Dyes and Pigments **11** (1989) 101–107

Synthesis and Characterization of Two Novel Formazan Dyes*

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(Received 1 June 1988; accepted 29 July 1988)

ABSTRACT

*Bis[*N,N′*-(2,2′-dihydroxy-5,5′-dichlorodiphenyl)] formazan (DCDF) and bis[*N,N′*-(2,2′-dihydroxy-4,4′-disulfodinaphthyl)] formazan (DSNF) were synthesized by coupling the diazonium salts of 2-amino-4-chlorophenol (ACP) and 1-amino-2-naphthol-4-sulfonic acid (ANS), respectively, with levulinic acid in alkaline media. These reddish-brown bis(formazans) contain two formazan groups in the* trans-*position. The structure of the two dyes, which showed high fastness properties on various textile fibers, were confirmed by elemental analysis and* ^{1}*H-NMR, IR and UV–VIS spectra. The molecular weight of the potassium salts was determined by osmometric methods.*

INTRODUCTION

Formazans and their metal complexes are of interest in the area of dye chemistry.[1] The oxidation products of formazans, namely tetrazolium salts, have attracted attention as bio-indicators and the formazans themselves are important in dyeing textile fibers.[2]

The structure of the formazans, which have an N═N—C═N—NH skeleton, was first determined by Bamberger.[3,4] According to the number of formazan groups in each molecule, these compounds are named as formazans or bis(formazans). Tautomerism is extremely important in the

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* This work is supported by the Research Fund of Karadeniz Technical University.

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structure of the formazans and the intramolecular hydrogen bridge is a specific feature of reddish formazans.[5-7]

The diazo-coupling reaction can be carried out under various conditions,[8] and the active methylene groups in compounds such as acetoacetic acid, cyanoacetic acid, malonic acid, nitromethane, benzoylacetone, acetanilide and levulinic acid are especially suitable for coupling reactions under strongly basic conditions.

Fichter & Schiess[9] reported the preparation of formazans with sulfonic acid groups and their alkali salts and also investigated their dye properties. However, the practical application of formazans as dyes was initially described by Ciba Ltd in 1946[10] and the dyeing capability of the copper(II) complexes of formazans with *o*-hydroxy and carboxy substituents was presented for the first time in this patent (see also Ref. 8).

In the present study, two new formazans were synthesized from intermediates (ACP and ANS) which are frequently used in the synthesis of dyes for cotton and wool.

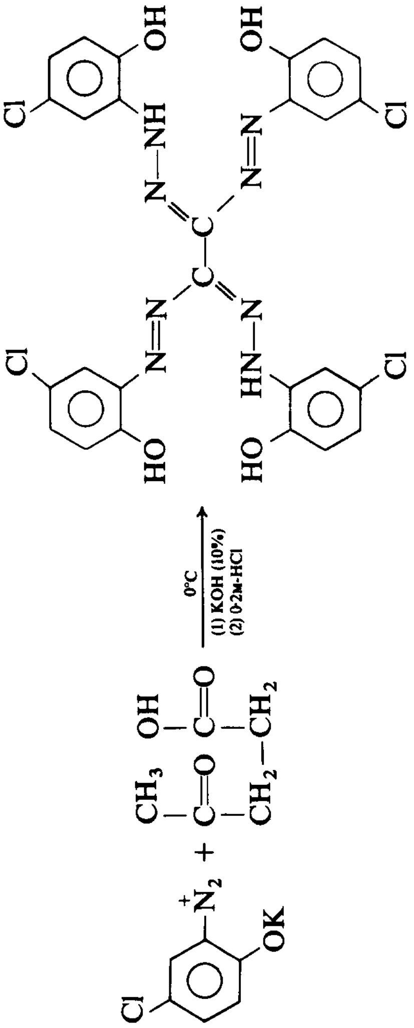
RESULTS AND DISCUSSION

The new formazans prepared by coupling the diazonium salts of 2-amino-4-chlorophenol (ACP) or 1-amino-2-naphthol-4-sulfonic acid (ANS) with levulinic acid under strongly basic conditions at 0°C are analogs of bis(*N*,*N'*-diphenylformazan) (Schemes 1 and 2). The structures of the two bis(formazans) were allocated on the basis of their elemental analysis, ^{1}H-NMR, IR and UV–VIS spectra, and molecular weight determination by osmometric methods.

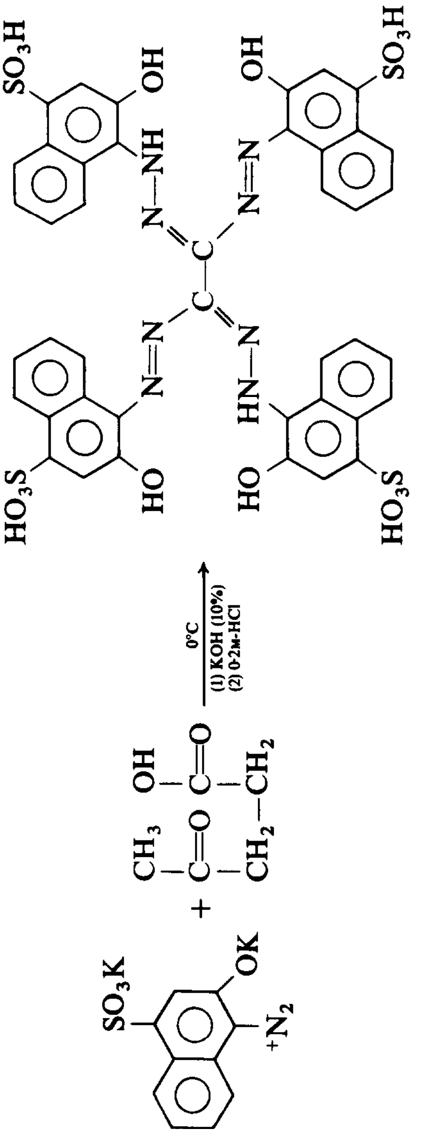
The primary aromatic amine protons of ACP, appearing at 3·50 ppm as a singlet in the ^{1}H-NMR spectrum, disappear after the coupling reaction and the NH protons of the formazan group appear at 7·90 ppm. As a result of tautomerism in the formazan skeleton, this singlet is rather weak.[11] There is no significant shift in the aromatic protons (multiplet) and phenolic protons (singlet) (Table 1). In the case of ANS, the chemical shift of primary aromatic amine at 4·70 ppm also disappears after the coupling reaction and the NH protons of the formazan (DSNF) are observed at 8·40 ppm as a weak band as seen in DCDF. The chemical shifts of the other protons are very similar in both ANS and DCDF (Table 1).

The stretching vibrations of the aromatic amine groups around 3400–3340 cm^{-1} in the IR spectrum of ACP changed into a single band at 3340 cm^{-1} after the coupling reaction.

The formation of C═N and N═N bonds was confirmed by the appearance of characteristic stretching absorptions at 1670 and 1400 cm^{-1}



Scheme 1



Scheme 2

TABLE 1
^{1}H-NMR Chemical Shifts δ (ppm) Data for ACP, ANS, DCDF and DSNF

Compound	*OH*	*NH_2*	*Aromatic H*	*N—H*	*SO_2—OH*
ACP[a]	5·50 (s, 1H)	3·45 (s, 2H)	6·30–6·70 (m, 3H)	—	—
ANS[b]	5·90 (s, 1H)	4·70 (s, 2H)	7·70–8·20 (m, 5H)	—	9·40 (s, 1H)
DCDF[a]	5·45 (s, 4H)	—	6·60–7·20 (m, 12H)	7·90 (s, 2H)	—
DSNF[c]	5·60 (s, 4H)	—	7·60–8·30 (m, 20H)	8·40 (s, 2H)	10·20 (s, 4H)

[a] DMSO-d_6 + $CDCl_3$.
[b] DMSO-d_6 + pyridine-d_5.
[c] DMSO-d_6 + acetone-d_6.

TABLE 2
Characteristic IR Bands of ACP, ANS, DCDF and DSNF (cm^{-1}) (KBr Pellets)

Compound	$\nu(OH)$	$\nu(NH_2)$	$\nu(N{-}H)$	$\delta(NH_2)$	$\nu(C{=}N)$	$\nu(C{-}H)$	$\nu(SO_2{-}OH)$	$\nu(N{=}N)$
ACP	3 140	3 400	—	1 650	—	3 020	—	—
ANS	3 120	3 250	—	1 640	—	3 020	2 650	—
DCDF	3 200	—	3 340	—	1 670	3 030	—	1 400
DSNF	3 220	—	3 370	—	1 660	3 020	2 680	1 430

for DCDF. Even though N═N stretching vibrations are infrared-inactive for symmetrical *trans*-azo compounds, they appear in the 1400–1450 cm^{-1} region for azo-groups.[12] Skeleton vibrations[13] of C—N═N—C or C═N—N—C (CNNC) groups appear at 1000 cm^{-1} in DCDF. The comparison of the absorption frequencies of ACP and DCDF in Table 2 indicates a small shift for ν(OH) and almost identical values of ν(C—H) and ν(C═C).

Whilst $\nu(NH_2)$ vibrations are observed at 3250–3200 cm^{-1} and $\delta(NH_2)$ vibrations at 1640 cm^{-1} in the IR spectrum of ANS, after the formation of bis(formazan) N—H stretches are present at 3370 cm^{-1}. The formation of the bis(formazan) is further confirmed by C═N and N═N stretching vibrations at 1670 and 1430 cm^{-1} respectively. The skeleton vibration of formazan appears at 975 cm^{-1}. The shift of ν(C═N) in formazans is a result of the structure $—N_2C═N—$.[12] The aromatic C—H, C═C, and $—SO_3H$ vibrations had very similar values in both ANS and DSNF.

The UV–VIS spectrum of DCDF in DMF exhibits a peak at 354 nm ($\varepsilon = 7400$) which corresponds to the characteristic $n \rightarrow \pi^*$ transition of azo compounds. This transition varies according to the steric structure of the molecule.[14] Strong absorptions in the UV region follow the results given in the literature.[8,15] The absorption at 268 nm ($\varepsilon = 25\,700$) corresponds to the combination of benzenoid B and phenolic K bands.[16] In the case of DSNF, the $n \rightarrow \pi^*$ transition is observed at 352 nm ($\varepsilon = 5700$) and the combined absorption of the naphthenic E and phenolic K bands is at 280 nm ($\varepsilon = 23\,700$). Both dyes had long-wavelength absorption in the 515 nm and 550 nm regions and their potential use as colorants will be reported later.

EXPERIMENTAL

Bis[*N,N′*-(2,2′-dihydroxy-5,5′-dichlorodiphenyl)]formazan (DCDF)

A mixture of 2-amino-4-chlorophenol (7·175 g, 0·05 mol) and $NaNO_2$ (3·45 g, 0·05 mol) in 125 ml of NaOH solution (5%) was cooled to −5°C and diazolization effected by gradual addition of conc. HCl (14 ml) maintaining the temperature below 0°C. The diazonium solution was then treated with 10% of KOH solution (110 ml) at 0°C and a further 25 ml of 10% KOH solution was then added. A cooled solution of levulinic acid (5·3 g, 0·05 mol) in 125 ml of 10% KOH solution was run into the above diazonium liquor with continuous stirring. During this procedure, the claret-red color of the solution turned to brown and CO_2 was evolved. The reaction mixture was stirred at 0°C for 4 h and the product was precipitated by acidification of the brown solution with 0·2M-HCl. It was filtered, washed with water and then dried. The product was dissolved in ethanol (Norit) and precipitated by the addition of water. This process was repeated to yield the pure product: 7·04 g (87%); m.p. 218°C; soluble in ethanol, pyridine, DMF, DMSO, acetone and dioxane.

$C_{26}H_{18}Cl_4N_8O_4$ requires: C, 48·15; H, 2·9; N, 17·3; Cl, 21·9. Found: C, 48·0; H, 2·6: N, 17·0; Cl, 22·1%.

The calculated molecular weight of the potassium salt ($C_{26}H_{14}Cl_4N_8O_4K_4$) and the value found osmometrically were 800 and 797·8 g mol^{-1} respectively.

UV–VIS λ_{max}(log ε) (in DMF): 554 nm (25 180), 515 nm (24 650), 438 nm (27 200), 354 nm (7400), 298 nm (19 970), 268 nm (24 700), 247 nm (20 140).

Bis[*N,N'*-(2,2'-dihydroxy-4,4'-disulfodinaphthyl)]formazan (DSNF)

1-Amino-2-naphthol-4-sulfonic acid (ANS) (2·39 g, 0·01 mol) was dissolved in 50 ml of 0·2M-NaOH solution and $NaNO_2$ (0·69 g, 0·01 mol) dissolved in 15 ml of water was added. The solution was diazotized by addition of 0·2M-HCl (60 ml), maintaining the temperature below 0°C. The diazonium liquor was treated with cooled 10% KOH (25 ml) solution and 5 ml of the same solution was then added. A cooled solution of levulinic acid (1·06 g, 0·01 mol) 10% KOH (25 ml) was run into the diazonium liquor with continuous stirring. The color of the solution became reddish and CO_2 was evolved. After stirring the mixture for a further 4 h at 0°C, 0·2M-HCl was added to give pH 4·90 and the dark-red formazan was precipitated. This was filtered, washed with water and dried. The product was purified by dissolving it in ethanol (Norit) and precipitating with water. Yield: 1·85 g (72%); m.p. 270°C; soluble in ethanol, pyridine, DMF, acetone and DMSO.

$C_{42}H_{30}N_8O_{16}S_4$ requires: C, 48·9; H, 2·9; N, 10·9; S, 12·4. Found: C, 48·8; H, 2·8; N, 10·65; S, 12·2.

The calculated molecular weight of the potassium salt ($C_{42}H_{22}N_8O_{16}S_4K_8$) and the value found by the osmometric method were 1334 and 1332·2 g mol^{-1} respectively.

UV–VIS λ_{max}(log ε) (in DMF: 554 nm (31 500), 515 nm (12 240), 472 nm (23 400), 435 nm (28 900), 395 nm (22 650), 352 nm (5700), 314 nm (18 400), 280 nm (21 370), 270 nm (20 090).

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