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# New Dyes Containing the 1,3-Benzodithiole Residue

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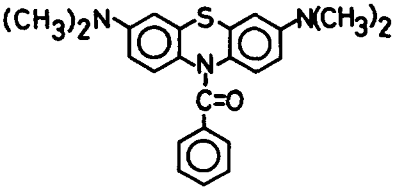
## SUMMARY

*The synthesis of various compounds containing the 1,3-benzodithiole residue is reported . The compounds are examined for application as functional dyes for carbonless duplicating systems and are found to develop slowly on silica gel, and to have good fastness to light. Especially useful was 1,1-bis(p-dimethylaminophenyl)-2-(1′,3′-benzodithiol-2′-yl)-ethylene* (**5**), *which developed blue on silica gel; the developing rate and fastness properties of this derivative are compared with those of benzoyl leuco Methylene Blue.*

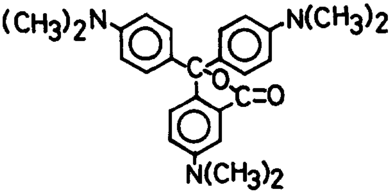
## 1. INTRODUCTION

Benzoyl leuco Methylene Blue (BLMB; **1**), which is used as a dye for carbonless paper, is a typical representative of a slow colour developing compound. Phthalide compounds, such as Crystal Violet lactone (CVL; **2**), are not fast to sunlight and cannot be used alone.



**(1)**

Benzoyl leuco Methylene Blue



**(2)**

Crystal Violet lactone.

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BLMB plays an important role in compensating for this defect of CVL. It develops a blue colour very slowly, and the developed colour does not fade in sunlight; therefore records on carbonless paper can be kept for many years.

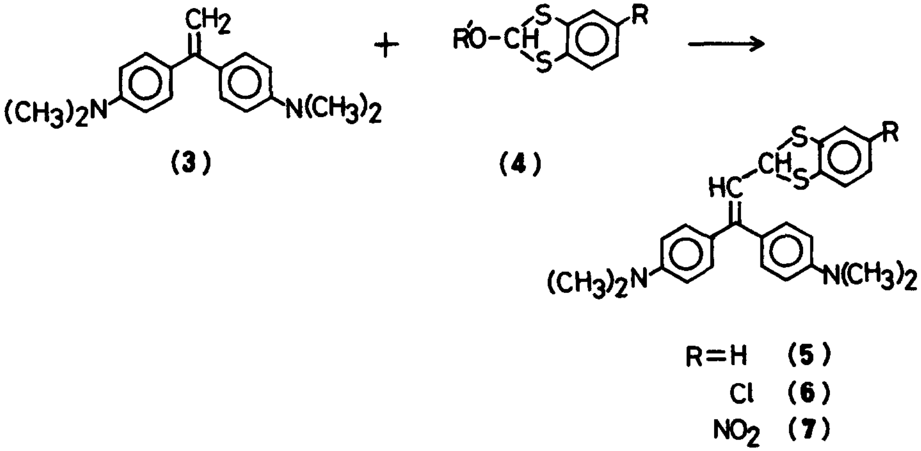
One defect of BLMB is that it cannot contribute to the development of colour in the initial period; thus, the colour developed from BLMB appears only slowly, so that the initial colour seen is that from CVL, which fades fairly quickly, and is replaced permanently by that from BLMB.

This paper describes the synthesis and fastness properties of new dyes containing the 1,3-benzodithiole nucleus and an investigation into their applicability for use in carbonless paper.

## 2. RESULTS AND DISCUSSION

Michler's ethylene (3) was the starting material used in the synthesis of the dyes. Whilst this compound develops a blue colour on silica gel, the developed colour fades easily. The colour developed by 1,1-bis(*p*-dimethylaminophenyl)-2-(1′,3′-benzodithiol-2′-yl)ethylene (5) was however found to be fast to light.

Thus, whilst Michler's ethylene was found to commence to fade one hour after colour developing on silica gel, the compound (5) showed no fade. The developed colour of 1,1-bis(*p*-dimethylaminophenyl)butadiene



The reaction of Michler's ethylene and benzodithiole derivatives.

was found to change more rapidly than that of the benzodithiole substituted compound (**10**).

Introduction of the benzodithiole residue was effected by reactions using either 2-alkoxy-1,3-benzodithiole (**4**) in acetic acid or 1,3-benzodithiolium tetrafluoroborate[1,2] in acetonitrile. A convenient synthesis of 2-alkoxy-1,3-benzodithiole has been previously reported.[3,4] 1,3-Benzodithiole is formed by the addition of alcohols to the carbene produced from carbon disulphide and the benzyne generated by aprotic diazotization of anthranilic acid. By these methods, compounds **5**–**12** containing the 1,3-benzodithiole residue were synthesized. Developed colours are given in section 3. We could not obtain the symmetrically substituted bis(benzodithiole) compound (**14**). Reaction of Michler's ethylene (**3**) with 2-isoamyloxy-1,3-benzodithiole gave, at room temperature, the monocondensed derivative (**5**); the use of higher reaction temperatures did not give the bis-condensed derivative (**14**), but compound **9**, in which the second benzodithiole ring system is substituted into one of the dimethylaminophenyl residues.

The reaction with leuco Crystal Violet did not give the expected tris(*p*-dimethylaminophenyl)-1,3-benzodithiol-2-ylmethane (**13**), but yielded compound **12** in 11% yield.

The colour developing rates of 1,1-bis(*p*-dimethylaminophenyl)-2-(1′,3′-benzodithiol-2′-yl)ethylene (**5**) and BLMB are given in Fig. 1. The wavelengths of maximum absorption are 640 nm for the benzodithiole compound (**5**) and 670 nm for BLMB (**1**). Reflection intensity was

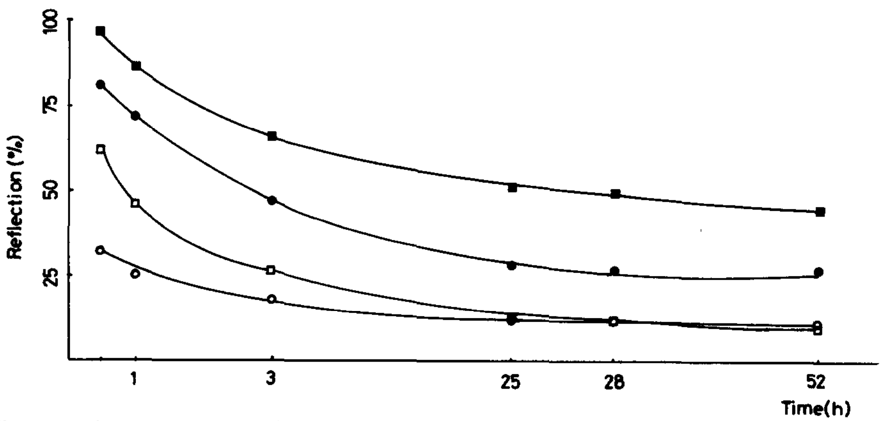
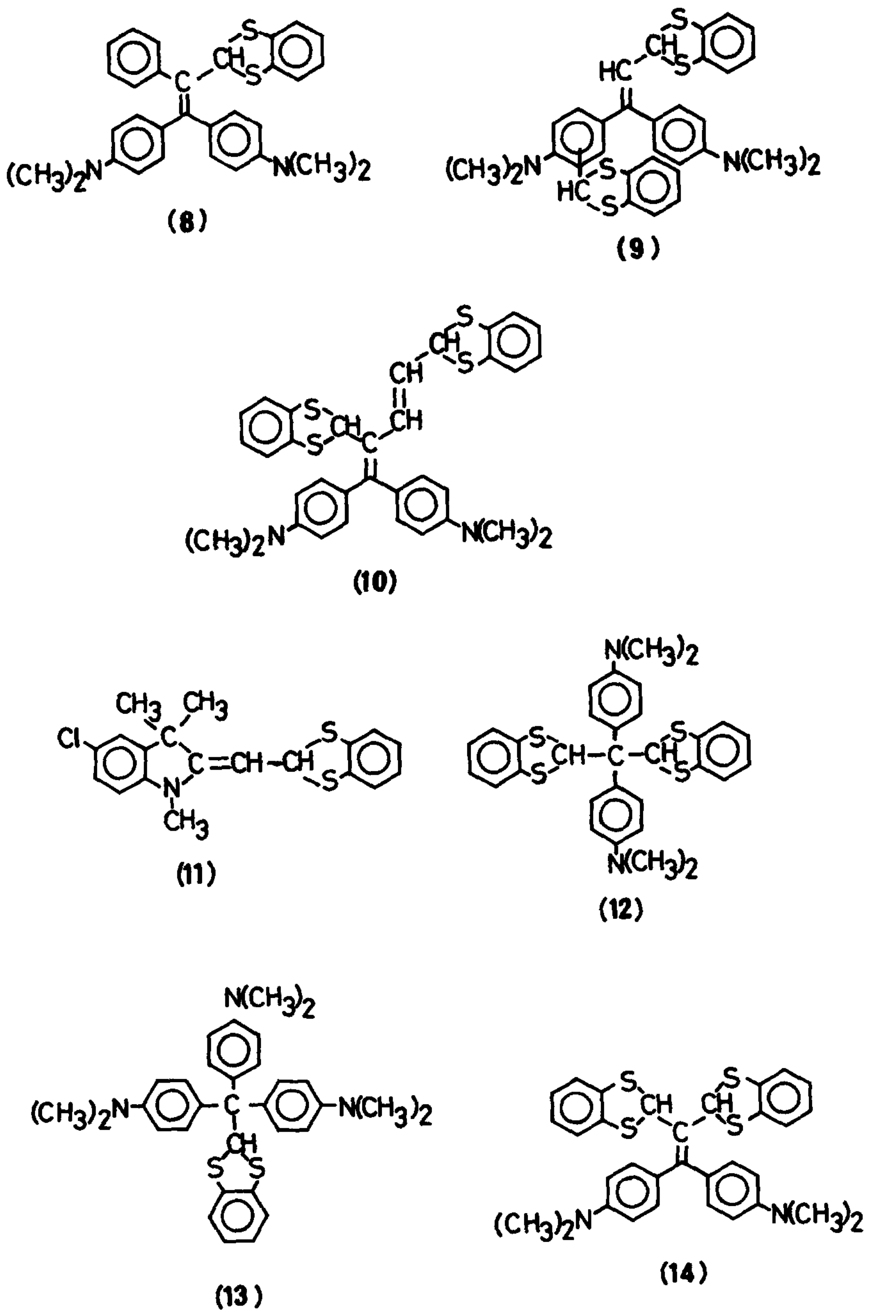


Fig. 1. The colour developing rates of compound **5** and of BLMB (**1**). ○, Compound **5**–clay (Siltone); □, BLMB–clay (Siltone); ●, compound **5**–zinc salicylate; ■, BLMB–zinc salicylate. (Siltone is a silica–alumina clay; Mizusawa Kagaku, Japan.)



(8) (9) (10) (11) (12) (13) (14)

Dyes containing benzo-1,3-dithiole.

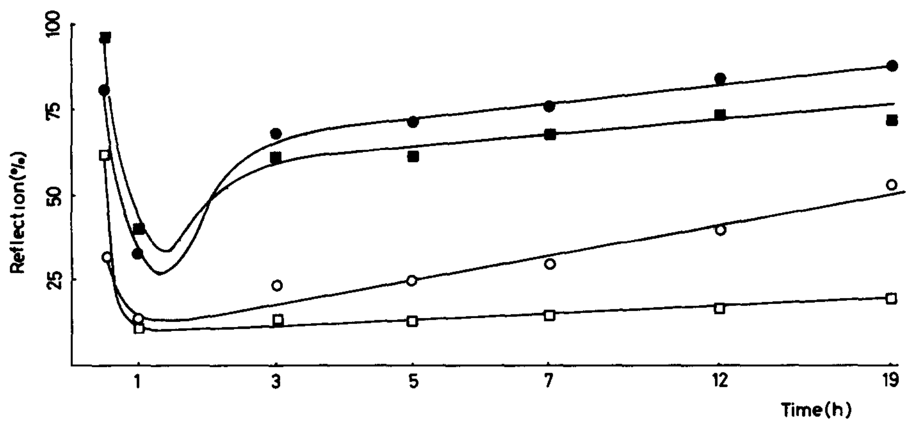


**Fig. 2.** Fastness (sunlight) of compound **5** and of BLMB (**1**). ○, Compound **5**–clay (Siltone); □, BLMB–clay (Siltone); ●, compound **5**–zinc salicylate; ■, BLMB–zinc salicylate.

measured at these wavelengths after colour developing by coating 2 wt % dye solution on to the developer coated paper. The rate of colour development of the benzodithiole compound (**5**) is thus seen to be faster than that of BLMB.

The lightfastness behaviour of compound **5** and of BLMB are given in Fig. 2. The fastness of the benzodithiole compound (**5**) is weaker than that of BLMB, its reflection intensity being reduced to 53 % after 19 h sunlight exposure; its usefulness is however better than that of Michler's ethylene.

## 3. EXPERIMENTAL

The general procedure used in the synthesis is as follows.

To a solution of the appropriate vinyl compound (2·0 mmol) in acetic acid (12 ml) was added a solution of 2-isoamyloxy-1,3-benzodithiole derivative (2·0 mmol) in acetic acid (4 ml) with stirring which was continued under the conditions described below for the individual compounds. After completion of the reaction, the precipitate was filtered and washed with water.

The vinyl compounds used as starting material were as follows: Michler's ethylene (for compounds **5**, **6**, **7** and **9**), 1,1-bis(*p*-dimethylaminophenyl)-2-phenylethylene (for compound **8**), 1,1-bis(*p*-dimethylaminophenyl)butadiene (for compound **10**) and 5-chloro-2-methylene-1,3,3-trimethylindoline (for compound **11**).

### 3.1. 1,1-Bis(*p*-dimethylaminophenyl)-2-(1′,3′-benzodithiol-2′-yl)ethylene (5)

Stirring was continued for 3·5 h at room temperature. The product was recrystallized from methanol/ethyl acetate (yield: 560 mg, 66·7 %), m.p. 171–174 °C.

The developed colour on silica gel was blue. NMR($CDCl_3$, $\delta$): 2·95 (s, 6H, $(CH_3)_2N$); 3·02 (s, 6H, $(CH_3)_2N$); 5·92 (d, 1H, $J = 11$ Hz, HC═C—); 6·40 (d, 1H, $J = 11$ Hz, S—CH—S); 6·61–7·32 (m, 13H, aromatic). (Calcd for $C_{25}H_{26}N_2S_2$: C, 71·73; H, 6·26: N, 6·69 %. Found: C, 71·73; H, 6·14; N, 6·53 %.)

### 3.2. 1,1-Bis(*p*-dimethylaminophenyl)-2-phenyl-2-(1′,3′-benzodithiol-2′-yl)-ethylene (8)

Stirring was continued for 1 h at 50 °C. The product was recrystallized from MeOH–THF (yield: 600 mg, 60·4 %), m.p. 257–259 °C.

The developed colour on silica gel was blue. NMR ($CDCl_3$, $\delta$): 2·78 (s, 6H, $(CH_3)_2N$); 2·95 (s, 6H, $(CH_3)_2N$); 6·21–7·38 (m, 18H, aromatic and S—CH—S). (Calcd for $C_{31}H_{30}N_2S_2$: C, 75·26; H, 6·11; N, 5·66 %. Found: C, 75·05; H, 6·20; N, 5·41 %.)

### 3.3. 1,1-Bis(*p*-dimethylaminophenyl)-2-(5′chloro-1′-3′-benzodithiol-2′-yl)-ethylene (6)

This compound was obtained by allowing the reactants to stand for ten days at room temperature. (yield: 250 mg, 27·0 %), m.p. 170–172 °C.

The developed colour on silica gel was blue. NMR($CDCl_3$, $\delta$): 2·88 (s, 6H, $(CH_3)_2N$); 2·92 (s, 6H, $(CH_3)_2N$); 5·80 (d, 1H, $J = 10·8$ Hz, C═CH—); 6·15 (d, 1H, $J = 10·8$ Hz, S—CH—S); 6·55–7·13 (m, 11H, aromatic). (Calcd for $C_{25}H_{25}ClN_2S_2$: C, 66·27; H, 5·56; N, 6·18 %. Found: C, 66·33; H, 5·60; N, 6·00 %.)

### 3.4. 1,1-Bis(*p*-dimethylaminophenyl)-2-(5′-nitro-1′,3′-benzodithiol-2′-yl)-ethylene (7)

Stirring was continued for 44 h at 50 °C. The product (yield: 850 mg, 91·9 %) was recrystallized from ethanol as orange crystals, m.p. 180–182 °C.

The developed colour on silica gel was green. NMR($CDCl_3$, $\delta$): 2·80 (s, 6H, $(CH_3)_2N$); 2·87 (s, 6H, $(CH_3)_2N$); 5·85 (d, 1H, $J = 9{\cdot}8$ Hz; C═CH—); 5·98 (d, 1H, $J = 9{\cdot}8$ Hz; S—CH—S); 6·22–7·62 (m, 11H, aromatic). (Calcd for $C_{25}H_{25}N_3O_2S_2$: C, 64·76; H, 5·44; N, 9·06%. Found: C, 64·92; H, 5·45; N, 8·82%.)

### 3.5. 1-(*p*-Dimethylaminophenyl)-1-[(1′,3′-benzodithiol-2′-yl)-*p*-nimethylaminophenyl]-2-(1′,3′-benzodithiol-2′-yl)ethylene (9)

The reaction mixture was refluxed for 3 h. The product was obtained by column chromatography (using benzene as eluant) and was recrystallized from benzene/*n*-hexane as pale yellow crystals, m.p. 170–172 °C (yield: 110 mg, 9·5%).

The developed colour on silica gel was pale blue. NMR($CDCl_3$, $\delta$): 2·66 (s, 6H, $(CH_3)_2N$); 2·90 (s, 6H, $(CH_3)_2N$); 5·63 (d, 1H, $J = 11$ Hz; —CH═C); 6·13 (d, 1H, $J = 11$ Hz; S—CH—S); 6·45–7·10 (m, 15H, aromatic and S—CH—S); 7·70 (d, 1H, $J = 2$ Hz, aromatic). Mass spectra: *m/e* 570 ($P^+$); *m/e* 555 ($P^+ - 15$).

### 3.6. 1,1-Bis(*p*-dimethylaminophenyl)-2,4-bis(1′,3′-benzodithiol-2′-yl)-butadiene (10)

Stirring was continued for 3 h at 50 °C. The product was purified by column chromatography using dichloromethane as eluant and was obtained as yellow crystals, m.p. 230–233 °C (yield: 230 mg, 19·3%).

The developed colour on silica gel was green. NMR($CDCl_3$, $\delta$): 2·88 (s, 6H, $(CH_3)_2N$); 2·92 (s, 6H, $(CH_3)_2N$); 6·07 (s, 1H, S—CH—S); 6·36 (m, 19H, aromatic, S—CH—S and —CH═C). Mass spectra: *m/e* 596 ($P^+$); *m/e* 455 ($P^+ - 141$); *m/e* 443 ($P^+ - 153$). (Calcd for $C_{34}H_{32}N_2S_4$: C, 68·42; H, 5·40; N, 4·69%. Found: C, 68·34; H, 5·56; N, 4·57%.)

### 3.7. 5-Chloro-2-(1′,3′-benzodithiol-2′-yl)methylene-1,3,3-trimethylindoline (11)

Stirring was continued for 3 h at room temperature. The product was recrystallized from aqueous ethanol , m.p. 186–187 °C (yield: 245 mg, 34·1%).

The developed colour on silica gel was orange. NMR($CDCl_3$, $\delta$): 1·46 (s, 6H, C—$CH_3$); 2·93 (s, 3H, N—$CH_3$); 4·76 (d, 1H, $J = 11$ Hz, C═CH—); 6·56 (d, 1H, $J = 11$ Hz, S—CH—S); 6·27–7·15 (m, 7H, aromatic). (Calcd for $C_{19}H_{18}ClNS_2$: C, 63·40; H, 5·04; N, 3·89%. Found: C, 63·28; H, 5·03; N, 3·75%.)

### 3.8. Bis(*p*-dimethylaminophenyl)bis(1,3-benzodithiol-2-yl)methane (12)

A solution of bis(*p*-dimethylaminophenyl)methane (2·0 mmol) and 2-isoamyloxy-1,3-benzodithiole (2·0 mmol) in acetic acid (16 ml) was stirred for 2 days at room temperature. The reaction mixture was extracted with dichloromethane. The organic layer was washed with water, sodium carbonate solution and water, dried with sodium sulphate, and then concentrated at reduced pressure. The residue was separated by column chromatography using benzene as eluant and gave 80 mg (13·7%) of product, m.p. 116–118 °C. The product was unstable on exposure to air.

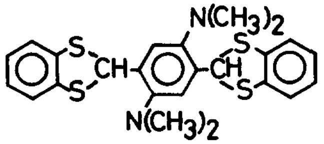
The colour developed on silica gel was red. NMR($CDCl_3$, $\delta$): 2·95 (s, 12H, $(CH_3)_2N$); 6·32 (s, 2H, S—CH—S); 6·60–7·58 (m, 16H, aromatic).

### 3.9. The reaction of leuco Crystal Violet and 2-isoamyloxy-1,3-benzodithiole

To a solution of leuco Crystal Violet (500 mg) in acetic acid (12 ml) was added a solution of 2-isoamyloxy-1,3-benzodithiole (320 mg) in acetic acid (3 ml) with stirring. Stirring was continued for one day at room temperature and the reaction mixture was then extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulphate, and then concentrated at reduced pressure. The residue was separated by column chromatography using benzene as eluant and gave 85 mg (11·4%) of product, m.p. 116–118 °C.

The product was identified as compound **13** by comparison of its NMR and IR spectra with those of an authentic sample.

### 3.10. 2,2′-[2,5-Bis(dimethylamino)-1,4-phenylene]bis(1,3-benzodithiole) (15)



(15)

This compound , m.p. 187–188 °C, was obtained by the procedure described in ref. 5. It did not develop colour on silica gel.

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