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SYNTHESIS OF 3,5-BIS(*m*- OR *m*,*m*′-DI-SUBSTITUTED-*p*-AMINOPHENYL)-*N*-AMINO-1,2,4-TRIAZOLE AND ITS APPLICATION TO BENZIDINE YELLOW TYPE PIGMENT

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SUMMARY

3,5-*Bis*(m- *or* m,m′-*di-substituted*-p-*aminophenyl*)-N-*amino*-1,2,4-*triazoles* (4) *were synthesized by the oxidative dimerization of the hydrazine adduct of* m- *or* m,m′-*di-substituted*-p-*aminobenzonitriles* (3) *followed by acid-catalysed rearrangement. They were used to prepare Benzidine Yellow type pigments* (8), *the thermal stability of which was definitely superior to that of Benzidine Yellow* (7) *while a slight blue shift of absorption maximum was observed.*

1. INTRODUCTION

One of the most serious problems in the field of dye chemistry is the toxicity and carcinogenicity of benzidine which has been an indispensable diamine component of many commercial azo dyes and pigments. In attempts to replace benzidine by relatively less toxic diamine compounds, *o*-tolidine,[1] *o*-dianisidine,[2] 4,4′-diaminodiphenylsulphide,[3] 4-aminobenzoyl-4′-aminoanilide,[4] 4,4′-diaminodiphenylamine,[5] 4,4′-diaminodiphenylurea[6] or 1,5-diaminonaphthalene[7] have been used to prepare new azo dyes. Their properties, however, were unsatisfactory in view of carcinogenicity, substantivity, hue, and colour fastness. In a preceding paper[8] we have reported that 3,5-bis(*p*-aminophenyl)-1,2,4-triazole (1) does not show toxicity or carcinogenicity and that the Direct Deep Black EX type dye (2) derived from (1) has good properties, i.e. shade, substantivity, and fastness to light and washing. Although this type of compound offers versatile application as a substitute for benzidine, an effective preparation method for the triazole derivatives has never been established.

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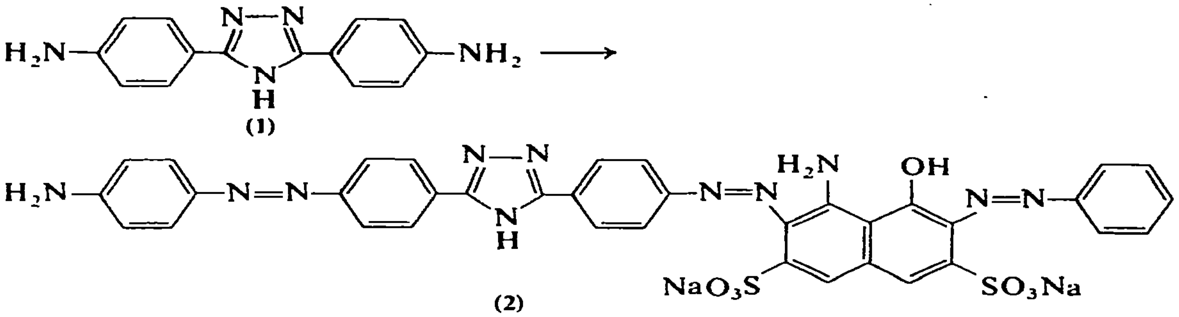


(1)

(2)

We now wish to report the synthesis of 3,5-bis(*p*-aminophenyl)-*N*-amino-1,2,4-triazoles having substituents adjacent to the amino group on the phenyl ring and Benzidine Yellow type pigments derived from them. The substituent effect on the properties of the triazoles and pigments is also discussed on the basis of the absorption spectra and thermal analysis.

2. RESULTS AND DISCUSSION

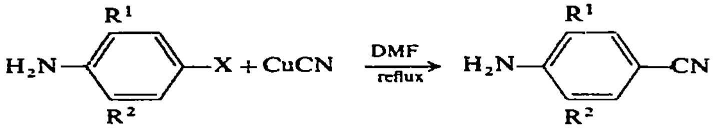
As is well known, cuprous cyanide is available for the cyanation of aromatic halides.[9] Friedman and Shechter reported that direct cyanation of aromatic halides took place smoothly using a slight excess of cuprous cyanide in DMF.[10] We obtained five aminobenzonitriles (**3a**–**e**) from the corresponding haloanilines through a modified method. That is, the mixture of haloaniline and 20% excess cuprous cyanide was refluxed in DMF and then treated with ethylene diamine.[11] The results are summarized in Table 1.

We have already found that 3,5-bis(*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4a**) is obtainable in a good yield by the reaction of *p*-aminobenzonitrile with hydrazine hydrate in the presence of mercaptoethanol[12] and hydrazine dihydrochloride at 100 °C for several hours.[8] As shown in Table 2, *m*-chloro (**4b**), *m*-methyl (**4d**), and *m*,*m*′-dimethyl (**4e**) derivatives of the triazoles were obtained in good yields under the same reaction conditions as for **4a**.

When *p*-amino-*m*,*m*′-dichlorobenzonitrile (**3c**) was subjected to the same reaction condition, 3,6-bis(*m*,*m*′-dichloro-*p*-aminophenyl)-1,2,4,5-tetrazine (**6c**) was obtained quantitatively after recrystallization from pyridine. We were able to obtain 3,5-bis(*m*,*m*′-dichloro-*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4c**) in 82% yield by using a large amount of acetic acid. The i.r. spectrum of **6c** is extremely simple because of the molecular symmetry and shows absorption at 1608 and 1402 cm^{-1} due to the tetrazine ring, while absorptions at 1623 and 1475 cm^{-1} characteristic of the triazole ring are observed in the i.r. spectrum of **4c**. Furthermore, the electronic absorption maximum of **6c** at 377 nm differs definitely from that of **4c** at 297 nm.

TABLE 1

CYANATION OF SUBSTITUTED HALOANILINES (3a–e)



(3a–e)

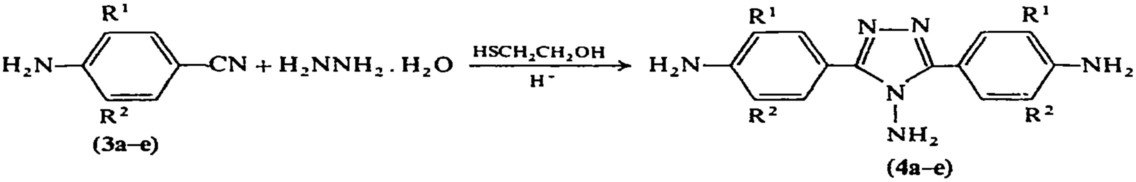
Substrate			Time	Product	Yield
R^1	R^2	X	(h)		(%)
H	H	Br	4	(3a)	83[a]
H	Cl	Br	5·5	(3b)	63
Cl	Cl	Br	5	(3c)	82
H	CH_3	Br	5	(3d)	50
H	CH_3	I	5	(3d)	70
CH_3	CH_3	Br	4	(3e)	62

[a] Published result by L. Friedman *et al.*[10]

It is known that dihydrotetrazine (5) is formed at the first stage of this reaction and rearranged to *N*-amino-1,2,4-triazole (4) under acidic condition or alternatively air-oxidized to tetrazine (6) (Scheme 1). The rate of the acid-catalyzed rearrangement is extremely low in the case of tetrachloro substituted dihydrotetrazine (5c) due to the electron-withdrawing effect of the substituent, which destabilizes a cationic intermediate developing in the course of this type of rearrangement.

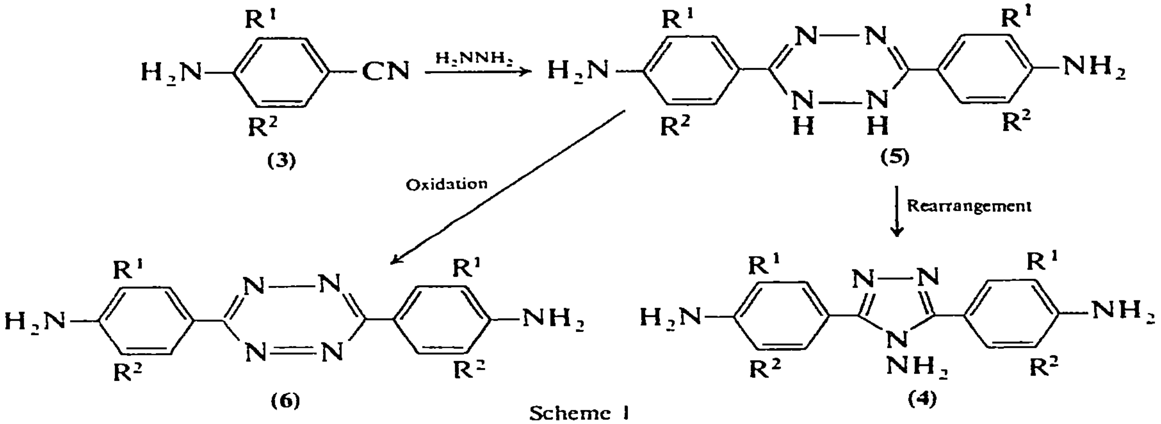
TABLE 2

PREPARATION OF *m*-SUBSTITUTED TRIAZOLES



Compound	R^1	R^2	Reaction conditions[a]	Time (h)	Yield (%)	Spectrum in MeOH	
						λ_{max} (nm)	$\varepsilon \times 10^{-1}$
a	H	H	A	4	75	293	3·48
b	H	Cl	A	5	78	294	3·56
c	Cl	Cl	B	40	82	297	3·63
d	H	CH_3	A	4·5	70	295	3·56
e	CH_3	CH_3	A	4·5	62	297	3·54

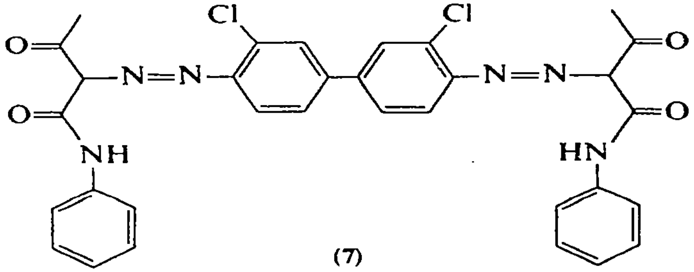
[a] A, 3:hydrazine hydrate:2-mercaptoethanol:hydrazine dihydrochloride = 1:4:1:0·4.
B, 3:hydrazine hydrate:2-mercaptoethanol:acetic acid = 1:4:1·2:15.



Scheme 1

Absorption maxima and molar extinction coefficients of the triazoles (**4a–e**) are shown to be insensitive to the change of substituent on the phenyl ring (Table 2).

In order to examine the applicability of the triazole as a substitute for benzidine, the yellow pigment corresponding to Benzidine Yellow (7)[13] was prepared. It has been confirmed already that **4a** is easily tetrazotized by $NaNO_2$ in HCl solution with concomitant elimination of the *N*-amino group.[8] As the compounds (**4a–e**) are sparingly soluble in aqueous HCl solution, tetrazotization of these triazoles was achieved by addition of acetic acid as a co-solvent. Coupling of the tetrazonium compounds with acetacetanilide was performed according to the synthetic procedure of (7) to give yellow pigments (**8a–e**) in excellent yields as shown in Table 3. Visible spectra of **8a**, **8b** and **8d** show a slight blue shift of the absorption maxima in comparison with that of **7**, which has an absorption maximum at 424 nm in DMF. The molar extinction coefficients of these three pigments are the same as that of 7 (ε, 6·6 × 10^{-4}). On the other hand, the spectral properties of the tetra-substituted pigments **8c** and **8e** are considerably different. This fact can be attributed to the steric crowding around an azo linkage imposed by the di-substitution at the *ortho* position relative to the azo group, giving rise to a loss of planarity of the π-conjugated system.[14]



(7)

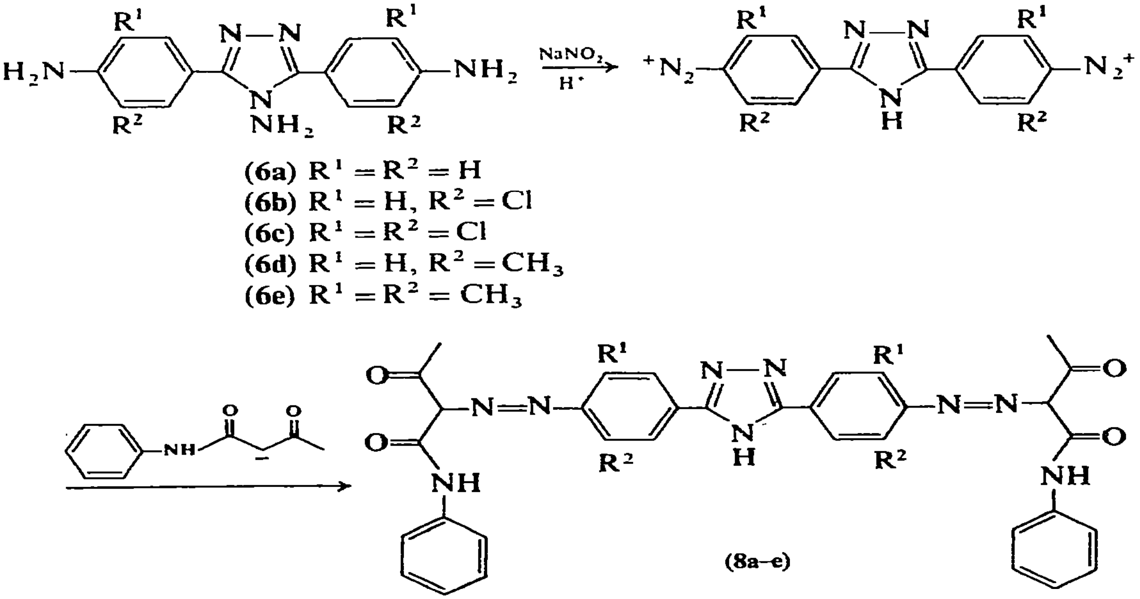
TABLE 3

PREPARATION OF YELLOW PIGMENTS (**8a–e**) AND THEIR VISIBLE SPECTRA

Product	*Yield* (%)	λ_{max} (*nm*)	$\varepsilon \times 10^{-4}$ *in DMF*	*Microanalysis* (%)					
				Found			*Calculated*		
				C	*H*	*N*	*C*	*H*	*N*
8a	74	403	6·8	64·77	4·27	19·29	65·07	4·66	20·08
8b	80	404	6·7	58·14	3·90	16·57	58·45	4·19	18·04
8c	84	389	4·6	52·79	3·29	15·53	53·35	3·29	16·47
8d	92	412	6·8	65·64	4·97	18·47	65·94	5·07	19·22
8e	64	396	5·5	64·40	5·64	18·02	66·75	5·46	18·43

Figure 1 shows the result of differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) for yellow pigments **8a**, **8b** and **8d**. Two distinct endothermic processes were observed for the tetra-substituted pigments **8c** and **8e**, which were shown to be thermally less stable than the other pigments. The decomposition temperature was found to rise in the order **8d** (290 °C) < **7** (302 °C) < **8a** (306 °C) < **8b** (308 °C). When the thermal stability is estimated on the basis of 10 % weight loss temperature, **8a** (316 °C) and **8b** (320 °C) are considerably superior to Benzidine Yellow (7; 200 °C).

The above observation unambiguously indicates that the newly synthesized yellow pigment **8b** can serve as a practical substitute for Benzidine Yellow.



(**6a**) $R^1 = R^2 = H$
(**6b**) $R^1 = H, R^2 = Cl$
(**6c**) $R^1 = R^2 = Cl$
(**6d**) $R^1 = H, R^2 = CH_3$
(**6e**) $R^1 = R^2 = CH_3$

Scheme 2

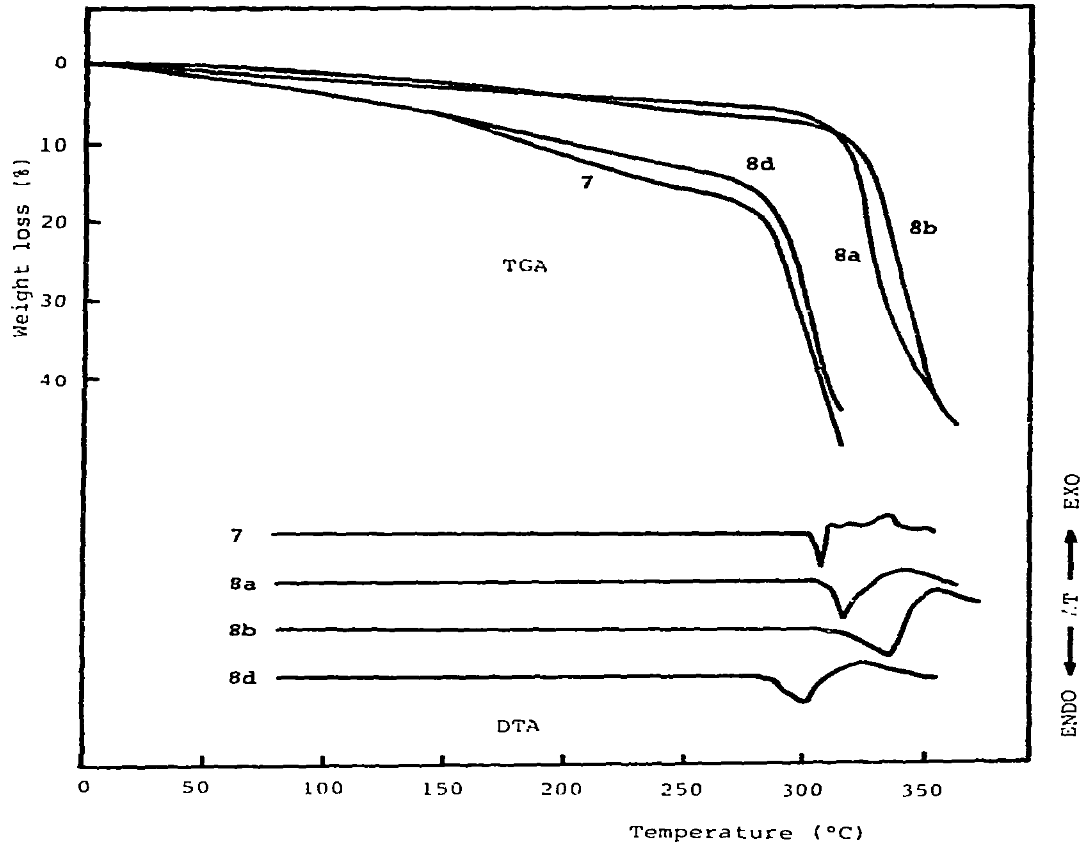


Fig. 1. TGA and DTA of yellow pigments 7, 8a, 8b and 8d. Heating rate 10°C min^{-1}, N_2 stream.

3. EXPERIMENTAL

3.1. *p-Aminobenzonitrile derivatives (general method)*

After a mixture of *p*-haloaniline (20 mmol), CuCN (2·15 g; 24 mmol), and DMF (10 ml) was heated at reflux temperature for about 5 h, ethylene diamine (20 ml) was added to the hot reaction mixture and stirred for 2 h. Following the addition of 40 ml of ice water, generated crystals were filtered, dried, and purified by chromatography on silica gel (eluent: chloroform) and recrystallization from benzene–hexane. The reaction conditions and yields are shown in Table 1. *p*-Aminobenzonotrile (**3a**): m.p. 85–86°C (85–86°C).[10] *p*-Amino-*m*-methylbenzonitrile (**3d**): m.p. 93–94°C (95°C).[15] *p*-Amino-*m*-chlorobenzonitrile (**3b**): m.p. 105°C; ν (C$\equiv$N) 2280 cm^{-1}; Calculated for $C_7H_5N_2Cl$ (%): C, 55·10; H, 3·30;

N, 18·36; Found (%): C, 55·42; H, 3·32; N, 18·16. *p*-Amino-*m*,*m*′-dichlorobenzonitrile (**3c**): m.p. 115 °C; ν (C$\equiv$N) 2300 cm^{-1}; Calculated for $C_7H_4N_2Cl_2$ (%): C, 44·92; H, 2·14; N, 14·97; Found (%): C, 44·73; H, 2·10; N, 14·97. *p*-Amino-*m*,*m*′-dimethylbenzonitrile (**3e**): m.p. 110–111 °C; ν (C$\equiv$N) 2240 cm^{-1}. Calculated for $C_9H_{10}N_2$ (%): C, 73·94; H, 6·90; N, 19·16; Found (%): C, 73·66; H, 6·89; N, 19·05.

3.2. *3,5-Bis*(p-*aminophenyl*)-N-*amino-1,2,4-triazole* (**4a**) (*method A*)

When a mixture of *p*-aminobenzonitrile (1·18 g; 10 mmol), hydrazine hydrate (1·94 ml; 40 mmol), 2-mercaptoethanol (0·7 ml; 10 mmol) and hydrazine dihydrochloride (0·42 g; 4 mmol) was heated at 100 °C for 4 h, the colour of the reaction mixture turned from yellow to white. Then it was treated with 50 ml of 10% NaOH. The precipitate formed was washed with water, dried under vacuum, and recrystallized from methanol–water to yield 1·89 g (75%) of 3,5-bis(*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4a**): m.p. 225–227 °C (dec.); i.r. (KBr) 3390–3140, 1610, 1500, 1290, 1186 cm^{-1}. Calculated for $C_{14}H_{14}N_6$ (%): C, 63·16; H, 5·26; N, 31·58. Found (%): C, 63·18; H, 5·26; N, 31·48.

3.3. *3,5-Bis*(m-*chloro*-p-*aminophenyl*)-N-*amino-1,2,4-triazole* (**4b**)

m-Chloro-*p*-aminobenzonitrile (1·53 g; 10 mmol) was treated following method A. The crude product was recrystallized from methanol–water to yield 2·61 g (78%) of 3,5-bis(*m*-chloro-*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4b**): m.p. 259–261 °C (dec.); i.r. (KBr) 3340–3160, 1626, 1482, 1325, 1168 cm^{-1}. Calculated for $C_{14}H_{12}N_6Cl_2$ (%): C, 50·16; H, 3·61; N, 25·17. Found (%): C, 50·31; H, 3·65; N, 25·56.

3.4. *3,5-Bis*(m-*methyl*-p-*aminophenyl*)-N-*amino,1,2,4-triazole* (**4d**)

m-Methyl-*p*-aminobenzonitrile (1·32 g; 10 mmol) was treated according to method A. Recrystallization of the crude product gave 2·06 g (70%) of 3,5-bis(*m*-methyl-*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4d**): m.p. 248–252 °C (dec.); i.r. (KBr) 3320–3140, 1632, 1492, 1295, 1140 cm^{-1}. Calculated for $C_{16}H_{20}N_6$ (%): C, 65·28; H, 6·16; N, 28·55. Found (%): C, 64·46; H, 6·27; N, 28·40.

3.5. *3,5-Bis*(m,m′-*dimethyl*-p-*aminophenyl*)-N-*amino-1,2,4-triazole* (**4e**)

m,*m*′-Dimethyl-*p*-aminobenzonitrile (1·46 g; 10 mmol) was treated according to method A. Recrystallization from methanol–water afforded 2·00 g (62%) of 3,5-bis(*m*,*m*′-dimethyl-*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4e**): m.p. 251–255 °C (dec.); i.r. (KBr) 3370–3200, 2880, 1620, 1475, 1320–1290, 1140 cm^{-1}. Calculated for $C_{18}H_{22}N_6$ (%): C, 67·05; H, 6·88; N, 26·07. Found (%): C, 67·51; H, 6·89; N, 26·08.

3.6. *3,5-Bis*(m,m′-*dichloro*-p-*aminophenyl*)-N-*amino-1,2,4-triazole* (**4c**) (*method B*)

A mixture of *m*,*m*′-dichloro-*p*-aminobenzonitrile (1·87 g; 10 mmol), hydrazine hydrate (1·94 ml, 40 mmol), and 2-mercaptoethanol (0·84 ml; 12 mmol) was heated at 100 °C for 15 min to result in the deposition of a yellow solid. After 5·72 ml of acetic acid was added to this mixture and heating at 100 °C was continued for a further 40 h, 50 ml of 10 % NaOH was added. The mixture was cooled to room temperature, then the white solid formed was washed sufficiently with water, dried under vacuum and recrystallized from methanol to give 3·31 g (82 %) of 3,5-bis(*m*,*m*′-dichloro-*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4c**): m.p. 296–298 °C (dec.); i.r. (KBr) 3450–3200, 1623, 1475, 1320, 1180 cm^{-1}. Calculated for $C_{14}H_{10}N_6Cl_4$ (%): C, 41·61; H, 2·49; N, 20·80. Found (%): C, 41·57; H, 2·48; N, 19·22.

3.7. *3,6-Bis(*m,m′*-dichloro-*p*-aminophenyl)-1,2,4,5-tetrazine* (**6c**)

When *m*,*m*′-dichloro-*p*-aminobenzonitrile was treated according to method A, 3,6-bis(*m*,*m*′-dichloro-*p*-aminophenyl)-1,2,4,5-tetrazine (**6c**) was obtained quantitatively as red crystals after recrystallization from pyridine: m.p. 300 °C (dec.); i.r. (KBr) 3360, 1608, 1402 cm^{-1}; visible (DMF) λ_{max} 377 nm (ε, $4{\cdot}4 \times 10^{-4}$). Calculated for $C_{14}H_8N_6Cl_4$ (%): C, 41·78; H, 1·99; N, 20·89. Found (%): C, 41·60; H, 2·11; N, 21·04.

3.8. *Preparation of non-substituted pigment* (**8a**)

3,5-Bis(*p*-aminophenyl)-*N*-amino-1,2,4-triazole (**4a**) (0·61 g; 2·3 mmol) was dissolved in 15 ml of 1·5N HCl solution by heating. A tetrazonium solution was prepared by pouring 1·18 ml of 40 % sodium nitrite solution into this solution at 0–10 °C. A solution of acetacetanilide (1·12 g; 6·3 mmol), sodium acetate (0·37 g), calcium carbonate (0·45 g) and 20 ml of 0·2N HCl was added to the tetrazonium solution. This reaction mixture was stirred at room temperature for 15 h and then at 100 °C for 1 h. The yellow precipitate was collected by filtration at 70 °C from the reaction mixture, washed with water and dried at 65 °C under reduced pressure. Recrystallization from DMF gave a yellow pigment (**8a**). The yield, absorption maximum, and microanalysis are shown in Table 3; i.r. (KBr) 3050, 1658, 1500, 1275, 958, 768 cm^{-1}.

3.9. *Di- or tetra-substituted pigments* (**8b–e**)

After a mixture of di- or tetra-substituted triazole (2·3 mmol), 10 ml of acetic acid, and 10 ml of water was dissolved by heating, 40 % sodium nitrite solution (1·18 ml) was poured into this solution at 0–10 °C. Acetacetanilide solution prepared as in section 3.8 was added to the tetrazonium solution. The yellow pigments (**8b–e**) were obtained after the same treatment described for **8a** above. The results were summarized in Table 3. Infrared spectra in KBr are described below:

8b: 3100, 1658, 1590, 1500, 1245, 1182, 955, 763 cm^{-1}
8c: 3100, 1660, 1590, 1508, 1270, 1170, 958, 768 cm^{-1}
8d: 3100, 1660, 1592, 1515, 1265, 1195, 958, 768 cm^{-1}
8e: 3030, 1657, 1594, 1514, 1295, 1208, 960, 765 cm^{-1}

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