Novel conjugated polynitriles based on aminal acetal of dimethylaminomethylenemalonaldehyde

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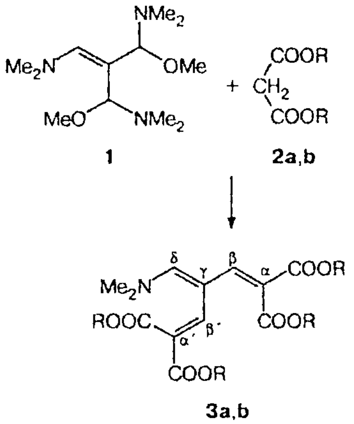
Depending on the reaction conditions, dimethylaminomethylenemalonaldehyde aminal acetal reacts with malonodinitrile or alkyl cyanoacetates to give various neutral or ionic cross-conjugated polynitriles. Cation-anionic cyanine dyes were obtained from tri- and tetracyanopolymethine salts. The conformation and geometric parameters of the tetramethyl 3-dimethylaminomethylenepenta-1,4-diene-1,1,5,5-tetracarboxylate molecule were established by X-ray diffraction analysis.

Key words: 1,3-bis(dimethylamino)-2-[(dimethylamino)methoxymethyl]-1-methoxyprop-2-ene, reactions with malonodinitrile and alkyl cyanoacetates; cross-conjugated polynitriles, polycyanopolymethine salts, cation-anionic dyes; X-ray diffraction analysis.

Recently we synthesized 1,3-bis(dimethylamino)-2-[dimethylamino(methoxy)methyl]-1-methoxyprop-2-ene (**1**) and, using its condensation with alkyl malonates esters (**2a,b**) as an example, we showed that owing to the presence of two reactive groups, this compound can react with two moles of malonate to give previously unknown triene tetraesters (**3a,b**).[1]

Scheme 1

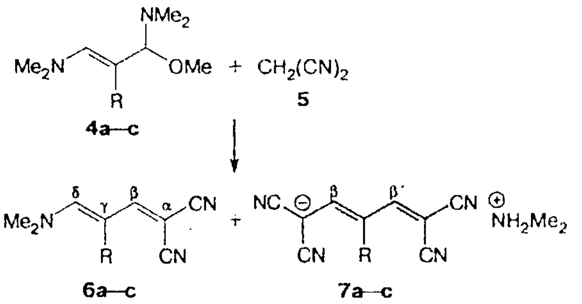


R = Me (**a**); Et (**b**)

The present work is devoted to the reaction of aminal acetal **1** with other CH acids.

Previously[2,3] we showed (Scheme 2) that condensation of aminals of conjugated β-dimethylaminoaldehydes (**4**) with malonodinitrile (**5**) affords conjugated diene δ-dimethylaminodinitriles (**6**) and tetracyanotrimethines (**7**).

Scheme 2



R = H (**a**), Ph (**b**), NMe$_2$ (**c**)

Tetracyanotrimethines are anionic dyes and, in addition, they are used as the anionic components in the synthesis of new cation-anionic cyanine dyes possessing a number of specific properties.[4—9]

While studying the reaction of aminal acetal **1** with malonodinitrile **5**, we found that, depending on the conditions, the reaction can follow two pathways giving compounds **8** and **11** (Scheme 3).

When the reaction is carried out in ether at 30—35 °C and the ratio of reagents **5** : **1** = 2 : 1 (**5** is added to **1**), it gives triene δ-dimethylaminotetranitrile **8** in 22% yield. The structure of this product was confirmed by ^{1}H NMR and UV data. When the reaction is carried out in benzene at 5 °C and the ratio **5** : **1** = 3 : 1 (**1** is added to **5**), it gives cross-conjugated salt **11**, containing four nitrile groups, in 45% yield; the structure of this salt was established using ^{1}H NMR, ^{13}C NMR, and UV spectroscopy and elemental analysis.

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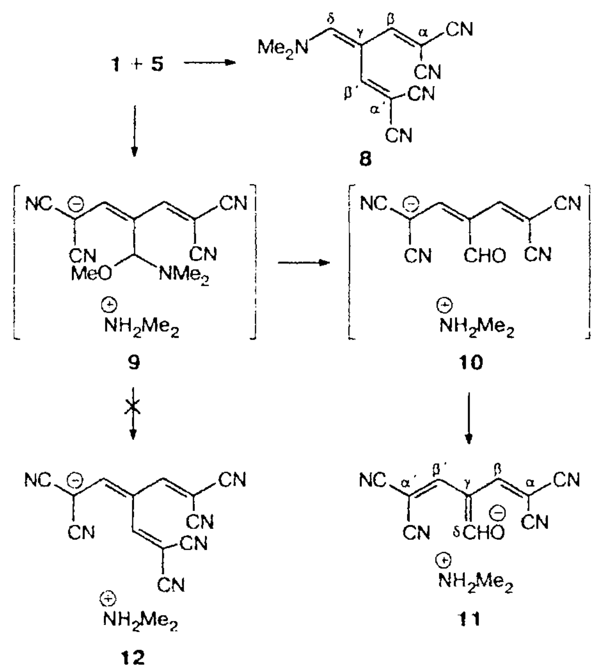
Scheme 3



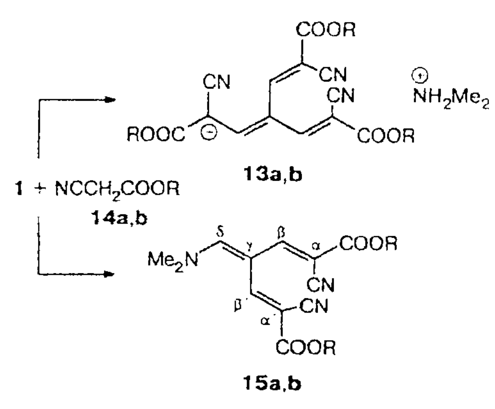
The enol structure **11** was preferred over aldehyde structure **10** based on the NMR data. The ^1H NMR spectrum of the reaction product (in CD_3OD) exhibits signals at 7.81, 8.31 (^4J = 2.5 Hz), and 8.57 ppm (^4J = 2.5 Hz), which correspond to the protons at δ-C, β-C, and β'-C, respectively, and the ^{13}C NMR spectrum contains signals at 157.40 (J = 180 Hz), 144.81 (J = 169 Hz), and 156.23 ppm (J = 163 Hz) corresponding to the δ-C, β-C, and β'-C atoms, respectively. If this product was aldehyde **10** rather than enolate **11**, the ^1H NMR spectrum would contain a signal for the CHO-group proton, whereas the signals of protons at β-C and β'-C, and the ^{13}C signals of the β-C and β'-C atoms would coincide, as has been observed for salts **7a—c** synthesized previously.[3]

Salt **12**, containing six CN groups, which would be expected to form upon condensation of intermediate **9** with malonodinitrile **5**, was not detected. However, similar salts (**13a,b**) are formed in high yields (84—87%) when aminal acetal **1** reacts with cyanoacetates (**14a,b**) (Scheme 4).

This reaction does not require a catalyst and occurs very rapidly (over a period of 5—10 min) in ether or benzene at 20 °C.

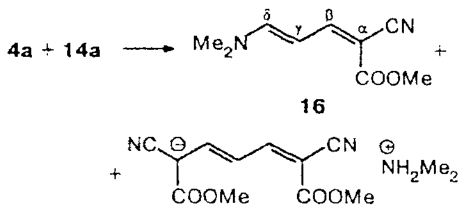
The formation of traces of triene δ-dimethylamino nitrilo esters **15a,b** can be detected only in the UV spectrum of the reaction mixture: in addition to the very intense absorption band with λ_{max} = 471 nm, the spectra of salts **13a,b** contain a weak band with λ_{max} = 400 nm corresponding to esters **15a,b**. The triene δ-dimethylamino nitrilo ester **15a** could be isolated in a low yield (10%) when the reaction was carried out in ether at 30—35 °C and the reactants were mixed in the opposite order (**14a** was added to aminal acetal **1**). It should be noted that, unlike the reaction of aminal acetal **1** with cyanoacetate **14a**, the reaction of **14a** with aminal **4a** studied previously resulted in the formation of δ-dimethylamino nitrilo ester **16**, whereas the yield of dimethylammonium salt **17** was no more than 5—7%.[2]

Scheme 4



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

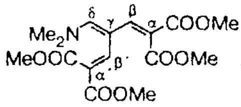
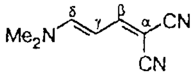
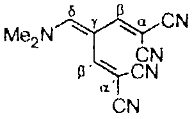
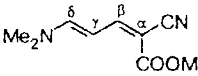
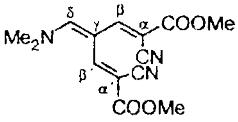
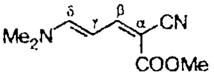
Scheme 5



Comparison of the electronic absorption spectra of cross-conjugated triene δ-dimethylamino compounds **8** and **15a** with the spectra of δ-dimethylamino compounds **6a** and **16** (Table 1) indicates that the introduction of a $-CH{=}C(CN)_2$ or $-CH{=}C(CN)COOMe$ fragment into the γ-position (compounds **8** and **15a**) results in a substantial bathochromic shift of the absorption maximum by 19 and 17 nm, respectively, indicating enhanced donor-acceptor interactions between the terminal substituents in the triene compounds.

These data are consistent with the ^1H NMR spectra. Table 1 presents chemical shifts of the protons at the β-C, β'-C, and δ-C atoms. In compound **8**, the signals for the β-H, β'-H, and δ-H protons are shifted downfield in relation to those of the β-H and δ-H protons in compound **6a** by 1.25, 1.44, and 0.4 ppm, respectively; the signals of the β-H, β'-H, and δ-H protons in compound **15a** are shifted downfield in relation to those

Table 1. UV and ^{1}H NMR spectra of compounds **3a**, **6a**, **8**, **15a**, **16**, and **18a***

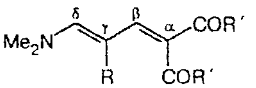
Compound		UV spectrum (EtOH), λ_{max}/nm	^{1}H NMR spectrum (CDCl$_3$), δ, J/Hz		
			β-H	β′-H	δ-H
	**3a**	372	7.52 s	7.52 s	6.99 s
	**6a**	376	7.17 (d, $^3J_{\beta,\gamma}$ = = 12)		7.1 (d, $^3J_{\gamma,\delta}$ = = 12)
	**8**	395	8.42** (d, $^4J_{\beta,\beta'}$ = = 2.5)	8.61** (d, $^4J_{\beta,\beta'}$ = = 2.5)	7.50 s
	**16**	383	7.79 (d, $^3J_{\beta,\gamma}$ = = 12.2)		7.08 (d, $^3J_{\gamma,\delta}$ = = 12)
	**15a**	400	8.59** (d, $^4J_{\beta,\beta'}$ = = 2.0)	8.78** (d, $^4J_{\beta,\beta'}$ = = 2.0)	8.10 s
	**18a**	374	7.68 (d, $^3J_{\beta,\gamma}$ = = 12)		6.96 (d, $^3J_{\gamma,\delta}$ = = 12)

* The full ^{1}H NMR spectra of compounds **8** and **15a** are given in the Experimental, that of compound **3a** is presented in Ref. 1, and the spectra of compounds **6a**, **16**, and **18a** are given in Ref. 2.

** The signal assignment to the β-H and β′-H protons is arbitrary.

for the β-H and δ-H protons in compound **16** by 0.8, 1.0, and 1.0 ppm, respectively. The introduction of a —CH=C(COOMe)$_2$ fragment in the γ-position (Table 1, tetraester **3a** [1]) does not cause the above-mentioned changes in the UV and ^{1}H NMR spectra.

In the case of tetraester **3a**, only a slight hypsochromic shift of λ_{max} is observed; the band shifts by 2 nm compared to that for diene diester **18a**.[2]



R = H, R′ = OMe (**a**);
R = H, R′ = Me (**b**);
R = CN, R′ = Me (**c**)

18a—c

The signals of the β-H, β′-H, and δ-H protons in compounds **3a** and **18a** are exhibited almost in the same region of the ^{1}H NMR spectrum. Since tetraester **3a** has four bulky methoxycarbonyl groups, some of these groups apparently deviate from the plane of the cross-conjugated system and actually do not participate in conjugation. This assumption was confirmed by an X-ray diffraction study.

Table 2. Coordinates (×10^4) and isotropic or (for nonhydrogen atoms) equivalent thermal parameters (×10^3) of atoms in structure **3a**

Atom	x	y	z	U/Å^2
O(1)	−51(1)	−3591(1)	1344(1)	48(1)
O(2)	781(1)	−3536(1)	1230(1)	29(1)
O(3)	−397(1)	−852(1)	627(1)	53(1)
O(4)	59(1)	886(1)	1476(1)	43(1)
O(5)	2684(1)	87(1)	4338(1)	34(1)
O(6)	2570(1)	2179(1)	3591(1)	27(1)
O(7)	1535(1)	2557(1)	2417(1)	45(1)
O(8)	1732(1)	889(1)	1473(1)	27(1)
N(1)	1464(1)	−3958(1)	3476(1)	22(1)
C(1)	857(1)	−837(1)	2194(1)	24(1)
C(2)	422(1)	−1395(1)	1628(1)	26(1)
C(3)	346(1)	−2927(1)	1397(1)	27(1)
C(4)	763(1)	−5059(2)	1128(1)	39(1)
C(5)	−16(1)	−464(2)	1186(1)	33(1)
C(6)	−355(1)	1866(3)	1102(2)	57(1)
C(7)	1758(1)	−899(1)	3210(1)	22(1)
C(8)	1953(1)	407(1)	3072(1)	22(1)
C(9)	2432(1)	836(1)	3732(1)	23(1)
C(10)	3036(1)	2684(2)	4223(1)	33(1)
C(11)	1716(1)	1416(1)	2313(1)	22(1)
C(12)	1490(1)	1752(2)	678(1)	40(1)
C(13)	1278(1)	−1574(1)	2793(1)	22(1)
C(14)	1155(1)	−2913(1)	3123(1)	21(1)
C(15)	2013(1)	−4098(2)	3418(1)	28(1)
C(16)	1258(1)	−5154(1)	3930(1)	27(1)
H(1)	873(5)	186(15)	2224(9)	23(3)
H(4A)	531(7)	−5330(18)	552(12)	48(5)
H(4B)	1119(8)	−5320(20)	1135(12)	59(5)
H(4C)	644(6)	−5487(18)	1650(12)	41(4)
H(6A)	−432(11)	1875(31)	415(18)	56(8)
H(6B)	−712(10)	1451(29)	1247(16)	46(7)
H(6C)	−233(12)	2862(32)	1363(20)	72(9)
H(7)	1969(5)	−1401(14)	3709(9)	20(3)
H(10A)	3005(6)	2501(17)	4883(11)	39(4)
H(10B)	3340(7)	2171(19)	4091(11)	46(4)
H(10C)	3066(8)	3672(24)	4070(14)	70(6)
H(12A)	1690(7)	2637(22)	707(12)	54(5)
H(12B)	1115(7)	1960(18)	703(12)	49(5)
H(12C)	1517(7)	1175(21)	147(13)	59(5)
H(14)	794(5)	−3101(14)	3113(8)	18(3)
H(15A)	2087(5)	−3454(16)	2942(10)	28(4)
H(15B)	2066(6)	−5069(17)	3243(11)	36(4)
H(15C)	2235(6)	−3890(18)	4012(12)	43(4)
H(16A)	1462(6)	−5222(16)	4577(11)	39(4)
H(16B)	1293(6)	−6056(17)	3578(10)	35(4)
H(16C)	876(7)	−4981(17)	3890(11)	39(4)

Tables 2—5 contain bond lengths and bond and torsion angles, and Fig. 1 shows the general view of molecule **3a**. It can be seen from the figure that the carbon skeleton of the molecule branches out at the γ-C atom giving two equivalent donor-acceptor polyene systems (*A*, *B*).

Table 3. Bond lengths (*d*) in molecule **3a**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(3)	1.202(2)	N(1)—C(14)	1.310(2)
O(2)—C(3)	1.346(2)	N(1)—C(15)	1.465(2)
O(2)—C(4)	1.443(2)	N(1)—C(16)	1.468(2)
O(3)—C(5)	1.205(2)	C(1)—C(2)	1.365(2)
O(4)—C(5)	1.343(2)	C(1)—C(13)	1.434(2)
O(4)—C(6)	1.441(2)	C(2)—C(5)	1.480(2)
O(5)—C(9)	1.214(1)	C(2)—C(3)	1.488(2)
O(6)—C(9)	1.345(1)	C(7)—C(8)	1.363(2)
O(6)—C(10)	1.447(2)	C(7)—C(13)	1.426(2)
O(7)—C(11)	1.199(2)	C(8)—C(9)	1.469(2)
O(8)—C(11)	1.334(1)	C(8)—C(11)	1.493(2)
O(8)—C(12)	1.451(2)	C(13)—C(14)	1.413(2)

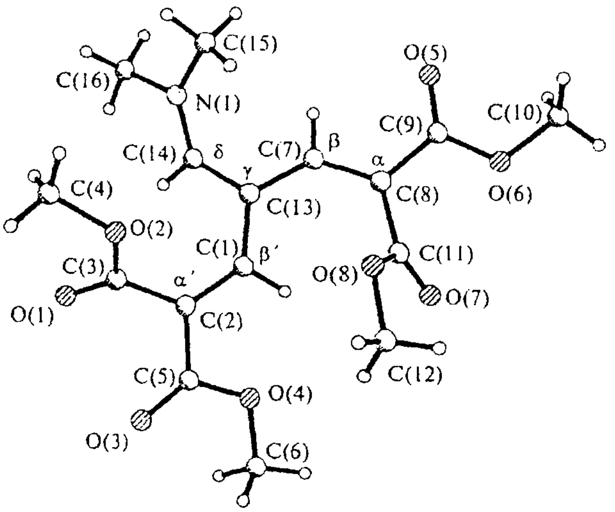


Fig. 1. General view of molecule **3a**:
N(1)—C(14)—C(13)—C(7)—C(8) is polyene system *A*;
N(1)—C(14)—C(13)—C(1)—C(2) is polyene system *B*.

It can be seen from Fig. 1 and Table 5 that the double bonds have the *S-trans*-configuration in system *A* and the *S-cis*-configuration in system *B*. The data of Table 5 also indicate that in both system *A* and system *B*, one of the methoxycarbonyl groups is out of the chain of conjugation, while the other group actually lies in the plane of the conjugated system: the O(1)—C(3)—C(2)—C(1) and O(7)—C(11)—C(8)—C(7) torsion angles are 139.4° and 115.1°, respectively, while the O(3)—C(5)—C(2)—C(1) and O(5)—C(9)—C(8)—C(7) angles are 174.5° and 5.7°. The effect of substituents at the α-C, α′-C, γ-C, and N atoms is manifested both as a substantial increase in the bond angles at the β-C, β′-C, and γ-C atoms (131.6(1)°, 128.3(1)°, 129.8(1)°, respectively) compared to a standard value of 120° typical of an sp^2-hybridized C atom and as a noticeable twisting of the γ-C—δ-C bond (the N(1)—C(14)—C(13)—C(1) and N(1)—C(14)—C(13)—C(7)

Table 4. Bond angles (ω) in molecule **3a**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(3)—O(2)—C(4)	115.60(11)	O(1)—C(3)—O(2)	121.54(13)	O(5)—C(9)—O(6)	122.42(11)
C(5)—O(4)—C(6)	116.1(2)	O(1)—C(3)—C(2)	126.34(12)	O(5)—C(9)—C(8)	125.28(11)
C(9)—O(6)—C(10)	115.48(10)	O(2)—C(3)—C(2)	112.11(10)	O(6)—C(9)—C(8)	112.30(10)
C(11)—O(8)—C(12)	115.85(10)	O(3)—C(5)—O(4)	123.15(13)	O(7)—C(11)—O(8)	122.81(11)
C(14)—N(1)—C(15)	125.28(10)	O(3)—C(5)—C(2)	124.81(14)	O(7)—C(11)—C(8)	126.19(11)
C(14)—N(1)—C(16)	119.97(10)	O(4)—C(5)—C(2)	112.03(11)	O(8)—C(11)—C(8)	111.00(10)
C(15)—N(1)—C(16)	114.67(10)	C(8)—C(7)—C(13)	131.58(11)	C(14)—C(13)—C(7)	119.75(10)
C(2)—C(1)—C(13)	128.29(12)	C(7)—C(8)—C(9)	116.52(10)	C(14)—C(13)—C(1)	116.15(10)
C(1)—C(2)—C(5)	120.54(12)	C(7)—C(8)—C(11)	125.11(11)	C(7)—C(13)—C(1)	122.64(11)
C(1)—C(2)—C(3)	124.52(11)	C(9)—C(8)—C(11)	118.37(10)	N(1)—C(14)—C(13)	129.82(11)
C(5)—C(2)—C(3)	114.94(11)				

Table 5. Torsion angles (α) in compound **3a**

Angle	α/deg	Angle	α/deg	Angle	α/deg
C(13)—C(1)—C(2)—C(3)	−11.4	O(4)—C(5)—C(2)—C(1)	−5.1	O(7)—C(11)—C(8)—C(7)	115.1
C(13)—C(1)—C(2)—C(5)	169.1	O(4)—C(5)—C(2)—C(3)	175.3	O(7)—C(11)—C(8)—C(9)	−64.6
O(1)—C(3)—O(2)—C(4)	−9.1	C(9)—C(8)—C(7)—C(13)	171.0	O(8)—C(11)—C(8)—C(7)	−65.2
C(2)—C(3)—O(2)—C(4)	171.7	C(11)—C(8)—C(7)—C(13)	−8.7	O(8)—C(11)—C(8)—C(9)	115.1
C(1)—C(2)—C(3)—O(1)	139.4	C(10)—O(6)—C(9)—O(5)	−1.2	C(2)—C(1)—C(13)—C(7)	167.4
C(1)—C(2)—C(3)—O(2)	−41.6	C(10)—O(6)—C(9)—C(8)	179.3	C(2)—C(1)—C(13)—C(14)	−26.5
C(5)—C(2)—C(3)—O(1)	−41.1	O(5)—C(9)—C(8)—C(7)	5.7	C(8)—C(7)—C(13)—C(1)	−9.3
C(5)—C(2)—C(3)—O(2)	138.0	O(5)—C(9)—C(8)—C(11)	−174.5	C(8)—C(7)—C(13)—C(14)	−175.0
C(6)—O(4)—C(5)—O(3)	2.0	O(6)—C(9)—C(8)—C(7)	−174.8	C(13)—C(14)—N(1)—C(15)	−14.6
C(6)—O(4)—C(5)—C(2)	−178.4	O(6)—C(9)—C(8)—C(11)	4.9	C(13)—C(14)—N(1)—C(16)	168.9
O(3)—C(5)—C(2)—C(1)	174.5	O(7)—C(11)—O(8)—C(12)	−3.1	C(1)—C(13)—C(14)—N(1)	161.5
O(3)—C(5)—C(2)—C(3)	−5.1	C(8)—C(11)—O(8)—C(12)	177.2	C(7)—C(13)—C(14)—N(1)	−31.9

Scheme 6

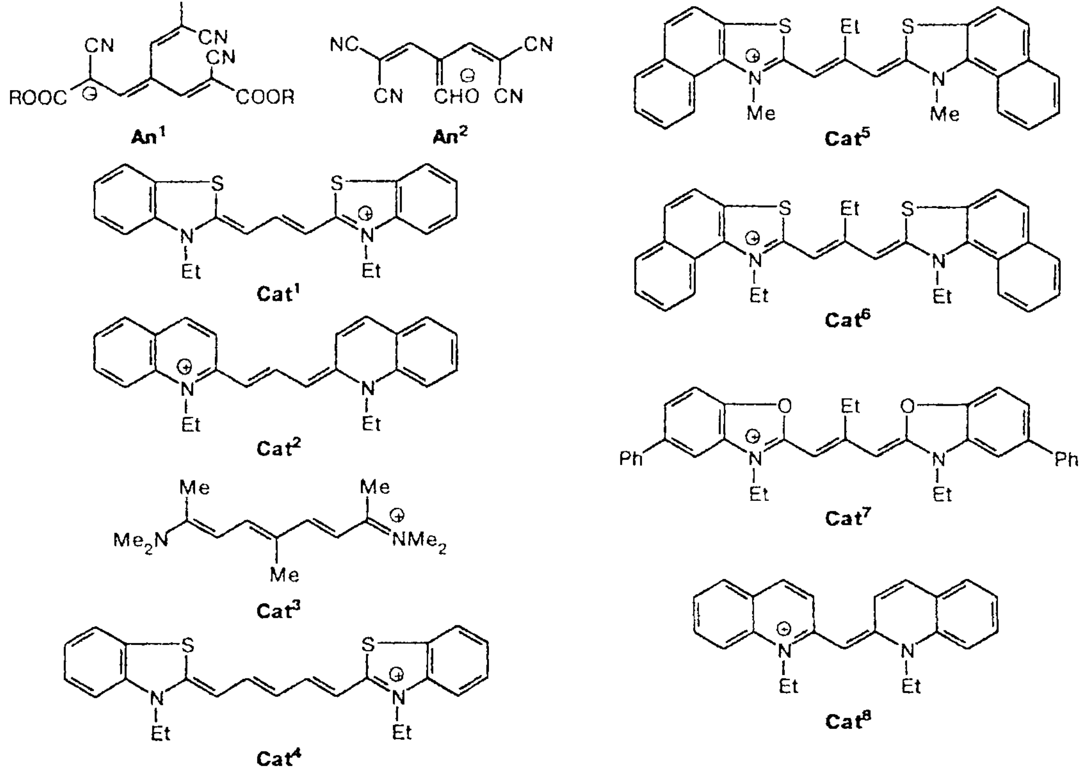


Table 6. Cation-anionic polymethine dyes **19—29**

Compound	An	Cat	Yield (%)	M.p./°C	Molecular formula	Found / Calculated (%)				UV spectrum, λ_{max}/nm (ε)		
						C	H	N	S	EtOH	$CHCl_3$	Toluene
19	**An^1**	**Cat^1**	81	229—231	$C_{37}H_{33}N_5O_6S_2$	62.72 62.78	4.67 4.70	9.82 9.90	8.70 9.06	468 (65700), 565 (193000)	470, 570	—
20	**An^1**	**Cat^2**	54	230—232	$C_{43}H_{39}N_5O_6$	71.50 71.55	5.59 5.45	9.63 9.70		468 (42300), 610 (160000)	480, 620	477, 620
21	**An^1**	**Cat^3**	98	178—180	$C_{30}H_{37}N_5O_6$	64.26 63.92	6.85 6.62	12.84 12.43		470 (54500), 540 (166000)	465, 547	464, 563
22	**An^1**	**Cat^4**	64	179—183	$C_{39}H_{35}N_5O_6S_2$	63.56 63.83	5.13 4.81		9.10 8.74	468 (54500), 670 (250000)	477, 680	477, 690
23	**An^1**	**Cat^5**	61	117—120	$C_{45}H_{37}N_5O_6S_2$	66.33 66.89	5.03 4.62	8.75 8.67	7.97 7.94	470 (49000), 585 (109000)	475, 600	475, 615
24	**An^1**	**Cat^6**	57	202—205	$C_{47}H_{41}N_5O_6S_2$	68.02 67.52	5.31 4.94	8.49 8.38	7.60 7.67	470 (73000), 585 (161000)	475, 600	485, 620
25	**An^1**	**Cat^7**	48	100—104	$C_{51}H_{45}N_5O_8$	71.18 71.56	5.57 5.30			480 (133000), 510 (193000)	480, 515	460, 520
26	**An^1**	**Cat^8**	54	167—169	$C_{39}H_{35}N_5O_6$					480 plateau (65200), 532 (74200)	468, 540	468, 540
27	**An^2**	**Cat^1**	61	225—228	$C_{31}H_{24}N_6OS_2$	66.48 66.40	3.97 4.31		10.81 11.44	565 (163000)	575	510, 585
28	**An^2**	**Cat^7**	85	235—239	$C_{45}H_{36}N_6O_3 \cdot$ $\cdot 0.5\ H_2O$	74.99 75.29	4.97 5.20			485 sh (127000), 510 (189000)	495 sh, 518 508, 600	495 sh, 520 —
29	**An^2**	**Cat^5**	50	249—252	$C_{39}H_{28}N_6OS_2$					480 (36000), 585 (83300)		

torsion angles are 161.5° and −31.9°, respectively). The nitrogen atom has a planar trigonal configuration, and the sum of bond angles at this atom is 360°.

The data obtained previously for a number of conjugated linear ω-aminocarbonyl compounds with donor- and acceptor substituents at the terminal carbon atoms showed that in relatively short systems, the C—C bond lengths become equal; this occurs, for example, in diketone **18b**[10] [1.395(4) (α—β), 1.405(4) (β—γ), 1.378(5) Å (γ—δ)] and in diester **18a**[11] [1.376(4), 1.408(4), 1.360(4) Å]. The introduction of an electron-withdrawing CN group to the γ-C atom in diketone **18b** decreases the degree of delocalization of conjugated bonds. Thus in diketone **18c**,[12] the bond lengths are 1.345(3) (α—β), 1.437(3) (β—γ), 1.427(3) (C—CN), and 1.381(3) Å (γ—δ).

The bond lengths in the conjugated systems *A* (1.365(2), 1.434(2), 1.413(2)) and *B* (1.363(2), 1.426(2), 1.413(2)) in molecule **3a** are practically equal and, in general, they resemble the corresponding systems in molecule **18c**. The difference between the γ-C—δ-C bond lengths in **3a** (1.413(2) Å) and **18c** (1.381(3) Å) can apparently be explained by additional steric effects (twisting of the γ-C—δ-C bond) in molecule **3a** not observed in **18c**.

We showed that the cations in salts **11** and **13a** can be easily replaced by the cation of a cyanine dye; this gives new cation-anionic dyes **19**—**29** (Table 6) in which the anionic and cationic components have the structures shown in Scheme 6.

The results of studies of spectral and luminescence properties ofr dyes **19**—**29** will be reported later.

Experimental

UV spectra were recorded on a Specord UV VIS spectrophotometer. ^{1}H NMR spectra were measured on a Bruker MW-250 instrument (^{1}H, 250 MHz) relative to TMS, and ^{13}C NMR spectra were run on a Bruker MW-300 spectrometer (75.432 MHz). Mass spectra (EI) were recorded on an MS-30 instrument (70 eV).

1,1,5,5-Tetracyano-3-dimethylaminomethylenepenta-1,4-diene (8). A solution of malonodinitrile **5** (0.24 g, 3.6 mmol) in 1.5 mL of anhydrous ether was added to a boiling solution of aminal acetal **1** (0.5 g, 1.8 mmol) in 2 mL of anhydrous ether. The reaction mixture was refluxed for 10 min and concentrated. Anhydrous EtOH was added to the oily residue, the mixture was cooled to −70 °C, and the precipitate was separated and washed with anhydrous EtOH and anhydrous ether. Then the precipitate (130 mg) was dissolved in 3 mL of $CHCl_3$, the insoluble part was separated, and the filtrate was concentrated. The oily residue was crystallized by trituration with anhydrous ether, and the precipitate was filtered off to give 90 mg (22%) of compound **8** as yellow crystals, m.p. 142—144 °C. UV (EtOH), λ_{max}/nm (ε): 358 sh, (17100), 395 (32000). ^{1}H NMR ($CDCl_3$), δ: 3.50 (s, 6 H, NMe_2); 7.05 (s, 1 H, δ-H); 8.42 (d, 1 H, β-H, *J* = 2.5 Hz); 8.61 (d, 1 H, H-β′, *J* = 2.5 Hz). MS (EI): *m/z* (I_{rel} (%)): 223 $[M]^+$ (81), 208 $[M-Me]^+$ (100), 153 $[M-NMe_2-CN]^+$ (34), 127 $[M-NMe_2-2CN]^+$ (8.3), 101 $[M-NMe_2-3CN]^+$ (7.9).

Dimethylammonium 4,4-dicyano-2-(2,2-dicyanovinyl)buta-1,3-dien-1-olate (11). A solution of aminal acetal **1** (1 g, 3.69 mmol) in 2 mL of dry C_6H_6 was added dropwise with stirring at 5 °C over a period of 5 min to a suspension of malonodinitrile **5** (0.76 g, 11.1 mmol) in 2.5 mL of dry C_6H_6. The reaction mixture was kept at 0—5 °C for 30 min, and the resulting precipitate was filtered off and washed successively with dry C_6H_6, $CHCl_3$, and anhydrous ether. Recrystallization of anhydrous MeOH gave 400 mg (45%) of compound **11** as bright red crystals, m.p. 173—176 °C. UV (EtOH), λ_{max}/nm (ε): 487 (33000). Found (%): C, 60.61; H, 4.09; N, 30.49. $C_{12}H_{11}N_5O$. Calculated (%): C, 59.74; H, 4.60; N, 29.03. ^{1}H (CD_3OD, δ: 2.73 (s, 6 H, NMe_2); 7.81 (s, 1 H, δ-H); 8.31 (d, 1 H, β-H, *J* = 2.5 Hz); 8.57 (d, 1 H, β′-H, *J* = 2.5 Hz). ^{13}C NMR (CD_3OD), δ: 35.77 (NMe_2, *J* = 141 Hz); 97.25 (α-C and α′-C); 110.94 (γ-C); 115.69 (CN); 116.37 (CN); 117.63 (CN); 118.44 (CN); 144.81 (β-C, *J* = 169 Hz); 156.23 (β′-C, *J* = 163 Hz); 157.40 (CHO, *J* = 180 Hz).

Dimethylammonium 1,5-dicyano-3-(2-cyano-2-methoxycarbonylvinyl)-1,5-dimethoxycarbonylpenta-2,4-dien-1-ide (13a). At 20 °C, cyanoacetate **14a** (0.75 mL, 8.5 mol) was added to a solution of aminal acetal **1** (0.76 g, 2.8 mmol) in 4 mL of dry benzene. After 5 min (the reaction is exothermic!), a voluminous precipitate was formed. After 20 min, the reaction mixture was diluted with dry chloroform, and the bright orange precipitate was filtered off and washed with $CHCl_3$ and C_6H_6 to give 920 mg (84%) of salt **13a**, m.p. 198—203 °C. UV (EtOH), λ_{max}/nm (ε): 443 sh (55800), 471 (61800). Found (%): C, 55.31; H, 5.31; N, 13.78. $C_{18}H_{20}N_4O_6$. Calculated (%): C, 55.66; H, 5.19; N, 14.43. ^{1}H NMR (CD_3OD), δ: 2.71 (s, 6 H, NMe_2); 3.81 (s, 9 H, COOMe); 8.57 (s, 3 H, C$\underline{H}$=).

Dimethylammonium 1,5-dicyano-3-(2-cyano-2-ethoxycarbonylvinyl)-1,5-diethoxycarbonylpenta-2,4-dien-1-ide (13b). Ethyl cyanoacetate **14b** (0.59 mL, 5.5 mmol) was added to aminal acetal **1** (0.5 g, 1.8 mmol) in 2 mL of anhydrous benzene. After 20 min, the reaction mixture was concentrated. Anhydrous ether was added to the oily residue, and the resulting precipitate was triturated, filtered, and washed with anhydrous ether to give salt **13b** as yellow-orange crystals, m.p. 146—151 °C (87%). UV (EtOH), λ_{max}/nm (ε): 458 sh (55800); 470 (64400). ^{1}H NMR ($CDCl_3$), δ: 1.32 (t, 9 H, C$\underline{H}_3$—Et); 2.88 (s, 6 H, NMe_2); 4.23 (q, 6 H, C$\underline{H}_2$—Et); 8.83 (s, 3 H, C$\underline{H}$=).

Dimethyl 1,5-dicyano-3-dimethylaminomethylenepenta-1,4-diene-1,5-dicarboxylate (15a). A solution of cyanoacetate **14a** (0.33 mL, 3.6 mmol) in 1.5 mL of anhydrous ether was added at 30 °C to a solution of aminal acetal **1** (0.5 g, 1.8 mmol) in 1.5 mL of anhydrous ether. After 10 min, the resulting precipitate was filtered off and washed with anhydrous ether (~2 mL). The ethereal mother solution was concentrated. Anhydrous EtOH was added to oily residue, and the resulting precipitate was filtered off and washed successively with anhydrous EtOH and anhydrous ether to give 50 mg (10%) of the product as yellow crystals, m.p. 156—159 °C. UV (EtOH), λ_{max}/nm (ε): 350 (sh) (ε 6300); 400 (ε 16600). ^{1}H NMR ($CDCl_3$), δ: 3.16 (s, 6 H, NMe_2); 3.91 (s, 3 H, COOMe); 3.93 (s, 3 H, COOMe); 8.10 (s, 1 H, δ-H); 8.59 (d, 1 H, β-H, *J* = 2 Hz); 8.78 (d, 1 H, β′-H, *J* = 2 Hz).

The precipitate from the reaction mixture (λ_{max} 400 and 470 nm) was a mixture of compounds **13a** and **15a**, which could not be separated.

Cation-anionic dyes 19—29. A filtered solutions containing a known cyanine dye ($[\mathbf{Cat^1}]^+I^-$, $[\mathbf{Cat^2}]^+I^-$, $[\mathbf{Cat^3}]^+I^-$, $[\mathbf{Cat^4}]^+I^-$, $[\mathbf{Cat^6}]^+Br^-$, $[\mathbf{Cat^7}]^+EtSO_4^-$, $[\mathbf{Cat^8}]^+Cl^-$ in a mixture of 12 mL of EtOH and 4 mL of CH_2Cl_2 or $[\mathbf{Cat^5}]^+Cl^-$ in a mixture of 12 mL of EtOH and 2 mL of CH_2Cl_2) (0.12 mmol) and a solution of anionic dye **11** or **13a** (0.12 mmol) in 10—12 mL of EtOH were poured together. The cation-anionic dye was isolated either by filtering off the resulting precipitate (as in the case of compounds **19**, **20**, **23**, **24**, and **27—29**) or as the precipitate formed after removal of the solvent *in vacuo* and addition of 6—7 mL of H_2O (dyes **21**, **22**, **25**, and **26**). The resulting dyes were washed successively by H_2O, EtOH, and ether and dried.

X-ray diffraction analysis of tetraester 3a. Crystals of **3a** ($C_{16}H_{21}NO_8$, $M = 355.34$) are monoclinic, space group *C*2/*s*; at −120 °C $a = 26.210(4)$, $b = 9.4251(12)$, $c = 14.628(2)$ Å, $\beta = 102.23(1)°$, $V = 3531.4(8)$ Å^3, $Z = 8$, $d_{calc} = 1.337$ g cm^{-3}. The unit cell parameters and the intensities of 3648 reflections were measured on a Siemens P3/PC four-circle automated diffractometer (153 K, λMoKα, graphite monochromator, θ/2θ scan mode, $\theta_{max} = 28°$). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms, localized objectively in the difference Fourier synthesis, were refined in the isotropic approximation. The final residual factors were $R_I = 0.033$ over 2962 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.088$ over 3536 independent reflections. All the calculations were carried out on an IBM PC/AT-386 using the SHELXTL PLUS and SHELXL-93 programs. The coordinates and isotropic thermal parameters of atoms are listed in Table 2, while bond lengths and bond and torsion angles are given in Tables 3—5, respectively.

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