Dyes and Pigments **25** (1994) 241–248

0143-7208/94/$7.00

Yellow Functional Dyes Derived from 4,4'-Diaminodiphenylmethanes

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(Received 7 January 1994; accepted 11 March 1994)

ABSTRACT

A series of yellow dyes derived from 4,4'-diaminodiphenylmethane and acetoacetanilide derivatives has been synthesized. The flow birefringent properties of the dyes have been studied. The chemical structure of the dyes, and the concentration, viscosity and temperature of dye solutions all influenced the flow birefringent properties. New birefringent compounds have been obtained.

1 INTRODUCTION

Flow birefringence is a birefringent effect which is produced under the action of a shearing force to investigate the flow of a liquid or the flow field quantitatively by means of light scattering. In order to detect the three-dimensional flow field, a viscous fluid containing a birefringent functional dye is preferably used as a detection medium.

Materials such as V_2O_5, sesame oil and polyethylcellulose can be used as detection medium, but these compounds have high viscosity and their properties as detection media are unsatisfactory. A material suitable for flow birefringence, viz. C.I. Acid Yellow 44 (C.I. 23900) was reported by Peebles in 1953,[1] but, this dye has high adhesivity on the instrument wall and its synthesis from 2-nitrotoluene involves many stages.

In this paper, some derivatives of 4,4'-diaminodiphenylmethane, acetoacetanilide and derived yellow dyes have been synthesized; the synthesis of some bis(aminophenylmethane) derivatives has been previously reported.[2]

The relation between chemical structure and the flow birefringence of solutions has been studied and some new compounds having evident birefringence have been found.[3]

2 EXPERIMENTAL

2.1 General synthesis of diaminodiphenylmethane derivatives (Fig. 1, A-1–A-VI)

Aniline (75 ml, 0·8 mol) and hydrochloric acid (43 ml, 0·5 mol) were stirred at 70°C and HCHO (36%, 27 ml, 0·2 mol) was added dropwise over 30 min. The mixture was then refluxed for 4 h, cooled to 60°C, and the pH adjusted to 9. The aqueous layer was separated, the remaining liquor was washed with H_2O, and aniline was removed with steam and the residue added to cold water. On filtering, a white residue of compound **A-1** was obtained; yield 83%, m.p. 91°C (found: C, 78·75; H, 7·09; N, 14·10; calculated: C, 78·79; H, 7·07; N, 14·14). Similarly prepared were: **A-11**, m.p. 141–142°C, 87%; **A-III**, m.p. 91–92°C, 85%; **A-IV**, m.p. 227–228°C, 83%, and **A-V**, m.p. 102–104°C (95%).

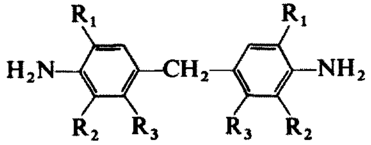
2.2 Synthesis of acetoacetanilide derivatives (Fig. 1, B-I–B-III)

4-Aminobenzenesulfonic acid ((99% purity) 35 g, 0·2 mol) was dissolved, with stirring, in water (160 ml) and Na_2CO_3 (10·6 g, 0·1 mol). The solution was cooled to 10°C, the pH was adjusted to 4, and diketene (23 ml, 0·3 mol) was added dropwise over 1 h. After stirring for 2 h, compound **B-I** was obtained (90% yield). The other compounds were prepared in a similar manner.

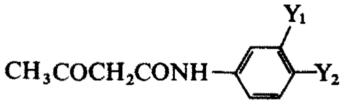
2.3 Synthesis of yellow functional dyes (Fig. 1, C-I–C-XII)

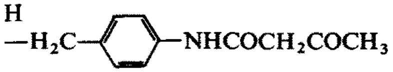
4,4'-Diaminodiphenylmethane (4 g, 0·02 mol) in hydrochloric acid (36%, 10 ml, 0·1 mol) and water was diazotized at 0–2°C by addition of sodium nitrite (3·5 g, 0·04 mol), followed by stirring for 30 min.

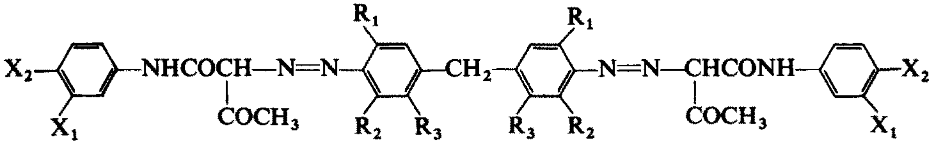
Acetoacetanilide-4-sulfonic acid (C-I, 10·8 g, 0·042 mol) was dissolved in aqueous NaOH and the clear solution cooled to below 5°C. The diazo liquor (0·02 mol) was then added dropwise with stirring, maintaining the pH between 8·2 and 8·8. After stirring for 2 h, sodium chloride was added to precipitate the dye (**C-I**). The other dyes were prepared in a similar manner.



No.	R_1	R_2	R_3
A-I	H	H	H
A-II	CH_3	H	H
A-III	OCH_3	H	H
A-IV	CH_3	CH_3	H
A-V	Cl	H	H
A-VI	H	H	SO_3H



No.	Y_1	Y_2
B-I	H	SO_3H
B-II	SO_3H	H
B-III	H	



No.	X_1	X_2	R_1	R_2	R_3
C-I	H	SO_3H	H	H	H
C-III	H	SO_3H	CH_3	H	H
C-V	H	SO_3H	OCH_3	H	H
C-VII	H	SO_3H	CH_3	CH_3	H
C-IX	H	SO_3H	Cl	H	H
C-XI	H	SO_3H	H	H	SO_3H
C-II	SO_3H	H	H	H	H
C-IV	SO_3H	H	CH_3	H	H
C-VI	SO_3H	H	OCH_3	H	H
C-VIII	SO_3H	H	CH_3	CH_3	H
C-X	SO_3H	H	Cl	H	H
C-XI	SO_3H	H	H	H	SO_3H

Fig. 1. Structure of dyes.

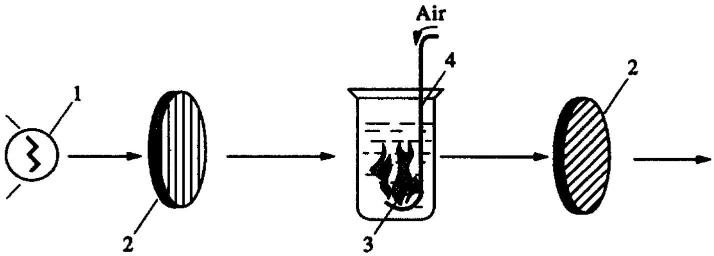


Fig. 2. Determination of the birefringence: (1) light source; (2) polarizer; (3) dye solution; (4) air blow pipe.

2.4 Determination of dye solution birefringence

The apparatus shown in Fig. 2 was used for the qualitative observations. It consists of a light source and two polarizers. The appropriate dye solution to be placed in glass is sampled using an air blow pipe; observations of the color linear pattern (marking) can then be made.

The cyclic flow and optical systems used for quantitative evaluations are shown in Fig. 3.[4]

3 RESULTS AND DISCUSSION

3.1 Structure of dyes and birefringence properties

The dyes varied in hue from greenish yellow to yellow and their absorption maxima are shown in Table 1. The birefringent effect of aqueous solutions of the dyes was observed using the apparatus shown in Fig. 2.

The results show that dyes **C-III–C-VIII**, which contain —CH_3 or —OCH_3 substituents in the diphenylmethane rings have a very strong birefringent effect, while dyes **C-IX–C—XII**, which contain Cl or —SO_3H groups do not show the effect. The use of unsubstituted diphenylmethane

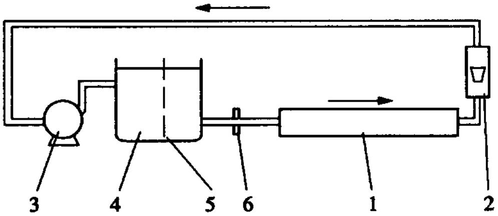


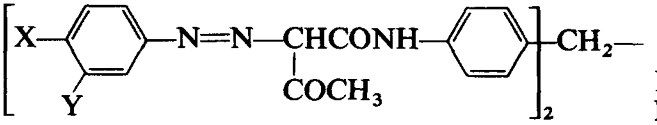
Fig. 3. Apparatus for quantitative determination of flow system birefringence: (1) experimental section; (2) rotameter; (3) pump; (4) water tank; (5) rectifier (to obtain evenness of flow orientation); (6) valve.

Table 1
Flow Birefringent Effect of the Dyes

No.	*Color*	λ_{max} *(nm)*	*Solution conc. (%)*	*Birefringent effect*[a]
C-I	Greenish yellow	382	2·0	+++
C-III	Greenish yellow	392	2·0	+++
C-V	Yellow	396	2·0	+++
C-VII	Yellow	395	2·0	+++
C-IX	Greenish yellow	390	2·0	+
C-XI	Yellow	395	2·0	+
C-II	Yellow	403	2·0	+++
C-IV	Yellow	395	2·0	+++
C-VI	Yellow	404	2·0	+++
C-VIII	Yellow	405	2·0	+++
C-X	Yellow	405	2·0	+
C-XII	Yellow	406	2·0	+
D-I	Greenish yellow	385	2·0	++
D-II	Greenish yellow	375	2·0	++

[a] +++: Very strong; ++: medium; +: weak.

derivatives such as the diazo component (dye **C-I** and **C-II**) results in a stronger birefringent effect compared with the analogous dyes **D-1** and **D-II** in which the diphenylmethane derivatives are used as coupling components.



D-I: (X:SO_3H, Y:H)
D-II: (X:H, Y:SO_3H)

It has been noted that color materials with linear molecular chains are arranged orderly, hence increasing the isotropic character and raising the birefringent effect.[5] To obtain an evident pattern of light and dark lines, it is necessary to choose an optimum concentration of the dye.

3.2 Viscosity of dye solution and birefringence

The viscosity of dyes **C-1**, **C-III** and **C-VII** at various aqueous concentration at 20°C were determined. The birefringence of the solutions is shown in Table 2. It was found that dye solutions of higher viscosity show a stronger birefringent effect. However, the increase in the concentration of the dye solution should also be considered, since this may be a cause of the high viscosity and low flowability, the solution becoming micellar, hence improving the birefringent action. The optimum concentration was about 1·5%.

Table 2
Viscosity and Birefringent Effect of Dyes C-I, C-III and C-VII

Ref. no.	*Concentration (%)*	*Viscosity (cP)*	*Birefringent effect*
C-I	0·6	10·5	None
	1·10	21·2	++
	1·45	80·0	+++
	1·52	116·4	+++
	2·18	656·0	+++
	2·50	1 928·0	+++
C-III	0·70	4·6	None
	1·15	7·4	++
	1·57	17·0	+++
	2·10	45·2	+++
	2·58	137·2	+++
C-VII	0·50	5·5	None
	1·01	8·0	++
	1·45	186·4	+++
	2·11	203·0	+++
	2·54	731·0	+++

3.3 Temperature of solution and birefringence

On comparison of the birefringence of the dyes, it is seen that the birefringence effect becomes weaker when the temperature is increased and alters at different temperatures for different dyes. Increase in temperature

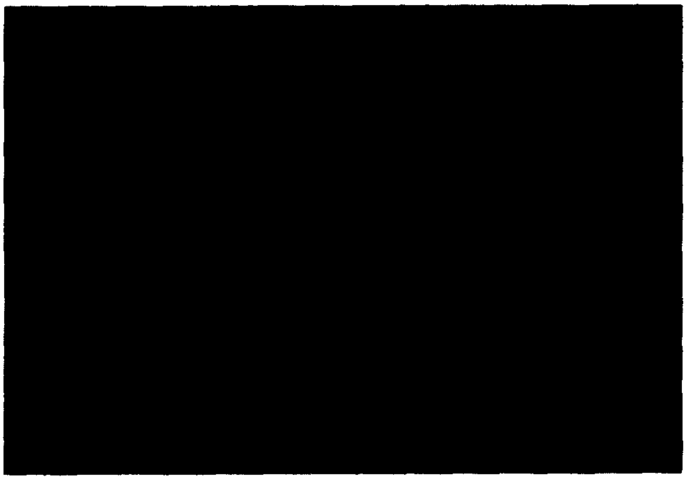


Fig. 4. Birefringent pattens for the laminar flow of dye C-III.

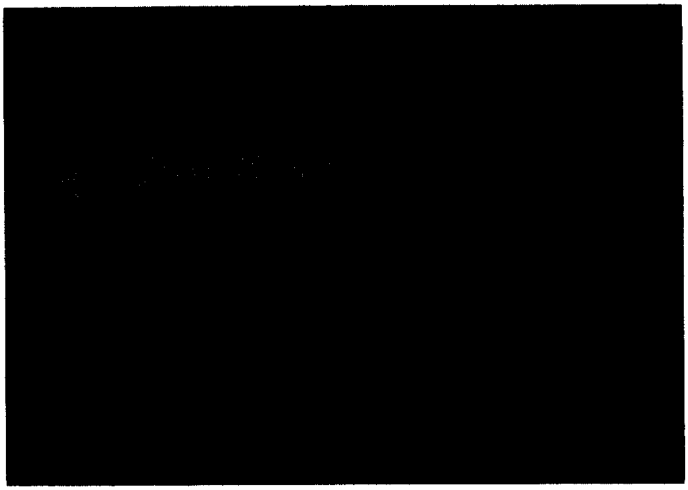


Fig. 5. Birefringent pattens for the laminar flow of dye **C-III** in a rectangular pipe with a column.

causes a decrease in the viscosity of the solution and hence a change in the micelle state of the dye; the birefringent effect diminishes at 60, 50 and 55°C for dyes **C-I**, **C-III** and **C-VII**, respectively.

The results measured using compound **C-I** at a concentration of 1·45% at 20°C are shown in Figs 4 and 5. The technique used to investigate the flow has been previously described.[6]

4 CONCLUSION

Some linear yellow azo dyes were synthesized from 4,4'-diaminodiphenylmethanes and acetoacetanilide derivatives. It is suggested that some of these materials, such as **C-I**, and **C-III**, are useful for flow birefringence detection. Dyes having —CH_3 or —OCH_3 substituents give an obvious birefringent effect in viscous solutions, and with the increase in viscosity (concentration) of the dye solution, the birefringent intensity is higher, but the effect decreases with increase in temperature.

ACKNOWLEDGEMENTS

The authors would like to thank Jin Jiahao and Xu Changxun for their part in the experimental work.

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