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# Polycyclic Compounds: Part III†—Colour and Chemical Constitution of 2-Aryl Phenalen-1-one Derivatives‡

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## *SUMMARY*

*The UV–visible spectra of several 3-substituted 2-aryl phenalen-1-ones and dyes such as C.I. Disperse Red 303 which incorporate the phenalen-1-one as the basic chromophore are recorded and colour–chemical constitution aspects of these compounds have been studied. The fluorescence spectral data of C.I. Disperse Red 303 revealed that the component* **1** *was more fluorescent than the component* **2**, *although* **2** *was more bathochromic compared with* **1**. *The difference in the fluorescence intensity has been explained on the basis of difference in polarity of the carbonyl group brought about by the positional difference of the electron donor ring sulphur atom. Confirmation of these observations was obtained by X-ray crystallographic study of component* **1** *of C.I. Disperse Red 303.*

## 1. INTRODUCTION

Derivatives of benzothioxanthene dicarboxylic acid anhydride such as the perinones, imides and pyrazolines have been reported as giving brilliant yellow to red dyeings on polyester with excellent dyeing and fastness properties.[1] We have previously reported data on C.I. Disperse

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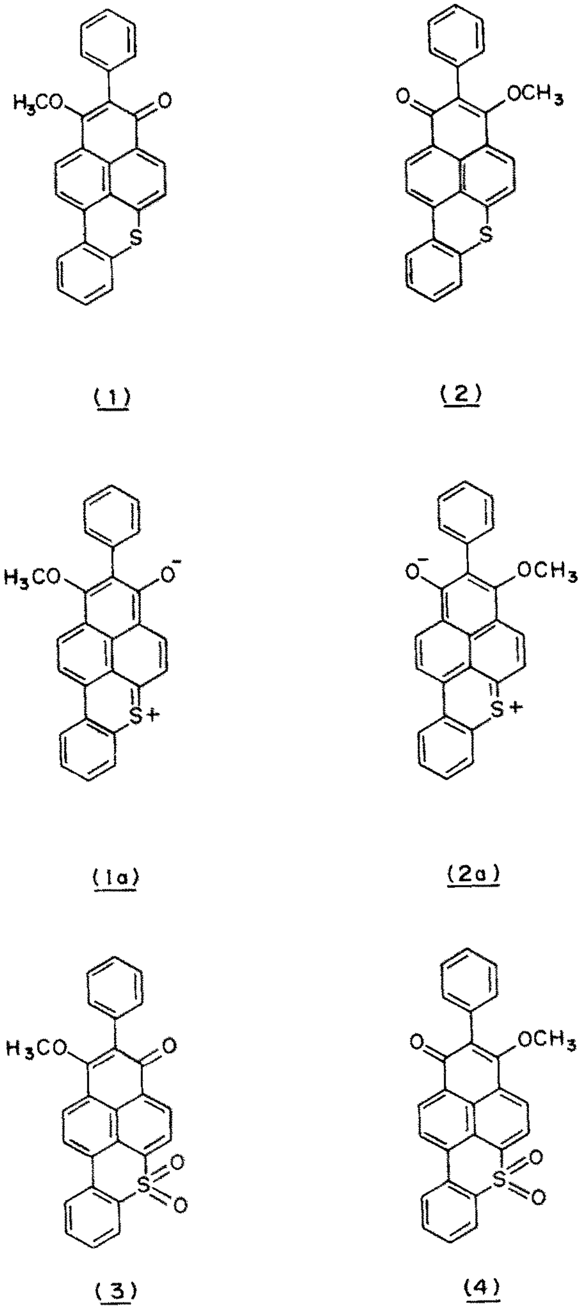
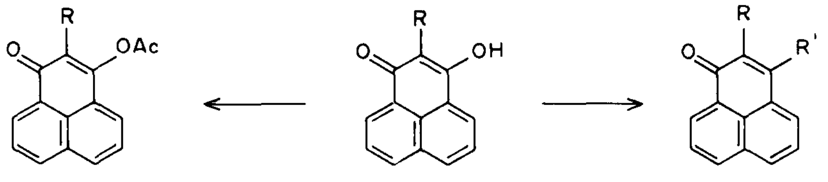
† For Part II, see Ref. 2.

‡ NCL Communication No. 3830.



**Scheme 1.**



(7)

(a) R = Ph
(b) R = $\alpha$-$C_{10}H_7$

(5)

(a) R = Ph
(b) R = $\alpha$-$C_{10}H_7$
(c) R = Quinolinyl

(6)

(a) R = Ph , R' = OMe
(b) R = Ph , R' = OEt
(c) R = $\alpha$-$C_{10}H_7$, R' = OEt
(d) R = Ph , R' = Cl
(e) R = $\alpha$-$C_{10}H_7$ , R' = Cl
(f) R = Ph , R' = $NH_2$

**Scheme 2.**

Red 303 and shown it to be a mixture of two components, 1-methoxy-2-phenyl-3*H*-naphtho[2,1,8-*mna*]thioxanthen-3-one (**1**) and 3-methoxy-2-phenyl-1*H*-naphtho[2,1,8-*mna*]thioxanthen-1-one (**2**) (Scheme 1).[2] These components derived from benzothioxanthene dicarboxylic acid anhydride can be viewed as a 2-phenyl phenalen-1-one ring fused to a benzothioxanthene moiety. The synthesis of various 2-aryl phenalen-1-one derivatives containing 3-acetoxy (**7**), 3-alkoxy or 3-chloro (**6**) substituents (Scheme 2) has been reported earlier by us.[3] This involved the reaction of naphthalic anhydride with aryl acetic acids. Similar condensation of naphthalic anhydride with quinaldine gave 3-hydroxy-2-quinolinyl phenalen-1-one (**5c**). The synthesis of 3-methoxy-2-phenyl phenalen-1-one was achieved by a method reported in the literature.[4] In this present paper, we wish to discuss the colour and constitution of 2-aryl-phenalen-1-one derivatives and related dyes.

## 2. RESULTS AND DISCUSSION

### 2.1. UV–visible spectra

The UV–visible spectra of phenalen-1-one derivatives were recorded and the results are summarised in Table 1. All the 2-aryl phenalen-1-one

**TABLE 1**
Comparison of UV–Visible Spectra of 2-Aryl Phenalen-1-one Derivatives

| *Compound* | $\lambda_{max}$(*nm*) (*log* $\varepsilon$) | | | | | |
|---|---|---|---|---|---|---|
| **1** | 260 (5·6) | — | 360 (4·5) | — | — | 499 (5·5) |
| **2** | 256 (5·6) | — | 356 (5·6) | — | — | 512 (5·3) |
| **3** | — | — | 370 (4·4) | 395 (4·1) | — | — |
| **4** | — | — | — | 395 (4·4) | — | — |
| **5a** | 238 (4·6) | 340 (4·0) | — | 394 (3·6) | 407 (3·0) | — |
| **5b** | 225 (4·1) | 352 (4·2) | — | 395 (3·8) | 405 (3·7) | — |
| **5c** | — | — | — | — | 405 (4·3) | 415 (4·3) |
| **6a** | 258 (4·2) | 343 (3·9) | 358 (4·2) | 395 (3·9) | — | — |
| **6b** | — | 343 (4·1) | 358 (4·0) | 395 (3·8) | — | — |
| **6c** | 227 (4·1) | 343 (4·5) | 358 (4·2) | 390 (3·6) | — | — |
| **6d** | 252 (4·4) | — | 363 (4·2) | 390 (4·2) | — | — |
| **6e** | 251 (4·4) | 330 (3·8) | 364 (4·0) | 385 (4·0) | — | — |
| **6f** | 238 (4·6) | 342 (4·7) | — | — | — | 443 (3·5) |
| **7a** | 249 (4·4) | — | 360 (4·0) | 393 (3·9) | — | — |
| **7b** | — | 340 (4·1) | — | 390 (3·8) | — | — |

derivatives exhibit a characteristic wavelength maximum at 385–395 nm with almost similar intensities of absorption. The auxochromic effect of the hydroxy substituent results in a bathochromic shift of about 15–30 nm, as shown by compounds **5a–c**, whereas the amino group in compound (**6f**) has a greater effect, increasing the wavelength maximum from 390 nm to 443 nm. The fairly constant $\lambda_{max}$ exhibited by **6a–e** and **7a, b** leads to the conclusion that substituents at the 2-position, such as 2-phenyl or 2-($\alpha$-naphthyl), have no significant effect on the colour of 2-aryl phenalen-1-one derivatives. The presence of the quinolinyl substituent in **5c** gives a moderate shift of about 10 nm. It would, therefore, appear that the aryl ring in the 2-position is not in the same plane as the phenalenone ring, ruling out the possibility of extended conjugation by resonance interaction. This has been confirmed by the X-ray crystallographic study of compound (**1**) wherein a 2-phenyl phenalen-1-one derivative has been fused to a benzothioxanthene moiety. The benzothioxanthene ring, containing a donor sulphur atom, gives a considerable bathochromic shift of the order of 109–112 nm, as shown in compounds **1** and **2**.

The compounds **1** and **2**, on oxidation, gave the corresponding sulphones **3** and **4**, thereby considerably reducing the electron donor nature of the sulphur atom; the $\lambda_{max}$ values of these compounds at 395 and

370 nm respectively are comparable with those of simple 2-aryl phenalen-1-ones (Table 1). These observations lead to the conclusion that the basic chromophore contributing to the colour of the 2-aryl phenalen-1-one class of dyes is the phenalenone ring itself. The parent or the basic chromophore has been defined either as the structure which has nearly the same absorption wavelength as the dye under consideration or as the substructure which is electronically most closely related to the dye.[5]

## 2.2. Crystal structure analysis of 1

Studies were carried out on a crystal of dimensions (mm) 0·33 × 0·25 × 0·35 obtained from a benzene solution. Cell dimensions (Table 2) were determined by a least-squares fit using 21 reflections ($18 \leq 2\theta \leq 28°$). Intensity data were collected on an Enraf–Nonius CAD-4F 11M diffractometer (MoK$\alpha$, graphite monochromated); 2968 reflections in the range $2\theta = 2$ to 48° were measured using $\omega/2\theta$ scan mode. The intensities of three standard reflections measured at intervals of one hour did not show any evidence of crystal decay during the entire data collection. Lorentz and polarisation corrections were applied but none was made for absorption and extinctions.

The structure was solved by trial and error methods by extracting possible peaks from a Patterson synthesis. Earlier attempts to solve the structure by direct methods using MULTAN 78[6] had failed. The solution

**TABLE 2**
Cell Data of Compound **1**

| | |
|---|---|
| Composition | $C_{26}H_{16}SO_2$ |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 7·500 (2) |
| $b$ (Å) | 9·164 (1) |
| $c$ (Å) | 14·330 (2) |
| $\alpha$ (°) | 108·06 (1) |
| $\beta$ (°) | 83·71 (1) |
| $\gamma$ (°) | 100·72 (1) |
| $V$ (Å$^3$) | 918·67 |
| $Z$ | 2 |
| Number of reflections included in least-squares refinement | 1 798 |

**TABLE 3**
Final Fractional Atomic Coordinates of **1** with E.S.D. in Parentheses and Equivalent Isotropic Temperature Factor ($B_{eq}$)

| | $X$ | $Y$ | $Z$ | $B_{eq.}$[a] |
|---|---|---|---|---|
| S | 0·3874(2) | 0·0763(2) | −0·1958(1) | 4·6 |
| O(1) | 0·6352(5) | 0·5213(4) | 0·3280(2) | 4·8 |
| O(2) | 0·1184(5) | 0·6037(5) | 0·2014(3) | 6·3 |
| C(1) | 0·5803(6) | 0·0038(5) | −0·1901(4) | 4·0 |
| C(2) | 0·6266(7) | −0·1124(6) | −0·2770(4) | 4·6 |
| C(3) | 0·7789(8) | −0·1763(6) | −0·2838(4) | 4·9 |
| C(4) | 0·8895(7) | −0·1269(6) | −0·2062(4) | 4·7 |
| C(5) | 0·8459(7) | −0·0164(6) | −0·1213(4) | 4·3 |
| C(6) | 0·6901(6) | 0·0538(5) | −0·1110(3) | 3·3 |
| C(7) | 0·6449(6) | 0·1723(5) | −0·0196(3) | 3·5 |
| C(8) | 0·4901(5) | 0·2450(5) | −0·0076(3) | 3·1 |
| C(9) | 0·3686(6) | 0·2136(5) | −0·0827(3) | 3·5 |
| C(10) | 0·2218(6) | 0·2924(6) | −0·0691(4) | 4·0 |
| C(11) | 0·1896(6) | 0·3995(6) | 0·0196(4) | 4·0 |
| C(12) | 0·2992(6) | 0·4315(5) | 0·0964(3) | 3·3 |
| C(13) | 0·4514(6) | 0·3563(5) | 0·0837(3) | 3·0 |
| C(14) | 0·5660(6) | 0·3947(5) | 0·1626(4) | 3·2 |
| C(15) | 0·7202(6) | 0·3259(6) | 0·1480(4) | 3·7 |
| C(16) | 0·7591(6) | 0·2167(6) | 0·0599(4) | 3·7 |
| C(17) | 0·5203(7) | 0·5015(5) | 0·2566(4) | 3·6 |
| C(18) | 0·3688(7) | 0·5689(5) | 0·2731(4) | 3·6 |
| C(19) | 0·2528(7) | 0·5407(6) | 0·1917(4) | 3·9 |
| C(20) | 0·7387(9) | 0·6710(7) | 0·3654(5) | 6·3 |
| C(21) | 0·3116(7) | 0·6658(6) | 0·3722(4) | 3·8 |
| C(22) | 0·2993(8) | 0·6155(7) | 0·4542(4) | 4·9 |
| C(23) | 0·2402(9) | 0·7057(8) | 0·5450(5) | 5·8 |
| C(24) | 0·1937(8) | 0·8499(8) | 0·5557(5) | 5·8 |
| C(25) | 0·2076(8) | 0·8989(7) | 0·4733(5) | 5·4 |
| C(26) | 0·2604(8) | 0·8103(6) | 0·3837(4) | 4·7 |

[a] $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab + \beta_{13}ac + \beta_{23}bc)$.

from a Patterson synthesis was not straightforward either. The occurrence of a large number of parallel vectors due to the planarity of the molecule appears to be the main reason for not obtaining the structure from these traditional methods. Sulphur was located by assuming the absence of the centre of symmetry, and computed Fourier maps based on this position gave centrosymmetrically related fragments. With this, the actual centre of symmetry was located and the resultant Fourier maps yielded all the atoms. The *R* index converged after refinement of positional and thermal parameters (hydrogen atom positions stereochemically fixed, also located in a difference map) in a full matrix least-squares procedure to 0·063. The final atomic parameters are given in Table 3.

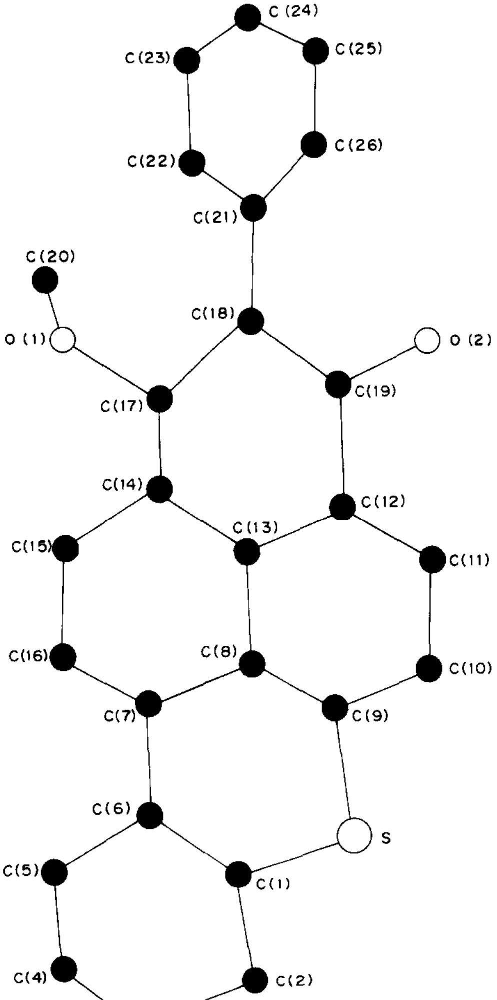


**Fig. 1.** A perspective view of the molecule **1**.

## TABLE 4

Bond Lengths Involving Non-hydrogen Atoms of **1** and Bond Angles with E.S.D. in Parentheses

| | *Bond length* (Å) | | *Bond length* (Å) |
|---|---|---|---|
| S—C(1) | 1·720(5) | C(10)—C(11) | 1·373(8) |
| S—C(9) | 1·727(5) | C(11)—C(12) | 1·372(7) |
| O(1)—C(17) | 1·357(6) | C(12)—C(13) | 1·408(7) |
| O(1)—C(20) | 1·418(8) | C(12)—C(19) | 1·473(7) |
| O(2)—C(19) | 1·226(7) | C(13)—C(14) | 1·412(7) |
| C(1)—C(2) | 1·423(8) | C(14)—C(15) | 1·384(7) |
| C(1)—C(6) | 1·384(7) | C(14)—C(17) | 1·448(8) |
| C(2)—C(3) | 1·359(8) | C(15)—C(16) | 1·387(8) |
| C(3)—C(4) | 1·371(8) | C(17)—C(18) | 1·356(8) |
| C(4)—C(5) | 1·373(8) | C(18)—C(19) | 1·461(8) |
| C(5)—C(6) | 1·409(7) | C(18)—C(21) | 1·488(8) |
| C(6)—C(7) | 1·472(6) | C(21)—C(22) | 1·378(8) |
| C(7)—C(8) | 1·412(6) | C(21)—C(26) | 1·403(8) |
| C(7)—C(16) | 1·412(7) | C(22)—C(23) | 1·384(9) |
| C(8)—C(9) | 1·413(6) | C(23)—C(24) | 1·387(10) |
| C(8)—C(13) | 1·427(6) | C(24)—C(25) | 1·376(10) |
| C(9)—C(10) | 1·390(7) | C(25)—C(26) | 1·352(9) |

| | *Bond angle* (*degrees*) | | *Bond angle* (*degrees*) |
|---|---|---|---|
| C(1)—S—C(9) | 103·7(2) | C(13)—C(12)—C(19) | 121·0(4) |
| C(17)—O(1)—C(20) | 117·7(4) | C(8)—C(13)—C(12) | 120·5(4) |
| S—C(1)—C(2) | 114·5(4) | C(8)—C(13)—C(14) | 120·8(4) |
| S—C(1)—C(6) | 125·0(4) | C(12)—C(13)—C(14) | 118·7(4) |
| C(2)—C(1)—C(6) | 120·5(5) | C(13)—C(14)—C(15) | 118·3(5) |
| C(1)—C(2)—C(3) | 120·7(5) | C(13)—C(14)—C(17) | 120·3(4) |
| C(2)—C(3)—C(4) | 119·4(5) | C(15)—C(14)—C(17) | 121·3(5) |
| C(3)—C(4)—C(5) | 120·7(5) | C(14)—C(15)—C(16) | 121·6(5) |
| C(4)—C(5)—C(6) | 121·9(5) | C(7)—C(16)—C(15) | 121·6(5) |
| C(1)—C(6)—C(5) | 116·7(4) | O(1)—C(17)—C(14) | 114·6(4) |
| C(1)—C(6)—C(7) | 121·8(4) | O(1)—C(17)—C(18) | 122·9(5) |
| C(5)—C(6)—C(7) | 121·4(4) | C(14)—C(17)—C(18) | 122·4(5) |
| C(6)—C(7)—C(8) | 122·5(4) | C(17)—C(18)—C(19) | 119·1(5) |
| C(6)—C(7)—C(16) | 119·6(4) | C(17)—C(18)—C(21) | 122·5(5) |
| C(8)—C(7)—C(16) | 117·8(4) | C(19)—C(18)—C(21) | 118·4(5) |
| C(7)—C(8)—C(9) | 123·1(4) | O(2)—C(19)—C(12) | 119·9(5) |
| C(7)—C(8)—C(13) | 119·8(4) | O(2)—C(19)—C(18) | 121·9(5) |
| C(9)—C(8)—C(13) | 117·1(4) | C(12)—C(19)—C(18) | 118·2(5) |
| S—C(9)—C(8) | 123·7(3) | C(18)—C(21)—C(22) | 122·0(5) |
| S—C(9)—C(10) | 115·1(4) | C(18)—C(21)—C(26) | 120·1(5) |
| C(8)—C(9)—C(10) | 121·2(4) | C(22)—C(21)—C(26) | 117·8(5) |
| C(9)—C(10)—C(11) | 120·0(5) | C(21)—C(22)—C(23) | 120·9(6) |
| C(10)—C(11)—C(12) | 121·5(5) | C(22)—C(23)—C(24) | 120·7(6) |
| C(11)—C(12)—C(13) | 119·6(4) | C(23)—C(24)—C(25) | 117·7(6) |
| C(11)—C(12)—C(19) | 119·4(4) | C(24)—C(25)—C(26) | 122·2(6) |

## 2.3 Molecule and crystal structure of 1

A perspective view of the molecule is shown in Fig. 1. The bond lengths and angles of non-hydrogen atoms are given in Table 4. The phenyl group at C(18) (2-phenyl) is twisted out of the molecular plane by 49·9°(8). It may be noted that the sulphur atom is on the same side as the keto group [C(19)—O(2)] while the methoxy group is on the other side. The crystal structure confirms our original assignment of this structure as the orange isomer of Disperse Red 303, as reported in a previous communication.[2] In assigning the structure, the hypsochromic shift was attributed to the reduced conjugation between the donor sulphur atom and the acceptor carbonyl group.

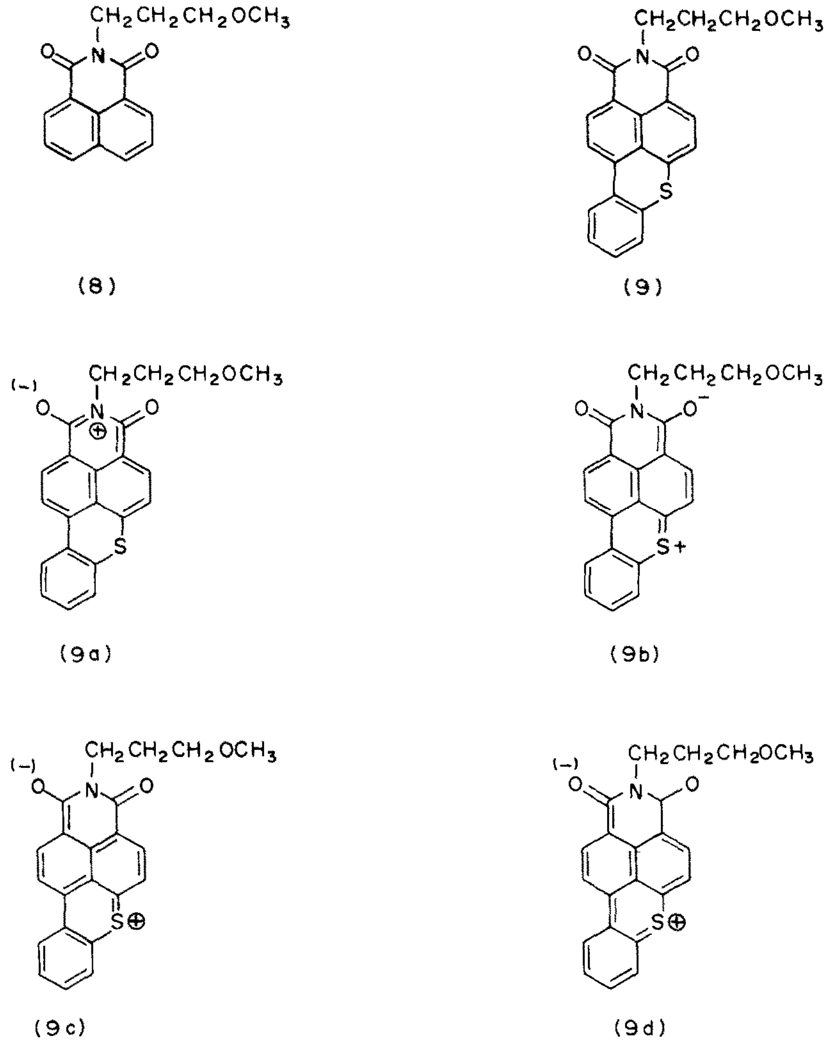
## 2.4. Fluorescent spectra

Derivatives of phenalen-1-one are known to exhibit fluorescence in the visible region, with fluorescence maxima at about 525 nm.[7] In the case of naphthalic anhydride derivatives, the possibility of polarisation of the ring carbonyl group by UV excitation and the enhancement in polarity of the same function by suitably situated electron donating groups such as amino groups have been cited as major factors contributing towards fluorescence.[8] In the light of the above considerations, the fluorescence spectra of the 2-aryl phenalenone derivatives were studied.

The fluorescent spectral data are summarised in Table 5. The compounds **6a–e** and **7a, b** show negligible fluorescence. Likewise, the naphthalimide derivative (**8**) showed negligible fluorescent intensity. The fluorescent spectra of individual isomers of commercial C.I. Disperse Red 303 showed a marked difference in the intensity of fluorescence. This

TABLE 5
Fluorescent Spectral Data

| *Compound* | $\lambda_{max}$ *(nm)* | | *Intensity* |
|---|---|---|---|
| | *Excitation* | *Emission* | |
| **1** | 470 | 550 | 1·38 |
| **2** | 480 | 575 | 0·41 |
| **8** | 310 | 392 | 0·07 |
| **9** | 450 | 510 | 5·70 |



**Scheme 3.**

difference can be explained on the basis of the polarity of the carbonyl group. The degree of polarisation of the carbonyl group in compounds **1** and **2** is determined by the relative position of the sulphur atom. The shorter distance of conjugation over three double bonds of sulphur in the former (as compared with that of six double bonds in the latter) results in an increased polarisation of the carbonyl group. This phenomenon results in a three-fold increase in the intensity of fluorescence of compound **1** compared with that of **2**. This is further exemplified by a nearly 14-fold increase in the relative intensity of fluorescence exhibited by C.I. Disperse Yellow 105 (**9**). This can be attributed to the high degree of polarisation of both the carbonyl groups in compound (**9**) (*vide* structures **9a–d**) brought about by the donor alkylamino nitrogen and ring sulphur atoms. When the electron donating nature of the ring sulphur atom is diminished by its conversion to the sulphones (**3** and **4**), a considerable decrease to a negligible intensity of fluorescence is observed.

## 3. EXPERIMENTAL

Melting points are uncorrected. Electronic spectra were recorded on a Beckman 216 spectrophotometer, IR spectra on a Perkin–Elmer 221 spectrophotometer and mass spectra on a CEC 21-110B mass spectrometer at minimum source temperature.

### 3.1. 1-Methoxy-2-phenyl-3*H*-naphtho[2,1,8-*mna*]thioxanthen-3-one-6,6-dioxide (3)

To a solution of compound **1** (0·5 g, 0·0012 mol) in glacial acetic acid (10 ml), hydrogen peroxide (3 ml, 30 % v/v) was added. The mixture was refluxed for 1 h. The reaction mass initially turned violet and finally assumed an orange-yellow colour. The reaction mass was diluted with water (50 ml) and, on cooling, an orange yellow product separated out. This was filtered, washed and dried to give the crude **3** (0·49 g, 75 %). The crude product was crystallised from methanol to give orange-yellow leaflets of **3** (0·25 g, 47·5 %), m.p. 270–272 °C. Visible ($CHCl_3$): $\lambda_{max}$ 370 (log ε, 4·4), 395 nm (4·1); IR (nujol): 1625, 1565, 1370, 1290, 1165, 1130, 1120 and 1020 $cm^{-1}$; MS: *m/z* 424 ($M^+$, 100 %), 423 (95), 409 (32), 396 (32), 393 (27), 361 (41), 360 (32). Found: C, 73·5; H, 3·9; S, 7·4. $C_{26}H_{16}O_4S$ requires: C, 73·6; H, 3·8; S, 7·5 %.

### 3.2. 3-Methoxy-2-phenyl-1*H*-naphtho[2,1,8-*mna*]thioxanthen-1-one-6,6-dioxide (4)

The oxidation of compound **2** was carried out exactly in the same manner as described above to yield the sulphone **4** (0·3 g, 57 %), m.p. 274 °C. Visible ($CHCl_3$): $\lambda_{max}$ 396 nm (log ε, 4·4); IR (nujol): 1625, 1565, 1280, 1190, 1150, 1120, 1050 cm$^{-1}$; MS: *m/z* 424 ($M^+$, 100%), 423 (96), 409 (32), 393 (22), 361 (41), 360 (32). Found: C, 73·5; H, 3·9; S, 7·2. $C_{26}H_{16}O_4S$ requires: C, 73·6; H, 3·8; S, 7·5%.

## ACKNOWLEDGEMENT

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