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STUDIES ON THE CHEMISTRY OF HETEROCYCLICS. XIII. TRIARYLMETHANE DYES CONTAINING A THIOPHENE RING[1]

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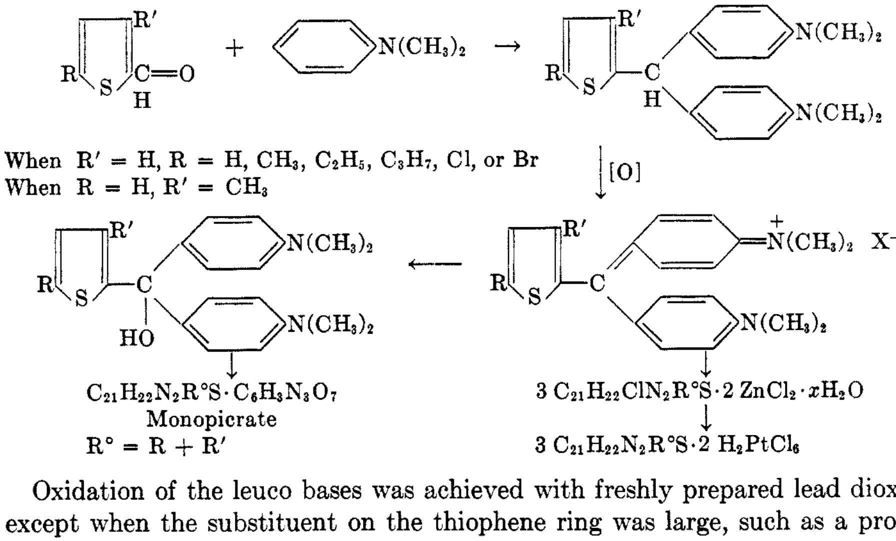
Although the presence of the thiophene nucleus in triarylmethane dyes has long been realized (1, 2, 3), the effect of the heterocyclic portion on the properties of these dyes has not been rigorously demonstrated. In view of the fact that 2-thenaldehyde and several substituted 2-thenaldehydes have been recently made readily available (4), the synthesis of a variety of dyes of this class was undertaken, in an attempt to ascertain not only the effect of the thiophene ring itself but also various substituents attached to the heterocyclic moiety.

The method of preparation consisted in the condensation of the various substituted aldehydes and dimethylaniline with anhydrous zinc chloride to form the leuco bases, oxidation to the corresponding dyes, and isolation of the different derivatives as presented in Chart I.

CHART I



When $R' = H, R = H, CH_3, C_2H_5, C_3H_7$, Cl, or Br

When $R = H, R' = CH_3$

$C_{21}H_{22}N_2R^{\circ}S \cdot C_6H_3N_3O_7$ Monopicrate

$R^{\circ} = R + R'$

$3\ C_{21}H_{22}ClN_2R^{\circ}S \cdot 2\ ZnCl_2 \cdot xH_2O$

$3\ C_{21}H_{22}N_2R^{\circ}S \cdot 2\ H_2PtCl_6$

Oxidation of the leuco bases was achieved with freshly prepared lead dioxide except when the substituent on the thiophene ring was large, such as a propyl group or halogen atom. In the case of the latter, oxidation with manganese dioxide proved more efficient.

The dyes were isolated as the zinc chloride complex salts, all of which have a metallic luster and are readily soluble in alcohol and water. The zinc salts of Thiophene Malachite Green[2] and 3-Methylthiophene Malachite Green color these solutions green, while the remaining zinc salts give different shades of blue.

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[1] 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.

[2] Name assigned to the unsubstituted dye by Levi (1).

Platinum chloride formed complex salts with the dyes; the formula of these salts has been assigned on the basis of the consistency of analysis, as indicated in Table I. These salts are dark brown amorphous powders practically insoluble in all common solvents. However if they are repeatedly boiled with water a yellow platinum salt is obtained. This is believed to be an example of the Anderson reaction (5).

The formation of picrate salts was limited to dyes of a definite structural feature. It was found that when the 5-position of the thiophene ring was unsubstituted, monopicrates were readily obtainable. The picrate salt of Thiophene Malachite Green forms beautiful golden plates while the picrate of the 3-methyl substituted dye is copper-colored. Repeated attempts to form picrates with the remaining dyes were unsuccessful.

TABLE I

LEUCO BASES AND PLATINUM CHLORIDE COMPLEXES OF CORRESPONDING DYES

LEUCO BASES							PLATINUM COMPLEXES					
Tetramethyldiamino-diphenyl	Yield, %	M.P.,[a] °C.	Analyses				Analyses[d]					
			Calc'd		Found		Calc'd			Found		
			C	H	C	H	C	H	Pt	C	H	Pt
(2-Thienyl)methane	66	92–92.5[b]	74.95	7.18	74.75	6.98	41.42	4.00	21.37	41.05	3.90	21.30
(5-Methyl-2-thienyl)methane	60	131–131.5[c]	75.38	7.47	75.35	7.14	42.42	4.23	20.89	42.20	4.01	20.50
(3-Methyl-2-thienyl)methane	62	90.5–91	75.38	7.47	75.10	7.34	42.42	4.23	20.89	42.40	4.58	20.65
(5-Ethyl-2-thienyl)methane	66	121–121.5	75.70	7.74	75.55	7.55	43.48	4.45	20.43	43.35	4.52	20.17
(5-Propyl-2-thienyl)methane	64	127.5–128	76.12	7.98	75.90	7.70	44.28	4.66	19.98	44.35	4.55	19.35
(5-Chloro-2-thienyl)methane	74	134.5–135	67.90	6.25	67.80	6.32	39.17	3.62	20.20	39.03	3.37	20.10
(5-Bromo-2-thienyl)methane	70	151.5–152	60.07	5.58	60.20	5.44	39.66	3.39	18.91	36.42	3.01	18.60

[a] All melting points are uncorrected. [b] Ref. (1) gives 92–93°. [c] Ref. (2) gives 131.4-131.8°. [d] For: $3C_{21}H_{22}N_2R^{\circ}S + 4HCl + 2PtCl_4$; where R° is the substituent on the thiophene ring.

Although Levi (1) was unable to isolate the dye base of Thiophene Malachite Green in a crystalline state, we obtained pure white crystals of the carbinol by careful crystallization from a benzene-petroleum ether mixture. By dissolving the zinc chloride complex in methyl alcohol and neutralizing with sodium methoxide, the methyl ether of the dye was also isolated. Thus it was possible to determine its absorption spectrum and compare it with the original Malachite Green. No appreciable difference could be observed in the spectrum between the carbinol and the methyl ether. The absorption spectrum of Malachite Green was found to be in excellent agreement with the results of Branch (6).

The absorption spectrum of triarylmethane dyes is of a particular type between 800 to 240 mμ (7). Three principal bands are observed which are referred to as the *x*-, *y*-, and *x*′-bands. The *x*- and *y*-bands are in the visible, and in dilute solutions are practically symmetrical. The *x*-band is the main band and has the highest extinction. According to the prevailing theory, the main absorption band of Malachite Green is characterized by an oscillation of an electron cloud across the molecule between the two auxochromes. The *y*-band corresponds to an oscillation through the phenyl group, while the *x*′-band has been associated with a secondary oscillation of higher amplitude. Any alteration in the structure of Malachite Green which effects the phenyl group, such as replacement with the

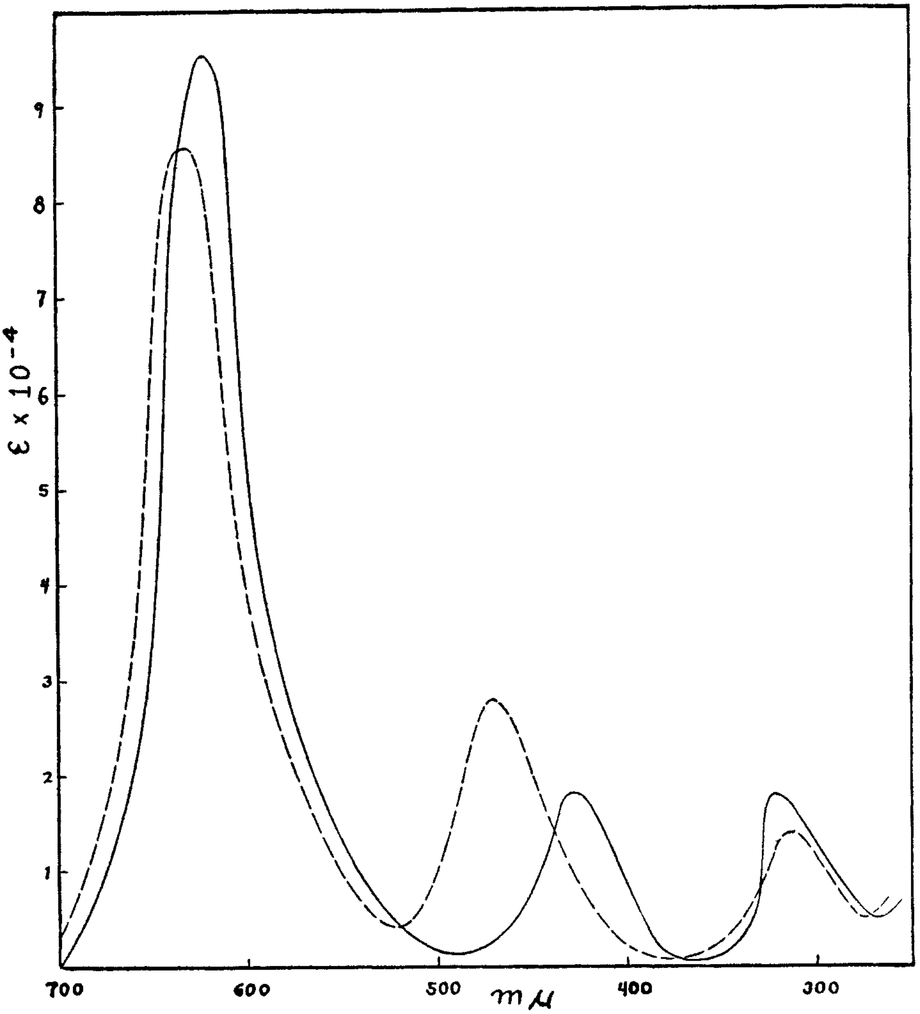


Fig. 1. Absorption Spectra of Malachite Green and Thiophene Malachite Green in Acetic Acid. Malachite Green ———; Thiophene Malachite Green - - - - - -.

2-thienyl group, will be most pronounced in the shift of the *y*-band (8). The result of the replacement can be seen in Figure 1.

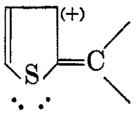
It can be readily recognized that while the *x*-band shifted slightly to a longer wave length, the main change noticeable is in the *y*-band. Although the intensity of the *x*-band has decreased that of the secondary band has increased. Comparative figures for the two dyes are recorded in Table II.

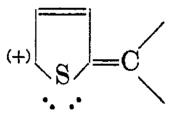
The bathochromic effect produced by the 2-thienyl group is believed to be due to a superior electron-releasing power of the thiophene ring as compared to the benzene ring. It is more capable of donating electrons to the central atom, thus effectively increasing the nitrogen atoms' basicity and consequently, lowering the absorption frequency. The role of the thiophene ring as the electron donor may be depicted as proceeding from the following resonating structures (9):

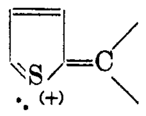
TABLE II

ABSORPTION MAXIMA AND THEIR MOLECULAR EXTINCTION COEFFICENTS IN ACETIC ACID

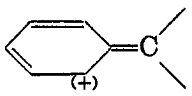
DYE	λ_x IN mμ	$\epsilon_x \times 10^{-4}$	λ_y IN mμ	$\epsilon_y \times 10^{-4}$	λ_x' IN mμ	$\epsilon_x' \times 10^{-4}$
Malachite Green	620	9.58	428	1.88	320	1.76
Thiophene Malachite Green	629	8.60	469	2.85	312	1.46







According to available data (10), the continuous conjugated structure makes the largest contribution and it is impressive to note that the phenyl group in Malachite Green cannot attain a corresponding structure:



This may be an explanation of the bathochromic effect observed in Thiophene Malachite Green.

The absorption spectra of the substituted and additional thiophene dyes will be presented and discussed in a forthcoming communication.

EXPERIMENTAL[3]

Preparation of intermediates. 2-Thenaldehyde and its alkylated and halogenated derivatives were synthesized according to the previously described procedure (4). The preparation of all the leuco bases, their oxidation, and the isolation of derivatives was carried out utilizing the procedure of Levi (1), with various modifications. As an example, the preparation of Thiophene Malachite Green and its derivatives is presented.

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[3] The thiophene used in this investigation was obtained through the courtesy of Dr. G. A. Harrington of the Socony-Vacuum Oil Company.

Tetramethyldiaminodiphenyl-(2-thienyl)methane. 2-Thenaldehyde (22 g., 0.20 mole) was mixed with 50 g. (0.41 mole) of dimethylaniline on the steam-bath and 42 g. (0.30 mole) of anhydrous zinc chloride was gradually added with stirring. The thick mass was occasionally stirred over a period of six hours. Hot water was then added and the contents transferred to a round-bottom flask. After excess dimethylaniline and aldehyde had been steam-distilled, the residue was cooled and washed with water. Recrystallization from ethyl alcohol gave 43 g. (65% yield) of white needles, m.p. 92–93°. If the leuco base separated as an oil, additional ethyl alcohol was used.

Oxidation of tetramethyldiaminodiphenyl-(2-thienyl)methane. The leuco base (11 g., 0.04 mole) was dissolved in 80 ml. of 2 *N* hydrochloric acid, and to the clear solution 800 ml. of water was added. Freshly prepared lead dioxide (9 g., 0.04 mole) suspended in 30 ml. of water was then added with cooling and stirring. After two hours 15 g. (0.05 mole) of sodium sulfate was added and the dye solution was filtered twice.

Zinc chloride complex. To 400 ml. of the dye solution was added 6 g. (0.03 mole) of zinc chloride dissolved in the minimum amount of water, followed by 800 ml. of saturated brine solution. The copper-colored crystals were filtered and cautiously washed with water. Yield, 6 g. (83%).

Anal. Calc'd for 3 $C_{21}H_{23}ClN_2S$ + 2 $ZnCl_2$ + 3 H_2O: N, 6.30. Found: N, 6.38.

Platinum chloride complex. To 20 ml. of the above dye solution was added 50 mg. of platinum chloride dissolved in water. The brown precipitate was filtered, washed with ethanol until the washings were clear, then with ether. The salt was dried in a vacuum.

Anal. Calc'd for 3 $C_{21}H_{23}N_2S$ + 4 HCl + 2 $PtCl_4$: C, 41.42; H, 4.00; Pt, 21.37.
Found: C, 41.05; H, 4.10; Pt, 21.30.

Anderson reaction. The platinum chloride complex was repeatedly boiled with water until the color of the salt changed to a light yellow.

Anal. Calc'd for $C_{21}H_{23}N_2S$ + 2 HCl + $PtCl_4$ + 2 H_2O: Pt, 24.96. Found: Pt, 25.10.

Tetramethyldiaminodiphenyl-(2-thienyl)methanol. Sodium hydroxide (1 g., 0.025 mole) dissolved in 10 ml. of water was slowly added to 400 ml. of the dye solution with stirring. The crude carbinol formed was filtered and washed with water. After drying in a desiccator the carbinol was pulverized, dissolved in benzene, filtered, and petroleum ether (60–75°) was added. The white crystals which formed were recrystallized from petroleum ether (60–75°), and dried in a vacuum, m.p. 88–90°.

Anal. Calc'd for $C_{21}H_{24}N_2OS$: C, 71.59; H, 6.82.
Found: C, 71.80; H, 6.56.

Picrate. To a portion of the carbinol dissolved in benzene was added a hot saturated chloroform solution of picric acid. The picrate was recrystallized from chloroform, m.p. 177–178°.

Anal. Calc'd for $C_{21}H_{23}N_2S \cdot C_6H_3N_3O_7$: C, 57.43; H, 4.64.
Found: C, 57.25; H, 4.65.

Tetramethyldiaminodiphenyl-(2-thienyl)methyl methyl ether. To 6 g. (0.005 mole) of the zinc chloride complex dissolved in methyl alcohol was added 1 g. (0.02 mole) of sodium methoxide in methyl alcohol. After all the ether had formed, the solution was extracted with benzene, washed thoroughly with water, separated, and dried over sodium sulfate. The solution was filtered and concentrated followed by the addition of petroleum ether (60–75°). The product which separated was recrystallized from petroleum ether, m.p. 97–97.5°.

Anal. Calc'd for $C_{22}H_{26}N_2OS$: C, 72.18; H, 7.10.
Found: C, 72.57; H, 6.99.

Methyl ether of Malachite Green. This was prepared according to an earlier procedure (6).

Absorption spectra. These measurements were taken with a Beckman quartz spectrophotometer, over a range from 255 to 700 mμ. Readings were made every 10 mμ in the visible region and every 5 mμ in the ultraviolet. Solutions of the dyes were made by dissolving weighed amounts of the methyl ethers or carbinol in acetic acid. The molarities of the dye solutions were between 8×10^{-6} and 1.2×10^{-5}.

SUMMARY

1. The preparation of new thiophene dyes and their derivatives has been presented and discussed.

2. The absorption spectrum of Thiophene Malachite Green has been determined and compared with Malachite Green.

3. An interpretation of the bathochromic effect of thiophene in triarylmethane dyes has been offered.

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