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2-Mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]substituted furan, thiophene and *N*-methylpyrrole were synthesized by mono- and dilithiation of furan, thiophene and *N*-methylpyrrole, respectively, and subsequent reaction with Michler's ketone. The title compounds develop black or dark-blue colors in acidic media.

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Metallations of furan [1-2], thiophene [3] and *N*-methylpyrrole [4-5] with lithium reagents (*n*-butyllithium, *tert*-butyllithium) leading to  $\alpha$ -monolithio derivatives are well documented. Direct lithiation without the assistance of a complexing agent generally gives relatively low yields, and it was reported that the metallation benefits from the presence of *N,N,N,N*-tetramethylethylenediamine [6-7]. Reactions of these  $\alpha$ -lithio intermediates with various electrophiles, such as halides, aldehydes, ketones and amides, provide a variety of 2-substituted derivatives. Dimetallations of furan, thiophene and *N*-methylpyrrole have been effected with butyllithium/potassium *tert*-butoxide or butyllithium/tetramethylethylenediamine at high temperatures [7-8]. Ashii *et al* reacted these dilithiated intermediates with diaryl ketones to prepare 2,5-bis(diarylhydroxymethyl)furans, -thiophenes and -*N*-methylpyrroles in good yields [9].

2-mono- and 2,5-bis[bis[4-(*N,N*-dimethylamino)phenyl]hydroxymethyl]-substituted five-membered heteroaromatic compounds. We now report the details.

#### Results and Discussion.

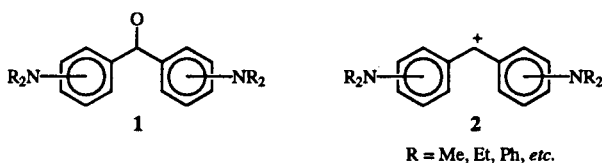
Treatment of furan **3a** with two equivalents of butyllithium in the presence of two equivalents of tetramethylethylenediamine at  $-30^\circ$  for 15 minutes followed by refluxing in hexane for 30 minutes and subsequent quenching with Michler's ketone afforded the desired product **5a** in 42% yield. Compounds **5b** and **5c** were similarly prepared in 55% and 63% yields, respectively. Compounds **5a-c** are sparingly soluble in common organic solvents such as chloroform, acetone and ethyl acetate and were thus purified by boiling in ethyl acetate and filtering the deposit.

In the above-mentioned procedure, the mono-substituted products **7a-c** were obtained in 30-60% yields when only one equivalent of butyllithium was used. Unlike the 2,5-disubstituted derivatives, compounds **7a-c** show high solubility in chloroform, acetone and ethyl acetate, and can be purified by recrystallization from a mixture of ethyl acetate and hexane (2:1). The structures of all compounds prepared were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectroscopy and elemental analyses.

Compounds **7a**, **7b**, and **7c** have been prepared *via* lithiation of furan, thiophene, and *N*-methylpyrrole and reaction with Michler's ketone. The effect of these compounds on *Trypanosoma cruzi* and their  $^{13}\text{C}$  nmr spectra have been reported [10-12].

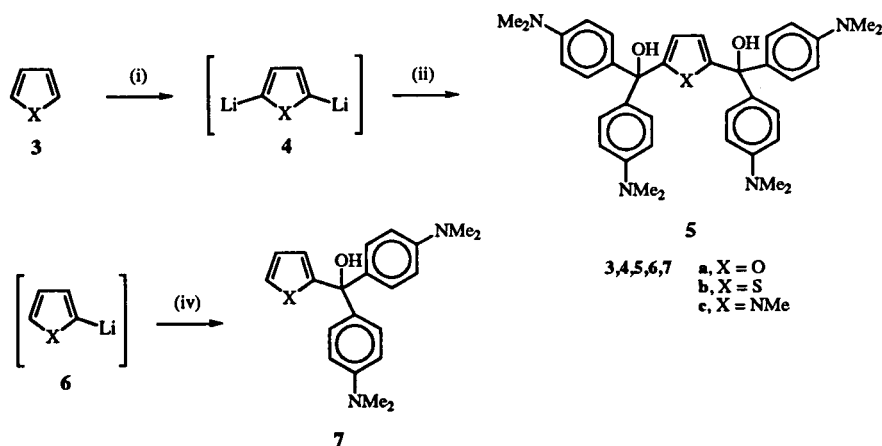
2-Mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furans, thiophenes and *N*-methylpyrroles can be used in carbonless paper imaging in which an image is formed by the application of pressure to a sheet of carbonless paper. For carbonless paper products, one of the reactants is typically encapsulated to prevent

Block 1



Compounds containing a fragment of type 1 are color-formers. Under acidic conditions, the oxygen atom (from a hydroxy or ester group) is cleaved to form cation 2 which exhibits a dark color due to the strong electron-donating effects of the dialkylamino groups and the existence of a large conjugated system in the molecule. During the course of investigation of new color-formers, we found that lithiations of furan, thiophene and *N*-methylpyrrole, as previously described [7-8], and subsequent reactions with Michler's ketone (4,4'-bis-(dimethylamino)benzophenone) furnish a new class of

Scheme 1



premature reaction of the color-forming compound with the developer. Preferably, a fill solution of the color-forming compound or compounds in a hydrophobic solvent is encapsulated or contained in microcapsules. When activating pressure is applied to the carbonless paper, such as from a stylus or a typewriter key, the capsules rupture, the solution of encapsulated color-forming compound is released, and a reaction between the previously separated reactants occurs. In general, the resulting reaction will form a colored image corresponding to the path traveled by the stylus or the pattern of pressure provided by the stylus or key. Common uses of carbonless papers include credit card receipts and multi-part forms.

2-Mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furans, thiophenes and *N*-methylpyrroles can also be used in thermal imaging constructions which rely on the use of heat to produce an image and generally comprise a support, such as paper, glass, plastic, metal, *etc.*, coated with (a) an acid developable color-forming compound; (b) an acidic developer; and (c) binder. At elevated temperatures the developer reacts with the acid developable color-forming compound to form a colored image corresponding to the pattern in which heat was applied to the thermal imaging construction. The image may be applied by contacting the imaging construction with a thermal print head or by other heating means. Typically, the activating temperature is in the range from 60 to 225°.

Additionally, these 2-mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furans, thiophenes and *N*-methylpyrrole compounds can be used in a composition comprising a color-forming compounds and a solvent, carried by a variety of materials such as woven, non-woven or film transfer ribbons for use

in impact marking systems such as typewriters and the like. In these uses, the color-forming compound is transferred to a record surface containing a developer by impact transfer means.

Further, these compounds can also be used in composition comprising a color-forming compound and a solvent, absorbed in a porous pad for subsequent transfer to a coreactive record surface by transfer means such as a portion of the human body, *e.g.*, a finger, palm, foot or toe, for providing fingerprints or the like.

Commonly used classes of color-forming compounds for carbonless paper applications and thermal imaging include fluorans, rhodamines, and triarylmethane lactone color-forming compounds. All of these compounds react with commonly used classes of acidic developers, such as Lewis acids, salicylic acids, phenolic compounds, or acidic clays, to form highly colored species by the opening of a lactone ring. Specific, examples of such compounds are Pergascript Black I-R (a fluoran) and crystal violet lactone (a triarylmethane lactone).

2-Mono[bis[(4-amino)phenyl]hydroxymethyl]-substituted furan, thiophene, and pyrrole compounds and 2,5-bis[bis[(4-amino)phenyl]hydroxymethyl]-substituted furan, thiophene, and pyrrole color-forming compounds are generally colorless to lightly colored, and impart little or no color when coated on imaging substrates. In addition, these compounds rapidly form stable, intense colors upon reaction with developer systems typically used in carbonless papers and thermal imaging systems. 2-Mono[bis[(4-amino)phenyl]hydroxymethyl]-substituted furan, thiophene and pyrrole compounds and 2,5-bis[bis[(4-amino)phenyl]hydroxymethyl]-substituted furan, thiophene and pyrrole color-forming compounds also satisfy the requirements of solubility in suitable

solvents for encapsulation, nonsolubility in aqueous media, non-reactivity with fill solvents, and color-forming compounds mixed therewith, and compatibility with existing carbonless paper and thermal imaging developer systems.

If desired, a mixture of color-forming compounds may be used and images of varying colors can be formed by the reaction between a developer and the color-forming compounds. Appropriate mixtures to form black images are particularly useful. In systems where the color-forming compounds are encapsulated, the system may provide either one type of capsule containing a mixture of color-forming compounds or may comprise a mixture of capsules, each containing a separate encapsulated color-forming compound solution. In the latter instance, color is formed by the mixing of the color-forming compounds upon capsule rupture and reaction with the developer.

2-Mono[bis[(4-amino)phenyl]hydroxymethyl]-substituted furan, thiophene, and pyrrole and 2,5-bis[bis[(4-amino)phenyl]hydroxymethyl]-substituted furan, thiophene, and pyrrole color-forming compounds are preferably encapsulated by means of interfacial polymerization encapsulation. They are soluble in the fill solvents commonly used in the encapsulation process. Such solvents are aqueous immiscible solvents and include but are not limited to xylene, toluene, cyclohexane, diethyl phthalate, tributyl phosphate, benzyl benzoate, diethyl adipate, butyl diglyme, and the like. Preferably, the color-forming compound is present in the microcapsules in an amount from about 0.2 to about 10% by weight based on weight of the fill of the microcapsule.

## EXPERIMENTAL

### Determination of Color.

The colors formed by reaction of the color-forming compound and developer in the examples below, were determined by preparing a 1% solution of the colorforming compound or mixture of color-forming compounds in an appropriate solvent. Images were formed by applying two stripes of the solution to a 3M Scotchmark™ CF developer (receptor) sheet using a cotton tipped applicator swab. This sheet contains a zincated phenolic resin (an alkyl Novolak™ resin) as the Lewis acid developer. Rapid and complete color development of the image was achieved by passing the sheet through a hot shoe adjusted to 102°, making a revolution every 10 seconds.

The color and the CIELAB coordinates for the developed color-forming compounds were measured and recorded for each sample. In the CIELAB System three mutually perpendicular axes ( $L^*$ ,  $a^*$ , and  $b^*$ ) are needed to define a color. " $L^*$ " (+z axis) represents the lightness or darkness of the image ( $L$  of 100 is white,  $L$  of 0 is black); " $a^*$ " (x axis) represents the amount of red or green (+ $a^*$  is red, - $a^*$  is green); and " $b^*$ " (y axis) represents the amount of yellow or blue (+ $b^*$  is yellow, - $b^*$  is blue).

By measuring a material's  $L^*$ ,  $a^*$ , and  $b^*$  values, the color of one sample can be compared with that of other samples [13].

The  $L^*$ ,  $a^*$ , and  $b^*$  color coordinates of the more uniform stripe were automatically measured on a Gretag SPM-100 Spectrophotometer using no color filters, a standard Observer of 2°; and using illuminant D-50. The sample was illuminated at 45° and read at 0°.

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. The  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectra were recorded on a Varian VXR 300 MHz spectrometer in deuteriochloroform using tetramethylsilane as an internal reference for  $^1\text{H}$  spectra and deuteriochloroform for  $^{13}\text{C}$  spectra. Elemental analyses were performed on a Carlo Erba-1106 instrument.

All materials used in the following examples are readily available from standard commercial sources such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. The following additional terms and materials were used.

Color measurements were made on a Gretag SPM-100 Spectrophotometer. This instrument is available from Gretag Aktiengesellschaft, Regensdorf Switzerland.

All percentages are by weight unless otherwise indicated.

Mondur™ MRS (CAS No. 9016-87-9) is a polymethylene-polyphenylene-polyisocyanate and is available from Bayer Chemical Company, Pittsburgh, PA.

Pergascript Red I-6B, Pergascript Orange I-SR, and Pergascript Black I-R are fluoran color-forming compounds available from Ciba-Geigy, Greensboro, NC.

Sodium alkyl naphthalenesulfinate dispersant was obtained from Emkay Chemical Co., Elizabeth, NJ.

Sure Sol™ 290 [CAS RN 81846-81-3] is a 4,4'-bis-butylated-1,1'-biphenyl and is available from Koch Refining Co., Corpus Christi, TX.

### General Procedure for the Preparation of Compounds 5a-c, 7a-c.

To a solution of furan, thiophene, or *N*-methylpyrrole (20 mmoles) and tetramethylethylenediamine (40 mmoles) in hexane (20 ml) at -30° was added butyllithium (40 mmoles for 5a-c, 20 mmoles for 7a-c). The solution was kept at this temperature for 15 minutes, refluxed for 30 minutes then cooled from -30 to -50°. A solution of 4,4'-bis(dimethylamino)benzophenone (40 mmoles for 5a, 20 mmoles for 7a-c) in tetrahydrofuran (200 ml) was then added, and the mixture stirred at room temperature overnight. After adding water (50 ml), the mixture was extracted with ethyl acetate (3 x 120 ml). The combined extracts were dried over magnesium sulfate and the solvent evaporated to give a residue. In the cases of 5a-c, 7a and 7c, pure products were obtained upon boiling this residue in ethyl acetate (-80 ml) and filtering the deposit. Product 7b was purified by column chromatography on silica gel (hexane:ethyl acetate = 3:1).

### 2,5-Bis[bis(*p*-dimethylaminophenyl)hydroxymethyl]furan (5a).

This compound was obtained in 42% yield, mp 186-188°;  $^1\text{H}$  nmr:  $\delta$  2.88 (s, 24H), 5.60 (br, 2H), 5.77 (s, 2H), 6.58 (d, 8H,  $J$  = 8.7 Hz), 7.10 (d, 8H,  $J$  = 8.5 Hz);  $^{13}\text{C}$  nmr:  $\delta$  40.1, 76.1, 107.5, 111.0, 127.7, 134.1, 148.9, 159.1.

Anal. Calcd. for  $\text{C}_{38}\text{H}_{44}\text{N}_4\text{O}_3$ : C, 75.45; H, 7.34; N, 9.27. Found: C, 75.34; H, 7.40; N, 9.26.

### 2,5-Bis[bis(*p*-dimethylaminophenyl)hydroxymethyl]thiophene (5b).

This compound was obtained in 55% yield, mp 194-196°;  $^1\text{H}$  nmr:  $\delta$  2.82 (s, 24H), 6.12 (s, 2H), 6.42 (s, 2H), 6.61 (d, 8H,

$J = 8.8$  Hz), 7.20 (d, 8H,  $J = 8.5$  Hz);  $^{13}\text{C}$  nmr:  $\delta$  40.2, 78.2, 111.2, 124.2, 127.9, 136.1, 149.1, 153.3.

*Anal.* Calcd. for  $\text{C}_{38}\text{H}_{44}\text{N}_4\text{O}_2\text{S}$ : C, 73.51; H, 7.15; N, 9.03. Found: C, 73.29; H, 7.23; N, 8.92.

2,5-Bis[bis(*p*-dimethylaminophenyl)hydroxymethyl]-*N*-methylpyrrole (5c).

This compound was obtained in 63% yield, mp 204-206°;  $^1\text{H}$  nmr:  $\delta$  2.88 (s, 24H), 3.08 (s, 3H), 5.03 (s, 2H), 5.70 (s, 2H), 6.58 (d, 8 H,  $J = 7.5$  Hz), 7.05 (d, 8 H,  $J = 7.32$  Hz);  $^{13}\text{C}$  nmr:  $\delta$  34.2, 40.1, 76.9, 107.8, 127.8, 135.5, 148.5.

*Anal.* Calcd. for  $\text{C}_{39}\text{H}_{47}\text{N}_5\text{O}_2$ : C, 75.81; H, 7.67; N, 11.34. Found: C, 75.54; H, 7.68; N, 11.34.

2-Bis(*p*-dimethylaminophenyl)hydroxymethyl]furan (7a).

This compound was obtained in 60% yield, mp 107-110°;  $^1\text{H}$  nmr:  $\delta$  2.89 (s, 12 H), 5.88-5.94 (m, 1 H), 6.22-6.28 (m, 1 H), 6.64 (d, 4 H,  $J = 8.2$  Hz), 7.13 (d, 4 H,  $J = 7.9$  Hz), 7.34 (s, 1 H);  $^{13}\text{C}$  nmr:  $\delta$  40.4, 77.4, 108.6, 109.7, 111.7, 128.0, 133.2, 142.0, 142.0, 149.6, 159.2.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$ : C, 74.96; H, 7.19; N, 8.33. Found: C, 74.87; H, 7.10; N, 8.21.

2-Bis(*p*-dimethylaminophenyl)hydroxymethyl]thiophene (7b).

This compound was obtained in 30% yield, mp 50°;  $^1\text{H}$  nmr:  $\delta$  2.92 (s, 12 H), 6.64 (d, 4 H,  $J = 9.0$  Hz), 6.69-6.71 (m, 1 H), 6.89-7.01 (m, 1 H), 7.17-7.23 (m, 5 H);  $^{13}\text{C}$  nmr:  $\delta$  40.5, 79.7, 111.6, 124.9, 126.0, 126.1, 129.2, 128.1, 135.2, 149.6, 153.8.

2-Bis(*p*-dimethylaminophenyl)hydroxymethyl]-*N*-methylpyrrole (7c).

This compound was obtained in 30% yield, mp 154-156°;  $^1\text{H}$  nmr:  $\delta$  2.91 (s, 12 H), 3.40 (s, 3 H), 5.49-5.51 (m, 1 H), 5.92-5.94 (m, 1 H), 6.58-6.59 (m, 1 H), 6.65 (d, 4 H,  $J = 8.9$  Hz), 7.08 (d, 4 H,  $J = 8.9$  Hz);  $^{13}\text{C}$  nmr:  $\delta$  35.8, 35.9, 40.5, 78.1, 105.2, 111.7, 124.2, 127.9, 134.6, 137.4, 149.4.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{27}\text{N}_3\text{O}$ : C, 75.60; H, 7.79; N, 12.03. Found: C, 75.20; H, 7.79; N, 11.66.

Example 1.

A 1% solution of each of color-forming compounds 5a-c and 7a-c was prepared in a mixture of diethyl phthalate:cyclohexane (1:1). Each solution was swabbed onto a sheet of 3M Scotchmark™ CF paper using a cotton tipped applicator swab. This CF sheet contains a zincated phenolic resin as the developer. In all cases, an immediate reaction occurred. The following colors were obtained:

Color-Former	Image Color	L*	a*	b*
5a	Blue	37.73	3.86	-22.83
5b	Blue-black	45.84	7.47	-31.43
5c	Cyan	42.85	1.53	-30.30
7a	Green-yellow	64.17	-22.28	6.88
7b	Green	58.87	-39.15	5.91
7c	Blue	40.95	0.41	-45.26

Example 2.

The following Example demonstrates that 2-mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furan, thiophene and *N*-methylpyrrole compounds can be encapsulated and coated to prepare a carbonless paper form-set construction.

Encapsulation of Compound 5b.

A capsule fill solution was prepared by placing 1.5 g of color-forming compound 5b and 290.5 g of Sure Sol™ 290 into an Ehrlenmeyer flask. Stirring was begun and the mixture heated to ensure complete dissolution of the color-forming compound. Upon dissolution, the solution was allowed to slowly cool to room temperature and 8.0 g of Mondur™ MRS was added. The total color-forming compound concentration was 0.5 wt%.

This fill solution was added to a stirred solution of 492.97 g of water, 10.3 g of sodium alkylnaphthalenesulfinate dispersant, and a sufficient amount of 50% sodium hydroxide solution to bring the pH to 11.00. The flask was then placed in a water bath maintained at 21.1°. When the solution had warmed, 20 g of a 25% solution of tetraethylene pentamine in water was added dropwise over 1 hour. Polyurea capsules containing color-forming compound 5b were formed.

The capsules obtained were spherical with a median volumetric diameter of 21.5  $\mu\text{m}$ . The capsule dispersion contained approximately 34.77% capsules.

Various amounts of capsule slurry were added to 65 g of a 1.5% aqueous sodium alginate solution. The mixture was applied to a coated paper using a bar coater with a 3 mil (76.2 mm) gap. The coating was allowed to dry at room temperature.

The coated CB sheet was imaged using a 3M Scotchmark™ CF sheet containing a zincated phenolic resin as the developer. Image color, speed, ultimate image reflectance, and L\*, a\*, and b\* were determined as described above. The L\*, a\*, b\* values for this Example are slightly different from those of Example 1 above as the concentrations of color-forming compound are different.

Amount capsule slurry	Image Color	L*	a*	b*
10 g	Blue	71.66	0.45	-14.59
15 g	Blue	69.25	1.03	-16.58
20 g	Blue	64.89	1.50	-18.38
25 g	Blue	63.93	1.79	-18.98

Example 3.

The following Example demonstrates the use of 2-mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furan, thiophene and *N*-methylpyrrole color-forming compounds in combination with fluoran color-forming compounds to provide blue-black image. Fluoran color-forming compounds develop by the opening of a lactone ring. A 1% solution of a mixture of color-forming compounds was prepared in a mixture of diethyl phthalate:cyclohexane (1:1). The color-forming compound solution had the following composition:

Compound	wt%
Compound 5b	16%
Compound 7b	22%
Pergascript Red I-6B	8%
Pergascript Orange I-5R	5%
Pergascript Black I-R	49%

The solution was swabbed onto a sheet of 3M Scotchmark™ CF paper using a cotton tipped applicator swab. This CF sheet contains a zincated phenolic resin as the developer. An immediate reaction occurred to form a black image.

Example	Image Color	L*	a*	b*
3	Black	54.39	2.77	4.64

## Example 4.

The following Example demonstrates the use of 2-mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furan, thiophene and N-methylpyrrole color-forming compounds in a fingerprinting system. An index finger was placed lightly onto a piece of filter paper saturated with the 1% solution of a mixture of color-forming compounds of Example 3. The finger was then pressed against a sheet of 3M Scotchmark™ CF paper. A reaction occurred to form a dark black fingerprint.

## Example 5.

The following Example further demonstrates the use of 2-mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furan, thiophene and N-methylpyrrole color-forming compounds in combination with fluoran color-forming compounds to provide blue-black image. A 1% solution of a mixture of color-forming compounds was prepared in a mixture of diethyl phthalate:cyclohexane (1:1 wt/wt). The color-forming compound solution had the following composition:

Compound	wt%
Compound 5b	32%
Compound 7b	44%
Pergascript Red I-6B	16%
Pergascript Orange I-5R	8%

The solution was swabbed onto a sheet of 3M Scotchmark™ CF paper using a cotton tipped applicator swab. This CF sheet contains a zincated phenolic resin as the developer. A reaction occurred to form a dark blue-black image.

Example	Image Color	L*	a*	b*
5	Blue-black	48.93.39	7.04	-23.51

## Example 6.

The following Example demonstrates the use of 2-mono- and 2,5-bis-[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furan, thiophene, and N-methylpyrrole color-forming compounds in a fingerprinting system. An index finger was placed lightly onto a piece of filter paper saturated with the 1% solution of a mixture of color-forming compounds of Example 5. The finger was then pressed against a sheet of 3M Scotchmark™ CF paper. An immediate reaction occurred to form a dark blue-black fingerprint.

## Example 7.

The following example demonstrates the use of 2-Mono- and 2,5-bis[bis[(4-dimethylamino)phenyl]hydroxymethyl]-substituted furan, thiophene and N-methylpyrrole color-forming compounds in a thermal imaging element.

An aqueous slurry of 1.00 g of color-forming compound 5b, 3.00 g of styrene maleic anhydride resin (Stymer S), and 96 g of water was ball milled for 24 hours.

A thermal imaging dispersion was prepared by mixing the materials shown below.

Component	Wet Weight - g	Dry Weight - g
Water	40.0	—
Rice Starch [a]	7.20	7.20
Cellose QPO9-L (7%) [b]	16.26	1.38
Stymer S (25%) [c]	16.26	2.85
Standapol ES (28%) [d]	0.11	0.03
Bisphenol A (30%)	24.54	7.36
Slurry of 5b (1.75%)	6.00	0.10
Total	105.52	18.92

[a] Rice starch is available from Sigma Chemical Co., St. Louis, MO. 63178. [b] Cellose QPO9-L is available from the Specialty Chemical Division of Union Carbide, Danbury, CT 06817. [c] Stymer S is the sodium salt of a styrene-maleic anhydride resin. It is available from Monsanto. [d] Standapol ES-3 is an anionic surfactant used as a dispersing agent. It is available from Henkel Inc., Teaneck, NJ 07666.

The dispersion was coated using a wire wound rod (Meier bar) onto bond paper and dried. The thermographic element was imaged using the tip of a heated screwdriver to simulate a thermal print head. A strong blue image resulted.

In summary, a new class of color-formers has been prepared with potentially important industrial applications in a wide variety of products, including carbonless papers, thermographic recording, and fingerprinting.

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