The Synthesis and Properties of Dyes and Pigments Containing a 9,9′-Spirobifluorene Residue

F. K. SUTCLIFFE,
HASSAN MOAVEN SHAHIDI and
DAVID PATTERSON

Department of Colour Chemistry
The University
Leeds LS2 9JT

The synthesis and properties of several azo and anthraquinonoid dyes containing a 9,9′-spirobifluorene residue are described. The azo dyes were prepared by diazotization of 2,2′-diamino-9,9′ spirobifluorene and coupling to various commonly used coupling components. The anthraquinonoid dyes were made by condensation of the appropriate aminoanthraquinones with 9,9′-spirobifluorene-2,2′-dicarboxylic acid dichloride. The fastness to light of the so prepared has been compared with that of their non-spiro analogues.

Introduction

It has been suggested that the presence of the spiro structure in metal-chelated dye molecules improves their photochemical stability [1], but it also tends to produce broad absorption bands and hence dull colours. Because of this, such dyes are of limited application in the textile industry. However, it was of interest to prepare dyes containing a similar spiro configuration, but having a tetrahedral carbon atom in place of the metal atom, in order to investigate the influence of the spiro structure on photochemical stability. Spiro structures may have favourable crystal packing properties, leading to a high degree of aggregation of the dyes in commercial usage, thus providing improved light-fastness properties [2]. The elimination of the chelating metal may also afford dyes of brighter colours. One way of preparing such dyes is to link chromogens to a non-conjugating hydrocarbon spiro system. Ideally the spiro nucleus should be chemically stable and be easily substituted by reactive groups, to facilitate incorporation of suitable chromogens, and to enable the dyes to be applied to fibre without degradation. Most aliphatic spirans, e.g. spiroalkenes, do not fulfil these requirements, whereas certain spiro–aromatic systems appear to have suitable properties. This paper describes the synthesis of several colorants containing simple azo and anthraquinone chromogens linked to the 9,9′-spirobifluorene parent system.

EXPERIMENTAL

This work will be described in two sections. The first deals with the preparation of 9,9′-spirobifluorene. From this 2,2′-diamino-9,9′-spirobifluorene and 9,9′-spirobifluorene-dicarboxylic acid were made. The second section describes the preparation from these latter two compounds of some azo and anthraquinone dyes, respectively.

I – Synthetic Routes to 9,9′-Spirobifluorene and its 2,2′-Diamino and 2,2′-Dicarboxylic Acid Derivatives

(a) ROUTE TO 9,9′-SPIROBIFLUORENE

1. Preparation of 2-Bromobiphenyl

2-Bromoamine (47.3 g), benzene (1 l) and amyl nitrite (47 g) were warmed until reaction commenced as shown by the evolution of N_2. After evolution of gas had ceased, the mixture was refluxed for 2 h, cooled, and then washed successively with 10% NaOH, and finally water. The low-boiling components were removed by distillation on a steam bath, and the residue was fractionally distilled under reduced pressure, giving 2-bromobiphenyl as a yellow oil, (yield 39.5 g, 60.9%) b.p. 152°C/0.1 mm Hg.

2. Preparation of 9-(2-Biphenyl)-9′-fluorenol and 9.9′-Spirobifluorene

Dry magnesium turnings (0.585 g) were refluxed gently with 2-bromobiphenyl (6.1 g) in dry ether (10 ml) until reaction was completed (ca 1 h). An ethereal solution of fluorenone (4.2 g) was added in small portions and the mixture heated under reflux overnight. The precipitated yellow magnesium complex was collected and washed with dry ether. The solid was stirred into ice-cold ammonium chloride solution (10%, 200 ml), and after 2 h the precipitate was collected and dried in vacuo. Recrystallization from ethanol afforded the desired carbinol as colourless plates (5.4 g, 61.7%) m.p. 170–172°C. Clarkson and Gomberg cite m.p. 169–170°C [3]. The carbinol (4.25 g) was dissolved in boiling acetic acid (7 ml) and one drop of concentrated hydrochloric acid was added. An immediate reaction took place and the mixture solidified. The 9,9′-spirobifluorene was filtered off, and recrystallized from ethanol to give colourless plates (3.55 g, 89.1%) m.p. 198°C; Clarkson and Gomberg quote the same value.

(b) ROUTE TO 2,2′-DIAMINO-9,9′-SPIROBIFLUORENE

1. Nitration of 9,9′-Spirobifluorene

A mixture of concentrated nitric acid (390 ml) and glacial acetic acid (390 ml) was added dropwise to a boiling solution of the spiro compound (39.0 g) in acetic acid (700 ml) over 2 h, and the reaction mixture was refluxed for a further 2 h. An equal volume of water was added to the cooled solution and the precipitated yellow nitro compound was filtered off. Recrystallization from acetic acid afforded 2,2′-dinitro-9,9′-spirobifluorene (31 g, 62.6%) as yellow crystals, m.p. 232–234°C.

2. Reduction of 2,2′-Dinitro-9,9′-spirobifluorene to the Corresponding Diamino Compound

To a stirred suspension of 2,2′-dinitro-9,9′-spirobifluorene (25 g) in 95% ethanol (200 ml) heated to 50°C, was added a 10% palladium on charcoal catalyst (0.1 g). Hydrazine hydrate (5 ml) was then added dropwise over 30 min. More catalyst (0.1 g) was next added and the mixture gently refluxed. After 1 h the nitro compound had dissolved and the supernatant liquor was almost colourless. The reaction mixture was filtered and the filtrate poured into water. The precipitated amine was collected and recrystallized from ethanol to give pure colourless crystals (1.9 g, 89.2%) m.p. 243°C; Weissburger *et al.* cite m.p. 242–248°C [4].

(c) ROUTE TO 9,9′-SPIROBIFLUORENE-2,2′-DICARBOXYLIC ACID

1. Preparation of 2,2′-Dibromo-9,9′-spirobifluorene

9,9′-Spirobifluorene (3.26 g) was dissolved in methylene chloride (30 ml) and ferric chloride (5 mg) added as a catalyst. The flask was covered with aluminium foil to protect the reaction from light. Bromine (1.12 ml) in methylene chloride (5 ml) was added dropwise over 30 min with stirring, and after 24 h the resultant brown solution was washed with saturated sodium bicarbonate solution and water to remove bromine and hydrobromic acid. The methylene chloride was then removed by evaporation under reduced pressure. The white residue was recrystallized from methanol to give 2,2′-dibromo-9,9′-spirobifluorene (3,45 g, 69.8%) as white crystals m.p. 239–240°C. Found: C, 62.85; H, 2.85; Br 33.6. $C_{25}H_{14}Br_2$ requires C, 63.3; H, 2.95; Br, 33.75.

2. Preparation of 2,2′-Dicyano-9,9′-spirobifluorene

Following a method due to Friedman and Shechter [5], 2,2′-dibromo-9,9′-spirobifluorene (1.19 g) and cuprous cyanide (0.54 g) were heated under reflux for 6 h in dimethylformamide (5 ml). The reaction was mildly exothermic. The resulting brown solution was poured into a mixture of hydrated ferric chloride (3 g) and concentrated hydrochloric acid (1.5 ml) in water (20 ml). After the mixture had been maintained at 60–70°C for 20 min to decompose the complex, the hot aqueous layer was extracted with toluene twice, and the extracts were combined with the organic layer, and washed successively with dilute hydrochloric acid, water and 10% aqueous sodium hydroxide. The organic layer was filtered to remove insoluble material and the solvent was evaporated under reduced pressure. The residual yellow solid was recrystallized from methanol to give 2,2′-dicyano-9,9′-spirobifluorene (0.72 g, 79.9%) as pale yellow crystals, melting over 215 to 245°C. A strong infrared absorption at 2220 cm^{-1} confirmed that the cyano derivative had been formed. It was not purified further, but directly hydrolysed to the dicarboxylic acid, as described below.

3. Preparation of 9,9′-Spirobifluorene-2,2′-dicarboxylic acid

2,2′-Dicyano-9,9′-spirobifluorene (3 g.) was refluxed with 30% sodium hydroxide (25 ml) and ethanol (30 ml) for 6 h. The sodium salt of 9,9′-spirobifluorene-2,2′-dicarboxylic acid was deposited as a yellow solid. This was filtered off and heated in 25% hydrochloric acid to give the free carboxylic acid. The acid was then recrystallized from acetic acid giving 9,9′-spirobifluorene-2,2′-dicarboxylic acid (2.2 g, 66.6%) as white crystals m.p. 376°C. Found C, 79.16; H, 4.0. $C_{27}H_{16}O_4$ requires C, 80.2 H, 3.96; a strong infrared absorption at 1685 cm^{-1} showed the presence of an aromatic acid C=O group. The dicarboxylic acid appeared to be pure, but the carbon analysis is 1% low. However, the correct analysis given below for dyes prepared from this dicarboxylic acid supports the view that the structure of the acid is correct.

II – Preparation of Dyes Containing the 9,9′-Spirobifluorene Residue

(a) Spiro-azo Dyes

2,2′-Diamino-9,9′-spirobifluorene (0.34 g) was diazotized by dissolving it in concentrated hydrochloric acid (3 ml), cooling the solution to 0–5°C, and adding an aqueous solution of sodium nitrite (0.14 g) slowly with stirring at 0°C. The resultant ice-cold diazonium solution was used for coupling to the various coupling components. The structures of the dyes prepared are given in Table 1. The elemental analyses were as follows:

Dye I(a) 62.8% yield; (found: C, 53;75 H, 3.20; N, 8.7. $C_{45}H_{30}N_6S_4O_{14}$ requires C, 53.67; H, 2.98; N, 8.35%.)

Dye I(b) 76.2% yield; (found: C, 82.05; H, 4.6; N, 8.45. $C_{45}H_{28}N_4O_2$ requires C, 82.31; H, 4.3; N, 8.5%.)

Dye I(c) 75.5% yield; (found: C, 79.45; H, 4.7; N, 10.35. $C_{37}H_{24}N_4O_2$ requires C, 79.86; H, 4.3; N, 10.1%.)

Dye I(d) 89.8% yield; (found: C, 75.5; H, 4.4; N, 15.3. $C_{43}H_{32}N_8O_2$ requires C, 75.42; H, 4.4; N, 15.56%.)

Dye I(e) 88.6% yield; (found: C, 74.75; H, 4.95; N, 11.25. $C_{45}H_{34}N_6O_4$ requires C, 75.2; H, 5.07; N, 11.2)

(b) Spiro-anthraquinone Dyes

The 2,2′-dicarboxylic acid chloride was first prepared as follows. 9.9′-Spirobifluorene-2,2′-dicarboxylic acid, (0.025 mmol), phosphorus pentachloride (0.55 mmol) and *o*-dichlorobenzene (30 ml) were heated under reflux for 1 h. Excess phosphorus pentachloride and phosphorus oxychloride were removed by adding *o*-dichlorobenzene (100 ml) to the solution and distilling off 100 ml of the solvent. The dye was prepared as follows. To the solution of the dicarboxylic acid chloride (Dye Type II, R=COCl) was added the appropriate aminoanthraquinone (0.5 mmol) and the mixture refluxed for 6 h. The product was filtered off and dried after cooling. The structures of the dyes are again listed in Table 1 and the following yields and analytical data were obtained:

Dye II(a) condensation with 1-aminoanthraquinone
40.5% yield; (found: C, 80.9; H, 3.6; N, 3.4.
$C_{55}H_{30}N_2O_6$ requires C, 81.1; H, 3.7; N, 3.4%.)
Dye II(b) condensation with 1,4-diaminoanthraquinone
45% yield; (found: C, 77.8; H, 3.9; N, 6.95.
$C_{55}H_{32}N_4O_6$ requires C, 78.0; H, 4.0; N, 6.6%.)
Dye II(c) condensation with 1,5-diaminoanthraquinone
47.4% yield; (found C, 78.10; H, 4.05.
$C_{55}H_{32}N_4O_6$ requires C, 78.01; H, 4.01).

Results and Discussion

SYNTHESIS

The preparation of 9,9′-spirobifluorene can be carried out by the method of Clarkson and Gomberg [3] in which the alcohol formed by a Grignard reaction between fluorenone and 2-iodobiphenyl was subjected to acid catalysed dehydration. However, yields were considerably improved by the use of 2-bromobiphenyl in the Grignard reaction. It was found to be preferable to prepare 2-bromophenyl from 2-bromoaniline and benzene by the Cadogan reaction, thus avoiding the carcinogenic 2-aminobiphenyl as an intermediate. The desired spiro compound was obtained in 62% yield from 2-bromobiphenyl.

The method used for introducing suitable reactive substituents into spirobifluorene was to nitrate and reduce it, giving 2,2′-diamino-9,9′-spirobifluorene. This compound was obtained in 94% yield, using hydrazine and palladium on charcoal as a catalyst for the reduction. The diamino compound was obtained as colourless crystals in a high state of purity by recrystallizing from ethanol.

Corresponding non-spiro analogues of the colorants were prepared for comparison of their general, physical and photochemical properties. The non-spiro analogue used was 2-amino fluorene. It was noted that extinction coefficients of the spiro-compounds were in many cases about twice those of the corresponding non-spiro analogues.

PROPERTIES OF THE PREPARED DYES

Some physical and spectroscopic properties of the dyes are listed in Table 2. The azo dyes were high melting (> 240°C) solids, although in some cases decomposition occurred without melting. Their colours closely resembled those of the non-spiro analogues, and their extinction coefficients were high, generally having twice the value of the non-spiro compound as might be anticipated from their doubled molecular size.

The water-soluble dye, I(a), could be applied to wool and nylon fibres by normal dyeing techniques, whereas the other colorants were more suitable for use as pigments.

The anthraquinonoid dyes (II) were higher melting solids, and in the case of II(b) and II(c) were evidently polymeric. Thus they were insoluble in most organic solvents, their solubility being so low as to preclude molecular weight determinations. The 1,4-diacylaminoanthraquinone derivative II(b) could be purified by soxhlet extraction with dimethylformamide to remove impurities, and the resultant dark brown pigment gave a satisfactory elemental analysis. No suitable means for purifying II(c) could be found however. The disadvantage of dyes of this type is that linking the anthraquinone chromogen to the spiro system by acylation causes a loss of the useful colour properties of the chromogen.

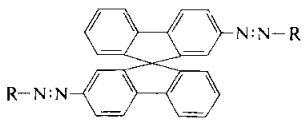
The insolubility of II(a) and II(c) precluded the measure-

TABLE 1

Dye Structures

(i) Structures of Spiro Azo Dyes

Dye Type I



Dye I(a)
Coupling component 3-amino-naphthol-3, 6-disulphonic acid (H acid)

Dye I(b)
Coupling component 2-naphthol

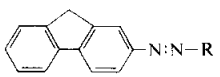
Dye I(c)
Coupling component phenol

Dye I(d)
Coupling component 1-phenyl-3-methyl-5-pyrazolone

Dye I(e)
Coupling component acetoacetanilide

(ii) Structures of Non-spiro Azo Dyes

Dye Type I′

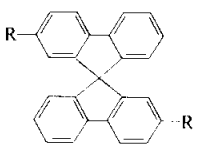


azo component 2-amino fluorene

The coupling component in Dye I(a)′ is the same as that in Dyeing I(a) and so on.

(iii) Structures of Spiro Anthraquinone Dyes

Dye Type II



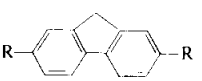
Dye II(a)
R = 1-aminoanthraquinone

Dye II(b)
R = 1,4-diaminoanthraquinone

Dye II(c)
R = 1,5-diaminoanthraquinone

(iv) Structures of Non-spiro Anthraquinone Dyes

Dye Type II′



T he anthraquinone derivatives used to prepare Dyes (II(a)′, II(b)′ and II(c) were the same as those used to make Dyes II(a), II(b) and II(c).

TABLE 2

Comparison of Physical Properties of Spiro and Non-spiro Dyes

SPIRO DYES							CORRESPONDING NON-SPIRO DYES						
Dye	Colour (a)	λ_{max} (nm)	$\epsilon_{max} \times 10^{-3}$	Solvent	M.p. (°C) (b)	Fastness to light	Dye	Colour (a)	λ_{max} (nm)	$\epsilon_{max} \times 10^{-3}$	Solvent	M.p. (°C) (b)	Fastness to light
I(a)	dull greenish grey	554	22.6	water	304	5–6	I(a)′	dull greenish grey	544	14.1	water	155	5–6
I(b)	bright red	498	40.6	CH_2Cl_2	350	4	I(b)′	bright red	490	20.6	CH_2Cl_2	224	4
I(c)	dull reddish yellow	375	26.1	CH_2Cl_2	>500 (c)	4–5	I(c)′	dull yellowish orange	375	26.5	CH_2Cl_2	207	3
I(d)	bright reddish orange	432	54.2	CH_2Cl_2	247	4–5	I(d)′	dull yellowish orange	434	28.7	CH_2Cl_2	185	4–5
I(e)	dull reddish yellow	406	66.8	CH_2Cl_2	>500 (c)	3	I(e)′	bright yellowish orange	405	33.9	CH_2Cl_2	157	3
II(a)	greenish yellow	424	11.2	o-$C_6H_4Cl_2$	442	4–5	II(a)′	bright yellowish	424	5.83	o-$C_6H_4Cl_2$	325	4–5
ii(b)	dark brown			(d)	>500 (c)	5–6	II(b)′	dull bordeaux	510	7.62	o-$C_6H_4Cl_2$	>500	4
II(c)	dull brown			(d)	>500	4	II(c)′	dull brown	454	10.5	o-$C_6H_4Cl_2$	417	7–8

Notes:
(a) The colour described is that of a dispersion of the dye in lithographic varnish
(b) melting points were measured in a differential Thermal Analyser
(c) no melting was observed up to the temperature quoted
(d) no solvent could be found

ment of their visible absorption spectra in solution. The i.r. spectra showed characteristic amide and quinone carbonyl bands between 1600 and 1690 cm^{-1}. The dyes of this type could all be reduced to water-soluble leuco derivatives by the action of sodium hydrosulphite and alkali, and regenerated by oxidation.

Since one of the objects of this work was to test the view that increased aggregation of dye molecules results in increased fastness to light according to Giles [2], the results of light-fastness testing are shown in Table 2. The fastness ratings of both spiro and non-spiro dyes of analogous structures are shown. Thus, if the presence of a spiro structure in these dyes results in more favourable crystal-packing properties, then the spiro dyes should have higher light-fastness properties than the non-spiro dyes, as is the case with metal chelates. Examination of Table 2 does not lend much support for this view. In five cases the fastness to light is exactly the same. In two cases the spiro dyes, I(c) and II(b), show an increase of 1½ steps in light-fastness rating compared with the non-spiro analogues I(c)′ and II(b)′. In the remaining instance the reverse effect is observed and the non-spiro dye, II(c)′, shows a 3½ step superiority over its spiro analogue, II(c).

All these light-fastness ratings were obtained by preparing the dyes for testing in the form of dispersions of 0.2 g of dye in 0.3 g of lithographic varnish using an automatic muller. A film of the dispersion was then drawn down on paper and exposed to a 500-watt high-pressure mercury vapour lamp along with ISO Blue Wool standards. This offers a method of comparative testing that can be used on all the dyes since not all of them could be dyed on substrates in the conventional way.

The results can only be claimed to be at best inconclusive. If the spiro structure does cause greater aggregation and improved fastness to light it may be that this effect was vitiated by differences in the physical state of the dyes as tested, arising from differences of hardness, dispersibility and initial particle size distribution. On the other hand, the relationship between aggregation and fastness to light may be ill-founded and semi- and photo-conductivity effects may predominate [6]. Only a further investigation in which the actual state of aggregation of the colorants being tested was measured could clear up this point, but it does seem fair to conclude that if aggregation is a factor in determining fastness to light, it is not an overwhelming factor.

References

1. Schetty, J.S.D.C., **71** (1955) 705.
2. Baxter, Giles, McKee and Macaulay, ibid., **71** (1955) 218, Giles, Baxter and Rahman, Text. Research J., **31** (1961) 831.
3. Clarkson and Gomberg, J. Amer. Chem. Soc., **52** (1930) 2881.
4. Weisburger, Weisburger and Ray, ibid., **72** (1950) 4250.
5. Friedman and Shechter, J. Org. Chem., **26** (1961) 2522.
6. Terenin, 'Symposium on Electrical Conductivity in Organic Solids', editors Kallman and Silver, (New York: Interscience, 1961). Horton, Patterson and Rizzo, J.S.D.C., **92** (1976) 269.

Spiro Dyes

From Dr C.H. Giles

Sir, With reference to the paper by Sutcliffe *et al.* [1], may I briefly record the background to the described research.

Spiro azo dyes were first synthesized in the period October 1963 to June 1965 in this Department, by Dr W. Lawrie and M.I. Shaikh [2]. They first prepared some spiro-2,2′-bisindane systems, but found that these were not readily converted into dyes. They then prepared diamino-2,2′-spiro-9,9′-bifluorene, by synthesis of the spiro-bifluorene, followed by nitration and then reduction. The diamino compound was then tetrazotized and coupled with several second components, respectively. Owing to shortage of time only one of these dyes could be evaluated for fastness to light against the corresponding 2-aminofluorene dyes (and also the dye from aniline). The second component in these cases was Brenthol AS; the spiro dye had the best light fastness.

The research was later continued here, from January 1967 to July 1970, by Dr D.C. Nonhebel, first with A.D. Mitchell, and subsequently with Dr A. Vaidyanathan from October 1968, supported by a SRC post-doctoral Fellowship. The results seemed to justify further development, but because of shortage of personnel here it was decided to approach Leeds University with the request that the research might be pursued in the Department of Colour Chemistry there. The writer discussed the matter with Professor I.D. Rattee and the late Dr F.K. Sutcliffe about February 1972, and they agreed to take up the project [1,3].

The original concept was based on the observation that the 1:2 metal-complex dyes, when interacted with spread monolayers of polymers on water surfaces, gave evidence of unusually strong self-association, believed to be due to their spiro structure, which had caused a particular and unusual type of intermolecular interlocking [4]. Thus it was considered that dyes containing a C–spiro-group might exhibit good fastness to light due to a pronounced tendency to associate, while not having the dullness of the metal-complex dyes.

There is, however, now found to be some degree of colour dulling introduced by the C-spiro configuration. As stated by the present authors [1], their use of insoluble azo dyes for the evaluation of fastness to light is not perhaps the best way to examine the concept under test, because of the complications introduced by the mechanical processes entailed in application of the dyes to the substrate. Possibly disperse dyes with the spiro structure would be better subjects for examination. Though this type of dye may well be present in hydrophobic fibres, largely in molecular form, particularly in the more highly organized structure of the polyester fibre, there is likely

to be a considerable proportion adsorbed in the associated form, in the voids in the fibre [5]. Such associated disperse dye has been detected in voids in cellulose acetate [6] and indirect evidence suggests its presence in polyester fibres dyed with insoluble azo dyes [7].

Yours faithfully,

C.H. GILES

Department of Pure and
Applied Chemistry
University of Strathclyde
Glasgow G1

References

1. Sutcliffe, Shahidi, and Patterson, J.S.D.C., **94** (July 1978) 306.
2. Shaikh, M.Sc. Thesis, University of Glasgow, June 1967.
3. Shahidi, Ph.D. Thesis, University of Leeds, 1975.
4. Giles and MacEwan, J. Chem. Soc. (1959) 1791.
5. Giles, in 'The Theory of Coloration of Textiles', ed. Bird and Boston (Bradford: Dyers Company Publications Trust, 1975), Chap. 2, pp. 93–94.
6. Kratky, Mittelbach and Sekora, Kolloid-Z., **200** (1964) 1.
7. Giles and De Bernat, Text. Research J., **46** (1976) 673.