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

A. L. Gershuns and A. A. Verezubova

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New 5,6-benzo-2,2'-diquinolyl derivatives were obtained. The optimum conditions for the formation of Cu(I) complexes were investigated. It is shown that the UV spectra of the synthesized compounds and the chromaticity of the complex are determined by the effect of the substituents, their planar orientation, and, mainly, by the planarity of the system.

Substituted 5,6-benzoquinolines can be obtained by condensation of the azomethines of β-naphthylamine with carbonyl compounds [1-5]. If the starting substances are azomethines of heterocyclic aldehydes, the condensation leads to heterocyclic systems. Considering that systems of two quinoline rings with an internuclear bond in the 2 position are inclined to form intensely colored compounds with Cu(I) ions, which explains their use as analytical reagents, we synthesized and investigated the complexing of a number of 5,6-benzo-2,2'-diquinolyl derivatives. The general formulas of the compounds obtained, their properties, yields, and analytical data are presented in Table 1.

The aim of the present study was not only the synthesis of new compounds but also the investigation of the dependence between the structure of the heterocycles and their capacity to form colored Cu(I) complexes. Of interest to us was the effect of the introduction of condensed and bonded benzene rings on the absorption intensity of the substance and its complex and the role of planarity of the substituents and the heterocyclic rings. The light-absorption curves of 5,6-benzo-2,2'-diquinolyl and its derivatives are presented in Fig. 1. It is seen that three absorption bands at 280-290, 320-345, and 365-370 nm are characteristic for I, II, V, and VI. The presence of phenyl groups increases the intensity of the absorption in the short-wave portion of the spectrum; this is seen on comparison of the curves of I, II, and VI with V. However, the effect of the substituents depends on their position, and the introduction of a phenyl group into the 4 position of 5,6-benzoquinoline ring has a lesser effect than is observed when the phenyl group is in the quinoline ring (compare VI and I). This is apparently explained by disruption of the planarity of the phenyl group, which is seen from Fig. 2a, in which the structural formula of VI is presented with allowance for the angles, internuclear distances, and hindrance radii [6]. The introduction of an additional cyclohexylene ring condensed in the 3, 4 position (III and IV) sharply changes the character of the absorption by causing a hypsochromic shift and disappearance of the absorption band in the long-wave portion of the spectrum. This effect is explained by disruption of the planarity of the entire system because of the steric hindrance created by the cyclohexylene group (Fig. 2b). Thus an investigation of the UV spectra demonstrated that the substituents and steric factors to a considerable extent determine the character of the absorption. It seemed of interest to ascertain the effect of steric factors on the spectral characteristics of colored Cu(I) complexes of the new compounds. The general method for the preparation of alcohol solutions of the complexes consisted in vigorous stirring of a butanol solution of the reagent with an aqueous solution containing hydroxylamine hydrochloride, acetate buffer (pH 6), and cuprous nitrate. The colored alcohol layer was separated, and the absorption spectra were recorded with an SF-4A spectrophotometer. A detailed investigation of the complexes demonstrated that all of them have a copper–reagent composition of 1 : 2, that they are stable at pH 6-7, and that the maximum optical density is reached when there is a threefold to fivefold excess of the reagent. The spectral characteristics of the colored Cu(I) complexes are presented in Table 1. It is known that the complex of 2,2'-diquinolyl has an extinction coefficient (ε) at $\lambda_{545} = 6440$.

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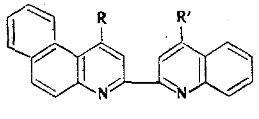
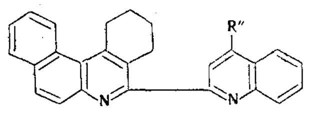
TABLE 1. 5,6-Benzo-2,2'-diquinolyl Derivatives



I, II, V, VI



III, IV

Compound	R	R'	R''	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %	Cu(I) complex	
						C	H	N	C	H	N		λ_{max}, nm	$\lg \varepsilon_{max}$
I	H	C_6H_5	—	229—230	$C_{28}H_{18}N_2$	87,6	4,3	7,1	87,9	4,7	7,3	20	540	3,9750
II	C_6H_5	C_6H_5	—	322—323	$C_{34}H_{22}N_2$	88,7	4,4	5,9	89,0	4,79	6,1	36	540	3,9294
III	—	—	H	133	$C_{26}H_{20}N_2$	86,4	5,2	7,6	86,6	5,5	7,7	27	510	3,5315
IV	—	—	C_6H_5	176—177	$C_{32}H_{24}N_2$	87,8	5,2	6,2	88,08	5,5	6,4	21	530	3,6474
V	H	H	—	—	—	—	—	—	—	—	—	58,7	535	3,8621
VI	C_6H_5	H	—	—	—	—	—	—	—	—	—	20	540	3,9320

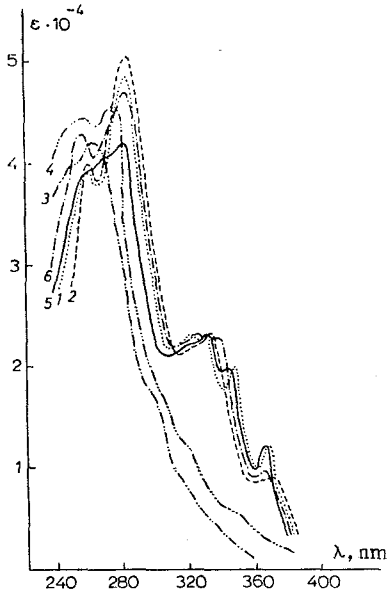
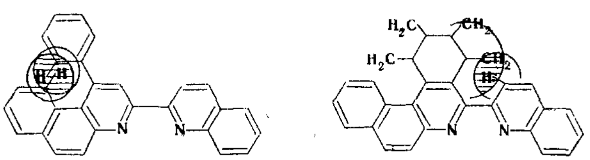


Fig. 1. UV absorption spectra in butanol: 1) 5,6-benzo-4-phenyl-2,2'-diquinolyl (I); 2) 5,6-benzo-4,4'-diphenyl-2,2'-diquinolyl (II); 3) 3,4-cyclohexylene-4'-phenyl-5,6-benzo-2,2'-diquinolyl (IV); 5) 5,6-benzo-2,2'-diquinolyl (V); 6) 5,6-benzo-4-phenyl-2,2'-diquinolyl (VI).



a

b

Fig. 2. Structural formulas of 5,6-benzo-4-phenyl-2,2'-diquinolyl (a) and 5,6-benzo-3,4-cyclohexylene-2,2'-diquinolyl (b) on a scale corresponding to the hindrance radii of the atoms and radicals.

A comparison of it with V shows that the introduction of a condensed benzene ring into the 5,6 position increases ε_{max} of the complex. The presence of phenyl groups in the 4 position has an even stronger effect on the increase in the intensity of the color, which also depends on the position of the substituent. The maximum effect is achieved when a phenyl group is introduced into the quinoline ring (I) rather than into the 5,6-benzoquinoline ring (VI). The reason for this is removal of the phenyl group from the planar state because of steric hindrance (Fig. 2a). Disruption of the planarity of the heterocyclic rings (Fig. 2b) has a much stronger effect on the interaction with Cu(I) ions. The ε_{max} value of the complex is almost halved (compare III and V and IV and I), and a hypsochromic effect is observed in addition to this.

The considerable change in the chromaticity of the complex when the planarity of the rings is disrupted is due to the fact that conjugation of the entire system is hindered, and the optimum distance between the heteroatoms responsible for the establishment of a bond with the metal changes.

Thus it was established that the above-examined factors that affect the UV absorption spectra of the compounds obtained also have an effect on the formation of colored metal complexes. This fact is important for the directed synthesis of systems of promise as analytical reagents.

EXPERIMENTAL

2-Formyl-4-phenylquinoline. This compound was obtained in 30% yield by oxidation of 4-phenylquinaldine with selenium dioxide [7] and had mp 85-86°.

4-Phenylquinolylidene-β-naphthylamine (VII). A solution of 3 g (0.02 mole) of β-naphthylamine in 15 ml of methanol was added to a solution of 3.8 g (0.016 mole) of 2-formyl-4-phenylquinoline in 15 ml of methanol, and the mixture was refluxed for 5 min. The mixture was cooled, and the yellow precipitate was separated and crystallized from ethanol to give 4.8 g (82%) of a product with mp 185°. Found: C 86.8; H 4.7; N 7.6%. $C_{26}H_{18}N_2$. Calculated: C 87.1; H 5.0; N 7.8%.

The azomethine of 2-formylquinoline was similarly obtained.

4'-Phenyl-5,6-benzo-2,2'-diquinolyl (I). A mixture of 1 g (0.003 mole) of VII in 40 ml of butanol, 3 ml (0.02 mole) of paraldehyde, and five drops of concentrated hydrochloric acid was refluxed on a water bath for 30 min, after which the solution was evaporated to half its volume and cooled. The resulting precipitate was separated, washed with methanol, and crystallized from dioxane. The light-yellow crystals were only slightly soluble in water but were quite soluble in alcohol, toluene, dioxane, benzene, dimethylformamide, and acetone.

4,4'-Diphenyl-5,6-benzo-2,2'-diquinolyl (II). A mixture of 1 g (0.003 mole) of VII in 50 ml of methanol, 1 ml (0.008 mole) of acetophenone, and five drops of concentrated hydrochloric acid was refluxed for 1 h on a water bath. Workup as in the case of the preparation of I gave light-yellow crystals that were only slightly soluble in water but quite soluble in alcohol, toluene, dioxane, benzene, acetone, and dimethylformamide.

3,4-Cyclohexylene-5,6-benzo-2,2'-diquinolyl (III). A mixture of 1 g (0.0035 mole) of 2-quinolylidene-β-naphthylamine in 40 ml of ethanol, 1 ml of concentrated hydrochloric acid, 3 ml of cyclohexanone, and 3 ml of nitrobenzene was sealed in an ampul and heated at 175° for 3 h. The contents of the ampul were then evaporated to half the original volume, and the precipitate was separated and washed with methanol and sodium carbonate solution. Crystallization from methanol gave a light-yellow crystalline powder that was only slightly soluble in water but quite soluble in alcohol, toluene, benzene, dioxane, acetone, and dimethylformamide.

4'-Phenyl-3,4-cyclohexylene-5,6-benzo-2,2'-diquinolyl (IV). This compound was obtained from 1 g (0.003 mole) of VII in 20 ml of isoamyl alcohol, 0.5 ml of concentrated hydrochloric acid, 3 ml of nitrobenzene, and 4 ml of cyclohexanone, as in the preparation of III. The light-yellow crystals (from isoamyl alcohol) were only slightly soluble in water but quite soluble in alcohol, toluene, benzene, dioxane, acetone, and dimethylformamide.

5,6-Benzo-2,2'-diquinolyl (V) and 4-phenyl-5,6-benzo-2,2'-diquinolyl (VI) were obtained via the method in [5].

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