Dyes and Pigments 4 (1983) 41–48

Polyfluoroalkyl Substituted Anthraquinone Dyes

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(Received: 4 January, 1982)

SUMMARY

A number of new amino- and hydroxy-anthraquinone dyes with 1,1-dihydropolyfluoroalkyl groups at the nitrogen and oxygen atoms have been prepared. The influence of polyfluoroalkyl groups on the colour of these anthraquinone dyes has been studied. The replacement of the hydrogen atom in the oxy group by polyfluoroalkyl radicals causes a stronger hypsochromic shift of the absorption maximum than the same replacement in the amino group.

1. INTRODUCTION

The influence of polyfluoroalkyl groups on the colour and properties of triphenylmethane and azo dyes has been studied previously.[1,2] In this respect the investigation of the same type of anthraquinone dyes containing polyfluoroalkyl groups is of special interest. Several amino-anthraquinone dyes with fluoroalkyl groups attached to the nitrogen atom have been described.[3] It is established that as it was observed earlier for azo dyes an increase in the number of fluorine atoms in the polyfluoroalkyl radical causes a hypsochromic shift of the absorption maximum, and the light fastness increases. A number of phenylaminoanthraquinone dyes with CF_3, CF_3CO and CF_3SO_2 groups in the phenyl moiety are also known.[4,5]

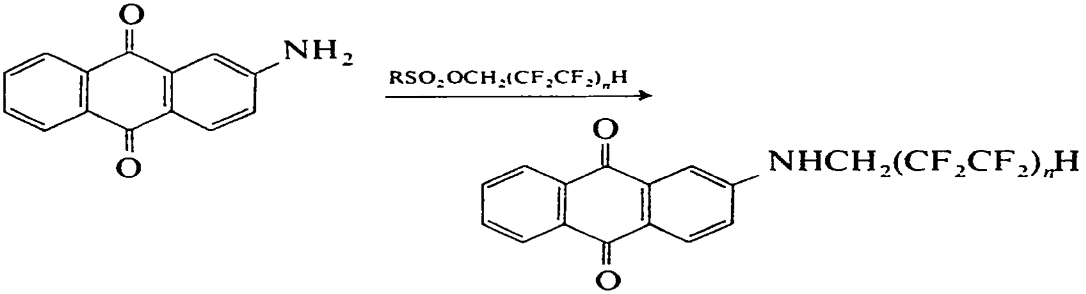
This paper is concerned with the synthesis of amino- and hydroxy-anthraquinone derivatives with polyfluoroalkyl groups at the nitrogen and oxygen atoms.

Dyes and Pigments 0143-7208/83/0004-0041/$03·00

2. SYNTHESIS OF DYES

2.1. Synthesis of polyfluoroalkylaminoanthraquinones

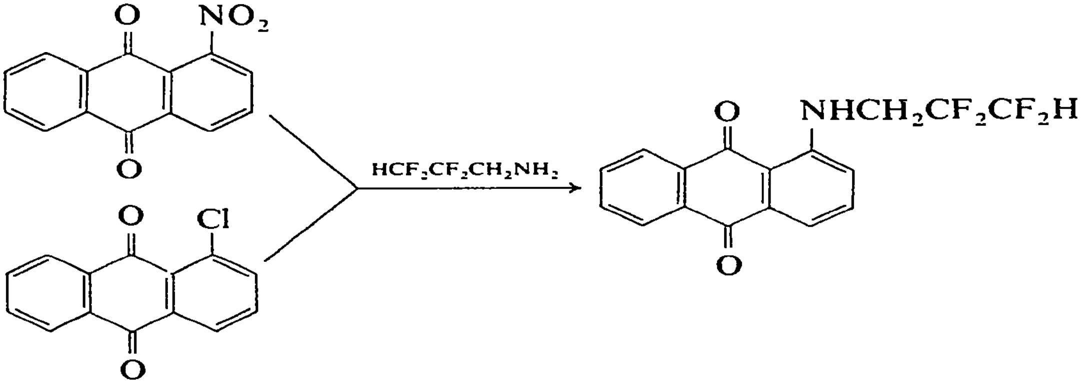
At first an attempt was made to alkylate aminoanthraquinones by polyfluoroalkylsulphonates as described earlier for arylamines.[6] It was found that mixtures of fluoro-containing and initial anthraquinones which were difficult to separate by either chromatography or crystallisation were usually obtained in this reaction. In this way it has been possible to alkylate in low yield only 2-amino- and 1,4-diamino-anthraquinones.



$R = p\text{-}CH_3C_6H_4,\ CF_2Cl,\ \text{iso-}C_3H_7OOCCF_2;\ n = 1, 2$

In contrast, polyfluoroalkylation of *p*-aminobenzophenone by isopropoxycarbodifluoromethanesulphonic acid tetrafluoropropyl ester leads to the formation of pure *p*-(*N*-2,2,3,3-tetrafluoropropyl)aminobenzophenone with 30% yield.

Other fluoroalkylaminoanthraquinones were obtained by the following methods. The interaction of α-nitroanthraquinone with polyfluoroalkylamine yields α-polyfluoroalkylaminoanthraquinone. This com-



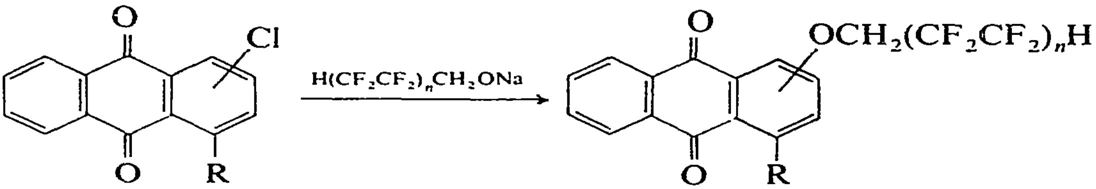
pound can also be obtained by the nucleophilic substitution of the chlorine atoms in α-chloroanthraquinone but the purification of the product from the traces of the initial compound is somewhat difficult.

β-Chloroanthraquinone does not undergo this conversion as the chlorine atom in the β-position is not so mobile as in the α-position.

1-Amino-4-hydroxyanthraquinone derivatives are deeply coloured. A number of 1-fluoroalkylamino-4-hydroxyanthraquinones were synthesised earlier by the interaction of leucoquinizarine with fluoroalkylamines followed by oxidation.[3,7] We have repeated the synthesis of 1-(*N*-2′,2′,3′,3′-tetrafluoropropyl)amino-4-hydroxyanthraquinone by this method as the absorption maximum of this dye was not described and the deviation of the fluorine analyses from the calculated value is more than 4%.[7] We did not obtain the product of the substitution of two hydroxy groups for polyfluoroalkylamino groups, described earlier.[7]

2.2. Synthesis of polyfluoroalkoxyanthraquinones

1,1-Dihydropolyfluoroalkoxyanthraquinones were not known previously. We have prepared them by the action of sodium alcoholates of telomeric alcohols on chloroanthraquinones.



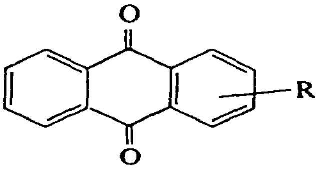
$R = H, NH_2, NHCOC_6H_5;\ n = 1,2$

α- and β-chloroanthraquinones undergo this reaction. Treatment of 1-benzoylamino-4-chloroanthraquinone with sodium 1,1,3-trihydrotetrafluoropropylate ($n = 1$) is accompanied by the saponification of the benzoylamino group and the same dye is obtained as from 1-amino-4-chloroanthraquinone.

3. RESULTS AND DISCUSSION

A comparison of the absorption maxima of α- and β-fluoroalkylaminoanthraquinones with the absorption maxima of α- and β-aminoanthraquinones[8] shows that the introduction of the 2,2,3,3-tetrafluoropropyl

TABLE 1
Absorption Maxima of Anthraquinones



Anthraquinone	*R*	λ_{max} (*nm*)	
		in CH_2Cl_2	*in* C_2H_5OH
1	1-NH_2	465	483
2	1-$NHCH_2CF_2CF_2H$	470	480
3	2-NH_2	410	452
4	2-$NHCH_2CF_2CF_2H$	420	450
5	2-$NHCH_2(CF_2CF_2)_2H$	—	442
6	1,4-di(NH_2)	545, 582	552, 593
7	1,4-di($NHCH_3$)	620	593, 641
8	1,4-di($NHCH_2CF_2CF_2H$)	555, 594	568, 608
9	1-OH	405	408
10	1-$OCH_2CF_2CF_2H$	336	367
11	1-$OCH_2(CF_2CF_2)_2H$	343	351
12	2-OH	365	380
13	2-$OCH_2CF_2CF_2H$	328	330
14	1-NH_2-4-OH	528, 554	534, 570
15	1-$NHCH_2CF_2CF_2H$-4-OH	534, 570	537, 571
16	1-NH_2-4-Cl	472	484
17	1-NH_2-4-$OCH_2CF_2CF_2H$	476	496
18	1-NH_2-4-$OCH_2(CF_2CF_2)_2H$	476	496

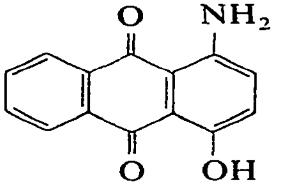
radical into the amino group exerts a slight (2–3 nm) hypsochromic shift of the absorption band in ethanol. The absorption maxima of dyes with fluoroalkyl groups and those without fluorine given for comparison in ethanol and dichloromethane are shown in Table 1. The hypsochromic shift increases with the length of the polyfluoroalkyl chain (i.e. the number of difluoromethylene groups).

The substitution of the hydrogen atom of the hydroxy group in 1-hydroxyanthraquinone has a stronger influence on the absorption maximum than the substitution of hydrogen in the corresponding amino derivative. The hypsochromic shift in this case reaches 50 nm. β-

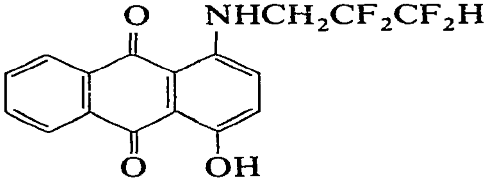
Fluoroalkylamino- and β-hydroxyanthraquinones are more highly coloured than the corresponding α-derivatives.

It was also interesting to ascertain the influence of fluoroalkyl groups on the colour of anthraquinone dyes containing two substituents in the 1- and 4-positions. The substitution of the two hydrogen atoms for tetrafluoropropyl radicals in 1,4-diaminoanthraquinone results in the deepening of the colour as both absorption maxima are displaced towards longer wavelengths (~ 15 nm). However dye **8** is noticeably more highly coloured than 1,4-bis(methylamino)anthraquinone (**7**).

The substitution of the hydrogen atom of the amino group in 1-amino-4-hydroxyanthaquinone by the polyfluoroalkyl radical results in a very insignificant deepening of the colour. At the same time the substitution of chlorine for the residue of telomeric alcohol ($n = 1, 2$) in 1-amino-4-chloroanthraquinone exerts a bathochromic shift of λ_{max} of 12 nm. Such dyes as 1-amino-4-hydroxypolyfluoroalkylanthraquinones, unlike the 1-amino-4-hydroxyanthraquinones, have only one absorption maximum in the visible region. The explanation of this fact can be found in the withdrawing of the electron pair of the oxygen atom by the polyfluoroalkyl radical. Due to this influence the electron pair of oxygen cannot participate in conjugation with the amino and carbonyl groups or form the hydrogen bonds. A comparison of the absorption maxima of two isomeric dyes **15** and **17** in ethanol shows that despite the substitution of

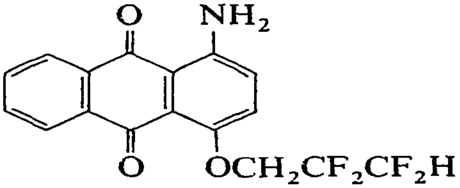


λ_{max}534, 570 nm



(**15**)

λ_{max}537, 571 nm



(**17**)

λ_{max}496 nm

the hydrogen atom of the amino group for the 1,1,3-trihydrotetrafluoropropyl radical, dye **15** has two absorption maxima in the visible region; that is, the polyfluoroalkylamino group, in contrast to the polyfluoroalkyloxy group, can participate in the formation of hydrogen bonds.

4. EXPERIMENTAL

4.1. p-(1,1,3-Trihydro-2,2,3,3-tetrafluoropropyl)aminobenzophenone

A mixture of 4-aminobenzophenone (2 g) and 2,2,3,3-tetrafluoropropylisopropoxycarbodifluoromethanesulphonate was heated for 8 h at 145 °C in a sealed stainless steel tube. The product was extracted with ether, the ether layer was washed with aqueous hydrochloric acid (1 : 1) and dried. Yield: 0·47 g (30 %): m.p. 82–84 °C (pentane). Analysis found (%): F 24·35, 24·50. Calculated for $C_{16}H_{13}F_4NO$: F, 24·44.

4.2. β-(1,1,3-Trihydro-2,2,3,3-tetrafluoropropyl)aminoanthraquinone

A mixture of β-aminoanthraquinone (0·5 g) and 2,2,3,3-tetrafluoropropylisopropoxycarbodifluoromethanesulphonate (1 g) in nitrobenzene (7 ml) was heated for 20 h at 160–170 °C in a sealed stainless steel tube, cooled and poured on ice. Water and nitrobenzene were decanted and the residue was mixed with hexane until crystallisation commenced. Yield 0·1 g (13·5 %): m.p. 215–217 °C (benzene). Analysis found (%): F 22·13, 22·20. Calculated for $C_{17}H_{11}F_4NO_2$: F 22·55.

4.3. β-(1,1,5-Trihydro-2,2,3,3,4,4,5,5-octafluoropentyl)aminoanthraquinone

A mixture of β-aminoanthraquinone and 2,2,3,3,4,4,5,5-octafluoropentyldifluorochloromethanesulphonate was heated for 15 h at 200 °C. The crude dye was purified by column chromatography on alumina using benzene as solvent. Yield 18 %, m.p. 242–244 °C (methanol). Analysis found (%): F 35·00, 35·26. Calculated for $C_{19}H_{11}F_8NO_2$: F 34·79.

4.4. 1,4-Di(1′,1′,3′-trihydro-2′,2′,3′,3′-tetrafluoropropyl)aminoanthraquinone[7]

A mixture of 1,4-diaminoanthraquinone, 2,2,3,3-tetrafluoropropyl tosylate and triethylamine was heated for 12 h at 240 °C. The crude dye was purified by column chromatography on alumina. Yield 9%, m.p. 180–182 °C (ethanol).

4.5. α-(1,1,3-Trihydro-2,2,3,3-tetrafluoropropyl)aminoanthraquinone

A mixture of α-nitroanthraquinone (0·5 g) and 1,1,3-trihydrotetrafluoropropylamine (0·6 g) in tetramethylene sulphone (4 ml) was heated for 15 h at 155–160 °C in a sealed stainless steel tube. The reaction mixture was poured in water (30 ml) and the crude dye was sucked off, washed with water, dried and recrystallised. Yield 0·24 g (35%), m.p. 141–143 °C (pentane). Analysis found (%): F 22·16, 22·34; N 4·58. Calculated for $C_{17}H_{11}F_4NO_2$: F 22·55, N 4·16.

This dye was also obtained in the same way in 29% yield, from α-chloroanthraquinone after heating for 25 h at 180–190 °C.

4.6. 1-(1′,1′,3′-Trihydro-2′,2′,3′,3′-tetrafluoropropyl)amino-4-hydroxyanthraquinone

This was prepared by the reaction of tetrafluoropropylamine and leucoquinizarine described earlier.[7] Yield 30%, m.p. 137–138 °C. Analysis found (%): F 20·53, 20·83. Calculated for $C_{17}H_{11}F_4NO_3$: F 21·53.

4.7. α-(1,1,3-Trihydro-2,2,3,3-tetrafluoropropoxy)anthraquinone

To sodium tetrafluoropropylate, prepared from telomeric alcohol ($n = 1$) (2 g) and sodium (0·06 g), α-chloroanthraquinone (1 g), pyridine (1·3 g) and copper powder (0·164 g) were added. The reaction mixture was boiled for 25 h, cooled, stirred with sulphuric acid (30 ml, 40%) at 0 °C and the product was extracted with ether. Yield 0·8 g (57%), m.p. 165–167 °C (benzene). Analysis found (%): F 22·29, 22·41. Calculated for $C_{17}H_{10}F_4O_3$: F 22·50.

4.8. α-(1,1,5-Trihydro-2,2,3,3,4,4,5,5-octafluoropentoxy)anthraquinone

This was obtained according to the previous procedure from telomeric alcohol ($n = 2$) and α-chloroanthraquinone. Yield 72%, m.p. 87–89 °C (hexane). Analysis found (%): F 35·23, 35·26. Calculated for $C_{19}H_{10}F_8O_3$: F 34·70.

4.9. β-(1,1,3-Trihydro-2,2,3,3-tetrafluoropropoxy)anthraquinone

This was obtained according to the previous procedure from telomeric alcohol ($n = 1$) and β-chloroanthraquinone. Yield 34%, m.p. 141–143 °C (heptane). Analysis found (%): F 22·17, 22·20. Calculated for $C_{17}H_{10}F_7O_3$: F 22·50.

4.10. 1-Amino-4-(1',1',3'-trihydro-2',2',3',3'-tetrafluoropropoxy)anthraquinone

This was prepared according to the previous procedure from 1-amino-4-chloroanthraquinone (yield 26%) or 1-benzoylamino-4-chloroanthraquinone (yield 26%), m.p. 158–160 °C (heptane). Analysis found (%): F 21·90, 22·08; N 3·63, 3·68. Calculated for $C_{17}H_{11}F_4NO_3$: F 21·53.

4.11. 1-Amino-4-(1',1',5'-trihydro-2',2',3',3',5',5'-octafluoropentoxy)-anthraquinone

This was prepared according to the previous procedure from 1-amino-4-chloroanthraquinone and sodium octafluoropentylate. Yield 47%, m.p. 126–128 °C (pentane). Analysis found (%): F 33·45, 33·48; N 3·01, 3·09. Calculated for $C_{19}H_{11}F_8NO_3$: F 33·55; N 3·09.

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