PREPARATION AND PROPERTIES OF 2-(4-ARYLAMINO-2-QUINOLYL) QUINOLINES

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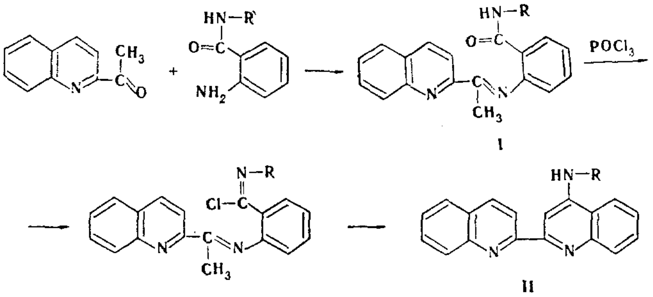
2-Acetylquinoline o-arylcarbamoylanils were synthesized and converted to 2-(4-arylamino-2-quinolyl)quinolines by intramolecular cyclization. The new compounds form colored complexes with copper (I).

A method for the preparation of 2-(2-quinolyl)cinchoninic acid by reaction of 2-acetylquinoline with isatin was described in [1]. Continuing our research on the synthesis of representatives of bonded heterocyclic systems we developed a new variant that consists in condensation of 2-acetylquinoline with anthranilic acid arylamides and subsequent intramolecular cyclization.

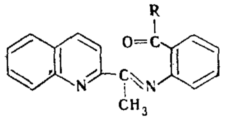


I, IIa $R = C_6H_5$; b $R = \alpha\text{-}C_{10}H_7$; c $R = p\text{-}CH_3OC_6H_4$; d $R = p\text{-}CH_3C_6H_4$;
e $R = p\text{-}BrC_6H_4$; f $R = C_6H_5NO_2$

It is apparent from the synthetic scheme that the intermediates are 2-acetylquinoline o-arylcarbamoylanils (I) (Table 1). In analogy with [2], imidochlorides are formed when I are heated with excess phosphorus oxychloride, and the final products are 2-(4-arylamino-2-quinolyl)quinolines (II) (Table 2).

Compounds I are white substances and II are light-yellow substances that dissolve on heating in organic solvents.

TABLE 1. 2-Acetylquinoline o-Arylcarbamoylanils



Compound	R	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
Ia	C_6H_5NH	222—223	$C_{24}H_{19}N_3O$	78,8	5,3	11,3	78.9	5,2	11,5	28
Ib	$\alpha\text{-}C_{10}H_7NH$	272—273	$C_{28}H_{21}N_3O$	81,2	5,0	10,2	81,0	5,1	10,1	29
Ic	$p\text{-}CH_3OC_6H_4NH$	248—249	$C_{25}H_{21}N_3O_2$	76,0	5,5	10,4	75,9	5,4	10,6	26
Id	$p\text{-}CH_3C_6H_4NH$	233—234	$C_{25}H_{21}N_3O$	79,3	5,5	11,2	79,1	5,6	11,1	25
Ie	$p\text{-}BrC_6H_4NH$	235—236	$C_{24}H_{18}BrN_3O$	64,8	4,2	9,3	64,9	4,1	9,5	20
If	$C_6H_5CH_2NH$	216—218	$C_{25}H_{21}N_3O$	79,3	5,8	11,0	79,1	5,6	11,1	23

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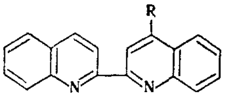
TABLE 2. 2-(4-Arylamino-2-quinolyl)quinolines



Compound	R	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %	Cu(I) complex	
				C	H	N	C	H	N		λ_{max}, nm	$\varepsilon \cdot 10^{3}$
IIa	C_6H_5NH	254—255	$C_{24}H_{17}N_{13}$	83,1	5,0	11,9	83,0	4,9	12,1	35	556	10,04
IIb	α-$C_{10}H_7NH$	199—200	$C_{28}H_{19}N_3$	84,7	4,6	10,7	84,6	4,8	10,6	42	558	10,40
IIc	p-$CH_3OC_6H_4NH$	184—185	$C_{25}H_{19}N_3O$	79,4	5,3	10,9	79,6	5,1	11,1	45	556	9,88
IId	p-$CH_3C_6H_4NH$	188—190	$C_{25}H_{19}N_3$	83,0	5,2	11,8	83,1	5,3	11,6	36	556	10,30
IIe	p-BrC_6H_4NH	227—228	$C_{24}H_{16}BrN_3$	67,5	3,6	9,9	67,6	3,8	9,8	33	556	10,72
IIf	$C_6H_5CH_2NH$	176—178	$C_{25}H_{19}N_3$	83,0	5,6	11,4	83,1	5,3	11,6	30	553	7,98

TABLE 3. UV Spectra of 2-Acetylquinoline o-Arylcarbamoylanils and 2-(4-Arylamino-2-quinolyl)quinolines

Compound	λ_{max}, nm(lg ε)	Compound	λ_{max}, nm (lg ε)
Ia	227 (4,7535), 315 (3,4357)	IIa	250 (4,6788), 320 (4,2598), 360 (3,8195)
Iб	225 (5,0558), 295 (4,0445)	IIб	250 (4,7589), 320 (4,3345), 360 (3,9777)
Iв	229 (4,7727), 325 (3,8558)	IIв	250 (4,7293), 320 (4,2840), 362 (3,8401)
Iг	228 (4,7281), 310 (3,3290)	IIг	250 (4,7203), 320 (4,2900), 360 (3,8573)
Iд	231 (4,7819), 325 (3,6709)	IIд	252 (4,7010), 324 (4,2856), 360 (3,9243)
Ic	226 (4,7350), 310 (3,4532)	IIe	262 (4,5541), 325 (4,1995), 361 (3,6998)

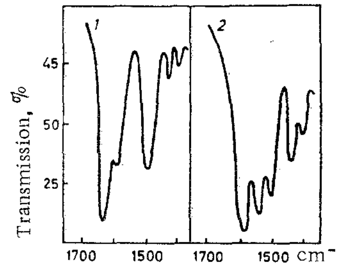


Fig. 1. IR spectra: 1) 2-acetylquinoline o-phenylcarbamoylanil; 2) 2-(4-anilino-2-quinolyl)quinoline.

An intense shortwave absorption band with a maximum at 225-231 nm and a longwave band at 295-325 nm are observed in the UV spectra of I (Table 3). The increase in the intensity of the shortwave band of Ib is associated with lengthening of the conjugation chain of the system.

The UV spectra of II are characterized by a bathochromic shift of the short-wave band (≈ 25 nm) and the appearance of an additional third band in the longwave portion of the spectrum (Table 3). The absorption of the synthesized compounds in the UV portion of the spectrum is due to $\pi \rightarrow \pi^*$ transitions.

The intense band at 1640 cm^{-1} in the IR spectra of I corresponds to the stretching vibrations of the carbonyl group and, of course, is absent in the spectra of II (Fig. 1). The stretching vibrations of the NH group are found at 3310-3315 and 3280-3290 cm^{-1} in the spectra of I and II, respectively. The appearance of intense bands related to the vibrations of heteroaromatic rings (1540 and 1590 cm^{-1}) is also characteristic for II.

The presence of a complexing grouping for monovalent copper in I and II provides a possibility for the formation of colored complexes. As a result of our investigation we established not only the fact that complexing does take place but also that the structural differences in I and II determine the intensity of the coloration of the complexes. The maximum molar absorption coefficient of the copper (I) complexes (Table 2) was obtained by reaction of compounds that are bonded systems made up of two heterocyclic rings with monovalent copper ions.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of the compounds in ethanol and the absorption spectra of the copper (I) complexes in isoamyl alcohol were recorded with an SF-4A spectrophotometer. The method used to prepare the solutions of the Cu(I) complexes was described in [1]. The anthranilic acid arylamides and 2-acetylquinoline were obtained by the methods in [3, 4].

2-Acetylquinoline o-Arylcarbamoylanils (I). A 0.01-mole sample of anthranilic acid arylamide was dissolved by heating in 10 ml of x-xylene, 0.01 mole of 2-acetylquinoline was added, and the mixture was refluxed for 6 h. It was then cooled, and the resulting precipitate was separated and crystallized from propanol.

2-(4-Arylamino-2-quinolyl)quinolines (II). A 0.01-mole of I was refluxed with 8 ml of phosphorus oxychloride for 1 h, after which the mixture was cooled, and the dark mass was poured over ice. The resulting precipitate was separated and dissolved by heating in 100 ml of propanol. The solution was filtered, ammonium hydroxide was added to the filtrate to pH 11, and water was added until precipitation of the product was complete. The liberated base was separated and crystallized from propanol.

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