

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 1×10^{-5} and 1×10^{-3} .

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NEW YORK 58, N. Y.

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Tetra-2-benzimidazolethylene, a New Yellow Chromophore

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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_{max}
13.5	40
12.4	100
6.20	20
5.85	30
5.42	20
3.80	20
3.65	15

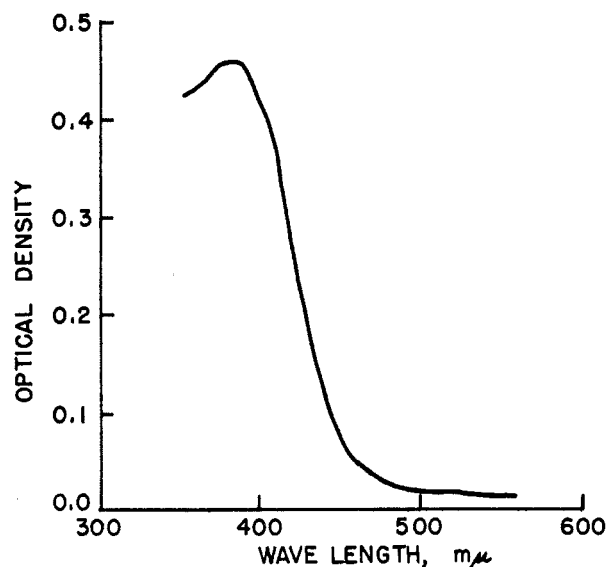


Fig. 1. Visible spectrum of tetra-2-benzimidazolethylene. One centimeter dimethylformamide solution, 0.0093 gram per liter

is 24,000 at 3800 \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.

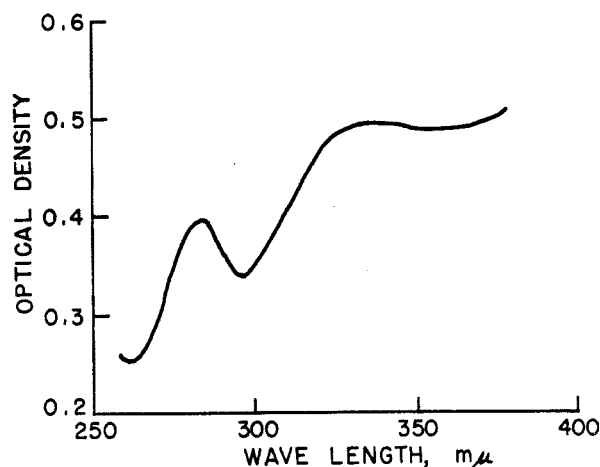


Fig. 2. Ultraviolet spectrum of tetra-2-benzimidazolethylene. One centimeter dimethylformamide solution, 0.0180 gram per liter

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.

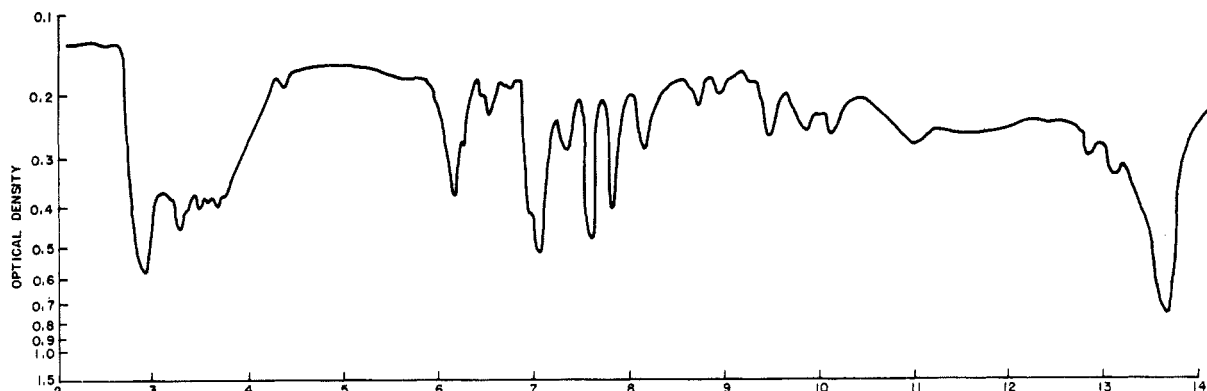
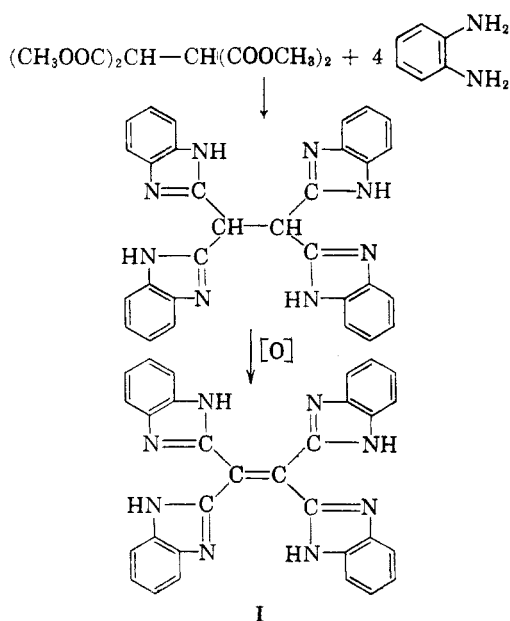


Fig. 3 Infrared spectrum of tetra-2-benzimidazolethylene, KBr Disk, NaCl Prism



Oxidation may be achieved in air at 210–250°, refluxing nitrobenzene, aqueous hydrogen peroxide, alkaline sodium hypochlorite, chlorine, bromine, or nitric acid. Chlorine, bromine, and nitric acid produce chloro, bromo, and nitro derivatives of I, respectively. Nitrobenzene is preferred for ease of operation, yield, and purity. Acidic potassium per-

manganate or chromic acid cannot be used since they destroy the product.

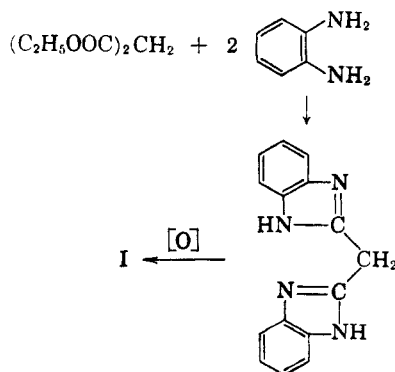
The second preparative route is reaction of diethylmalonate with *o*-phenylenediamine to give di-2-benzimidazolymethane, followed by bimolecular oxidation to I with air, nitrobenzene, sulfur, sodium hypochlorite, chlorine, or bromine. Chlorine and bromine give halogenated products.

Both routes are generally successful with *o*-phenylenediamine substituted with alkyl or alkoxy groups. Halogen or nitro substituents, on the other hand, prevent reaction.

Chlorination and bromination of I are readily effected by direct reaction with the elements in alcohol or acetic acid. As expected,¹ an appreciable amount of halogen is bound by the imidazole rings and is difficult to remove even by pasting in sulfuric acid. For this reason it is best to chlorinate with sulfuryl chloride and to brominate in a mixture of bromine, sulfuryl chloride, and trichlorobenzene. Products obtained in this way appear to be free of removable halogen and are characterized by very low solubility in nitrobenzene, a solvent for many of the *N*-halogenated compounds. A product containing approximately 11 nuclear chlorine atoms was found to be too insoluble in dimethylformamide to permit determination of the visible spectrum in that solvent. Determination of the spectrum on a mineral oil dispersion showed a maximum at 3600 Å. The infrared spectrum of this chlorinated derivative is reproduced in Fig. 4.

I and its derivatives are not affected noticeably by mild alkalis and weak acids. Strong alkalis and strong mineral acids cause shade changes, greener with alkalis, redder with acids. An exception is the completely chlorinated derivative which shows no sensitivity to either acids or bases.

The strong color and stability of I and its derivatives make these novel substances potentially useful as dyes and pigments.²



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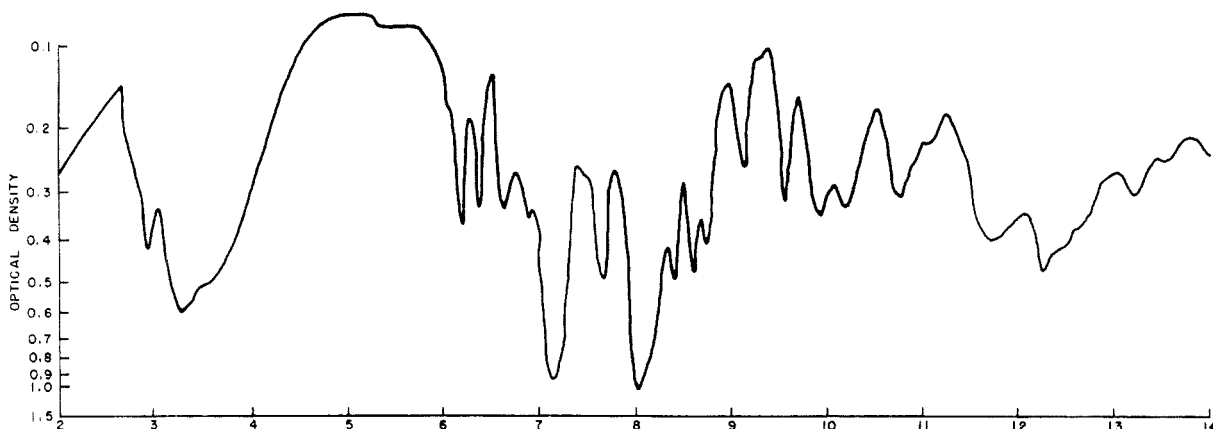


Fig. 4. Infrared spectrum of polychlorotetra-2-benzimidazoleethylene, KBr disk, NaCl prism

EXPERIMENTAL

The ultraviolet and visible spectra were determined with a Cary Model 11 Recording Spectrophotometer. The infrared spectrum was obtained with a Perkin-Elmer Model 12-C Spectrophotometer.

1,1,2,2-Tetra-2-benzimidazoleethylene dihydrate. One hundred grams (0.378 mole) of tetramethyl ethane-1,1,2,2-tetracarboxylate and 180 g. (1.66 mole) of *o*-phenylenediamine were dissolved in 750 ml. of trichlorobenzene at 85°. This solution was then added to 300 ml. of boiling trichlorobenzene at such a rate that the temperature did not drop below 180°. The reaction mixture was then boiled for 3 hr. The mixture was cooled to room temperature which caused a crystalline product to precipitate. After cooling, the mass was poured into several volumes of alcohol and filtered. The product was washed free of trichlorobenzene with alcohol and dried. The yield was 131.5 g. (65.5%).

Anal. Calcd. for $C_{30}H_{22}N_8(H_2O)_2$: C, 67.9; H, 4.92; N, 21.2. Found: C, 67.7, 67.3; H, 5.3, 5.3; N, 20.8, 20.9.

Tetra-2-benzimidazoleethylene monohydrate. A slurry of 70 g. (0.132 mole) of 1,1,2,2-tetra-2-benzimidazoleethylene dihydrate and 5 g. of potassium carbonate in 150 ml. of nitrobenzene was heated at reflux for 1 hr. The mixture, which became thick during heating, was cooled to room temperature and filtered. The filter cake was washed with benzene, then with alcohol, and dried. It was next dissolved in 30 ml. of 98% sulfuric acid at 10°, reprecipitated with water, filtered, and washed free of acid. When dry the bright orange product weighed 30 g. (44.7%).

Anal. Calcd. for $C_{30}H_{22}N_8(H_2O)$: C, 70.5; H, 4.31; N, 21.7. Found: C, 70.4, 70.5, 70.8; H, 4.25, 4.25, 4.23; N, 21.6, 21.9.

Oxidation of 1,1,2,2-tetra-2-benzimidazoleethylene dihydrate with nitric acid. A fine slurry was produced by ball-milling 56.4 g. (0.106 mole) of 1,1,2,2-tetra-2-benzimidazoleethylene dihydrate in 1 l. of water. An additional 1 l. of water was added, followed by 450 ml. of 70% nitric acid added in a slow stream. Stirring was continued for 30 min. and then the red reaction mass was made basic with 30% sodium hydroxide. The product was filtered, washed free of alkali, and dried. This material was dissolved in 15 parts of 96% sulfuric acid, reprecipitated with water, filtered, washed free of acid, and dried. The yield was 42 g. (71.3%) of a bright yellow solid.

Anal. Found: C, 63.2, 63.8; H, 3.74, 4.08; N, 22.6, 22.8; H_2O by weight loss at 200°, 3.14. This corresponds to a mixture of nitro derivatives with an average content of 1.2 nitro groups.

This product can be further nitrated with fuming nitric acid in 96% sulfuric acid at 25° to give a tetranitro derivative.

Oxidation of 1,1,2,2-tetra-2-benzimidazoleethylene dihydrate with bromine. Five grams (0.0094 mole) of 1,1,2,2-tetra-2-benzimidazoleethylene dihydrate was suspended in 100 ml.

of carbon tetrachloride containing 5 g. of dissolved bromine. After standing for 48 hr. at room temperature, the mixture was filtered. The product was washed with carbon tetrachloride and then with alcohol. When dry it was dissolved in 10 parts of 96% sulfuric acid, reprecipitated with water, washed free of acid, and dried again. The final product was a bright orange solid. The yield was 5.5 g. (87.3%).

Anal. Calcd. for $C_{30}H_{18}N_8Br_2(H_2O)$: C, 53.8; H, 2.99; N, 16.8; Br, 23.9. Found: C, 53.5, 54.0; H, 3.21, 3.41; N, 17.0, 17.4; Br, 23.5, 24.0.

Tetrakis(5 [or 6]methyl-2-benzimidazolyl)ethylene. This product was made in 56% yield by condensing 4-methyl-*o*-phenylenediamine with tetramethyl ethane-1,1,2,2-tetracarboxylate, followed by oxidation with nitric acid. The product was not nitrated and contained no water of crystallization.

Anal. Calcd. for $C_{34}H_{28}N_8$: C, 74.4; H, 5.14; N, 20.4. Found: C, 72.9, 73.0; H, 5.17, 5.21; N, 21.1, 21.0.

Tetrakis(5 [or 6]methoxy-2-benzimidazolyl)ethylene dihydrate. This product was prepared in 30% yield by condensing 4-methoxy-*o*-phenylenediamine with tetramethyl ethane-1,1,2,2-tetracarboxylate followed by oxidation with sodium hypochlorite.

Anal. Calcd. for $C_{34}H_{28}N_8O_4(H_2O)_2$: C, 62.9; H, 4.93; N, 17.3. Found: C, 62.1, 62.5; H, 5.04, 5.23; N, 17.0, 17.1.

Di-2-benzimidazolylmethane monohydrate. A mixture of 1,000 g. (9.25 moles) of *o*-phenylenediamine and 2,500 ml. of trichlorobenzene was heated to 170° in a flask equipped with an azeotroping head, and 740 g. (4.62 moles) of diethylmalonate was added over 90 min. The temperature was allowed to rise to 185° during addition of the malonate, and finally was maintained at 185–190° for 2 hr. more. During the reaction period, volatile material amounting to 641 g. was collected. The mixture was cooled to 25° whereupon a crystalline product precipitated. The product was filtered and the filter cake washed twice with 250-ml. portions of benzene, and then with 250 ml. of alcohol and 250 ml. of water. The sand-like yellow product was dried at 110°. The yield was 1,040 g. (84.5%).

Anal. Calcd. for $C_{15}H_{12}N_4(H_2O)$: N, 21.4. Found: N, 21.6, 21.6.

Tetra-2-benzimidazoleethylene monohydrate by oxidation of the corresponding methane. Two hundred g. (0.806 mole) of di-2-benzimidazolylmethane monohydrate, 200 g. of potassium carbonate, and 1200 ml. of nitrobenzene were heated at 160° for 4 hr. After cooling at room temperature, the reaction mass was poured into 2 l. of alcohol, filtered, and the filter cake washed with alcohol until free of nitrobenzene. The product was then stirred with 2 l. of water at 50°, filtered, washed with water until alkali-free, and dried at 110°. The yield was 160 g. (77.8%) of a bright yellow solid.

Anal. Calcd. for $C_{30}H_{20}N_8(H_2O)$: C, 70.5; H, 4.31; N, 21.7. Found: C, 70.2, 70.3, 70.8; H, 4.13, 3.95; N, 21.9, 21.9.

This product was identical with that prepared by oxida-

tion of the corresponding ethane with nitrobenzene. A small sample was dried for 3 days at 110° and analyzed before moisture could be regained.

Anal. Calcd. for $C_{30}H_{20}N_3$: C, 73.2; H, 4.10; N, 22.8. Found: C, 73.6, 73.7; H, 3.70, 3.80; N, 22.3, 22.5.

Chlorination of tetra-2-benzimidazolylethylene with sulfuryl chloride. Fifty g. (0.098 mole) of tetra-2-benzimidazolylethylene was finely ground and suspended in 650 ml. of trichlorobenzene. One g. of iodine was added, the mixture was heated to 150° and maintained at 150–155° while 200 ml. (2.47 moles) of sulfuryl chloride was added over 4 hr. The mixture was held at 155° for an additional 30 min., cooled, and poured into 2 l. of water. The product was filtered, washed with alcohol, and dried. The yield of crude material was 85 g. This was ground and extracted for 7 hr. in a Soxhlet extractor with benzene. The residue was then extracted twice with 500-ml. portions of nitrobenzene at 90°, washed free of nitrobenzene with alcohol, and dried. The yield was 59.5 g. (69.3%) of bright orange solid.

Anal. Found: C, 40.1, 40.6; H, 1.60, 1.70; N, 12.7, 12.7; Cl, 42.3, 42.4.

This corresponds to a mixture of monohydrates with an average content of 10.6 chlorine atoms.

This product can be further chlorinated to a chlorine content of 53.4% by autoclaving at 150° for 10 hr. with excess sulfuryl chloride.

Bromination of tetra-2-benzimidazolylethylene. A mixture of 10.5 g. (0.065 mole) of bromine and 10.5 g. (0.077 mole) of sulfuryl chloride was slowly added to a suspension of 4 g.

(0.008 mole) of tetra-2-benzimidazolylethylene in 100 ml. of trichlorobenzene. The temperature rose to 31°. The mixture was heated to 80°, held one hour, then heated to 130° and held one hour. After cooling, the mixture was filtered and the filter cake washed with alcohol. The dry product weighed 8 g., was insoluble in nitrobenzene, and contained 70.2% bromine, corresponding to 14 bromine atoms. No chlorine was found.

Sulfonation of tetra-2-benzimidazolylethylene. A mixture of 93 ml. of 100% sulfuric acid and 8 ml. of 65% oleum was cooled to 19°. Ten g. (0.203 mole) of finely ground tetra-2-benzimidazolylethylene was added slowly at 20–25°. The mixture was heated at 70° until a drop was just soluble in dilute sodium hydroxide (45 min.). The solution was then cooled and poured slowly into 200 ml. of water. Fifty ml. of 30% sodium hydroxide was added and, after filtration to remove any insoluble material, the filtrate was mixed with 150 ml. of 30% sodium hydroxide. After cooling again to room temperature, the product was filtered, redissolved in 400 ml. of water, and reprecipitated with 7 g. of potassium chloride. The product weighed 35 g. when dry.

Anal. Found: N, 4.63, 4.39; Organic S, 2.04, 2.04. This corresponds to a mixture of sulfonated derivatives averaging 1.5 sulfonic acid groups admixed with sodium and potassium salts.

This product dyes wool from a weakly acidic dyebath in red-yellow shades.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE RESEARCH DIVISION, BRISTOL LABORATORIES, INC.]

Dialkylaminoalkyl Ethers of Some 2,6-Dialkylphenols

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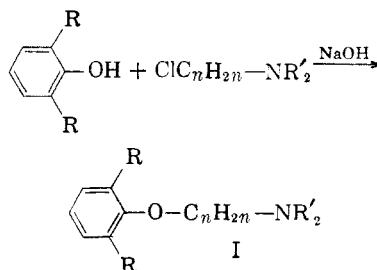
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A number of dialkylaminoalkyl ethers of some 2,6-dialkylphenols, particularly 2,6-diisopropylphenol, have been prepared in good yields by the Williamson synthesis using dialkylaminoalkyl chlorides. Attempts to prepare other ethers, *e.g.*, β -hydroxyethyl and β -haloethyl ethers, were almost completely unsuccessful, probably because of steric hindrance.

2,6-Dialkylphenols have recently become available on a scale such that their use as intermediates is now feasible.¹ Because of the fact that certain basic ethers of substituted phenols have shown utility as therapeutic agents, we set out to prepare some dialkylaminoalkyl ethers of these 2,6-dialkylphenols. This particular type of compound has received little attention, due in part to the previous accessibility of only the simpler dialkylphenols such as 2,6-xyleneol, and of the 2,4,6-trialkylphenols.

The majority of compounds to be described are ethers of 2,6-diisopropylphenol (DIP), and most of the discussion which follows refers to this phenol. The presence of two branched ortho substituents causes this phenol to be cryptophenolic, being insoluble in aqueous alkali, but soluble in Claisen's alkali. It does form a sodium salt quite readily on treatment in boiling toluene with either sodium hydride or sodium hydroxide.² This sodium 2,6-

diisopropylphenoxide is not typical, however, since it participates in the Williamson ether synthesis in widely varying degrees, depending on the nature of the halide used as the other reactant.



With dialkylaminoalkyl chlorides, the desired basic ethers (I) were obtained in quite acceptable yields. With other halides, the results were often negative. All attempts to prepare β -hydroxyethyl 2,6-diisopropyl ether were unsuccessful; neither ethylene chlorohydrin nor ethylene carbonate³ could be caused to react with DIP under a variety

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