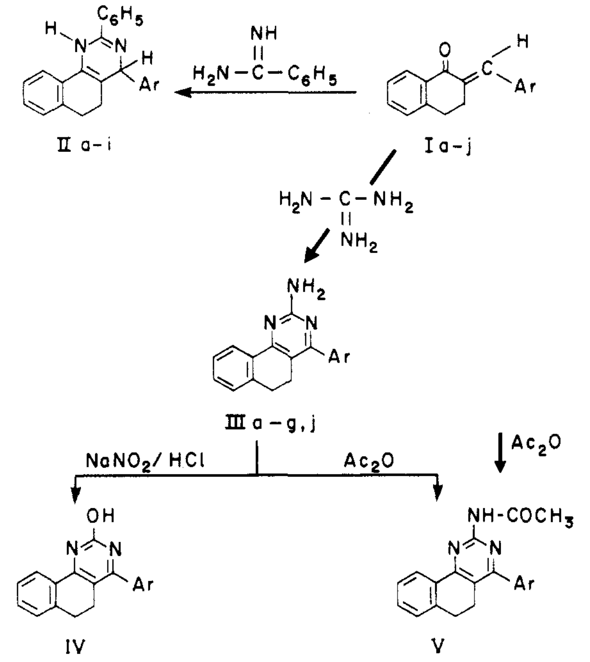
Scheme I



Compound	Ar	Compound	Ar
I - Va	C_6H_5	I - Vg	C_5H_6N (N-methyl-pyrrolyl)
b	p-OCH_3-C_6H_4	h	C_5H_5N (4-pyridyl)
c	p-Cl-C_6H_4	i	$C_{10}H_7$
d	m-Cl-C_6H_4	j	p-CH_3-C_6H_4
e	C_4H_3O (2-furyl)		
f	C_4H_3S (2-thienyl)		

ketone I (1 mol) and benzamidine or guanidine hydrochloride (1 mol) in ethyl alcohol was refluxed, while a solution of sodium hydroxide (5 mL) in water was added portion-wise during 2 h. Refluxing was continued for further 8 h and the reaction mixture was worked up as previously described (*10*). The products were crystallized from benzene/petroleum ether (60-80 °C) to give 4-arylbenzo[*h*]hexahydro-2-phenylquinazoline (II) and 2-amino-4-aryl-5,6-dihydrobenzo[*h*]quinazolines (III), respectivey (Table II).

Reaction of 2-Amino-4-aryl-5,6-dihydrobenzo[h]quinazolines (IIIc,f) with Nitrous Acid. An aqueous solution of sodium nitrite (1.5 g/10 mL H_2O) was added dropwise to a solution of the quinazoline III (1.0 g) in glacial acetic acid (15 mL). The precipitated product was crystallized from acetone to give the corresponding 2-oxoquinazolines (IV) (Table II).

Acetylation of 2-Amino-4-aryl-5,6-dihydro-benzo[h]quinazolines (IIIc,f). The 2-aminoquinazoline (1 g) was heated with acetic anhydride (3 mL) on a boiling water bath for 1 h. Addition of cold 50% ethyl alcohol (15 mL) precipitated a product which was crystallized from ethanol to give the corresponding 2-acetamido-4-aryl-5,6-dihydrobenzo[*h*]quinazolines (Vc,f) (Table II).

Registry No. Ia, 6261-32-1; Ib, 49629-37-0; Ic, 49545-70-2; Id, 61661-18-5; Ie, 54752-28-2; If, 54752-27-1; Ig, 106319-24-8; Ih, 14711-31-0; Ii, 55760-09-3; Ij, 54752-30-6; IIa, 106319-25-9; IIb, 106319-26-0; IIc, 106319-27-1; IId, 106319-28-2; IIe, 106319-29-3; IIf, 106319-30-6; IIg, 106319-31-7; IIh, 106319-32-8; IIi, 106319-33-9; IIIa, 97145-59-0; IIIb, 3977-36-4; IIIc, 97145-61-4; IIId, 97145-64-7; IIIe, 106319-34-0; IIIf, 106319-35-1; IIIg, 97145-66-9; IIIj, 97145-60-3; IVe, 106335-77-7; IVf, 106335-78-8; Ve, 106319-36-2; Vf, 106319-37-3; $C_6H_5C(=NH)NH_2$, 618-39-3; $H_2N=C(NH_2)_2 \cdot HCl$, 50-01-1.

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Physical Characteristics of Synthesized 1,4-Bis(arylamino)-2-(aryloxy)anthraquinone Dyes for Synthetic Polymer Fibers

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The synthesis and characteristics of a series of 1,4-bis(arylamino)-2-(aryloxy)anthraquinones are described. Replacing the hydrogen atom in the amino group in the 1-position of 1-amino-4-(arylamino)anthraquinone 2-ethers with aryl groups results in a bathochromic change in the absorption spectra of the new compounds from violet to green.

Experimental Section

All melting points are corrected. Microanalyses, thin layer chromatography, mass spectra, and visible absorption spectra of the dyes were effected as previously described (*1*).

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Table I. Characterization Data of 1,4-Bis(arylamino)-2-(aryloxy)anthraquinone (Dyes (IV)

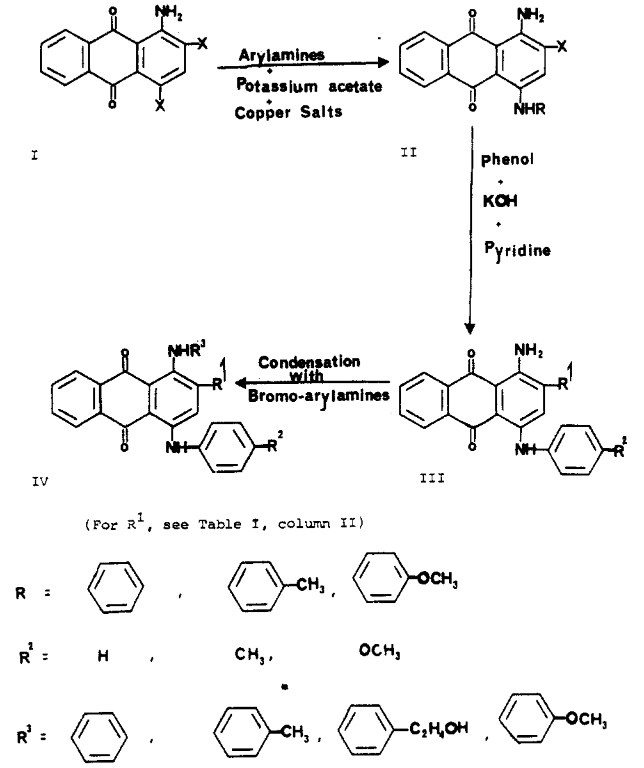
compd	R^1	R^2	R^3	synth method, recryst solv[a]	crude prod yield, %	λ_{max} (log ϵ) in C_6H_5Cl[b]	mp, °C
III	OC_6H_5	H	H	1	75.7	528 s (3.96), 536 (4.18), 600 (4.19)	189–90
IV.1	OC_6H_5	H	C_6H_5	1, A	81.0	560 s (3.92), 598 (4.10), 630 (4.08)	200
IV.2	$OC_6H_4CH_3$-*p*	H	C_6H_5	1, A	96.0	598 (4.08), 630 (4.08)	182
IV.3	$OC_6H_4OCH_3$-*p*	H	C_6H_5	1, B	79.0	597 (4.18), 628 (4.08)	182–4
IV.4	$OC_6H_4OCH_3$-*m*	H	C_6H_5	1, B	77.0	564 s (4.00), 600 (4.15), 634 (4.15)	150
IV.5	OC_6H_4OH-*p*	H	C_6H_5	1, B	115.4	564 s (3.89), 607 (4.05), 640 s (4.00)	174
IV.6	$OC_6H_4NH_2$-*p*	H	C_6H_5	1, C	104.0		206
IV.7	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	H	C_6H_5	1, C	76.1	600 (3.86), 624 s (3.85)	134
IV.8	OC_6H_5	H	$C_6H_4C_2H_4OH$-*p*	1, A	77.0	560 s (3.86), 602 (4.08), 634 (4.04)	164
IV.9	$OC_6H_4CH_3$-*p*	H	$C_6H_4C_2H_4OH$-*p*	1, B	97.3	562 s (3.92), 602 (4.11), 632 (4.09)	176
IV.10	$OC_6H_4OCH_3$-*p*	H	$C_6H_4C_2H_4OH$-*p*	1, B	94.1	562 s (3.90) , 600 (4.08), 632 (4.08)	168
IV.11	$OC_6H_4OCH_3$-*m*	H	$C_6H_4C_2H_4OH$-*p*	1, C	78.4	564 s (3.90), 602 (4.12), 634 (4.11)	120
IV.12	OC_6H_4OH-*p*	H	$C_6H_4C_2H_4OH$-*p*	1, C	117.0	615 (4.04), 640 (4.00)	140
IV.13	$OC_6H_4NH_2$-*p*	H	$C_6H_4C_2H_4OH$-*p*				
IV.14	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	H	$C_6H_4C_2H_4OH$-*p*	1, C	86.0	562 s (3.93), 600 (4.16), 632 (4.11)	168
IV.15	OC_6H_5	H	$C_6H_4CH_3$-*p*	1, A	81.6	560 s (3.85), 608 (4.04), 630 s (4.04)	170
IV.16	$OC_6H_4CH_3$-*p*	H	$C_6H_4CH_3$-*p*	1, C	106.0	560 s (3.86), 608 (4.11), 626 s (4.09)	210
IV.17	$OC_6H_4OCH_3$-*p*	H	$C_6H_4CH_3$-*p*	1, A	106.0	560 s (3.78), 624 (4.01)	220
IV.18	$OC_6H_4OCH_3$-*m*	H	$C_6H_4CH_3$-*p*	1, B/C	93.7	608 (3.92), 630 s (3.91)	80
IV.19	OC_6H_4OH-*p*	H	$C_6H_4CH_3$-*p*	1, C	111.0	612 (3.90), 638 s (3.88)	120
IV.20	$OC_6H_4NH_2$-*p*	H	$C_6H_4CH_3$-*p*	1, C	99.0	614 (4.04), 650 s (4.00)	164
IV.21	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	H	$C_6H_4CH_3$-*p*	1, C	91.0	564 s (3.85), 608 (3.97), 628 s (4.00)	165
IV.22	OC_6H_5	CH_3	C_6H_5	1, A	104.0	562 s (3.90), 600 (4.08), 632 (4.08)	230
IV.23	$OC_6H_4CH_3$-*p*	CH_3	C_6H_5	1, A	108.0	562 s (3.90), 600 (4.09), 630 (4.08)	256
IV.24	$OC_6H_4OCH_3$-*p*	CH_3	C_6H_5	1, D	91.3	562 s (3.91), 600 (4.09), 630 (4.04)	226
IV.25	$OC_6H_4OCH_3$-*m*	CH_3	C_6H_5	1, C	96.0	562 s (3.90), 602 (4.08), 634 (4.08)	190
IV.26	OC_6H_4OH-*p*	CH_3	C_6H_5	1, C	130.0	424 (3.92), 564 s (4.11), 606 (4.26), 657 (4.26)	240
IV.27	$OC_6H_4NH_2$-*p*	CH_3	C_6H_5	1, D	130.0	520 s (3.92), 606 (4.04), 650 (4.02)	200
IV.28	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	CH_3	C_6H_5	1, C	87.0	562 s (3.85), 602 (4.00), 620 (4.00)	220
IV.29	OC_6H_5	CH_3	$C_6H_4CH_3$-*p*	1, A	61.2	610 (4.08), 638 (4.08)	186
IV.30	$OC_6H_4CH_3$-*p*	CH_3	$C_6H_4CH_3$-*p*	1, A	73.5	564 s (3.92), 604 (4.11), 630 (4.11)	198
IV.31	$OC_6H_4OCH_3$-*p*	CH_3	$C_6H_4CH_3$-*p*	1, C	57.1	562 s (3.92), 604 (4.12), 622 (4.12)	184
IV.32	$OC_6H_4OCH_3$-*m*	CH_3	$C_6H_4CH_3$-*p*	1, C	75.5	564 s (3.95), 606 (4.15), 640 (4.15)	200
IV.33	OC_6H_4OH-*p*	CH_3	$C_6H_4CH_3$-*p*	1 B	46.9	560 s (3.85), 612 (4.08), 640 (4.08)	220–2
IV.34	$OC_6H_4NH_2$-*p*	CH_3	$C_6H_4CH_3$-*p*		86.5		
IV.35	$OC_6H_4C(CH_3)_2$*p*-C_6H_4OH-*p*	CH_3	$C_6H_4CH_3$-*p*	1, B	104.0	608 (4.04), 628 s (4.04)	186
IV.36	OC_6H_5	CH_3	$C_6H_4C_2H_4OH$-*p*	1, C	76.4	562 s (3.90), 606 (4.11), 634 (4.11)	182
IV.37	$OC_6H_4CH_3$-*p*	CH_3	$C_6H_4C_2H_4OH$-*p*	1, A	78.4	606 (4.08), 636 (4.08)	240
IV.38	$OC_6H_4OCH_3$-*p*	CH_3	$C_6H_4C_2H_4OH$-*p*	1 C	118.0	630 s (4.00), 606 (4.02)	158–60
IV.39	$OC_6H_4OCH_3$-*m*	CH_3	$C_6H_4C_2H_4OH$-*p*	1, C	78.4	630 s (4.01), 608 (4.02)	70
IV.40	OC_6H_4OH-*p*	CH_3	$C_6H_4C_2H_4OH$-*p*	1, B	118.0	610 (3.78), 642 (3.78)	158–60
IV.41	$OC_6H_4NH_2$-*p*	CH_3	$C_6H_4C_2H_4OH$-*p*		98.0		
IV.42	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	CH_3	$C_6H_4C_2H_4OH$-*p*	1, B	81.0	560 s (3.70), 606 (3.90), 630 (3.90)	120
IV.43	OC_6H_5	OCH_3	$C_6H_4OCH_3$-*p*	1, A	61.2	628 (4.12)	186
IV.44	$OC_6H_4CH_3$-*p*	OCH_3	$C_6H_4OCH_3$-*p*	1, A	73.5	626 (4.13)	198
IV.45	$OC_6H_4OCH_3$-*p*	OCH_3	$C_6H_4OCH_3$-*p*	1, C	57.1	626 (4.14)	184
IV.46	$OC_6H_4OCH_3$-*m*	OCH_3	$C_6H_4OCH_3$-*p*	1, C	75.5	560 s (3.91), 620 s (4.21), 638 (4.23)	200
IV.47	OC_6H_4OH-*p*	OCH_3	$C_6H_4OCH_3$-*p*	1, B	46.9	562 s (3.85), 626 (4.35), 640 (4.36)	220–2
IV.48	$OC_6H_4NH_2$-*p*	OCH_3	$C_6H_4OCH_3$-*p*		86.5		
IV.49	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	OCH_3	$C_6H_4OCH_3$-*p*	1, B	104.0	564 s (3.91), 626 (4.36), 640 (4.36)	186
IV.50	OC_6H_5	OCH_3	C_6H_5	1, C	91.3	566 s (3.90), 640 (4.11), 624 (4.10)	190
IV.51	$OC_6H_4CH_3$-*p*	OCH_3	C_6H_5	1, A	108.6	564 s (3.91), 602 (4.08), 622 (4.08)	250–52
IV.52	$OC_6H_4OCH_3$-*p*	OCH_3	C_6H_5	1, B	91.3	604 (4.09), 626 (4.09)	134
IV.53	$OC_6H_4OCH_3$-*m*	OCH_3	C_6H_5	1, B	113.0	562 s (3.73), 610 (3.92), 636 s (3.91)	98
IV.54	OC_6H_4OH-*p*	OCH_3	C_6H_5	1, B	130.0	560 s (3.90), 610 (4.12), 640 (4.18)	180
IV.55	$OC_6H_4NH_2$-*p*	OCH_3	C_6H_5	1, B	143.0	560 s (3.85), 605 (4.00), 618 s (3.98)	174
IV.56	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	OCH_3	C_6H_5	1, B	89.0	616 (4.08)	204
IV.57	OC_6H_5	OCH_3	$C_6H_4C_2H_4OH$-*p*	1, A	84.3	628 (4.12)	168–70
IV.58	$OC_6H_4CH_3$-*p*	OCH_3	$C_6H_4C_2H_4OH$-*p*	1, C	78.4	626 (4.13)	226
IV.59	$OC_6H_4OCH_3$-*p*	OCH_3	$C_6H_4C_2H_4OH$-*p*	1, C	80.0	626 (4.13)	192
IV.60	$OC_6H_4OCH_3$-*m*	OCH_3	$C_6H_4C_2H_4OH$-*p*	1, B	80.0	560 s (3.91), 620 s (4.21), 638 (4.23)	120
IV.61	OC_6H_4OH-*p*	OCH_3	$C_6H_4C_2H_4OH$-*p*	1, B	77.8	562 s (3.85), 626 s (4.35), 640 (4.36)	184
IV.62	$OC_6H_4NH_2$-*p*	OCH_3	$C_6H_4C_2H_4OH$-*p*		120.0		
IV.63	$OC_6H_4C(CH_3)_2$-*p*-C_6H_4OH-*p*	OCH_3	$C_6H_4C_2H_4OH$-*p*	1, B	104.0	640 (4.36)	124

[a] A = toluene; B = acetone; C = ethanol; D = benzene. [b] s = shoulder.

1-Amino-4-(arylamino)anthraquinone 2-ether dyes (III) used in the syntheses were obtained as reported elsewhere (*1*) (see Scheme I).

Synthesis of 1,4-Bis(arylamino)-2-(aryloxy)anthraquinones

Method 1. Synthesis of 1,4-Bis(anilino)-2-(phenoxy)-anthraquinone (IV.1) (2). III (4 g), bromobenzene (2.4 mL), Scheme I



potassium acetate (6.4 g), and cuprous chloride (0.4 g) were refluxed in nitrobenzene (40 mL) with stirring for 5 h at 198–206 °C and then cooled to room temperature. Nitrobenzene was steam distilled leaving a dark solid (3.8 g, 81%) which was shown by TLC to be homogeneous, Recrystallization from toluene gave dark violet needles (2 g), mp 200 °C. The compound was confirmed by elemental analysis and spectrometry.

Similar compounds were prepared by using different bromoarylamines (see Table I).

Registry No. III, 86397-46-8; IV.1, 105281-89-8; IV.2, 105281-90-1; IV.3, 105281-91-2; IV.4, 105281-92-3; IV.5, 105281-93-4; IV.6, 105281-94-5; IV.7, 105281-95-6; IV.8, 105281-96-7; IV.9, 105281-97-8; IV.10, 105281-98-9; IV.11, 105281-99-0; IV.12, 105282-00-6; IV.13, 105282-01-7; IV.14, 105282-02-8; IV.15, 105309-53-3; IV.16, 105282-03-9; IV.17, 105282-04-0; IV.18, 105282-05-1; IV.19, 105282-06-2; IV.20, 105282-07-3; IV.21, 105282-08-4; IV.22, 105282-09-5; IV.23, 105282-10-8; IV.24, 105282-11-9; IV.25, 105282-12-0; IV.26, 105282-13-1; IV.27, 105282-14-2; IV.28, 105282-15-3; IV.29, 105282-16-4; IV.30, 105282-17-5; IV.31, 105282-18-6; IV.32, 105282-19-7; IV.33, 105282-20-0; IV.34, 105282-21-1; IV.35, 105282-22-2; IV.36, 105282-23-3; IV.37, 105282-24-4; IV.38, 105282-25-5; IV.39, 105282-26-6; IV.40, 105282-27-7; IV.41, 105282-28-8; IV.42, 105282-29-9; IV.43, 105282-30-2; IV.44, 105282-31-3; IV.45, 105282-32-4; IV.46, 105282-33-5; IV.47, 105282-34-6; IV.48, 105282-35-7; IV.49, 105282-36-8; IV.50, 105282-37-9; IV.51, 105282-38-0; IV.52, 105282-39-1; IV.53, 105309-54-4; IV.54, 105282-40-4; IV.55, 105282-41-5; IV.56, 105282-42-6; IV.57, 105282-43-7; IV.58, 105282-44-8; IV.59, 105282-45-9; IV.60, 105282-46-0; IV.61, 105282-47-1; IV.62, 105282-48-2; IV.63, 105282-49-3.

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