Table I. Triaryl Phosphorothionates Prepared by Phase-Transfer Catalysis

no.	Ar	yield,[a] %	mp, °C	lit. mp °C	mass spectrum calcd	mass spectrum found
3a	C_6H_5	86	55	54[b]		
3b	$4H_3C-C_6H_4$	84	93-94	93-94[c]		
3c	$2,4(H_3C)_2C_6H_3$	76	63.0-64.5		426.1419	426.1428
3d	2naphthyl	83	94.5-96.0		492.0949	492.0957
3e	$3,5(H_3C)_2C_6H_3$	80	92-94		426.1419	426.1438
3f	$4Cl-C_6H_4$	88	84-86	108.5[d] 113[e] 85-86[f]	443.9310	443.9310
3g	$4O_2H-C_6H_4$	82[g]	177-179	174[h]	477.0032	477.0029
3h	$4NC-C_6H_4$	88	158-159		417.0336	417.0336
3i	$4Br-C_6H_4$	86	96.0-97.5	88-99[f]	575.7797	575.7799

[a] Yield of purified product after recrystallization from *n*-heptane; elemental analyses (C, H, N, P, S, Cl, Br) were submitted for review and agreed with the appropriate theoretical values. [b] Yamasaki, T. *Science Rep. Inst. Tohou Univ.* **1954**, *6*, 172; *Chem. Abstr.* **1955**, *49*, 6858i. [c] *Beilstein* 6 (3) 1372. [d] Mel'nikov, N. N.; Shevetsova, S.; Kagan, M. Y.; *Zh. Obshch. Khim.* **1960**, *30*, 2931; *Chem. Abstr.* **1961**, *55*, 9321a. [e] Kamai G.; Koshkina, E. S. *Tr. Kazan. Khim-Tekhnol. Inst.* **1955**, 11: *Chem. Abst.* **1956**, *50*, 6347a. [f] Mel'nikov, N. N.; Khokhlov, D. N. *Zh. Obsch. Khim.* **1953**, *23*, 1357; *Chem. Abstr.* **1954**, *48*, 9903e. [g] Recrystallized from acetone. [h] Ketelarr, J. A. A.; Gersmann, H. R. *J. Am. Chem. Soc.* **1950**, *72*, 5777.

Table II. Spectral Data of Triaryl Phosphorothionates

no.	IR, cm^{-1}	^1H NMR, ppm
3a	1587, 1185, 1158, 939, 798, 751, 685	7.35 (brs. 5 H)
3b	1493, 1181, 940, 923, 821, 748	2.33 (s, 3 H), 7.17 (s, 4 H)
3c	2880, 1477, 1242, 1180, 1098, 940, 902, 808, 763, 687	2.22 (s, 3 H), 2.24 (s, 3 H), 6.90 (d, 1 H, J = 7.5 Hz), 6.96 (brs, 1 H), 7.20 (d, 1 H, J = 7.5 Hz)
3d	1242, 1210, 1157, 981, 968, 946, 938, 875, 870, 741	7.43 (m, 3 H), 7.74 (s, 4 H)
3e	1281, 1125, 1018, 951, 854, 677	2.30 (s, 6 H), 6.87 (s, 3 H)
3f	1471, 1182, 1157, 1081, 921, 824, 786, 770	7.31 (dd, 2 H, J_{AB} = 8.3, J_{BP} = 1.5 Hz), 7.35 (d, 2 H, J_{AB} = 8.3 Hz)
3g	1587, 1523, 1485, 1356, 1190, 1162, 930, 858, 800, 750	7.73 (dd, 2 H, J_{AB} = 9.0, J_{BP} = 1.5 Hz), 8.44 (d, 2 H, J_{AB} = 9.0 Hz)
3h	1193, 1161, 923, 834	7.38 (dd, 2 H, J_{AB} = 9.0, J_{BP} = 2.0 Hz), 7.78 (d, 2 H, J_{AB} = 9.0 Hz)
3i	1185, 1158, 925, 828, 798, 765, 670	7.13 (dd, 2 H, J_{AB} = 9.0, J_{BP} = 1.5 Hz), 7.54 (d, 2 H, J_{AB} = 9.0 Hz)

phenyl) phosphorothionate had been reported in the literature on three occasions; however, each reference contains a different melting point, so this material was also fully characterized.

Experimental Section

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. Infrared spectra were determined with a Beckman Microlab MX-250 spectrophotometer as KBr disks; absorbance positions are reported in reciprocal centimeters (cm^{-1}). Proton magnetic resonance spectra were recorded on a Varian EM-390 spectrometer as solutions in chloroform-*d* unless otherwise stated. High-resolution mass spectra were recorded on a MAT instrument. Elemental analyses were determined by the General Electric Research and Development Center analytical services group.

Preparation of Triphenyl Phosphorothionate: Typical Example. A 500-mL round-bottomed flask equipped with a reflux condenser, mechanical stirrer, and addition funnel was charged with phenol (56.4 g, 0.6 mol) and sodium hydroxide solution, (24.0 g, 1.2 mol in 150 mL of water). To this solution was added Aliquot 336 (2.25 g) and 150 mL of dichloromethane. The solution was stirred rapidly while thiophosphoryl chloride (33.9 g, 0.2 mol) was added dropwise from the addition funnel over a period of 0.25 h. The solution was stirred at room temperature for 2 h and then the contents of the flask poured into a separatory funnel. The phases were separated and the aqueous layer extracted with two 100-mL portions of dichloromethane. The combined organic extracts were washed with brine and then dried over anhydrous magnesium sulfate. The solution was filtered and concentrated and the oil taken up in 100 mL of hot *n*-heptane whereupon crystals of pure thiophosphate formed, 48.8 g, (86%); mp 55 °C.

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Heterocycles. 11. Synthesis of Substituted Benzo[*h*]quinazolines

Nizar R. El-Rayyes,* Baikis Al-Saleh, and Fatima Al-Omran
Department of Chemistry, Kuwait University, Kuwait

2-Arylidene-1-tetralones (I) were condensed with benzamidine or guanidine to give the corresponding substituted benzo[*h*]quinazolines II and III, respectively. The structures of all products were established by chemical and spectroscopic methods.

Aryl aldehydes were previously reacted with 1-tetralones (*1*) to yield 2-arylidn-1-tetralones (I). These were condensed with benzamidine to produce the corresponding 4-aryl-2-phenylbenzo[*h*]hexahydroquinazolines (IIa-i) (cf. Scheme I). The structures of the products are different from those previously mentioned (*2*) and were substantiated by spectral and chemical

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Table I. Spectrometric Data of Compounds II–V

compd	IR (KBr) ν, cm^{-1}	bond	UV (ethanol) λ_{max}, nm	ϵ_{max}	compd	IR (KBr) ν, cm^{-1}	bond	UV (ethanol) λ_{max}, nm	ϵ_{max}
IIa	1590 (s)	C=C	250	21030	IVg	1590 (w)	C=N	260	6835
	1638 (m)	C=N	310	5735		1630 (br)	C=O	285	5580
	3200 (br)	NH				3000 (br)	NH	354	7670
IIIg	1610 (w)	C=C	226	19145				370	7670
	1630 (m)	C=N	297	4505	Vg	1660 (s)	C=O	226	7730
	3370 (m)	NH_2	350	1735		3220 (m)	NH	262	7405
	3480 (m)							295	7250
								339	5395
								349	5070

compd	NMR ($CDCl_3$) δ, ppm	assignment	compd	NMR ($CDCl_3$) δ, ppm	assignment
IIa	2.0–3.40	(m, 4, CH_2–CH_2)		5.96	(br, 1, NH)
	5.60	(s, 1, H_4)		6.96–9.32	(m, 13, Ar–H)
	6.0	(br, 1, NH)	IIi	2.18–3.25	(m, 4, CH_2–CH_2)
	7.40–9.41	(m, 14 Ar–H)		4.64	(br, 1, NH)
IIb	2.0–3.20	(m, 4, CH_2–CH_2)		5.82	(s, 1, H_4)
	4.0	(s, 3, OCH_3)		7.62–9.40	(m, 16, Ar–H)
	5.60	(s, 1 H_4)	IIIa	1.70–3.20	(m, 4, CH_2CH_2)
	6.02	(br, 1, NH)		7.30–7.75	(m, 9, Ar–H)
	7.30–8.81	(m, 13, Ar–H)		11.85	(s, 2, NH_2)
IIc	2.0–3.0	(m, 4, CH_2–CH_2)	IIIb	2.18–3.70	(m, 4, CH_2–CH_2)
	5.40	(s, 1, H_4)		4.10	(s, 3, OCH_3)
	5.81	(br, 1, NH)		7.25–8.85	(m, 8, Ar–H)
	7.41–9.0	(m, 13, Ar–H)		12.0	(s, 2, NH_2)
IId	2.01–3.30	(m, 4, CH_2–CH_2)	IIIc	3.05	(s, 4, CH_2CH_2)
	5.51	(s, 1, H_4)		7.33–8.30	(m, 8, Ar–H)
	6.30	(br, 1, NH)		11.85	(s, 2, NH_2)
	7.30–9.31	(m, 13, Ar–H)	IIId	1.45–3.05	(m, 4, CH_2–CH_2)
IIe	2.02–3.35	(m, 4, CH_2–CH_2)		6.80–7.4	(m, 8, Ar–H)
	5.63	(s, 1, H_4)		11.60	(s, 2, NH_2)
	6.08	(br, 1, NH)	IIIe	3.40	(s, 4, CH_2CH_2)
	6.74–8.92	(m,12, Ar–H)		7.42–8.60	(m, 7, Ar–H)
IIf	2.08–3.41	(m, 4, CH_2–CH_2)		12.0	(s, 2, NH_2)
	5.58	(s, 1, H_4)	IIIf	3.37	(s, 4, CH_2CH_2)
	6.13	(br, 1, NH)		6.90–8.40	(m, 7, Ar–H)
	6.85–8.87	(m, 12, Ar–H)		11.94	(s, 2, NH_2)
IIg	2.20–3.41	(m, 4, CH_2–CH_2)	IIIg	2.82–3.24	(m, 4, CH_2CH_2)
	3.98	(s, 3, N–CH_3)		3.98	(s, 3, N–CH_3)
	6.58	(br, 1, NH)		6.46–8.52	(m, 7, Ar–H)
	6.82–9.21	(m, 12, Ar–H)		11.86	(s, 2, NH_2)
IIh	2.13–3.52	(m, 4, CH_2–CH_2)	IIIj	2.56	(s, 3, CH_3)
	5.63	(s, 1, H_4)		3.07–4.0	(m, 4, CH_2CH_2)
				7.30–8.30	(m, 8, Ar–H)
				11.85	(s, 2, NH_2)

analyses (Table I). Thus, the infrared and the NMR spectra revealed the presence of the NH and Ar–CH moieties.

The reaction of the chalcones (I) with guanidine gave the corresponding 2-amino-4-aryl-5,6-dihydrobenzo[*h*]quinazolines (IIIa–i) (Scheme I). The structures of these products were deduced from their chemical and spectral analyses (Table I). The infrared spectra show absorption bands characteristic for the quinazoline system (*3*, *4*, *5a*, *6*). The electronic spectra show three major maxima which can be ascribed to the ^{1}La and ^{1}Lb bands of the benzo[*h*]quinazolines (*3*, *6*, *7*). The NMR spectra show signals which can be attributed to the different types of protons (*8*). The MS spectra of IIIe,f,j reveal molecular ion peaks at *m/e* 263 (100%), *m/e* 279 (38.63%), and *m/e* 287 (79.64%), respectively. The base peaks of IIIf,j are found at *m/e* 278 and *m/e* 286 corresponding to $(M - 1)^+$. Chemical reactions lend further support to the structure of compounds III. Thus, treatment of IIIc,f with nitrous acid gave the corresponding 4-aryl-5,6-dihydro-benzo[*h*]-2-oxo-quinazolines (IVc,f). Acetylation of IIIc,f with acetic anhydride gave the monoacetyl derivatives (Vc,f) (Scheme I). These show infrared (*5b*,*c*) and electronic spectra (*3*, *9*) consistent with their structures (Table I).

Table II. Melting Points and Yields of Compounds II–V

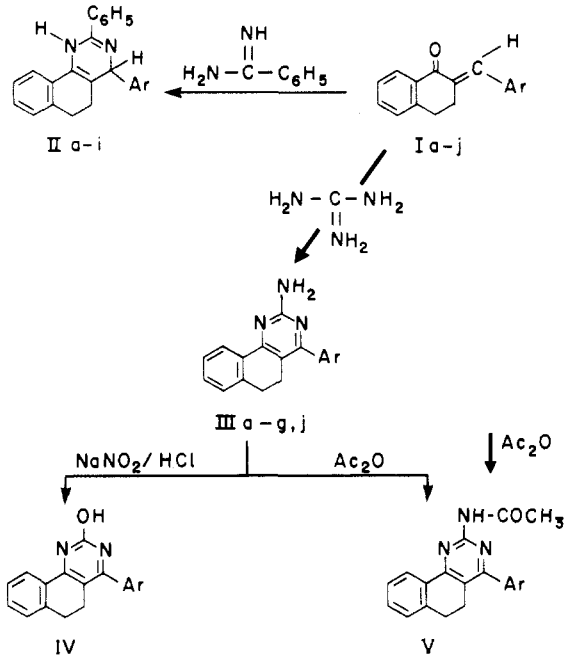
compd	mp, °C	yield, %	compd	mp, °C	yield, %
IIa	110	77	IIIc	222–223	80
IIb	199	80	IIId	173–174	78
IIc	143	82	IIIe	208–209	80
IId	154	81	IIIf	253–255	82
IIe	70	78	IIIg	156–157	81
IIf	153	75	IIIj	193–194	78
IIg	95	79	IVc	295–296	82
IIh	115	80	IVf	275–276	80
IIi	105	78	Vc	207–208	90
IIIa	138–139	76	Vf	214–215	92
IIIb	182–183	77			

Experimental Section

Microanalyses were performed by Prof. H. Malissa and G. Reuter Analytisches Laboratorium BRD. Infrared spectra (KBr disk) were measured on Perkin-Elmer 580B infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded for solutions in deuteriochloroform with tetramethylsilane as an external standard on a Varian T60A spectrometer. Electronic spectra were taken for solutions in ethyl alcohol on a Pye Unicam SP8000 recording spectrometer. The mass spectra were carried out with Varian MAT 311 A. Melting points were determined by using a Bock-Monoscop M (thermal microscope).

Reaction of the Chalcones I with Benzamidine or Guanidine. General Procedure. A mixture of the α,β-unsaturated

Scheme I



Compound	Ar
I - Ve	C_6H_5
b	p-OCH_3-C_6H_4
c	p-Cl-C_6H_4
d	m-Cl-C_6H_4
e	C_4H_3O (2-furyl)
f	C_4H_3S (2-thienyl)

Compound	Ar
I - Vg	C_5H_6N (N-methyl-pyrrolyl)
h	C_5H_5N (4-pyridyl)
i	$C_{10}H_7$
j	p-CH_3-C_6H_4

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, 97145-81-4; 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

David O. Ukponmwan,*† Malcolm Greenhalgh, and Arnold T. Peters

Dyestuff Research Laboratories, School of Colour Chemistry and Colour Technology, The University of Bradford, Bradford BD7 1DP, England

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*).

†Present address: Department of Chemistry, University of Benin, P.M.B. 1154, Benin City, Bendel State, Nigeria.

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