Dyes and Pigments 7 (1986) 289–298

Synthesis of 2,4-Dihydro-6-methyl-4-phenyl-2-(4-substituted phenyl)pyrazolo[3,4-*d*]-1,2,3-Triazole Derivatives and Their Use as Fluorescent Whiteners for Polyester Fibres

D. W. Rangnekar and P. V. Tagdiwala

Dyes Research Laboratory, Department of Chemical Technology,
University of Bombay, Matunga, Bombay 400 019, India

(Received: 5 November, 1985)

SUMMARY

Diazotised arylamines (**2a**–**2c**) *were coupled with 5-amino-3-methyl-1-phenylpyrazole* **1** *to give 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles* (**3a**–**3c**) *which were then oxidised, using cupric acetate and DMF in a current of air, to the 2,4-dihydro-6-methyl-4-phenyl-2-(4-substituted phenyl)pyrazolo[3,4-d]-1,2,3-triazoles* (**4a**–**4c**). *The carboxylic acid group in* **4c** *was further converted to the corresponding 2-[4-(benzimidazol-2-yl)phenyl], 2-[4-(benzoxazol-2-yl)phenyl] and 2-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]-derivatives* (**6a**, **6b** *and* **8** *respectively*). *2-Hydro-2-(4-aminophenyl)naphtho[1,2-d]-1,2,3-triazole* (**9**) *was diazotised and similarly converted to 2,4-dihydro-6-methyl-4-phenyl-2-[4-(2-hydronaphtho[1,2-d]-1,2,3-triazol-2-yl)phenyl]pyrazolo [3,4-d]-1,2,3-triazole* (**10**). *Benzidine* (**11**) *was tetrazotised and similarly converted to 2,2′-(1,1′-biphenyl-4,4′-diyl)bis(2,4-dihydro-6-methyl-4-phenylpyrazolo-[3,4-d]-1,2,3-triazole)* (**12**), *using 2 moles of* **1**. *The 2,4-dihydro-6-methyl-4-phenyl-2-(4-substituted phenyl)pyrazolo[3,4-d]-1,2,3-triazole derivatives* (**4a**–**4b**, **6a**–**6b**, **8** *and* **10**) *and 2,2′-(1,1′-biphenyl-4,4′-diyl)-bistriazole* (**12**) *were applied as fluorescent whiteners on polyester fibres and gave excellent results.*

1. INTRODUCTION

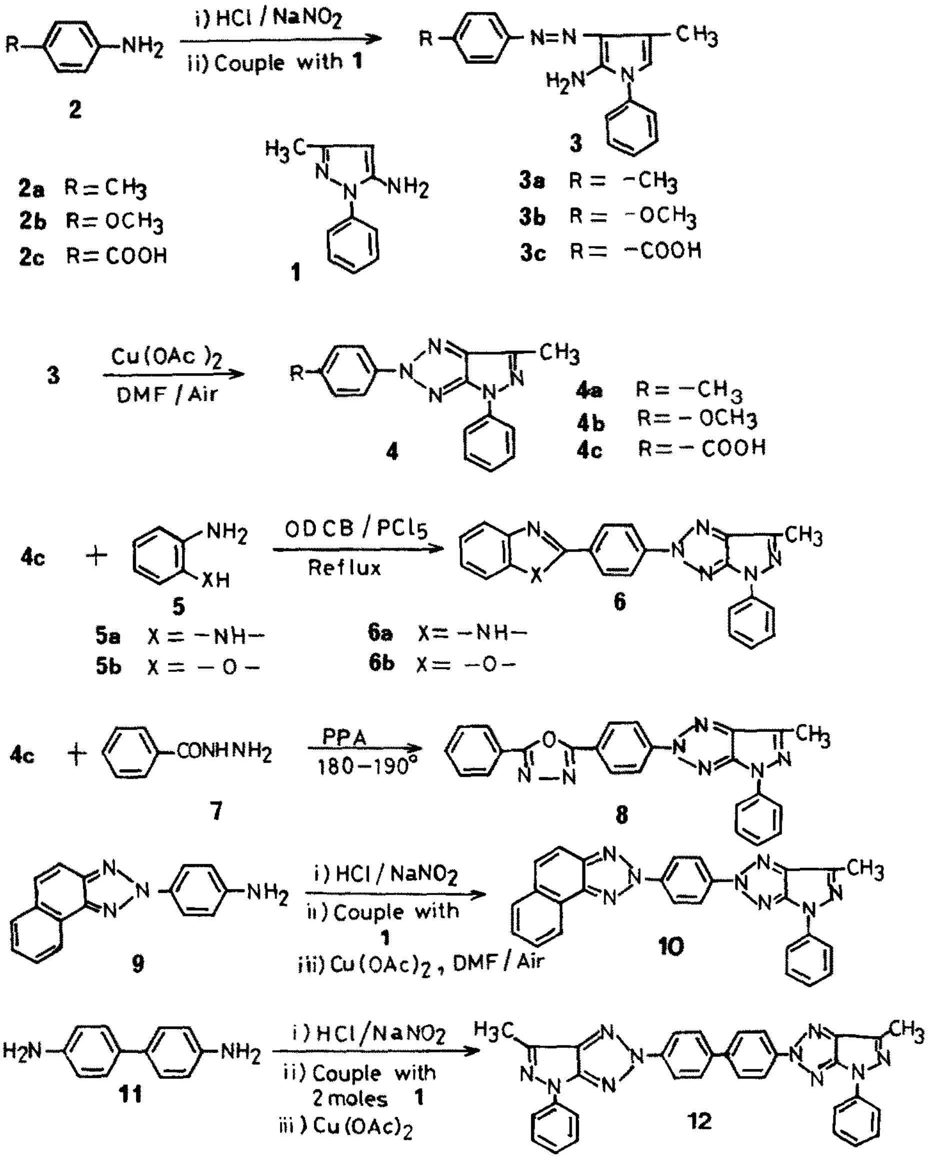
Many novel heterocyclic compounds have been synthesised in the search for fluorescent whiteners for polyester fibres. The general approach in the

Dyes and Pigments 0143-7208/86/$03·50 © Elsevier Applied Science Publishers Ltd, England, 1986. Printed in Great Britain

synthesis of heterocyclic systems for use as fluorescent whiteners has been mainly in two directions, in which the same or different heterocyclic systems are linked together with each other so as to increase the overall conjugation in the resulting molecule, or in which the same single or different heterocyclic systems are present in a fused system in order to increase the conjugation and provide planar rigidity to the resulting structure. We have previously reported the use of 1,3,4-oxadiazole derivatives as fluorescent whiteners[1] (an example of the first category) and in this present work, compounds containing two different heterocycles, pyrazole and 1,2,3-triazole, in a fused system are reported, as an example of the second category.

2. RESULTS AND DISCUSSION

To obtain compounds which may possess fluorescent properties, compounds containing the pyrazolo[3,4-*d*]-1,2,3-triazole system as one substituent in 1,4-bis-substituted phenylene derivatives, with variations in the other substituent, were synthesised. The substituents selected in the 4-position of the 1,4-bis-substituted phenylene derivatives were simple groups such as methyl and methoxy and favourable heterocyclic systems such as benzimidazol-2-yl, benzoxazol-2-yl, oxadiazol-2-yl and 1,2,3-triazol-2-yl derivatives. 5-Amino-3-methyl-1-phenylpyrazole (**1**) was used as the coupling component for preparing *o*-aminoarylazo dyes which were oxidised to the corresponding pyrazolo[3,4-*d*]-1,2,3-triazole derivatives. Thus *p*-toluidine (**2a**), *p*-anisidine (**2b**) and *p*-aminobenzoic acid (**2c**) were diazotised and coupled with **1** to give 5-amino-4-(4-methylphenyl)-azo-3-methyl-1-phenylpyrazole (**3a**), 5-amino-4-(4-methoxyphenyl)azo-3-methyl-1-phenylpyrazole (**3b**) and 5-amino-4-(4-carboxyphenyl)azo-3-methyl-1-phenylpyrazole (**3c**), respectively. These *o*-aminoaryl azo dyes were oxidised using cupric acetate and DMF in a current of air to give the corresponding 2,4-dihydro-6-methyl-4-phenyl-2-(4-methylphenyl)-pyrazolo[3,4-*d*]-1,2,3-triazole (**4a**), 2,4-dihydro-6-methyl-4-phenyl-2-(4-methoxyphenyl)pyrazolo[3,4-*d*]-1,2,3-triazole (**4b**) and 2,4-dihydro-6-methyl-4-phenyl-2-(4-carboxyphenyl)pyrazolo[3,4,-*d*]-1,2,3-triazole (**4c**), respectively. The carboxylic acid group in compound **4c** was further useful in building up a variety of heterocycles which are known fluorophores. Thus, compound **4c** was reacted with 1,2-diaminobenzene (**5a**) and with 2-aminophenol (**5b**), using phosphorus pentachloride in


i) HCl / NaNO2
ii) Couple with 1
2
2a R=CH3
2b R=OCH3
2c R=COOH
1
3
3a R= -CH3
3b R= -OCH3
3c R= -COOH
Cu(OAc)2
DMF / Air
4
4a R=-CH3
4b R=-OCH3
4c R=-COOH
ODCB / PCl5
Reflux
5
5a X=-NH-
5b X=-O-
6
6a X=-NH-
6b X=-O-
PPA
180-190°
7
8
i) HCl / NaNO2
ii) Couple with 1
iii) Cu(OAc)2, DMF / Air
9
10
i) HCl/NaNO2
ii) Couple with 2 moles 1
iii) Cu(OAc)2
11
12

o-dichlorobenzene at reflux, to give 2,4-dihydro-6-methyl-4-phenyl-2-[4-(benzimidazol-2-yl)phenyl]pyrazolo[3,4-*d*]-1,2,3-triazole (**6a**) and 2,4-dihydro-6-methyl-4-phenyl-2-[4-(benzoxazol-2-yl)phenyl]pyrazolo[3,4-*d*]-1,2,3-triazole (**6b**), respectively. Compound **4c** was also reacted with benzhydrazide (**7**) in PPA at 180–190 °C to give 2,4-dihydro-6-methyl-4-phenyl-2-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl]pyrazolo[3,4-*d*]-1,2,3-triazole (**8**).

p-Nitroaniline was diazotised and coupled to 2-aminonaphthalene-1-sulphonic acid and the resulting *o*-aminoarylazo dye was oxidised to give 2-hydro-2-(4-nitrophenyl)naphtho[1,2-*d*]-1,2,3-triazole. The nitro group was reduced with iron and hydrochloric acid to give 2-hydro-2-(4-aminophenyl)naphtho[1,2-*d*]-1,2,3-triazole (**9**). Compound **9** was then diazotised and coupled with **1** and the resulting *o*-amino hetaryl azo dye oxidised to yield 2,4-dihydro-6-methyl-4-phenyl-2-[4-(2-hydronaphtho-(1,2-*d*)-1,2,3-triazol-2-yl)phenyl]pyrazolo[3,4-*d*]-1,2,3-triazole (**10**).

The synthesis was also effected at a representative compound with a relatively closed structure having a 4,4′-bishetaryl-biphenylene system in place of the 1,4-bishetarylphenylene system present in the previously described compounds (**6a**–**6b**, **8** and **10**). Thus, benzidine (**11**) was tetrazotised and coupled with two moles of **1** to give 4,4′-(1,1′-biphenyl-4,4′-diyl)bisazo-bis(5-amino-3-methyl-1-phenylpyrazole), which was then oxidised to 2,2′-(1,1′-biphenyl-4,4′-diyl)bis(2,4-dihydro-6-methyl-4-phenyl-pyrazolo[3,4-*d*]-1,2,3-triazole) (**12**).

The various 2,4-dihydro-6-methyl-4-phenyl-2-(4-substituted phenyl)-pyrazolo[3,4-*d*]-1,2,3-triazole derivatives (**4a**–**4c**, **6a**–**6b**, **8** and **10**) were pale yellow to colourless compounds possessing blue (**4a**–**4c**), strong bluish violet (**6a**–**6b**, **8**) or strong violet fluorescence (**10**) in daylight in ethyl acetate, ethanol, etc. 2,2′-(1,1′-Biphenyl-4,4′-diyl)bis(2,4-dihydro-6-methyl-4-phenyl pyrazolo[3,4-*d*]-1,2,3-triazole) (**12**) was colourless and exhibited strong violet fluorescence in daylight in ethyl acetate. Compounds **4a**–**4b**, **6a**–**6b**, **8**, **10** and **12** were applied to polyester fibres as fluorescent whiteners. In general, the compounds showed excellent whitening effects of polyester fibre, being particularly outstanding in the case of compounds **6a**–**6b**, **10** and **12**. Despite their high molecular weights, the compounds were found to possess comparable spectral properties with known standard fluorescent whiteners.

The PMR spectrum of **4b** in acetone-d_6 showed a sharp singlet centred at 2·6 corresponding to three protons which could be attributed to the methyl group at C-6, a sharp singlet at 4·0 corresponding to three protons and attributable to the methoxy group at the 4-position of the phenyl ring at N-2, and a multiplet between 7·1 and 8·3 corresponding to nine protons, which could be attributed to the hydrogen atoms of the phenyl rings at N-2 and N-4.

The mass spectra of the compounds showed the molecular ion peaks in agreement with the proposed molecular weights, thus confirming the molecular formulae of these compounds, e.g. **6a** at *m/e* 391; **6b** at *m/e* 392 and **8** at *m/e* 419.

The IR spectra of the compounds **3a–3c**, **9**, the *o*-aminoarylazo dye from **9** in Nujol mull, and of the bis(*o*-aminoarylazo) dye from **11** in KBr disc, showed the presence of the amino group, absent in the spectra of compounds **4a–4c**, **10** and **12** in Nujol mull. The IR spectrum of **4c** also showed the presence of the carboxylic acid group (1700 cm^{-1}) and the spectrum of compound **6a** also showed absorption at 3180 cm^{-1}, corresponding to the imidic —NH— group.

The absorption maxima and the fluorescence emission maxima in the electronic spectra of all the compounds **4a–4c**, **6a–6b**, **8**, **10** and **12** are given in Table 1, together with those of a standard fluorescent compound, 7-*N*,*N*-diethylamino-4-methylcoumarin. The absorption maxima (nm) of the compounds varied from 297 nm to 358 nm. It is generally considered appropriate for absorption in the region close to 350–400 nm to occur for a compound to be considered suitable as a fluorescent whitener. In this respect compounds **6a–6b** and **10** satisfied the requirement. However, all

TABLE 1
Absorption and Fluorescence Emission Spectra of Pyrazolo[3,4-*d*]-1,2,3-triazole Derivatives

Compound	*Absorption max (nm)*	*Fluorescence emission max (nm)*	*log ε*	*Q (mg)*
4a	300	432	4·30	9·80
4b	305	445	4·34	8·73
4c	297	427	4·43	9·31
6a	342	457	4·80	1·42
6b	338	458	4·63	1·45
8	312	451	4·46	1·53
10	358	449	4·16	1·72
12	328	460	4·67	1·51
Standard	376	458	4·41	1·52

the compounds **4a–4c**, **6a–6b**, **8**, **10** and **12** had fluorescence emission maxima close to the blue to greenish-blue region (427–460 nm), thus satisfying the general requirement of a suitable fluorescent whitener. The amount of the compounds (Q), dissolved in 100 ml of solvent, required for 100 units of intensity indicated that the compounds **6a–6b**, **8**, **10** and **12** compared very favourably with the standard, whereas compounds **4a–4c** did not. The grades of the actual whitening of polyester fibres were as follows: **4a**, 2; **4b**, 1; **6a**, 3·5; **6b**, 3·5; **8**, 2; **10**, 3; and **12**, 3. It may be concluded that selected members of the class of compounds reported in this investigation are very satisfactory fluorescent whiteners.

3. EXPERIMENTAL

All melting points are uncorrected and are in °C. Absorption and fluorescence emission spectra in DMF solutions were recorded on a Beckman Model 25 spectrophotometer and an Aminco–Bowman spectrophotofluorimeter respectively. Infrared spectra were recorded on a Perkin–Elmer Model 397 spectrometer. The PMR spectra were recorded on a Varian 60 MHz instrument EM-360-L using TMS as internal standard; the chemical shifts are given in δ (ppm).

3.1. Preparation of starting materials

5-Amino-3-methyl-1-phenylpyrazole (**1**),[2] m.p. 116° (literature[2] m.p. 114–6°) and benzhydrazide (**7**),[3] m.p. 112° (literature[3] m.p. 112–5°) were prepared by known methods.

3.2. 5-Amino-3-methyl-1-phenyl-4-(4-methylphenyl)azopyrazole (3a)

p-Toluidine (1·07 g, 0·01 mol) was diazotised at 0–5° using sodium nitrite (0·76 g, 0·011 mol) and dilute (1:1) hydrochloric acid (10 ml). The excess of nitrous acid was destroyed by addition of urea (0·25 g). The diazo solution was run slowly into a solution of 5-amino-3-methyl-1-phenylpyrazole (1·73 g, 0·01 mol) in acetic acid (5 ml) at 0–5°, the pH being adjusted to 4–5 by addition of sodium carbonate. The coupling reaction was completed in about 6 h, after which time the pH was adjusted to 7 with sodium acetate and the dye filtered, washed with water and dried. It was recrystallised from ethanol as orange crystals (85 %), m.p.

160°. Calculated for $C_{17}H_{17}N_5$: C, 70·1; H, 5·8; N, 24·1. Found: C, 69·9; H, 5·4; N, 24·0%.

The other azopyrazoles (**3b**–**3c**) and the azopyrazole from **9** were prepared in the same manner.

3.3. 5-Amino-3-methyl-1-phenyl-4-(4-methoxyphenyl)azopyrazole(3b)

Crystallised from ethanol as orange crystals (80%), m.p. 195°. Calculated for $C_{17}H_{17}N_5O$: C, 66·2; H, 5·5; N, 22·7. Found: C, 66·1; H, 5·2; N, 22·4%.

3.4. 5-Amino-3-methyl-1-phenyl-4-(4-carboxyphenyl)azopyrazole(3c)

Crystallised from ethanol as orange needles (78%), m.p. 265°. Calculated for $C_{17}H_{15}N_5O_2$: C, 66·2; H, 4·7; N, 21·8. Found: C, 66·0; H, 4·5; N, 21·7%.

3.5. 2,4-Dihydro-6-methyl-4-phenyl-2-(4-methylphenyl)pyrazolo[3,4-*d*]-1,2,3-triazole(4a)

Compound **3a** (2·91 g, 0·01 mol) was heated with cupric acetate (1 g, 0·0052 mol) in DMF (10 ml) at 90–95° for 1 h. A current of air was continuously passed through the reaction mixture during this period and the reaction mixture was then added to ice-cold dilute (5%) hydrochloric acid (50 ml). The separated compound was filtered and the last traces of the dye **3a** were removed by addition of zinc dust (0·05 g) in dilute (1:1) acetic acid (10 ml). The resulting product was recrystallised from acetic acid (65%), m.p. 180°. Calculated for $C_{17}H_{15}N_5$: C, 70·6; H, 5·2; N, 24·2. Found: C, 70·5; H, 5·0; N, 24·0%.

The other triazoles **4b**–**4c**, 2-hydro-2-(4-nitrophenyl)naphtho[1,2-*d*]-1,2,3-triazole, **10** and **12** were synthesised by following this typical procedure.

3.6. 2,4-Dihydro-6-methyl-4-phenyl-2-(4-methoxyphenyl)pyrazolo[3,4-*d*]-1,2,3-triazole(4b)

Crystallised from acetic acid (68%), m.p. 130°. Calculated for $C_{17}H_{15}N_5O$: C, 67·9; H, 4·9; N, 22·9. Found: C, 67·7; H, 4·5; N, 22·7%.

3.7. 2,4-Dihydro-6-methyl-4-phenyl-2-(4-carboxyphenyl)pyrazolo[3,4-*d*]-1,2,3-triazole(4c)

Crystallised from acetic acid (67%), m.p. 280°. Calculated for $C_{17}H_{13}N_5O_2$: C, 64·9; H, 4·1; N, 21·9. Found: C, 64·6; H, 4·0; N, 21·7%.

3.8. 2,4-Dihydro-6-methyl-4-phenyl-2-[4-(benzimidazol-2-yl)phenyl]-pyrazolo[3,4-*d*]-1,2,3-triazole(6a)

The triazole carboxylic acid **4c** (1·6 g, 0·005 mol) and 1,2-diaminobenzene **5a** (0·54 g, 0·005 mol) were refluxed in a mixture of *o*-dichlorobenzene (40 ml) and phosphorus pentachloride (1·5 g) for 10 h. The reaction mixture was cooled and added to petroleum ether. The separated solid was filtered, washed with petroleum ether and dried. The resulting compound was recrystallised from DMF as colourless crystals (63%), m.p. 340°. Calculated for $C_{23}H_{17}N_7$: C, 70·6; H, 4·4; N, 25·1. Found: C, 70·3; H, 4·2; N, 25·0%.

The compound **6b** was synthesised in the same manner.

3.9. 2,4-Dihydro-6-methyl-4-phenyl-2-[4-(benzoxazol-2-yl)phenyl] pyrazolo[3,4-*d*]-1,2,3-triazole(6b)

Crystallised from DMF as colourless crystals (59%), m.p. 195°. Calculated for $C_{23}H_{16}N_6O$: C, 70·4; H, 4·1; N, 21·4. Found: C, 70·1; H, 4·0; N, 21·0%.

3.10. 2,4-Dihydro-6-methyl-4-phenyl-2-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenyl]pyrazolo[3,4-*d*]-1,2,3-triazole(8)

The triazole **4c** (1·6 g, 0·005 mol) and benzhydrazide (0·54 g, 0·005 mol) was added to freshly prepared polyphosphoric acid (PPA) (10 g) [prepared by heating P_2O_5 (7 g) and H_3PO_4 (3 ml) at 180° for 0·5 h] at 100°. The reaction mixture was heated at 180–190° for 6 h, cooled to room temperature and slowly added to cold water (100 ml). The resultant solid was filtered, washed with water and dried. It was recrystallised from DMF as pale yellow crystals (86%), m.p. 190°. Calculated for $C_{22}H_{17}N_7O$: C, 66·8; H, 4·3; N, 24·8. Found: C, 66·6; H, 4·0; N, 24·5%.

3.11. 2,4-Dihydro-6-methyl-4-phenyl-2-[4-(2-hydronaphtho[1,2-*d*]-1,2,3-triazol-2-yl)phenyl]pyrazolo[3,4-*d*]-1,2,3-triazole(10)

p-Nitroaniline (1·38 g, 0·01 mol) was diazotised at 0–5° using sodium nitrite (0·76 g, 0·011 mol) and dilute (1:1) hydrochloric acid (10 ml). Excess nitrous acid was destroyed by the addition of urea (0·25 g) and the diazo solution was run slowly into a solution of 2-aminonaphthalene-1-sulphonic acid (Tobias acid) (2·23 g, 0·01 mol) in acetic acid (5 ml) at 0–5°, the pH being adjusted to 4–5 by the addition of sodium carbonate. The coupling reaction was complete in about 6 h, when the pH was brought to 7 using sodium acetate. The separated dye was filtered, washed with water and dried. It was recrystallised from ethanol as red crystals of 2-amino-1-(4-nitrophenyl)azonaphthalene (82%), m.p. 250°. Calculated for $C_{16}H_{12}N_4O_2$: C, 65·8; H, 4·1; N, 19·2. Found: C, 65·6; H, 4·0; N, 19·0%.

The above *o*-aminoarylazo compound was oxidised with cupric acetate and DMF in a current of air, following the procedure described above for **4a**. The resultant compound was recrystallised from acetic acid as pale yellow crystals of 2-hydro-2-(4-nitrophenyl)naphtho[1,2-*d*]-1,2,3-triazole (69%), m.p. 350°. Calculated for $C_{16}H_{10}N_4O_2$: C, 66·2; H, 3·5; N, 19·3. Found: C, 66·0; H, 3·4; N, 19·0%.

To the above nitro compound (2·9 g, 0·01 mol) in acetic acid (20 ml) was slowly added zinc dust (1·95 g, 0·03 mol) at 50–60° with stirring. The reaction mixture was refluxed for 6 h, filtered hot, and the filtrate cooled and added to cold water (100 ml). The separated solid was filtered, washed with water and dried. The compound was recrystallised from DMF as off-white crystals of 2-hydro-2-(4-aminophenyl)naphtho[1,2-*d*]-1,2,3-triazole (**9**) (77%), m.p. 180°. Calculated for $C_{16}H_{12}N_4$: C, 73·9; H, 4·6; N, 21·5. Found: C, 73·6; H, 4·3; N, 21·4%.

The arylamine **9** was diazotised and coupled with **1** following the procedure described above for **3a**. The resultant 5-amino-3-methyl-1-phenyl-[4-(2-hydronaphtho[1,2-*d*]-1,2,3-triazol-2-yl)phenyl]azopyrazole was recrystallised from a DMF–ethanol (1:1) mixture as orange-red needles (72·0%), m.p. 120°. Calculated for $C_{26}H_{20}N_8$: C, 70·3; H, 4·5; N, 25·2. Found: C, 70·0; H, 4·3; N, 25·0%.

The above *o*-aminoarylazo compound was oxidised with cupric acetate and DMF in a current of air following the procedure described above for **4a**. The resulting compound was recrystallised from DMF as colourless crystals of the triazole **10** (81%), m.p. 270°. Calculated for $C_{26}H_{18}N_8$: C, 70·6; H, 4·1; N, 25·3. Found: C, 70·5; H, 4·1; N, 25·2%.

3.12. 2,2′-(1,1′-Biphenyl-4,4′-diyl)bis(2,4-dihydro-6-methyl-4-phenylpyrazolo[3,4-*d*]-1,2,3-triazole)(12)

Benzidine dihydrochloride (2·57 g, 0·01 mol) was dissolved in 30% hydrochloric acid (5 ml) and water (15 ml) at 70°. The clear solution was cooled at 30–40° and ice (about 10–15 g) was added causing part of the hydrochloride to separate. Tetrazotisation was carried out after further addition of 30% hydrochloric acid (3–5 ml) in water (10–15 ml), followed by slow addition of sodium nitrite (1·4 g, 0·02 mol) in water (7 ml) at 10–12°. The clear solution was slowly run into a solution of **1** (3·46 g, 0·02 mol) in water (50 ml) at 0°. The reaction liquor was maintained at 5° for 1 h, then slowly raised to 20°, maintained for 5 h, further raised to 30°, maintained for 24 h and then heated to 55°. After completion of the coupling, the reaction mixture was cooled to room temperature and the product filtered and washed with water. The dull red coloured dye was dried at 60–70° and recrystallised from benzene (87%), m.p. 235°. Calculated for $C_{32}H_{28}N_{10}$: C, 70·6; H, 5·1, N, 25·4. Found: C, 70·4; H, 5·0; N, 25·2%.

The above diaminobisazo dye (2·76 g, 0·005 mol) was heated with cupric acetate (1·05 g, 0·0055 mol) in DMF (20 ml) at 90–95° for 2 h in a continuous current of air. The oxidation procedure described above for **4a** was followed. The resulting compound was recrystallised from DMF to give pale yellow crystals of the bistriazole **12** (73%), m.p. 310°. Calculated for $C_{32}H_{24}N_{10}$: C, 70·1; H, 4·4; N, 25·6. Found: C, 70·0; H, 4·3; N, 25·4%.

ACKNOWLEDGEMENT

One of us (P. V. T.) thanks the University Grants Commission, New Delhi, for the award of Junior and Senior Research Fellowships.

REFERENCES

1. D. W. Rangnekar and R. C. Phadke, *Dyes and Pigments*, **6**, 293 (1985).
2. S. Searles, Jr and W. R. Hire, Jr, *J. Amer. Chem. Soc.*, **79**, 3175 (1957).
3. J. Stolle, *J. Prakt. Chem.*, **69**, 145 (1904).