

crude solid disulfide from a 95% aqueous ethanol/*n*-hexane mixture, disulfide was obtained in two crops of 117 g. of yellow-orange crystals, m.p. 87.3–88.3°, (36.8%) and 17.5 g. of very fine pale yellow crystals, m.p. 81–83° (5.3%). The melting point of the higher melting crop was increased to m.p. 89.7–90.6° by recrystallization from 95% aqueous acetic acid. Titrimetric analysis of this product by the sodium sulfite silver nitrate method,<sup>24</sup> indicated a purity of 99% of XII.

*1-Naphthyl allyl sulfide* (XIII). By treating 60.8 g. of 1-thionaphthol (0.380 mole) with equivalent quantities of alcoholic potassium hydroxide and allyl bromide (Halogen Chem. Co.) in much the same manner as that used to prepare III, the crude mixed sulfide was isolated as a golden oil. By distilling this oil, two fractions of desired sulfide were obtained: 1. 26.8 g., b.p. 153.3–155.3°/4.2 mm., and 2. 22.3 g., b.p. 154.3–157.4°/4.2 mm., both distillates being

fluorescent yellow oils (78%) with distinct garlic-like odors. Fraction 1 was used as a sample for both ultraviolet absorption spectrum determination and element analysis.

*Acknowledgment.* We are grateful to Mr. Robert W. Schrock and to Dr. Glen E. Meyer for their efforts in determining mercaptan and disulfide content of various compounds, to Messrs. Richard J. Coleman, Albert J. Costanza, and to Dr. Edward F. Devlin, for determining the ultraviolet absorption spectra of various compounds, and to Dr. Teh Fu Yen for preparing some di-1-naphthyl disulfide. We are indebted to Dr. H. J. Osterhof for permission to publish this work.

AKRON, OHIO

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## Studies on the Chemistry of Heterocyclics. XXXII.\* Preparation and Absorption Spectra of Triarylmethane Dyes Containing a Thiophene or a Thianaphthene Ring

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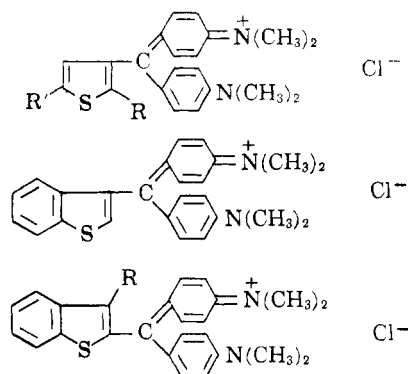
Received September 19, 1957

The preparation of some new thiophene and thianaphthene dyes and their derivatives has been presented and discussed. The absorption spectra of 3-Thianaphthene Malachite Green, 2-Thianaphthene Malachite Green and its derivatives, 3-Thiophene Malachite Green and its derivatives have been determined and compared with the absorption spectra of Malachite Green. An interpretation of the bathochromic effects of the thiophene and thianaphthene rings in triarylmethane dyes has been offered.

It was demonstrated earlier<sup>3</sup> that replacement of one of the phenyl rings in Malachite Green by a thiophene ring produces a bathochromic shift of the secondary absorption band. In a continuation of the study of the effect on the absorption spectrum of Malachite Green, of replacing one of the phenyl rings by a heterocyclic ring, a number of dyes containing either a thiophene ring or a thianaphthene ring were prepared and their absorption spectra measured. Furthermore, dyes containing various substituents on the heterocyclic moiety were also prepared to investigate the effects of these substituents.

The dyestuffs studied were those shown in the accompanying formulas.

The general method of preparation consisted of the condensation of the appropriate aldehyde or the substituted aldehyde with two molecules of dimethylaniline using anhydrous zinc chloride as the condensing agent. The oxidation of the leuco compounds so obtained to the dyes was achieved



Where R = H, CH<sub>3</sub>, Br or Cl and R' = H, CH<sub>3</sub>.

using manganese dioxide and sulfuric acid. The dyes were isolated as their zinc chloride complex salts. The dye bases were prepared by basification of the dye solutions with aqueous sodium hydroxide solution. During the course of purification of the dye bases, a considerable polymerization was encountered. This observation was first made in the case of the dye base of 2-Thiophene Malachite Green.<sup>3</sup> It could be avoided to a certain extent by isolating the dye bases immediately upon formation.

\* For communication XXXI of this series see *J. Org. Chem.*, 21, 419 (1956).

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(3) C. D. Mason and F. F. Nord, *J. Org. Chem.*, 16, 722 (1951).

The identities of the dyes were established by their methods of preparation, analyses of the leuco bases and the dye bases and by their characteristic absorption spectra.

Of the aldehydes and the substituted aldehydes required for the preparation of these dyes, 3-bromo-, 3-chloro-, and 3-methyl-2-thianaphthenecarboxaldehyde have not been reported previously. These were prepared from the respective 3-substituted thianaphthene derivatives which are known, metalating them using *n*-butyllithium and treating the aryllithium compounds with *N*-methylformanilide. Hydrolysis of the complexes so formed gave the desired aldehydes.

**Absorption spectra.** The absorption spectra of triarylmethane dyes are of a particular type between 800 and 200  $m\mu$ . Three principal bands are observed, which have been referred to as the x, y, and the x' bands.<sup>4</sup> The x and the y bands are in the visible region and in dilute solutions practically symmetrical. The x band is the main band and has the highest extinction.

According to the prevailing theory,<sup>4</sup> the main absorption band of Malachite Green is characterized by an oscillation of the electron cloud across the molecule between the two auxochromes. The y band corresponds to an oscillation through the phenyl group along an axis perpendicular to the main axis, while the x' band has been associated with a secondary oscillation of a higher amplitude. In a dye such as Malachite Green, the y band is of a shorter wave length, since the resonance in the y direction involves a carbonium ion, which has a lower stability than an ammonium nitrogen atom. Any alteration in the structure of Malachite Green which affects the phenyl group such as replacement with a thienyl or a thianaphthenyl group, will be most pronounced in the shift of the y band. Results of these replacements can be seen in Figs. 1 and 2.

The x' band is observed in the ultraviolet region of the spectrum. According to Lewis and Bigeleisen,<sup>5</sup> the main band of a molecule of a frequency  $V$  corresponds to the difference in energies between the ground state and the first excited state. When a molecule receives a higher excitation to the second excited state, resulting in an electronic oscillation of a higher amplitude in the direction of polarizability, a second band of frequency  $V'$  is found, which is related to the x' band. Since the differences in the energy levels are equal, the ratio  $V'/V$  should be exactly 2; however, the probability of such a jump is zero. In a molecule, in which the electronic oscillations are not entirely harmonic, as in the case of dye molecules, the energy levels of the successive excited states will lie closer together. In this case the ratio  $V'/V$  will be less than 2 and

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

(5) G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 2107 (1943).

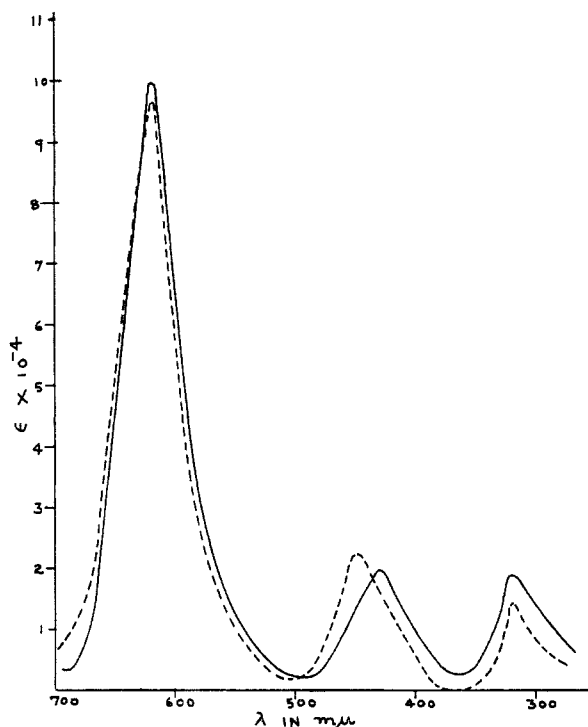


Fig. 1. Absorption spectra of Malachite Green and 3-Thiophene Malachite Green. Malachite Green, —; 3-Thiophene Malachite Green, - - -

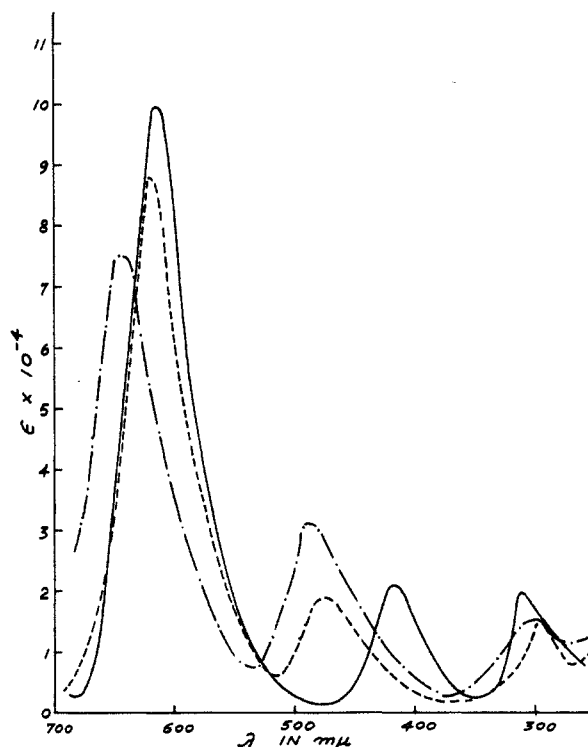


Fig. 2. Absorption spectra of Malachite Green and 2- and 3-Thianaphthene Malachite Greens. Malachite Green, —; 3-Thianaphthene Malachite Green, - - -; 2-Thianaphthene Malachite Green, - . - .

the ratio  $\epsilon_{x'}/\epsilon_x$  greater than zero. However the ratio  $V'/V$  may be greater than 2, depending on the amplitude of the electronic displacements rela-

TABLE I

ABSORPTION MAXIMA AND MOLECULAR EXTINCTION COEFFICIENTS OF 3-THIOPHENE MALACHITE GREEN AND SUBSTITUTED DYES

Dye	$\lambda_x$ , m $\mu$	$\epsilon_x \times 10^{-4}$	$\lambda_y$ , m $\mu$	$\epsilon_y \times 10^{-4}$	$\lambda_{x'}$ , m $\mu$	$\epsilon_{y'} \times 10^{-4}$	$\nu_{x'}/\nu_x$	$\epsilon_{x'}/\epsilon_x$
Malachite Green	620	9.91	428	1.88	320	1.76		
3-Thiophene Malachite Green	617	9.71	444	2.31	316	1.51	1.95	0.158
2,5-Dimethyl-3-Thiophene Malachite Green	619	10.4	464	1.92	321	1.28	1.93	0.123
2-Bromo-3-Thiophene Malachite Green	640	9.0	441	1.28	318	1.42	2.02	0.175
2-Chloro-3-Thiophene Malachite Green	642	10.70	441	1.63	318	1.88	2.01	0.158

TABLE II

ABSORPTION MAXIMA AND MOLECULAR EXTINCTION COEFFICIENTS OF THIANAPHTHENE MALACHITE GREEN DYES COMPARED WITH THOSE OF MALACHITE GREEN

Dye	$\lambda_x$ , m $\mu$	$\epsilon_x \times 10^{-4}$	$\lambda_y$ , m $\mu$	$\epsilon_y \times 10^{-4}$	$\lambda_{x'}$ , m $\mu$	$\epsilon_{x'} \times 10^{-4}$	$\nu_{x'}/\nu_x$	$\epsilon_{x'}/\epsilon_x$
Malachite Green	620	9.90	428	1.88	316	1.91		
3-Thianaphthene Malachite Green	627	8.87	476	1.86	304	1.53	2.06	0.171
2-Thianaphthene Malachite Green	645	7.56	492	3.10	311	1.50	2.07	0.198
3-Methyl-2-Thianaphthene Malachite Green	645	9.03	495	2.19	309	1.68	2.07	0.185
3-Bromo-2-Thianaphthene Malachite Green	661	8.10	480	1.54	309	1.65	2.13	0.203
3-Chloro-2-Thianaphthene Malachite Green	667	7.80	485	1.70	310	1.61	2.15	0.206

tive to the dimensions of the molecule.<sup>5</sup> Since the amplitude of the electron displacement depends on the polarizability of the molecule, it will be greater for those dyes with larger maximum wave lengths of absorption. Hence, in a series of similar compounds, as the value of  $\lambda_{max}$  of the x band increases, the ratio of the frequencies of the x' and the x band,  $V'/V$ , will increase even to the extent of exceeding 2, and simultaneously the ratio  $\epsilon_{x'}/\epsilon_x$  will decrease. When the thianaphthene dyes are placed in the order of increasing  $\lambda_x$  a gradation of the ratio of frequencies is evident, as can be seen in Table II. However, such a gradation is not seen in the case of the thiophene dyes (Table I).

Both the heterocyclic rings produce a bathochromic shift of the y band of Malachite Green, as can be seen from the data listed in Tables I and II. It will also be recognized that there is a bathochromic shift of 64 m $\mu$  of the y band when the phenyl ring in Malachite Green is replaced by a 2-thianaphthenyl ring. This is much larger in comparison with a similar shift of 41 m $\mu$  observed in the case of 2-Thiophene Malachite Green.<sup>3</sup> This comparatively larger shift may be due to the higher electron releasing power of the thianaphthene ring as compared to that of the thiophene ring. It is therefore capable of donating more electrons to the central carbon atom, thereby increasing the basicity of the nitrogen atom and consequently lowering the absorption frequency.

It has been reported previously<sup>6</sup> that when one of the phenyl rings of Malachite Green is replaced by an  $\alpha$ -naphthyl or a  $\beta$ -naphthyl group, prominent secondary bands are observed. Although no shift of the secondary band was mentioned in either case, it was noted that the second band is twice as high in the  $\beta$ - as in the  $\alpha$ -compound. This has been attributed<sup>6</sup> partly to the greater extension in the y direction of the former molecule and partly to its nearer approach to coplanarity. However, in the present case, where one of the phenyl groups is replaced by a 2- or 3-thianaphthenyl ring, it is found that the second band is twice as high in the former compound as in the latter. Since the extension of the molecule in the y direction is the same in both the thianaphthene substituted dyes, it appears that the higher extinction in the case of the former dye is due to its nearer approach to coplanarity. However, it might also be due to a greater extent of conjugation from the 2- than from the 3-thianaphthenyl group.

It will be noticed from the data listed in Table II that there is practically no effect of the methyl substituent on the absorption spectrum of 2-Thianaphthene Malachite Green, while there is a bathochromic shift of the y band of 3-Thiophene Malachite Green (Table I). According to Lewis<sup>6a</sup>

(6) G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 2102 (1943).

(6a) G. N. Lewis, *J. Am. Chem. Soc.*, **67**, 770 (1945).

an ortho substituent on the phenyl ring in Malachite Green should have a bathochromic effect on the main band due to a steric effect, which forces the phenyl group out of the nearly coplanar configuration, thus diminishing its share in the general resonance. Since, however, such a shift is not noticed, it appears that the introduction of either heterocyclic ring has increased the atomic distance sufficiently so that no steric hindrance is encountered. This finding is similar to previous observations regarding the effect on the absorption spectra of 2-Thiophene Malachite Green by the methyl substituent in the ortho position of the thienyl ring.<sup>3</sup>

The absorption spectra of the halogenated dyes reveal that there is a bathochromic shift of the x band. The deepening of the color produced by these electronegative atoms is apparently due to their ability to remove electrons from the heterocyclic ring, thus increasing the positive charge that is present.

#### EXPERIMENTAL

*Preparation of the starting substances.* Thianaphthene-2-carboxaldehyde was prepared from thianaphthene.<sup>7</sup> Thianaphthene-3-carboxaldehyde was prepared from thianaphthene by applying the Sommelet reaction.<sup>8</sup> 3-Methylthianaphthene was prepared by cyclization of phenyl acetyl sulfide.<sup>9</sup> 3-Bromothianaphthene was prepared by bromination of thianaphthene.<sup>10</sup> 3-Thienaldehyde was prepared according to Campaigne,<sup>11</sup> 2,5-dimethyl-3-thiophene carboxaldehyde according to Blanchette,<sup>12</sup> and 2-halo-3-thiophenecarboxaldehydes according to Campaigne and Le Suer.<sup>13</sup>

*Preparation of 3-methylthianaphthene-2-carboxaldehyde.* 3-Methylthianaphthene (29.6 g., 0.2 mole) in 60 ml. of anhydrous ether was metalated by addition to an ethereal solution of *n*-butyllithium prepared from *n*-butyl bromide (41.2 g., 0.3 mole) in 50 ml. ether and lithium metal (5.04 g., 0.72 g.-atom) in 100 ml. ether. To the organometallic compound was added slowly with stirring a solution of *N*-methylformanilide (27.0 g., 0.2 mole) in 45 ml. of ether. After completion of the addition, the mixture was heated to reflux for one hour and then hydrolyzed by pouring it into a mixture of 2*N* hydrochloric acid and crushed ice. The ether layer was separated and the aqueous layer extracted three times with ether. The residue after the removal of the solvent was dissolved in the minimum amount of ethanol, and 150 ml. of an aqueous saturated solution of sodium bisulfite was added. The mixture was shaken for 0.5 hr., and the bisulfite addition compound which separated was filtered, washed with ether, and decomposed with a hot, saturated aqueous solution of sodium carbonate, yielding a colorless product

(18.1 g.). On two further crystallizations from acetone it gave colorless needles, m.p. 88–88.5°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>OS: C, 68.19; H, 4.55; S, 18.19%. Found: C, 68.28; H, 4.54; S, 18.50.

The phenylhydrazone crystallized from alcohol in yellow needles, m.p. 178–179°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>S: N, 10.53. Found: N, 10.90.

By applying a similar procedure, 3-bromothianaphthene (42.6 g., 0.2 mole) gave colorless needles of 3-bromothianaphthene-2-carboxaldehyde, m.p. 123–124°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>SBRO: C, 44.81; H, 2.08; S, 13.28%. Yield 5.1 g. Found: C, 45.28; H, 1.98; S, 13.50.

The phenylhydrazone crystallized from alcohol in pale yellow needles, m.p. 158–159°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>11</sub>BrN<sub>2</sub>S: C, 54.39; H, 3.57; Br, 24.18; S, 9.67%. Found: C, 54.53; H, 3.57; Br, 24.20; S, 9.61.

3-Chlorothianaphthene-2-carboxaldehyde, prepared similarly from 3-chlorothianaphthene crystallized in colorless needles from ethanol, m.p. 106–107°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>ClOS: C, 54.95; H, 2.52; Cl, 18.06%. Found: C, 55.00; H, 2.23; Cl, 18.48.

The phenylhydrazone crystallized from ethanol in orange flakes, m.p. 172–173°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>11</sub>ClN<sub>2</sub>S: N, 9.08%. Found: N, 9.50.

*Preparation of intermediates.* The preparation of all the leuco bases, their oxidation and the isolation of derivatives was carried out utilizing the procedure of this laboratory.<sup>3</sup> The yields, melting points, and analyses of the various intermediates are listed in Tables III, IV, V, and VI. As an example, preparation of 2-Thianaphthene Malachite Green is presented.

*Preparation of p-p'-tetramethyldiaminodiphenyl(2-thianaphthényl)methane (I).* 2-Thianaphthene carboxaldehyde (12.75 g., 0.079 mole) was mixed with dimethylaniline (19.5 g., 0.16 mole) in a 100-ml. three-necked flask. The mixture was heated on a steam bath and anhydrous zinc chloride (16.1 g., 0.118 mole) was gradually added under stirring. The thick mass was heated under stirring for 6 hr. After the excess of dimethylaniline and the unreacted aldehyde had been steam distilled, the residue was cooled and washed with water. The colorless product (25.8 g.), obtained on four crystallizations from benzene and petroleum ether (b.p. 60–75°), gave colorless needles, m.p. 142–143°.

*Oxidation of (I).* The leuco base (I) (7.8 g., 0.0202 mole) was dissolved in 2*N* sulfuric acid (30 ml.) and water (500 ml.). To the clear solution pulverized manganese dioxide (2.3 g., 0.0272 mole) was gradually added, with stirring. After the addition was completed, the mixture was stirred vigorously for 2 hr. It was then filtered and the residue extracted with 100 ml. of boiling water. The washings were added to the dye solution, which was finally made to 800 ml.

*Zinc chloride complex of 2-Thianaphthene Malachite Green.* To 400 ml. of the dye solution was added 1.36 g. (0.01 mole) of anhydrous zinc chloride dissolved in minimum amount of water followed by 600 ml. of saturated brine solution. The copper colored crystals were filtered and washed carefully with ice cold water.

*Preparation of p-p'-tetramethyldiaminodiphenyl(2-thianaphthényl)methanol.* Aqueous sodium hydroxide (10 ml. of 10% solution) was added to 300 ml. of the dye solution with vigorous stirring. The carbinol, which precipitated, was filtered and washed with water. It was then dried *in vacuo* in a desiccator. The dry product was extracted in a Soxhlet extractor with petroleum ether (b.p. 60–75°) for 6 hr. The pink colored crystals obtained gave colorless needles on repeated crystallizations from petroleum ether (b.p. 60–75°).

*Absorption spectra.* These measurements were taken with a Beckman DU Quartz Spectrophotometer over a range from 260–700 m $\mu$ . Readings were taken at every 10 m $\mu$  intervals in the visible region and at every 5 m $\mu$  intervals in the ultraviolet. Near the points of maxima readings were

(7) D. A. Shirley and M. J. Danzig, *J. Am. Chem. Soc.*, **74**, 2935 (1952).

(8) W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

(9) E. G. G. Werner, *Rec. Trav. Chim.*, **68**, 509 (1949).

(10) J. Szmuszkovicz and E. J. Modest, *J. Am. Chem. Soc.*, **72**, 571 (1950).

(11) E. Campaigne, R. C. Bourgeois, and W. C. McCarthy, *Org. Synthesis*, **33**, 93 (1953).

(12) G. Blanchette, dissertation, Fordham University (1951).

(13) E. Campaigne and W. M. Le Suer, *J. Am. Chem. Soc.*, **71**, 333 (1949).

TABLE III  
 LEUCO BASES AND ZINC CHLORIDE COMPLEXES OF THIOPHENE MALACHITE GREEN

Tetramethyl- diamino- diphenyl-	Yield, %	M.P., <sup>a</sup> °C.	Leuco Bases										Zinc Chloride complexes <sup>b</sup>					
			Analyses										Analyses					
			Calcd.					Found					Calcd.	Found				
C	H	N	S	Hal.	C	H	N	S	Hal.	N	N							
(3-Thienyl)- methane	59.3	111-112	75.00	7.14	8.35						74.97	7.17	8.65			5.84	5.60	
(2,5- Dimethyl- 3-thienyl)- methane	49.0	139-140	75.76	7.76		8.80					75.05	7.91		8.92			5.77	5.75
(2-Bromo-3- thienyl)- methane	65.3	115-117	60.07	5.59			19.24	60.14	5.54						19.30	5.02	5.59	
(2-Chloro-3- thienyl)- methane	57.0	122-123	67.98	6.26			9.56	68.00	6.14					9.89	5.45	5.50		

<sup>a</sup> All melting points are uncorrected. <sup>b</sup> For  $C_{21}H_{22}ClN_2R^{\circ}S \cdot 2ZnCl_2 \cdot 3H_2O$  where  $R^{\circ}$  is a substituent on the thiophene ring.

 TABLE IV  
 BASES OF THIOPHENE MALACHITE GREEN DYES

Tetramethyldiamino- diphenyl-	M.p., <sup>a</sup> °C.	Analyses												
		Calcd.					Found							
C	H	N	S	Hal.	C	H	N	S	Hal.					
(3-Thienyl)methanol	183-184	71.60	6.82	7.96						71.57	6.37	7.93		
(2,5-Dimethyl-3-thienyl)- methanol	152-153	72.58	7.43		8.43					73.16	7.71		8.35	
(2-Bromo-3-thienyl)- methanol-	143-144	58.47	5.38			18.52	58.54	5.48						19.42
(2-Chloro-3-thienyl)- methanol-	140-142	65.17	6.00			9.16	65.12	6.58						9.80

<sup>a</sup> All melting points are uncorrected.

 TABLE V  
 LEUCO BASES AND ZINC CHLORIDE COMPLEXES OF THIANAPHTHENE MALACHITE GREEN DYES

Tetramethyldiamino- diphenyl-	M.P., <sup>a</sup> °C.	Yield, %	Leuco Bases										Complexes <sup>b</sup>			
			Analyses										Analyses			
			Found					Calcd.					Calcd.	Found		
C	H	S	Hal.	C	H	S	Hal.	C	H	S	Hal.	N	N			
(3-Thianaphthenyl)- methane	148-149	84.8	78.01	7.40	8.34					77.71	6.74	8.30			5.27	4.85
(2-Thianaphthenyl)- methane	142-143	80.4	77.34	6.69	7.96					77.71	6.74	8.30			5.27	5.11
(3-Methyl-2-thianaph- thenyl)methane	157-158	34.3	77.68	6.59	7.66					78.00	7.00	8.00			5.15	4.94
(3-Bromo-2-thianaph- thenyl)methane	126-127	39.8	64.25	5.45		17.40	64.50	5.38					17.21	4.60	5.22	
(3-Chloro-2-thianaph- thenyl)methane	139-140	61.3	71.19	5.89			71.35	5.95						6.40	5.82	

<sup>a</sup> All melting points are uncorrected. <sup>b</sup> For  $3 C_{23}H_{23}ClN_2R^{\circ}S \cdot 2ZnCl_2 \cdot 3H_2O$  where  $R^{\circ}$  is a substituent on the thianaphthene ring.

 TABLE VI  
 CARBINOL BASES OF THE THIANAPHTHENE MALACHITE GREEN DYES

Tetramethyldiaminodiphenyl-	M.P., <sup>a</sup> °C.	Analyses					
		Found			Calculated		
		C	H	S	C	H	S
(3-Thianaphthenyl)methanol	170	74.95	6.47	7.78	74.63	6.47	7.96
(2-Thianaphthenyl)methanol	193-194	74.57	6.82	8.16	74.63	6.47	7.96
(3-Methyl-2-thianaphthenyl)methanol	182-183	75.00	6.73	7.69	74.61	6.54	7.69
(3-Bromo-2-thianaphthenyl)methanol	212-213	62.79	5.40	7.30	62.38	5.20	6.65
(3-Chloro-2-thianaphthenyl)methanol	188	69.13	6.01		68.71	5.73	

<sup>a</sup> All melting points are uncorrected.

taken at every  $m\mu$ . Solutions of the dyes were made by dissolving weighed amounts of analytically pure carbinols in glacial acetic acid. The molarities of the dye solutions were between  $1 \times 10^{-5}$  and  $1 \times 10^{-3}$ .

*Acknowledgments.* This investigation was aided by grants from the National Science Foundation

and the U.S. Public Health Service. The thianaphthene used was obtained through the courtesy of Dr. W. J. Coppoc of the Texas Company, Beacon, N. Y.

NEW YORK 58, N. Y.

[CONTRIBUTION NO. 248 FROM THE RESEARCH DIVISION, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

## Tetra-2-benzimidazolethylene, a New Yellow Chromophore

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Received August 12, 1957

Tetra-2-benzimidazolethylene (I) has been prepared and its ultraviolet, visible, infrared, and x-ray diffraction spectra determined. Nitro, chloro, bromo, sulfo, methyl, and methoxyl derivatives of I have been made.

In the course of an investigation of novel dye structures, tetra-2-benzimidazolethylene (I) was prepared and found to be a strong yellow chromophore. The visible spectrum in dimethylformamide is shown in Fig. 1. The molar extinction coefficient

$d, \text{\AA}$	$I/I_{\text{max}}$
13.5	40
12.4	100
6.20	20
5.85	30
5.42	20
3.80	20
3.65	15

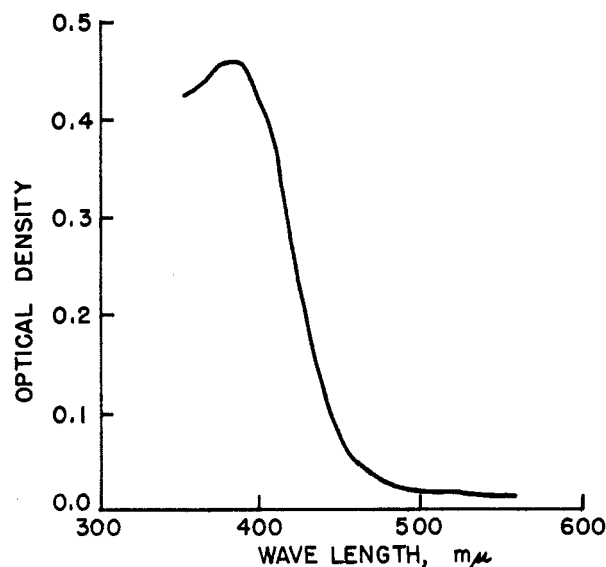


Fig. 1. Visible spectrum of tetra-2-benzimidazolethylene. One centimeter dimethylformamide solution, 0.0093 gram per liter

is 24,000 at 3800  $\text{\AA}$ . I is insoluble in water at any pH and in most organic solvents. It can be dissolved to a small extent in dimethylformamide and is completely soluble in 100% sulfuric acid from which it is recovered unchanged by dilution with water. I is crystalline and is characterized by an x-ray diffraction pattern having seven peaks at the following interplanar spacings:

The ultraviolet and infrared spectra of I are reproduced in Figs. 2 and 3, respectively. From a study of molecular models, it is concluded that I should be hydrogen-bonded between the 4 adjacent nitrogen pairs.

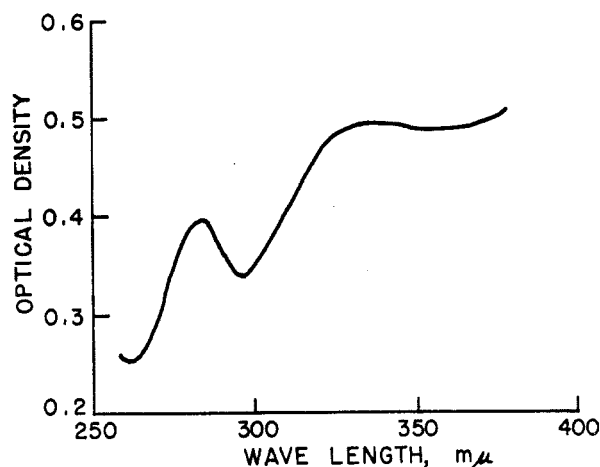


Fig. 2. Ultraviolet spectrum of tetra-2-benzimidazolethylene. One centimeter dimethylformamide solution, 0.0180 gram per liter

Two routes to I were found. The first is reaction of tetramethyl ethane-1,1,2,2-tetracarboxylate with *o*-phenylenediamine to give 1,1,2,2-tetra-2-benzimidazolethylene which is subsequently oxidized to I.