SYNTHESIS AND INVESTIGATION OF SOME CONNECTED HETEROCYCLIC SYSTEMS

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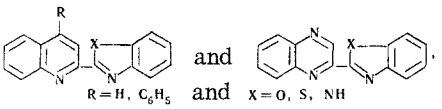
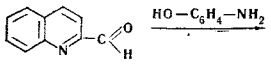
New connected heterocyclic systems consisting of quinoline or quinoxaline nuclei connected in position 2 with benzoxazole, benzothiazole, or benzimidazole rings have been synthesized. The UV spectra of the new substances have been studied and it has been found that the formation of a connected system causes an increase in the intensity of the absorption and a shift in the long-wave part of the spectrum.

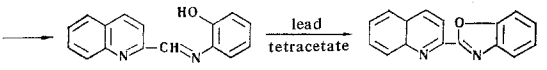
Connected nitrogen-containing heterocyclic systems in which the nitrogen atoms are adjacent to the bond joining the nuclei are interesting because of their capacity for forming colored complexes with metal ions. Systems of two pyridine or quinoline nuclei are well known to analysts who use these compounds for the photometry of iron and copper. Less well studied are the connected systems consisting of two different heterocycles. In the present work we faced the problem of synthesizing compounds containing quinoline or quinoxaline nuclei in addition to condensed five-membered heterocycles with two heteroatoms. The general formulas of the connected systems that we obtained are:



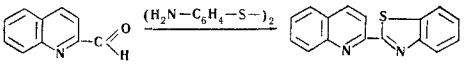
Of the nine substances that we obtained, only 2-(benzothiazol-2'-yl)quinoline [1] (IV) and 2-(benzimidazol-2'-yl)quinoline [2] (VII) have been described in the literature. But for these compounds, as well, we have simplified the method of synthesis and considerably increased the yield.

We synthesized connected heterocyclic systems containing the benzoxazole ring in two stages comprising the preparation of the o-hydroxyanil of the heterocyclic aldehyde and the oxidation of the anil with lead tetraacetate:



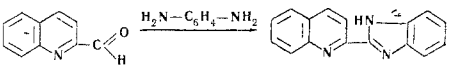


Compounds containing benzothiazole rings were obtained by condensing the corresponding aldehyde with di(2-aminophenyl) disulfide



This method enables a higher yield to be obtained than that described in the literature [1] consisting in heating the anil, sulfur, and quinaldine.

The substances with a benzimidazole ring were obtained by heating a heterocyclic aldehyde with o-phenylenediamine in the presence of copper acetate:



This synthesis leads to higher yields and is considerably simpler than the method described for 2-(benzimidazol-2'-yl)quinoline, which requires the use of special catalysts [2].

The properties, yields, and analyses of the compounds that we obtained are given in the table.

We have studied the UV spectra of the heterocyclic compounds. For this purpose light-absorption curves both of the connected heterocycles and of the compounds composing the given system were recorded. The results are given in Figs. 1–4. It can be seen from these that the formation of a connected heterocyclic system is always accompanied by a marked increase in the intensity of the absorption and by a shift in the absorption band towards the long-wave part of the spectrum by 40–50 nm. This is equally valid for symmetrical heterocyclic systems consisting of similar (Fig. 4) and of different (Figs. 1–3) nuclei. This

Characteristics of the Compounds Synthesized

Compound	Name	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
				N	S	N	S	
I	2-(Benzoxazol-2'-yl)quinoline	173—4	$C_{16}H_{10}N_2O$	11.01	—	11.38	—	26
II	2-(Benzoxazol-2'-yl)-4-phenylquinoline	183—4	$C_{22}H_{14}N_2O$	8.55	—	8.69	—	39
III	2-(Benzoxazol-2'-yl)quinoxaline	183	$C_{15}H_9N_3O$	17.41 17.26	—	17.00	—	57
IV	2-(Benzothiazol-2'-yl)quinoline	199—200	$C_{16}H_{10}N_2S$	10.75	12.0	10.67	12.21	84
V	2-(Benzothiazol-2'-yl)-4-phenylquinoline	240—1	$C_{22}H_{14}N_2S$	8.56	9.25	8.28	9.46	62
VI	2-(Benzothiazol-2'-yl)quinoxaline	227—8	$C_{15}H_9N_3S$	16.15	11.88	15.95	12.16	51
VII	2-(Benzimidazol-2'-yl)quinoline	220	$C_{16}H_{11}N_3$	16.98	—	17.14	—	45
VIII	2-(Benzimidazol-2'-yl)-4-phenylquinoline	220—1	$C_{22}H_{15}N_3$	13.38	—	13.08	—	95
IX	2-(Benzimidazol-2'-yl)quinoxaline	249—50	$C_{15}H_{10}N_4$	22.58	—	22.73	—	50

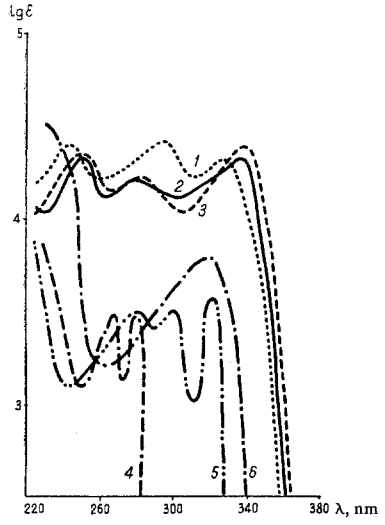


Fig. 1. UV spectra: 1) 2-(benzoxazol-2'-yl)-4-phenylquinoline (II); 2) 2-(benzoxazol-2'-yl)quinoline (III); 4) benzoxazole (X); 5) quinoline (XI); 6) quinoxaline (XII).

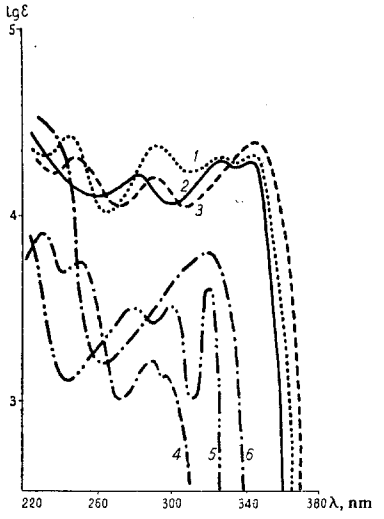


Fig. 2. UV spectra: 1) 2-(benzothiazol-2'-yl)-phenylquinoline (V); 2) 2-(benzothiazol-2'-yl)quinoline (IV); 3) 2-(benzothiazol-2'-yl) quinoxaline (VI); 4) benzothiazole (XIII); 5) quinoline (XI); 6) quinoxaline (XII).

effect is obviously connected with an enhancement of conjugation over the whole molecule through conjugation between the connected nuclear systems. This can also explain the increase in the intensity of absorption of the 280–300 nm band when a phenyl group is introduced into position 4 of the quinoline ring (curve 1 in Figs. 1–3).

It is also interesting to note that the unsymmetrical connected heterocyclic systems have monotypical light-absorption curves with three bands (225–235, 270–290, and 340–350 nm), while the UV spectra of the components of these systems differ markedly fron one another in dependence on the heteroatom.

EXPERIMENTAL

2-(Benzoxazol-2'-yl)quinoline (I). A solution of 7.85 g (0.05 mole) of quinoline-2-aldehyde in 35 ml of methanol was mixed with a solution of 5.45 g (0.05 mole) of o-aminophenol in 25 ml of methanol. The mixture was heated to the boil, and after 15 min it was cooled and the hydroxyanil of quinoline-2-aldehyde that had deposited was filtered off. The dried product was triturated with 35 ml of glacial acetic acid and the suspension was added to a solution of 25 g of lead tetracetate in 70 ml of glacial acetic acid. The mixture was left to stand at room temperature for 30 min and was then diluted with water to 300 ml. The brown precipitate that deposited was filtered off, dried, and purified by vacuum sublimation. The yield of pure product with mp 173–175° C was 3.2 g or 26% of theory.

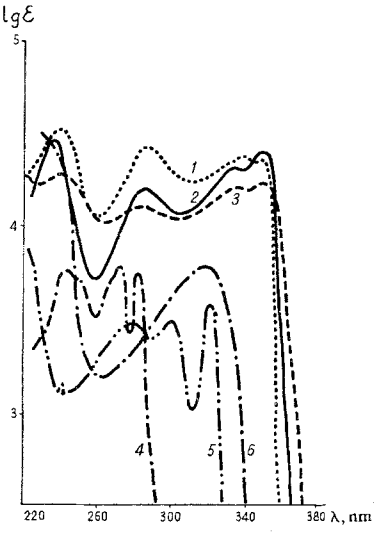


Fig. 3. UV spectra: 1) 2-(benzimidazol-2'-yl)-4-phenylquinoline (VIII); 2) 2-(benzimidazole-2'-yl)quinoline (VII); 3) 2-(benzimidazol-2'-yl)quinoxaline (IV); 4) benzimidazole (XIV); 5) quinoline (XI); 6) XII.

2-(Benzoxazol-2'-yl)-4-phenylquinoline (II) and **2-(benzoxazol-2'-yl)-quinoxaline (III)** were obtained similarly using the corresponding aldehydes as the starting materials. Their yields and characteristics are given in the table. They form colorless crystalline products soluble in alcohols, ether, dichloroethane, xylene, and pyridine, and sparingly soluble in water.

2-(Benzothiazol-2'-yl)quinoline (IV). A mixture of 7.85 g (0.05 mole) of quinoline-2-aldehyde, 12.4 g (0.05 mole) of di(2-aminophenyl)disulfide, and 40 ml of xylene was boiled under reflux for 2 hr. After cooling, yellow needles of 2-(benzothiazol-2'-yl)quinoline were filtered off, washed on the filter with methanol, and recrystallized from xylene.

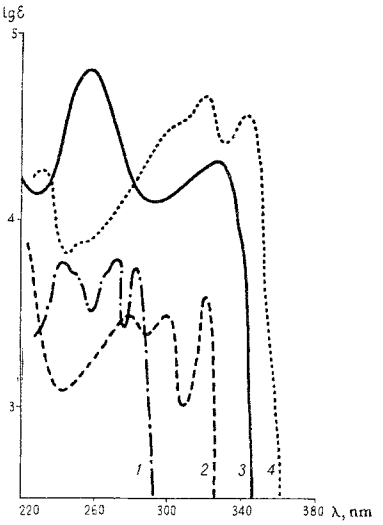


Fig. 4. UV spectra: 1) benzimidazole (XIV); 2) quinoline (XI); 3) 2,2'-biquinolyl (XV); 4) 2,2'-bibenzimidazolyl (XVI).

2-(Benzothiazol-2'-yl)-4-phenylquinoline (V) and **2-(benzothiazol-2'-yl)-quinoxaline (VI)** were obtained by a similar method but starting from 4-phenylquinoline-2-aldehyde and quinoxaline-2-aldehyde. The yields and characteristics of the compounds obtained are given in the table. The substances are soluble in xylene, ether, dichloroethane, and pyridine, sparingly soluble in water, and moderately soluble in cold ethanol.

2-(Benzimidazol-2'-yl)quinoline (VII). A 1-liter round-bottomed flask fitted with a reflux condenser was charged with a solution of 10.8 g (0.1 mole) of o-phenylenediamine in 150 ml of propanol, a solution of 7.85 g (0.05 mole) of quinoline-2-aldehyde in 100 ml of propanol, and 30 g of copper acetate dissolved in 300 ml of water. The mixture was heated in the water bath for 1 hr, during which the blue color of the copper acetate gradually disappeared and a brown precipitate of the copper salt of 2-(benzimidazol-2'-yl)quinoline separated out. Then it was cooled and the filtered-off residue was mixed with 300 ml of hot 70% methanol, and hydrogen sulfide was passed through until the copper had been completely precipitated. The copper sulfide was filtered off and washed with 75 ml of hot methanol, and the alcoholic extract was added to the previous filtrate. After the addition of 200 ml of water, a yellow precipitate of 2-(benzimidazol-2'-yl)quinoline precipitated, and this was crystallized from methanol. Yield 11.6 g.

2-(Benzimidazol-2'-yl)-4-phenylquinoline (VIII) and **2-(benzimidazol-2'-yl)quinoxaline (IX, table)** were obtained similarly from the corresponding aldehydes. The substances are readily soluble in alcohols, pyridine, and chloroform, and sparingly soluble in water.

The UV spectra of the substances dissolved in specially purified 95% ethanol were recorded on an SF-4A instrument.

REFERENCES

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