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A New Synthesis of Triphenodithiazines and Triphenodithiazinequinoes

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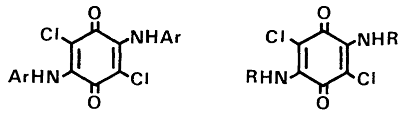
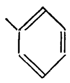
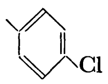
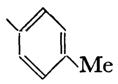
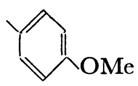
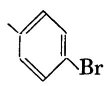
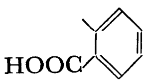
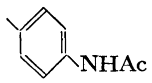
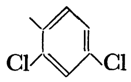
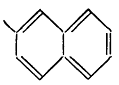
A new class of 6,13-bis(arylamino)triphenodithiazines has been synthesized by condensing chloranil with arylamines followed by the reaction of the resulting 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones with zinc 2-aminobenzenthiolates (**4**) in the presence of a base in Methyl Cellosolve. On the other hand, the reaction of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone (**3a**) with **4** in DMF proceeded unexpectedly to give 7,14-dihydro-6,13-triphenodithiazinequinones by eliminating the anilino groups of **3a**.

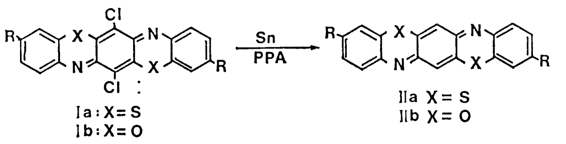
Few triphenodithiazine ([1,4]benzothiazino[2,3-*b*]-phenothiazine) derivatives have been studied in comparison with triphenodioxazine derivatives, which are useful dyes and pigments.[1] Recently, however, Mital and Jain *et al.* have reported[2,3] the synthesis of 6,13-dichlorotriphenodithiazine and its derivatives. In a previous paper, we ourselves studied[4,5] the dechlorination of some 6,13-dichlorotriphenodithiazine (**Ia**) and -dioxazine (**Ib**) with tin powder in polyphosphoric acid (PPA), as is shown in Scheme 1. Then, it was

Table 1. 2,5-Bis(arylamino)-3,6-dichloro-1,4-benzoquinone derivatives **3**



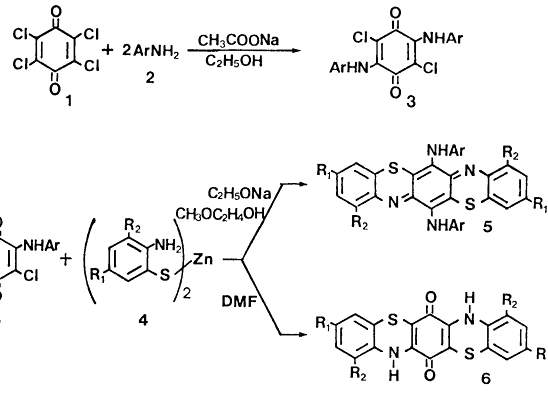
Compd No.	Substituent Ar or R	Yield / %	Mp θ_m/°C	Appearance	N-Anal. Found (Calcd) (%)	Cl Br-Anal. Found (Calcd) (%)
3a		88	312—313	Black plates	7.88 (7.80)	20.5 (19.7)
3b		76	305—308	Black plates	6.65 (6.54)	34.6 (33.1)
3c		84	312—315	Black plates	7.34 (7.24)	19.4 (18.3)
3d		88	300—302	Dark green plates	6.85 (6.68)	17.0 (16.9)
3e		76	324—326	Brown needles	5.61 (5.42)	—
3f		48	365 (decomp)	Brown needles	6.35 (6.24)	16.1 (15.9)
3g		80	350 (decomp)	Greenish brown needles	12.1 (11.8)	15.4 (15.0)
3h		73	310 (decomp)	Dark brown needles	9.41 (9.38)	11.8 (11.9)
3i		32	304—306	Brown needles	5.68 (5.63)	— (42.8)
3j		80	288 (decomp)	Black plates	6.32 (6.10)	16.7 (15.4)
3k		66	240—241	Reddish purple needles	7.86 (7.55)	18.7 (19.1)
3l	$-C_4H_9$	87	199—200	Reddish purple needles	8.91 (8.78)	22.0 (22.3)

clarified that the replacement of two chlorine atoms at the 6 and 13 positions by hydrogen atoms brought about a decrease in the melting point and a strong hypsochromic shift in the electronic spectrum.



Scheme 1.

Furthermore, it will be interesting to ascertain the effects on the physical properties of the introduced bulky substituents at these positions. We wish here to report the synthesis and several properties of the new triphenodithiazines (**5**) and 7,14-dihydro-6,13-triphenodithiazinequinones (**6**). We have established these novel synthetic routes to be as is shown in Scheme 2. These compounds may be suited for new organic pigments.



Scheme 2.

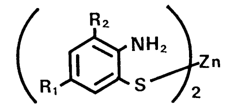
Results and Discussion

The condensation of chloranil **1** (1 : 2 molar ratio) with amines **2** in ethanol containing sodium acetates gave 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones (**3**) in good yields by using Mital's method.[2] These findings are summarized in Table 1.

Zinc 2-aminobenzenethiolate (**4a**) was prepared from commercial 2-aminobenzenethiol by Nodiff's method.[6] Zinc 2-aminobenzenethiolate derivatives **4b**—**h** were synthesized by improving Mital's method.[2] The basic hydrolysis of substituted 2-aminobenzothiazoles with 50% aqueous potassium hydroxide afforded the corresponding potassium 2-aminobenzenethiolates in the solution. These salts were converted to zinc 2-aminobenzenethiolates **4b**—**h** by the following treatment. That is, the potassium-salt solution was adjusted with acetic acid to pH 8 and filtered; then, methanol and zinc chloride in a 15% acetic acid solution were added to this filtrate. Some examples of these results are summarized in Table 2. The use of Compound **4** was necessary to cause the following reaction to proceed smoothly without forming a tarry product.

In the presence of sodium ethoxide, Compound **3** reacted with Compound **4** in 2-methoxyethanol (Methyl Cellosolve) to give 6,13-bis(arylamino)triphenodithiazine derivatives **5** as a new class of heterocycles. The synthetic results of Compound **5** are listed in Table 3. When the molar ratio of sodium ethoxide : Compound **3a** (Ar=phenyl) were equal to 1, 2, 4, and 8, Compound **5a** was obtained in yields of 26, 40, 42, and 29% respectively. The best yield of Compound **5a** was afforded by using a 1.5-fold excess of **4a** in relation to the **3a** in Methyl Cellosolve.

Table 2. Zinc 2-aminobenzenethiolate derivatives



Compd No.	Substituent R$_1$	Substituent R$_2$	Yield %	Mp[a) θ_m/°C (decomp)	N-Anal. Found (Calcd) (%)	Mass M$^+$ (mol wt)
4a	H	H	87	282	9.05 (8.93)	312 (313.76)
4b	Cl	H	86	274	7.40 (7.32)	380 (382.64)
4c	Me	H	87	300	8.44 (8.20)	340 (341.82)
4d	OMe	H	89	280	7.80 (7.50)	372 (373.82)
4e	Br	H	83	262	6.12 (5.94)	— (469.74)
4f	5,6-Benzo	H	53	244	6.93 (6.77)	412 (413.88)
4g	Cl	Cl	70	272	6.21 (6.20)	448 (451.52)
4h	Me	Me	54	248	7.64 (7.58)	368 (369.88)

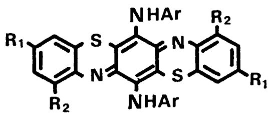
a) These results were obtained by DTA.

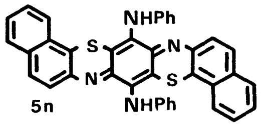
The decomposition point of Compound **5**, as examined by DTA, was observed to be as high as the other triphenodithiazines previously reported by us.[4,5] Especially, the replacement of two chlorine atoms at the 6 and 13 positions in Compound **Ia** to phenyl groups caused a rise in the decomposition point. Compound **5** was easily soluble in organic solvents. However, by the introduction of *p*-(benzamido)anilino groups at the 6 and 13 positions Compound **5** became sparingly soluble as compared with that of other arylamino groups.

The UV and visible absorption spectra showed 320—358 nm in H_2SO_4 and 555—621 nm in dioxane respectively. When the R$_1$ and R$_2$ substituents were hydrogen atoms, the UV and visible spectra of Compound **5** were found in the narrow regions of 320—328 nm and 555—560 nm respectively. These values were nearly the same as those of 6,13-dichlorotriphenodithazine[5] (**Ia**) (UV: λ_{max} 332 nm, visible: λ_{max} 560 nm) and triphenodithiazine[5] (**IIa**) (UV:$\lambda_{max}(H_2SO_4)$ 321 nm, visible: λ_{max}(dioxane) 560 nm). It was suggested that the spectral change caused by conjugation effect was very little, for 6,13-disubstituted arylamino groups could not be coplanar with the triphenodithiazine ring.

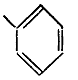
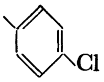
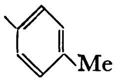
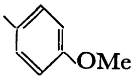
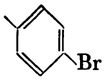
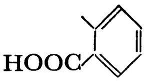
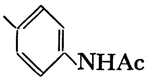
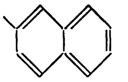
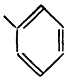
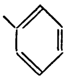
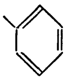
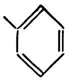
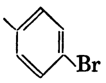
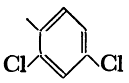
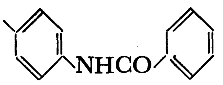
The bathochromic effect was observed by introducing the substituents, R$_1$ and/or R$_2$. Especially, the annelation compound **5n** showed a remarkable shift in both UV and visible spectra. The streak colors of

TABLE 3. 6,13-BIS(ARYLAMINO)TRIPHENODITHIAZINE DERIVATIVES **5**



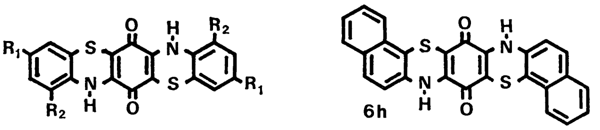


5n

Compd No.	Substituent			Yield	Mp[a)	Appearance (Streak color)	N-Anal.	Cl Br -Anal	Visible[b)	UV[c)
	Ar	R_1	R_2	%	θ_m/°C (decomp)		Found (Calcd) (%)	Found (Calcd) (%)	λ_{max}/nm ($\varepsilon\times10^{-4}$)	λ_{max}/nm ($\varepsilon\times10^{-4}$)
5a		H	H	50	500	Green needles (Purple)	11.6 (11.2)	—	555 (5.0)	328 (5.9)
5b		H	H	60	455	Green needles (Purple)	9.93 (9.84)	12.8 (12.5)	555 (4.3)	323 (4.4)
5c		H	H	42	460	Green needles (Purple)	10.8 (10.6)	—	557 (4.0)	320 (4.3)
5d		H	H	14	463	Brown needles (Purple)	10.2 (9.99)	—	559 (5.2)	324 (5.3)
5e		H	H	48	480	Brown needles (Purple)	8.54 (8.51)	25.1 (24.2)	555 (4.4)	323 (4.8)
5f		H	H	24	432	Blue needles (Purple)	9.38 (9.52)	—	558 (4.0)	330 (5.1)
5g		H	H	29	428	Brown needles (Purple)	13.9 (13.7)	—	560 (—)	328 (6.1)
5h		H	H	25	450	Purple powder (Purple)	11.5 (11.4)	—	560 (—)	326 (3.6)
5i		H	H	34	450	Brown needles (Purple)	9.36 (9.33)	—	557 (3.4)	326 (3.5)
5j		Cl	H	19	465	Brown needles (Violet)	9.85 (9.84)	12.7 (12.5)	579 (4.2)	337 (4.2)
5k		Me	H	20	495	Dark blue powder (Violet)	10.7 (10.6)	—	591 (5.2)	352 (5.1)
5l		OMe	H	16	460	Green needles (Violet)	10.2 (9.99)	—	578 (4.6)	336 (4.3)
5m		Br	H	25	390	Violet powder (Violet)	8.73 (8.51)	23.8 (24.2)	591 (3.6)	339 (3.5)
5n		3,4-Benzo	H	26	500	Brown needles (Blue)	9.37 (9.33)	—	621 (4.2)	358 (4.7)
5o		Br	H	28	500	Violet powder (Violet)	7.05 (6.87)	— (39.2)	586 (3.7)	336 (3.2)
5p		Cl	Cl	26	443	Violet powder (Violet)	7.29 (7.22)	— (36.6)	599 (3.5)	345 (3.0)
5q		Cl	H	32	390	Violet powder (Violet)	10.6 (10.4)	8.81 (8.78)	590 (3.9)	337 (4.3)

a) These results were obtained by DTA. b) In dioxane. c) In H_2SO_4.

Table 4. 6,13-Triphenodithiazinequinone derivatives **6**



Compd No.	Substituent		Yield %	Mp[a) θm/°C (decomp)	Appearance (Streak color)	N-Anal. Found (Calcd) (%)	Cl Br-Anal. Found (Calcd) (%)	Visible[b) λ_{max}/nm ($\varepsilon\times10^{-4}$)	UV[b) λ_{max}/nm ($\varepsilon\times10^{-4}$)	IR	
	R_1	R_2								ν_{N-H} cm^{-1}	$\nu_{C=O}$ cm^{-1}
6a	H	H	73	393	Blue powder (Blue)	7.91 (8.00)	—	723 (5.6)	334 (6.2)	3240	1635
6b	Cl	H	68	414	Blue powder (Blue)	6.65 (6.68)	17.1 (17.9)	733 (6.8)	337 (6.3)	3240	1630
6c	Me	H	66	357	Blue powder (Blue)	7.45 (7.40)	—	749 (6.4)	335 (6.2)	3250	1635
6d	OMe	H	64	342	Blue powder (Greenish blue)	6.89 (6.83)	—	773 (5.2)	331 (6.4)	3200	1630
6e	Br	H	55	417	Dark blue powder (Greenish blue)	5.63 (5.51)	30.6 (31.4)	749 (5.6)	340 (5.2)	3250	1635
6f	Cl	Cl	15	417	Green powder (Greenish blue)	5.81 (5.74)	28.9 (29.1)	748 (6.7)	348 (6.8)	3240	1640
6g	Me	Me	34	372	Dark blue powder (Blue)	6.94 (6.89)	—	750 (6.8)	342 (6.7)	3250	1640
6h	3,4-Benzo	H	57	420	Green powder (Green)	6.32 (6.22)	—	860 (5.7)	362 (6.6)	3250	1620

a) These results were obtained by DTA. b) In H_2SO_4.

Compound **5** were from purple to blue.

The IR absorption spectra in KBr showed the N–H stretching band (around 3300 cm^{-1}) and the disappearance of the C=O stretching band (around 1660 cm^{-1}) of Compound **3**.

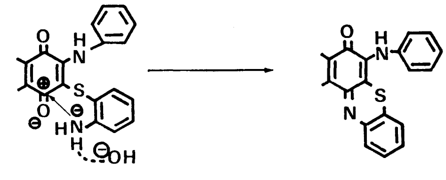
On the other hand, the reaction of Compound **3a** (Ar=phenyl) with Compound **4** in *N,N*-dimethyformamide (DMF), in the absence of a base, afforded 7,14-dihydro-6,13-triphenodithiazinequinone derivatives **6** by eliminating the anilino groups of Compound **3a**.7) The synthetic results of Compound **6** are listed in Table 4. Some of the triphenodithiazinequinones have already been synthesized by another synthetic route.8) A good yield of Compound **6a** (unsubstituted) was obtained only when the molar ratio of **3a**:**4a** was 1:2 in DMF. This reaction was tested in various solvents: chlorobenzene, nitrobenzene, anisole, acetic acid, cyclohexanol, Methyl Cellosolve, DMF, *etc.* Consequently, DMF was found to be the best solvent for dissolving **3** together with **4**.

Several **3** compounds as well as **3a** reacted with **4a** to give the same compound, **6a**, in 60—68% yields. When **3k** (R=cyclohexyl) or **3l** (R=butyl) was used as the starting material, however, Compound **6a** was obtained in a low yield.

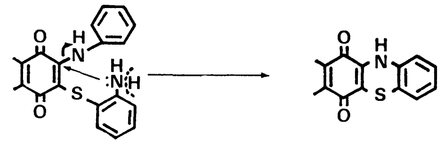
The **6** compounds decomposed at 342—420 °C, and the streak colors were from blue to green. Because the **6** compounds were sparingly soluble in the usual solvents, then UV and visible absorption spectra were measured as 331—362 nm and 723—860 nm respectively in H_2SO_4. Accordingly, the visible spectra were actually observed in the near-infrared region. The bathochromic effect of Compound **6** was observed as well as that of Compound **5**.

The IR absorption spectra in KBr showed a N–H stretching band (around 3250 cm^{-1}) and a C=O stretching band (around 1630 cm^{-1}).

It may be assumed that the reaction mechanisms are based on Pearson's HSAB (Hard and Soft Acids and Bases) principle9), as is shown in Schemes 3a and 3b. The mechanisms in the residual side of the intermediate can also be similarly.



Scheme 3a. Hard acid and hard base type.



Scheme 3b. Soft acid and soft base type.

Experimental

The melting points are uncorrected. The DTA was measured on Rigaku Denki YGHD. The IR spectra were taken with a JASCO IRA-2 apparatus. The UV and visible spectra were recorded with a Hitachi EPS-3T apparatus.

*Condensation of Chloranil **1** with Amines **2**.* To a stirred suspension of **1** (0.025 mol) and sodium acetate (0.061 mol in ethanol (50 ml), we added arylamine **2** (0.10 mol). The mixture was then heated under reflux for 3—5 h and filtered while still hot. The residue was washed with ethanol, hot water, and water, and dried. Recrystallization from the appropriate solvents gave 2,5-bis(arylamino)-3,6-dichloro-1,4-benzoquinones (**3**) in a good yield. The yield and properties of **3** are listed in Table 1.

Preparation of 6,13-Dianilino-type ***5***. A mixture of **3** (0.0025 mol), zinc salt of substituted 2-aminobenzenethiol **4** (0.0025 mol), and sodium ethoxide (0.0075 mol) was refluxed for 6—8 h in Methyl Cellosolve (150 ml) and then cooled overnight. The precipitated solid was collected, washed with Methyl Cellosolve, ethanol, hot 3 M HCl (1 M=1 mol dm^{-3}), and water, and dried. Recrystallization from *o*-dichlorobenzene produced 6,13-bis(arylamino)triphenodithiazines (**5**). The yield and properties of **5** are listed in Table 3.

Preparation of 6,13-Quinone-type ***6***. A mixture of **3** (0.0025 mol) and **4** (0.0050 mol) in DMF (50 ml) was refluxed for 12 h and filtered while still hot. The residue was washed with hot DMF until the filtrate was almost colorless, washed with ethanol, and dried. Further, the solid was washed with hot 3 M HCl for a long time and then with water, and dried. Sublimation *in vacuo* gave 7,14-dihydro-6,13-triphenodithiazinequinones (**6**). The yield and properties of **6** are listed in Table 4.

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