Dyes and Pigments **12** (1990) 145–155

Characterization of the Products Derived from the Nitration of 1,5-Dihydroxyanthraquinone (*Anthrarufin*) and 1,8-Dihydroxyanthraquinone (*Chrysazin*)

D. O. Ukponmwan & H. S. Freeman*

Department of Textile Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8302, USA

(Received 8 November 1988; accepted 16 December 1988)

ABSTRACT

When 1,5-dihydroxyanthraquinone (Anthrarufin) and 1,8-dihydroxyanthraquinone (Chrysazin) were nitrated using a mixture of concentrated sulfuric and nitric acids in the presence of boric acid at 10–25°C, three major products formed in each reaction. The products were separated by low-pressure column chromatography and identified by ^{1}H-NMR and mass spectrometric analyses in tandem. The products identified result from the mono-, di- and tetra-nitration of these dihydroxyanthraquinones.

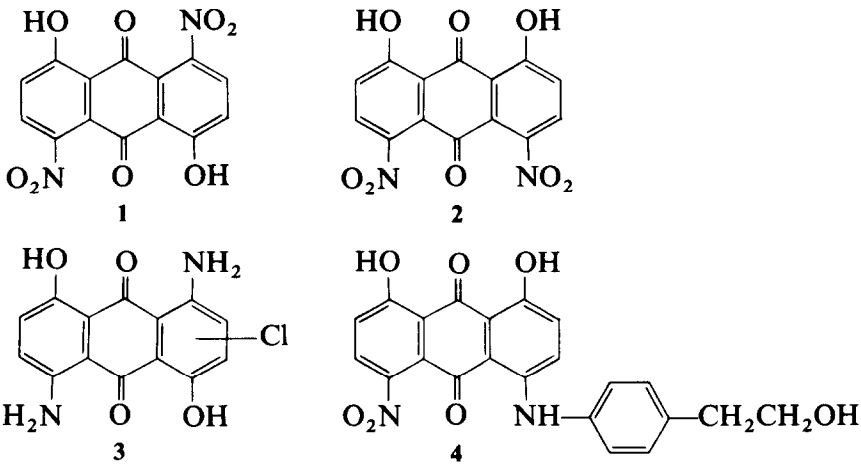
INTRODUCTION

It is known from the chemical literature[1–3] that 4,8-dinitroanthrarufin (**1**; 4,8-DNA) and 4,5-dinitrochrysazin (**2**; 4,5-DNC) are very useful chemical intermediates in the synthesis of disperse blue anthraquinone dyes possessing good lightfastness and sublimation fastness.[3] Two examples of such dyes that enjoy commercial success are CI Disperse Blue 56 (**3**) and CI Disperse Blue 27 (**4**).

During the course of synthesizing some analogs of dyes **3** and **4**, the authors elected to prepare the required intermediates (**1** and **2**) according to the literature.[1,4] TLC analysis of the crude products revealed that the two nitration reactions afforded a mixture of three or more compounds in nearly

* Author to whom correspondence should be addressed.

Dyes and Pigments 0143-7208/89/$03·50



equal proportions. Each of the three major products of the two reactions was isolated with the aid of flash column chromatography[5] and identified by a combination of ^{1}H-NMR (250 MHz) and mass spectrometry using chemical ionization (CI) and fast atom bombardment (FAB) techniques.

EXPERIMENTAL

General

The samples of Anthrarufin and Chrysazin used in this study were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin 53233, USA) and were 95·0% and 97·0%, respectively. The melting points of the reaction products were recorded on a Mel-Temp melting-point apparatus and are uncorrected. The ^{1}H-NMR spectra were recorded on a Bruker 250-MHz instrument using DMSO-d_6 as the solvent and TMS as the internal reference. The CI mass spectra were recorded on a Hewlett–Packard 5958 mass spectrometer by direct probe using methane gas as a carrier, while the FAB mass spectrum was recorded on a JEOL HX110HF double-focusing mass spectrometer equipped with a DA-5000 data system. In the FAB work, thioglycerol was used as the matrix. This matrix gives rise to major peaks at *m/e* 107, 215 and 321. The use of methane in the CI experiments always gives an $M+1$ peak and occasionally an $M+28$ peak. The visible absorption spectra were recorded on a Perkin–Elmer 559A spectrophotometer at a concentration of 4×10^{-5} M in chlorobenzene or in methanol.

Nitration of Anthrarufin[4]

To a mixture of anthrarufin (25 g, 0·104 mol) and boric acid (12·5 g, 0·202 mol) in 250 ml of conc. H_2SO_4 at 10°C, small portions of KNO_3 (25 g,

0·247 mol) were added at a rate such that the reaction temperature did not exceed 15°C. The resulting reaction mixture was stirred at 20–25°C for 8 h and then diluted by pouring it into 2 litres of cold H_2O. The crude product was collected by vacuum filtration and dried to give 17 g of an orange–red solid. Low-pressure column chromatography[5] of 1·0 g of crude product using silica gel (230–400 mm mesh) and initially PhMe:EtOAc (4:1) and near the end PhMe:EtOAc:HOAc (8:2:1) afforded a small quantity of starting material, 0·4 g of the expected orange product (**1**), m.p. 360–362°C; 0·3 g of a reddish violet component (**5**), m.p. 236°C (from MeOH); and 0·25 g of a violet component (**6**), m.p. >400°C (from MeOH). TLC data on silica gel using PhMe:EtOAc:HOAc (8:2:1) are: $R_f = 0{\cdot}767$ for **1**, 0·875 for **5**, and 0·786 for **6**.

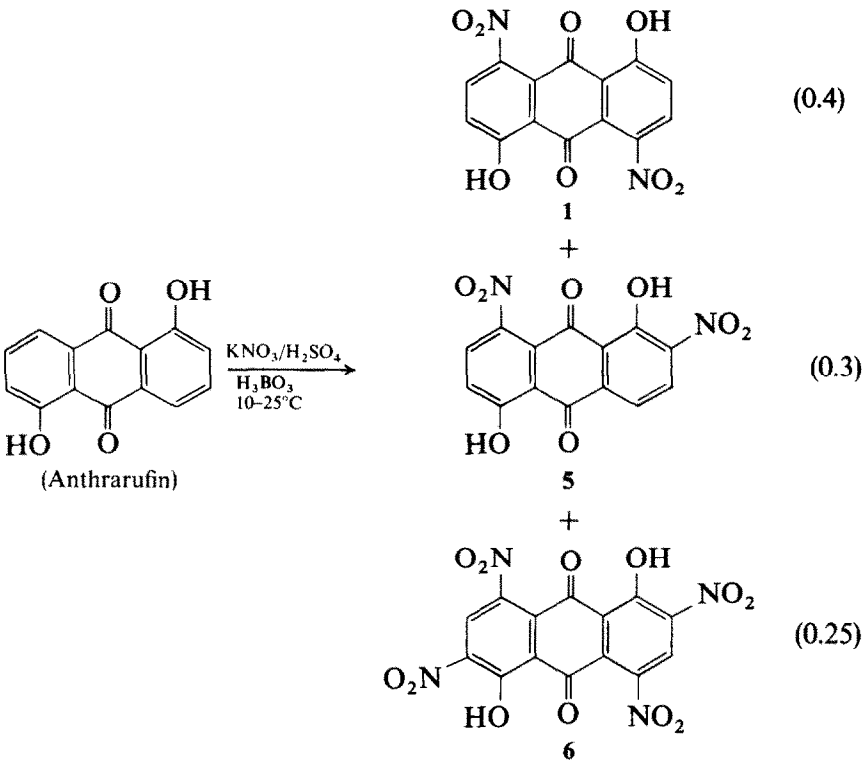
Nitration of Chrysazin[1]

Chrysazin (12 g, 0·05 mol) was added over a period of 30 min to a well-stirred mixture of conc. H_2SO_4 (41 ml) and boric acid (6 g, 0·09 mol) at 30°C. The resulting mixture was stirred for 1·5 h and then cooled to 10°C. At that point, a mixture of 12·43 ml of conc. H_2SO_4 and 4·65 ml of conc. HNO_3 was added at a rate such that the reaction temperature did not exceed 15°C (this required 1 h). The reaction temperature was allowed to increase to room temperature and kept near 25°C for 8 h. The crude product was isolated by pouring the reaction mixture into 750 ml of cold H_2O, vacuum filtration, and air-drying. Purification of 0·3 g of the crude product by flash column chromatography followed by recrystallization from MeOH afforded 0·05 g of pure **7**, m.p. 272–274°C; 0·07 g of a second orange solid (**8**), m.p. 234°C; and 0·07 g of a reddish-orange solid (**2**), m.p. 290–292°C. TLC data on silica gel using PhMe:EtOAc:HOAc (8:2:1) are: $R_f = 0{\cdot}873$ for **2**, 0·818 for **7**, and 0·327 for **8**.

RESULTS AND DISCUSSION

When Anthrarufin is nitrated using the method of Allen *et al.*,[4] the reaction proceeds as shown in Scheme 1. The structure of each product of this reaction was determined using ^{1}H-NMR and mass spectrometry in tandem. The spectra obtained are shown in Figs 1–3.

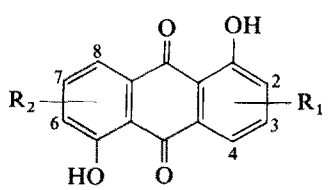
CI mass spectrometry indicated that compounds **1** and **5** were isomers ($M + 1 = m/e$ 331) that resulted from dinitration. The presence of only two signals in the ^{1}H-NMR spectrum of **1** but four signals in the spectrum of **5** led to the assignments recorded in Table 1. The third product of the nitration of Anthrarufin required mass spectrometric analysis by the FAB technique,[6,7]



Scheme 1. Nitration of Anthrarufin at 10–25°C.

TABLE 1

Chemical Shifts (ppm), Multiplicities[a] and Coupling Constants (Hz) for the Ring Protons of **1**, **5** and **6**



Compound	*H-2*	*H-3*	*H-4*	*H-6*	*H-7*	*H-8*	*Coupling constants*
1 $R_1 = 4\text{-}NO_2$; $R_2 = 8\text{-}NO_2$	7·52 (d)	8·10 (d)	—	7·52 (d)	8·10 (d)	—	$^3J_{23} = 9{\cdot}0$
5 $R_1 = 2\text{-}NO_2$; $R_2 = 8\text{-}NO_2$	—	8·22 (d)	7·82 (d)	7·45 (d)	7·83 (d)	—	$^3J_{34} = 8{\cdot}2$ $^3J_{67} = 8{\cdot}9$
6 $R_1 = 2,4\text{-}(NO_2)_2$; $R_2 = 6,8\text{-}(NO_2)_2$	—	8·37 (s)	—	—	8·37 (s)	—	—

[a] Abbreviations: s, singlet; d, doublet.

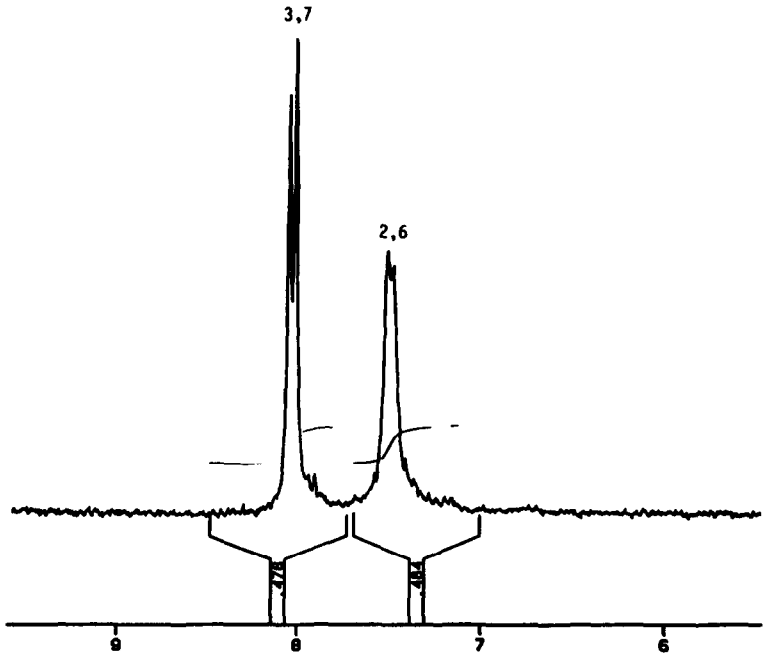
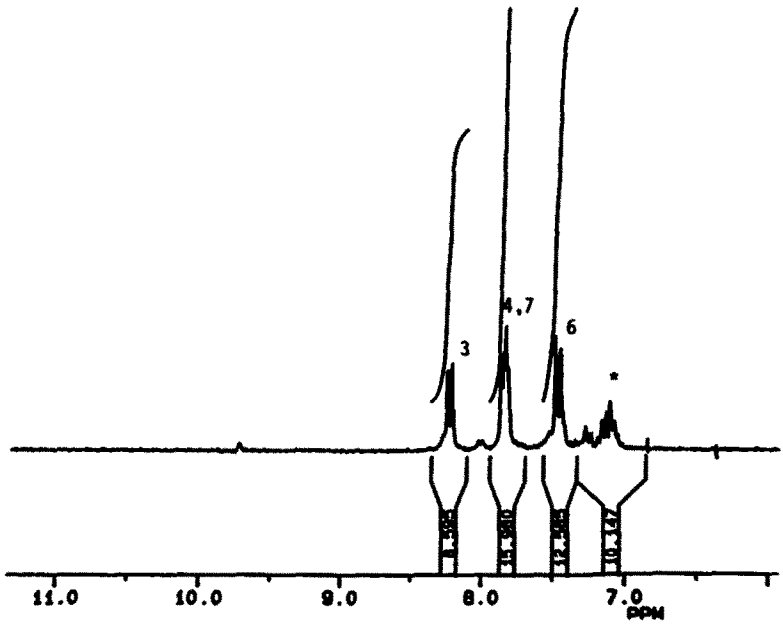


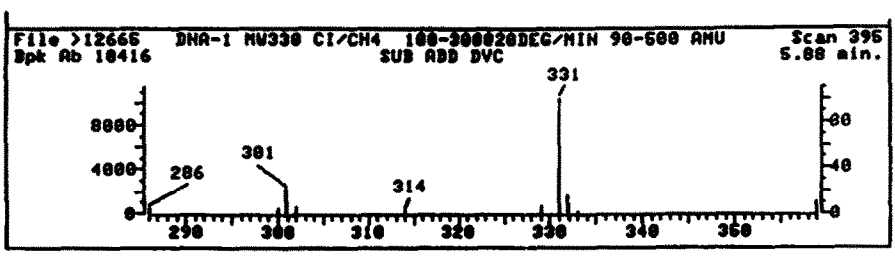
Fig. 1. ^{1}H-NMR spectrum (a) and CI mass spectrum (b) of 4,8-dinitroanthrarufin (**1**).

due to its very low volatility, and was shown to have resulted from tetranitration ($m/e = 420$). The ^{1}H-NMR spectrum of **6** contained a lone signal (a singlet) at 8·37 ppm.

When Chrysazin was nitrated using the method of Buxbaum & Terss,[1] the reaction proceeded as outlined in Scheme 2. The products were identified as 4,5-dinitrochrysazin (**2**), 2,5-dinitrochrysazin (**7**) and 4-nitrochrysazin (**8**). The ^{1}H-NMR and mass spectra are shown in Figs 4–6. As in the previous nitration, the nitration of Chrysazin produces a pair of isomers (**2** and **7**). ^{1}H-NMR again showed two different kinds of protons in one of the isomers and four different kinds of protons in the other. Thus, the assignments of **2** and **7**



(a)

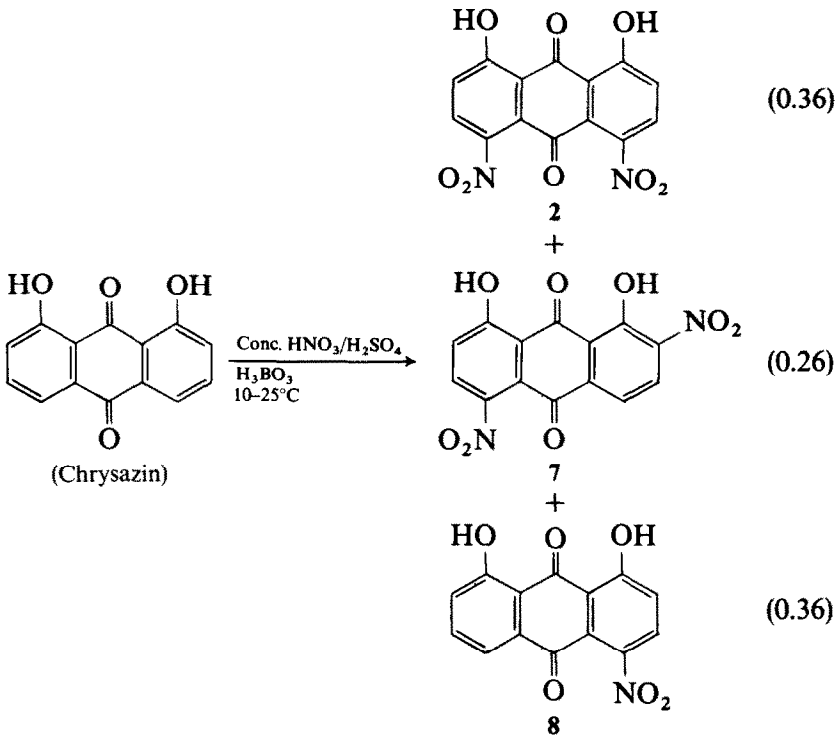


(b)

Fig. 2. ^{1}H-NMR spectrum (a) and CI mass spectrum (b) of 2,8-dinitroanthrarufin (**5**).

are as outlined in Table 2. Interestingly, the NMR data obtained from the analysis of **1**, **2**, **5** and **6** indicate that 1,4- or 5,8-disubstitution produces a $^3J_{23}$ or $^3J_{67}$ of 9 Hz, whereas 1,2- or 5,6-disubstitution produces a $^3J_{34}$ or $^3J_{56}$ of 8·2–8·3 Hz. These results were used to help assign the structure of the mononitrated product **8**. The lone nitro group must be *para* to an —OH group, in that the $^3J_{23}$, δ H-2, and δ H-3 values are essentially the same as observed for compound **2**.

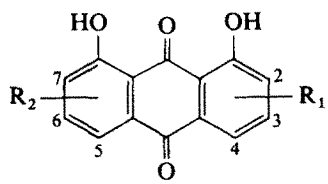
Visible absorption spectra were recorded on **1**, **2**, **5**, **7** and **8** using chlorobenzene as the solvent and on **6** using MeOH. The data that resulted



Scheme 2. Nitration of Chrysazin at 10–25°C.

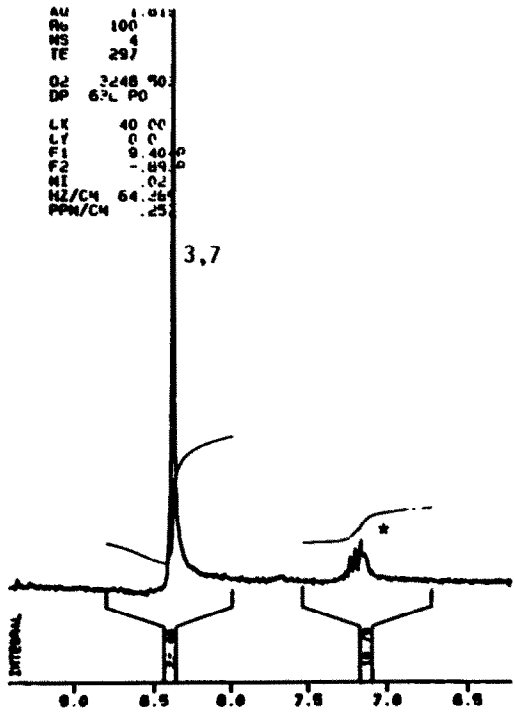
TABLE 2

Chemical Shifts (ppm), Multiplicities[a] and Coupling Constants (Hz) for the Ring Protons of **2**, **7** and **8**



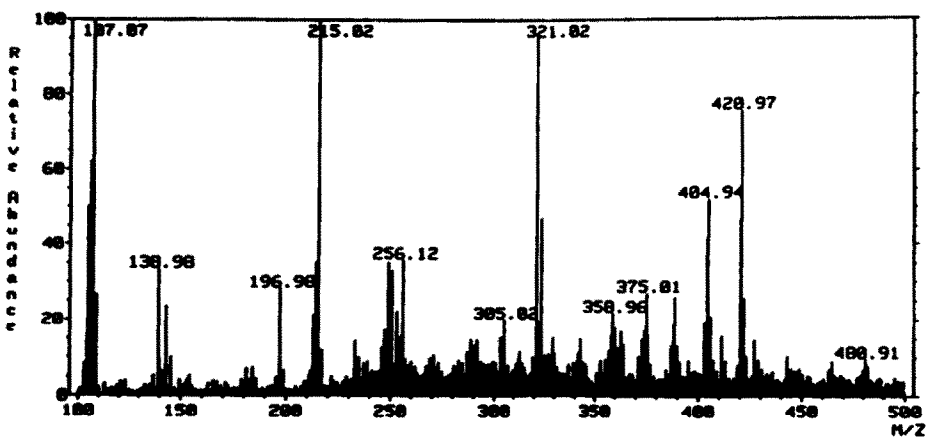
Compound	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*Coupling constants*
2 $R_1 = 4\text{-}NO_2$; $R_2 = 5\text{-}NO_2$	7·48 (d)	8·08 (d)	—	—	8·08 (d)	7·48 (d)	$^3J_{23} \doteq 9{\cdot}0$
7 $R_1 = 2\text{-}NO_2$; $R_2 = 5\text{-}NO_2$	—	8·38 (d)	7·70 (d)	—	8·10 (d)	7·55 (d)	$^3J_{34} = 8{\cdot}3$ $^3J_{67} = 9{\cdot}0$
8 $R_1 = 4\text{-}NO_2$; $R_2 = H$	7·49 (d)	8·05 (d)	—	7·61 (dd)	7·80 (t)	7·39 (dd)	$^3J_{23} = 9{\cdot}0$ $^3J_{56} = 8{\cdot}3$ $^3J_{67} = 8{\cdot}2$ $^4J_{57} = 1{\cdot}0$

[a] Abbreviations: d, doublet; dd, doublet of doublets; t, triplet.



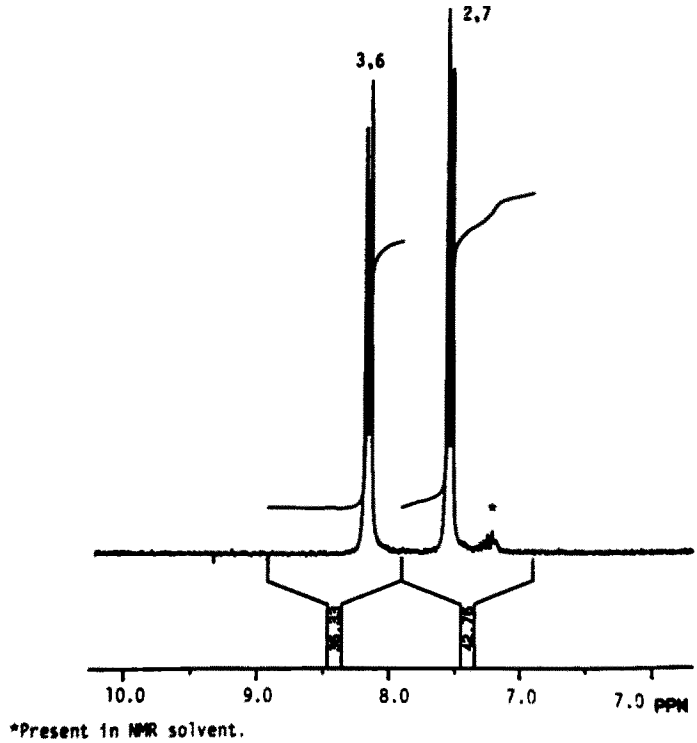
*Present in NMR solvent

(a)

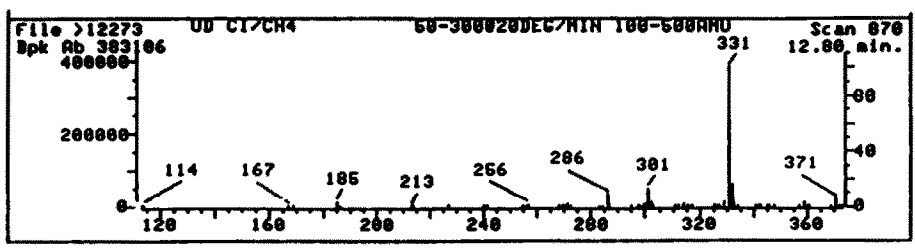


(b)

Fig. 3. ^{1}H-NMR spectrum (a) and FAB mass spectrum (b) of 2,4,6,8-tetranitroanthrarufin (**6**).



(a)

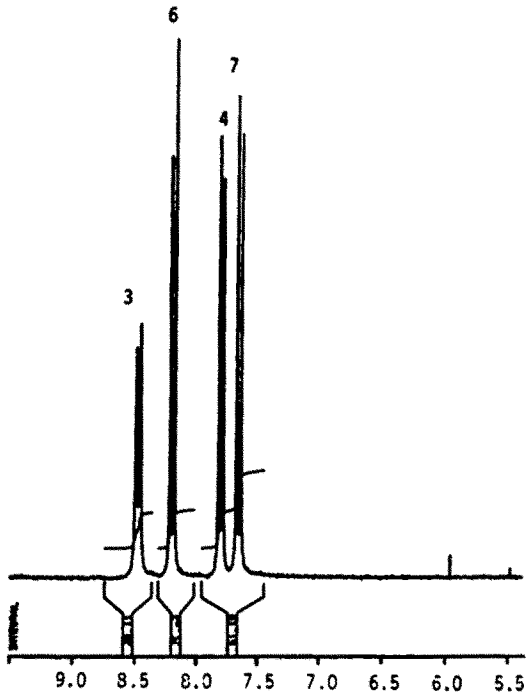


(b)

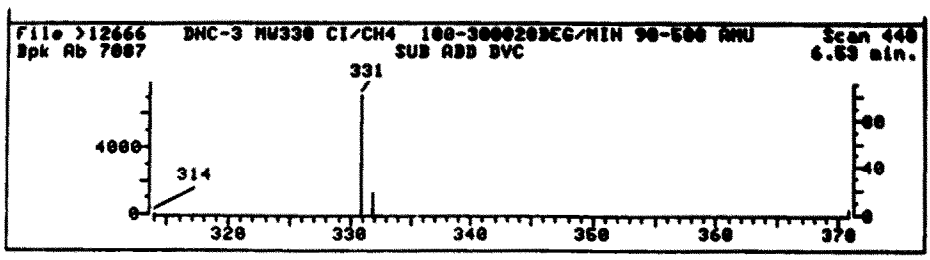
Fig. 4. ^{1}H-NMR spectrum (a) and CI mass spectrum (b) of 4,5-dinitrochrysazin (**2**).

are provided in Table 3. Compound **6** was too insoluble in most other organic solvents to give a useful spectrum. However, it was possible to observe a $\lambda_{max} = 500$ nm by using MeOH.

It has been shown through this study that although the nitration of Anthrarufin and Chrysazin leads to a mixture of mono-, di- and tetra-nitrated compounds, the reaction products are relatively easy to separate and characterize using chromatographic and instrumental techniques. The



(a)



(b)

Fig. 5. ^{1}H-NMR spectrum (a) and CI mass spectrum (b) of 2,5-dinitrochrysazin (**7**).

TABLE 3
Visible Absorption Data for Compounds **1**, **2**, **5**, **7** and **8** in Chlorobenzene

Compound	λ_{max} (*nm*)	*Log* ε
1	435	3·98
2	439	3·95
5	436, 504	3·79, 3·51
7	436	4·09
8	438	4·02

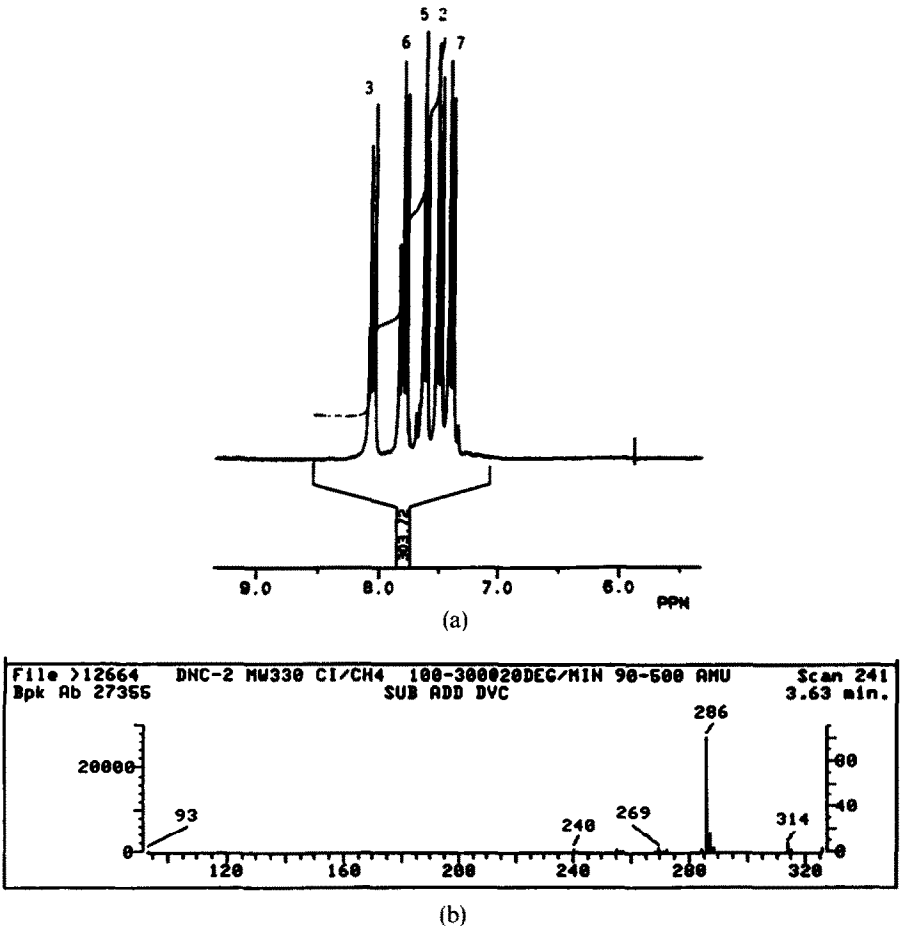


Fig. 6. ^{1}H-NMR spectrum (a) and CI mass spectrum (b) of 4-nitrochrysazin (**8**).

results of this study also help to explain why dyes of varying colors of blue → green result when different laboratory samples of 4,8-DNA and 4,5-DNC are employed.

REFERENCES

1. Buxbaum, E. & Terss, R. H., US Patent, 3 082 218 to E.I. Dupont (19 March 1963).
2. British Celanese, British Patent 420 593 (1933).
3. Lee, C.-S. & Peters, A. T., *J. Soc. Dyers Colourists*, **98** (1982) 343.
4. Allen, C. F. H., Frame, G. F. & Wilson, C. V., *J. Org. Chem.*, **6** (1944) 732; *Chem. Abstr.*, **36** (1942) 460[4].
5. Still, W. C., Kahn, M. & Mitra, A., *J. Org. Chem.*, **43** (1978) 2923.
6. Bowie, J. H., *Mass Spectrom.*, **8** (1985) 161.
7. Balasanmugam, K. & Miller, J. M., *Org. Mass Spectrom.*, **23** (1988) 267.