INVESTIGATION OF THE STRUCTURAL PECULIARITIES AND CHEMICAL TRANSFORMATIONS OF CARBAZOLE AND ITS DERIVATIVES

XXXVIII.* INTERRELATIONSHIP BETWEEN THE STRUCTURE AND CHROMATICITY OF CARBAZOLE-BASED AZOMETHINES

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Nineteen azomethines based on aminocarbazoles were synthesized, and their electronic absorption spectra were measured. The problems of the interrelationship between the structure and chromaticity of azomethines of the carbazole series are discussed on the basis of the results obtained.

In the previous paper [2], we described the synthesis and several properties of azomethines based on carbazole [2]. The goal of this investigation is a study of the interrelationship between the structure and chromaticity of carbazole-containing azomethines. The K-chromophoric system of the compounds that we synthesized includes a carbazole ring and a benzene ring or a system of condensed benzene rings bonded by an azomethine group (–CH=N–) (Table 1).

In order to study the effect of the unshared pair of electrons of the heterocyclic nitrogen atom on the conjugation system, we made a comparison of the UV spectra of azomethines obtained from m-aminobiphenyl (XX), p-aminodiphenylamine (XXI), and 3-aminocarbazole (II) (Fig. 1).

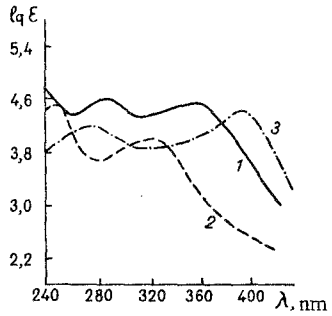

Fig. 1. UV spectra: 1) 3-(o-hydroxybenzylideneamino)carbazole; 2) m-(o-hydroxybenzylideneamino)biphenyl; 3) p-(o-hydroxybenzylideneamino)diphenylamine.

A bathochromic shift of the absorption maximum by 38 nm due to lengthening of the conjugation chain and the planarity of the carbazole molecule is observed on passing from biphenyl derivatives to carbazole derivatives. On the other hand, a hypsochromic shift of the absorption maximum by 35 nm is observed on passing from diphenylamine derivatives to carbazole derivatives. This is explained by the fact that the unshared pair of electrons of the heterocyclic nitrogen atom is in conjugation with the π electrons of the carbazole ring and does not participate in polarization of the molecule [3].

An analysis of the results presented in Table 1 demonstrated that the introduction of electron-donor substituents into the benzylidene portion of the molecules of the azomethines (3-aminocarbazole derivatives) leads to a shift in the absorption maximum to the long-wavelength region and to an increase in the absorption intensity. Thus, when there is a dimethylamino group in the para position of the benzene ring, the bathochromic shift can be explained by $p-\pi$ conjugation of the electron pair of the nitrogen atom with the benzene ring that is part of the chromophoric system [4]. An OH group in the ortho posi-

* See [1] for communication XXXVII.

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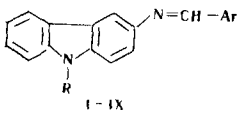
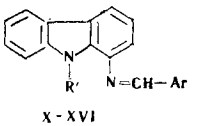
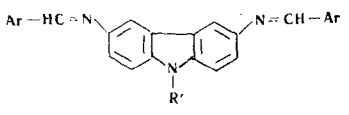
TABLE 1



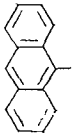
I - IX



X - XVI

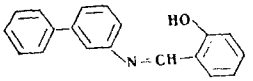


XVII - XIX

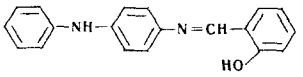
Compound	Ar	R'	Azomethine color	Mp, deg C	UV spectra λ_{max}, nm	UV spectra $\varepsilon \cdot 10^{-4}$	Empirical formula	N, % Found	N, % Calc.	Yield %
I	C_6H_5	H	Light yellow	209[a]	345	1,86	$C_{19}H_{14}N_2$	10,1	10,4	81
II	o-HOC_6H_4	H	Yellow	223—224[b]	360	3,47	$C_{19}H_{14}N_2O$	9,4	9,8	93
III	p-$O_2NC_6H_4$	H	Red	215—216[a]	405	2,18	$C_{19}H_{13}N_3O_2$	13,0	13,3	87
IV	p-$(CH_3)_2NC_6H_4$	H	Yellow	247[a]	370	4,08	$C_{21}H_{19}N_3$	13,6	13,4	79
V	o-$O_2NC_6H_4$	H	Orange	131—133[c]	380	1,7	$C_{19}H_{13}N_3O_2$	13,0	13,3	64
VI	C_6H_5	CH_3	Light yellow	197—198[d]	350	2,5	$C_{20}H_{16}N_2$	9,6	9,9	68
VII	C_6H_5	CH_2CH_2CN	Yellow	212—214[a]	360	1,64	$C_{22}H_{17}N_3$	13,6	13,0	75
VIII	2-Naphthyl	H	Yellow	254—255[e]	377	2,23	$C_{23}H_{16}N_2$	8,4	8,8	79
IX		H	Orange	218—220[a]	442	3,6	$C_{27}H_{18}N_2$	7,0	7,6	72
X	C_6H_5	H	Yellow	200—201[a]	355	1,0	$C_{19}H_{14}N_2$	10,9	10,4	42
XI	o-HOC_6H_4	H	Greenish yellow	211[d]	363	1,42	$C_{19}H_{14}N_2O$	9,8	9,8	69
XII	p-$(CH_3)_2NC_6H_4$	H	Yellow	235—237[a]	367	1,75	$C_{21}H_{19}N_3$	13,7	13,4	76
XIII	p-$O_2NC_6H_4$	H	Dark orange	180[c]	402	1,2	$C_{19}H_{13}N_3O_2$	13,0	13,3	81
XIV	p-$O_2NC_6H_4$	H	Yellow	157—160[c]	347	0,97	$C_{19}H_{13}N_3O_2$	13,7	13,3	53
XV	C_6H_5	CH_3	Light yellow	249—250[a]	330	0,84	$C_{20}H_{16}N_2$	9,8	9,9	78
XVI	C_6H_5	CH_2CH_2CN	Yellow-green	263—265[a]	320	0,42	$C_{22}H_{17}N_3$	12,7	13,0	74
XVII	C_6H_5	H	Orange	286—288[f]	383	3,7	$C_{26}H_{19}N_3$	11,7	11,3	57
XVIII	o-HOC_6H_4	H	Orange	295—296[f]	397	4,9	$C_{26}H_{19}N_3O_2$	9,9	10,4	62
XIX	p-$O_2NC_6H_4$	H	Red	267—268[f]	456	4,1	$C_{26}H_{17}N_5O_4$	15,0	15,1	71

[a] From acetone.
[b] From n-butyl alcohol.
[c] From ether.
[d] From ethanol.
[e] From glacial acetic acid.
[f] From dimethylformamide.

tion relative to the azomethine grouping has the same effect due to the formation of an intramolecular



XX



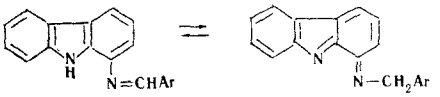
XXI

hydrogen bond. The introduction of an NO_2 group in the para position of the benzene ring induces a still larger bathochromic shift of the absorption maximum. This can be considered to be a consequence of the strong polarization of the molecule and an increase in the length of the conjugated system [5]. The hypsochromic shift of the absorption maximum in azomethines with a nitro group in the ortho position is probably caused by disruption of the coplanarity of the nitro group and the plane of the benzene ring and, consequently, by the decrease in its participation in conjugation.

Lengthening of the conjugation chain through an increase in the number of condensed benzene rings in the benzylidene portion of the molecule (I, VIII, and IX) and through the formation of bisazomethines (XVII-XIX), as expected, leads to a shift in the absorption maximum to the long-wavelength region.

When the hydrogen of the NH group of the carbazole ring is replaced by CH_3 and CH_2CH_2CN groups, the electron-donor properties of the heterocyclic nitrogen and, consequently, the effect of conjugation increase, and this leads to a bathochromic shift of the absorption maximum.

The same principles are observed for azomethines based on 1-aminocarbazole, except for benzal-1-aminocarbazole (X), in which the absorption maximum is shifted to the longer-wavelength region; this is probably explained by the formation of a quinoid structure.



The shift in the absorption maximum to the short-wavelength region in azomethines with substituents attached to the heteroatom is apparently explained by the withdrawal of the azomethine grouping from the plane of conjugation in connection with steric factors.

The reduction of the absorption intensity in azomethines based on 1-aminocarbazole occurs as a result of even greater disruption of the coplanarity of the system than in the azomethines from 3-aminocarbazole.

EXPERIMENTAL

The carbazole-based azomethines were obtained by the method in [2]. m-Aminobiphenyl was obtained by the reduction of m-nitrobiphenyl [6].

p-Aminodiphenylamine. A total of 100 ml of saturated NaOH solution was added to 10 g (0.03 mole) of tropaeoline (azo dye), and 12 g (0.184 g-atom) of zinc dust was added gradually in portions. The mixture was heated with stirring on a boiling-water bath for 2.5-3 h until the solution was completely decolorized. It was then filtered, and the filtrate was cooled to give 3.7 g of p-aminodiphenylamine.

The absorption spectra of $3 \cdot 10^{-5}$ to $6 \cdot 10^{-5}$ M alcohol solutions of the azomethines were recorded with an SF-4 spectrophotometer.

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