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DESIGN, SYNTHESIS AND INVESTIGATION OF PROPERTIES OF FUNGICIDAL DYES*

D.N. KUZNETSOV, A.G. RUCHKINA, K.I. KOBRAKOV, M.B. DMITRIEVA, M.O. GLOTOVA

(Moscow State Textile University "A.N. Kosygin")
E-mail: kki@staff.msta.ac.ru

This article describes a methodology for the synthesis of new biocidal pyrazole-containing azo dyes, which consists in the sequential formation of biophore and chromophore groups. It was established that the synthesized azo compounds provide good operational characteristic of colourings on fabrics obtained with their aid and protection from mold fungi.

Keywords: azopyrazoles, pyrazol-5-ions, 4-nitrophenylazo-3, 5-dimethylpyrazole, methylphloroglucin, fungicidal dyes, biological activity.

Hygienic conditions of life and work of a large number of people in an environment lacking the appropriate level of hygiene (transportation, shift work, expeditions, field conditions of soldiers, rescue work), can be significantly improved by the use of biocide-protected textile materials.

Biocide treatment of textile materials, developed over half a century ago, and which is widely used today in many countries in Europe, America, Asia and Russia, as a rule, is limited to processing of textile materials with various environmentally stringent fungicidal drugs.

Ever-increasing environmental requirements to chemical and technological processes in the textile and finishing manufacture of textiles require a change in approach to existing methods of protection of textile materials.

One way to solve the mentioned problem is the synthesis of new effective fungicide dyes which could independently, without using additional biocidal products, protect textiles from the action of the most common fungi (micromycetes). This makes it possible to reduce power consumption, extent and degree of contamination of wastewater by combining the stages of finishing processes.

In this study, we examined the fungicidal properties of some synthetic dyes and attempted to identify the relationship between the structure and level of fungicidal activity exhibited by them.

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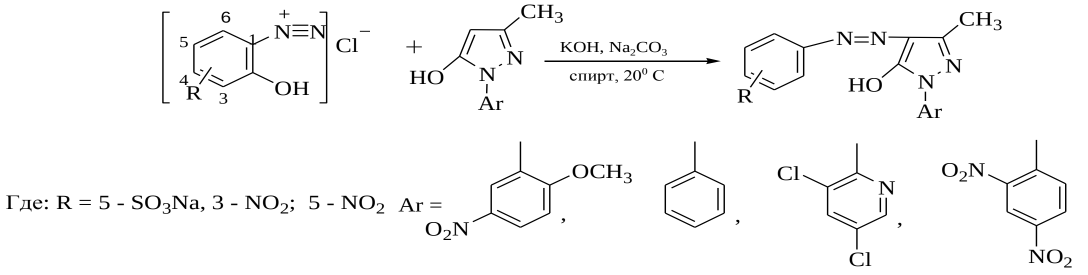
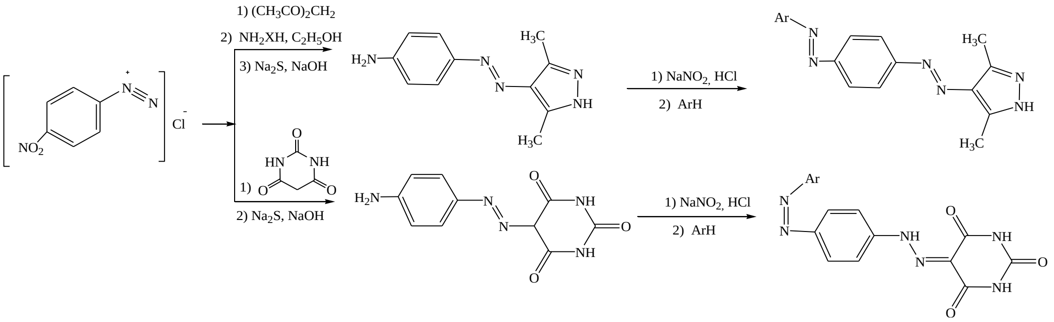
Synthesis of dyes studied in the paper has been carried out in three ways:

1. by a method, based on the use of azo-components as a potential biophore, and polyfunctional aromatic amines were used as a diazo component. Various pyrazolone derivatives act as azo components , which as shown in studies conducted by the department earlier, possess a pronounced fungicidal action [1], [2]. Selection of aromatic diazo components depends on what functional class and what color is necessary to be imparted to final dyes.



2. by a method, based on the use of heterocyclic amines as a potential biophore, and polyfunctional amines and hydroxyl compounds are used as azo components. This paper contains a detailed description of this approach [3]

3. From our point of view, the most effective method is a hybrid approach that includes stagewise design of a biophore and chromophore system which allows already at the stage of synthesis to simulate the specified colour and level of biological effect.



Using the first and third methods, we obtained 18 previously undocumented new azo compounds, yields, melting point and EAS (electronic absorption spectrum) of which are given in Tables 1, 2 and 3.

Polyazo compounds 1-18 were tested as dyes for fabrics made from fibers of different types.

Azo compounds 1...4, 9, 13, 16 were tested as acid dyes for dyeing of polypeptide fibers (wool). Dyeing of wool material was carried out by the method of dyeing by average-levelling dyes in weak acidic medium (pH=4...6) [4].

Dyeing with the dye 11 of cellulosic material was carried out under standard dyeing conditions with direct dyes [4].

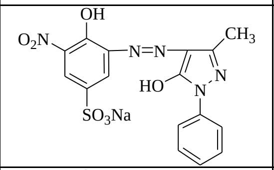
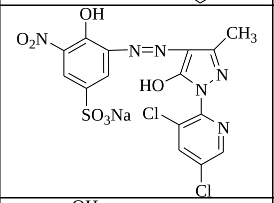
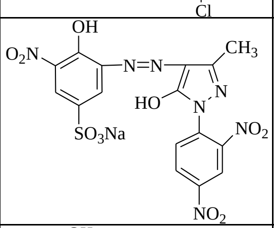
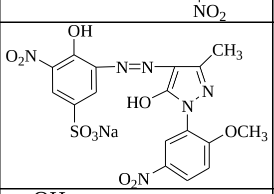
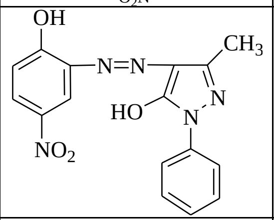
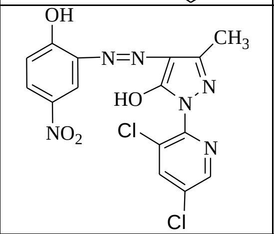
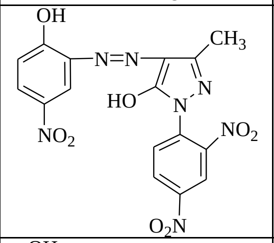
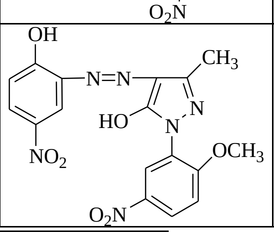
Azo compounds 5...8, 10, 12, 14, 15, 17, 18 – were tested as disperse dyes for dyeing of polyamide fibre (nylon) under standard dyeing conditions with disperse dyes [4].

The samples dyed with dyes 1...4, have a reddish-brown colour, with the dyes 9, 11 and 16 violet colour, with the dye 13 – lilac. The samples dyed with the dyes5-8, 14, 15, 18 have a reddish-brown color; the sample coloured with the dye 12 yellow colour and with the dyes 10 и 17- bright scarlet colour.

The obtained samples were tested for fastness to dry and wet rubbing according to GOST 9733.27-83, to wet treatment according to GOST 9733.4-83 (MS ISO 105CO5) [5...7]. Colouring stability of the samples was assessed on a 5-point scale of gray standards on a spectrophotometer Datacolor mod.3880 using the software package for solving problems of the textile colouristic "Pavlin". The test results of colourings are presented in Tables 1, 2, 3.

T a b l e 1

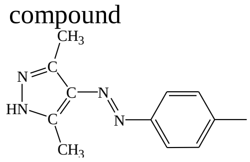
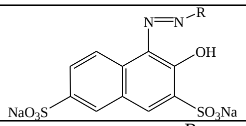
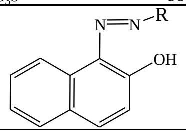
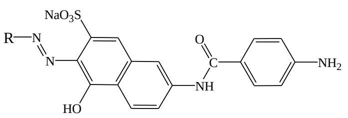
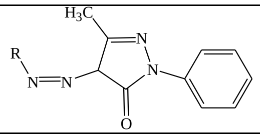
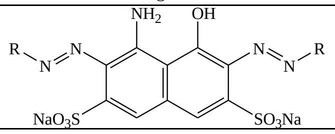
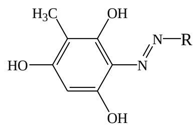
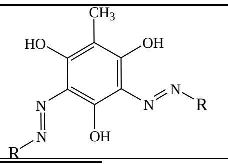
Characteristics of the synthesized azo compounds 1-8

Compound number	The structural formula of azo compound	T_{mp}., °C	R_f^*	Yield, %	EAS, λ_{max}, нм (lg ε)*	Fastness of coloured materials to the physical and chemical effects			
						Dry rubbing	Wet rubbing	Laundering	Sweat
1		-	0,76	90	496,0 (4,21)	5/5	4-5/3-4	1/3/2	4/2/3
2		-	0,63	80	500,0 (3,86)	5/5	4/4-5	1/3/1	2/3/4
3		-	0,79	83	504,0 (4,24)	5/5	5/3-4	1/4/1	4/1/4
4		-	0,71	76	498,0 (2,84)	5/5	4/4-5	1/4/2	4/2/4
5		330	0,69	85	409,8 (3,78)	5/5	5/5	4/3/5	1/3/3
6		350	0,63	80	426,6 (3,75)	5/5	5/5	4/4/5	1/3/3
7		170	0,66	89	419,4 (4,18)	5/5	5/5	4/3/5	1/3/3
8		185	0,54	80	417,2 (3,97)	5/5	5/5	4/5/5	1/4/4

* - Purity of the synthesized compounds 1-4 was monitored by paper chromatography, [on paper “Filtrak”, eluent: water- NH_4OH 25% solution-ethanol = 1:1:1]; purity of compounds 5-8 – TLC. For TLC Silufol UV-254 plates for dyes 5-8 in in ethyl acetate were used; ** - The spectra of azo compounds1-4 recorded in ethanol; 5-8 – in water.

Table 2

Characteristics of the synthesized disazo compounds 9-15

Compound number	The structural formula of azo compound  Where R =	$T_{mp.}$, °C	R_f*	Yield, %	EAS, □max, нм (lg □)**	Fastness of coloured materials to the physical and chemical effects			
						Dry rubbing	Wet rubbing	Laundering	Sweat
9		-	0,36	67	520,8 (4,49)	5/5	3/4	3-4/1/1	4/1/1
10		290	0,54	80	509,4 (4,20)	5/5	5/5	4/4/4	5/4/4
11		-	0,27	70	512,3 (4,11)	5/5	3/4	3/1/1	3/1/1
						5/5***	5/5	4/2/2	4/3/3
12		276	0,64	86	432,53 (4,59)	5/5	5/4	5/4/4	5/5/4
13		-	0.86	75	553,09 (4,21)	5/4	3/4	1/4/1	4/4/2
14		280	0,52	57	453,90 (4,37)	5/5	5/5	4/3/3	4/2/2
15		350	0,35	60	491,67 (4,11)	5/5	5/5	5/4/4	4/3/3

* - Purity of the synthesized compounds 9, 11, 13 - was monitored by paper chromatography, [on paper "Filtrak", eluent: water- NH_4OH 25%-solution-ethanol = 1:1:1]; purity of compounds 10, 12, 14, 15 – TLC (Silufol UV-254 plates in ethyl acetate); ** The spectra of azo compounds 9, 11, 13 are recorded in water; 10, 12, 14, 15 – in ethanol. *** Additional fixation of colouring was carried out by diazotization

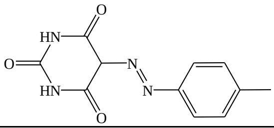
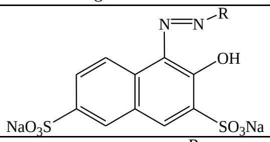
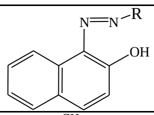
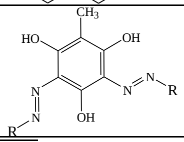
The tests of fungicidal properties of the synthesized compounds have been conducted in the biological laboratory GosNIIR according to GOST 9.048-75 [8].

As the test cultures micromycetes of fungi were used which often can be found on textile materials causing both mechanical and chemical destruction of fibers: *Aspergillus niger*, *Chaetomium globosum*, *Penicillium chrysogenum*, *Aspergillus flavus*.

The test results are presented in Table 4. Test cultures grown under the same conditions, but without adding of dyes, served as a control. On the third day, the nature of fungal growth on 6-point scale according to the following percentages of growth inhibition was assessed. Fungicidal activity (in % / points): 0/5 - abundant growth of mycelium, sporulation is present, 20 / 4 - limited growth of mycelium, suppressed sporulation, 40 / 3 - inhibiting the growth of mycelium, 60 / 2 - web-like mycelium; 80 / 1 - the complete suppression of growth; 100 / 0 - full inhibition of growth, the formation of the inhibition of growth.

Table 3

Characteristics of the synthesized disazo compounds 16-18

Compound number	The structural formula of azo compound Where R = 	$T_{mp.}$, °C	R_f*	Yield, %	EAS, λ_{max}, нм (lg ε)**	Fastness of dyed materials to the physical and chemical effects			
						Dry rubbing	Wet rubbing	Laundering	Sweat
16		-	0,80	80	527,42 (4,48)	5/4	3/4	1/4/1	1/1/1
17		225	0,68	85	504,03 (4,05)	5/5	5/4	4/2/2	5/3/3
18		380	0,71	75	495,54 (4,20)	5/5	5/4	3/3/5	3/4/5

* - Purity of the synthesized compounds 16 -   was monitored by paper chromatography, [on paper "Filtrak", eluent: water-pyridine butanol = 1:1:0,5]; purity of compounds 17, 18 – TLC (Silufol UV-254 plates in ethyl acetate); ** The spectra of azo compounds 16 are recorded in water; 18 – in DMF.

Table 4

Results of determination of fungicidal activity of synthesized compounds 1-18 (in points)

Substance		Test-cultures			
№	Concentration, %	Aspergillus niger (v. Teigh)	Ulocladium ilicis (Thom)	Aspergillus flavus (Link Fr.)	Penicillium chrysogenum (Thom)
1	1	5	5	5	5
	0,1	5	5	5	5
2	1	5	5	5	5
	0,1	5	5	5	5
3	1	3	5	3	5
	0,1	3	5	4	5
4	1	4	5	5	4
	0,1	4	5	5	5
5	1	3	5	4	4
	0,1	4	5	4	4
6	1	3	5	5	4
	0,1	4	5	5	5
7	1	3	5	4	4
	0,1	3	5	3	4
8	1	4	5	5	4
	0,1	5	5	5	4
9	1	5	5	5	5
	0,5	5	5	5	5
10	1	1	0	2	3
	0,5	2	1	3	5
11	1	1	1	5	5
	0,5	2	3	5	5
12	1	2	4	3	3
	0,5	3	5	3	4
13	1	3	4	3	4
	0,5	4	5	3	5
14	1	2	3	4	5
	0,5	3	5	5	5
15	1	2	3	2	5
	0,5	3	4	4	5
16	1	3	4	4	4
	0,5	4	5	4	5
17	1	2	4	3	3
	0,5	2	5	3	4
18	1	4	4	4	4
	0,5	4	5	4	5

Analysis of the results, given in Table 4, enables to make definitive conclusions regarding the influence of the structure of groups comprising the molecule composition on the fungicidal properties exhibited by a compound.

Group of compounds 1...8 is divided in two subgroups 1...4 and 5...8 in which logic of change in the structure is as follows. During transition from compound 1 to compound 4 structure of azo component changes, but diazo component remains the same. In the series of compounds 5...8 another diazo component is used, but the azo component is changed according to the same scheme.

It has been revealed as a result of conducted tests that the compound 1 remained inactive under all test objects. Replacement of the phenyl radical by dichlorpyridine radical had no influence on the level of activity (compound 2). At the same time, the introduction in position 2 and 4 of the phenyl radical of the two nitro groups (compound 3) increased fungicidal activity with respect to the group of fungi *Aspergillus* by 30...40%. Substitution of one nitro group by the electron-donor methoxy group causes some loss of activity (compound 4).

In compounds 5...8 sulphonic group is absent in the diazo component, and the nitro group is not in the ortho position in relation to the OH group, but in the para-position. This causes increase in activity in relation to test cultures of fungi *Aspergillus* compared with the structural analogs (compound 1...4). Like in the case of compound 4 substitution of the nitro group by the methoxy group (compound 8) decreases the activity. The compounds 1-8 appeared to be completely inactive with respect to fungi *Ulocladium ilicis* and *Penicillium chrysogenum*.

When analyzing the results of testing compounds 9-18, some of the above mentioned regularities were found. The presence of the sulfo group in the molecule causes a notable reduction in activity (compound 9, 13, 16)

In the case of identical azo component (compound 10, 17) affect of the diazo-component's composition is clearly visible. Presence of pyrazole ring in the structure of diazo component (compound 10) causes a sharp increase in activity of all test objects, and the substitution of the pyrazole fragment by barbituric one (compound 17) results in decrease of activity.

A similar effect was observed in the case of compound 15 and18. From the comparison of dyes 14 and 15 it follows that the introduction of the second azo group with the pyrazole ring doubles the fungicidal activity with respect to the fungus *Aspergillus flavus,* in this case, activity against other fungi remains at the same level.

In general, the most promising structure that deserves attention as a basis for further design of molecules with desired properties seems to be the structure 10.

It is further noted that all substances investigated (compound 9...18) appeared to be virtually inactive with respect to the fungus *Penicillium chrysogenum*.

C O N C L U S I O N S

1. Complex approach to the synthesis of new azo dyes for textiles with fungicidal properties has been proposed.
2. Up to 18 new azo compounds have been obtained under the proposed scheme.
3. The synthesized compounds can be used as independent agents to suppress the growth of Aspergillus niger, Chaetomium globosum, Aspergillus flavus and as dyes for textiles with strong biocidal properties

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