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SYNTHESIS AND COLOR OF 2-(N, N-DIETHYL-p-QUINONEDIIMINE)-INDAZOLONES

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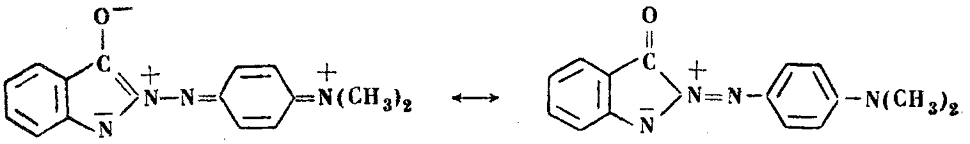
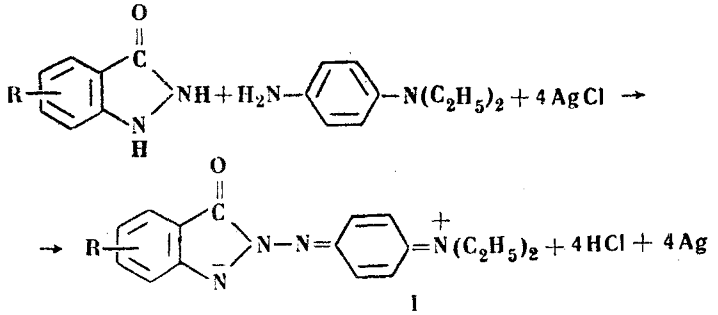
A number of substituted 2-(N, N-diethyl-p-quinonediimine)indazolones have been synthesized, and their optical properties investigated. It has been shown that introduction of electrophilic substituents into the benzene ring of an indazolone gives rise to a bathochromic shift in the absorption spectra of 2-(N, N-diethyl-p-quinonediimine)indazolones in alcohol and benzene solution.

It is found that reaction of indazolones with p-nitrosodimethylaniline gives mesoionic dyes [1, 2]:



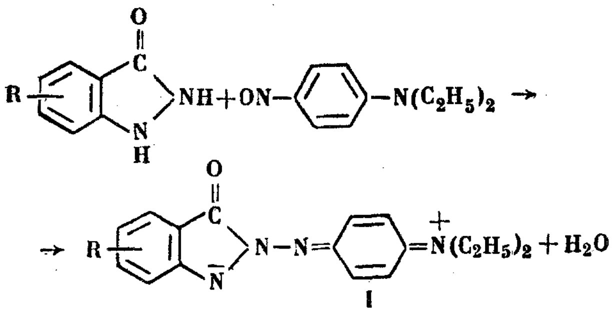
A study is also made of formation in the photographic layer during light development, of a purple dye from indazolone and its derivatives [3]. The dyes formed have not been investigated in detail.

The synthesis and study of such dyes is of definite interest for elucidating the connection between chemical structure and color. Dye I has been synthesized by simultaneously oxidizing, with silver chloride in slightly alkaline medium as the oxidizing agent, indazolones and N, N-diethyl-p-phenylenediamine:



I (A)

and also by reacting indazolones with p-nitrosodiethylaniline in alcohol:



I (B)

In both cases the reaction products were separated by chromatography on active aluminum oxide. The first to be eluted was a yellow-orange dye, which proved to be identical with 4, 4'-bis(diethylamino)azobenzene.

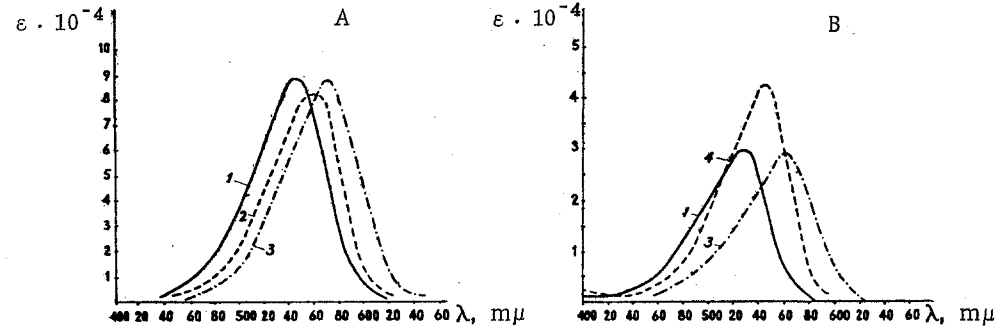
The 2-(N, N-diethyl-p-quinonediimine)indazolones (I) are crystalline and have sharp melting points (see table). Alcohol solutions of these compounds are distinguished by a narrow light absorption band with a maximum in the limits 547-580 mμ; in benzene the absorption maximum is found to be shifted by 15-25 mμ hypsochromically as compared with alcohol solutions (see figure).

On a basis of structure I, one would expect a shift of the light absorption maximum towards the long wavelength region on introducing into the benzene ring those indazolone substituents which are able to delocalize the negative

2-(N, N-Diethyl-p-quinonediimine)indazolones (I).

Compound no.	R	Preparation method	Yield, %	Mp, °C	Position of absorption maximum and coefficient of extinction in ethanol: λ_{max} mμ	log ε	Formula	Element	Found, %	Calculated, %
1	H	A	21,6	179—180	550	4,95	$C_{17}H_{18}N_4O$	N H	19.0 6.0	19.0 6.1
2	5-Cl	K	16,0	193	558	4,83	$C_{17}H_{17}ClN_4O$	N	16.6	17.0
3	5-Br	Б	17,3	177—178	562	4,89	$C_{17}H_{17}BrN_4O$	C H	54.6 4.6	54.7 4.8
4	6-Cl	K	14,6	179	562	4,92	$C_{17}H_{17}ClN_4O$	N	16.8	17.0
5	5,7-Cl_2	A	10,4	183—184	570	4,74	$C_{17}H_{16}Cl_2N_4O$	Cl	19.5	19.5
6	4-NO_2	A	8,8	174—175	576	4,81	$C_{17}H_{17}N_5O_3$	N	20.4	20.6
7	6-NO_2	A	2,0	175—176	580	4,92	$C_{17}H_{17}N_5O_3$	N	20,3	20.6
8	5-$C_{17}H_{35}CONH$	K	17,4	213—214	547	5,04	$C_{35}H_{53}N_5O_2$	C H	72,6 9.2	72.9 9.4

charge. Actually, when hydrogen is replaced by halogen, a bathochromic shift of the maximum by 8-12 mμ is observed (see table, nos. 2-5), and when it is replaced by the nitro- group, by 26-30 mμ, (see table, nos. 6, 7). Introduction of the stearoylamino- group is practically without effect on the color of the dye.



Absorption spectra of 2-(N, N-diethyl-p-quinonediimine)indazolones (A — in ethanol, B — in benzene); 1) 2-(N, N-diethyl-p-quinonediimine)indazolone; 2) 2-(N, N-diethyl-p-quinonediimine)-6-chloroindazolone; 3) 2-(N, N-diethyl-p-quinonediimine)-6-nitroindazolone; 4) 2-(N, N-diethyl-p-quinonediimine)-5, 7-dichloroindazolone.

Experimental*

Information has previously been published regarding the syntheses of the starting indazoles [4]. The dyes were prepared by the following typical methods.

A. 2-(N, N-Diethyl-p-quinonediimine)indazolone. A solution of 2. 8 g soda in 14 ml water and 0. 573 g (2 mmole) indazolone was added to a silver chloride suspension prepared from 2. 32 g (36 mmole) sodium chloride and 6. 12 g (36 mmole) silver nitrate in 56 ml water. A solution of 1. 16 g (7 mmole) N, N-diethyl-p-phenylenediamine sulfate in 28 ml water was added over 10 min, with stirring, and stirring then continued for 2 hr. The precipitate was filtered off, washed with water, and dried in a vacuum. The dye was extracted with 150 ml chloroform, and the solvent distilled off from the filtrate. The residue was dissolved in 10 ml dry benzene plus 3 ml chloroform, and chromatographed on aluminum oxide. Development of the chromatogram showed yellow and purple layers. The yellow dye was recovered from the benzene eluate (0. 25 g), mp 166-167. 5°, light absorption maximum at 465 mμ in alcohol, in agreement with the literature [5] data for 4, 4'-bis(diethylamino)azobenzene. Repeated chromatographing and recrystallization from ethanol gave 0. 254 g of the purple dye.

B. 5-Stearoylamino-2-(N, N-diethyl-p-quinonediimino)indazolone. A solution of 0. 415 g (0. 8 mmole) 5-stearoylaminoindazolone, with 0. 178 g (1 mmole) p-nitrosodiethylaniline and 3 drops of piperidine in 5. 3 ml absolute ethanol, was heated for 3 hr. The solvent was evaporated in a vacuum on a water bath, the residue dissolved in 10 ml chloroform, and run on to an alumina column. Development of the chromatogram revealed yellow and purple bands. Two chromatographings purified the purple dye, and gave a chloroform solution of it; the chloroform was distilled off in a

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vacuum, and the residue recrystallized from ethanol, yield 0.10 g.

The absorption spectra of the dyes synthesized were measured with an SF-4 spectrophotometer. Solvents used were spectroscopically pure benzene and ethanol. The concentrations of the dye solutions were 10^{-3}-10^{-4} mole/*l*.

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