BENZO[c,d]INDOLE CARBOCYANINES

Ya. B. Shteinberg

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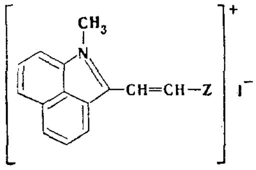
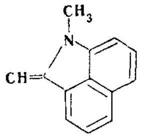
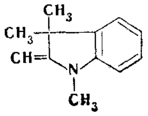
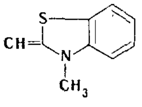
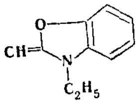
A symmetrical and some asymmetrical carbocyanines (benzo[c,d]indole derivatives) were synthesized.

2-(β-Anilinovinyl)-1-methylbenzo[c,d]indolinium iodide (I) was obtained from the previously described 1,2-dimethylbenzo[c,d]indolinium iodide [1] and diphenylformamidine. Compound I was converted to asymmetrical carbocyanines (III-VIII) by reaction with quaternary salts of the corresponding 2-methyl-N-alkylheterocyclic bases. A symmetrical carbocyanine (II) was synthesized by heating 1,2-dimethylbenzo[c,d]indolinium iodide with ethyl orthoformate. An alcohol solution of II has a green coloration with λ_{max} 757 nm.

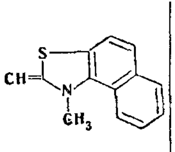
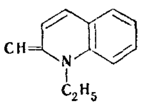
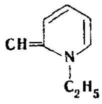
TABLE 1



Compound	Z	mp, °C	Empirical formula	N, % found	N, % calc.	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)
1	2	3	4	5	6	7
I	NHC_6H_5	227—228	$C_{20}H_{17}IN_2$	6,7	6,8	511(1,99)
II		Does not melt up to 400°	$C_{27}H_{21}IN_2$	5,5	5,6	690(5,36), 757(11,62)
III		248—249	$C_{26}H_{25}IN_2$	5,9	5,7	614(6,25), 662(8,58)
IV		252—253	$C_{23}H_{19}IN_2S$	5,9	6,0	611(5,27), 658(6,53)
V		249—251	$C_{24}H_{21}IN_2O$	5,6	5,8	580(4,55), 625(5,82)

Rubezhnoe Branch, Scientific-Research Institute of Organic Intermediates and Dyes, Rubezhnoe. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 340-341, March, 1973. Original article submitted January 26, 1972.

TABLE 1 (continued)

1	2	3	4	5	6	7
VI		190—192	$C_{27}H_{21}IN_2S$	5,4	5,3	630(4,84), 675(4,60)
VII		259—260	$C_{26}H_{23}IN_2$	5,9	5,7	658(8,64)
VIII		214—216	$C_{22}H_{11}IN_2$	6,2	6,3	570(3,72)

The depth of its color considerably surpasses that of the analogous derivatives of the most widespread dinuclear and trinuclear heterocyclic bases [2]. The accessibility and depth of color of the benzo[c,d]indolecarbocyanines make it possible to assume that the subsequent synthesis of polymethine dyes of this series may prove to be of promise for the discovery of compounds of interest for the photographic industry.

EXPERIMENTAL

2-(β-Anilinovinyl)-1-methylbenzo[c,d]indolinium Iodide (I). A mixture of 1.0 g (3.2 mmole) of 1,2-dimethylbenzo[c,d]indolinium iodide, 0.80 g (4.1 mmole) of diphenylformamidine, and 8.0 ml of propanol was refluxed for 1 h, after which it was cooled, and the precipitate was removed by filtration and washed with benzene to give 1.12 g (84%) of product.

Bis(1-methylbenzo[c,d]-2-indoline)trimethylidynecyaninium Iodide (II). A mixture of 0.50 g (1.6 mmole) of 1,2-dimethylbenzo[c,d]indolinium iodide, 0.50 ml (3.2 mmole) of ethyl orthoformate, and 3.0 ml of acetic anhydride was refluxed for 2 h, after which it was cooled, and the precipitate was removed by filtration and washed with ether to give 0.37 g (92%) of product.

Asymmetrical Benzo[c,d]indole Carbocyanines (II-VIII). A mixture of 1.2 mmole of I, 1.4 mmole of 2-methyl-N-alkyl iodide of the appropriate heterocyclic base, 2.0 ml of pyridine, and a few drops of acetic anhydride was refluxed for 1 h. The mixture was then diluted with ether, and the resulting precipitate was removed by filtration and washed with ether and water to give the products in 70-80% yield. Dye I was crystallized from methanol, while II-VIII were crystallized from water.

The absorption spectra of alcohol solutions of the dyes were recorded with SF-2M (I and III-VIII) and SF-4 (II) spectrophotometers.

LITERATURE CITED

1. N. S. Dokunikhin and Ya. B. Shteinberg, Zh. Obshch. Khim., 30, 1989 (1960).
2. F. M. Hammer, The Cyanine Dyes and Related Compounds, Interscience, New York (1964), p. 102.