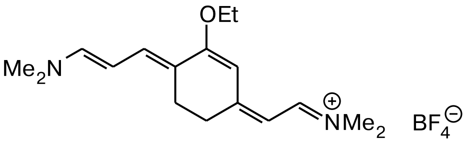


92a—m

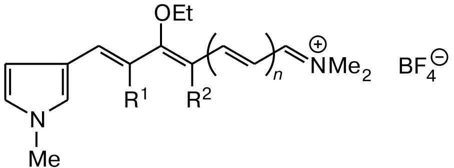
n = 1, R^3 = H, R^1 = R^2 = H, (**a**), R^1 + R^2 = $(CH_2)_2$ (**b**), $(CH_2)_3$ (**c**), $(CH_2)_4$ (**d**), $(CH_2)_2CHMe$ (**e**), $CH_2CH(Me)CH_2$ (**f**), $CH_2CH(Me)CH(Me)$ (**g**), $CH_2OCH(Me)$ (**h**);
R^1 = H, R^2 = Me (**i**), R^1 + R^2 = $(CH_2)_2$, R^3 = F (**j**);
R^1 + R^2 = $(CH_2)_3$, R^3 = F (**k**);
n = 2, R^1 + R^2 = $(CH_2)_3$, R^3 = H (**l**);
n = 0, R^1 = R^2 = R^3 = H (**m**);
X = BF_4, $MeSO_4$, I.



92n

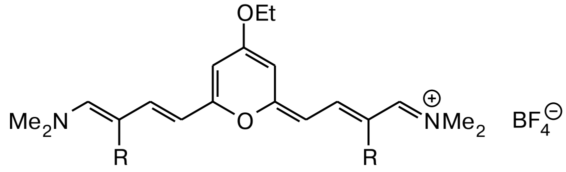


93



94b,c, **95a—c**

n = 0 (**94**), 1 (**95**);
R^1 = R^2 = H (**a**), R^1 + R^2 = $(CH_2)_2$ (**b**), $(CH_2)_3$ (**c**).

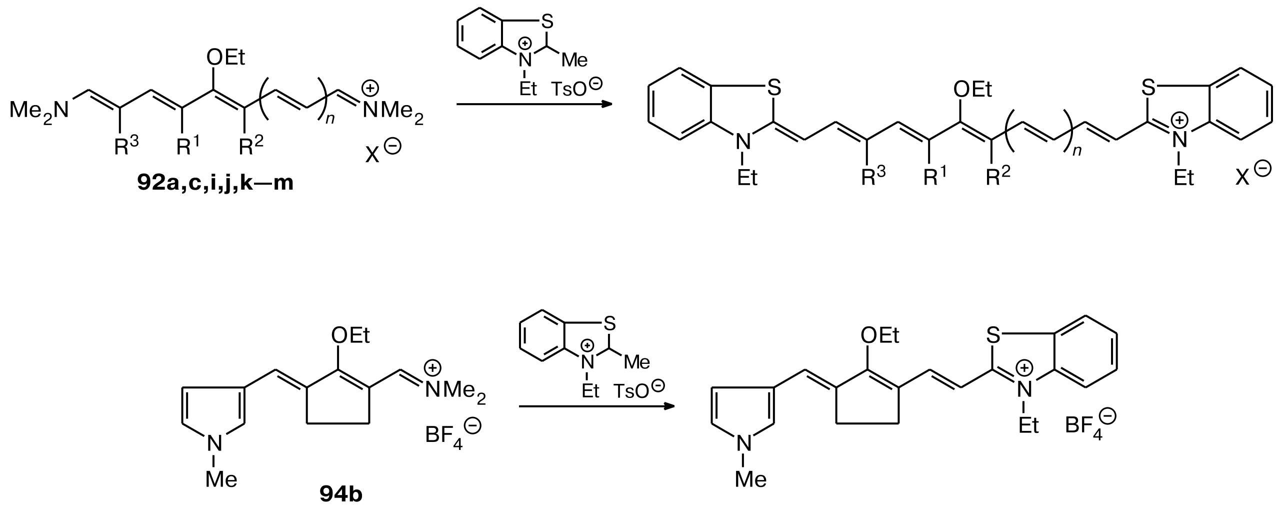


96a—c

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

Polymethine salts are the major intermediate products in the synthesis of cyanine dyes, which have found exten-

Scheme 26



92a,c,i,j,k—m

94b

sive use as sensitizers for silver halide emulsions in photographic materials and for quantum electronics. Dyes with extended systems of conjugated double bonds are especially significant for the development of materials used in the infrared and far-infrared spectral regions (900—1300 nm).

Table 1. Synthesis of alkoxypolymethine salts

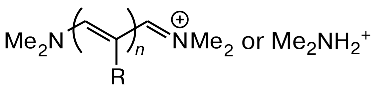
Salt	Ketone	Yield (%)	Method*	Ref.
92a	**20a**	73	A	23
92b	**20b**	96	B	23
92c	**20c**	96, 86	A, B	23
92d	**20d**	65	C	23
92e	**20e**	89	C	23
92f	**20f**	95	C	23
92g	**20g**	67	C	23
92h	**20h**	78	C	23
92i	**20i**	80	A	23
92j	**21f**	90	A	40
92k	**21h**	90	A	40
92l	**25d**	85	A	54
92m	**32a**	93	A	23
92n	**34a**	85	A	15
93	**33a**	95	A	69
94b	**74b**	92	A	15
94c	**74c**	58	A	15
95a	**75a**	66	A	15
95b	**75b**	17	A	15
95c	**75c**	80	A	15
96a	**45a**	62	A	15, 45
96b	**45b**	27	A	15, 45
96c	**45c**	34	A	15, 45

* Alkylation with $Et_3O^+BF_4^-$ (A), KI (B), Et_2SO_4 (C).

Polymethine salts **92a,c,i,j,k—m** [40,54] and **94b** [15] were employed to synthesize new mesoalkoxythiapenta- and thiahexacarbocyanine dyes (Scheme 26).

4. Synthesis of cation-anionic polymethine dyes with the anionic components based on oxanine salts and salt-like conjugated polynitriles

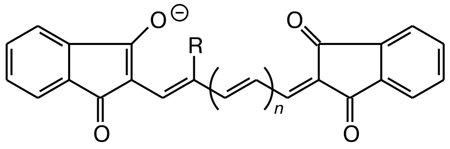
The oxanine salts (see Sections 1.3 and 2.2) and salt-like conjugated polynitriles (see Sections 1.1 and 2.3) are anionic dyes. We found that the cation


$Me_2N(CH{=}C(R))_nCH{=}\overset{+}{N}Me_2$ or $Me_2NH_2^+$

in these compounds can be easily replaced by the cyanine dye cation; this reaction affords cation-anionic dyes of a new type in high yields.[36,40,52,53] The presence of chromophores in both the cationic and anionic parts of these dyes gives rise to two absorption bands with high extinction coefficients in the electronic spectrum.

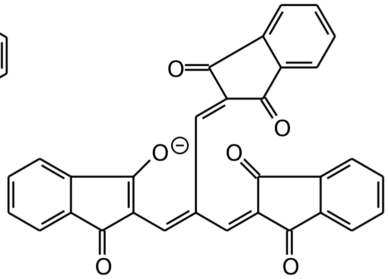
By using various combinations of oxanine salts **62a—c**, **63**, **82**, **65b**, **64a,b**, and **66** or salt-like polynitriles **13** ($n = 0$, R = H, Me, CN, F; $n = 1$, R = H; $n = 2$, R = H), **86**, and **90a** and cyanine dyes C_1—C_{11}, we synthesized a large set of cation-anionic dyes A_iC_j that absorb over a broad spectral range (Table 2). The structures of the anions and the cations in these dyes are as follows:

Anion structure

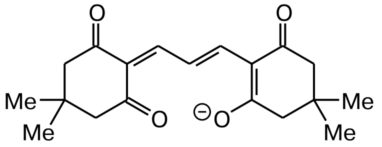


A_1—A_4

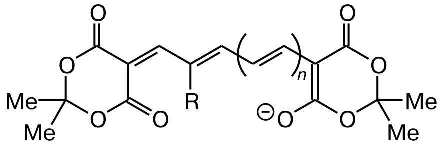
n = 0, R = H (A_1), Me (A_2), F (A_3);
n = 1, R = H (A_4)



A_5

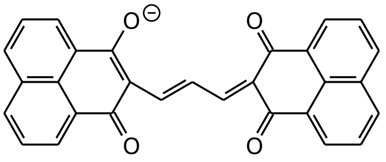


A_6

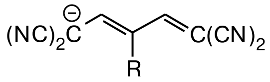


A_7, A_8

n = 0, R = Me (A_7); n = 1, R = H (A_8)

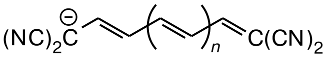


A_9



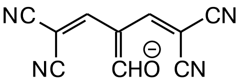
A_{10}—A_{13}

R = H (A_{10}), Me (A_{11}), CN (A_{12}), F (A_{13})

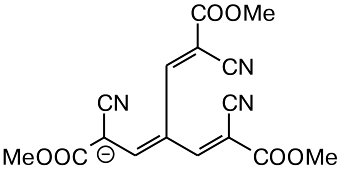


A_{14}, A_{15}

n = 1 (A_{14}), 2 (A_{15})

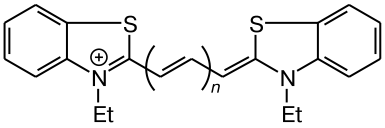


A_{16}



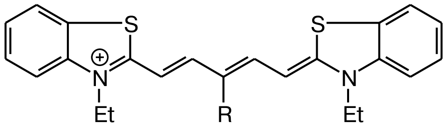
A_{17}

Cation structure



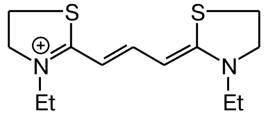
C_1, C_2

n = 0 (C_1), 1 (C_2)

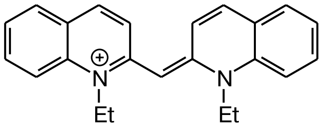


C_3, C_4

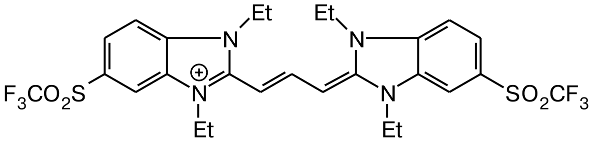
R = H (C_3), Me (C_4)



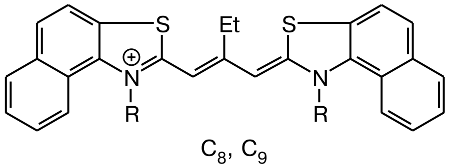
C_5



C_6

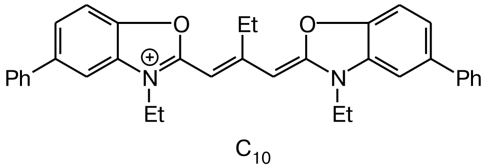


C_7

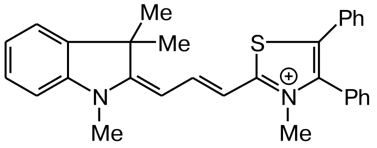


C_8, C_9

R = Me (C_8), Et (C_9)



C_{10}



C_{11}

Table 2. Spectral characteristics of the cation-anionic polymethine dyes prepared by two methods

Method A

Anion	Cation	λ_{max}^{abs}/nm		
		in EtOH	in $CHCl_3$	in toluene
A_1	C_1	555 An 420 Cat	571, 425	575, 427
A_1	C_2	555 An 560 Cat	—	527, 566
A_1	C_3	555 An 655 Cat	560, 680	555, 668
A_1	C_5	555 An 445 Cat	561, 446	564, 448
A_1	C_6	555 An 495 Cat 530 Cat	570, 462, 500	—
A_2	C_3	560 An 655 Cat	543, 657	568, 682
A_2	C_4	560 An 653 Cat	554, 664	561, 666
A_3	C_4	570 An 653 Cat	574, 665	574, 666
A_4	C_4	655 An and Cat	600, 666	598, ~670 (sh)
A_5	C_2	540 An 560 Cat	—	— *
A_5	C_3	565 An 655 Cat	—	—
A_5	C_8	555 An 575 Cat	—	—
A_6	C_3	510 An 655 Cat	510, 660	—
A_7	C_3	467 An 655 Cat	480, 680	471, 675
A_8	C_4	560 An 655 Cat	—	—
A_9	C_3	565 An 655 Cat	—	—

Method B

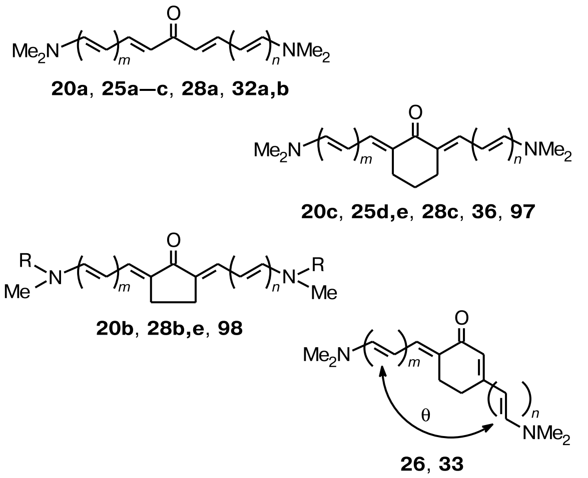
Anion	Cation	λ_{max}^{abs}/nm		
		in EtOH	in $CHCl_3$	in toluene
A_{10}	C_2	440 An 560 Cat	450, 565	446, 574
A_{10}	C_5	444 An and Cat	420, 446	420, 452
A_{11}	C_5	443 An and Cat	420, 448	420, 458
A_{12}	C_5	416 An 444 Cat	420, 455	408, 462
A_{13}	C_4	455 An 653 Cat	460, 662	458, 675
A_{14}	C_2	550 An and Cat	567	535, 555
A_{14}	C_7	530 An and Cat	531	531, 549
A_{14}	C_{11}	545 An and Cat	550	520, 549
A_{16}	C_2	565 An and Cat	—	—
A_{16}	C_{10}	485 An 510 Cat	—	—
A_{17}	C_2	468 An 560 Cat	—	—
A_{17}	C_3	468 An 655 Cat	—	—
A_{17}	C_6	470 An 532 Cat	—	—
A_{17}	C_8	470 An 585 Cat	—	—
A_{17}	C_9	470 An 585 Cat	—	—
A_{17}	C_{10}	470 An 510 Cat	—	—

Note. Method A. Equimolar amounts of the oxanine salt and cyanine dye tosylate are dissolved in ethanol or in an ethanol/dichloromethane mixture. At 20 °C or on cooling, the cation-anionic dye crystallizes, while the tosylate $Me_2N-(CH=CH)_n-CH=C(R)-CH=NMe_2{}^+TsO^-$ or $Me_2NH_2{}^+TsO^-$ remains in the mother liquor. Method B. Cyanine dyes were used as halides or tosylates. The resulting dye separates as a crystalline solid either immediately or after the removal of the solvent and addition of a small amount of water.

5. Effects of chromophore interaction in the photonics of ketocyanines and polymethine salts based on them

The absorption and fluorescence properties of BDAK (ketocyanines) are listed in Table 3. It can be seen that these compounds exhibit long-wavelength absorption bands in the visible spectral region characterized by high extinction coefficients typical of dyes. The absorption bands of symmetrical ketocyanines (containing two aminopolyene fragments of the same length) are shifted bathochromically with respect to those of the unsymmetrical BDAK with the same total length of the polyene chain (*cf.* ketocyanines **32b** and **20a**; **25b** and **28a**; **25e** and **28c**; even unsymmetrical BDAK **25c** in which the whole chain is longer than that in symmetrical BDAK **28a** has a shorter-wavelength absorption spectrum than **28a)**. This feature of ketocyanines can be explained in terms of the theory of chromophore interaction based on dipole—dipole interaction.[55,56] Previously, this theory has been used successfully, in particular, to describe the absorption spectra and interpret the photochemical behavior of a number of biscyanine dyes.[55—57] The grounds for

Table 3. Absorption (λ_{max}^{abs}) and fluorescence (λ_{max}^{fl} in *n*-propanol) maxima and extinction coefficients (ε) for ketocyanines (in ethanol)



20a, **25a—c**, **28a**, **32a,b**

20c, **25d,e**, **28c**, **36**, **97**

20b, **28b,e**, **98**

26, **33**

R = Me (**20b**, **28b,e**), Ph (**98**)[17]

Keto-cyanine	*m*	*n*	λ_{max}^{abs} /nm	$\varepsilon \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	λ_{max}^{fl} /nm
20a	1	1	470	6.4	540
20b	1	1	508	8.16	570
20c	1	1	450	5.45	550
25a	1	2	507	8.55	625
25b	1	3	522	10.4	—
25c	1	4	530	—	—
25d	1	2	512	6.6	625
25e	1	3	532	—	—
26	1	2	505	7.85	—
28a	2	2	550	8.66	673
28b	2	2	585	5.91	700
28c	2	2	550	7.9	668
28e	3	3	625	—	—
32a	0	1	430	7.27	—
32b	0	2	450	5.45	—
33	1	1	469	6.68	565
36	2	3	575	—	—
97 [18]	0	1	440	5.64	—
98 [17]	1	1	503	—	580

such interpretation stem from the π-electronic structure of ketocyanine. This structure can be described as being intermediate between two canonical resonance structures (Fig. 1, structures **I** and **II**). Structure **I** has alternating bonds in the polyene chain and the lack of charge separation. Structure **II** has fully equalized polyene bonds (full π-electron conjugation over the whole polyene chain) and is characterized by charge separation (a zwitter-ionic structure with a negative charge on the oxygen atom and positive charges on two nitrogen atoms). The latter structure is typical of a cationic polymethine salt having the longest-wavelength absorption spectrum; therefore, the shift of the real ketocyanine structure **III** toward structure **II** would induce a bathochromic shift of the ketocyanine absorption band. This shift may be due, in particular, to the solvation of ketocyanine in polar and, especially, proton-donating solvents that specifically solvate the carbonyl group, resulting in the enhancement of charge separation in the ketocyanine molecule. This accounts for the pronounced positive solvatochromism[19,20] and thermochromism of ketocyanines,[21] which are observed experimentally.

It is known that the spectral properties of polymethine dyes are well described by the "free electron" model.[58] According to this model, the dye chromophore is described as a potential box whose width corresponds to the chromophore length. Then the ketocyanine molecule can be described as two potential boxes corresponding to two aminopolyene fragments (two chromophores) separated by a potential barrier (see Fig. 1). This barrier is caused by the presence of two single bonds at the carbonyl group of ketocyanine; the highest barrier is found in **I**, while in structure **II** with full (barrierless) π-electron conjugation, the barrier is missing. Thus, the real ketocyaine structure has an average potential barrier to conjugation, which decreases with increase in solvation. The increase in solvation entails gradual coalescence of the two aminopolyene chromophores into a single chromophore, *i.e.*, a conjugated polymethine system responsible for the longest-wavelength absorption.

The singlet excited states of the chromophores in ketocyanine can interact in two ways, either by dipole—dipole interaction or by conjugation through the potential barrier. The former corresponds to the exciton interaction in the Davydov model[59] and the latter, to the electron tunneling through the barrier. The dipole—dipole interaction brings about symmetrical splitting of the singlet levels of the chromophores;[58] the conjugation leads to further separation and lowering of these levels[57] (Fig. 2). The highest interaction energy (and the greatest splitting of the excited singlet levels) is observed for dyes with identical chromophores (symmetrical). In the linear ketocyanines **20**, **25**, **28**, **32**, **36**, and so on, the $S_0 \leftrightarrow S_2$ radiative transition is forbidden, while the $S_0 \leftrightarrow S_1$ transition is allowed. The chromophore interaction in linear ketocyanines reveals as a bathochromic shift of the long-wavelength absorption band ($S_0 \rightarrow S_1$). Thus, the longer-wavelength position of the absorption band of symmetrical ketocyanines compared to that for unsymmetrical ketocyanines can be attributed to stronger interaction of the chromophores in symmetrical ketocyanines.

In nonlinear ketocyanines, both transitions, $S_0 \leftrightarrow S_1$ and $S_0 \leftrightarrow S_2$, are allowed and the energy splitting $\Delta\nu$ between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption bands can serve as a measure of interaction of the chromophores in these molecules. Indeed, the $\Delta\nu$ value for nonlinear symmetrical ketocyanine **33** is greater than for unsymmetrical BDAK **26** (Fig. 3; $\Delta\nu_1$ = 4400 cm^{-1}, $\Delta\nu_2$ = 3500 cm^{-1}).

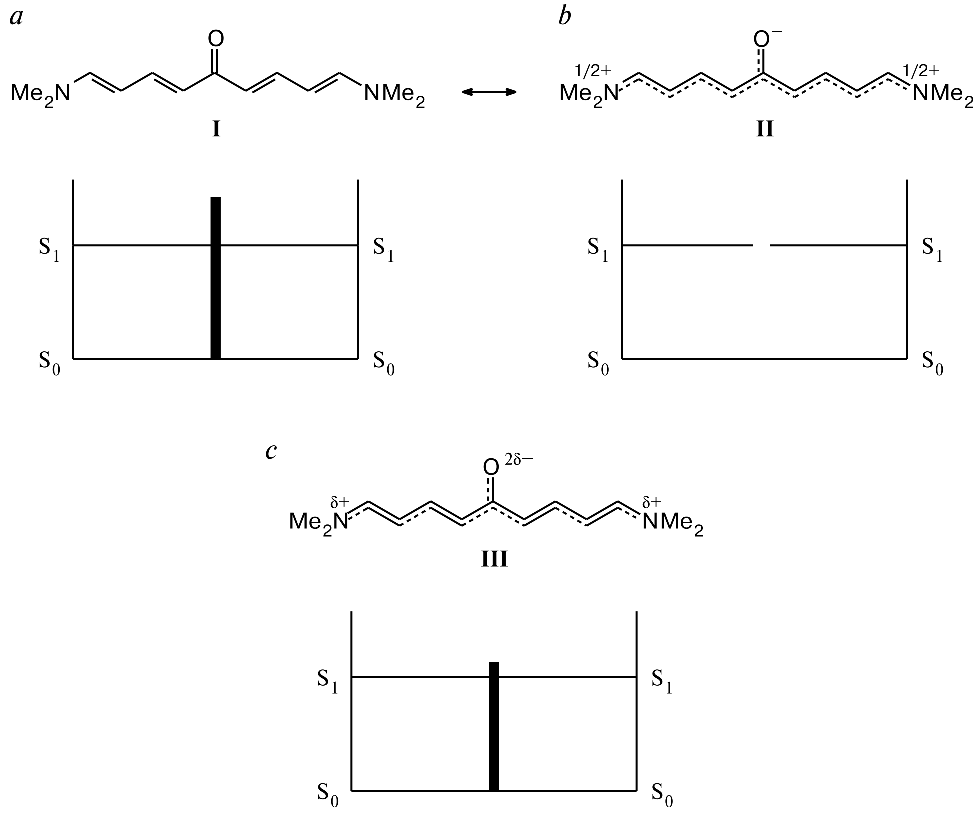


Fig. 1. π-Electronic structure of ketocyanine dyes: (*a*) structure **I**, high potential barrier; (*b*) structure **II**, no potential barrier; (*c*) real structure **III**, average potential barrier.

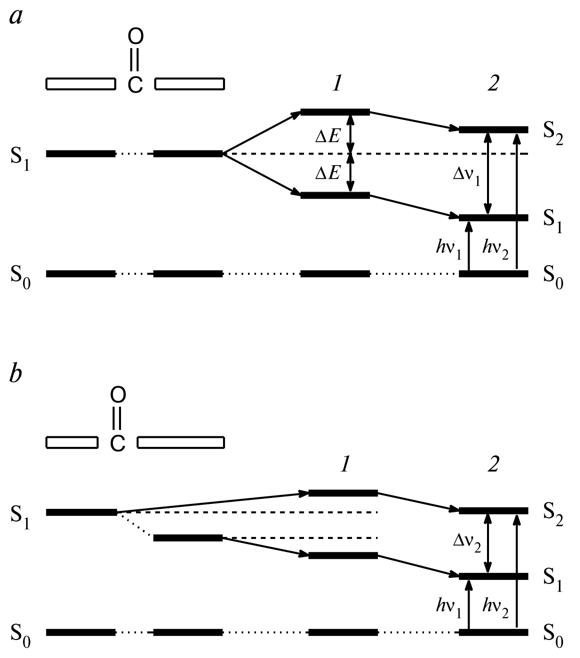


Fig. 2. Interaction of chromophores (in excited singlet states) in symmetrical (*a*) and unsymmetrical (*b*) ketocyanines. (*1*) dipole—dipole interaction, (*2*) dipole—dipole interaction + conjugation.

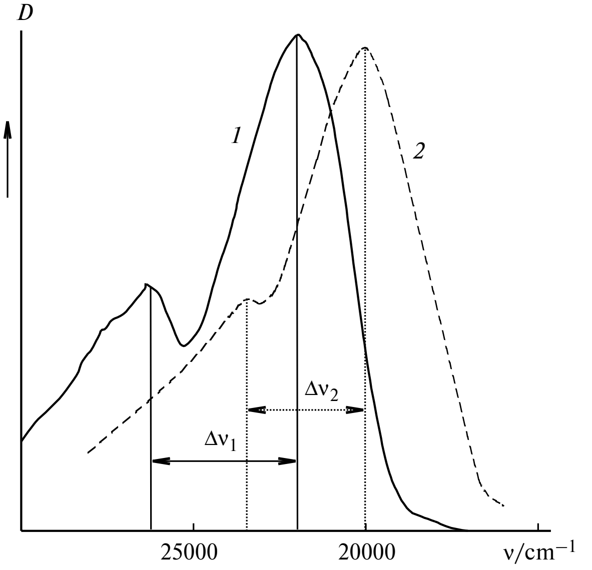


Fig. 3. Absorption spectra of dyes **33a** (*1*) and **26** (*2*) in *n*-propanol.

Let us consider the properties of ketocyanines with the central pyranone fragment **45a—d**. The absorption spectra of these compounds exhibit specific features that

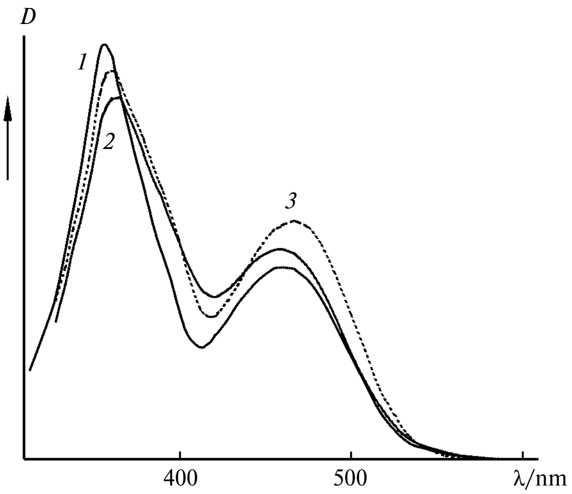
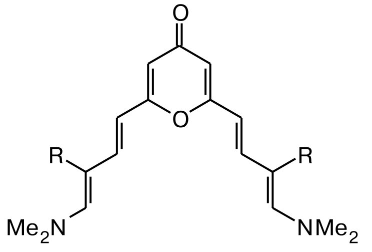


Fig. 4. Absorption spectra of dyes **45a** (*1*), **45b** (*2*), and **45c** (*3*) in Pr^{i}OH.

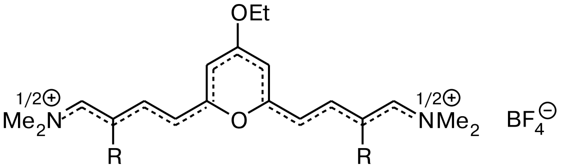
sharply distinguish them from the ketocyanines studied previously. Whereas the longest-wavelength absorption band (located in the visible or near-UV region) in the spectra of the latter is most intense (the extinction coefficient can be as high as 10^5 L mol^{-1} cm^{-1}; see Table 3), the spectra of ketocyanines **45a—d** contain a short-wavelength band (shifted by about 100 nm with respect to the long-wavelength band), which is substantially more intense than the long-wavelength band (Fig. 4).^{45} This unusual spectral pattern found for compounds **45a—d** can also be interpreted in terms of the chromophore interaction theory. The absorption spectra of such compounds are split, in the general case, into two bands whose intensity is related to the angle θ between the chromophores, in particular, if the angle θ is obtuse, the short-wavelength band is less intense than the long-wavelength one, while for an acute angle, the opposite is true.^{55} In particular, for linear ketocyanines (where θ ≈ 180°), virtually only the long-wavelength absorption band is observed and the intensity of the short-wavelength band is slight (the short-wavelength transition is forbidden). Meanwhile, the absorption spectra of the ion pairs of the cation-anionic polymethine dyes where the chromophores are parallel to each other (θ ≈ 0) and strongly interact with each other exhibit an intense short-wavelength band, the long-wavelength band being appreciably depressed (see Ref. 60 and Section 6). The spectra of ketocyanines **33** and **26**, in which the chromophores are arranged at the angle θ ≈ 120°, have both bands, the long-wavelength band being more intense than the short-wavelength one (see Fig. 3). In the case of ketocyanines **45a—d**, the short-wavelength band is more intense, which is in line with the acute angle between the chromophores. Taking into account the fact that the protons at the double bonds in ketocyanines **45a—d** occupy *trans*-positions and the whole molecules exist mainly as *S-trans*-conformers, the molecules of ketocyanines **45a—d** can be described as structures with a acute angle θ consistent with the observed absorption spectra.



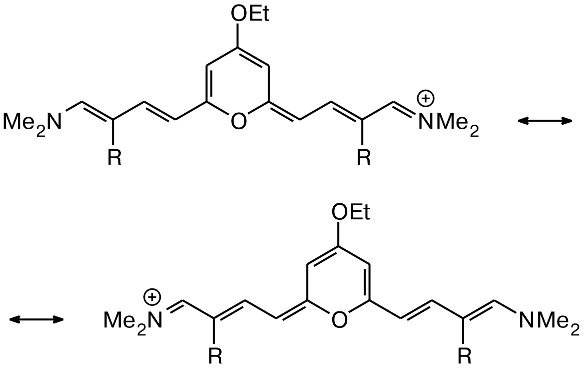
45a—d

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

It is noteworthy that the absorption spectra of ethoxytridecamethine salts **96a—c** are also unusual. Salts **96a—c**, like other similar polymethine salts,^{61} are assumed to have a symmetrical π-electron structure of a perfect polymethine dye with fully equalized bonds in the polymethine chain, this structure being intermediate between two resonance structures.



96a—c



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

Usually, salts of this type give rise to a narrow long-wavelength absorption band with high intensity (ε ~ 10^5 L mol^{-1} cm^{-1}) and no significant short-wavelength absorption in the visible or near-UV region.^{58} However, the absorption spectra of salts **96a—c**, similarly to those of ketocyanines **45a—c**, do exhibit a short-wavelength band, which is much more intense (for **96a** λ_{max} = 378 nm, ε_1 = 136800 L mol^{-1} cm^{-1}) than the long-wavelength one (for **96a**, λ_{max} = 615 nm, ε_2 = 42900 L mol^{-1} cm^{-1}; Fig. 5). These spectral features can

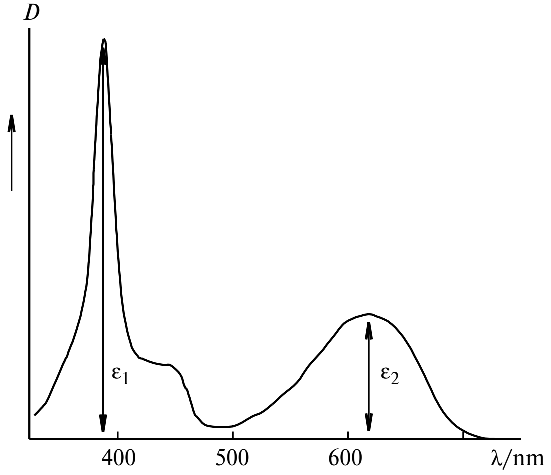
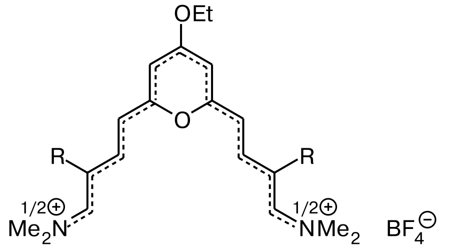
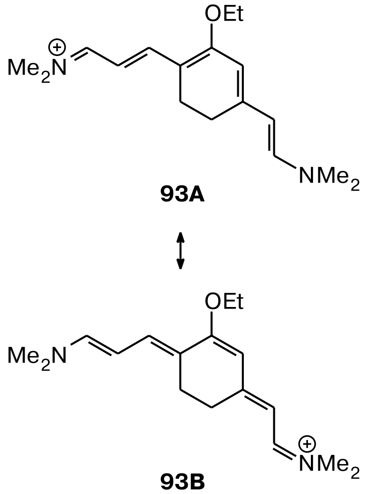


Fig. 5. Absorption spectra of polymethine salt **96a** in Pr^iOH.

be explained only in terms of the model of interaction of the chromophores, *i.e.*, the halves of the polymethine chains in salts **96a—c**. Since the most stable form of polymethine salts usually has a *trans*-configurations for each polymethine bond, the structure of salts **96a—c** should be shown as follows:



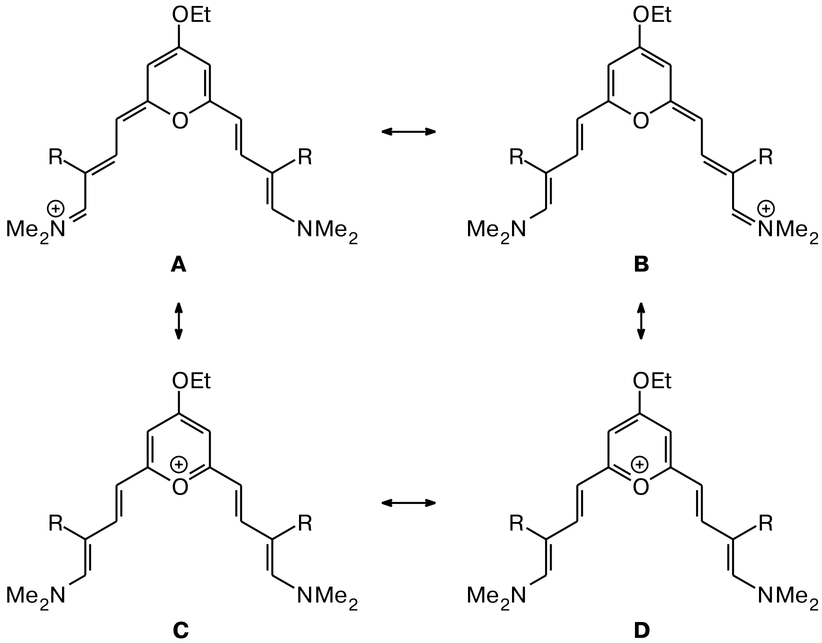
96a—c



In this case, the chromophores present in the molecule are arranged at an acute angle, which is consistent with the pattern of the absorption spectra.

The interpretation of the spectra of salts **96a—c** in terms of the theory of chromophore interaction is justified if the salt structure has some barrier to their interaction (otherwise, the whole system of conjugation should be considered as a single chromophore). Such a barrier is created, apparently, by the pyran ring. Indeed, among the resonance structures of salts **96a—c**, one can see structures **C** and **D** with an aromatic pyrylium fragment, which can serve as an obstacle to conjugation of the polymethine fragments to form a single system.

Evidently, no such obstacle is present if the salt structure does not have the central pyran fragment. Indeed, the absorption spectrum of dimethylene-bridged salt **93**



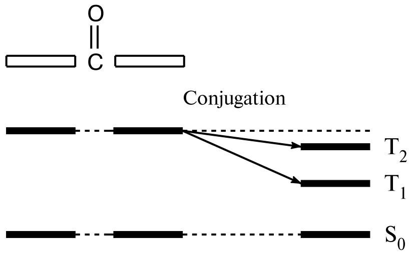


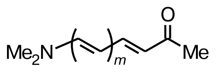
Fig. 6. Interaction of the chromophore triplet states in ketocyanines.

obtained from ketocyanine **33a** has no anomalous features (no noticeable short-wavelength band in the visible or near-UV region),[21] although the halves of the polymethine chains are arranged in this structure at an angle to each other. This is due to the lack of the barrier to conjugation in the polymethine chain.

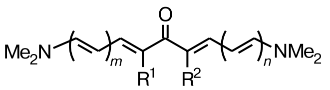
Unlike the singlet levels, the lowest triplet levels of the chromophores in ketocyanines can interact with each other only *via* conjugation, without the dipole—dipole coupling because the dipole moment of the $S_0 \leftrightarrow T_1$ transitions is close to zero. This interaction induces splitting and lowering of the triplet levels similarly to the excited singlet levels (Fig. 6). In this case, one can expect lower T_1 levels for symmetrical ketocyanines with respect to the corresponding asymmetrical molecules.

The energies of the lowest triplet levels (E_T) for a number of ketocyanines are listed in Table 4.[62] It can be seen that the symmetry of the dye is not the crucial factor determining these energies and that dyes with the same length of the longer chromophore (equal *n* values) have virtually identical E_T in toluene, irrespective of their symmetry (*cf*. dyes **25a**, **28a** and **32b**; **19l**, **25b**, **28e**, and **36**). Hence, the lowest triplet level of ketocyanines in toluene is determined only by the length of the longer chromophore and does not depend on the shorter one. Thus, it can be concluded that the T_1 levels of chromophores virtually do not interact with each other in the ketocyanine molecule (in toluene), which is apparently due to a low triplet energy insufficient for overcoming the potential barrier to the chromophore interaction (conjugation). In a polar proton-donating solvent, *n*-propanol, this barrier decreases due to solvation and the interaction of the triplet levels becomes noticeable, which results in a somewhat lower triplet level observed for symmetrical ketocyanine **28a** compared to those of unsymmetrical dyes **32b** and **25a** (see Table 4).

Table 4. Triplet energies (E_T) of ketocyanine dyes in toluene and *n*-propanol (the E_T value for merocyanine **19l** is also given)



19l



25a—c, **28a,e**, **32b**, **36**

Dye	*m*	*n*	R^1, R^2	R^1+R^2	E_T/cm^{-1}	
					toluene	*n*-propanol
19l	3	—	—	—	~11500	—
25a	1	2	H, H	—	13330	13020
25b	1	3	H, H	—	11500	—
25c	1	4	H, H	—	~10250	—
28a	2	2	H, H	—	13190	12440
28e	3	3	—	$(CH_2)_2$	~11500	—
32b	0	2	H, H	—	13580	13510
36	2	3	—	$(CH_2)_3$	~11500	—

6. Chromophore interaction in the cation-anionic polymethine dyes

The cation-anionic polymethine dyes exhibit, in the general case, two absorption bands (in some cases, they coincide), their behavior in polar solvents (acetonitrile, methanol) being similar to that of a mixture of a cationic and an anionic dye with simple counter-ions. However, in nonpolar solvents or in solvents with low polarity, the absorption spectra of these dyes can substantially change due to the formation of ion pairs and the interaction of chromophores of the cationic and anionic components. Previously,[63—65] the absorption and fluorescence properties of some cation-anionic dyes where the absorption bands of the cation and the anion differed appreciably and the chromophore interaction was feebly pronounced have been studied. More recently,[60,66] we studied the photonics of a large number of cation-anionic polymethine dyes in polar and nonpolar solvents and solvents with low polarity.

On passing to low-polarity or nonpolar solvents (chloroform, dioxane, toluene), the absorption and fluorescence spectra of usual polymethine dyes or cation-anionic dyes with appreciably different bands for the cation and the anion shift to longer wavelengths (by 5—10 nm), as the refractive indices of these solvents are greater than those of polar solvents (acetonitrile, alcohols), but no significant changes in the spectral pattern usually take place. However, in the case of cation-anionic dyes with close positions of absorption bands of the cation and the anion (A_1C_2, A_1C_6, A_4C_4, $A_{10}C_5$, $A_{11}C_5$, *etc*.), the absorption spectra change substantially on passing to low-polarity and nonpolar solvents, which is manifested first of all as the appearance of an additional short-wavelength band and a sharp decrease in the intensity of the long-wavelength absorption (Fig. 7). Since the spectral pattern in the nonpolar solvents does not depend on the dye concentration (in the range of 10^{-7}—10^{-6} mol L^{-1}), the formation of the additional band cannot be due to aggregation processes. The fact that the cation-anionic dyes exist in nonpolar solvents as ion pairs (as shown by conductometric measurements) implies that the additional

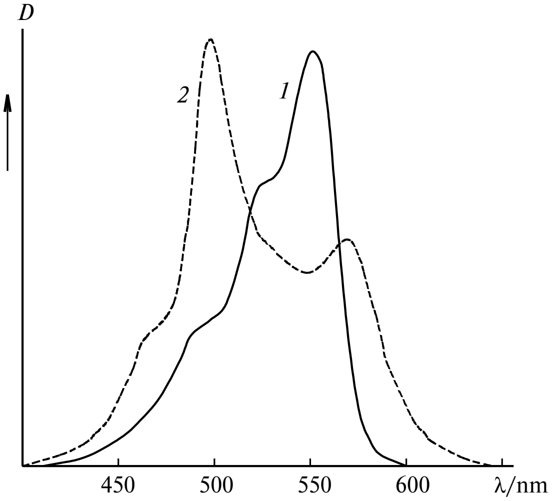


Fig. 7. Absorption spectra of the cation-anionic dye A_1C_6 in acetonitrile (*1*) and chloroform (*2*).

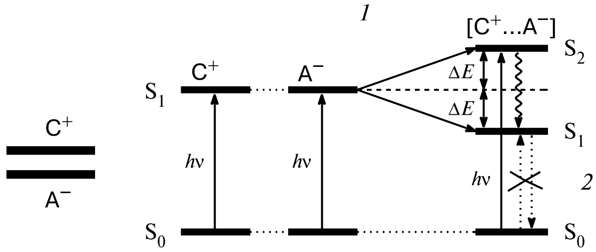


Fig. 8. Interaction of the chromophores in the cation-anionic dyes. (*1*) dipole—dipole interaction, (*2*) radiative transitions are forbidden.

short-wavelength band is due to the interaction between the cation and anion chromophores in the ion pair of the cation-anionic dye and characterizes this interaction. For efficient interaction of the chromophores, first, the absorption bands due to the cation and the anion should be close to each other and, second, these ions should be arranged in close proximity in the ion pair. The latter is, apparently, determined by the chemical nature of the cation and the anion and the specific interaction between them. For example, the absorption bands of the anion and the cation of dye $A_{14}C_2$ are close to each other (in ethanol and other polar solvents, their spectra coalesce to give a single band, see Table 2), which is expected to induce effective interaction of the cation and anion chromophores. However, the absorption spectrum of this dye in chloroform is similar to the spectrum in acetonitrile (except that the spectrum in chloroform is shifted to longer wavelength by 18 nm), and only in toluene, a short-wavelength band appears near the maximum of the original long-wavelength band. This attests to a relatively weak interaction of the chromophores in the ion pair, perhaps, due to insufficient proximity of the cation and the anion. Meanwhile, in the case of dyes A_1C_6 and $A_{12}C_5$, where the absorption maxima of the cation and the anion do not coincide but are close to each other, the absorption spectra in toluene, dioxane, and even chloroform undergo sharp changes (see Fig. 7), indicating a substantial interaction of the chromophores. As follows from the theory of chromophore interaction,[55,56,59] in the case of a parallel orientation, in an ion pair, of the anion and cation polymethine chains having identical (or similar) absorption spectra, the interaction of their chromophores in the absorption spectra of the dye should give rise to a new short-wavelength band (Fig. 8), whereas in the case of head-to-tail linear orientation, a long-wavelength band should appear. The fact that only short-wavelength bands appear in the absorption spectra of the cation-anionic dyes existing as ion pairs and no new long-wavelength bands are observed points to the lack of head-to-tail orientations of the cation and the anion and to more likely parallel orientation (a long-wavelength shoulder or bands remaining in the absorption spectra of ion pairs in place of the band of the dissociated dye are, probably, due to the presence of ion pairs with weak interaction, apparently, solvent-separated ion pairs). With this orientation of the chromophores, the long-wavelength transition is forbidden for the ion pair in the absorption and fluorescence spectra (see Fig. 8). This is responsible for the lack of fluorescence upon excitation to the short-wavelength absorption band resulting from the chromophore interaction, as fast nonradiative $S_2 \rightsquigarrow S_1$ deactivation brings the ion pair into the nonfluorescent excited state S_1. However, excitation to the long-wavelength region of the spectrum often brings about essential fluorescence, which comes apparently from solvent-separated ion pairs.

The spectral and fluorescent properties of the cation-anionic dyes A_1C_2, A_4C_4, and A_3C_4 were studied in detail (both experimentally and using quantum-chemical calculations). For the first two dyes, the absorption bands of the cation and the anion virtually coincide, while in the third case, they are markedly different (see Table 2).[67] In conformity with the theory of chromophore interaction, the A_1C_2 and A_4C_4 ion pairs (in toluene), show substantial spectral changes, manifested, first of all, as origination of a new short-wavelength band, whereas for the A_3C_4 ion pairs, only the change in intensity is observed for the existing absorption bands. In the case of the A_1C_2 pairs, the intense original (long-wavelength) band is retained in the spectrum together with the new band, whereas only a shoulder (Fig. 9, *a*, *b*) is retained in the long-wavelength region in the case of A_4C_4. The distance between the new and original bands, which can serve as a measure of chromophore interaction, is much greater for A_4C_4 (~70 nm) than for A_1C_2 (~38 nm). The observed spectral changes are due to the formation of contact ion pairs of the dyes exhibiting no fluorescence. On the basis of calculations, it was concluded that these ion pairs can

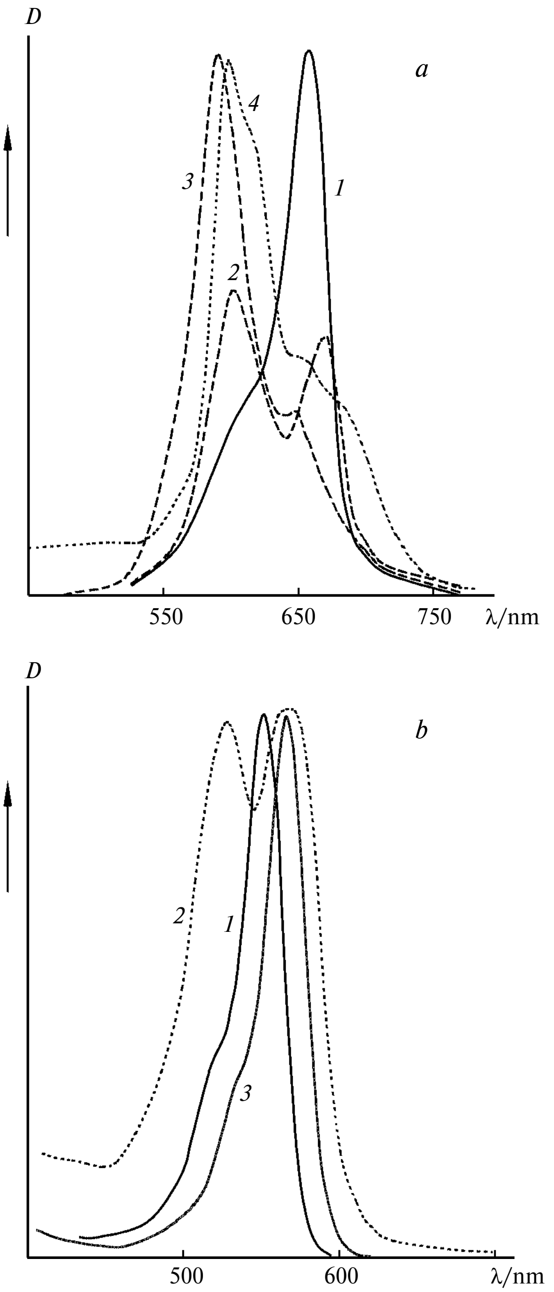


Fig. 9. (*a*) Absorption spectra of the cation-anionic dye A_4C_4 in acetonitrile (*1*), chloroform (*2*), dioxane (*3*), and toluene (*4*). (*b*) Absorption spectra of the cation-anionic dye A_1C_2 in acetonitrile (*1*) and toluene (*2*), and the anionic dye A_1 with the simple $Me_2N—CH=CH—CH=NMe_2^+$ cation in toluene (*3*).

form two stable configurations, with either parallel or perpendicular arrangement of the chromophores. The former configuration corresponds to the A_4C_4 pairs, while in the case of the A_1C_2 pairs, the second configuration makes a substantial contribution. This accounts for the weaker interaction of chromophores in the A_1C_2 pairs compared to A_4C_4. The calculation also shows that an additional low-lying (in the IR region) excited singlet state with a charge transfer nature appears in the contact ion pairs in question. The radiative transition from this state is forbidden, which accounts for the absence of fluorescence in these pairs. The data obtained suggest that the perpendicular (along with the parallel) orientation can also occur for chromophores in the ion pairs of other cation-anionic polymethine dyes, resulting in a decrease in the effect of chromophore interaction.

The close proximity of ions in the ion pairs formed by the cation-anionic dyes creates, in addition to the chromophore interaction effects, a sort of "microreactor" for performing various reactions between the dyes in the absence of mutual diffusion. This provides easy conducting of photochemical processes such as electronic excitation energy transfer and photoinduced electron transfer without creating high concentrations of reactants. In the former case, photoexcitation of the energy donor ion induces fluorescence of the acceptor ion;[66] in the latter case, photoexcitation of ion pairs is accompanied by electron transfer from the anion to the cation to give the corresponding dye radicals.[68] Due to these specific features, cation-anionic dyes are attractive objects both for the study of fundamental photophysical and photochemical processes and for various photochemical systems used for practical purposes, for example, for the conversion of solar energy, information recording, and so on.

Conclusion

Thus, the use of aminals of ω-amino-substituted unsaturated aldehydes offers extensive opportunities for the synthesis of polyfunctional conjugated polyenes of diverse structures. Moreover, some of these compounds are formed in unusual chemical transformations of aminals or products derived from aminals.

Systematic photophysical and photochemical research of a great number of synthesized compounds showed that many polyenes, in particular, bisamino-substituted cross-conjugated ketones, possess unusual optical properties, which have been successfully interpreted resorting to the theory of chromophore interaction.

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