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STUDIES ON THE CHEMISTRY OF HETEROCYCLICS. XX. THE ABSORPTION SPECTRA OF SOME TRIARYLMETHANE DYES CONTAINING A THIOPHENE RING

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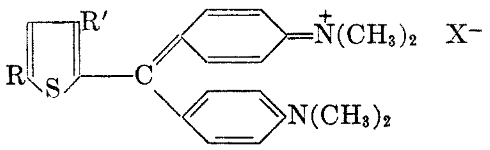
In a previous communication from this laboratory (1), the preparation of a variety of triarylmethane dyes containing a thiophene ring was presented. It was also demonstrated that when the phenyl ring in Malachite Green is replaced with the 2-thienyl group, a bathochromic effect is produced. In a continuation of our investigation on these dyestuffs, the absorption spectrum of Thiophene Malachite Green[3] in different solvents as well as the spectra of some thiophene-substituted dyes were determined in an endeavor to ascertain not only the effect produced by the medium on this dye, but also that of various substituents attached to the heterocyclic moiety. The dyestuffs studied are as follows:



When R′ = H, R = H, CH_3, C_2H_5, C_3H_7, Cl or Br
When R = H, R′ = CH_3

The identities of the dyes were determined by the method of preparation (1), the analyses of their bases, and their characteristic spectra. The formation of the dye bases was achieved by neutralization of the dye solutions with dilute solutions of sodium hydroxide or ammonium hydroxide. During the course of purification of the carbinols, a considerable amount of polymerization was always encountered. The preparation of the methyl ethers of the carbinols proved unsuccessful in eliminating this undesirable side reaction. These products are highly colored amorphous powders, insoluble in most organic solvents. From their analyses which are recorded in Table I, they appear to be condensation products of the dye cations. Susceptability to polymerization caused by thiophene in triarylcarbinols has been observed previously (3–5). In order to alleviate this reaction, it was found necessary to isolate the dye bases immediately upon formation. In this way, appreciable amounts of the carbinols could be obtained. It is noteworthy that only those dyes which formed crystalline picrates (1) yielded crystalline dye bases.

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[1] The contents of this paper were taken from a part of a dissertation submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This investigation was aided in part by a grant from the Office of Naval Research. The analyses were carried out by Dr. F. Bühler and A. A. Sirotenko of this department.

[3] Name assigned to the thiophene analog of Malachite Green by Levi (2).

TABLE I

DYE BASES AND CORRESPONDING POLYMERS OF THE VARIOUS THIOPHENE MALACHITE GREEN DYES

TETRAMETHYLDIAMINODIPHENYL-	DYE BASE					POLYMER				
	Formula	Analysis				Formula[c]	Analysis			
		Calc'd		Found			Calc'd		Found	
		C	H	C	H		C	H	C	H
(5-Methyl-2-thienyl)methanol	$C_{22}H_{26}N_2OS$	72.40	7.11	72.01	7.05	$(C_{22}H_{25}N_2S)_x$	75.64	7.16	75.80	6.97
(3-Methyl-2-thienyl)methanol	$C_{22}H_{26}N_2OS$[a]	72.40	7.11	72.53	6.82	$(C_{22}H_{25}N_2S)_x$	75.64	7.16	75.48	7.10
(5-Ethyl-2-thienyl)methanol	$C_{23}H_{28}N_2OS$	72.62	7.36	—[b]	—	$(C_{23}H_{27}N_2S)_x$	76.03	7.43	75.90	7.53
(5-Propyl-2-thienyl)methanol	$C_{24}H_{30}N_2OS$	73.09	7.61	—[b]	—	$(C_{24}H_{29}N_2S)_x$	76.39	7.69	76.34	7.62
(5-Chloro-2-thienyl)methanol	$C_{21}H_{23}ClN_2OS$	65.27	5.95	65.49	6.03	$(C_{21}H_{22}ClN_2S)_x$	72.11	6.45	72.32	6.25
(5-Bromo-2-thienyl)methanol	$C_{21}H_{23}BrN_2OS$	63.67	5.67	63.49	5.66	$(C_{21}H_{22}BrN_2S)_x$	65.86	5.69	65.55	5.37

[a] Melting point 112–113°, uncorrected. [b] No satisfactory analysis was obtained. [c] Melting points too vague to be recorded.

The absorption spectra of triarylmethane dyes are of a particular type between 800 to 220 mμ. Three principal bands are observed which have been referred to as the x, the y, and the x'-bands. The x and y-bands are in the visible region and in dilute solutions are practically symmetrical (6). The x-band is the main band and has the highest extinction.

During the process of purification of the dye bases, little change was observed in the values of λ_x and λ_y. The molecular extinction values increased slightly until a constant value was obtained (7). No extinction was recorded until it was constant and could be duplicated. In the case of the 5-ethyl- and 5-propyl-substituted dyes, satisfactory analyses could never be obtained. Since the values obtained for λ_x and λ_y agree so well with the values for the series of dyes, it has been concluded that the samples were the required dyes contaminated with colorless impurities. Additional evidence for this assumption is furnished by their characteristic spectrum and the ease with which the absorption maxima could be duplicated. Owing to the impurity, however, their molecular extinction coefficients were not recorded.

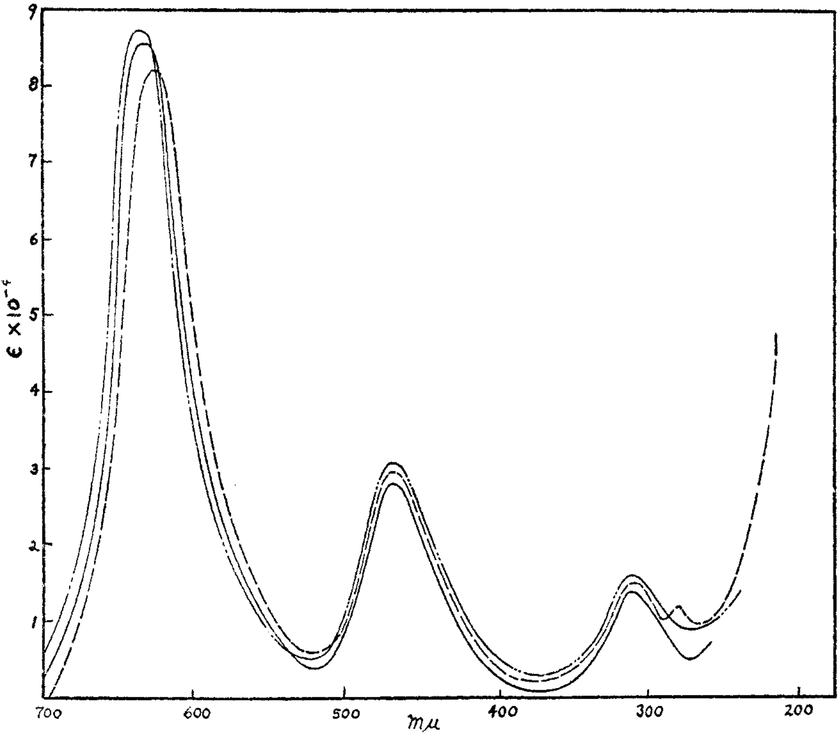

FIG. 1. EFFECT OF SOLVENT ON THE ABSORPTION SPECTRUM OF THIOPHENE MALACHITE GREEN: ———, in acetic acid; - - - , in water; —··—, in chloroform

The influence of solvent on the spectrum of Thiophene Malachite Green has been studied by observing the spectrum in three different types of solvents: water, a hydroxylated solvent with a high dielectric constant; acetic acid, a hydroxylated solvent with a low dielectric constant; and chloroform, a solvent with a low dielectric constant. As can be seen from Figure 1, the medium has not changed λ_x and λ_y to any noticeable extent. In chloroform, the wave lengths are a little longer than in the other two solvents. In changing from acetic acid to chloroform, λ_x increased by 4 mμ, while λ_y increased by 3 mμ. In changing from acetic acid to water, λ_x was decreased by 4 mμ and λ_y by 2 mμ. The absorption maxima and molecular extinction coefficients for the dyes in the different solvents are recorded in Table II. The fact that acetate was the negative ion when the solvent used was acetic acid, but the chloride ion when the other solvents were employed, appears to have had no effect on the spectrum. For this reason the spectra of all the substituted dyes were determined only in acetic acid. It is noteworthy that the effect of medium on the spectrum of Thiophene Malachite Green is qualitatively similar to that of Malachite Green (8, 9). When water was employed as the solvent, a fourth peak was observed, located in the ultraviolet region.

TABLE II

ABSORPTION MAXIMA AND MOLECULAR EXTINCTION COEFFICIENTS OF THIOPHENE MALACHITE GREEN IN DIFFERENT SOLVENTS

SOLVENT	λ_x in mμ	$\epsilon_x \times 10^{-4}$	λ_y in mμ	$\epsilon_y \times 10^{-4}$	λ_x' in mμ	$\epsilon_x' \times 10^{-4}$
AcOH	629	8.60	469	2.85	312	1.46
$CHCl_3$	633	8.75	472	3.14	311	1.63
H_2O	625	8.20	467	2.94	310	1.53
					280	1.21

The influence of methyl substitution on the absorption spectrum of Thiophene Malachite Green is evident in Figure 2. It can be readily recognized that while the x-bands have shifted slightly to shorter wavelengths, the y-bands have been displaced to longer wavelengths. Simultaneously, the intensities of the main bands have been decreased as the secondary bands have increased. In the case of 5-Methylthiophene Malachite Green a large bathochromic shift of the secondary band is observed when compared to the 3-methyl-substituted dye. This is understandable since the positive substituent in the *para*-position is more structurally similar to Crystal Violet in which the x and y-bands coincide (10). The absorption maxima and molecular extinction coefficients of the methyl-substituted dyes as well as the remaining substituted dyes are listed in Table III.

According to Lewis (11), an *ortho* substituent on the phenyl group of Malachite Green should shift the main band to longer wave lengths due to a steric factor which forces the phenyl group out of the nearly coplanar configuration, thus diminishing its part in the general resonance, and forcing some of the characteristic charge towards the auxochromes. Since a bathochromic shift is not observed for the 3-methyl-substituted thiophene dye, it appears that the presence of the thiophene ring has increased the atomic distance sufficiently so that no steric hinderance is encountered. Any interference should also alter the intensity

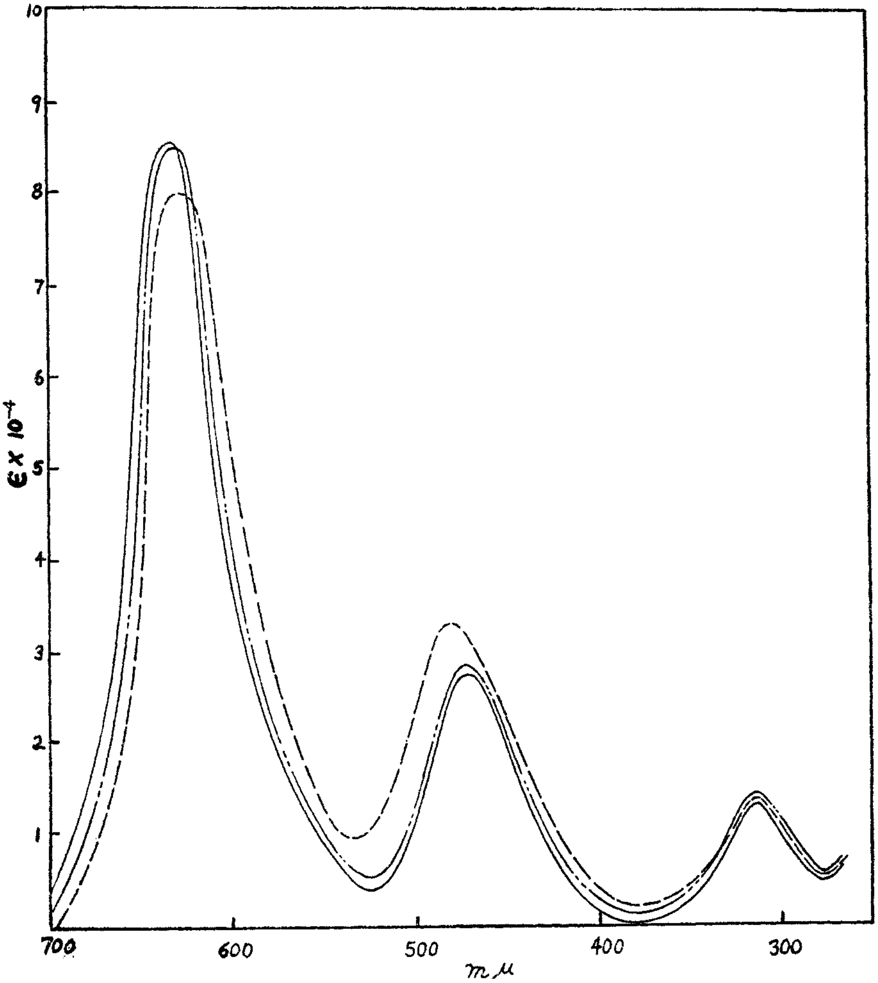

Fig. 2. Effect of Methyl Substitution on the Absorption Spectrum of Thiophene Malachite Green: ———, Thiophene Malachite Green; – – –, 5-Methylthiophene Malachite Green; —·—, 3-Methylthiophene Malachite Green

TABLE III

Absorption Maxima, Molecular Extinction Coefficients, Ratio of the x and x'-Bands and Molecular Extinction Coefficients of the Thiophene Malachite Green Dyes in Acetic Acid

DYE	λ_x in mμ	$\epsilon_x \times 10^{-4}$	λ_y in mμ	$\epsilon_y \times 10^{-4}$	$\lambda_{x'}$ in mμ	$\epsilon_{x'} \times 10^{-4}$	$V_{x'}/V_x$	$\epsilon_{x'}/\epsilon_x$
5-Propyl-T.M.G.*..........	624	—	488	—	310	—	2.013	—
5-Ethyl-T.M.G.............	625	—	487	—	310	—	2.015	—
3-Methyl-T.M.H.	626	8.51	472	2.88	311	1.58	2.015	0.187
5-Methyl-T.M.G............	627	7.96	485	3.34	311	1.48	2.015	0.185
T.M.G.....................	629	8.60	469	2.85	312	1.46	2.017	0.170
5-Bromo-T.M.G.............	635	5.20	482	2.10	310	1.01	2.050	0.194
5-Chloro-T.M.G.	637	7.41	478	3.04	310	1.25	2.050	0.168

* T. M. G. indicates Thiophene Malachite Green.

of absorption (12). However, no major alteration in intensity was observed as can be seen from Figure 2. This finding is in accord with the fact that the presence of thiophene in certain biaryls increases the atomic distance between the *ortho* substituents to the extent that diminished steric hinderance is observed (13).

The hypsochromic influence exerted by the methyl groups on the main band of Thiophene Malachite Green increases with the size of the alkyl group present. Thus, 5-Ethyl- and 5-Propyl-thiophene Malachite Green absorb at still shorter wavelengths while the secondary bands are displaced to longer wave lengths. The ability of the alkyl groups on the 5-position of the thiophene ring to remove some of the positive charge (11) is in the order, propyl, ethyl, methyl. However, as the size of the substituents is increased its effectiveness in shifting the main band is progressively diminished. This is also observed with the secondary bands; and the increase in size from ethyl to propyl shifted the y-band only one millimicron.

The absorption spectra of the halogenated thiophene dyes reveal the bathochromic effect produced by these electronegative substituents. While the presence of the chlorine atom on the thiophene ring has shifted the main band to the longer wavelength than does a bromine atom in the corresponding position, the relation is reversed with the secondary band. This may be due, possibly, to the more positive character of the bromine atom. Although the intensity of the main band of 5-Chlorothiophene Malachite Green is decreased in comparison to the unsubstituted dyestuff, the secondary band is increased, as can be seen in Figure 3. The brominated dye, however, shows a reduction in the intensity of both bands. The absorption maxima and molecular extinction coefficients for the halogenated dyes are presented in Table III.

According to Lewis and Bigeleisen (14), when a series of similar dyestuffs are arranged in the order of increasing wavelengths of the main bands, the ratio of the frequencies of the x and x'-bands, $V_{x'}/V_x$, will increase and simultaneously the ratio of the intensities, $\epsilon_{x'}/\epsilon_x$, will decrease. When the thiophene dyestuffs are placed in the order of increasing λ_x, a gradation of the ratio of the frequencies and molecular extinction coefficients is evident as can be seen in Table III. It is interesting to note that the ratio of the frequencies of the thiophene dyes exceeds 2. If the substituents on the thiophene ring were stronger auxochromes, the points of maxima for the respective dyes would have spread farther over the spectrum and a better relationship would probably have been observed. The impurities that accompanied the 5-ethyl- and 5-propyl-substituted dyes should be expected to alter the position of the x'-band located in the ultraviolet region. Since the value obtained for the ratio of the frequencies of these dyestuffs agrees so well with the remaining dyestuffs, it appears that their x'-bands have not been subject to much error. For this reason, they have been recorded.

EXPERIMENTAL[4]

The procedure for the preparation of the carbinols consisted essentially of employing the method that has been described previously (1), with various modifications. As an ex-

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[4] The thiophene used in this investigation was obtained through the courtesy of Drs. C. A. Hochwalt and O. J. Weinkauff of the Monsanto Chemical Company, St. Louis, Mo.

ample, the preparation of tetramethyldiaminodiphenyl(3-methyl-2-thienyl)methanol is presented.

Tetramethyldiaminodiphenyl(3-methyl-2-thienyl)methanol. Tetramethyldiaminodiphenyl-(3-methyl-2-thienyl)methane (1), (10 g., 0.028 mole) was dissolved in 25 ml. of dilute sulfuric acid and 1000 ml. of water was added. To the clear solution, 3.0 g. (0.029 mole) of pulverized manganese dioxide was gradually added. The mixture was stirred vigorously for two hours and filtered. The precipitate obtained was extracted with 50 ml. of warm water, filtered, and the extract added to the dye solution.

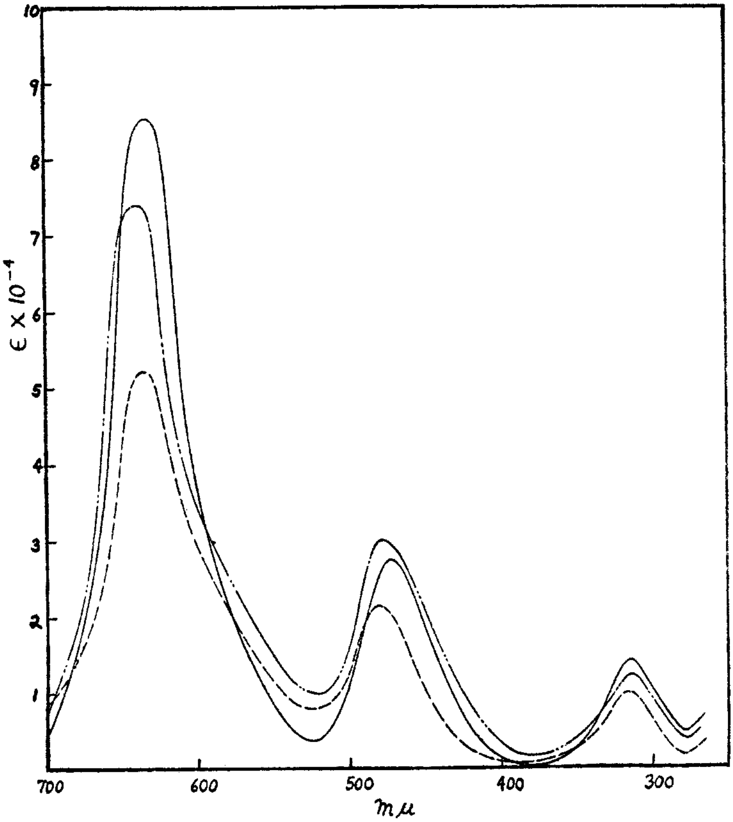

FIG. 3. EFFECT OF HALOGEN SUBSTITUTION ON THE ABSORPTION SPECTRUM OF THIOPHENE MALACHITE GREEN: ————, Thiophene Malachite Green; —··—, 5-Chlorothiophene Malachite Green; – – –, 5-Bromothiophene Malachite Green.

Sodium hydroxide (1 g., 0.025 mole) dissolved in 50 ml. of water was added slowly to 400 ml. of the dye solution with stirring. The crude carbinol which formed was filtered and washed with water. It was immediately transferred to a drying pistol containing sodium sulfate and dried at reduced pressure for two hours. The carbinol was then continuously extracted with petroleum ether (60–75°). The petroleum ether solution was purified with Nuchar C-145 and filtered. The product which separated on cooling was recrystallized from petroleum ether to give white crystals, m.p. 112–113°.

Anal. Calc'd for $C_{22}H_{26}N_2OS$: C, 72.40; H, 7.11.

Found: C, 72.53; H, 6.82.

Absorption spectra. These measurements were taken with a Beckman quartz spectrophotometer, over a range from 220 to 700 mμ. Readings were made every 10 mμ in the visible region and every 5 mμ in the ultraviolet. When a point of maximum was observed, readings were taken every millimicron and repeated to insure accuracy of determination.

Solutions of the dyes were prepared by dissolving weighed amounts of the carbinols in acetic acid. When distilled water was employed, the dye base was treated with the calculated amount of hydrochloric acid of molarity 1.0×10^{-2}. A chloroform solution of the dye was prepared utilizing a previously described procedure (15). In all cases, the molarities of the dye solutions were between 8×10^{-6} and 1.2×10^{-5}.

Dye base of Thiophene Malachite Green. This was prepared according to an earlier procedure (1).

SUMMARY

1. The formation of the dye base of some triarylmethane dyes containing a thiophene ring has been presented and discussed.

2. The effect of solvent on the absorption spectrum of Thiophene Malachite Green has been studied and evaluated.

3. The absorption spectra of the various substituted dyes have been determined and compared with the spectrum of Thiophene Malachite Green.

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