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A NEW TRIAL FOR THE SYNTHESIS OF DIRECT DYES TO REPLACE BENZIDINE TYPE DYE (1) —— TRISAZO DYES FROM 3,5-BIS(p-AMINOPHENYL)-1,2,4-TRIAZOLE, 2,5-BIS(p-AMINOPHENYL)-1,3,4-OXADIAZOLE AND 2,5-BIS(p-AMINOPHENYL)IMIDAZOLE

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New trisazo dyes from 3,5-bis(p-aminophenyl)-1,2,4-triazole and 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole which are found to have no toxicity and no carcinogenicity, and 2,5-bis(p-aminophenyl)-imidazole have been prepared to replace benzidine type dye, Direct Deep Black EX. Dyeing with these dyes was carried out on cotton, silk, wool and 6-nylon. These dyes have been shown to have very good dye-ability and also to be very similar to benzidine type dye in colour and fastnesses to light and washing.

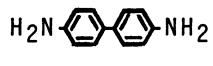
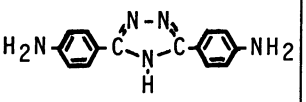
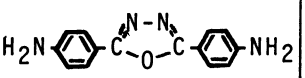
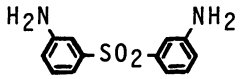
One of the most important problems in the field of dye chemistry is the carcinogenicity of benzidine and benzidine dyes. It has been reported that benzidine is resuscitated as a metabolic product of benzidine dye by rat, mouse, Escherichia coli and soil bacteria[1]. The interest and demand for non-toxic and antipolluted dyes have been originated from the discontinuance of benzidine production. By using o-tolidine[2], o-dianisidine[3], 4,4'-diaminodiphenylsulfide[4], 4-aminobenzoyl-4'-aminoanilide[5], 4,4'-diaminodiphenylamine[6], 4,4'-diaminodiphenylurea[7] or 1,5-diaminonaphthalene[8] as a diamine to replace benzidine, new type of direct dyes have been proposed by some dye makers, but the carcinogenicity, substantivity, hue and colour fastness of those dyes are in serious problem.

The biological toxicity, LD_{50} which were determined in female mice by Litchfield-Wilcoxon method[9], of 3,5-bis(p-aminophenyl)-1,2,4-triazole and 2,5-bis(p-amino-

phenyl)-1,3,4-oxadiazole were 10g/kg (oral feeding) either. Supposing LD_{50} of benzidine is 1.25g/kg[9], these azoles have extremely lower toxicity.

The carcinogenicity of 3,5-bis(p-aminophenyl)-1,2,4-triazole and 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole were evaluated in young female Sprague-Dawley rats during 9 months after the oral feeding of 10 doses by the similar method of Griswold, Jr., et. al.[10] (Table 1). Striking differences in activity between benzidine and

Table 1 The carcinogenicity test to female Sprague-Dawley rats

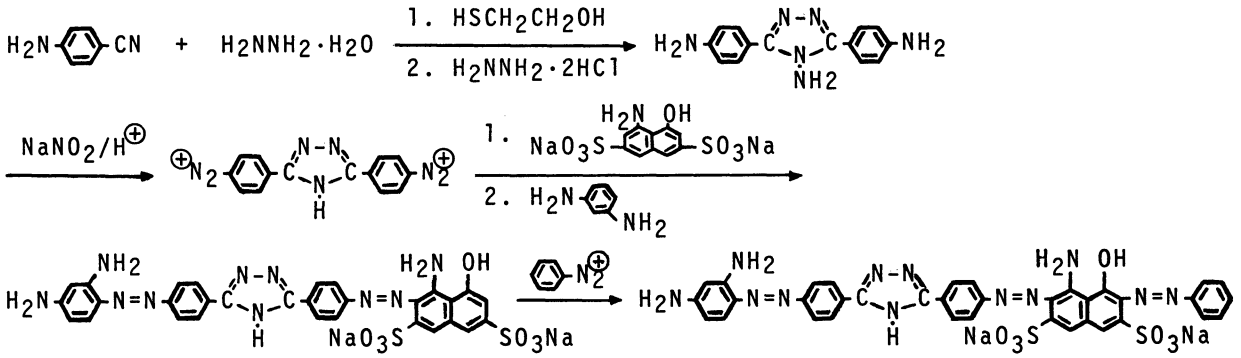
Compound	Total*1 Dosage mg/rat	No. of Observed Rats	No. of Rats with Tumor (months) 0 2 3 4 5 6 7 8 9	Total	
	25	25	0 0 10 13 14 15 13*2 14 14	16	Single Tumor 6 Multiple Tumor 10
	300	25	0 0 1 1 1 1 2 2 2	2	Single Tumor 2 Multiple Tumor 0
	300	25	0 0 1 0*2 0 0 0 2 2	3	Single Tumor 3 Multiple Tumor 0
	300	25	0 0 0 0 0 0 0 0 0	0	Single Tumor 0 Multiple Tumor 0
(Control) Sesame Oil	-	25	0 0 0 0 0 0 1 1 1	1	Single Tumor 1 Multiple Tumor 0

*1 Each rat received 10 equal doses at 3 day intervals, starting at 40 days of age
*2 Decrease by natural extinction of tumors

the related compounds were found. Thus, benzidine was quite active, but triazole and oxadiazole compounds were considerably less, and 3,3'-diaminodiphenylsulfone had no activity. However, o-tolidine[10], o-dianisidine[11] and 3,3'-dichlorobenzidine[12] are known to have carcinogenicity. On the other hand, 4,4'-diaminodiphenylsulfone[10], 4,4'-diaminodiphenylmethane[10] and 4,4'-diaminodiphenylether[10] are reported not or scarecely to have the activity.

Therefore, an inference that the toxicity and the carcinogenic activity of the benzidine related compound may be lowered considerably or extremely by introduction of heterocyclic group such as triazole, oxadiazole and imidazole, or interposed group such as sulfone, methylene and ether between the two benzene rings of benzidine, may be drawn, and this matter constitutes a pattern of substitute component for benzidine.

By the way, while investigating the reaction of nitriles with hydrazine hydrate[15], we have found that the reaction of p-amino benzonitrile with hydrazine hydrate in the presence of mercaptoethanol and hydrazine dihydrochloride offers a convenient synthetic route to 3,5-bis(p-aminophenyl)-4-amino-1,2,4-triazole. This compound reacts with nitrous acid to eliminate N-amino group and then to form tetrazonium salt, which is continuously treated with suitable coupling components to obtain dye corresponding to benzidine type ones.

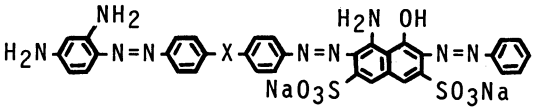


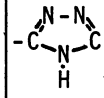
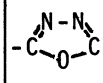
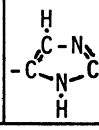
Several black direct dyes were prepared from 3,5-bis(p-aminophenyl)-4-amino-1,2,4-triazole (mp 225-7°C), 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole (mp 299-301 °C)[16] and 2,5-bis(p-aminophenyl)-4-aminoimidazole (mp 185°C)[17] as a diamine to replace benzidine of Direct Deep Black EX type dye. The preparation was conducted by a normal method by coupling tetrazotized substituted diamines with H-acid and subsequently with m-phenylenediamine under acidic condition, and then coupling benzene diazonium salt with H-acid part of these compounds under alkaline condition. These dyes were purified by the cellulose column chromatography using ammonia-water solution developer. The Rf and the Rm values[18] on cellulose thinlayer plate "Abisel SF" and the absorption maximum values determined in 2×10^{-5} mole per litre pH 10 (Na_2CO_3-$Na_2B_4O_7$) buffer solution at room temperature were shown in Table 2.

The dyeing with these dyes was carried out on cotton (under mild alkaline condition), silk, wool and 6-nylon (under acidic condition) (the liquor ratio, 20:1; the dye, 10% on the weight of fibre), and their applicability, colour and colour fastness were examined. The measurement of colour was done by determining reflectances with a Shimadzu Spectrophotometer model RC-330 and Adams Chromatic Values with a Hitachi Electronic Computer model HITAC-10. The light fastness was determined by a progression comparing with the Gakushin blue scale using a Toyo Rika Fade-O-tester model

FA-1 and the washing fastness was determined by the method of JIS L0844-1970(Table 3).

Table 2 Rf, Rm and absorption maximum values of the direct dyes of the type



Dye No.	X	Rf Values*1		Rm Values*2		Absorption Maximum*3	
		28%NH_4OH(3) : H_2O(7)	$C_6H_5CH_2OH$(3) : DMF(2) : H_2O(2)	28%NH_4OH(3) : H_2O(7)	$C_6H_5CH_2OH$(3) : DMF(2) : H_2O(2)	λmax (nm)	εmax ($\times10^{-4}$)
1	——	0.07	0.43	1.124	0.123	403 597	1.7 2.0
2		0.03	0.40	1.510	0.176	410 479 590	1.9 2.5 1.7
3		0.01	0.38	1.996	0.213	394 493 610	- - -
4		0.08	0.40	1.061	0.176	379 500 678	2.1 2.6 1.3

*1 On cellulose thinlayer plate "Abisel SF"

*2 Rm=log(1/Rf-1)

*3 In 2×10^{-5}mol/l pH 10 (Na_2CO_3-$Na_2B_4O_7$) buffer solution at room temperature

Table 3 Adams chromatic values and fastness results of the direct dyes

No.	X	Cotton ΔE	Cotton ΔL*1	Cotton L	Cotton W*2	Silk ΔE	Silk ΔL	Silk L	Silk W	Wool ΔE	Wool ΔL	Wool L	Wool W	6-Nylon ΔE	6-Nylon ΔL	6-Nylon L	6-Nylon W
1	——	-	-	5	3-4	-	-	5	4	-	-	5	4	-	-	5	4
2		2.1	-1.0	5	3-4	1.1	0.0	5	4	2.8	0.7	5	4	2.7	-2.3	5	4
3		3.1	-2.4	5	3-4	2.5	-1.3	5	4	4.1	-4.1	5	4	2.5	-2.0	5	4
4		1.6	-2.3	5	3-4	2.8	-5.3	5	4	6.1	1.4	5	4	4.8	-3.2	5	4

*1 Adams Colour Order System

Colour Difference : $\Delta E=40\left\{[\Delta(Vx-Vy)]^2+[0.4\Delta(Vz-Vy)]^2+(0.23\Delta Vy)^2\right\}^{\frac{1}{2}}$ (N.B.S.)

Luminance Difference : $\Delta L=0.23\Delta Vy$ (N.B.S.)

*2 Fastness : L=Light, W=Washing

As the result of dyeing with these dyes and treating by the above mentioned method, the good dyeings comparable to that with the Direct Deep Black EX dye were obtained not only on cotton but also on silk, wool and 6-nylon, and it seems that they may be used as a black direct dye to replace benzidine type dye. The fastnesses made no great difference and were generally good because of the deep colour dyeing, namely the light fastness was graded about 5 and washing about 3-4 or 4.

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