3,3-Diaryl-3*H*-2,1-benzoxathiole 1-oxides: new sultine colour-formers for carbonless imaging

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Lithiations of *N*-phenylbenzenesulfinamides followed by treatment with Michler's ketone and subsequent cyclizations during acidic workup provide 3,3-diaryl-3*H*-2,1-benzoxathiole 1-oxides in reasonable to good yields. The title compounds **11a, c–e, h** develop dark-blue colours in acidic media.

Heteroatom-assisted *ortho*-metallation has evolved as an important strategy in many aromatic and heterocyclic syntheses.[1,2] The common directing groups involved in such lithiations contain nitrogen (amino, amido, hydrazono, N-heterocycles, *etc.*), oxygen (alkoxide, ether, acetal, ketal), or sulfur (sulfide, sulfone, sulfonamide, thio heterocycle).[1] Each directing group has its own distinct effects, which depend mainly on the electron-withdrawing ability and coordinative properties. *ortho*-Lithiation of aromatic carboxylic or thiocarboxylic derivatives and subsequent reaction with aldehydes,[3,4] ketones,[5–7] or formamides[8,9] followed by cyclization, provides a convenient access to various α,β-benzolactones and α,β-benzolactams. Mamaeva *et al.*[10] prepared 2-(*tert*-butylsulfonyl)-3-(diphenylhydroxymethyl)benzoic acid **2** by double lithiation and subsequent reaction with benzophenone and carbon dioxide. Acid **2** was transformed into the *o*-carboxylic acid substituted sultine **3** by either heating or treatment with hydrochloric acid. However, it was reported that *tert*-butyl *o*-(1-hydroxy-1,1-diphenylmethyl)phenyl sulfone **1**, the analogue without the carboxylic group, did not undergo cyclization under the same conditions. The driving force in the cyclization has therefore been attributed to the steric 'pressure' between the carboxylic group and the adjacent *tert*-butylsulfonyl substituent.[10]

Recently, our group reported a novel heteroatom-assisted lithiation of benzenesulfinamides. The lithio intermediates were treated with a variety of electrophiles to generate *ortho*-substituted derivatives.[11] When aryl ketones or aldehydes were used as the electrophiles, the intermediates underwent simultaneous cyclization during aqueous workup to give sultine derivatives **5**. This methodology has now been further investigated and utilized for the synthesis of potentially important sultine colour-formers for carbonless imaging.

Compounds of type **6** (R^1, R^2 = alkylaminophenyl, dialkylaminophenyl, or alkylamino substituted polycycle) have been shown to be good colour formers for carbonless imaging.[12–14] Under acidic conditions, the lactone ring opens to form cations **7** which exhibit a dark colour due to the strong electron-donating effects of the alkylamino groups and the existence of extensive conjugated systems in the molecules. During a course of exploration into new colour-formers, we found that lithiations of *N*-phenylbenzenesulfinamides followed by reactions with an aryl ketone and subsequent cyclization during acidic workup provided 3,3-diaryl-3*H*-2,1-benzoxathiole 1-oxides in reasonable yields. We now report the details.

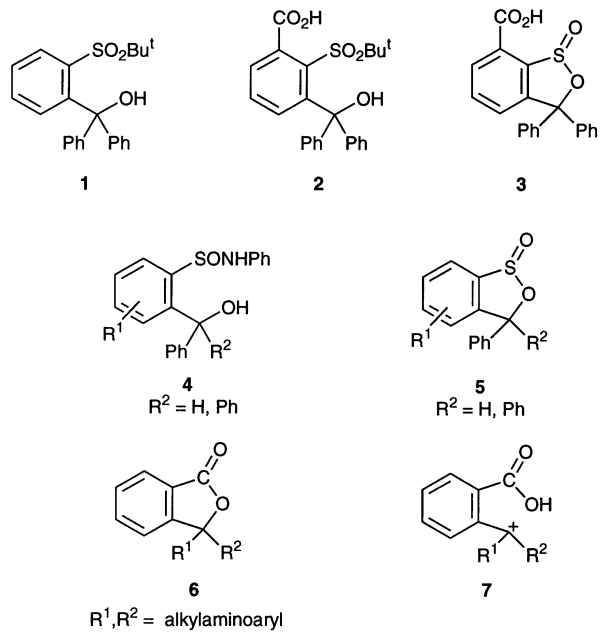
Results and Discussion

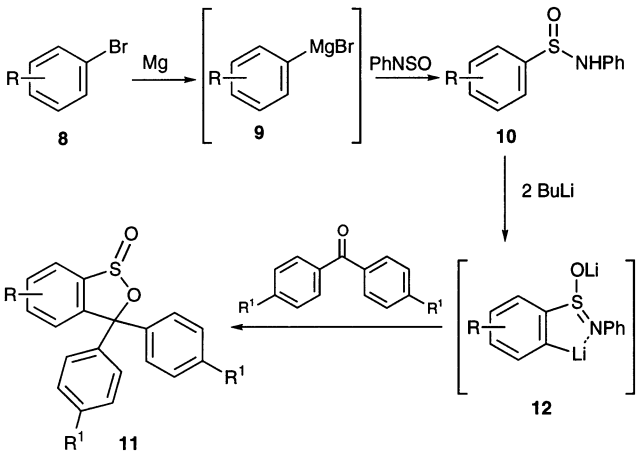
Chemistry

According to the literature procedure,[15,11] we first prepared *N*-phenylbenzenesulfinamides **10a–d** by reaction of *N*-sulfinylaniline with the appropriate Grignard reagents. For example, treatment of Grignard reagent **9a** with *N*-sulfinylaniline in tetrahydrofuran (THF) at −10 °C for 30 min then at 20 °C overnight afforded sulfinamide **10a** in 84% yield. Derivatives **10b–d** were similarly obtained in 60–95% yield. It should be mentioned that Grignard reagent **9c** was prepared in refluxing THF whereas diethyl ether was used for **9a**, **b**, **d**.

Treatment of **10a** with 2 equiv. of BuLi at −5 to 0 °C for 1 h gave a red–orange solution of dianion **12a**. Subsequent reaction with Michler's ketone followed by acidic workup gave the expected sultine **11a** in 48% yield (Scheme 1). Compounds **11b**, **d–h** were similarly prepared in 30–78% yields by reactions with the appropriate aryl ketones. Sultines **11a**, **b**, **d–h** were purified by column chromatography on silica gel.

We have also found that sulfinamides **10** can be easily prepared by the lithium–bromine exchange from **8** followed

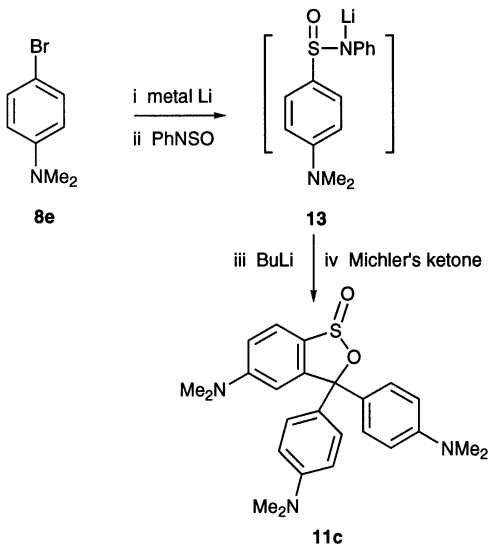




8,9,10,12 **a** R = H
b R = 3-Me
c R = 3-NMe_2
d R = 3-OMe

11 **a** R = H, R^1 = NMe_2
b R = H, R^1 = OMe
c R = 5-NMe_2, R^1 = NMe_2
d R = 6-Me, R^1 = NMe_2
e R = 6-NMe_2, R^1 = NMe_2
f R = 6-NMe_2, R^1 = H
g R = 6-NMe_2, R^1 = OMe
h R = 6-OMe, R^1 = NMe_2

Scheme 1



Scheme 2

by reactions with *N*-sulfinylaniline, which undergo further lithiation by BuLi and reaction with Michler's ketone to produce the desired sultines in a one-pot operation. Thus, heating 4-(*N,N*-dimethylamino)bromobenzene **8e** with 2 equiv. of metallic Li in diethyl ether for 3 h followed by reaction with *N*-sulfinylaniline gave the intermediate **13**. Further treatment of this intermediate **13** without separation with 1 equiv. of BuLi at −5 to 0 °C for 20 min then reaction with Michler's ketone afforded sultine **11c** in 68% overall yield (Scheme 2).

The structures of all products and the isolated intermediates were confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analyses (see Experimental). The sole unexpected feature was that broad proton peaks were observed in the aromatic region for compounds **11a**, **c–e**, **h**. We attribute this to fast reversible sultine ring-opening in deuterochloroform which affords a small amount of the corresponding cations with structure similar to the cations **7** formed from the analogous lactones due to the strong electron-donating ability of the dimethylamino group.

Compounds **11a**, **c–e**, **g**, **h** develop dark blue colours in acidic media, while compounds **11b**, **f** appear colourless under the same conditions. This indicates that the substituents on the sultine play an important role in the colour formation. It appears that at least one of R^1, R^2 and R^3 must be an amino group and at least one of the remaining substituents R^1, R^2 and R^3 must be a strongly electron-donating group. In other words, each sultine must have one amino group substituent and a second substituent which is a strongly electron-donating group. Examples of amino groups include amino, alkylamino and dialkylamino. Examples of strongly electron-donating groups include hydroxy, alkoxy and alkylthio.

Applications

Sultine compounds **11** can be used as colour-formers 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 premature reaction of the colour-forming compound with the developer. Preferably, a fill solution of the colour-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 colour-forming compound is released, and a reaction between the previously separated reactants occurs. In general, the resulting reaction will form a coloured image corresponding to the path travelled by the stylus or the pattern of pressure provided by the stylus or key. Common uses of carbonless papers include credit card receipts and multipart forms.

Sultine compounds **11** can also be used as colour-formers 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 colour-forming compound; (*b*) an acidic developer; and (*c*) binder. At elevated temperatures the developer reacts with the acid developable colour-forming compound to form a coloured 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 60–225 °C.

Additionally, these sultine compounds **11** can be used in a composition comprising colour-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 colour-forming compound is transferred to a record surface containing a developer by impact transfer means.

Further, compounds **11** can also be used in composition comprising a colour-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 colour-forming compounds for carbonless paper applications and thermal imaging include fluorans, rhodamines, and triarylmethane lactone colour-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 coloured 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).

Our sultine compounds **11** are generally colourless to lightly coloured, and impart little or no colour when coated on imaging substrates. In addition, these compounds rapidly form stable, intense colours upon reaction with developer systems

typically used in carbonless papers and thermal imaging systems. They also satisfy the requirements of solubility in suitable solvents for encapsulation, non-solubility in aqueous media, non-reactivity with fill solvents, and colour-forming compounds mixed therewith, and compatibility with existing carbonless paper and thermal imaging developer systems.

If desired, a mixture of the colour-forming compounds **11** may be used and images of varying colours can be formed by the reaction between a developer and the colour-forming compounds. Appropriate mixtures to form black images are particularly useful. In systems where the colour-forming compounds are encapsulated, the system may provide either one type of capsule containing a mixture of colour-forming compounds or may comprise a mixture of capsules, each containing a separate encapsulated colour-forming compound solution. In the latter instance, colour is formed by the mixing of the colour-forming compounds upon capsule rupture and reaction with the developer.

Sultine compounds **11** are preferably encapsulated by means of aminoplast 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 colour-forming compound **11** is present in the microcapsules in an amount from *ca.* 0.2–10% by weight based on weight of the fill of the microcapsule.

In summary, a new class of sultine colour-formers has been prepared in a two-step procedure. These compounds may be of potential importance in industrial applications.

Experimental

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Gemini VXR 300 MHz spectrometer in deuterochloroform using tetramethylsilane as an internal reference for ^{1}H spectra and deuterochloroform for ^{13}C spectra; *J*/Hz. Elemental analyses were performed on a Carlo Erba-1106 instrument.

Compound **10a** was prepared according to the literature procedure[11]: mp 113–114 °C (lit., mp 113–114 °C). Compounds **10b**, **d** were prepared by adaptation of a literature procedure.[11]

N-Phenyl-3-methylbenzenesulfinamde 10b

Yield 90%. Mp 60–61 °C; δ_H (300 MHz; $CDCl_3$, Me_4Si) 2.34 (s, 3 H), 6.95–7.02 (m, 1 H), 7.04–7.10 (m, 3 H), 7.15–7.35 (m, 4 H), 7.45 (d, 1 H, *J* 7.6), 7.51 (s, 1 H); δ_c (75 MHz; $CDCl_3$) 21.2, 118.5, 122.5, 123.0, 125.8, 128.7, 129.2, 131.8, 138.9, 140.7, 144.1 (Found: C, 67.85; H, 5.86; N, 5.89. Calc. for $C_{13}H_{13}NOS$: C, 67.51; H, 5.67; N, 6.06%).

N-Phenyl-3-methoxybenzenesulfinamde 10d

Yield 81%. Mp 128–129 °C; δ_H (300 MHz; $CDCl_3$, Me_4Si) 3.80 (s, 3 H), 6.76 (s, 1 H), 6.99–9.10 (m, 4 H), 7.22–7.37 (m, 5 H); δ_c (75 MHz; $CDCl_3$) 55.5, 109.9, 117.6, 117.7, 118.8, 123.4, 129.3, 129.9, 140.7, 145.9, 160.1 (Found: C, 63.31; H, 5.33; N, 5.61. Calc. for $C_{13}H_{13}NO_2S$: C, 63.14; H, 5.30; N, 5.67%).

N-Phenyl-3-(dimethylamino)benzenesulfinamide 10c

A solution of *N*,*N*-dimethyl-3-bromoaniline (20 mmol) in dry THF (60 ml) was added dropwise to magnesium turnings and a trace of iodine at room temp. The mixture was heated under reflux for 4 h to give Grignard reagent **9c**. To a solution of *N*-thionylaniline (15 mmol) in dry diethyl ether (50 ml) Grignard reagent **9c** was added at *ca.* −10 °C. The mixture was stirred at this temperature for 30 min then at room temp. for 10 h. The reaction was then quenched with aqueous NH_4Cl (10%), extracted with diethyl ether (3 × 50 ml) and dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane–ethyl acetate; 3:1). Yield 60%. Mp 86–87 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.98 (s, 6 H), 6.32 (s, 1 H), 6.80 (m, 1 H), 6.99–7.11 (m, 5 H), 7.23–7.32 (m, 3 H); δ_c (75 MHz; $CDCl_3$) 40.3, 108.0, 112.5, 114.7, 118.4, 123.2, 129.4, 129.7, 141.0. 150.8 (Found: C, 64.32; H, 6.23; N, 10.69. Calc. for $C_{14}H_{16}N_2OS$: C, 64.59; H, 6.20; N, 10.77%).

Preparation of sultines 11a, b, d–h by lithiation of 10a, b, d–h

To a stirred solution of *N*-phenylbenzenesulfinamide **10** (10 mmol) in THF (70 ml) at −5 to 0 °C was added butyllithium (20 mmol). The solution was stirred at this temperature for 2 h. Then Michler's ketone [4,4′-bis(dimethylamino)benzophenone] in THF (80 ml) was added slowly. The mixture was kept at this temperature for 1 h then at room temp. overnight. Aqueous NH_4Cl (10%) was added and the solution extracted with ethyl acetate (2 × 100 ml), dried with $MgSO_4$ and evaporated to give a residue. The pure product was obtained by column chromatographic separation on silica gel (hexane–ethyl acetate, 3:1).

3,3-Bis(4-dimethylaminophenyl)-3*H*-2,1-benzoxathiole 1-oxide 11a

Yield 48%. Mp 174–176 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.90 (s, 12 H), 6.62 (4 H, d, *J* 8.9), 7.20 (br s, 4 H), 7.32–7.35 (m, 1 H), 7.46–7.51 (m, 2 H), 7.70–7.73 (m, 1 H); δ_C (75 MHz; $CDCl_3$) 40.2, 106.3 (sp^3 q), 111.5, 123.7, 125.3, 128.7, 129.1, 131.8, 144.1, 146.3, 150.1 (Found: C, 70.23; H, 6.31; N, 7.01. Calc. for $C_{23}H_{24}N_2O_2S$: C, 70.38; H, 6.17; N, 7.14%).

3,3-Bis(4-Methoxyphenyl)-3*H*-2,1-benzoxathiole 1-oxide 11b

Obtained as an oil. Yield 74%; δ_H (300 MHz; $CDCl_3$; Me_4Si) 3.73 (s, 3 H), 3.75 (s, 3 H), 6.82 (d, 4 H, *J* 7.1), 7.13 (d, 2 H, *J* 8.7), 7.33 (d, 3 H, *J* 9.1), 7.46–7.58 (m, 2 H), 7.74 (d, 1 H, *J* 7.9); δ_C (75 MHz; $CDCl_3$) 54.9, 55.0, 104.6 (sp^3 q), 113.3, 113.4, 123.7, 125.1, 128.7, 128.9, 129.4, 131.9, 134.1, 134.6, 143.4, 146.2, 159.2, 159.5 (Found: C, 68.61; H, 4.90; Calc. for $C_{21}H_{18}O_4S$: C, 68.84; H, 4.96%).

6-Methyl-3,3-bis(4-dimethylaminophenyl)-3*H*-2,1-benzoxathiole 1-oxide 11d

Yield 41%. Mp 100–103 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.39 (s, 3 H), 2.89 (s, 12 H), 6.61 (d, 4 H, *J* 8.8), 7.29 (br s, 4 H), 7.31(d, 2 H, *J* 7.9), 7.49 (s, 1 H); δ_C (75 MHz; $CDC1_3$) 20.9, 40.2, 106.1 (sp^3 q), 111.4, 123.6, 124.9, 128.6, 132.0, 132.9, 139.4, 141.4, 146.5, 150.0 (Found: C, 70.88; H, 6.56; N, 7.00. Calc. for $C_{24}H_{26}N_2O_2S$: C, 70.91; H, 6.45; N, 6.90%).

6-Dimethylamino-3,3-bis(4-dimethylaminophenyl)-3*H*-2,1-benzoxathiole 1-oxide 11e

Yield 34%. Mp 183–184 °C; δ_H (300 MHz; $CDC1_3$; Me_4Si) 2.91 (s, 12 H), 2.98 (s, 6 H), 6.63 (d, 4 H, *J* 9.0), 6.85 (dd, 1 H, *J* 8.6, 2.5), 6.92 (d, 1 H, *J* 2.4), 7.14 (d, 2 H, *J* 8.6), 7.13–7.23 (m, 3 H); δ_C (75 MHz; $CDCl_3$) 40.3, 40.5, 105.1 (sp^3 q), 111.6, 116.4, 125.4, 128.7, 131.0, 131.4, 147.8, 150.0, 151.2 (Found: C, 68.77; H, 6.75; N, 9.57. Calc. for $C_{25}H_{29}N_3O_2S$: C, 68.93; H, 6.72; N, 9.65%).

6-Dimethylamino-3,3-diphenyl-3*H*-2,1-benzoxathiole 1-oxide 11f

Yield 45%. Mp 140–142 °C; δ_H (300 MHz; $CDC1_3$; Me_4Si) 2.99 (s, 6 H), 6.86–6.93 (m, 2 H), 7.18–7.31 (m, 9 H), 7.43 (dd, 2 H, J 8.0, 1.3); δ_C (75 MHz; $CDCl_3$) 40.4, 104.3 (sp^3 q), 105.1, 116.3, 125.5, 127.4, 127.5, 127.8, 128.1, 128.2, 128.3, 129.8, 142.9,

143.3, 147.9, 151.4 (Found: C, 72.28; H, 5.48; N, 3.97. Calc. for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01%).

6-Dimethylamino-3,3-bis(4-methoxyphenyl)-3*H*-2,1-benzoxathiole 1-oxide 11g

Yield 60%. Mp 77–79 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.90 (s, 6 H), 3.67 (s, 3 H), 3.69 (s, 3 H), 6.77–6.89 (m, 6 H), 7.11–7.18 (m, 3 H), 7.34 (d, 2 H, *J* 8.6); δ_C (75 MHz; $CDCl_3$) 40.0, 54.8, 54.9, 104.2 (sp^3 q), 104.6, 113.0, 113.1, 116.1, 125.1, 128.5, 128.7, 130.0, 134.9, 135.5, 147.4, 151.0, 158.8, 159.2 (Found: C, 67.20; H, 5.53; N, 3.27. Calc. for $C_{23}H_{23}NO_4S$: C, 67.46; H, 5.67; N, 3.42%).

6-Methoxy-3,3-bis(4-dimethylaminophenyl)-3*H*-2,1-benzoxathiole 1-oxide 11h

Yield 30%. Mp 85–87 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.91 (s, 12 H), 3.60 (s, 3 H), 6.62 (d, 4 H, *J* 9.1), 6.96 (d, 1 H, *J* 8.1), 7.18–7.33 (m, 4 H), 7.46 (t, 2 H, *J* 7.90); δ_C (75 MHz; $CDCl_3$) 40.1, 55.7, 107.9 (sp^3 q), 111.0, 114.9, 115.6, 128.3, 129.5, 131.5, 148.1, 149.9, 154.8 (Found: C, 67.81; H, 6.41; N, 6.25. Calc. for $C_{24}H_{26}N_2O_3S$: C, 68.22; H, 6.21; N, 6.63%).

One-pot preparation of 11c from 8e

To a solution of **8e** (10 mmol) in diethyl ether (50 ml) was added lithium metal (which had been cut into small pieces in diethyl ether) (0.12 g, 20 mmol) and the mixture was refluxed for 3 h. After the solution had been cooled to −5 to 0 °C, *N*-sulfinylaniline (10 mmol) was added and the mixture stirred for 1 h at this temperature. Then butyllithium (2.5 M; 4 ml, 10 mmol) was added and the lithiation was continued for another 1 h. Michler's ketone in THF (80 ml) was added slowly. The mixture was kept at this temperature for 1 h then at room temp. overnight. Aqueous NH_4Cl (10%) was added and the solution extracted with ethyl acetate (2 × 100 ml), dried with $MgSO_4$ and evaporated to give a residue. The pure product **11c** was obtained by column chromatographic separation on silica gel (hexane–ethyl acetate, 3:1). Yield 68%. Mp 182–184 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.90 (s, 12 H), 2.93 (s, 6 H), 6.41 (d, 1 H, *J* 2.2), 6.63 (d, 4 H, *J* 7.5), 6.71 (dd, 1 H, *J* 8.8, 1.3), 7.14 (d, 2 H, *J* 7.7), 7.34 (d, 2 H, *J* 7.9), 7.51 (d, 1 H, *J* 8.7) (Found: C, 69.24; H, 6.72; N, 9.58. Calc. for $C_{25}H_{29}N_3O_2S$: C, 68.93; H, 6.72; N, 9.65%).

Determination of colour

The colours formed by reaction of the colour-forming compound and developer in the examples below were determined by preparing a 1% solution of the colour-forming compound **11** or mixture of colour-forming compounds **11** 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 colour development of the image was achieved by passing the sheet through a hot shoe adjusted to 102 °C, making a revolution every 10 s.

The colour and the CIELAB coordinates for the developed colour-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 colour. 'L^*' ($+z$ axis) represents the lightness or darkness of the image ($L^*=100$ is white, $L^*=0$ 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 colour of one sample can be compared with that of other samples.[16]

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

All materials used in the following examples are readily available from standard commercial sources such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. Colour measurements were made on a Gretag SPM-100 Spectrophotometer. This instrument is available from Gretag Aktiengesellschaft, Regensdorf, Switzerland. All percentages are by mass unless otherwise indicated.

AE 700 is a di-C_6 to C_8 branched alkyl ester of benzene-1,2-dicarboxylic acid (CAS RN 71888-89-6), and is available from Exxon Chemical Americas, Houston, Texas. Luracol is a partially methylated, methylolated melamine formaldehyde resin and is available from BASF Corp. Lupasol PA-140 is an arylamidosulfonic acid, sodium salt and is available from BASF Corp. Norpar 12 is a liquid paraffinic hydrocarbon (CAS RN 64771-72-8), and is available from Exxon. Pergascript Red I-6B, Pergascript Orange I-5R, and Pergascript Black I-R are fluoran colour-forming compounds available from Ciba-Geigy, Greensboro, NC. 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. Crystal Violet Lactone is 3,3′-bis(*p*-dimethylaminophenyl)-6-dimethylaminophthalide and (CAS RN 1552-42-7). The Leuco Green Fluoran Color-Former is 3′-(diethylamino)-7′-(dibenzylamino)-6′-(diethylamino)fluoran (CAS RN 34372-72-0).

Example 1

A 1% solution of each of colour-formers **11a, c–e, h** and comparative sultine **11b** 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. In samples **11a–e, h**, an immediate reaction occurred. The following colours were obtained immediately after imaging and without further development with heat, Table 1.

Example 2

The following example demonstrates the use of the sultine compounds as colour-formers in combination with lactone colour-formers to provide blue–black image. A 1% solution of a mixture of colour-formers was prepared in diethyl phthalate–cyclohexane (1:1). The colour-former solution had the composition in Table 2.

The solution was swabbed onto a sheet of 3M Scotchmark CF paper using a cotton tipped applicator swab. An immediate reaction occurred to form an intense blue–black image, Table 3.

Table 1

colour-former	image colour	L^*	a^*	b^*
11e	blue	48.07	8.12	−66.07
11d	green	70.91	−55.36	−6.97
11a	green	71.95	−50.79	−13.93
11h	green	74.35	−48.98	−9.42
11c	green	72.54	−41.04	−16.05
11b	no colour			

Table 2

compound	mass%
sultine **11e**	22%
sultine **11d**	16%
pergascript red I-6B	8%
pergascript orange I-5R	5%
pergascript black I-R	49%

Table 3

image colour	L^*	a^*	b^*
blue–black	54.02	−10.34	−13.28

Example 3

The following example demonstrates the use of sultine compounds as colour-formers 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 colour-formers of Example 2. 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 4

A 1% solution of sultine **11e** colour-former was prepared in diethyl phthalate–cyclohexane (1 : 1). A second 1% solution of crystal violet lactone was also prepared in diethyl phthalate–cyclohexane (1 : 1). Each solution was swabbed onto several samples of 3M Scotchmark CF paper using a cotton tipped applicator swab. In all cases, an immediate reaction occurred. Blue colour developed in each sample immediately after imaging. The colour coordinates of these samples are shown in Table 4.

Each imaged sample was put through a hot roll device at 102 °C and the colour coordinates were then remeasured. The colour of the sultine colour-former sample changed from a deep blue to a deep red–blue. The colour of the Crystal Violet Lactone sample did not change. The colour coordinates of each sample were remeasured and are given in Table 5.

The same colour change in the sultine was observed after 90 min at room temp. This colour change in the sultine colour-former is believed to result from oxidation of the sulfinate form to the sulfonate form.

Example 5

Freshly prepared, unheated sultine images from Example 4 were placed in a light box for 3 d. One half of the sample was exposed to light, the other half of the sample was covered with paper. The samples were placed on a rotating carousel *ca.* 7.6 cm from a circular bank of twelve 20 W fluorescent light bulbs for 3 d. The colour coordinates of both the covered and uncovered portions of each sample were then remeasured.

The results (Table 6) demonstrate that the developed sample of crystal violet lactone that had been exposed to light faded badly. This is shown by the high L value and the low a^* and b^* values. The developed sample of sultine **11e** that had been in the dark, turned to a deep red–blue colour. The light-exposed sample of Sultine **11e** retained a blue colour. The values obtained are in Table 6.

Table 4 Initial development

	L^*	a^*	b^*
sultine **11e**	55.16	6.11	−45.11
CV lactone	51.19	8.18	−47.17

Table 5 After heating

	L^*	a^*	b^*
sultine **11e**	33.06	26.83	−85.99
CV lactone	51.19	8.18	−47.17

Table 6 Initial development

	L^*	a^*	b^*
sultine **11e**	55.16	6.11	−45.11
CV lactone	51.19	8.18	−47.17
After light exposure—covered portion			
	L^*	a^*	b^*
sultine **11e**	33.06	26.83	−85.99
CV lactone	51.19	8.18	−47.17
After light exposure—uncovered portion			
	L^*	a^*	b^*
sultine **11e**	56.57	0.68	−16.24
CV lactone	77.58	−3.07	−7.60

Example 6

The developed, heated samples of sultine colour-former and crystal violet lactone colour-former prepared in Example 4 were heated in an oven at 49 °C for one week. No further colour change in the samples was observed. Both images displayed good stability over this time at this temperature.

Example 7

The following example demonstrates that sultine compounds can be encapsulated and coated to prepare a carbonless paper form-set construction.

Encapsulation of compound 11e. A 35 g capsule fill solution containing 0.3 mass% of Crystal Violet Sultine **11e** colour-former in a 75 : 25 mass% mixture of AE 700 and Norpar 12 was prepared.

Into a 118 ml glass bottle were placed 6.9 g of Luracol, 39.9 g of water, and 6.4 g of a 20% solution of Luprasol PA-140. The pH was adjusted to 3.60 with dilute sulfuric acid. A capsule fill solution (31 g) containing 0.3 mass% of Crystal Violet Sultine colour-former in a 75 : 25 mass% mixture of AE 700 and Norpar 12 was added. A Silverson mixer L4R was immersed in the mixture and the mixture stirred at a setting of 3.2. After 5 min, the pH remained at 3.60. Due to the energy of the mixing, the temperature rose to approximately 55 °C after *ca.* 20 min. After 90 min the temperature was still *ca.* 57 °C. Inspection of an aliquot under a microscope showed stable capsules had formed. The Silverson mixer was removed, the jar was placed on a hot plate, stirred with a marine propeller stirrer. Heating and stirring for 90 min at 60 °C was followed by cooling and addition of aqueous ammonium hydroxide solution to bring the pH to *ca.* 8.5.

The capsules obtained were spherical with a median volumetric diameter of 6.77 μm. They had a slight indentation in one portion of the wall. The capsule dispersion contained approximately 40% capsules. The capsule slurry was used to prepare CB sheets without further modification.

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 temp. for 1 h.

The coated CB sheet was imaged using a 3M Scotchmark CF sheet. Image colour, speed, ultimate image reflectance, and L^*, a^* and b^* were determined as described above. The L^*, a^* and b^* values for this example are slightly different from those of the examples above as the concentrations of colour-forming compound are different, Table 7.

Table 7

amount capsule slurry/g	speed	ultimate	image colour	L^*	a^*	b^*
2	73.40	67.8	Blue	87.86	−2.96	−4.61
4	66.00	60.95	Blue	82.52	−4.71	11.40
6	64.00	57.45	Blue	80.11	−5.23	15.27
8	58.00	53.25	Blue	77.94	−5.53	18.07
10	53.85	45.05	Blue	73.31	−5.58	23.19

Table 8

component	wet mass/g	dry mass/g
water	40.0	—
rice starch[a]	7.20	7.20
cellosize QPO9-L (7%)[b]	11.40	1.14
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 1 (1.75%)	6.00	0.11
total	105.51	18.69

[a]Rice starch is available from Sigma Chemical Co., St. Louis, MO. 63178. [b]Cellosize 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.

Example 8

The following example demonstrates the use of sultine compounds as colour-formers in a thermal imaging element.

An aqueous slurry of 1.00 g of colour-forming sultine **11e**, 3.00 g of styrene maleic anhydride resin (Stymer S), and 96 g of water was ball milled for 24 h.

A thermal imaging dispersion was prepared by mixing the materials shown, Table 8.

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.

Example 9

A 1% solution of each of sultine colour-former **11g** and comparative sultines **11b** and **11f** were prepared in a mixture of diethylphthalate and cyclohexane (1 : 1). Each solution was swabbed onto a sheet of 3M Scotchmark CF paper using a cotton tipped applicator swab. In all cases, no colour developed.

A 1% solution of $ZnCl_2$ in acetone was then swabbed over the stripe of sultine colour-former on the CF sheet. The coating of sultine **11g** gave an intense blue–black colour. The coatings of comparative sultines **11b** and **11f** remained colourless.

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