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Synthesis of Aizen Spilon Black TRH and its Derivatives

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ABSTRACT

A series of new azoic coupling components, derivatives of Naphthol AS, have been synthesized by reacting phenyl 3-hydroxy-2-naphthoate with para-substituted anilines. The coupling of Naphthol AS or its derivative with diazotized picramic acid was initially carried out in alkaline aqueous solutions following an original patent procedure. However, all the reactions were incomplete and the azo products were contaminated with the corresponding couplers. This may be due to the low solubility of the couplers in aqueous NaOH solution. Successful coupling reactions were finally achieved, giving pure azo dyes in about 90% yields, by carrying out the reaction in DMF in the presence of sodium acetate. Metallization of the azo dyes with sodium chromium salicylate gave TRH and its derivatives in 60–100% yield.

INTRODUCTION

Organic metal complexes have long been used in electrophotographic applications. For example, certain neutral organic metal complexes are good photoconductors or sensitizers for photoconductors and have been utilized in the fabrication of photoconductive layers.[1] Recently, a class of negatively charged 2:1 azo metal complexes, previously described for application as dyestuffs,[2,3] has been shown to be excellent negative charge control agents (CCA).[4,5] Aizen Spilon Black TRH (TRH for short, shown below), a 2:1 azo dye chromium complex developed by Hodogaya Chemical Co., is one of the most widely used CCAs of the class.[6]

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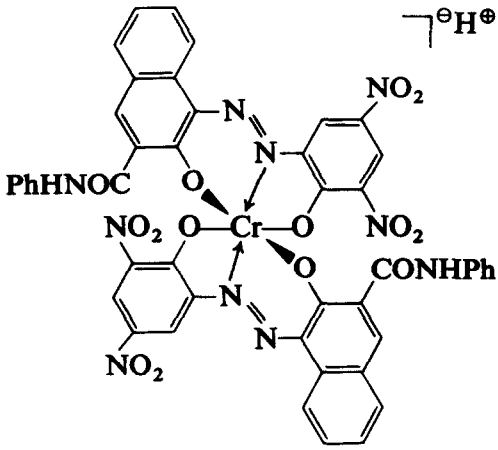


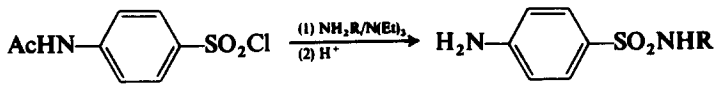
A CCA is added to the toner bulk or onto toner particle surfaces to modify toner charging characteristics. A high level of dispersion for a CCA is needed to ensure optimal charge control performance. However, complexes such as TRH have relatively high melting temperatures and limited solubility in non-polar organic solvents. A high degree of dispersion in a typical non-polar toner resin such as the copolymer of styrene and butyl methacrylate is difficult. This may be the limiting factor for the charge control performance for TRH-like complexes. To improve the processibility of TRH and hence its charge control ability, we decided to prepare derivatives of TRH containing solubilizing groups such as sulfanamides or long chain alkyls. The synthesis of these materials is described in this paper.

RESULTS AND DISCUSSION

Synthesis of naphthol as derivatives

As shown in Scheme 1, several para-substituted anilines (**2a–2f**) were prepared by reacting N-acetylsulfanilyl chloride, **1**, with the respective amines in the presence of triethylamine, followed by acid hydrolysis with 70% sulfuric acid. (Hydrolysis in alkaline solution gave impure products.) The yields were higher than 90% for most cases, except for **2d** and **2e**, which were obtained in 72% and 28% yields, respectively. The very low yield of **2e** was due to the cleavage of *t*-octylsulfanamide groups; large amounts of *t*-octylamine were isolated as the side product during the work-up. No attempt was made to improve the yield by adjusting the condition of hydrolysis. Due to the low yield, **2e** was not used in the subsequent reaction.

The condensation reaction between **2** and **3**, as shown in Scheme 2, was carried out initially in *o*-dichlorobenzene or 1-chloronaphthalene at reflux

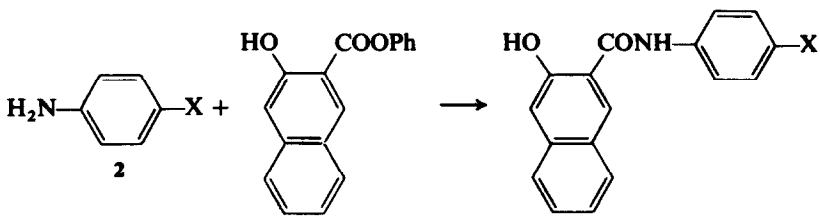


1 2

a	R = —$(CH_2)_2CH_3$
b	—$(CH_2)_4CH_3$
c	—$(CH_2)_7CH_3$
d	—$CH_2CH(CH_2CH_3)[(CH_2)_3CH_3]$
e	—$CH(CH_3)_2CH_2C(CH_3)_3$
f	—$(CH_2)_{15}CH_3$

Scheme 1

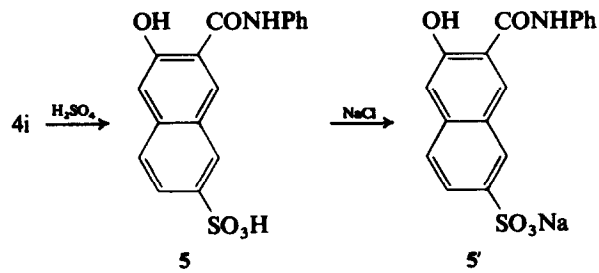
temperature for 3–5 h to give **4**. The crude yields were only ~50%. This is due partly to the solubility of **4** in the chloro-solvents. In addition, the solvents were difficult to remove completely from **4**. To prevent these problems, water miscible N-methyl pyrrolidinone was used as the solvent. The product was isolated by precipitating the reaction mixture into water, followed by filtration and recrystallization. Pure **4a–4d** were readily obtained in *c.* 60% yields. Because of steric effects, compound **2f**, which has the longest alkyl chain, reacted poorly with **3**. The unreacted **2f** and **3** were removed by extracting the crude product mixture with chloroform; pure **4f** was obtained in 39% yield. Under the same conditions, **4g** and **4h** were obtained in 81% and 84% yields, respectively. This result is attributable to the highly nucleophilic amino groups of **2g** and **2h**, which undergo effective condensation reaction with **3**. On the other hand, the electron withdrawing sulfanamide groups of **2a–2d** reduce the nucleophilicity of their amino groups and retard the condensation reaction. This could account for the moderate yields of the corresponding products.



2 3 4

a	X = —$SO_2NH(CH_2)_2CH_3$
b	—$SO_2NH(CH_2)_4CH_3$
c	—$SO_2NH(CH_2)_7CH_3$
d	—$SO_2NHCH_2CH(CH_2CH_3)[(CH_2)_3CH_3]$
e	—$SO_2NHCH(CH_3)_2CH_2C(CH_3)_3$
f	—$SO_2NH(CH_2)_{15}CH_3$
g	—$O(CH_2)_4CH_3$
h	—$(CH_2)_{11}CH_3$
i	—H

Scheme 2

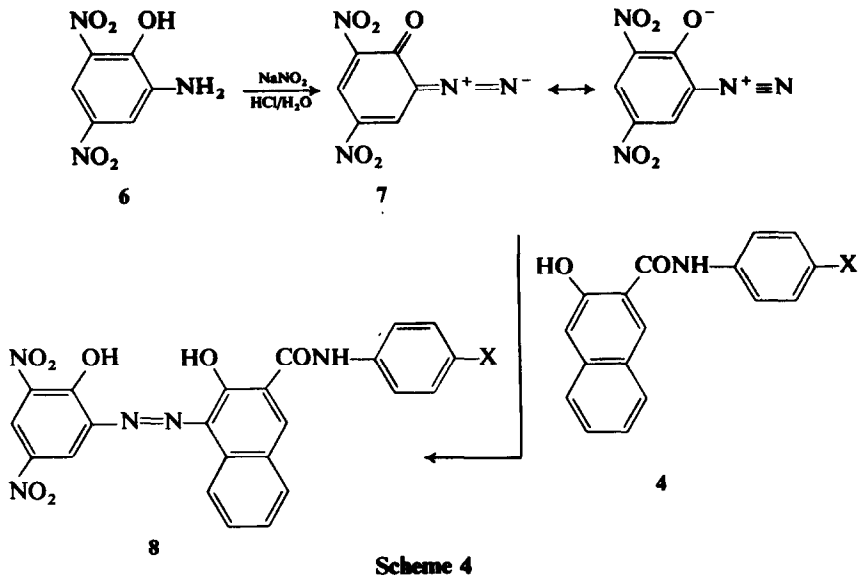


Scheme 3

We were also interested in introducing sulfanamide groups into the naphthalene ring of Naphthol AS, **4i**, via direct sulfonation. Sulfonation of **4i** with concentrated sulfuric acid has been previously reported[7,8] to give **5** (Scheme 3). The object was to convert **5** to the corresponding sulfonyl chloride and then react it with amines to form sulfamide groups. We reinvestigated the sulfonation reaction and found that a by-product, presumably the disulfonated species, was formed at 60–90°C, which were the reaction temperatures reported in the literature. The best result was obtained by heating the mixture of **4i** and H_2SO_4 at 45–50°C for 3–5 h. The sodium salt of **5**, **5'**, was, however, isolated only in low yield (~30%), due largely to the difficulties involved in the work-up and purification. Reaction of **5'** with thionyl chloride gives a mixture of products, according to NMR. This could be due to the reactive C4 site of **4i**, which could attack thionyl chloride or any sulfonyl chloride group derived from **5'**. Because of the many problems, this direct derivatization approach was not investigated further.

Synthesis of azo precursor

According to the original patent,[6] the azo precursor for TRH was prepared from **4i** and diazotized picramic acid (**7**) in water, as shown in Scheme 4. One equivalent of picramic acid (**6**) was diazotized with sodium nitrite in aqueous HCl (3 equivalent) solution to give a dark yellow suspension of **7**. This suspension was then added to the suspension of **4i** (1 equivalent) in aqueous NaOH (3·5 equivalent) solution at 10°C to form the azo dye. We repeated the reaction many times and found that the products were contaminated with unreacted **4i**. Under the same conditions, **4a** and **4b**, which were soluble in the NaOH solution, gave the corresponding products with a small amount of unreacted materials. The products which resulted from **4g** and **4h** showed little solubility in the NaOH solution and were highly contaminated by the respective couplers. These results indicated the importance of complete dissolution of the couplers in aqueous NaOH solution. The solubility of **4i** was improved by heating, the suspension of **4i** turning into a cloudy yellow



Scheme 4

solution on heating. Reaction of the cooled solution with the suspension of **7** gave a product with improved purity. Compounds **4g** and **4h** remained relatively insoluble in boiling NaOH solution and, again, gave highly contaminated products.

It is reasonable that the solubility of a naphthol coupler in NaOH solution will influence the ease of forming the corresponding naphtholate ion, the active entity of the coupling reaction.[9] The hydrophobic alkyl chains of **4g** and **4h** reduce their solubility and thus hinder the generation of the corresponding naphtholate ions. This could explain the incomplete reactions for the couplers. On the other hand, the solubility of **4a** or **4b** is promoted by the additional ionizable proton of the sulfanamide group. The naphtholate ion of **4a** or **4b** can be easily formed, enabling a relatively complete reaction. Diazotized picramic acid, **7**, was isolated as a dark yellow powder. Compound **7** is very stable; no appreciable decomposition was detected by IR even after 1 month at ambient conditions. Because of its high stability, **7** was prepared on a large scale and stored in a freezer in its powder form for ready application. The desired amount of **7** was then weighed, redispersed in water, and added to the alkaline solution or suspension of a coupler to give the azo product. This simplifies considerably the reaction procedure. In addition, **8i** thus obtained, though still containing a trace of **4i**, was pure enough for metallization.

It is to be noted that the structure of **7**, shown in Scheme 4, is given in the resonance forms of quinone diazide and diazophenol zwitterion. This type of resonance structure has been established for many *o*-diazophenols.[10–12]

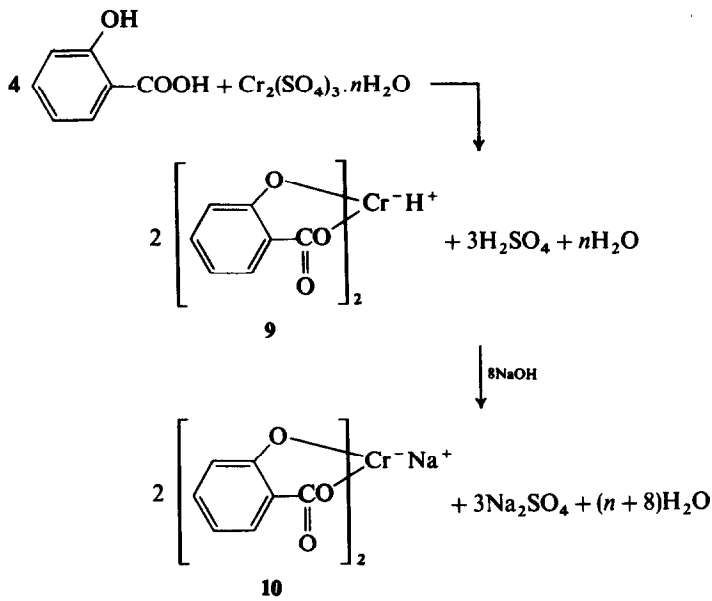
The bond between two nitrogen atoms is between a double bond and a triple bond, and absorbs in the range of 2173–2014 cm^{-1}. This is lower than the $2261 \pm 20\,cm^{-1}$ found normally for aryl diazonium salts.[10–12] The 2200 cm^{-1} peak in the IR spectrum of **7** suggests its quinone diazide structure. The peak at 1641 cm^{-1}, ν(C=O) of the quinone diazide, is lower than the absorptions of conjugated ketone carbonyls (1667–1678 cm^{-1}). This can be attributed to the resonance effect.[10–12] The ^{13}C NMR spectrum of **7** shows the oxygen carbon peak at 164·33 ppm, revealing the partial C=O character. Based on the spectroscopic results, the quinone diazide structure of **7** was assigned. It is to be noted that **7** was first prepared under a different reaction condition by Griess in 1858[10,13] and was the first diazo compound ever isolated.

In order to obtain pure **8**, new reaction conditions were investigated. Pure **8i** was eventually synthesized by reacting the isolated **7** with **4i** in DMF in the presence of sodium acetate. The use of a weak base such as sodium acetate could prevent the formation of diazo hydroxide Ar-N=N-OH. Since **4i** was soluble in DMF, the reaction went to completion and gave pure **8i** quantitatively. In addition, **8i** formed relatively large crystals in DMF, allowing convenient work-up and isolation. This is in contrast to the aqueous reaction where work-up and isolation of **8i** was very difficult, due to its fine crystal sizes. The coupling reaction in DMF is universal as most of the azoic coupling components are soluble in DMF. Under similar conditions, **8a–8d** and **8f–8h** were prepared in excellent yields (80–100%) and purities.

Synthesis of sodium chromium salicylate

Chromium salts of chelating organic acids, such as salicylic acid, oxalic acid and the like, are among the best reagents for the preparation of 2:1 chromium complexes of azo dyes.[2] The use of such complexes has a two-fold advantage. First, the difficulty of displacing strongly coordinated water from the hydrated chromium(III) ion is removed. Therefore, 2:1 chromium azo complexes can be prepared under relatively mild conditions. Second, the reaction can be carried out at high pH values without precipitation of chromium hydroxide, so that the desired chromium complexes can be isolated in high purities.

Sodium chromium salicylate (**10**, Scheme 5) is one of the most popular metallizing agents and was used for the preparation of TRH.[6] However, the preparation of **10** was not disclosed in the TRH patent. We found from early patents that **10** was generally obtained in an aqueous alkaline solution and was used *in situ* without isolation.[14–16] This may be due to difficulty in isolating the pure **10**. As a result, the physical properties of its salts have rarely been described. The synthesis of **10** is outlined in Scheme 5. Four equivalents of salicylic acid were heated with $Cr_2(SO_4)_3 . nH_2O$ ($n = 7$–8) in



Scheme 5

water to form **9** and H_2SO_4. The mixture of **9** was then treated with a large excess of aqueous NaOH (15 equivalents, only 8 equivalents are needed according to the equation) solution to give a green suspension, instead of a green solution reported in the patents. This presents a problem because the amount of **10** needed for the metallization reaction cannot be measured accurately from the suspension. To prevent this problem, water was evaporated from the suspension to give a green powder, code name Cr-1. Its Cr content was 6·6% according to elemental analysis, lower than the calculated value of 8·1%. This may be due to water association. Alternatively, the mixture of **9** was treated with 12 or 8 equivalents of NaOH, followed by evaporation of water to give the green powders, Cr-2 or Cr-3, respectively. The former still contained excess NaOH, the latter did not. Their respective Cr contents were 8·0% and 9·4%, in good agreement with the calculated values of 8·7% and 9·3%. With the known Cr concentrations, one can readily calculate the amount of the reagent needed for a metallization reaction.

The IR spectra for Cr-1 and Cr-2 were almost identical with a strong carbonyl peak at 1602 cm^{-1} and a medium sulfate peak at 1142 cm^{-1}. On the other hand, a strong sulfate peak at 1183 cm^{-1} was observed for Cr-3.

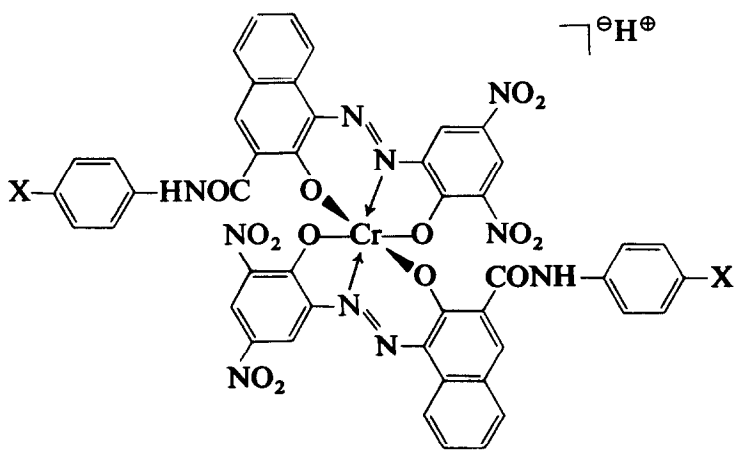
Synthesis of Spilon Black TRH

Initially, Cr-1 was used as the metallizing agent. One equivalent of **8i** was reacted with ~0·6–0·7 equivalent, calculation based on the percentage of

chromium(III), of Cr-1 in ethylene glycol at 110–115°C for 2 h to give the corresponding complex with Na^+ as the counter ion. The complex was washed thoroughly with 5% aqueous NaOH solution until washes had become almost colorless. The washed powder was treated with 1% HCl to give TRH in about 60% yield. The moderate yield was attributed initially to the weak alkaline strength of Cr-1. Therefore, a small amount of NaOH was added in the next experiment. Unexpectedly, the black powder obtained showed a completely different IR spectrum from that of TRH. This result indicated that the added NaOH could cause unknown side reactions under the described reaction conditions.

Cr-3, which is relatively neutral, was used to react with **8i** with or without the use of sodium acetate. There were no obvious differences in terms of purity and the yields (60–70%) among the TRHs derived from the different chroming agents. However, the reaction using Cr-3 in the presence of sodium acetate gave the highest yield of 81%.

It has been reported that sodium salts of *o,o'*-dihydroxyazo dyes react more rapidly with the metallizing agent.[2] In many practices, the sodium salts of the dyes were used to react with chromium salicylate to form the corresponding azo chromium complexes.[14–16] The use of sodium acetate may assist the formation of the sodium salt of **8i** and may thus improve the yield.



X = —H	**TRH**
—$SO_2NH(CH_2)_2CH_3$	**TRH3**
—$SO_2NH(CH_2)_4CH_3$	**TRH5**
—$SO_2NH(CH_2)_7CH_3$	**TRH8**
—$SO_2NHCH_2CH(CH_2CH_3)[(CH_2)_3CH_3]$	**TRH8A**
—$SO_2NH(CH_2)_{15}CH_3$	**TRH16**
—$SO_2NH(CH_2)_4CH_3$	**TRH5A**
—$(CH_2)_{11}CH_3$	**TRH12**

The derivatives of TRH (shown below) were prepared accordingly from the respective azo precursors in about 70–100% yields. All the complexes were obtained in good purities, 95%+ according to elemental analyses. A code name is assigned for each complex. The number associated with the code name denotes the number of carbon atoms on the alkyl side chain, while the letter A is used to prevent conflict between two complexes having the same carbon atoms on the alkyl chains. All the TRH derivatives, except TRH5A, are reasonably soluble in polar solvents such as acetone and methanol, but they are not soluble in less polar solvents such as ethyl acetate, chloroform and dichloromethane.

In conclusion, we have developed a convenient and versatile procedure for the synthesis of TRH and its derivatives. These compounds were obtained in high yields and purities.

EXPERIMENTAL

Instrumentation

All melting points were taken with a Haake Buchler melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1750 Fourier transform spectrometer and are given in cm^{-1}. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. UV–IR spectra were recorded on a Hewlett–Packard 8451A diode array spectrophotometer. Solution ^{13}C NMR spectra were recorded on a Bruker CXP spectrometer operating at 50·3 MHz in a Cryomagnet Systems, Inc. superconducting magnet system.

Materials

N-Acetylsulfanilyl chloride, phenyl 3-hydroxy-2-naphthoate and Naphthol AS were from Aldrich. Picramic acid was from Tokyo Chemical Industry Co. All the chemicals were used as received.

N^1-*n*-Propylsulfanilamide (2a) (general procedure)

A mixture of acetone (40 ml), propylamine (4 g, 0·07 mol) and triethylamine (6 g, 0·06 mol) was cooled to about 5°C, and compound **1** (11·7 g, 0·05 mol) was then gradually added. (A brown product was obtained when **1** was added too quickly.) A precipitate of $NH(Et)_3Cl$ formed during the addition. The resulting mixture was stirred for 10 min and placed in a refrigerator overnight. The mixture was poured into water (400 ml) with vigorous

stirring. The solid, the N^4-acetyl derivative of **2a**, namely N^4-acetyl-N^1-propylsulfanilamide, was collected by filtration and treated with 70% H_2SO_4 (50 ml). (70% H_2SO_4 was prepared by gradually adding conc. H_2SO_4, 300 ml, to 225 g of ice-water.) The mixture was heated to 120°C for 1 h and then cooled. The resulting mixture was poured into water (300 ml). The solution was cooled with ice-water and then neutralized by gradually adding conc. NH_4OH. The pale precipitate was collected by filtration, washed with small portions of water, and air dried to give crude **2a** (10 g, 93%): m.p. 83–85°C (lit.[17] m.p. 85°C); IR 3411 (m), 3341 (m), 3248 (m), 3148 (m), 2961 (m), 2934 (w), 2875 (w), 1636 (m), 1598 (s), 1500 (m), 1142 (s), 1094 (s), 678 (m), 546 (s).

N^1-*n*-Pentylsulfanilamide (2b)

This was obtained analogously from **1** (23·3 g, 0·1 mol), pentylamine (9·6 g, 0·11 mol) and triethylamine (12·0 g, 0·12 mol), followed by acid hydrolysis. The crude yield was 23·4 g (97%) and crude **2b** showed: m.p. 127°C; IR 3412 (m), 3336 (m), 3244 (m), 3149 (m), 2958 (m), 2932 (m), 2858 (m), 1632 (m), 1598 (s), 1501 (m), 1306 (s), 1144 (s), 1096 (s), 680 (m), 547 (s).

N^1-*n*-Octylsulfanilamide (2c)

This was obtained analogously from **1** (11·7 g, 0·05 mol), *n*-octylamine (6·5 g, 0·05 mol) and triethylamine (6·0 g, 0·06 mol), followed by acid hydrolysis. The crude yield was 13·0 g (91%) and the crude **2c** showed: m.p. 119–120°C (lit.[18] m.p. 114–119·5°C); IR 3409 (m), 3337 (m), 3248 (m), 3137 (m), 2956 (m), 2927 (s), 2855 (m), 1634 (m), 1598 (s), 1500 (m), 1304 (s), 1142 (s), 1096 (s), 679 (m), 546 (s).

N^1-(2-Ethylhexyl)sulfanilamide (2d)

This was prepared analogously from **1** (23·0 g, 0·1 mol), 2-ethylhexylamine (13·0 g, 0·1 mol) and triethylamine (12 g, 0·12 mol), followed by acid hydrolysis. The crude yield was 21 g (72%) and the crude **2d** showed: m.p. 139–142°C; IR 3412 (m), 3341 (m), 3248 (m), 3147 (m), 2960 (m), 2930 (m), 2873 (m), 2860 (m), 1632 (m), 1597 (s), 1501 (m), 1304 (m), 1143 (s), 1095 (s), 681 (m), 548 (s).

N^1-(1,1,3,3-Tetramethylbutyl)sulfanilamide (2e)

The N^4-acetyl derivative of **2e** (29·5 g, 90%) was prepared analogously from **1** (23·0 g, 0·1 mol), *t*-octylamine (14·0 g, 0·1 mol) and triethylamine (12 g,

0·12 mol). Hydrolysis was carried out in 50% H_2SO_4 (150 ml) at 70°C for 3 h. To the resulting solution was added 100 g of ice and it was then cooled with an ice-water bath. Sodium hydroxide (30 g) was added gradually, followed by addition of conc. NH_4OH to give pH = 8. The precipitate was collected and air dried to give crude **2e** (14·3 g) with a very broad melting point (166–185°C). Recrystallization twice from chlorobenzene/DMF (200 ml/15 ml) gave **2e** as pale crystals (8 g, 28%): m.p. 167–169°C; IR 3479 (m), 3377 (s), 3321 (m), 3269 (m), 3245 (m), 1628 (m), 1597 (s), 1505 (m), 1313 (s), 1149 (s), 1095 (m), 828 (m), 740 (m), 697 (m), 562 (m), 543 (m). (The yield may be improved under a milder hydrolysis condition.)

N^1-*n*-Hexadecylsulfanilamide (2f)

The N^4-acetyl derivative of **2f** was prepared from **1** (26 g, 0·11 mol), *n*-hexadecylamine (36 g, 0·15 mol) and triethylamine (14 g, 0·14 mol) in acetone (350 ml) following the general procedure. The acetyl derivative was added to 70% H_2SO_4 (200 ml) and the mixture refluxed for 2 h and cooled. (Stirring should be avoided to prevent severe foaming during the hydrolysis.) Work-up, as described in the general procedure, gave **2f** as a pale powder (44 g, 100%): m.p. 110–116°C; IR 3413 (w), 3333 (w), 3225 (w), 3118 (w), 2920 (s), 2851 (s), 1630 (w), 1597 (m), 1307 (m), 1144 (m), 1096 (m).

4′-(Propylsulfamido)-3-hydroxy-2-naphthanilide (4a) (general procedure)

A mixture of **3** (5 g, 0·019 mol), **2a** (5 g, 0·023 mol) and N-methyl-pyrrolidinone (10 ml) was refluxed for 5 h and allowed to stand overnight at room temperature. The solidified mixture was poured into water (300 ml) and the resulting mixture was stirred vigorously to break up the large solid pieces. The powder was collected by filtration and air dried to a brown powder (7·5 g). This crude product, which contained traces of starting materials according to TLC, was recrystallized from chlorobenzene and vacuum dried overnight (70°C) to give pure **4a** (4·7 g, 65%): m.p. 182–185°C; IR 3279 (br, m), 2966 (m), 2934 (w), 2876 (w), 1663 (m), 1629 (m), 1592 (s), 1533 (s), 1323 (s), 1157 (s). Anal. calcd for $C_{20}H_{20}N_2O_4S$: C 62·50, H 5·21, N 7·29. Found: C 62·53, H 5·65, N 6·79.

4′-(*n*-Pentylsulfamido)-3-hydroxy-2-naphthanilide (4b)

This was prepared analogously from **2b** (10 g, 0·04 mol) and **3** (10 g, 0·038 mol) in N-methylpyrrolidinone (10 ml). The yield of **4b** was 10 g (64%) and it showed: m.p. 181–185°C; IR 3283 (br, m), 3059 (w), 2957 (m), 2931 (m), 2876

(w), 1663 (s), 1629 (m), 1592 (s), 1533 (s), 1326 (s), 1156 (s). Anal. calcd for $C_{22}H_{24}N_2O_4S$: C 64·08, H 5·83, N 6·80. Found: C 63·48, H 6·04, N 6·31.

4′-(*n*-Octylsulfamido)-3-hydroxy-2-naphthanilide (4c)

This was prepared analogously from **2c** (12 g, 0·042 mol) and **3** (10·5 g, 0·038 mol) in N-methylpyrrolidinone (10 ml). The yield of **4c** was 11·5 g (64%) and it showed: m.p. 191–195°C; IR 3281 (br, m), 2926 (m), 2855 (m), 1663 (s), 1629 (m), 1592 (s), 1533 (s), 1324 (s), 1156 (s). Anal. calcd for $C_{25}H_{30}N_2O_4S$: C 66·08, H 6·61, N 6·17. Found: C 65·23, H 6·57, N 5·66.

4′-(2-Ethylhexylsulfamido)-3-hydroxy-2-naphthanilide (4d)

This was prepared analogously from **2d** (11 g, 0·04 mol) and **3** (10 g, 0·038 mol) in N-methylpyrrolidinone (10 ml). The yield of **4c** was 10·5 g (60%) and it showed: m.p. 220–223°C; IR 3296 (br, m), 3059 (w), 2959 (m), 2929 (m), 2872 (m), 1664 (s), 1629 (m), 1591 (s), 1533 (s), 1327 (s), 1156 (s). Anal. calcd for $C_{25}H_{30}N_2O_4S$: C 66·08, H 6·61, N 6·17. Found: C 66·15, H 6·79, N 6·13.

4′-(*n*-Hexyldecylsulfamido)-3-hydroxy-2-naphthanilide (4f)

A mixture of **2f** (15 g, 0·042 mol), **3** (10 g, 0·038 mol) and N-methylpyrrolidinone (20 ml) was heated at reflux for 7 h. The resulting mixture, solidified after standing overnight at room temperature, was transferred into an aqueous 5% Na_2CO_3 solution (500 ml). The mixture was stirred for 3 h. The solid was collected by filtration and air dried. The dried product was Soxhlet extracted with $CHCl_3$ overnight to remove the unreacted starting materials. The remaining solid was collected and air dried to give 5·2 g (24%) of **4f**. Additional product (2 g, 9%), which crystallized from the cooled $CHCl_3$ solution, was isolated. The obtained product showed: m.p. 201–203°C; IR 3285 (br, m), 2920 (s), 2851 (s), 1647 (m), 1630 (m), 1611 (m), 1597 (m), 1555 (m), 1536 (m), 1322 (m), 1157 (s). Anal. calcd for $C_{33}H_{46}N_2O_4S$: C 69·96, H 8·13, N 4·95. Found: C 69·10, H 8·03, N 4·34.

4′-(*n*-Pentoxy)-3-hydroxy-2-naphthanilide (4g)

This was prepared according to the general procedure from **2g** (8 g, 0·044 mol) and **3** (10 g, 0·038 mol) in N-methylpyrrolidinone (10 ml). Compound **4g** (11 g, 81%) was obtained as a dark green powder and it showed: m.p. 201–203°C; IR 3294 (w), 3078 (m), 2958 (m), 2933 (m), 2872 (w), 1640 (s), 1624 (s), 1568 (s), 1512 (s), 1252 (m). Anal. calcd for $C_{22}H_{23}NO_3$: C 75·64, H 6·59, N 4·01. Found: C 75·45, H 7·12, N 3·99.

4′-(*n*-Dodecyl)-3-hydroxy-2-naphthanilide (4h)

This was prepared according to the general procedure from **2h** (10 g, 0·038 mol) and **3** (9·5 g, 0·038 mol) in N-methylpyrrolidinone (10 ml). Compound **4h** (13·2 g, 84%) was obtained as a pale powder and it showed: m.p. 170–172°C; IR 3310 (w), 3055 (br, m), 2922 (s), 2852 (s), 1637 (s), 1624 (s), 1559 (m). Anal calcd for $C_{29}H_{37}NO_2$: C 80·74, H 8·58, N 3·25. Found: C 80·53, H 8·74, N 2·80.

Sodium 3-hydroxy-7-sulfo-naphtholate anilide (5′)

A mixture of conc. H_2SO_4 (250 ml) and **4i** (60 g, 0·23 mol) was heated at 45–50°C for 3 h. After cooling, the black solution was poured into crushed ice (2000 g). The aqueous mixture was stirred overnight and centrifuged. The aqueous layer was decanted and the solid was transferred into a beaker containing water (1500 ml) and NaCl (300 g) added. Large amounts of precipitate formed immediately. The solution was heated to boiling with stirring for 2 h. After cooling, the mixture was centrifuged and the solid was heated in boiling saturated brine (1000 ml) until neutral pH. After cooling, the solid was filtered, washed with brine and vacuum dried to give 93 g of product. This was added to boiling DMF (200 ml) and the remaining solid, which was mainly NaCl, was filtered off while hot. Upon cooling, **5′** crystallized. This was collected and vacuum dried to give **5′** (28 g, 34%) as a white powder: IR 3700–2900 (br, w), 1670 (s), 1642 (s), 1625 (s), 1599 (s), 1562 (s), 1495 (m), 1445 (m), 1328 (m), 1195 (s), 1109 (m), 1045 (s). Anal. calcd for $C_{17}H_{12}NNaO_5S$: C 55·87, H 3·29, N 3·84, Na 6·30, S 8·77. Found: C 54·28, H 3·82, N 3·71, Na 5·63, S 8·78.

4,6-Dinitro-1,2-benzoquinone-2-diazide (7)

A mixture of **6** (20 g, 0·1 mol) and conc. HCl (30 g, 0·3 mol) and water (400 ml) was cooled to *c.* 5–10°C. An aqueous solution of sodium nitrite (8 g in 40 ml water) was added dropwise and the resulting mixture was stirred for 2–3 h to give a dark yellow suspension. The solid was filtered and air dried to give **7** (21 g, 85%) as a dark yellow powder.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-3-hydroxy-2-naphthanilide (8i)

Method I: A mixture of **4i** (4·7 g, 0·018 mol) and NaOH solution (2·0 g in 60 ml water) was heated with stirring until a yellow cloudy solution was obtained. This was cooled to ~10°C (or lower). A mixture of **7** (4·5 g, 0·02 mol) in 200 ml water was then gradually added and the resulting mixture

stirred for 5 h. The black solid was filtered. (This was a very slow process. Centrifuging allowed faster work-up.) The collected product was washed at least three times with water (*c.* 1000 ml each time) until the water layer became clear. The washed product was filtered to give **8i** (4·6 g, 54%). The moderate yield was due to loss of material during the work-up. This product, though containing traces of unreacted **4i** according to TLC, was pure enough for metallization.

Method II (general procedure): A mixture of **4i** (3·9 g, 0·015 mol) and 70 ml DMF was cooled to *c.* 10°C with stirring. A solution of **7** (3·6 g, 0·017 mol) in DMF (50 ml) was then added all at once. To the resulting dark purple mixture was added sodium acetate solution (7·5 g in 12 ml water). The mixture was stirred at room temperature for 3 h and quenched with ice-water (400 g). The precipitate was filtered and washed by stirring in water (400 ml each time) until a light color wash obtained. The black powder was vacuum dried overnight to give pure **8i** (7·0 g, 100%): m.p. >300°C; UV–IR (DMF) $\lambda_{max} = 574$ nm; IR 3440 (br, m), 3098 (w), 1657 (m), 1603 (s), 1550 (s), 1496 (s), 1476 (s), 1448 (s), 1325 (s), 1327 (s), 1177 (s), 1154 (s), 1018 (m). Anal. calcd for $C_{23}H_{15}N_5O_7 . 3H_2O$: C 52·37, H 3·98, N 13·28. Found: C 52·26, H 3·63, N 13·37.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-4″-(propylsulfamido)-3-hydroxy-2-naphthanilide (8a)

This product (4·7 g, 78%) was obtained analogously from the following reactants: **4a** (3·9 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF (50 ml) and sodium acetate (5 g) in water (10 ml). (It was difficult to isolate **8a** by filtration because it was a very fine powder. Some product was lost during isolation. This can account for the lower yield of **8a** as compared with that of **8i**. It may be possible to improve the yield by centrifuge.) The **8a** obtained showed: UV–IR (DMF) $\lambda_{max} = 570$ nm; IR 3700–3000 (br), 2966 (w), 2934 (w), 2876 (w), 1666 (m), 1604 (s), 1592 (m), 1535 (s), 1498 (s), 1475 (s), 1448 (s), 1403 (m), 1324 (s), 1275 (s), 1154 (s). Anal. calcd for $C_{26}H_{22}N_6O_9S . 2H_2O$: C 49·52, H 4·13, N 13·33. Found: C 49·78, H 3·98, N 12·91.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-4″-(pentylsulfamido)-3-hydroxy-2-naphthanilide (8b)

This product (4·9 g, 79%) was obtained analogously from the following reactants: **4a** (4·1 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF (50 ml) and sodium acetate (5 g) in water (10 ml). (Some product was lost during isolation because **8b** was also a fine powder.) The **8b** obtained showed: UV–IR (DMF) $\lambda_{max} = 570$ nm; IR 3700–3000 (br), 2955 (w), 2931

(w), 2860 (w), 1668 (m), 1605 (s), 1535 (s), 1498 (s), 1475 (s), 1448 (s), 1403 (m), 1324 (s), 1275 (s), 1153 (s). Anal. calcd for $C_{28}H_{26}N_6O_9S.2H_2O$: C 51·06, H 4·56, N 12·77. Found: C 51·61, H 4·49, N 12·56.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-4″-(*n*-octylsulfamido)-3-hydroxy-2-naphthanilide (8c)

This compound (6·7 g, 100%) was obtained analogously from the following reactants: **4c** (4·6 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF (50 ml) and sodium acetate (5 g) in water (10 ml). Compound **8c** showed: UV–IR $\lambda_{max} = 576$ nm; IR 3700–3000 (br, w), 2926 (m), 2855 (w), 1669 (m), 1605 (s), 1592 (s), 1535 (s), 1498 (s), 1474 (s), 1449 (s), 1403 (m), 1325 (s), 1275 (s), 1155 (s). Anal. calcd for $C_{31}H_{32}N_6O_9S.2H_2O$: C 53·14, H 5·14, N 12·00. Found: C 53·51, H 4·79, N 11·95.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-4″-(2-ethylhexylsulfamido)-3-hydroxy-2-naphthanilide (8d)

This compound (6·7 g, 100%) was obtained analogously from the following reactants: **4d** (4·6 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF (50 ml) and sodium acetate (5 g) in water (10 ml). Compound **8d** showed: IR 3700–3000 (br, w), 2958 (m), 2928 (m), 2859 (w), 1672 (m), 1606 (s), 1592 (s), 1537 (s), 1497 (s), 1475 (s), 1449 (s), 1403 (m), 1324 (s), 1274 (s), 1154 (s). Anal. calcd for $C_{31}H_{32}N_6O_9S.2H_2O$: C 53·14, H 5·14, N 12·00. Found: C 52·94, H 4·69, N 11·92.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-4″-(*n*-hexadecylsulfamido)-3-hydroxy-2-naphthanilide (8f)

This product (6·6 g, 84%) was obtained analogously from the following reactants: **4f** (5·8 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF (50 ml) and sodium acetate (5 g) in water (10 ml). Compound **8f** showed: IR 3700–3000 (br, m), 2924 (s), 2853 (s), 1656 (m), 1592 (s), 1536 (s), 1499 (s), 1469 (s), 1449 (s), 1403 (m), 1325 (s), 1275 (s), 1155 (s). Anal. calcd for $C_{39}H_{48}N_6O_9S.2H_2O$: C 57·64, H 6·40, N 10·34. Found: C 57·94, H 6·02, N 10·09.

4-[(3′-5′-Dinitro-2′-hydroxybenzene)azo]-4″-(pentoxy)-3-hydroxy-2-naphthanilide (8g)

This compound (5·7 g, 100%) was obtained analogously from the following reactants: **4g** (3·6 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF

(50 ml) and sodium acetate (5 g) in water (10 ml). Compound **8g** showed: UV–IR $\lambda_{max} = 582$ nm; IR 3600–3000 (br, w), 2928 (m), 2869 (w), 1662 (m), 1605 (s), 1551 (s), 1511 (s), 1496 (s), 1475 (s), 1449 (s), 1391 (w), 1325 (s), 1313 (s), 1271 (s), 1250 (s), 1176 (s), 1153 (s). Anal. calcd for $C_{28}H_{25}N_5O_8 . 2H_2O$: C 56·47, H 4·87, N 11·76. Found: C 56·61, H 4·77, N 11·89.

4-[(3′,5′-Dinitro-2′-hydroxybenzene)azo]-4″-(*n*-dodecyl)-3-hydroxy-2-naphthanilide (8h)

This product (6·4 g, 100%) was obtained analogously from the following reactants: **4h** (4·3 g, 0·01 mol) in DMF (50 ml), **7** (2·5 g, 0·01 mol) in DMF (50 ml) and sodium acetate (5 g) in water (10 ml). Compound **8h** showed: UV–IR $\lambda_{max} = 564$ nm; IR 3700–3000 (br, w), 2924 (s), 2853 (m), 1652 (m), 1605 (s), 1576 (m), 1551 (s), 1496 (s), 1476 (s), 1449 (s), 1415 (m), 1326 (s), 1275 (s), 1177 (s), 1154 (s). Anal. calcd for $C_{35}H_{39}N_5O_7 . 2H_2O$: C 62·04, H 6·35, N 10·34. Found: C 61·87, H 6·35, N 10·34.

Sodium chromium salicylate

A mixture of salicylic acid (13·8 g, 0·1 mol), $Cr_2(SO_4)_3 . nH_2O$ (13·5 g, 0·025 mol) and water (30 ml) was heated (*c.* 105°C) to boiling for 30 min. Foaming was controlled by temporarily removing the flask from the heat source. A relatively homogeneous green mixture was obtained. The mixture was cooled to about 50°C and 30% NaOH (50, 35 or 28 g) was added. Water was removed from the resulting dark green solution by heating at 70°C with stirring until a viscous residue was obtained. This was dried further in vacuum at 50°C overnight. The dried product was ground into a powder to give Cr-1 (31 g), Cr-2 (33 g) or Cr-3 (29 g) depending on the amount of NaOH used. The Cr contents for each sample were 6·6%, 8·04% or 9·44%, respectively.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH)

General procedure I

A mixture of Cr-1 (1·0 g) and ethylene glycol (10 ml) was stirred and heated to form a deep green solution. Compound **4i** (1·0 g, from the DMF reaction) was then added and the resulting mixture was heated at 100–115°C for 2 h. The hot mixture was poured into ice-water (150 ml) and the black solid was filtered, washed with water, and added to aqueous 1% HCl solution (100 ml). After stirring for 1 h, the solid was collected and vacuum dried overnight at 50°C to give a black powder (1·1 g). This material was further purified by

washing with 5% NaOH (3 × 100 ml), acidified with 1% HCl and vacuum dried to give TRH (0·6 g, 60%): UV–IR (DMF) $\lambda_{max} = 582$ nm; IR 3700–3000 (br, w), 1657 (m), 1596 (s), 1549 (s), 1495 (s), 1459 (s), 1382 (w), 1361 (m), 1329 (s), 1290 (s), 1262 (m), 1231 (w), 1203 (s), 1153 (s), 1116 (w), 1078 (w), 754 (m). Anal. calcd for $C_{46}H_{27}N_{10}O_{14}Cr.5H_2O$: C 50·88, H 3·41, N 12·90, Cr 4·79. Found: C 51·02, H 3·61, N 11·54, Cr 4·88.

General procedure II

A mixture of Cr-3 (1·2 g), sodium acetate trihydrate (1·5 g) and ethylene glycol (30 ml) was heated to 60°C with stirring. Compound **4i** (1·4 g) was added and the mixture heated at 110–120°C for 2 h. The hot mixture was poured into ice cold 5% NaOH solution (200 ml). After stirring for 5 min the precipitate was filtered and the product was slurried in 5% NaOH solution (3 × 250 ml). The washed product was then stirred into water (300 ml), conc. HCl (3 ml) added and the mixture stirred for 5 min before filtering. The product was dried in a vacuum oven at 50°C overnight to give TRH (1·2 g, 81%). This material showed identical UV–IR and IR to those described above.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(propylsulfamido)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH3)

This was prepared by reacting **8a** with Cr-3 following the general procedure II. However, the crude product was soluble in 5% NaOH solution and could not be purified by-washing with the alkaline solution. No addition effort was made to purify it.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(*n*-pentylsulfamido)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH5)

This compound (0·9 g, 68%) was obtained according to the general procedure II from the following reagents: **8b** (1·3 g), Cr-3 (0·9 g) and sodium acetate (1 g) in ethylene glycol (25 ml). TRH5 showed: IR 3700–3000 (br, w), 2955 (w), 2930 (w), 2869 (w), 1677 (w), 1594 (s), 1529 (s), 1495 (m), 1459 (s), 1420 (w), 1403 (w), 1382 (w), 1361 (m), 1329 (s), 1290 (s), 1230 (m), 1204 (s), 1154 (s). Anal. calcd for $C_{56}H_{49}N_{12}S_2Cr.H_2O$: C 51·25, H 3·73, N 12·81, Cr 3·96. Found: C 51·29, H 4·23, N 11·94, Cr 4·43.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(*n*-octylsulfamido)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH8)

This product (1·0 g, 70%) was obtained according to the general procedure II from the following reagents: **8c** (1·3 g), Cr-3 (0·9 g) and sodium acetate (1 g) in

ethylene glycol (25 ml). TRH8 showed: UV–IR (DMF) $\lambda_{max} = 576$ nm; IR 3600–3000 (br, m, peak at 3275), 2972 (m), 2856 (w), 1677 (w), 1593 (s), 1531 (s), 1496 (m), 1459 (s), 1419 (w), 1403 (w), 1382 (w), 1360 (m), 1329 (s), 1290 (s), 1264 (m), 1230 (m), 1203 (s), 1154 (s). Anal. calcd for $C_{62}H_{61}N_{12}O_{18}S_2Cr.H_2O$: C 53·33, H 4·52, N 12·04, Cr 3·72. Found: C 53·17, H 4·80, N 11·00, Cr 3·93.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(2-ethylhexylsulfamido)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH8A)

This compound (1·1 g, 74%) was obtained according to the general procedure I from the following reagents: **8d** (1·3 g), Cr-1 (0·9 g) and sodium acetate (1 g) in ethylene glycol (25 ml). TRH8A showed: IR 3700–3000 (br, w, peak at 3287), 2958 (w), 2928 (m), 2871 (w), 1677 (w), 1594 (s), 1531 (s), 1496 (m), 1459 (s), 1420 (w), 1403 (w), 1382 (w), 1361 (m), 1329 (s), 1291 (s), 1231 (m), 1203 (s), 1154 (s). Anal. calcd for $C_{62}H_{61}N_{12}O_{18}S_2Cr.5H_2O$: C 50·72, H 4·84, N 11·45, Cr 3·54, S 4·36. Found: C 50·72, H 5·04, N 11·45, Cr 4·83, S 4·30.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(*n*-hexyldecylsulfamido)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH16)

This compound (1·5 g, 91%) was obtained according to the general procedure I from the following reagents: **8f** (1·3 g) and Cr-1 (1·1 g) in ethylene glycol (30 ml). TRH16 showed: IR 3700–3000 (br, w, peak at 3274), 3101 (w), 2924 (s), 2852 (s), 1681 (m), 1593 (s), 1531 (s), 1496 (m), 1459 (s), 1420 (w), 1403 (w), 1381 (w), 1360 (m), 1328 (s), 1290 (s), 1264 (m), 1230 (m), 1202 (s), 1154 (s). Anal. calcd for $C_{78}H_{93}N_{12}O_{18}S_2Cr.5H_2O$: C 55·94, H 6·16, N 10·04, Cr 3·11, S 3·83. Found: C 55·94, H 6·21, N 9·51, Cr 2·87, S 4·09. (Trace of starting **8d** was detected on TLC.)

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(*n*-pentoxy)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH5A)

This product (1·5 g, 100%) was obtained according to the general procedure I from the following reagents: **8h** (1·4 g) and Cr-1 (1·4 g) in ethylene glycol (30 ml). TRH5A showed: UV–IR (DMF) $\lambda_{max} = 578$ nm; IR 3700–3100 (br, w, peak at 3286), 3096 (w), 2955 (w), 2932 (w), 2870 (w), 1652 (m), 1595 (s), 1548 (s), 1529 (s), 1511 (s), 1458 (s), 1417 (w), 1381 (w), 1361 (m), 1329 (s), 1290 (s), 1252 (s), 1232 (s), 1202 (s), 1153 (s). Anal. calcd for $C_{56}H_{47}N_{10}O_{16}Cr.6H_2O$: C 52·70, H 4·62, N 10·98, Cr 4·14. Found: C 52·80, H 4·59, N 9·77, Cr 5·18.

Bis{4-[(3′,5′-dinitro-2′-hydroxybenzene)azo]-4″-(*n*-dodecyl)-3-hydroxy-2-naphthanilide} chromate (-1) hydrogen (TRH12)

This compound (1·5 g, 100%) was obtained according to the general procedure I from the following reagents: **8h** (1·3 g) and Cr-1 (1·2 g) in ethylene glycol (30 ml). TRH12 showed: UV–IR (DMF) $\lambda_{max} = 578$ nm; IR 3700–3100 (br, w, peak at 3285), 3098 (w), 2924 (s), 2853 (s), 1651 (m), 1596 (s), 1531 (s), 1493 (m), 1459 (s), 1415 (w), 1360 (m), 1331 (s), 1289 (s), 1262 (m), 1230 (m), 1203 (s), 1153 (s). Anal. calcd for $C_{70}H_{75}N_{10}O_{14}Cr \cdot 6H_2O$: C 58·37, H 6·04, N 9·72, Cr 3·61. Found: C 57·05, H 5·63, N 8·26, Cr 4·97.

REFERENCES

1. Kosche, H. H. In *Current Problems in Electrophotography*, ed. W. F. Berg & K. Hauffe. Walter de Gruyter, Berlin, New York, 1972, p. 310.
2. Price, R. In *The Chemistry of Synthetic Dyes*, Vol. III, ed. K. Venkataraman. Academic Press, New York, 1970, p. 303 and references therein.
3. Zollinger, H., *Color Chemistry*. VCH, New York, 1987, pp. 120–30 and references therein.
4. Gregory, P., *Dyes and Pigments*, **7** (1986) 1.
5. Gruber, R. J., SID International Symposium Digest of Technical Papers, Vol. XVIII, New Orleans, Louisiana, 1987, p. 272.
6. US Patent 4 433 040.
7. German Patent 397 313.
8. Dziewonski, R. & Loewenhof, A., *Bull. Intern. Acad. Polonaise*, **A** (1927) 521 (CA, 1928, 2560).
9. Putter, R., *Angew. Chem.*, **63** (1951) 188.
10. Saunders, K. H. & Allen, R. L. M., *Aromatic Diazo Compounds*. Edward Arnold, London, Baltimore, 1985, p. 42 and references therein.
11. Bellamy, L. J., *The Infra-red Spectra of Complex Molecules*, Vol. I. John Wiley, New York, 1975, p. 304 and references therein.
12. Le Febre, R. J. W., Sousa, J. B. & Werner, R. L., *J. Chem. Soc.*, **1954**, 4686.
13. Griess, P., *Ann. Chim.*, **106** (1858) 123.
14. US Patent 2 565 898.
15. British Patent 637 404.
16. British Patent 756 874.
17. Mangini, A., *Atti Accad. Italia, Rend. Classe Sci. Fis., Mat. Nat. [7]*, **1** (1940) 452 (CA, 1943, 98).
18. Crossley, M. L., Northey, E. H. & Hultquist, M. W., *J. Am. Chem. Soc.*, **62** (1940) 532.