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The Preparation and Characterization of New Thioanthraquinone Dyes

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SUMMARY

A synthetic route to derivatives of 1,8-dihydroxy-2,7-diisobutyl-4-thioaryl-anthraquinones and 1,5-dihydroxy-2,6-diisobutyl-4-thioarylanthraquinones is described. The new red and purple dyes are fully characterized. The effect of the substituents of the thiophenoxy group on the color of the dyes is correlated to the Hammett σ values of the substituents.

INTRODUCTION

The color of an anthraquinone dye is related to the chemical nature and position on the anthraquinone of substituents known as 'auxochromes' which are, traditionally, groups such as hydroxy, alkoxy, aryloxy, amino, alkyl- and aryl-amino, or halogens.[1] The thioalkyl and thioaryl groups have been added to this series of auxochromes, to generate new dyes used mostly as colorants in liquid crystal displays or as textile dyes. Anthraquinones having one to four thioaryl groups as the only auxochromes have been synthesized[2–4] (Table 1). Their colors range from yellow to red and no blues or greens can be obtained using such a structural basis. The preparation of such thioanthraquinones is based on a nucleophilic replacement of a halogen or nitro substituent with a mercaptan in the presence of a base.

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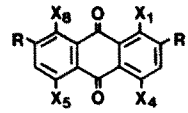
Taking advantage of the difference in reactivity between the nitro and halogen groups it is possible to prepare unsymmetrical bis-, tris-, and tetrakis-phenylthioanthraquinones. For example, reaction of 1,4-dichloro-5-nitroanthraquinone with *p*-chlorothiophenol at 40°C leads to 1,4-dichloro-5-(*p*-chlorothiophenoxy)-anthraquinone which in turn is converted to 1,4-[di-(*p*-*tert*-butylthiophenoxy)]-5-(*p*-chlorothiophenoxy)-anthraquinone by reaction with *p*-*tert*-butylthiophenol at 120°C. The color of the dye is related to the number of thiophenoxy substituents and their positional isomerism. However, chemical substituents on the thiophenoxy groups themselves do not influence strongly the color of the dyes. Only minor changes in color shades have been reported to occur when the thiophenoxy ring substituents are effective electron-withdrawing or electron-donating groups. When thiol-substituted heterocycles, such as mercaptobenzothiazoles, were linked to the anthraquinone framework brown dyes were obtained.[5]

The thiophenoxy group can also be used in conjunction with other auxochromes in the anthraquinone molecule and this enables a much broader spectrum of colors to be attained. The first extensive study of the preparation and uses of such anthraquinones was disclosed in a 1962 patent to Ciba.[7] Over 15 chromophores ranging from lemon yellow to dark blue were prepared by substitution of halogens with a thiophenol in the presence of a strong base (Table 1). The dyes were used as vat dyes for cotton or disperse dyes for poly(ethylene terephthalate). At about the same time Bayer disclosed the preparation of two new violet–blue anthraquinones substituted with thiophenoxy groups, 1,8-dihydroxy-5-nitro-4-thiophenoxyanthraquinone and 1,8-dihydroxy-5-amino-4-thiophenoxyanthraquinone.[8]

Recently, pleochroic dyes based on thioanthraquinones have been prepared.[9-14] Of particular interest are 4-arylamino-1,5-dihydroxy-8-thiophenoxyanthraquinone and 4-arylamino-1,8-dihydroxy-5-thiophenoxyanthraquinone, the colors of which range from blue to green, the green color resulting from the replacement of the phenylamino group with a *p*-phenylazophenylamino group. Small changes in the shade of the dyes are reported as a function of the substitution pattern of the thiophenoxy and arylamino groups. A few anthraquinones possessing two thiophenoxy groups together with other auxochromes have been reported. Examples of such dyes are the bluish-violet anthraquinones, 1,8-dihydroxy-4,5-di-(thiophenoxy)-anthraquinones, 1,5-dihydroxy-4,8-di-(thiophenoxy)-anthraquinones, and 1,4-dihydroxy-5,8-di-(thiophenoxy)-anthraquinones.[11] Effects of the substitution pattern of the anthraquinone nucleus on the color of the dye are described in a qualitative manner, as well as small effects due to changes in the substitution of the thiophenoxy ring.

We report here the preparation of new thioanthraquinone dyes in which

TABLE 1



X_1	X_4	X_5	X_8	R	*Color*[a]	*Reference*
SAr	H	H	H	H	Yellow	2, 3
SAr	H	SAr	H	H	Yellow	2, 3
SAr	SAr	H	H	H	Red	2, 3
SAr	SAr	SAr	H	H	Red	2, 3
Cl	H	SAr	H	H	Lemon yellow	5
NO_2	H	SAr	H	H	Greenish yellow	5
NHR	H	SAr	H	H	Orange	5
OH	OH	SAr	H	H	Orange	5
NHR	SAr	NHR	H	H	Red–brown	5
OH	NHAr	SAr	OH	H	Dark blue	5
NH_2	SAr	NH_2	H	H	Ruby red	5
SAr	SAr	NH_2	H	H	Pink	5
OH	SAr	NH_2	OH	H	Violet	6
OH	SAr	NO_2	OH	H	Violet–blue	6
OH	SAr	OH	NO_2	C_8H_{17}	NR	2
OH	SAr	OH	NH_2	C_8H_{17}	NR	2
OH	SAr	NH_2	OH	$C_{12}H_{25}$	NR	2
OH	SAr	NO_2	OH	$C_{12}H_{25}$	NR	2
OH	SAr	NHCOR	NHR	H	Turquoise	9
OH	SAr	NH_2	NHR	H	NR	9
OH	SAr	NHR	OH	H	NR	7
OH	SAr	OH	OH	H	Purple	10, 11
OH	SAr	OH	NHR	H	Green–blue	7
NHAr	SAr	NHAr	SAr	H	Blue–violet	5
OH	SAr	OH	SAr	H	Navy blue	5
OH	SAr	SAr	OH	$C_{12}H_{25}$	NR	2
OH	SAr	SAr	OH	H	Bluish violet	11
OH	OH	SAr	SAr	H	Reddish violet	11

NR, Not reported.

the anthraquinone nucleus bears alkyl substituents in addition to the thiophenoxy group. These dyes combine the excellent solubility characteristics of the alkylated anthraquinones with the color-tuning capability of the thiophenoxy substituent. The new red and purple dyes were synthesized by nucleophilic replacement of nitro groups with mercaptans or thiophenoxides, starting from dialkylated nitroanthraquinones. They were characterized by IR and ^{1}H-NMR spectroscopy. The effect of substituents of the thiophenoxy group on the color of the dyes was investigated and correlated to the Hammett σ-values of the substituents.

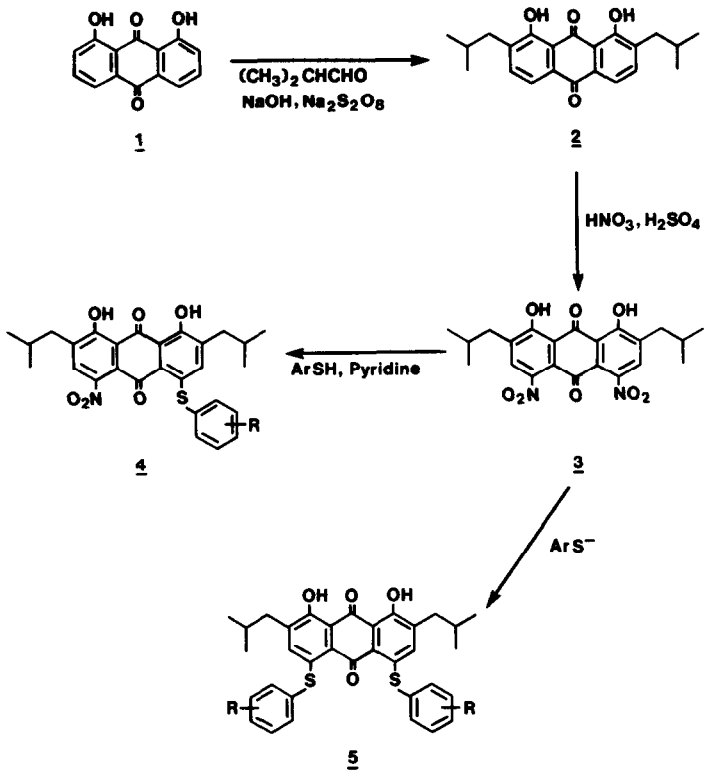
RESULTS AND DISCUSSION

Preparation of the dyes

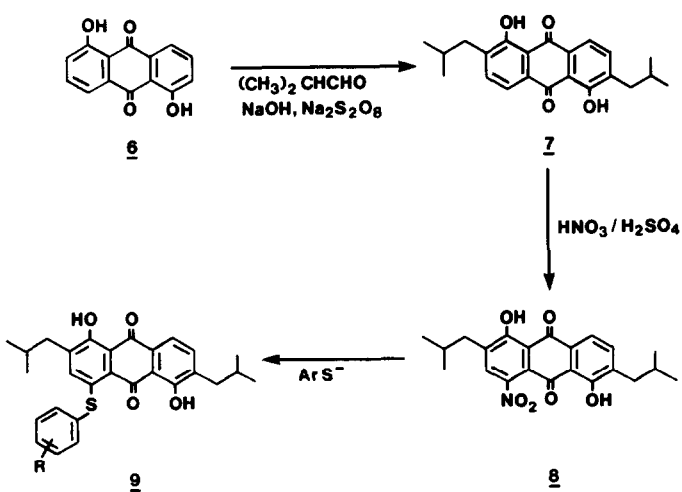
The overall synthetic routes are outlined in Schemes 1 and 2. The dialkylation was performed by reaction of isobutyraldehyde with leuco-dihydroxyanthraquinones in alkaline and reductive medium. This reaction, first reported by Marshalk,[15] results in regiospecific alkylation *ortho* to the hydroxy groups. Starting from either 1,5-dihydroxyanthraquinone or 1,8-dihydroxyanthraquinone the reaction gave acceptable yields, provided that all the starting materials were pure. Particular attention had to be paid to the purity of isobutyraldehyde and of the reducing agent, sodium hydrosulfite (for the titration of sodium dithionite, see Ref. 16). The second step of each synthesis involved the nitration of the isomeric dialkyl-dihydroxyanthraquinones **2** and **7**. Hydroxyanthraquinones are known to be nitrated easily (see for example Ref. 17), and in general α-hydroxy groups direct nitration to the *ortho* and *para* positions. Since in compounds **2** and **7** both *ortho* positions are substituted, only the *para* positions can be nitrated. As expected, 1,8-dihydroxy-2,7-di-isobutylanthraquinone, when nitrated at room temperature, gave a single compound, identified as 1,8-dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone (**3**). Under identical conditions, 1,5-dihydroxy-2,6-di-isobutylanthraquinone gave the corresponding dinitro compound. Selective mononitration was achieved by lowering the strength of the nitrating mixture and decreasing the reaction temperature to ~0°C. In all three nitrations boric acid was added to control side-reactions.

The key step in each synthesis involved the replacement of the nitro group with a mercaptan. In the case of the mononitrated anthraquinone **8** the substitution was performed by treatment of **8** with a thiophenoxide prepared by reaction of potassium hydroxide with the mercaptan prior to the substitution. Since the thiophenoxide is an excellent nucleophile, the substitution of the nitro group was effected in quantitative yields in a short period of time. Structure **9** (R = H) was assigned to the red dye obtained with benzenethiol on the basis of its spectroscopic properties, in particular the presence of C–S stretching bands in the IR at 800–600 cm^{-1}. The ^{1}H-NMR spectrum of **9** (R = H), discussed in detail in the next section, corroborated the structural assignment.

We then investigated the feasibility of selective substitution of a single nitro group of 1,8-dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone (**3**) with a mercaptan. The substitution reaction was performed first under the conditions described previously, but with only one equivalent of reactive mercaptan. In this case the reaction led always to a mixture of mono- and di-thio compounds, together with unreacted starting material. In order to



Scheme 1.



Scheme 2.

prevent disubstitution the reaction had to be carried out under milder conditions. For most aryl mercaptans monosubstitution was accomplished successfully by treatment of **3** with one equivalent of the mercaptan in the presence of an amine such as pyridine, at room temperature. However under these conditions cyclohexylmercaptan was unreactive. The substitution required preliminary preparation of the cyclohexylthioxide, which was reacted with **3** in isopropanol at 45°C. The reaction was quenched as soon as some product of disubstitution was detected by TLC. Only a modest yield of the desired mono-substituted compound was achieved.

^{1}H-NMR spectra of the dyes

The 80 MHz ^{1}H-NMR spectra of 1,5-dihydroxy-2,6-di-isobutyl-4-thiophenoxyanthraquinone (**9**, R = H) and 1,8-dihydroxy-2,7-di-isobutyl-4-nitro-5-(3′-*p*-methoxy)-thiophenoxyanthraquinone (**4**, R = *p*-MeO) are shown in Figs 1 and 2. They are typical of the two classes of compounds and several features of the spectra useful to confirm the structure of the dyes are apparent. The presence of two isobutyl substituents on the anthraquinone framework is evidenced by characteristic signals in the high-field region. For example, in the spectrum of **9**, R = H, there are two six-proton doublets (*J* 6·5 Hz) at 0·78 and 0·96 ppm, assigned to the isobutyl methyl protons. Two two-proton doublets (*J* 7 Hz) at 2·38 and 2·66 ppm are due to the resonances of the benzylic methylene protons. A complex two-proton multiplet between

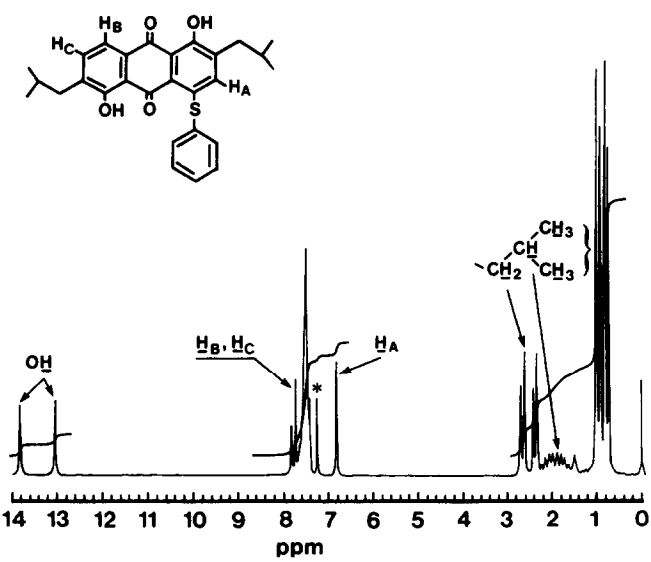


Fig. 1. ^{1}H-NMR spectrum of 1,5-dihydroxy-2,6-di-isobutyl-4-thiophenoxyanthraquinone (**9**, R = H).

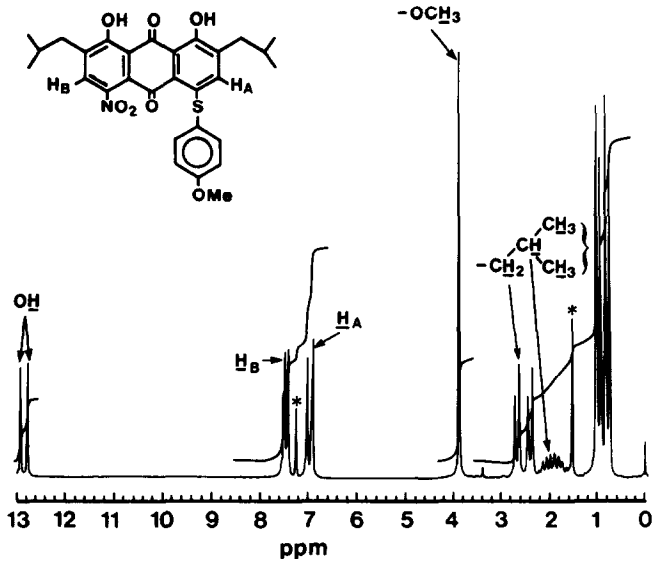


Fig. 2. ^{1}H-NMR spectrum of 1,8-dihydroxy-2,7-di-isobutyl-4-nitro-5-(4'-methoxythiophenoxy)anthraquinone (**4**, R = OMe).

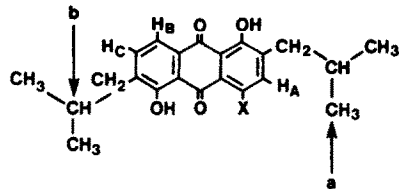
1·6 and 2·2 ppm is attributed to the two methine protons. In the aromatic region, the thiophenoxy protons resonate as an undefined five-proton multiplet. The three anthraquinoid protons resonances appear as two distinct signals. The proton *ortho* to the sulfide H_A resonates as a broad singlet at 6·80 ppm, as expected from the fact that it only undergoes long-range coupling with the isobutyl methylene protons. The two aromatic protons H_B and H_C appear as an AB quartet, of which only one part is visible (at 7·46 and 7·75 ppm); the second part is obscured by the thiophenoxy protons resonances. Two exchangeable singlets at 13·79 and 13·00 ppm are assigned to the phenolic protons. The exceptionally low-field position of resonances of these protons reflects the occurrence of intramolecular hydrogen bonds between the hydroxyl groups and the carbonyl groups. The spectrum of **4**, R = *p*-OMe (Fig. 2) presents similar features. The chemical shifts of all compounds synthesized are listed in Tables 2 and 3.

Visible absorption spectra of the dyes

A specific object of this study was to examine the influence of the thiophenoxide structure on the color of the red anthraquinone chromophores. It was expected that by changing the nature of the substituent R of the thiophenoxy ring one could modify slightly the absorption spectrum of the chromophore. Only a small effect was anticipated since the thiophenoxy substituent does not enter in direct conjugation with the anthraquinone

TABLE 2

Chemical Shift Values for the 1,5-Dihydroxy-2,6-di-isobutylanthraquinones (ppm)



X	CH_3		CH_2		*OH*	*OH*	H_A	H_B, H_C[a]
	a	*b*	*a*	*b*				
H	0·95	0·95	2·63	2·63	13·08	13·08	7·46, 7·75	7·46, 7·75
NO_2	0·98	1·02	2·70	2·62	13·12	13·58	7·40	7·58, 7·74
SPh	0·78	0·96	2·38	2·66	13·00	13·79	6·80	7·46, 7·74
SPh-*p*-Br	0·84	1·00	2·44	2·68	13·00	13·80	6·88	—[c]
SPh-*p*-OMe	0·80	0·98	2·42	2·68	13·08	13·82	6·82	—[c]
SPh-*m*-NH_2	0·84	0·98	2·44	2·68	13·10	13·86	—[c]	7·54, 7·78
SC_6H_{11}	0·98	1·02	2·68	2·68	13·08	13·94	7·40	7·48, 7·78
SPh-*m*-Cl	0·84	1·00	2·44	2·68	12·98	13·80	6·94	7·78[b]
SPh-*p*-Cl	0·84	0·98	2·44	2·72	13·00	13·82	6·84	7·80[b]
SPh-*p*-NO_2	0·84	0·98	2·48	2·68	12·86	13·80	6·92	8·26[b]
SPh-*t*-Bu	0·78	0·98	2·40	2·68	13·08	13·82	6·78	7·76[b]

[a] AB quartet (*J* 7·7 Hz).

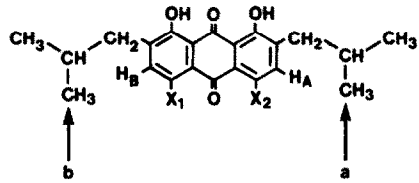
[b] Part of the AB quartet; the rest is obscured by the thiophenoxy protons.

[c] Masked by the thiophenoxy protons.

itself. The exact magnitude of this effect was unknown. Indeed all the dyes having the 1,5-dihydroxy-2,6-di-isobutyl-4-thiophenoxyanthraquinone chromophore were red, but their shade varied from orange red to cherry red in solution or in polymer films. The 1,8-dihydroxy-2,7-di-isobutyl-4-nitro-5-thiophenoxyanthraquinone chromophore also covered a range of shades, in this case from red to purple, as a result of shifts in maximum absorbance wavelength upon changes of the thiophenoxy ring substituent. In Figs 3 and 4 are presented the visible absorption spectra of the two series of dyes. The maximum absorbance wavelengths exhibit a bathochromic shift with substituents R of increasing electron-donating properties (see Tables 4 and 5, Experimental Section). This effect is emphasized on a plot of the changes of absorption energy as a function of the Hammett σ-values[18] (Fig. 5). The relationship between σ-values of the thiophenoxy substituent and the energy (or wavelength of absorption) can be used to predict the color of dyes with a specific substituent R, provided that its σ-value is known. The feature can be very useful if one wants to change solubility properties of dyes without altering their color.

TABLE 3

Chemical Shift Values for the 1,8-Dihydroxy-2,7-diisobutylanthraquinones (ppm)



X_1	X_2	CH_3		CH_2		OH	OH	H_B	H_A
		b	*a*	*a*	*b*				
H	H	0·95	0·95	2·62	2·62	12·37	12·37	7·47	7·75[a]
NO_2	NO_2	1·00	1·00	2·70	2·70	12·30	12·50	7·64	7·64[a]
NO_2	SPh	0·98	0·78	2·39	2·68	12·78	12·92	—[b]	6·90
NO_2	SPh-*p*-Br	0·98	0·82	2·42	2·68	12·70	12·88	—[b]	6·92
NO_2	SPh-*p*-OMe	0·98	0·79	2·41	2·68	12·74	12·92	7·48	6·90
NO_2	SC_6H_{11}	0·98	0·98	2·68	2·68	12·88	12·88	7·50	7·47
NO_2	SPh-*m*-Cl	0·99	0·82	2·45	2·65	12·80	12·88	—[b]	6·92
NO_2	SPh-*p*-Cl	1·00	0·82	2·44	2·70	12·74	12·90	7·50	6·90
NO_2	SPh-*p*-NO_2	0·98	0·82	2·48	2·70	12·72	12·85	7·71	7·00
NO_2	SPh-*t*-Bu	0·96	0·78	2·40	2·70	12·76	12·92	—[b]	6·84
SPh	SPh	0·78	0·78	2·39	2·39	12·98	12·98	6·88	6·88
SPh-*p*-F	SPh-*p*-F	0·85	0·85	2·48	2·48	13·00	13·00	6·84	6·84

[a] AB quartet.

[b] Masked by thiophenoxy protons.

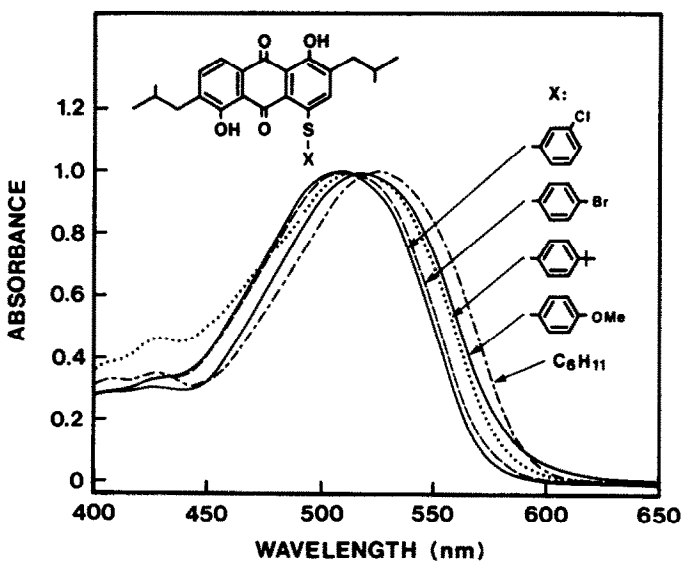


Fig. 3. Visible absorption spectra of the red dyes of general structure **9**.

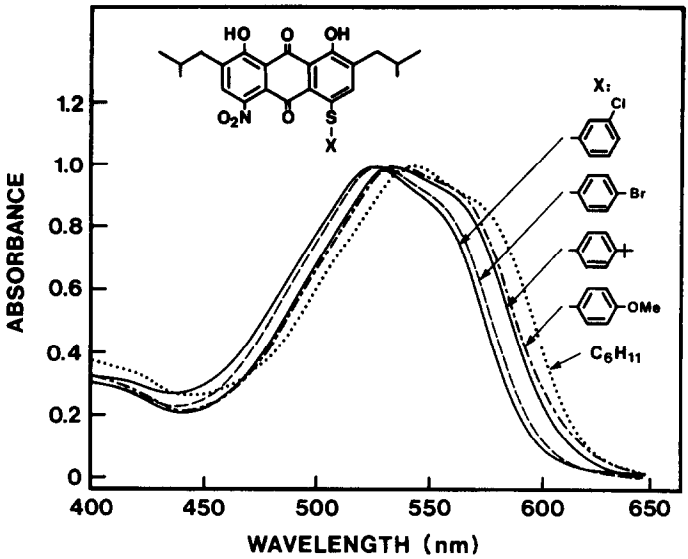


Fig. 4. Visible absorption spectra of the purple dyes of general structure **4**.

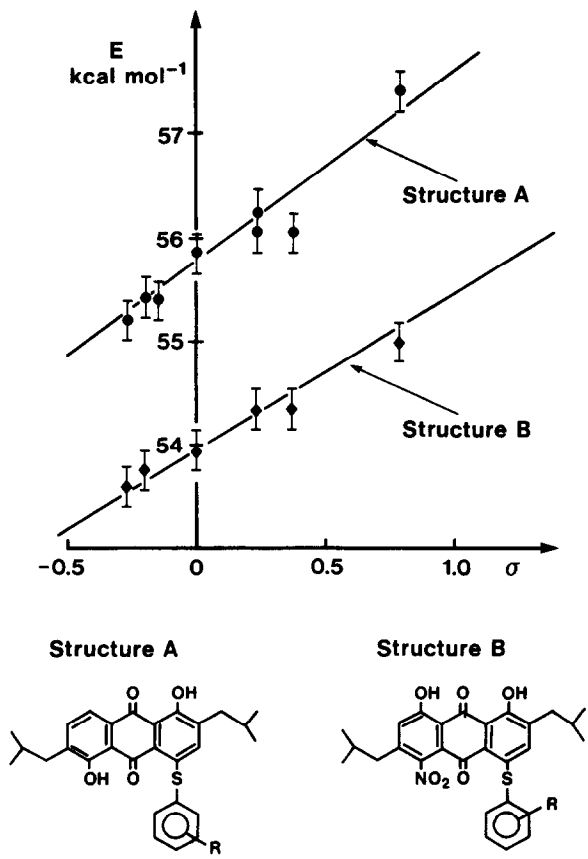


Fig. 5. Hammett plot of the absorbance maxima for the two series of red dyes.

TABLE 4
Preparation of 1,5-Dihydroxy-2,6-di-isobutyl-5-thiophenoxyanthraquinones (**9**): Summary of the Reaction Conditions

Mercaptan	*Solvent*	*Reaction time*	*Temperature* (°C)	*Yield* (%)
Benzenethiol	Isopropanol	30 min	50	85
4-*t*-Butylbenzenethiol	Isopropanol	1 h	50	76
4-Bromobenzenethiol	Isopropanol	45 min	50	93
4-Chlorobenzenethiol	Isopropanol	3·5 h	76	85
3-Chlorobenzenethiol	Isopropanol	1 h	50	95
4-Nitrobenzenethiol	Isopropanol	1·8 h	110	42
4-Methoxybenzenethiol	Isopropanol	1·5 h	44	60
4-Aminobenzenethiol	Isopropanol	45 min	50	59
Cyclohexyl mercaptan	Isopropanol	1·3 h	45	51

Properties of 1,5-Dihydroxy-2,6-di-isobutyl-4-thiophenoxyanthraquinones (**9**)

R	*M.p.* (°C)	*m/z* (M^+)	λ_{max} (*nm*)	ε	*Solvent of recrystallization*
Phenyl	175–176	460	512	14 000	Ethyl acetate
4-*t*-Butylphenyl	161–164	516	516	13 000	Ethyl acetate
4-Bromophenyl	210–211	540	510	15 000	Ethyl acetate
4-Chlorophenyl	204–207	496	510	16 000	Ethyl acetate
3-Chlorophenyl	185–186	496	508	14 200	Ethyl acetate
4-Nitrophenyl	202–207	505	498	13 700	Methoxyethanol
4-Methoxyphenyl	197–199	490	518	16 100	Ethyl acetate
3-Aminophenyl	180–182	475	516	14 000	Methanol/acetone, 5/1 v/v
Cyclohexyl	172–176	468	524	13 000	Methoxyethanol

EXPERIMENTAL

Equipment

^{1}H-NMR spectra were recorded at 80 MHz with a Bruker WP-80 spectrometer. ^{13}C-NMR spectra were recorded at 20·1 MHz with a Bruker WP-80 spectrometer. The spectra were run in chloroform-d containing 0·1% TMS as internal standard. IR spectra were taken with an IR 4250 Beckman spectrophotometer. The samples were dispersed in KBr pellets. UV–visible spectra were recorded with a Hewlett Packard 8450A diode array spectrometer. Unless otherwise stated the solvent was dichloromethane. Mass spectra were recorded in a Finnigan-MAT Model 4500 quadrupole mass spectrometer. Samples were introduced through a heated solid probe

TABLE 5
Preparation of 1,8-Dihydroxy-2,7-di-isobutyl-4-nitro-5-thiophenoxyanthraquinones (**4**): Summary of the Reaction Conditions

Mercaptan	*Solvent*	*Reaction time*	*Temperature* (°C)	*Yield* (%)
Benzenethiol	Pyridine	30 min	25	83
4-*t*-Butylbenzenethiol	Pyridine	15 min	25	94
4-Bromobenzenethiol	Pyridine	40 min	25	99
4-Chlorobenzenethiol	Pyridine	2 h	25	88
3-Chlorobenzenethiol	Pyridine	2 h	25	88
4-Nitrobenzenethiol	Pyridine	2 h	100	18
4-Methoxybenzenethiol	Pyridine	20 min	100	90
Cyclohexyl mercaptan	Isopropanol	4 h	45	50

Properties of 1,8-Dihydroxy-2,7-di-isobutyl-4-nitro-5-thiophenoxyanthraquinones (**4**)

R	*M.p.* (°C)	*m/z* (M^+)	λ_{max} (*nm*)	ε	*Solvent of recrystallization*
Phenyl	231–232	505	530	16000	Methoxyethanol
4-*t*-Butylphenyl	220–222	561	532	16000	Methanol
4-Bromophenyl	233–234	585	526	13400	Methoxyethanol
4-Chlorophenyl	193–196	541	526	12200	Methanol
3-Chlorophenyl	233–238	541	526	12200	Methanol
4-Nitrophenyl	215–217	550	520	11600	Methanol
4-Methoxyphenyl	232–234	535	536	14400	Ethyl acetate
Cyclohexyl	232–237	511	542	7000	Ethanol

inlet system. Typical scan ranges were 60–650 a.m.u. over 2 s. Spectra were calibrated against FC43 using an Incor 2000 data system. Elemental analyses were performed by Canadian Microanalytical Service, New Westminster, BC, Canada.

1,8-Dihydroxy-2,7-di-isobutylanthraquinone (2)

A mixture of 1,8-dihydroxyanthraquinone (200·0 g, 0·833 mol; Aldrich Chemicals), water (1·7 litres), sodium hydroxide (294·0 g, 7·35 mol) in water (300 ml) and sodium dithionite (356·0 g, 2·0 mol, freshly opened) was stirred under nitrogen. The deep red solution was heated to 50°C and isobutyraldehyde (200·0 g, 2·8 mol; Aldrich Chemicals, Gold Label) was added dropwise over 2 h. At the end of the addition the temperature was increased to 70°C over 1 h, then to 85°C and was maintained for 17 h. The reaction mixture was tested for the presence of starting material by TLC on

silica gel plates eluted with toluene. If after 17 h starting material was detected, sodium dithionite and isobutyraldehyde were added to the reaction mixture kept at 70°C. When completion of the reaction was ascertained, the reaction vessel was opened to the air, cooled to 40°C and air was bubbled in for 1·5 h. The reaction mixture was then cooled to room temperature and its pH brought to ~8 by addition of dilute hydrochloric acid (1/1 v/v concentrated HCl/water). The mixture thus obtained was cooled in an ice bath for 2 h and filtered to give reddish-brown pellets which were washed with water (2 litres). These were slurried in water (2 litres) and on acidification to pH 2 with concentrated HCl the product became yellow. The mixture was stirred for 1 h, and filtered. After drying in an air oven overnight, the product (244 g) was recrystallized from ethyl acetate/glacial acetic acid (2 litres, 95/5 v/v) to give **2** as fine orange needles (180·6 g, 62%); m.p. 139–140°C (138–140°C);[3] $\lambda_{max}(CH_2Cl_2)$ 440 nm, ε 14 000; ν_{max}(KBr) 2980 (m), 2890 (w), 1680 (m), 1625 (s), 1435 (s), 1300 (s), 1270 (s), 1055 (m), 750 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 0·95 (d, 12H, *J* 7·5 Hz) 1·80–2·25 (m, 2H), 2·62 (d, 4H, *J* 7 Hz), 7·47, 7·75 (AB-q, 4H, *J* 7·6 Hz), 12·37 (s, D_2O exchangeable) ppm; ^{13}C-NMR ($CDCl_3$) δ 22·5, 28·4, 39·1, 115·4, 119·3, 131·9, 137·9, 138·4, 161·1, 181·7, 193·9 ppm.

1,5-Dihydroxy-2,6-di-isobutylanthraquinone (7)

Compound **7** was prepared from 1,5-dihydroxyanthraquinone (Pfaltz and Bauer, unpurified) following the procedure described for 1,8-dihydroxy-2,7-di-isobutylanthraquinone; TLC eluant, hexanes/acetone 4/1 v/v; yield 76%, recrystallized from ethyl acetate (3 litres for 206 g of crude alkylation product); m.p. 196–198°C (188°C);[3] $\lambda_{max}(CH_2Cl_2)$ 448 nm, ε 15 100; ν_{max}(KBr) 3500 (br, w), 2970 (m), 2880 (m), 1630 (m), 1610 (s), 1590 (m), 1445 (s), 1320 (s), 800 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) 0·95 (d, 12H, *J* 7 Hz), 1·9–2·15 (m, 2H), 2·63 (d, 4H *J* 7 Hz), 7·46, 7·75 (ABq, 4H, *J* 7·6 Hz), 13·08 (s, D_2O exchangeable) ppm; ^{13}C-NMR ($CDCl_3$), δ 22·5, 28·4, 39·2, 115·5, 118·8, 137·2, 139·0, 161·3, 188·4 ppm.

1,8-Dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone (3)

A mixture of concentrated sulfuric acid (1·5 litres) and boric acid (92·3 g, 1·5 mol) was heated to 60°C for 30 min or until total dissolution of the boric acid. The solution was cooled to 50°C and 1,8-dihydroxy-2,7-di-isobutylanthraquinone (170 g, 0·48 mol) was added portionwise. The reaction mixture was stirred at room temperature for 1 h, when a violet solution was obtained. To it, a mixture of concentrated nitric acid and concentrated sulfuric acid (340 ml, 33/67 v/v) was added dropwise at a rate

such that the temperature of the reaction mixture did not exceed 32°C; it gradually became red. The reaction was monitored by TLC: a sample of the reaction mixture was taken and drowned into water (1 ml), dichloromethane (1 ml) was added, the mixture was shaken, then allowed to settle; a few drops of the organic phase were spotted on TLC plates (silica gel); elution with hexanes/acetone (4/1 v/v) led to the separation in order of decreasing R_f of the starting material, the mononitro and dinitro compounds. After stirring for 3 h at room temperature, the reaction mixture was poured onto ice (~4 litres) and the yellow solid was filtered and washed with water and methanol. It was then stirred in cold methanol (3 litres), filtered and dried and the resultant yellow solid (260 g) was recrystallized from nitroethane (1·5 litres) to give 1,8-dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone as orange needles (169 g, 79%); m.p. 251–252°C (250–252°C);[3] $\lambda_{max}(CH_2Cl_2)$ 444 nm, ε 15 000; ν_{max}(KBr) 2980 (m), 1690 (m), 1635 (m), 1550 (s), 1430 (m), 1380 (m) cm^{-1}; ^{1}H-NMR, see Table 3.

1,5-Dihydroxy-2,6-di-isobutyl-4-nitroanthraquinone (8)

A mixture of concentrated sulfuric acid (1·5 litres) and boric acid (109·0 g, 1·74 mol) was stirred and heated to 50°C until complete dissolution of the boric acid. 1,5-Dihydroxy-2,6-di-isobutylanthraquinone (200·0 g, 0·57 mol) was added and the reaction mixture was cooled slowly to room temperature and then to 0°C in an ice–salt bath. The nitrating mixture (200 ml concentrated nitric acid/concentrated sulfuric acid, 33/67 v/v) was added over 3 h, at such a rate that the temperature did not exceed 1°C. At the end of the addition the reaction mixture was warmed slowly to 4°C and kept at this temperature for 4–5 h or until disappearance of the starting material, as indicated by TLC. Only small amounts of the dinitro compound could be detected. The mixture was poured into ice (~5 litres) and filtered. The orange solid was washed with water and methanol, slurried in cold methanol, filtered and dried in high vacuum overnight. The orange solid (223 g) was recrystallized from nitroethane (1·6 litres) to give orange needles (186 g, 83%). The product appeared to be contaminated slightly with starting material and a second recrystallization from nitroethane gave pure **8**; m.p. 180–181·5°C; $\lambda_{max}(CH_2Cl_2)$ 446 nm, ε 13 400; ^{1}H-NMR, see Table 2.

General procedure for the preparation of the mercapto derivatives of 1,5-dihydroxy-2,6-di-isobutylanthraquinones (9) (see Table 4)

A mixture of isopropanol (25 ml), potassium hydroxide (1 equivalent), and the desired thiophenol (1 equivalent) was stirred under nitrogen and heated

to 40–50°C until total dissolution of the KOH (usually 10–15 min). 1,5-Dihydroxy-2,6-di-isobutyl-4-nitroanthraquinone (1 equivalent, usually 1·0 g) was added portionwise and the reaction monitored by TLC (eluant, hexanes/acetone, 4/1 v/v). Heating was discontinued when complete disappearance of the starting material was observed. The reaction mixture was cooled to room temperature and in an ice bath. The red product was separated by filtration, washed with methanol and dried. It was then recrystallized from an appropriate solvent.

General procedure for the preparation of the mercapto derivatives of 1,8-dihydroxy-2,7-di-isobutylanthraquinones (4) (see Table 5)

A mixture of pyridine (25 ml) and 1,8-dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone (1 equivalent, usually 1·0 g) was stirred under nitrogen and to the red–brown solution the thiophenol (1 equivalent) was added at room temperature. The reaction was followed by TLC (eluant, hexanes/acetone, 4/1 v/v) and if necessary the temperature of the reaction was increased slowly up to 100°C. When the reaction was complete the reaction liquor was cooled to room temperature. At this point the work-up procedure varied, depending on the solubility properties of the product. If the product appeared to be insoluble in pyridine the reaction vessel was cooled in an ice bath and the product was separated by filtration, washed with methanol and recrystallized. On the other hand, if the product was significantly soluble in pyridine the reaction mixture was poured into acidified water and the product separated by filtration, washed with methanol and recrystallized.

1,8-Dihydroxy-2,7-di-isobutyl-4,5-thiophenoxyanthraquinone (5, R = H)

A mixture of isopropanol (15 ml), benzenethiol (0·249 g, 2·26 mmol) and potassium hydroxide (0·126 g, 2·26 mmol) was stirred under nitrogen and heated to 50°C until total dissolution of the potassium hydroxide. Addition of 1,8-dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone (0·50 g, 1·13 mmol) to this solution led to the immediate formation of a reddish purple color. The mixture was heated at reflux for 1 h. TLC indicated complete conversion of the starting material to a single compound (eluant, hexanes/acetone 4·5/0·5 v/v). After cooling, the purple product was separated by filtration, washed with methanol, and dried (561 mg, 87%); m.p. 252–253°C; $\lambda_{max}(CH_2Cl_2)$ 544, 576 nm; ν_{max}(KBr) 3400 (br, w), 2980 (m), 2950 (m), 1620 (s), 1450 (s), 1420 (s), 1280 (m), 1225 (s), cm^{-1}; ^{1}H-NMR, see Table 3.

1,8-Dihydroxy-2,7-di-isobutyl-4,5-di(4′-fluorothiophenoxy)anthraquinone (5, R = *p*-F)

The procedure described for the preparation of **5** (R = H) was applied starting with 4-fluorobenzenethiol (0·289 g, 2·26 mmol) and 1,8-dihydroxy-2,7-di-isobutyl-4,5-dinitroanthraquinone (0·50 g, 1·13 mmol); yield 63%; m.p. 310–312°C; $\lambda_{max}(CH_2Cl_2)$ 572 nm, ε 13 000; ν_{max}(KBr) 2980 (m), 1640 (m), 1610 (s), 1510 (s), 1430 (s), 1280 (m), 1230 (s), 1130 (s) cm^{-1}; ^{1}H-NMR, see Table 3. Calculated for $C_{34}H_{32}O_4S_2$; C, 71·80; H, 5·67; S, 11·27; Found: C, 71·05; H, 5·66; S, 11·83%.

CONCLUSION

A simple preparation of new red and purple dyes has been reported. It has been shown that through the use of the thiophenoxy auxochrome it is possible to fine-tune the shade of anthraquinone chromophores. The dyes prepared here exhibit exceptional compatibility with polymers such as polyesters and styrene/methacrylate copolymers. The lightfastness of the dyes in several polymeric matrices has been investigated and the results of this study will be presented in a separate publication.[19]

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