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Physical Characteristics of Synthesized 1-Amino-4-(arylamino)anthraquinone 2-Ether Dyes for Synthetic-Polymer Fibers

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The synthesis and characteristics of a series of 2-ethers of 1-amino-4-(arylamino)anthraquinone by various preparative routes are described. Replacement of a bromine atom in the β-position by a phenoxy group increased the molecular size.

Experimental Section

Melting points were determined by using a Gallenkamp heated block apparatus. All the dyes synthesizied were purified where necessary by column chromatography on Silica Gel C. T. (Reeve A) and eluted with toluene. Analytical thin-layer chromatography (TLC) was done on 0.25-mm plates of Kisselgel$_{60}$ PF 244 + 365 (toluene/ethyl acetate/glacial acetic acid, 8:2:1). Microanalyses were performed by Butterworth Microanalytical Consultancy, Teddington, Middlesex.

Mass-spectrophotometric analyses were carried out by using an AEI-MS 902 mass spectrometer with a direct insertion probe.

Visible absorption spectra were recorded on a Unicam SP 800 in chlorobenzene at a concentration of 4×10^{-5} M.

Dye syntheses were carried out by utilizing the following typical preparation. 1-Amino-2-bromo-4-anilinoanthraquinone, II (R = phenyl) used in the syntheses was obtained in 85.2% yield, mp 220 °C (toluene), by refluxing 1-amino-2,4-dibromoanthraquinone (20 g), copper carbonate (1.72 g), potassium acetate (18 g), and aniline (120 mL) for 1 h at 130–140 °C, cooling the liquor to 80–90 °C, and adding methanol (60 mL) to give a dark blue solid (see Scheme I). Other intermediates (II, R = $PhCH_3$, $PhOCH_3$) were similarly prepared.

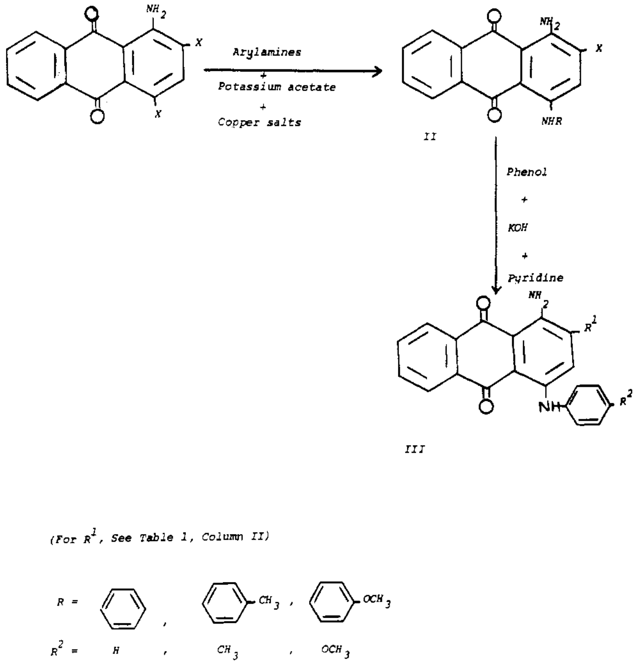
Synthesis of 1-Amino-4-(arylamino)anthraquinone 2-Ethers

Method 1. Synthesis of 1-Amino-2-phenoxy-4-anilinoanthraquinone (IIIc). II (10 g), phenol (20 g), potassium hydroxide (5 g), and pyridine (20 mL) were heated under reflux with stirring for 8 h between 125 and 135 °C. The reaction mixture was cooled to 80 °C and methanol (40 mL) was added to precipitate the crude product (7.8 g, 75.7%) which was filtered and washed with water. TLC showed a single spot of relatively low R_f value. Recrystallization of the product (2 g) from acetone gave violet glittering plates (1 g), mp 189–190 °C. The compound was confirmed by elemental analysis and mass spectrometry.

Reaction with other phenols gave dyes (III) listed in Table I with slight variation in method of preparation as described in method 2.

Method 2. Synthesis of 1-Amino-2-[(3-methoxyphenyl)oxy]-4-anilinoanthraquinone (IIIf). II (2 g), *m*-methoxyphenol (4 mL), potassium hydroxide (1 g), and pyridine (4 mL) were heated under reflux with stirring for 18 h between 125 and 135 °C. When the reaction mixture was cooled to 80 °C, ethanol (8 mL) was added to precipitate the crude product (1.6 g, 72.7%) as a sticky slurry. This was drowned in aqueous sodium hydroxide (200 mL), stirred for 3 h, and warmed to 60 °C for 1 h in order to remove excess of *m*-methoxyphenol. The solution was filtered and the precipitated product washed with water until free of alkali and then dried. TLC indicated the major component (approximately 70%) R_f violet together with equal amounts of three other bands (of lower R_f—blue, red, and yellow, respectively). Chromatographic separation on a silica gel column, using toluene as solvent and eluent, afforded from the main zone violet fluffy needles of IIIf, mp 120 °C (ethanol). Mass spectrometry and elemental analyses confirmed the structure of the compound.

Scheme I



Method 3. Synthesis of 1-Amino-2-methoxy-4-anilinoanthraquinone (IIIj). 1,4-Diamino-2-methoxyanthraquinone (2.67 g), bromobenzene (1.7 mL), potassium acetate (3.2 g), and cuprous chloride (0.2 g) were refluxed in nitrobenzene (30 mL) with stirring for 5 h at 198–206 °C and then cooled to room temperature. Nitrobenzene was steam distilled, leaving a dark solid (5.3 g) which was shown by TLC to contain three major components (approximately equal amounts) (green, violet, and blue bands), contaminated by a higher R_f yellow band and a lower R_f red band. Chromatographic separation of the crude product (2 g) on a silica preparative thick plate using toluene as solvent and toluene/ethyl acetate/acetic acid as eluent gave from the three major zones fine violet granules (violet band) (0.3

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Table I. Characterization Data of 1-Amino-4-anilinoanthraquinone 2-Ethers (Dyes III)

compd	R^1	R^2	synthesis method and recryst solv[a]	crude prod yield, %	λ_{max} (log ϵ) in C_6H_5Cl[b]	mp, °C
IIIa	H	H			454 s (3.93), 573 (4.11), 610 (4.12)	
IIIb	Br	H			584 (4.12), 621 (4.11)	
IIIc	OC_6H_5	H	1A	75.7	528 s (3.96), 536 (4.18), 600 (4.19)	189–190
IIId	$OC_6H_4CH_3$-*p*	H	1A	73.8	530 s (3.93), 562 (4.15), 600 (4.16)	168
IIIe	$OC_6H_4OCH_3$-*p*	H	1A	94.5	534 s (4.02), 562 (4.20), 600 (4.21)	184
IIIf	$OOCH_3$-*m*	H	2A	69.0	534 s (3.92), 564 (4.12), 600 (4.13)	120
IIIg	OC_6H_4OH-*p*	H	1A	80.3	534 s (3.94), 562 (4.14), 600 (4.14)	220
IIIh	$OC_6H_4NH_2$-*p*	H	1A	128.0	534 s (3.94), 561 (4.15), 600 (4.16)	202
IIIi	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	H	1A	54.7	536 s (3.90), 564 (4.15), 600 (4.16)	110
IIIj	OCH_3	H	3B	126.0	530 s (4.00), 552 (4.18), 582 (4.20)	165
IIIk	OCH_3	CH_3	3C	111.0	530 s (4.00), 554 (4.19), 5.93 (4.21)	118
IIIl	OC_6H_5	CH_3	1B	87.4	568 (3.15), 604 (4.15)	148
IIIm	$OC_6H_4CH_3$-*p*	CH_3	1C	85.7	566 (4.16), 602 (4.18)	194
IIIn	$OC_6H_4OCH_3$-*p*	CH_3	1C	81.8	534 s (3.91), 565 (4.16), 602 (4.18)	200
IIIo	OCH_3	OCH_3	1A	103.0	530 s (3.90), 556 (4.09), 592 (4.11)	118
IIIp	OC_6H_5	OCH_3	1A	82.5	536 s (3.98), 568 (4.18), 600 (4.18)	128
IIIq	$OC_6H_4CH_3$-*p*	OCH_3	1A	94.3	536 s (3.98), 602 (4.18), 602 (4.18)	182
IIIr	$OC_6H_4OCH_3$-*p*	OCH_3	1C	86.4	536 s (4.00), 568 (4.18), 600 (4.18)	204

[a] A = acetone. B = ethanol. C = toluene. [b] S = shoulder.

g), mp 165–166 °C. The compound was confirmed by mass spectrometry and elemental analysis.

The other bands were also isolated and their structures confirmed by mass spectrometry. Similarly prepared from appropriate bromoaryl compounds were other dyes (III) listed in Table I.

Registry No. I (X = Br), 81-49-2; II (R = H, X = CH_3O), 2872-48-2; IIIa, 4395-65-7; IIIb, 1564-71-2; IIIc, 86397-46-8; IIId, 90791-31-4; IIIe, 90791-32-5; IIIf, 90791-33-6; IIIg, 90791-34-7; IIIh, 90791-35-8; IIIi, 90791-36-9; IIIj, 90791-37-0; IIIk, 90791-38-1; IIIl, 90822-50-7; IIIm, 90791-39-2; IIIn, 90791-40-5; IIIo, 90791-41-6; IIIp, 90791-42-7; IIIq, 90791-43-8; IIIr, 90791-44-9; $C_6H_5NH_2$, 62-53-3; C_6H_5OH, 108-95-2; *m*-$CH_3OC_6H_4OH$, 150-19-6; C_6H_5Br, 108-86-1.

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Synthesis of Some Bis(ammonium) Salts of 2,4-Dinitro-3-(2-furyl)glutarodinitrile

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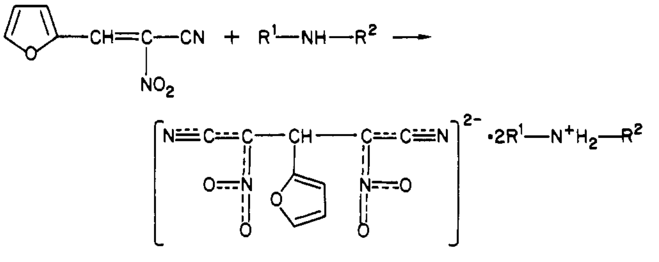
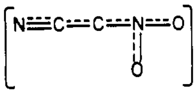
A number of bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile are synthesized from 1-nitro-1-cyano-2-(2-furyl)ethene via reaction with aliphatic and alicyclic amines. The structure of the products is supported by IR and NMR spectra.

In continuation of our investigations on the reaction of cyanonitroalkenes with amines (*1*–*4*), we carried out the reaction of 1-nitro-1-cyano-2-(2-furyl)ethene (*5*) with aliphatic and alicyclic amines and obtained the corresponding bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile (I–X).



I-X

The structures of the compounds follow from elemental analyses, spectroscopic data (Table I), and some chemical reactions. There are several absorption bands in the IR spectra in the region 1470–1080 cm^{-1} and a band at 2210–2195 cm^{-1} which correspond to the vibrations of the conjugated anionic system (*1*–*4*, *6*, *7*)



This anion is also confirmed by the presence of the three furyl protons at δ 7.40, 6.24, and 5.96 and one proton at δ 5.40 in NMR spectra. The presence of ammonium counterion is proved by the broad absorption band at 3300–2600 cm^{-1} in IR spectra (*6*, *8*), by a signal at δ 7.76 or 8.40 (D_2O exchanged) in NMR spectra, and also by acidification of the salts with excess hydrobromic acid, when the respective ammonium bromides were obtained quantitatively.

All salts are crystalline solids, easily soluble in water and polar solvents, insoluble in ether, benzene, chloroform, tetrachloromethane, and petroleum ether. They must be kept in dark