in vacuo; 50 ml. of water was added to the residue and it was made alkaline with 45% aqueous potassium hydroxide. After extraction with ether, the ethereal layer was concentrated and the residual oil fractionated to give 9.9 g. (59%) of a colorless oil, b.p. 87–89° (0.6 mm.), $n^{27}D$ 1.4720.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 71.07; H, 11.33; N, 8.29. Found: C, 70.68; H, 11.46; N, 9.01, 8.82.

The hydrochloride was recrystallized from methanol, m.p. 156–159°.

Anal. Calcd. for $C_{10}H_{20}ClNO$: N, 6.83; Cl, 17.30. Found: N, 6.97; Cl, 17.70.

The oxime was recrystallized from ethanol, m.p. 190–193° as white crystals.

Anal. Calcd. $C_{10}H_{21}ClN_2O$: C, 54.41; H, 9.62; N, 12.69; Cl, 16.06. Found: C, 54.33; H, 9.62; N, 12.89; Cl, 16.07.

2-Acetyl-trimethylene-1,3-bis-(hexahydro-1-azepine Dihydrochloride.—A mixture consisting of 9.2 g. (0.31 mole) of paraformaldehyde, 12.6 g. (0.21 mole) of acetone, 60 ml. of ethanol, 0.5 ml. of concentrated hydrochloric acid and 25 g. (0.18 mole) of hexahydroazepine hydrochloride was refluxed for 1 hour. After this period an additional 6 g. (0.2 mole) of paraformaldehyde was added and the heating was continued for another 2 hours. The mixture then was added to 500 ml. of hot acetone and allowed to cool. The white crystals which separated were recrystallized from ethanol to give 13 g. (20%) of product, m.p. 196–198°.

Anal. Calcd. for $C_{17}H_{34}Cl_2N_2O$: C, 57.84; H, 9.71; N, 7.94; Cl, 20.09. Found: C, 57.49; H, 9.66; N, 7.65; Cl, 19.99.

1-(3-Aminopropyl)-hexahydroazepine Dihydrochloride.—To 8 g. (0.21 mole) of lithium aluminum hydride in 500 ml. of ether, hexahydro-1-azepinepropionitrile (15.2 g., 0.1 mole) in 50 ml. of ether was added slowly. After the addition was completed, the solution was refluxed for an additional hour; 8 ml. of water was added slowly to decompose the excess hydride; this was followed by 6 ml. of 20% aqueous sodium hydroxide and an additional 28 ml. of water. After filtration and washing of the cake with ether, the solvent was removed *in vacuo* to give a yellow oil which was converted to the dihydrochloride with ethanolic hydrogen chloride and was recrystallized from ethanol to give 16.1 g. (70%) of white crystals, m.p. 114–115°.

Anal. Calcd. for $C_9H_{22}Cl_2N_2$: N, 12.23; Cl, 30.97. Found: N, 12.04; Cl, 31.18.

1-(3-Dimethylaminopropyl)-hexahydroazepine Dihydrochloride.—Hexahydroazepine (19.8 g., 0.2 mole) and 3-dimethylaminopropyl chloride (12.15 g., 0.1 mole) in 150 ml. of xylene were refluxed 2.5 hours, then cooled and filtered. The filtrate was gassed with hydrogen chloride and the solid so obtained was recrystallized from ethanol to give 16.72 g. (65%) of white crystalline material, m.p. 272–275°.

Anal. Calcd. for $C_{11}H_{26}Cl_2N_2$: N, 10.90; Cl, 27.59. Found: N, 10.76; Cl, 26.73, 26.83.

1-(2-Dimethylamino-1-methylethyl)-hexahydroazepine dihydrochloride was prepared in the manner described above. It was recrystallized from ethanol and gave white crystals in 70% yield, m.p. 218–220°.

Anal. Calcd. for $C_{11}H_{26}Cl_2N_2$: N, 10.90; Cl, 27.59. Found: N, 10.06; Cl, 27.37.

1-(2-Diethylaminoethyl)-hexahydroazepine dihydrochloride was prepared in the manner described above. It was recrystallized from ethanol and gave white crystals in 72% yield, m.p. 237–240°, lit.[22] m.p. 222–224° dec.

Anal. Calcd. for $C_{12}H_{28}Cl_2N_2$: N, 10.34; Cl, 26.17. Found: N, 10.23; Cl, 26.00.

Ethyl Hexahydro-1-azepinepropionate.—A mixture of 9.9 g. (0.1 mole) of hexahydroazepine and 9 g. (0.05 mole) of ethyl 3-bromopropionate in 100 ml. of benzene was refluxed for 1.5 hours. The solution darkened and precipitation occurred. After cooling, the reaction mixture was extracted with an equal volume of water and the benzene layer dried and then concentrated *in vacuo*. Fractionation of the residual oil gave 9 g. (90%) of the desired product, b.p. 125–132° (14 mm.), $n^{27}D$ 1.4580.

Anal. Calcd. for $C_{11}H_{21}NO_2$: C, 66.39; H, 10.64; N, 7.04. Found: C, 66.35; H, 10.36; N, 7.06.

Hexahydro-1-azepineacetaldehyde.—To a solution of 19.8 g. (0.2 mole) of hexahydroazepine in 400 ml. of benzene was added slowly 10.3 g. (0.1 mole) of 3-chloro-2-hydroxypropionitrile. The solution was refluxed 4 hours, allowed to stand overnight, filtered, concentrated and fractionated to give 8.7 g. (62%) of an oil, b.p. 69–71° (0.2 mm.), $n^{27}D$ 1.4821.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.14; H, 10.72; N, 9.93. Found: C, 67.87; H, 10.59; N, 10.04.

The hydrochloride salt melted at 92–94° with decomposition when recrystallized from ethanol.

Anal. Calcd. for $C_8H_{16}ClNO$: C, 54.13; H, 9.08; N, 7.89; Cl, 19.97. Found: C, 53.08; H, 9.24; N, 8.30; Cl, 20.45.

1-Benzylhexahydroazepine Hydrochloride.—With stirring, 12.6 g. (0.1 mole) of benzyl chloride in 50 ml. of benzene was added to a solution of 19.8 g. (0.2 mole) of hexahydroazepine in 400 ml. of benzene and refluxed for 2 hours. After cooling and filtering, the solution was concentrated and the residual yellow oil was fractionated, b.p. 80–82° (0.5 mm.), and gassed with hydrogen chloride. Recrystallization from ethanol–ether gave 13.7 g. (61%) of white crystalline material, m.p. 163–165°.

Anal. Calcd. for $C_{13}H_{20}ClN$: C, 69.33; H, 8.49; N, 6.22; Cl, 15.56. Found: C, 68.95; H, 8.99; N, 6.13; Cl, 15.50.

SUMMIT, NEW JERSEY

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(22) F. F. Blicke and E. B. Hotelling, THIS JOURNAL, **76**, 2422 (1954).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Polymethine Dyes. I. A Comparison of Several Vinylogous Series in which the Polymethine Chains Are Terminated by Aryl Groups[1]

BY WILLIAM B. TUEMMLER AND BERNARD S. WILDI[2]

RECEIVED DECEMBER 19, 1957

The preparation and absorption spectra of four series of polymethine dyes having polymethine chains terminated by aryl groups are described. By applying principles known from the triphenylmethane- and cyanine dyes, it is possible to identify x-, y- and x'-bands in these spectra. A large bathochromic shift of the y-band as well as the x-band occurs as conjugation in the chain is extended.

Introduction

The polymethine dyes have provided some of the outstanding examples of the successful correlation of color and constitution in organic molecules. Particularly significant studies in the cyanine field have been reported by Brooker and his colleagues[3]

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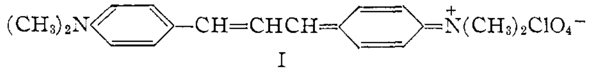
[1] Presented in part before the Organic Division of the American Chemical Society, 129th Meeting, Dallas, Texas, April 9, 1956.

[2] To whom inquiries should be directed.

[3] (a) L. G. S. Brooker, R. H. Sprague and H. N. J. Cressman, THIS

and by Hamer and her collaborators.[4] Because of their effectiveness as photographic sensitizers the cyanines are commercially important and a large number of them have been studied.

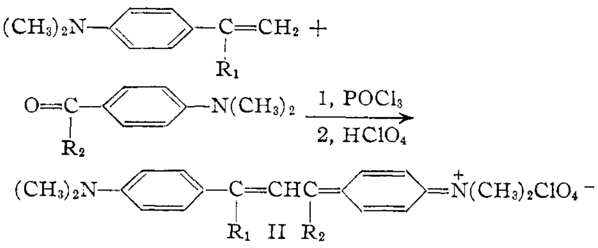
Polymethine dyes in which the polymethine chain is terminated at each end by substituted benzene rings have received relatively little study. Wizinger and his co-workers[5,6] have described the preparation of tri- and pentamethine dyes having terminal aryl groups, but have reported spectroscopic data on only a few. The vinylog I of the color salt of Michler hydrol also has been reported.[7]



I

We have extended the class of tetraaryl tri- and pentamethine dyes described by Wizinger to the heptamethine vinylogs and also have correlated the spectra of these compounds in greater detail. Several new tri- and pentamethine dyes also have been prepared.

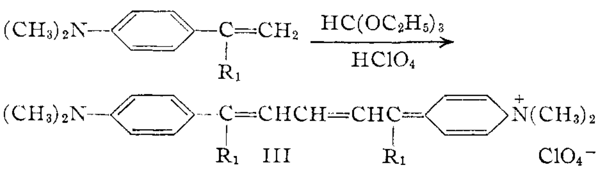
Preparation of Dyes.—The tri- and pentamethine dyes were prepared essentially according to Wizinger.[5,6] The reactions of the appropriate benzophenone with a 1,1-diarylethylene in phosphorus oxychloride, followed by treatment with perchloric acid, furnished the trimethine dyes II in 39–56% yield.



II

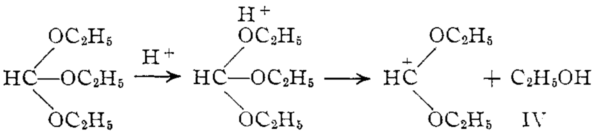
Other strong acids such as *p*-toluenesulfonic acid and trifluoroacetic acid can be used in place of perchloric acid, but yields are lower. The reaction failed when R_1 and R_2 were 2,4-dichlorophenyl, presumably because of steric interference by the *ortho* chlorine atoms.

The pentamethine dyes III were prepared by reaction of ethyl orthoformate with a 1,1-diarylethylene under anhydrous conditions in the presence of perchloric acid.



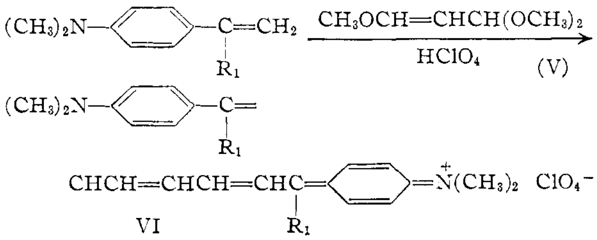
III

With the exception of III, R = 2,4-$Cl_2C_6H_3$, which was obtained in very low yield, yields were 50–99%. This reaction proceeded smoothly in acetic anhydride or in dry acetic acid, but failed when ordinary acetic acid was the solvent. This can be explained by a reaction mechanism in which coördination of the acid with the orthoester is followed by cleavage to the carbonium ion IV which then enters into a sequence of reactions with the polarized ethylene leading to the product.[8] However, if water is present it reacts preferentially with the carbonium ion IV to form ethyl formate and ethanol. This is in agreement with the observation[9] that carbonium salts resulting from the addition of acids to 1,1-diarylethylenes are readily hydrolyzed in aqueous media. The lower nucleophilicity of the ethylene compared to water prevents it from competing successfully for an electrophilic ion.



IV

The heptamethine dyes VI were prepared in 37–96% yields by using 1,3,3-trimethoxypropene-1 (V) instead of ethyl formate. This approach has been used successfully in the cyanine series.[10] These reactions proceeded more rapidly than those with ethyl orthoformate; in some cases maximum yields were obtained in less than one minute.



(V)

VI

The preparation and properties of the polymethine dyes are summarized in Table I.

Experimental

1,1,5,5-Tetrakis-(*p*-dimethylaminophenyl)-2,4-pentadien-1-ol perchlorate (VIII).—A mixture of 1.33 g. (0.005 mole) of 1,1-bis-(*p*-dimethylaminophenyl)-ethylene, m.p. 122–124°, 1.0 ml. of ethyl orthoformate and 5 ml. of acetic anhydride was treated all at once with a solution of 0.34 g. (0.0025 mole) of 71% perchloric acid in 5 ml. of acetic anhydride. (Caution is advised when adding perchloric acid to acetic anhydride. The reaction is strongly exothermic). The blue mixture was heated on the steam-bath for 70 minutes with occasional swirling. After cooling, the golden-brown needles which precipitated were collected, washed with acetic acid followed by ether and dried under vacuum to give 1.52 g. (94%) of VIII, m.p. 232–234° dec.

Essentially identical results were obtained when heating was omitted and the reaction mixture stood at room temperature for two days. Absolute acetic acid could be substituted for acetic anhydride as the solvent with equally good results.

1,7-Bis-(*p*-dimethylaminophenyl)-1,7-bis-(phenyl)-2,4,6-heptatrien-1-ol Perchlorate (XII).—A mixture of 7.63 g. (0.00342 mole) of 1-(*p*-dimethylaminophenyl)-1-phenylethylene, m.p. 55–58°, 3.5 ml. of 1,3,3-trimethoxypropene-1 (Eastman Kodak Co.), b.p. 30° (0.5 mm.), and 15 ml. of acetic anhydride was treated all at once with a solution of 2.30 g. (0.017 mole) of 71% perchloric acid in 30 ml. of

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JOURNAL, **67**, 1889 (1945), and earlier papers; (b) L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr., and G. Van Zandt, *Chem. Revs.*, **41**, 325 (1947).

(4) (a) N. I. Fisher and F. M. Hamer, *J. Chem. Soc.*, 189 (1933); (b) N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc.* (*London*), **154A**, 703 (1936); (c) F. M. Hamer, *Quart. Rev.*, **4**, 327 (1950).

(5) R. Wizinger and G. Renckhoff, *Helv. Chim. Acta*, **24**, 369E (1941).

(6) H. Lorenz and R. Wizinger, *ibid.*, **28**, 600 (1945).

(7) W. König and K. Seifert, *Ber.*, **67B**, 2112 (1934).

(8) Essentially the same mechanism has been proposed for the formation of cyanine dyes; A. B. Lal and V. Petrow, *J. Chem. Soc.*, S 115 (1949).

(9) R. Wizinger, *J. prakt. Chem.*, **154**, 1 (1939).

(10) W. König, U. S. Patent 1,524,791, Feb. 3, 1925.

TABLE I

PREPARATION OF POLYMETHINE DYES

Dye/ no.	Yield, %	Solvent	Time	Temp., °C.	M.p. (dec.),[a] °C.	Re-crystln. solv.	Color	Formula	Analyses, % Calcd.	Found
VII	46	$POCl_3$	5 hr.	90–100	247	EtOH	Red-brown	$C_{35}H_{41}ClN_4O_4$	C, 68.11	68.06
					(240)[a]				H, 6.70	7.05
VIII	94	Ac_2O	70 min.	90	232–234	EtOH	Golden-brown	$C_{37}H_{43}ClN_4O_4$	C, 69.08	69.45
	99	AcOH[c]	1 hr.	90	(231)[b]				H, 6.74	7.01
IX	96	AcOH–Ac_2O	4 hr.	20–30	224–226	Ac_2O	Brown	$C_{39}H_{45}ClN_4O_4$	C, 69.99	68.20[d]
									H, 6.78	7.08
X	39	$POCl_3$	5 hr.	100	201–202	EtOH	Copper	$C_{31}H_{31}ClN_2O_2$	C, 70.11	70.40
					(193–195)[b]				H, 5.88	6.03
									Cl, 6.68	6.75
XI	56	Ac_2O	1 hr.	85–95	210–211	AcOH	Copper	$C_{33}H_{33}ClN_2O_4$	C, 71.15	70.93
	67	AcOH[c]	2 hr.	85–95	201–205				H, 5.97	6.43
					(193–194)[b]					
XII	61	Ac_2O	3 min.	20–30	179–180	Ac_2O	Red-brown	$C_{35}H_{35}ClN_2O_4$	C, 72.09	70.26[d]
									H, 6.05	6.35
									N, 4.81	4.69
XIII	48	$POCl_3$	4 hr.	Reflux	218	EtOH	Golden green	$C_{31}H_{29}Cl_3N_2O_4$	C, 62.06	62.23
									H, 4.87	5.23
XIV	50	Ac_2O	7 min.	85–95	217–219	AcOH	Copper	$C_{33}H_{31}Cl_3N_2O_4$	C, 63.32	63.34
									H, 4.99	5.42
XV	55	Ac_2O	1 min.	20–30	195–196	Ac_2O	Red-brown	$C_{35}H_{33}Cl_3N_2O_4$	C, 64.47	63.43[d]
									H, 5.10	5.28
									N, 4.30	4.37
XVI	*ca.* 5[c]	Ac_2O	3 min.	85–95	230	AcOH	Red-brown	$C_{33}H_{29}Cl_5N_2O_4$[e]	C, 56.96	58.30
									H, 4.20	4.72
									N, 4.03	4.04
XVII	37	Ac_2O	1 min.	20–30	203–204	Ac_2O	Red-brown	$C_{35}H_{31}Cl_5N_2O_4$[e]	C, 58.31	57.77[d]
									H, 4.34	4.73
									N, 3.89	3.82

[a] The decomposition temperatures vary somewhat with the rate of heating and are not corrected. [b] The values in parentheses are those reported by Wizinger, ref. 5 and 6. [c] The acetic acid–perchloric acid mixture was dried before use by adding sufficient acetic anhydride to react with the water present. [d] The heptamethines persistently occluded solvent which was not removed on prolonged heating at 0.05 mm. The use of more easily removed recrystallization solvents was prevented by the insolubility of these compounds. [e] The precursor 2,4-dichloro-4′-dimethylaminobenzophenone has not been reported. It was prepared in 68% yield, m.p. 129–131°, by the procedure of Shah, Deshpande and Chaubel, *J. Chem. Soc.*, 642 (1932). *Anal.* Calcd. for $C_{15}H_{13}Cl_2NO$: C, 61.24; H, 4.45; N, 4.76. Found: C, 61.27; H, 4.58; N, 4.76. The benzophenone was converted to 1-(2,4-dichlorophenyl)-1-(4-dimethylaminophenyl)-ethylene, m.p. 65–68°, in 78% yield by the Grignard procedure. An analytical sample, m.p. 67–69°, was obtained by recrystallization from ethanol. *Anal.* Calcd. for $C_{16}H_{15}Cl_2N$: C, 65.76; H, 5.17; N, 4.79. Found: C, 66.24; H, 5.51; N, 4.46. [f] See Table II for structures.

acetic anhydride. The solution developed a purple color and became warm. After swirling for 3 minutes, the red-brown crystals were collected, washed with ethanol and ether and dried. There was obtained 6.0 g. (61%) of XII, m.p. 179–180° dec.

Determination of Absorption Spectra.—A Cary recording spectrophotometer, model 11 MS, was used in the 200–800 mμ region. A modified Gaertner infrared spectrophotometer was used from 520 mμ to the solvent cut-off in the near infrared around 1300 mμ. This instrument was equipped with a tungsten source, rock-salt optics, and a slit drive and was calibrated with a mercury discharge lamp. The reduction of this instrument in the region examined was very satisfactory. Reagent grade chloroform containing 0.75% ethanol was used as the solvent. Solutions were 10^{-5} to 10^{-6} molar and were measured in a 1-cm. cell.

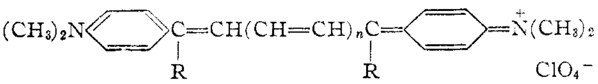
Discussion of Spectra

The vinylogous series A, B, C and D are summarized and the individual dyes are identified in Table II. The spectra of series A, B, C and D are shown in Figs. 1, 2, 3 and 4, respectively.

In general, the absorption spectra of these compounds consist of one intense band at long wave lengths and a number of less intense bands at shorter wave lengths. For a given series of dyes, as vinyl groups are introduced in the chain, the position of the long wave length band undergoes a bathochromic shift of 70–100 mμ per added vinyl group. These dyes thus resemble the cyanines in exhibiting non-convergence of the position of the principal absorption maxima as a vinylogous series is ascended.[11] Actually, an initial divergence is observed. The average shift in going from the trimethines to the pentamethines is 74 mμ, while the introduction of another vinyl group causes an average shift of 101.5 mμ.

TABLE II

IDENTITY OF POLYMETHINE DYE SERIES



n	Series A R = 4-(CH₃)₂NC₆H₄	Series B R = C₆H₅	Series C R = 4-ClC₆H₄	Series D R = 2,4-Cl₂C₆H₃
0	VII	X	XIII	...
1	VIII	XI	XIV	XVI
2	IX	XII	XV	XVII

The principal features of these spectra can be interpreted in terms of the work of Lewis and his collaborators.[12] A comparison of series A and B is

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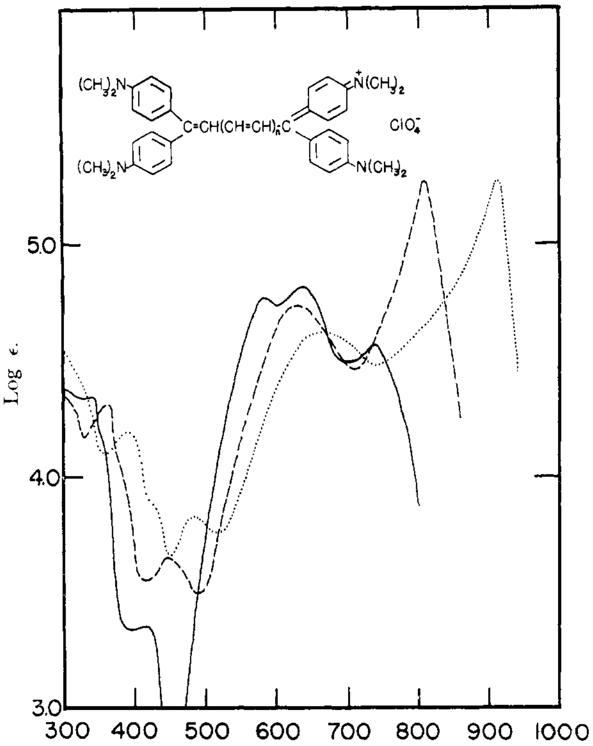
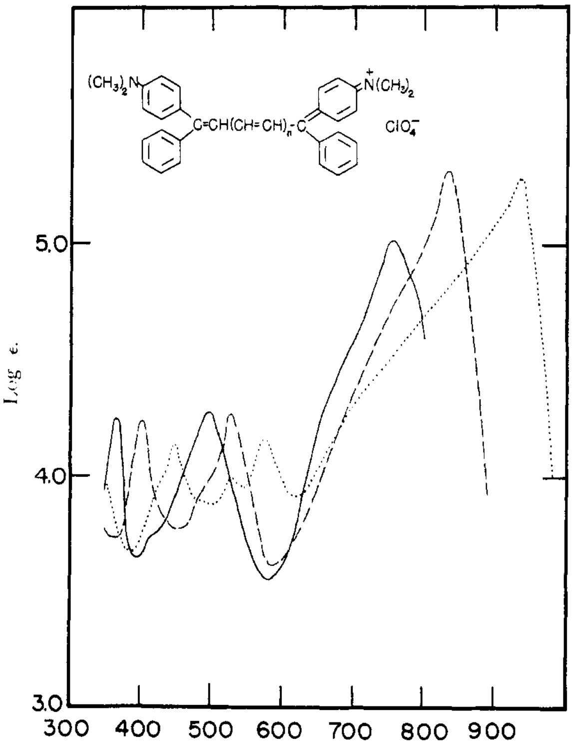
(11) L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth and P. F. Oesper, THIS JOURNAL, **63**, 3192 (1941).

(12) (a) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939);



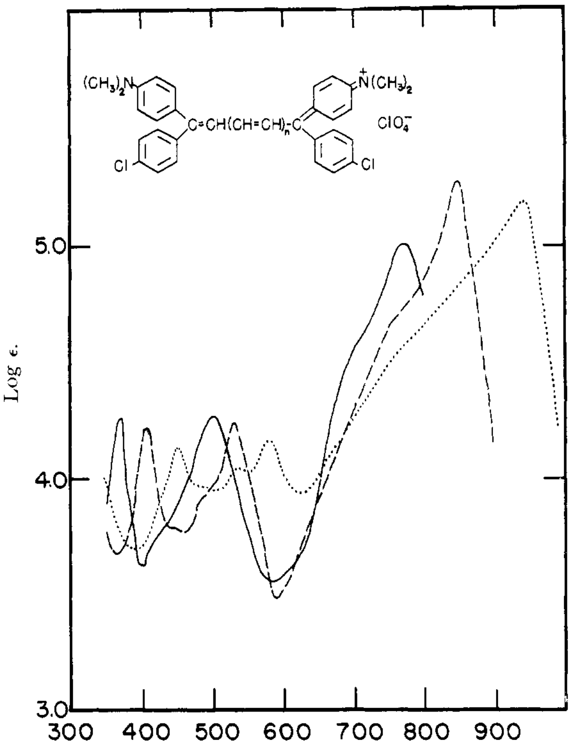
Wave length, mλ.

Fig. 1.—Series A: VII, $n = 0$, ———; VIII, $n = 1$, - - - -; IX, $n = 2$, ...



Wave length, mλ.

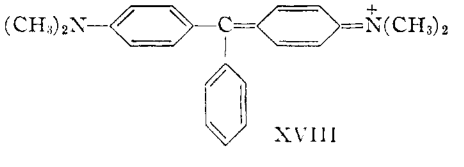
Fig. 2.—Series B: X, $n = 0$, ———; XI, $n = 1$, - - - -; XII, $n = 2$, ...



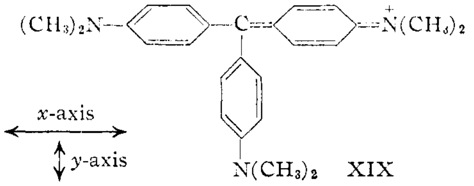
Wave length, mμ.

Fig. 3.—Series C: XIII, $n = 0$, ———; XIV, $n = 1$, - - - -; XV, $n = 2$, ...

interesting. The spectrum of VII, the first member of series A, is unlike those of the other dyes of these series and will be discussed more fully in a succeeding paper. The spectra of VIII and IX of series A consist of bands at 636 and 810 mμ and 663 and 910 mμ. respectively, with the long wave length bands being more intense. The comparable vinylogs XI and XII of series B have strong absorptions at 833 and 934 mμ, respectively, but no bands corresponding to the absorptions at 636 and 663 mμ in VIII and IX. Instead, XI and XII have considerably weaker absorptions at 527 and 575 mμ, respectively. The situation here is similar to that found in the spectra of malachite green (XVIII) and crystal violet (XIX).



XVIII



XIX

Malachite green has two absorption maxima in the visible at 423 mμ (log ε 4.20) and 625 mμ (log ε

(b) G. N. Lewis T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1774 (1942); (c) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 2102 (1943); (d) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 2107 (1943); (e) G. N. Lewis, *ibid.*, **67**, 550 (1945).

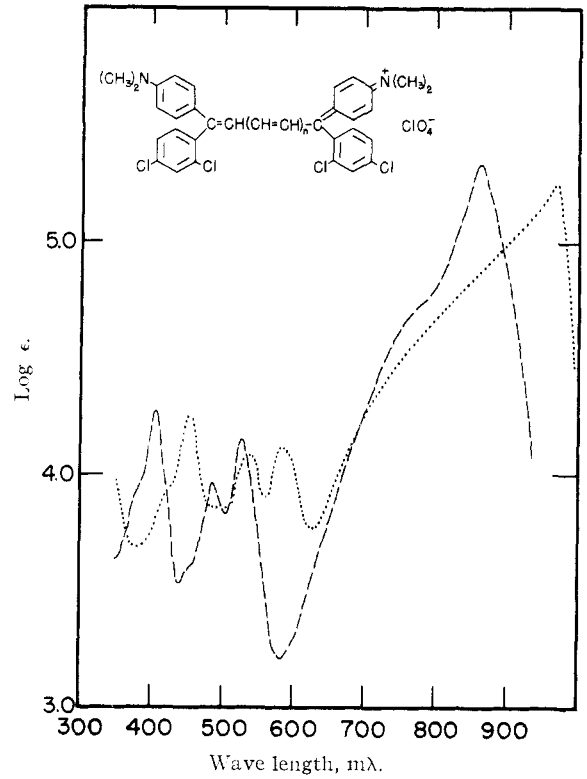
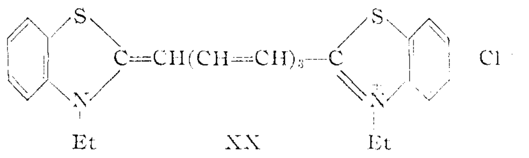


Fig. 4.—Series D: XVI, $n = 1$, - - - -; XVII, $n = 2$, ...

4.83) while crystal violet has but one band at 590 mμ (log ε 5.00). Lewis and Bigeleisen[12c] have shown that the more intense absorption of malachite green at 625 mμ is due to electronic oscillations along the x-axis of the molecule while the band at 423 mμ is due to oscillations along the y-axis. In crystal violet, the x- and y-axes are identical, and only one absorption band results. Because the transition along the y-axis of the dyes in series B involves resonance interaction between a phenyl- and a dimethylaminophenyl group rather than two dimethylaminophenyl groups, the energies of the extreme forms are widely different, and the transition becomes less probable and of higher energy than the one along the x-axis. By analogy with the triphenylmethane dyes, the intense, first absorption bands of the tetraarylpolymethines must be due to electronic oscillations along the long x-axis of the molecules while the weaker, second absorption bands arise from oscillations along the shorter y-axis. These will be referred to as x- and y-bands in agreement with the convention of Lewis and Calvin.[12a] Thus the band at 810 mμ in VIII is associated with resonance between dimethylaminophenyl groups at opposite ends of the chain, while the band at 636 mμ is ascribed to resonance between two dimethylaminophenyl groups at one end of the chain. Similarly, in XI the band at 833 mμ is due to resonance between the dimethylaminophenyl groups, and the band at 527 mμ is associated with resonance between a phenyl and a dimethylaminophenyl group. In agreement with the higher energy and lower probability of such a transition, the latter band is shifted to shorter wave lengths and the intensity is reduced relative to the y-band of VIII. The first and second absorption bands of the members of series C and D can be explained similarly. The y-bands of XI (series B) and XIV (series C) have pronounced shoulders which are resolved into separate bands in the higher vinylogs XII (series B) and XV (series C). The corresponding bands in XVI and XVII (series D) are well resolved. The origin of these shoulders and bands is not known. It is possible that they represent vibrational levels of the same electronic band, or that they are due to discrete isomers such as have been postulated for crystal violet.[12b]

It is perhaps significant that XVI and XVII show the most pronounced resolution of the y-bands. In these compounds, the presence of the *ortho* chlorines should reduce the coplanarity of the system relative to the corresponding vinylogs in series B and C and accentuate the energy differences between the species responsible for the bands.

The x-bands of the dyes of series B, C and D possess shoulders which are particularly pronounced in XIII, XIV and XVI. Since similar shoulders do not appear to be present in the x-bands of series A, it is possible that in series, B, C and D, they arise from *cis* and *trans* arrangements of the terminal groups. It seems likely that the more symmetrical *trans* configuration of the p-dimethylaminophenyl groups would be favored and give rise to absorption at longer wave length than the *cis* isomer. Zechmeister and Pinckard[13] have presented evidence that three *cis-trans* isomers of 3,3′-diethylthiatricarbocyanine chloride (XX) exist, although no isomers were detected in the corresponding iodide. However, these isomers equilibrated too rapidly in solution to permit measurement of their spectra. Presumably these isomers possessed different configurations of the polymethine chain. Molecular models show that, if coplanarity is to be maintained, the tetraarylpolymethines must have an all *trans* chain except for the heptamethines where the greater extension of the molecule permits one *cis* linkage.



XX

It is interesting that the y-bands undergo some bathochromic shift with increasing chain length. If the y-band is regarded simply as arising from polarization at right angles to the x-axis, then extending the x-axis should have little effect on the y-band, except insofar as the geometry of the terminal rings is modified by the greater extension of the molecule. It is evident that such a simple picture is inadequate for the complete interpretation of these spectra.

The third important absorption exhibited by these dyes lies in the 350–450 mμ region. These bands are evidently second-order x-bands (x'-bands) since they lie at approximately twice the frequencies of the first-order x-bands and are of about one-tenth the intensities of the first-order

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(13) L. Zechmeister and H. Pinckard, *Experientia*, **9**, 16 (1953).

bands. The data in the last two columns of Table III resemble those which Lewis and Bigeleisen[12d] obtained on a series of eight dyes except that $\bar{\nu}'/\bar{\nu}$, the ratio of the frequencies of the second- and first-order x-bands, is always greater than 2. The ratio $\bar{\nu}'/\bar{\nu}$ increases with increasing wave length of the x-band, as found by Lewis and Bigeleisen, but only within a given series. Furthermore, $\bar{\nu}'/\bar{\nu}$ is much larger for the trimethine dyes than for the higher vinylogs, and is in the range found for several triphenylmethane-type dyes. The values of $\bar{\nu}'/\bar{\nu}$ for the higher vinylogs are intermediate between those for the triphenylmethanes and several cyanines. The trimethine dye III again is anomalous, although $\bar{\nu}'/\bar{\nu}$ fits into the general pattern.

TABLE III

FIRST- AND SECOND-ORDER x-BANDS IN POLYMETHINE DYES

	First-order x-band		Second-order x-band			
Dye no.[a]	$\bar{\nu} \times 10^{-2b}$	$\epsilon \times 10^{-3}$	$\bar{\nu}' \times 10^{-2b}$	$\epsilon \times 10^{-3}$	$\bar{\nu}'/\bar{\nu}$	ϵ'/ϵ
VII	135.1	36.1	289	21.3	2.14	0.59
VIII	123.5[c]	183	276	20.1	2.24	.110
IX	109.8	186	255	15.5	2.32	.083
X	132.5	100	274	18.2	2.07	.182
XI	120.0[d]	208	249	17.3	2.08	.083
XII	107.0	195	224	13.8	2.09	.071
XIII	129.8	100	270	18.2	2.08	.182
XIV	118.4	187	247	16.4	2.08	.088
XV	106.2	151	222	13.8	2.09	.091
XVI	116.1	214	247	18.6	2.12	.087
XVII	103.0	178	221	17.8	2.15	.100

[a] See Table II for structures. [b] Frequency of absorption maxima in cm.$^{-1}$. [c] Wizinger (ref. 6) reported the absorption maximum at 11390 cm.$^{-1}$ (*i. e.*, 878 mμ) in acetic acid. Essentially no difference was detected in our curves in chloroform and in acetic acid. The value of 12350 cm.$^{-1}$ (810 mμ) was closely checked on a Beckman model DU spectrophotometer. Furthermore, the curve obtained on the Cary appeared to be rapidly approaching a maximum at 800 mμ. [d] Wizinger (ref. 6) reported $\lambda_{\max}^{\mathrm{AcOH}}$ 876 mμ (11410 cm.$^{-1}$); see footnote *c*.

Series B, C and D differ only in the progressive introduction of chlorine into the rings not bearing dimethylamino groups and the spectra of comparable vinylogs are similar, as would be expected from the weak auxochromic effect of chlorine. However, increasing the electron-withdrawing ability of the phenyl group by mono- and dichlorination results with one exception, in a slight bathochromic shift of the short wave length bands and a much larger shift of the long wave length band. The bathochromic effect of increasing the electron-withdrawing power of a substituent on the essential part of the chromophore finds a close analogy in the triphenylmethane dyes and has been attributed by Lewis[12e] to an increase in the fraction of the unit positive charge distributed between the auxochromic amino groups. The bathochromic shift of the y-bands as conjugation is extended requires further study. Possibly a quantum mechanical treatment of these dyes such as has been done by Dewar[14] on some triphenylmethane and related dyes would be helpful in arriving at a theoretical understanding of this effect.

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[14] M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950).

DAYTON, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CHAS. PFIZER & CO., INC.]

Oleandomycin (PA-105). II.[1,2] Chemical Characterization (I)

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The characterization and properties of the antibiotic oleandomycin, $C_{35}H_{61}NO_{12}$,[3] are described in detail. Degradation studies led to the characterization of oleandomycin as a polyhydroxy, epoxy, polymethyl ketolactone of the macrolide type,[4] containing glycosidically bound desosamine and L-oleandrose. Degradation products and derivatives are described and a partial structural formula is presented.

Molecular Formula and Characterization.—Oleandomycin (I) is a crystalline, colorless, basic compound (pK_a 8.5) with the molecular formula $C_{35}H_{61}NO_{12}$.[3] It is slightly soluble in water and ligroin, but dissolves readily in most of the other common organic solvents. The compound crystallizes from aqueous methanol or aqueous acetone solutions without solvent retention, melting at 110° with decomposition. The antibiotic forms characteristic solvated crystals with chlorinated solvents like methylene chloride or chloroform. The chloroform solvate, m.p. 120–121°, contains one equivalent of tenaciously bound solvent. Such preparations have been shown to be essentially pure by countercurrent distribution and paper chromatographic analysis utilizing several solvent-pair systems.[5]

Oleandomycin is readily soluble in acidic media and forms crystalline salts with a variety of mineral and organic acids. The specific optical rotation of

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(1) (a) Oleandomycin is the generic name proposed for PA-105; Matromycin is the trademark of Chas. Pfizer & Co., Inc., for this antibiotic. (b) B. A. Sobin, A. R. English and W. D. Celmer, "Antibiotics Annual 1954–1955," Medical Encyclopedia, Inc., New York, N. Y., p. 827.

(2) Presented in part at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956, p. 15-N.

(3) Present analytical data favor the $C_{35}H_{61}NO_{12}$ empirical formula over previously reported tentative formulations; ref. 1b and 2.

(4) R. B. Woodward, *Angew. Chem.*, **69**, 50 (1957).

(5) W. D. Celmer, Hans Els and K. Murai, Oleandomycin Derivatives—Preparation and Characterization, "Antibiotics Annual, 1957–1958," in press.