SYNTHESIS AND STUDY OF CERTAIN 4,4'-DISUBSTITUTED 5,6-BENZO-2,2'-DIQUINOLYLS

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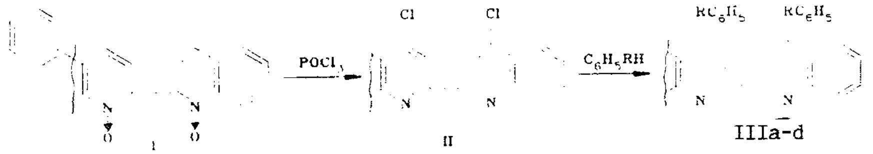
543.422.6

4,4'-Dianilino-, 4,4'-dibenzylamino-, 4,4'-diphenoxy and 4,4'-dithiophenoxy-5,6-benzo-2,2'-diquinolyls were synthesized. Their complexation with monovalent copper ions was studied, the spectral characteristics were given, and a postulation was made on the relationship between the structure of ligands and the color intensity of the metal complexes.

In continuation of our investigations [1, 2] on producing organic reagents for the photometric determination of monovalent copper, we synthesized new derivatives of 5,6-benzo-2,2'-diquinolyl:



III a R=NH, b R=NHCH$_2$, c R=O, d R=S

The structure and composition of the compounds were confirmed by elemental analysis and spectroscopy data. In the IR spectra of the heterocyclic compounds studied, bands were detected and identified which were due to the vibrations of the quinoline rings, as well as bands corresponding to the vibrations of the substituents [3]. Some characteristics of the compounds obtained are listed in Table 1.

We have already shown [1] the role of the phenyl residues at the 4,4' positions of the benzodiquinolyl ring in increasing the color intensity of the metal complexes. It was of interest to clarify the character of the interaction of the aryl and heterocyclic fragments through the bridging hetero atoms containing unshared pairs of p-electrons.

Figure 1 shows the light absorption curves in the UV region of the solutions of the compounds IIIa-d studied. For comparison, a light absorption curve of 4,4'-diphenyl-5,6-benzo-2,2'-diquinolyl IV is given [1]. Based on the intensity of the bands, and their reaction to transition from an inert to a polar solvent, it can be concluded that in the region of 250-255, 275-290, 320-330, and 350-365 nm, the compounds studied have π → π* type bands, which are characteristic for polynuclear derivatives of benzo(f)quinoline [4]. Figure 1 shows that the electronic nature of the bridging hetero atoms does not influence the character of the UV bands, but leads to some change in the intensity and the position of the bands. The pres-

TABLE 1. Characteristics of Compounds Studied

Compound	Empirical formula	mp, °C	Yield, %	Cu(I)-complex	
				λ_{max}, nm	ε
III a	$C_{34}H_{24}N_4$	248...249	21	535	13 000
III b	$C_{36}H_{28}N_4$	228...230	26	535	9750
III c	$C_{34}H_{22}N_2O_2$	275...276	13	525	8900
III d	$C_{34}H_{22}N_2S_2$	273...274	16	540	9500
IV	—	—	—	540	8500

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†Deceased.

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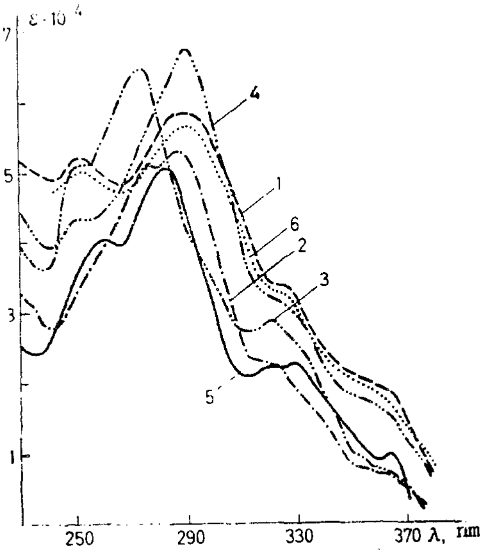

Fig. 1. UV absorption spectra of the compounds in ethanol: IIIa (1), IIIb (2), IIIc (3), IIId (4), 4,4'-biphenyl-5,6-benzo-2,2'-diquinolyl (5); in octane: IIIa (6).

ence in the compounds IIIa-d studied of the 2,2'-diquinolyl structural fragment ensures complexation with monovalent copper ions. The spectrophotometric investigation of the reaction of the new reagents with copper ions by the previously described method [1] showed that compounds IIIa-d form complexes with a composition of copper:reagent = 1:2, which are stable in the pH range of 5.5-6.7.

Comparison of the molar absorption coefficients of the complexes showed that the introduction of bridging hetero atoms does not weaken the intensity of the electronic influence of the aryl residues compared with a bridgeless system (compound IV). Increase in the extinction coefficient is due to the ability of the unshared electrons of the bridging hetero atom to enter into an electron-donor conjugation with the π-electronic system of both the quinolinyl and phenyl rings. The maximal effect in the direction of increase in the molar extinction coefficient when an imino group is introduced, is probably due to its stronger electron-donor properties, compared with the bridging —O— and —S— atoms. A similar behavior of the bridging hetero atoms was observed in [5] during the investigation of the electronic structure and the transferring power in the series of bridged pyridine derivatives. In the case of compound IIIb, the insulating effect of the methylene group is evident.

The experimental data obtained show that the complex forming properties of the heterocyclic compounds are dependent on the electronic nature of the bridging atoms and on the character of their interaction with molecular fragments.

EXPERIMENTAL

The UV spectra of compounds IIIa-d were run on an SF-46 spectrophotometer, and the concentration of the reagents was $2 \cdot 10^{-5}$ mole/liter in ethanol and octane; the IR spectra were obtained on a Specord IR-75 spectrophotometer in KBr tablets.

5,6-Benzo-2,2'-diquinolyl N,N-dioxide (I) was obtained by a method described in [6], mp 242-244°C.

4,4'-Dichloro-5,6-benzo-diquinolyl (II, $C_{22}H_{12}N_2Cl_2$). A 3.4 g portion (0.01 mole) of compound I was dissolved in 20 ml of phosphorus oxychloride, and the solution was heated for 1 h at 107°C. After cooling, the mixture was poured onto ice, neutralized with 20% solution of NaOH, and the product was washed with water. Yield, 1.6 g (43%), mp 220-222°C (from DMFA).

4,4'-Dianilino-5,6-benzo-2,2'-diquinolyl (IIIa). A mixture of 3.8 g (0.01 mole) of compound II and 10 ml of aniline was boiled for 1 h at 180°C. The reaction mixture was cooled and mixed with 100 ml of ether. The hydrochloride salt precipitate was dissolved with heating in 200 ml of ethanol. The base was isolated by making the solution alkaline with a 20% solution of KOH and was crystallized from toluene. IR spectrum: 3360 (NH); 3040 (CH); 1586, 1570, 1496 cm^{-1} (C=C; C=N).

4,4'-Dibenzylamino-5,6-benzo-2,2'-diquinolyl (IIIb) was obtained in a similar manner by boiling compound II at 180°C and crystallization from toluene. IR spectrum: 3360 (NH); 3030 (CH); 1600, 1580, 1500 ($C{=}C$; $C{=}N$); 2092 cm^{-1} (CH_2).

4,4'-Diphenoxy-5,6-benzo-2,2'-diquinolyl (IIIc). A 1.9 g portion (5 mmoles) of compound II was added to a solution of sodium phenolate (3 g of metallic sodium and 20 g of phenol) in 120 ml of dry dimethyl sulfoxide, and the mixture was heated for 1 h at 140°C. The dark red solution was poured onto ice, the reaction product was filtered, washed with water, and crystallized from benzene. IR spectrum: 3060 (CH); 1596, 1570, 1480 ($C{=}C$; $C{=}N$); 1246 cm^{-1} (C—O—).

4,4'-Dithiophenoxy-5,6-benzo-2,2'-diquinolyl (IIId). A mixture of 1.9 g (5 mmoles) of compound II and 30 ml of thiophenol was heated for 3 h at 170°C. After cooling, the reaction mixture was poured into 500 ml of absolute ethanol. The precipitate that separated out was filtered off, washed with alcohol, water, and crystallized from dioxane. IR spectrum: 3060 (CH); 1590, 1570, 1473 cm^{-1} ($C{=}C$; $C{=}N$).

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SYNTHESIS OF PYRIDO[2,3-d]PYRIMIDINE-2,4-DIONES FROM PYRIMIDO-[4,5-e]-1,2,4-TRIAZINE-6,8-DIONES BY REVERSED AZADIENE SYNTHESIS*

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It was shown that pyrimido[4,5-e]-1,2,4-triazine-6,8-diones enter the reversed azadiene synthesis reaction with ketones and vinyl ethyl ether in the presence of diethylamine or boron trifluoride etherate, and also with enamines. As a result of the reaction, pyrido[2,3-d]pyrimidine-2,4-diones are formed in good yield. Pyrimido[5,4-e]-1,2,4-triazine-5,7-diones do not undergo such reactions with acetone. The reasons for the unique behavior of the isomeric pyrimidotriazinediones in the reaction with acetone are discussed.

Recently interest has increased noticeably with respect to the reversed azadiene synthesis reactions, with which numerous compounds with a very complex structure can be synthesized, which are often unobtainable by other methods [2-4]. As the azadiene component, 1,2,4-triazines among other compounds are particularly widely used, giving in the reaction with electron-donor dienophiles, derivatives of pyridine, pyrimidine and 1,3,5-triazine. Until recently it was not possible to involve condensed aromatic systems in this reaction. We have

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*For a preliminary communication, see [1].

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