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SYNTHESIS AND INVESTIGATION OF STYRYL DERIVATIVES OF 5,6-BENZO-2,2'-DIQUINOLYL

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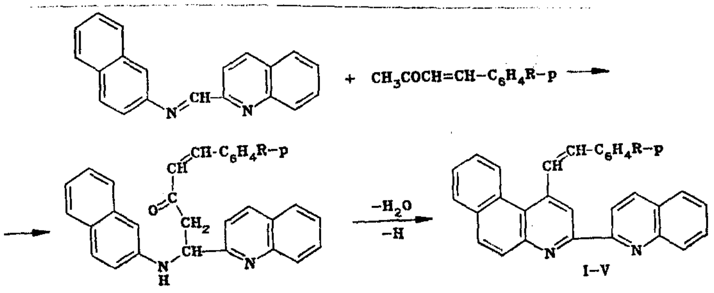
By catalytic condensation of quinolidene-β-naphthylamine with benzalacetone and its derivatives, previously undescribed styryl-5,6-benzo-2,2'diquinolyls have been synthesized. Complexes of these compounds with univalent copper ions have been studied, the spectral characteristics of the reagents and complexes have been reported, and a hypothesis has been advanced on the relationship between the structure of the ligands and the intensity of coloration of the metal complexes.

We had reported previously [1-3] of the possibility of using derivatives of 5,6-benzo-2,2'-diquinolyl for the photometric determination of copper. With the aim of further study of the dependence of the complex-forming properties of the ligands on their structure, it was of interest to synthesize new derivatives of benzoquinoline containing substituents with a multiple bond.

By catalytic condensation of quinolidene-β-naphthylamine with benzalacetone and its derivatives, new compounds were obtained through the scheme



I R=H, II R=Cl, III R=OCH_3, IV R=$N(CH_3)_2$, V R=NO_2

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TABLE 1. Characteristics of Compounds Synthesized

Compound	mp, °C	UV spectrum, λ_{max}, nm, ($\varepsilon \cdot 10^{-4}$)	Cu (I) comlex, λ_{max}, nm, ($\varepsilon \cdot 10^{-3}$)	Found, %			Empirical formula	Calculated, %			z_N	Yield, %
				C	H	N		C	H	N		
I	206	255 (5,01), 280 (5,05), 317 (3,10), 370 (0,80)	548 (11,7)	88,0	5,0	6,9	$C_{30}H_{20}N_2$	88,2	4,8	6,8	−0,2287	15,8
II	208—209	260 (5,25), 280 (5,50), 325 (2,95), 365 (0,95)	548 (12,5)	81,6	4,4	6,5	$C_{30}H_{19}ClN_2$	81,3	4,2	6,3	−0,2293	20,4
III	212—213	250 (4,75), 275 (5,70), 320 (2,77), 365 (1,35)	550 (12,7)	84,6	5,2	6,5	$C_{31}H_{22}N_2O$	84,9	5,0	6,4	−0,2298	16,2
IV	263—265	255 (5,60), 270 (6,10), 325 (2,87), 370 (1,27)	544 (12,6)	85,4	5,3	9,4	$C_{32}H_{25}N_3$	85,1	5,5	9,3	−0,2296	18,5
V	240—241	250 (4,75), 280 (6,25), 325 (3,77), 370 (1,60)	552 (12,8)	79,0	4,6	9,4	$C_{30}H_{19}N_3O_2$	79,2	4,4	9,3	—	19,0
VI	—	—	542 (8,5)								−0,2280	

The structure and composition of the compounds were confirmed by elemental analysis and IR and UV spectroscopy. Certain characteristics of the compounds that were obtained are listed in Table 1.

Examination of the IR absorption spectra showed that there were none of the bands near 1700 and 3400 cm^{-1} that are characteristic for stretching vibrations of N—H and C=O groups, thus indicating cyclization of the intermediate condensation product. The UV spectra of compounds I-V are complex systems of several absorption bands: 250-260, 270-280, 317-325, and 365-370 nm. The absorption by these compounds is due to $\pi \rightarrow \pi^*$ transitions. The form of the spectra is characteristic for polynuclear derivatives of benzo(f)quinolines [4].

As can be seen from the data of Table 1, regardless of the nature of the substituent R, the characteristic absorption spectrum remains essentially the same. Slight changes are observed in the intensity and position of the absorption bands of the compounds.

The presence of a structural fragment including two heteroatoms is responsible for the complex-forming properties of the new compounds. A study of their interaction with univalent copper ions, following procedures described in [1], showed that compounds I-V form colored complexes with a 1:2 ratio of copper to reagent in the pH interval 5.4-7.6. The spectral characteristics of alcohol solutions of the Cu(I) complexes of these compounds are listed in Table 1. Also listed for comparison are the spectral characteristics of 4-phenyl-5,6-benzo-2,2'-diquinolyl (VI). A comparison of the molar extinction coefficients for the complexes of compounds I and VI indicates that the introduction of the arylethylene grouping is accompanied by sharp bathochromic and hyperchromic effects, which indicates realization of an extended chromophoric system ($CH=CH—C_6H_5$). The introduction of various substituents R, differing in the electronic nature, into the para position relative to the ethylene group leads to an increase in intensity and a shift of the absorption maximum for the Cu(I) complexes. The greatest effect is produced by the NO_2 group: $\Delta\lambda = +4$ nm, $\Delta\varepsilon = 1100$.

On the basis of the results obtained in this work, we can conclude tentatively that in these compounds I-V, conjugation of the R-substituted aromatic ring with the benzoquinoline ring is maintained through the ethylene group —CH=CH—.

This view is supported by quantym-chemical calculations performed by the Pariser—Parr—Pople method. The changes in electron density on the heteroatoms responsible for complexation when various substituents R are introduced (values of the effective charge z_N are shown in Table 1) indicate a leading role of the ethylene group in position 4 between the π-systems of the phenyl and benzoquinoline rings [5].

EXPERIMENTAL

The UV spectra of compounds I-V were taken in an SF-4A spectrophotometer; the concentration of reagents was $2 \cdot 10^{-5}$ M in ethanol, absorbing layer thickness 1 cm. The IR spectra were taken in a Specord IR-75 spectrophotometer in KBr tablets.

4-Styryl-5,6-benzo-2,2'-diquinolyl (I). A 2.8-g quantity (0.01 mole) of quinolidene-β-naphthylamine and 1.46 g (0.01 mole) of benzalacetone were dissolved in 15 ml of ethanol, 5 drops of concentrated HCl were added, and the mixture was refluxed on a boiling water bath for 1 h. The precipitate that formed after cooling was filtered off and washed with methanol and ammonia.

Compounds II-V were obtained by an analogous procedure, by condensation of quinolidene-β-naphthylamine with p-chloro-, p-methoxy-, p-dimethylamino-, and p-nitrobenzalacetone, respectively. All of the compounds were purified by repeated recrystallizations from dioxane.

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