NOVEL POLYMETHINE DYES DERIVED FROM AMINALS AND

AMINAL-ACETALS OF CONJUGATED W-DIMETHYLAMINOALDEHYDES

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In a previous study [1] of the condensation reactions of aminals and aminal-acetals of conjugated ω -dimethylaminoaldehydes (I) (n = 0-2, R = H, Y OMe, NMe₂) with malondinitrile, it was found that, in addition to the principal reaction products, conjugated ω -dimethyl- \dot{CN} CH-(CH=CH)_nCH=C(CN)₂ aminodinitriles $Me_2N(CH=CH)_nCH=C(CN)_2$, tetracyanopolymethines

were also isolated, in yields of 12 (n = 1), 36 (n = 2), and 18% (n = 3), respectively.

Tetracyanopolymethines (TCPM) are anionic polymethine dyes, which may also be of interest as anionic components in the preparation of cation-anion dyes.

In the present paper we have developed conditions for the preparation of TCPM in high yields, and have also prepared for the first time a series of y-functionalized tetracyanopentadienes:

$$\begin{array}{c} \operatorname{Me_2N-}\left(\operatorname{CH=}^R_{\mathcal{O}}\right)_n - \operatorname{CH} \swarrow \stackrel{NMe_2}{Y} + \operatorname{CH_2(CN)_2} \rightarrow \underset{CN}{\overset{O}{\longrightarrow}} \stackrel{CN}{\overset{O}{\subset}} - \binom{\underset{I}{\overset{I}{\bigcap}}}{\underset{n}{\operatorname{CH}} = \operatorname{C(CN)_2} \stackrel{\oplus}{\overset{O}{\operatorname{N}}} \operatorname{H_2Me_2}}{\underset{III)-(XI)}{(II)-(XI)} \\ (I): n = 1, R = H, Me, Ph, Cl, Br, CN, OEt, NMe_2; n = 2, R = H; n = 3, R = H; \\ \mathbf{Y} = OMe, NMe_2; (II)-(XI): n \text{ and } R \text{ are given in Table 1.} \end{array}$$

Aminals and aminal-acetals of (I) readily undergo condensation with $CH_2(CN)_2$ in benzene solution at 20°C in the absence of a catalyst. At a (I):CH2(CN)2 ratio equal to 1:2, compounds (II)-(XI) are formed; their structures and properties are given in Table 1.

These newly synthesized TCPM are, with the exception of compounds (IV), (IX), and (X), easily isolated from the reaction mixtures in the form of their crystalline dimethylammonium salts; (IV), (IX), and (X) were isolated by chromatography on SiO_2 .

The conjugated ω -dimethylaminodinitriles which were obtained under the conditions described above were formed in small amounts (<10%) and remained in CHCl₃ solution after the isolation of the TCPM. Only the dinitriles $Me_2NCH = C(R) - CH = C(CN)_2$ ((XII): R = NMe₂, and (XIII): R = Ph) were formed in higher yields of 20-25%.

The structures of the TCPM were confirmed on the basis of their PMR spectra (for compounds (II)-(XI)), and also using ¹³C-NMR spectroscopy (compound (II)) (Table 1). The chemical shifts (CS) of the olefinic carbon atoms in the ¹³C-NMR spectrum of (II) reflect alter-

nating π -electron density $CN \xrightarrow{+}_{\beta} \xrightarrow{+}_{\beta} \xrightarrow{CN}_{\beta} \xrightarrow{N}_{\beta} \xrightarrow{N}_{\alpha} \xrightarrow{N}$

deficit is shifted downfield substantially ($\delta = 157.97$ ppm) compared to (\overline{C}_{α}) and (\overline{C}_{γ}), for which the CS values are 54.33 and 108.15 ppm, respectively. The very strong upfield shift of C_{α} is due to the influence of the two CN groups attached to C_{α} .

Based on the electronic spectra of the TCPM (Table 1), it is clear that λ_{max} undergoes a bathochromic shift of 100 nm upon extension of the polymethine chain by one (CH=CH) unit (compare compounds (II), (X), and (XI)); introduction of a substituent in the meso-position (with the exception of (VII)) exerts only a very small change on the position of the absorption maximum ($\Delta\lambda$ < 11 nm).

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| | | | (ô, ppm, CD ₃ OD) | other protons | 6,02 d.d(H ₇) 6,0 d.d(H ₇) | 2,2 (CH ₃) | 6,92-7,42 (Ph) | | | | 1,35 t (CH ₃ CH ₂) | 3.764 (CH ₃ CH ₂) (3H, H ₆ , H ₆ , H ₅) (3H, H ₆ , H ₇) | (4H, He, He, He, He,) | $ \begin{vmatrix} (3H, H_7, H_6, H_\eta) \\ (4H, H_6, H_6, H_6, H_6, H_0) \\ (3H, H_7, H_6, H_1) \end{vmatrix} $ | |
|----|---------------------------|----|---|---------------------------------|--|--|--|----------------|---|--|--|---|---|--|---|
| | | | spectrum | H _β n H _δ | 7,26 br.d 7,28 br.d | 6,83 | 6,92-7,42 | 6,98 | 7,23 | 7,35 | 6,66 | 6,88 7,09m 5,93+ | 7,08m | 0,00m 7,08m 6,08m | |
| | | | PMR S | NMe2 | 2,7 | 2,65 | | 2,65 | 2,68 | 2,67 | 2,68 | 2,47 | | 3,03 | |
| | | | Electronic spectrum in EtOH, λ_{max} , nm (ε) | | 440 (78 900) 440 (84 000) | 441 (125 300) | 438 (81 280) | 442 (111 150) | 440 (113 000) | 415 (95 706) | 451 (73 400) | 442 (83 290) 540 (90 000) | 643 (90 800) | 643 (90 857) | |
| | | | ated, | z | 30,6 | 30,3 30,57 30,83 | 22,61 22,61 | 27,68 27,68 | 23,82 | 16,62 | 24,6 95.45 | er,62 | | | |
| | ([] | • | Calcula % | H | 4,98 | 5,62 5,74 | | 3,77 | 3,51 | 3,42 4,49 <u>6.93</u> | 4 ¹ C-1 | 4,89 | 1 ,00 | | |
| | (II)—(X | | Found/ | υ | 57,22 | 57,10 63,33 63,43 | 21 600 | 53,09 | 44.71 | 40,20 60,19 | et, 00 | 57,96 | 00,10 | | |
| CN | $n - CH = C K^{\oplus}$ | CN | | Molecular formula | С ₉ Н ₁ N ₄ С1,Н11N ₅ .Н ₂ O | G ₁₂ H ₁₃ N ₅ | C ₁₅ II ₈ N ₄ | C1111.0N5Cl | C ₁₁ H ₁₀ N ₅ Br | C ₁₂ H ₁₀ N ₆ | C ₁₃ II ₁₅ N ₅ O · 1,5H ₂ Oé | G ₁₁ H ₉ N ₅ C ₁₁ H ₆ N ₄ ·2H ₂ O | C ₁₃ H ₈ N ₄ | C ₁₅ H ₁₅ N ₅ | |
| ш- | $\int_{C}^{O} -(CII = C)$ | GN | | Mp, °C M | 158-160 85-86 | 141-142 b | 215-218 | 147-150 c | 123-125 | 142-146d | 63-65 | 147-150d 185 f (dec.) | >250 | 129 (dec.) | |
| CN | | | Vield % | | 85 85 | 95 | 38 | 00 | 54 | 80 | 80 | 41 70 | 80 | 83 | |
| | .c Dyes | | | К | $_{\rm NH_2Me_2}^{ m H}$ | NH12Me2 | Н | NII2Mo2 | NH12Mc2 | NH2Me2 | NH2Me2 | HH | Н | NII2Me2 | |
| | iioii | | | u | | ~ | 1 | ÷ | | | क्रम | 40 | ന | e. | 1 |
| | • • A1 | | | ж | HH | Me | μ'n | ច | Br | CN | OEt | NMe ₂ H | Н | 11 | |
| | TABLE 1 | | Com- | punod | | (111) | (1I) | (x) | (IVI) | (III) | (IIII) | (XI) (X) | (IX) | (IX) | |

a) ¹³C-NMR spectrum (II), K = NH₂Me₂ (CDCl₃, δ , ppm; J, Hz): 35.52 q (NMe₂) J = 142.8), 54.33 (C_q), 108.15 d (C_q, J = 155.6), 157.97 d (C_g, J = 155.6), 118.4 and 120.6 (CN). b) 1:3 MeOH—ether. c) 1:1 Benzene—ether. d) After washing with acetone. e) H₂O: found 9.06%, calculated 9.5%. f) 5:1 Benzene-acetone.

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Fig. 1. Electronic absorption spectra of dyes in EtOH (a) and C₆H₆ (b): 1) (XXIV); 2) (XV), 3) (XXV).

The cation $(H^+ \text{ or } ^+NH_2Me_2)$ in these TCPM can be easily replaced by a cationic cyanine dye, resulting in the formation of the cation—anion cyanine dyes (XIV)-(XXV) in high yields; the structures of these dyes are given in Table 2.

The electronic spectra of these newly synthesized cation—anion dyes were investigated. In polar solvents (EtOH) the spectra contain two bands (Fig. 1a, curve 1), corresponding to absorption of the cationic and anionic components, respectively. When the absorption maxima of the two components are similar in wavelength, the bands coalesce to form one very intense absorption band (Fig. 1a, curves 2 and 3). Thus, for example, dye (XV) contains one absorption band in EtOH, λ_{max} 444 nm (ϵ 208,000), while its constituent dyes (II) and K₂+Ts⁻ exhibit λ_{max} 440 nm (ϵ 84,000) and 448 nm (ϵ 120,000).

As the index of refraction of the solvent is increased there is an accompanying characteristic shift of both absorption bands toward longer wavelength. This trend is followed in weakly polar solvents for most of the newly synthesized dyes, which is indicative of the universal nature of the effect of medium on the absorption spectra of these dyes, and of the absence of specific cation-anionic interaction in these solvents. Dyes (XV), (XXIV), and (XXV) are exceptions to this rule; in low dielectric constant solvents, such as benzene, or mixtures of tetrachloroethane or CCl_4 with CH_2Cl_2 (9:1), the electronic spectra of these dyes contain, in addition to the absorption bands of the cationic and anionic components, respectively, a new short-wavelength band (λ_{max} , 400-420 nm) (Fig. 1b). Since the ratio of band intensities does not depend on the dye concentration, the formation of this additional absorption band cannot be due to the effect of aggregation. The absorption spectra of the anionic dyes (II), (III), and (VII), and of the cationic thiazolinocarbocyanine tosylate dye (K₂+Ts⁻), which are the anionic and cationic components, respectively, of dyes (XV), (XXIV), and (XXV), do not contain these additional bands in analogous solvent systems. Based on these results we conclude that the absorption band in the 400-420 nm region for (XV), (XXIV), and (XXV) is due to specific cation-anion interactions within the dye molecules. This requires not only interaction of the chromophoric systems in the cationic and anionic components, but also stabilization via hydrogen bond formation between the nitrile groups in the anion and the heterocyclic methylene groups in the cation. It should be noted that the presence of only one of these factors is not sufficient to give rise to the appearance of specific cation-anion interaction.

In the type of complex formed by dyes (XV), (XXIV), and (XXV), the cation and anion are located in parallel with one another and stabilized in two directions via interaction of their terminal groups.



When stabilization can occur from only one direction, such as in dye (XVIII), due to different lengths of the chromophores in the two components, the interaction is not sufficient to give rise to an additional absorption band due to complex formation.

| | trum, | GeIIs | 448 674 | 421 447 | (plateau) 449 724 | 448 572 | 442 550 | 545 673 | 449 622 | 571 620 |
|------|---|-------|--------------------------------|-----------------------|-------------------------------|-------------------------------|---|--------------------------------|-------------------------------|--|
| | Electronic spec $\lambda \max, nm(\varepsilon)$ | EtOII | 440 (102 000) 655 (237 000) | 444 (208 000) | 440 (62 000) 709 (210 000) | 440 (60 000) 560 (152 000) | $\begin{array}{c} 442 \\ 540 \\ (128 \\ 000) \end{array}$ | 540 (162 000) 655 (223 000) | 440 (81 000) 607 (157 000) | 545 (138 000) 607 (180 000) |
| | % | s | 11,35 11,50 | $\frac{14,52}{14,65}$ | | 12,41 | | <u>10,75</u> 10,95 | | |
| | alculated | н | $\frac{5,04}{4,66}$ | 5,62 5,54 | 5,24 5,38 | 4,32 | | 4,64 | $\frac{5,52}{5,39}$ | 5,36 5,49 |
| | Found/C | C | <u>68,64</u> <u>68,70</u> | 60,18 60,54 | 78,05 78,40 | $\frac{67,40}{67,60}$ | | <u>69,50</u> <u>69,85</u> | 78,30 78,50 | 78,85 79,00 |
| , ČN | Molecular formula | | $C_{32}H_{26}N_6S_2$ | $C_{22}H_{24}N_8S_2$ | Ca4H28N6 | $C_{30}H_{24}N_6S_2$ | $C_{24}H_{26}N_6S_2$ | $C_{34}H_{28}N_6S_2$ | $C_{34}H_{28}N_6$ | C ₃₆ H ₃₀ N ₆ |
| | Mp, °C | | 193-195 | 111-011 | 101-104 | 202 - 204 | 80 with de- composition | 206-208 | 235237 | 135 138 |
| CN | Yield, % | | 75 | 56 | 99 | 80 | 50 | 75 | 65 | 68 |
| | Cation* | | Kı | K ₂ | K3 | Кı | K ₂ | Kı | Ks | K5 |
| | uo | u | | प् रून | Ļ | | 2 | 5 | Ţ | ณ |
| | Ani | В | = | Н | П | П | Н | П | II | Ξ |
| | Compound | | (XIV) | (XV) | (IAX) | (XVII) | (IIIAX) | (XIX) | (XX) | (IXX) |

(CH = C) ĆN Cation-Anion Dyes TABLE 2.

ĸ⊕ CN

EO-

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| pectrum, | C,H, | 542 borad band | 447 532 | 410 | 418 450 (plateau) | |
|------------------------------|----------------------|-------------------|-------------------------------|------------------------------|-------------------------|--------------------|
| Electronic s λ max, nm (ε | ЕСОН | 522 (270 000) | 441 (86 000) 522 (209 000) | 416 (98 400) 444 (98 400) | 443 (210 000) | |
| ced, % | s | | | <u>13,51</u> 13,88 | <u>13,92</u> 14,24 | E |
| l/Calculat | H | 3,85 4,03 | 3,85 4,03 | $\frac{5,24}{4,99}$ | 5,95 5,76 | - = + + |
| Found | υ | 54,50 54,15 | 52,45 52,85 | <u>60,27</u> 59,85 | $\frac{61,00}{61,20}$ | |
| | Molecular formula | C38H34N8O4S2F6 | C36H32N8O4S2F6 | C23H23N7S2 | C23H26N6S2 | |
| | мр, °С | 136-138 | 92-95 | 140-143 | 164-165 | |
| | Yield, % | 76 | 80 | 80 | 93 | |
| | Cation" | K6 | Кa | K, | K2 | $K_{a}^{+} =$ |
| ion | u | 5 | - | | - | |
| ΫŪ | Я | Н | Н | CN | Me | E-x |
| | Compound | (XXII) | (XXIII) | (XIX) | (XXV) | $* K_{i} + =$ |

TABLE 2 (continued)

The photographic properties of the cation—anion dyes (XX), (XXI), (XIV), and (XIX) were studied in an ammoniacal silver bromide—iodide emulsion, according to [2].

It was found that the absorption spectra of these dyes in the emulsion contained bands due to the cationic and anionic components only. As sensitizers these dyes were found to be somewhat better than their corresponding cationic dyes, resulting in 20-25% higher light sensivity of films than the carbocyanine dye K_5 +Cl⁻ and the dicarbocyanine dye K_1 +I⁻.

EXPERIMENTAL

Electronic absorption spectra were measured on Specord UV-VIS, Specord M-40, and SF-20 spectrophotometers, respectively; PMR spectra were recorded on a Tesla BS-467 spectrometer at an operating frequency of 60 MHz, while high resolution and ${}^{13}C-{}^{1}H$ decoupled spectra were obtained on a Bruker WM-250 spectrometer at a ${}^{13}C$ operating frequency of 62.89 MHz. Compounds in the series (I) were prepared according to [1]; the ratios of aminal (Y = NMe₂) and aminal—acetal (Y = OMe) in (I) were determined by NMR and found to be 9:1 (n = 1, R = H, Me, F, CN, Cl); 2:3 (n = 1, R = Ph; n = 3, R = H); 8:2 (n = 1, R = Br); 3:1 (n = 1, R = OEt); 0:1 (n = 1, R = NMe₂); 1:0 (n = 2, R = H).

<u>General Procedure for the Synthesis of Tetracyanopolymethines.</u> To a suspension of 12 mmoles $CH_2(CN)_2$ in 2 ml dry benzene was added 6 mmoles (I) in 4 ml dry benzene. After 1 h the reaction mixture was evaporated under vacuum. Compounds (III), (V)-(VIII), and ((XI), K = NH_2Me_2) were isolated by the addition of 5 ml CH_2Cl_3 to the residue and filtration and washing of the precipitate with 5 ml $CHCl_3$.

In order to isolate (II) (K = NH_2Me_2) the concentrated reaction mixture was dissolved in 10 ml absolute MeOH, cooled, and $Me_2NCH=CH-CH=C(CN)_2$ was removed (10%). The methanol solution was evaporated under vacuum. To the residue was added 5 ml CHCl₃ and (II) (K = NH_2Me^2) was isolated and washed with an additional 5 ml CHCl₃.

Compounds (II) and (XI) (K = H) were isolated by preparative TLC; (II) and (XI) (K = NH_2Me_2) on SiO₂ (EtOH:NH₄OH, 14:1). In order to isolate (X) the concentrated residue from the reaction mixture was washed with CHCl₃ and subjected to preparative TLC on SiO₂ (EtOH: NH_4OH , 14:1), then leached out with EtOH. Compounds (IV), (IX), (XII), and (XIII) were isolated after chromatography of the concentrated residues on SiO₂. The dinitriles (XII) and (XIII) were isolated by leaching with CHCl₃, (IV) and (IX) by leaching with a mixture of EtOH:NH₄OH, 14:1. (XIII) was prepared in 80% yield by carrying out the reaction in absolute MeOH for 48 h at 20°C. (XII), mp 140-142°C. UV spectrum (λ_{max} , nm, EtOH): 380 (ϵ 47,500). PMR spectrum (CDCl₃, δ , ppm): 2.45 (6H, NMe₂), 3.10 (6H, NMe₂), 6.95 (1H, H_β or H_δ), 6.63 br s (1H, H_β or H_δ). Found: C 62.97; H 7.11; N 29.47%. C₁₀H₁₄N₄. Calculated: C 63.16; H 7.37; N 29.47%. (XIII), mp 158-161°C (from ether—MeOH, 1:2). UV spectrum (λ_{max} , nm, EtOH): 378 (86,159). PMR spectrum (CDCl₃, δ , ppm): 2.48 and 3.15 (6H, NMe₂), 6.98 br s (1H, H_β or H_δ), 7.12 (1H, H_β or H_δ), 7.2-7.45 (5H, Ph). Found: C 75.77; H 5.93; N 18.58%. C₁₄H₁₃N₃. Calculated: C 75.34; H 5.83; N 18.83%.

<u>Cation—Anion Dyes (XIV)-(XXV).</u> Prefiltered solutions containing 0.1 mmole of the cyanine dye $(K_3^+I^-, K_4^+I^-, K_6^+I^-)$ in a mixture of 25 ml EtOH and 5 ml CH_2Cl_2 ; $K_2^+Ts^-$ in 5 ml EtOH; $K_1^+Ts^-$ and $K_5^+Cl^-$ in 15 ml EtOH) were layered with a solution containing 0.1 mmole of an one of the anionic dyes (II)-(XI) in 3-5 ml EtOH. The resulting dye was isolated either immediately in the form of a precipitate (XIV) and (XX), or else after evaporation of the solvent under vacuum and the addition of 3-5 ml H₂O. The dye was washed with H₂O, EtOH, and ether, and dried.

CONCLUSIONS

1. A series of tetracyanopolymethines has been synthesized by condensation of aminals and aminal—acetals of conjugated ω -dimethylaminoaldehydes with malonodinitrile.

2. These tetracyanopolymethines can be used as the anionic components in cation—anion cyanine dyes.

3. The electronic absorption spectra of these newly synthesized dyes were studied in both polar and nonpolar solvents. Specific cation—anion interaction and complex formation has been shown to occur in several of these cation—anion dyes in nonpolar solvents.

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OXIDATIVE δ -CHLORINATION OF ALIPHATIC ALCOHOLS IN THE SYSTEM LEAD TETRAACETATE—METAL CHLORIDE*

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Alkoxy radicals containing at least four carbon atoms in the chain are capable of undergoing rearrangement in solution with 1,5-H and 1,6-H migration $(K_{1,5-H}/K_{1,6-H} \approx 10 \ [2])$. Precursors of the alkoxy radicals may be alkanols, alkyl hypochlorites, alkyl nitrites, or alkyl hydroperoxides [3].

Functionalization of carbon-centered radicals at the radical center by external reagents gives functionally substituted alcohols, while intramolecular functionalization affords fivemembered cyclic ethers. For example, oxidation of aliphatic alcohols with five or more carbon atoms by lead tetraacetate (LTA) gives mostly α -alkyltetrahydrofurans [4], whereas photochemical decomposition of alkyl hypochlorites and reduction of alkyl hydroperoxides by Fe(II) chloride produces mainly the δ -chloroalkanols [5, 6].

We have now examined the oxidation of primary, secondary, and tertiary C_5-C_{11} aliphatic alcohols (I) in the system LTA-metal chloride, in order to determine the influence of the structure of the alcohol on the course of oxidation, and to synthesize δ -chloroalkanols. The reaction was carried out in benzene at 80°C. The principal product of the reaction was found to be the δ -chloroalkanol (II). To a small extent, (I) was oxidized to the ε -chloroalkanol (III), the carbonyl compound (IV), and the substituted alkyltetrahydrofuran (V), the overall yield of (III)-(IV) being 5-10%:



R¹, R², R³, R⁴ and R⁵=H, alkyl C₁--C₅, C₆H₅; M = Li, Na, K, Mg, Ca; n = 1, 2.

EPR was used to detect the radical steps in the oxidation of alcohols. It was found that the reaction between LTA and 1-hexanol in benzene in the presence of C-phenyl-N-tertbutylnitrone (PBN) gave rise to a triplet of doublets in the EPR spectrum ($a_{\rm N}$ = 13.8; $a_{\beta}^{\rm H}$ = 1.9 Oe) for the spin adduct (SA) of the alkoxy radicals (A) with PBN. Radicals of type (A) were also detected in the reaction of 1-hexanol with the system LTA-LiCl in the presence of PBN. The formation of carbon-centered secondary radicals was observed in the oxidation of 1-hexanol with LTA in the presence of 2-methyl-2-nitrosopropane (MNP). The EPR spectrum of

*For previous communication, see [1].

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