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Purification Procedures for Synthetic Dyes: Part 3—HPLC Separation of the Components of 1,4-Bis(2,6-diisopropylanilino)anthraquinone*

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SUMMARY

Reverse-phase thin-layer chromatography (TLC) of a laboratory-synthesized sample of 1,4-bis(2,6-diisopropylanilino)anthraquinone revealed that the dye contained three components (violet, blue and blue-green). Analytically HPLC then showed that the blue-green component was a mixture of blue-green and green dyes. The four dyes were separated by HPLC, and each was identified by ^{1}H-NMR and mass-spectral analysis. The latter three dyes were shown to be isomeric compounds which result from the presence of a small amount of 2,4-diisopropylaniline in commercial 2,6-diisopropylaniline.

1 INTRODUCTION

Previous papers from these laboratories have described[1,2] attempts to develop purification procedures for the generation of gram quantities of synthetic dyes. It was pointed out that while preparative HPLC is a viable method, its cost and requirement for large volumes of solvent for each purification limit its utility. In this paper, however, we present some results from a study of the analytical-scale HPLC purification of an anthraquinone dye, which gave a separation of components not readily obtainable by other techniques.

* Abstracted from the MS thesis of K. P. Mills, North Carolina State University (1984).

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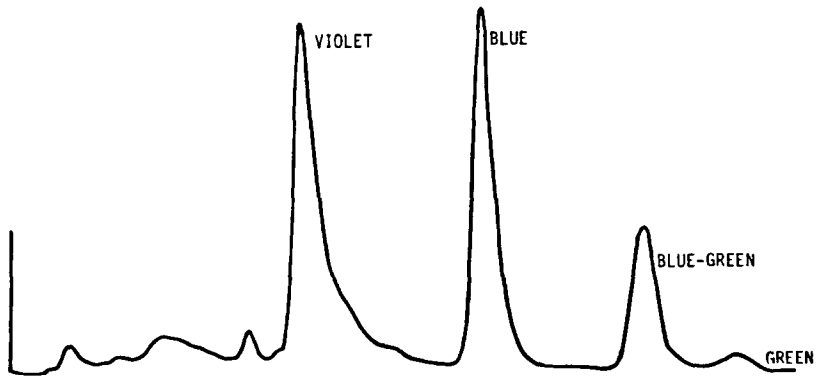
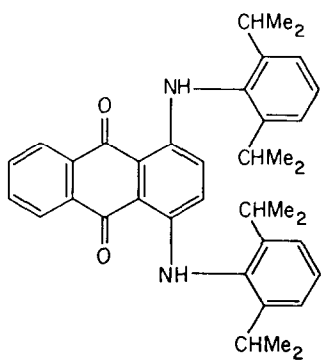


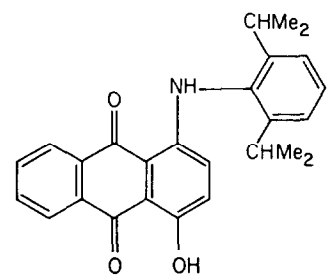
Fig. 1. HPLC chromatogram recorded on a sample of crude **I** using a silica-gel column.

It is well known that anthraquinone is the central chromophoric moiety of a large number of acid, disperse, mordant, solvent, vat and reactive dyes, as well as pigments.[3] Placing NH_2 groups in the 1- and 4-positions of anthraquinone produces the violet dye Disperse Violet 1. Derivatives of this which have an alkyl- or aryl-substituent on one or both the nitrogen atoms invariably possess blue or green colors,[4,5] and there are many such dyes which enjoy commercial use today.[6]

One interesting derivative of anthraquinone, though not of commercial importance, is 1,4-bis(2,6-diisopropylanilino)anthraquinone (**I**). We prepared this compound as part of a series of anthraquinone dyes of interest as colorants for certain refrigerants. HPLC (silica gel) evaluation of a sample of crude **I** indicated initially that the dye was a mixture of three components (violet, blue and blue-green). HPLC using a C-18 column showed that the blue-green component also contained a green dye (Fig. 1). The method of synthesis accounts for two products (i.e. **I** and **II**). The violet component would possess the structure **II**, and one of the remaining three would have



I



II

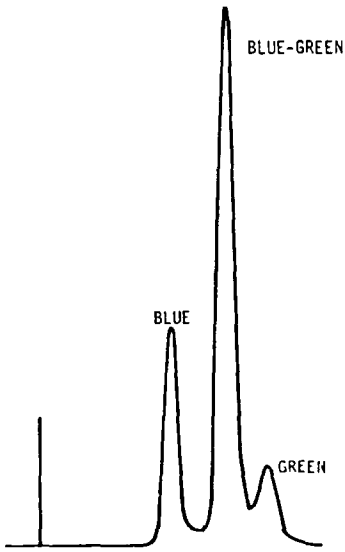


Fig. 2. HPLC chromatogram recorded on a sample of partially purified **I** using a C-18 column.

the structure drawn for compound **I**. It was not immediately clear what structures would correspond to the remaining two components, since the literature[7] indicates that the method used to synthesize 2,6-diisopropylaniline yields the 2,6-product, a trace amount of the 2,4,6-product, but none of the 2,4-isomer.

Sufficient quantities of the blue, blue-green and green components of partially purified **I** (Fig. 2) were isolated via an HPLC separation, and identified with the aid of ^{1}H-NMR and electron-impact mass-spectral analysis.

2 EXPERIMENTAL

2.1 General

The TLC analyses were conducted with Analtech RPSF Uniplates. The HPLC separations were performed using a Waters Model 440 ultraviolet detector equipped with a Model 600A solvent delivery pump, a Rheodyne injector and a Fisher Recordall Series 5000 recorder. (A C-18 column and a flow rate of 2 ml min^{-1} were used.) The ^{1}H-NMR spectra were recorded in $CDCl_3$ on a Bruker 250-MHz instrument, and the mass spectra on a Hewlett–Packard 5985B mass spectrometer using the electron-impact (EI) mode. The chemicals used in the synthesis of the dyes were purchased from Aldrich Chemical Company. The UV–visible spectra were recorded on a Perkin–Elmer Model 559A spectrophotometer.

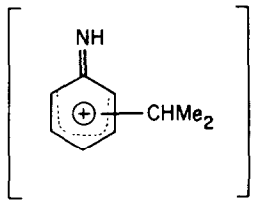
2.2 Synthesis of compounds V, VI and VII

A mixture of 2,6-diisopropylaniline (70·92 g, 0·4 mol), leucoquinizarin (4·84 g, 0·02 mol), boric acid (2·82 g, 0·046 mol) and propionic acid (1·6 ml, 0·02 mol) was gradually heated to 160°C, whereupon 2–3 ml of an aqueous distillate were collected. The distillation receiver was removed and the reaction was stirred under N_2 at 160°C for 4 h. At that point 50 ml of the arylamine were removed by vacuum distillation. The dark green residue which remained was cooled to 120°C, then poured into a mixture of 150 ml of ice–H_2O and 18 ml of conc. HCl with vigorous stirring. The mixture was stirred at 75°C for 15 min and filtered hot. The solid collected was washed repeatedly with H_2O and then suspended in 100 ml of methyl cellosolve. The temperature was raised to 110°C and kept near that temperature as air was bubbled through the reaction mixture for 4 h. Additional solvent was added periodically to maintain a volume of 100 ml. The reaction was cooled to room temperature and 50 ml of H_2O were added to complete precipitation of the crude dye. This was collected and dried *in vacuo* at 50°C for 4 h to give 8·0 g of a bluish-violet powder. TLC on reverse-phase silica-gel plates with cyclohexane:toluene (1:1) showed that the product contained three major components: violet ($R_f = 0{\cdot}45$), blue ($R_f = 0{\cdot}31$) and blue-green ($R_f = 0{\cdot}17$). A portion of the crude dye (110 mg) was dissolved in MeOH. The solution was filtered through a 0·5-μm filter and injected into the HPLC instrument. After numerous injections, eluting with cyclohexane:toluene (1:1), the blue component (50·12 mg) was isolated. A quantity of 50·15 mg of the blue-green dye was also obtained, but after passing it through the HPLC in the recycle mode 25 mg of pure blue-green dye ($R_f = 0{\cdot}17$) were obtained. A green dye (9 mg, $R_f = 0{\cdot}16$) was also isolated which contained a small amount of the blue-green dye. Further purification of the green component afforded 5·04 mg of the pure green dye.

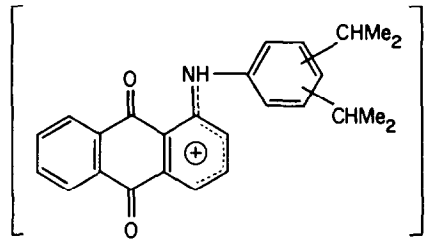
3 RESULTS AND DISCUSSION

Table 1 summarizes the results of the mass-spectral analysis of the blue, blue-green and green dyes which were separated by HPLC. The spectrum of each dye was characterized by three major peaks (*m/e* 133, 382 and 558). The molecular ion was of *m/e* 558, and the base peak for each dye appeared at *m/e* 382. The second most intense peak of the three spectra had *m/e* 133. The fragments of *m/e* 133 and 382 probably correspond to species **III** and **IV**, respectively, and the mass spectra results clearly showed that the three dyes were isomers.

Examination of the commercial sample of 2,6-diisopropylaniline con-



III: *m/e* 133



IV: *m/e* 382

firmed that a small amount of 2,4-diisopropylaniline was present. It was not possible to alter the amounts of the blue-green and green components of the crude dye mixture by distilling the commercial 2,6-diisopropylaniline prior to its use. However, when the unreacted 2,6-diisopropylaniline was collected and redistilled at the end of the dye-forming reaction, no green and very little blue-green dye formed when that freshly distilled sample was employed in a dye-forming reaction (Fig. 3). A twice-recycled sample of the diisopropylaniline produced no blue-green or green dye (Fig. 4).

Table 2 summarizes the ^{1}H-NMR results from the evaluation of the blue, blue-green and green dyes. The data permit the assignment of the structures of these dyes as **V**, **VI** and **VII**, respectively. These structures would account for the disappearance of the green dye when the recycled diisopropylaniline from a previous dye-forming reaction was used. The 2,4-diisopropylaniline would be expected to react faster than the 2,6-isomer, thus being used in the initial stages of the dye-forming reaction and consequently recycled arylamine contains progressively decreased amounts of it.

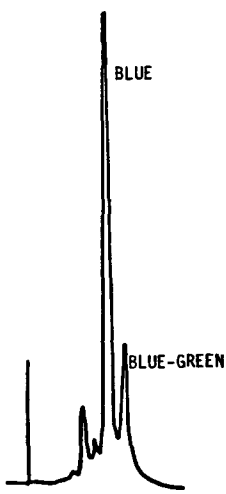


Fig. 3. HPLC chromatogram recorded on a sample of dye **I** prepared using once-reclaimed 2,6-diisopropylaniline.

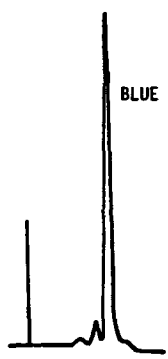


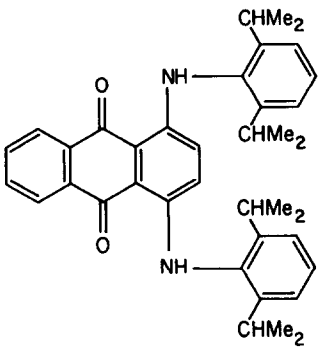
Fig. 4. HPLC chromatogram recorded on a sample of dye **I** prepared using twice-reclaimed 2,6-diisopropylaniline.

TABLE 1
Mass Spectral Data

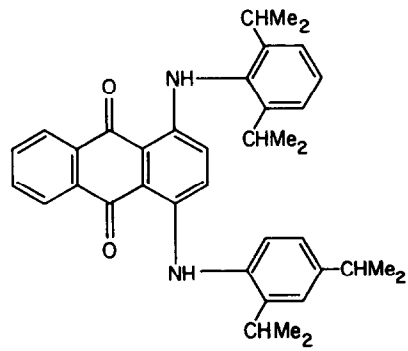
Dye	*m/e*	*Relative intensity (%)*
Blue (**V**)	133	67·8
	382	100·0
	558	9·7
Blue-green (**VI**)	133	65·8
	382	100·0
	558	31·6
Green (**VII**)	133	76·5
	382	100·0
	558	13·7

TABLE 2
^{1}H-NMR Data of Dyes **V**, **VI** and **VII**

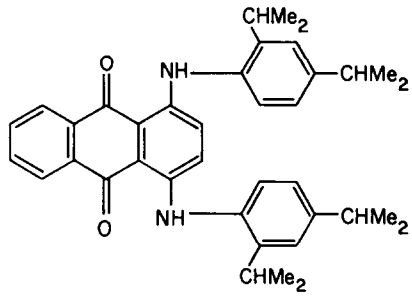
Dye	*Chemical shift, δ (ppm)*	*Multiplicity*	*Integrated number of protons*	*Assignment*
Blue (**V**)	1·05, 1·18	Doublets	12	—CH_3
	3·10	Heptet	4	—CH (isopropyl)
	6·55	Singlet	2	H-2, H-3
	7·28	Multiplet	6	—CH (aniline)
	7·77	Multiplet	2	H-6, H-7
	8·46	Multiplet	2	H-5, H-8
	11·90	Singlet	2	—NH
Blue-green (**VI**)	1·10, 1·19, 1·26	Doublets	12	—CH_3
	2·91, 3·10, 3·25	Heptets	4	—CH (isopropyl)
	6·59, 7·08	Doublets	2	H-2, H-3
	7·28	Multiplet	6	—CH (aniline)
	7·76	Multiplet	2	H-6, H-7
	8·44	Multiplet	2	H-5, H-8
	11·85, 12·18	Singlets	2	—NH
Green (**VII**)	1·25	Multiplet	12	—CH_3
	2·92, 3·27	Heptets	4	—CH (isopropyl)
	7·13	Multiplet	6	—CH (aniline)
	7·30	Singlet	2	H-2, H-3
	7·75	Multiplet	2	H-6, H-7
	8·43	Multiplet	2	H-5, H-8
	12·21	Singlet	2	—NH



V: Blue dye



VI: Blue-green dye



VII: Green dye

Although analytical HPLC is a quite tedious way to prepare large amounts of pure dye samples, it proved to be very useful in this present work in the separation of compounds **V**, **VI** and **VII**, isolation of which had not been possible by other conventional chromatography procedures.

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