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COLOR PHENOMENA IN AZOMETHINES CONTAINING A SEPARATED ELECTRON-DONOR SYSTEM

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The visible absorption of most organic substances, including dyes, can be explained (^{1}) by the presence in them of a chromophoric BKA system: a system of conjugated double bonds (K), coupled with acceptor (B) and donor (A) substituents. In order to clarify what effect the introduction of a separated electron-donor system ($A'K$) will have on the color of compounds containing the BKA system, we synthesized a series of azomethines of general formula 1.

$$\mathrm{O_2N{-}\between{-}CH{=}N{-}\between{-}CH_2CONH{-}\between{-}A'}, \quad \text{where } A' = \mathrm{H};\ \mathrm{OCH_3};\ \mathrm{OH};\ \mathrm{N(CH_3)_2}, \tag{1}$$

$$\mathrm{O_2N{-}\between{-}CH{=}N{-}\between{-}CH_3}, \tag{2}$$

$$\mathrm{O_2N{-}\between{-}CH{=}N{-}\between{-}CH_2CH_2CONH{-}\between{-}N(CH_3)_2}. \tag{3}$$

Compounds 1 may be regarded as derivatives of 4-nitrobenzylidene-*p*-toluidine (formula 2), to the methyl group of which the $A'K$ system is attached. The chromophoric BKA system of compounds 1 and 2 is a system of π-electrons of two benzene rings joined by an azomethine group, one of which contains an acceptor substituent, the nitro group, and the other a donor substituent, the methyl or methylene group. The electron-donor system $A'K$ of compounds 1—a benzene ring with two donor substituents: an acylamino group and the group A'—has, when $A' = \mathrm{H}$, $\mathrm{OCH_3}$, OH, relatively weak donor properties, but these increase sharply when A' is a dimethylamino group. The $A'K$ system is not conjugated with the BKA system owing to the presence of the group $-\mathrm{CH_2CONH}-$, which disrupts π,π-conjugation.

Table 1 gives, with indication of color in powder form, the compounds of general formula 1 and formula 2, as well as the analogous compound V (Table 1), which we synthesized, a derivative of hydrocinnamic acid of formula 3. Figure 1 shows the absorption spectra of the surfaces of powders of compounds 1, 2, and 3.

From the similarity of the visual colors—various shades of yellow—of compounds 1 (compounds II-IV, Table 1), containing a relatively weak electron-donor $A'K$ system, and compound 2 (I, Table 1), which contains no $A'K$ system at all, and also from the almost complete coincidence of the absorption curves of the surfaces of the powders of these compounds (I–IV, Fig. 1), it follows that the color of compounds II–IV is entirely determined by the chromophoric BKA system, while the influence of the $A'K$ system is insignificant and is ···

Table 1

Compounds of formula 2 (I), general formula 1 (II—V), and formula 3 (VI)

No. of compound	Name of compound	A′	Color of compound (in powder)	M.p., °C	Recrystallization solvent	Empirical formula	N, % found	N, % calculated
I	4-(p-nitrobenzylamino)toluene	—	Light yellow	123.5—124.5	Alcohol	$C_{14}H_{12}N_2O_2$	—	—
II	4′-[4-(p-nitrobenzylamino)phenacetamido]benzol	H	Light yellow	241—242	Pyridine	$C_{21}H_{17}N_3O_3$	11.78 11.85	11.69
III	4′-[4-(p-nitrobenzylamino)phenacetamido]anisole	OCH_3	Pale yellow	228—229	»	$C_{22}H_{19}N_3O_4$	11.08 11.21	10.79
IV	4′-[4-(p-nitrobenzylamino)phenacetamido]phenol	OH	Yellow	249—250	»	$C_{21}H_{17}N_3O_4$	11.54 11.57	11.20
V	4′-[4-(p-nitrobenzylamino)-N,N-dimethylaniline]	$N(CH_3)_2$	Orange-brown	(with decomp.)246—247	»	$C_{23}H_{22}N_4O_3$	14.41 14.46	13.92

No. of compound	Name of compound	A′	Color of compound (in powder)	M.p., °C	Recrystallization solvent	Empirical formula	N, % found	N, % calculated
VI	4′-[4-(p-nitrobenzylamino)-N,N-dimethylamino]-hydrocinnamanilide	$N(CH_3)_2$	Orange-brown	248–249	»	$C_{24}H_{24}N_4O_3$	13.38 13.52	13.45

is expressed only in a certain increase in the absorption intensity in the region of the maximum (400–402 mμ).

Compounds V and VI (Table 1), containing a strong electron-donor system A′K, differ sharply from the preceding compounds in their orange-brown coloration and in the position of the absorption curves. They are characterized by somewhat greater absorption in the region of the maximum and by the appearance of an additional broad band in the 500–700 mμ region (curves V and VI, Fig. 1). Reliable isolation of the A′K and BKA systems by the group $=CH_2CONH-$ and, especially, $-CH_2CH_2CONH-$excludes the possibility of formation of a single conjugated system in compounds V and VI, and the appearance in them of a long-wavelength absorption band can be caused only by intermolecular donor-acceptor interaction ([2]-[4]) of the A′K and BKA systems. The nitro group, which is part of the BKA system, is a strong acceptor substituent, whereas the donor properties of the alkyl radicals are comparatively small; therefore, as a whole the BKA chromophoric system possesses weak acceptor properties and is capable of entering into intermolecular interaction with strong electron-donor systems.

Experimental Part

Compound I (Table 1) was synthesized according to the literature data ([5]). Compounds II–IV (Table 1) were obtained by heating for half an hour in alcohol equimolecular amounts of *p*-nitrobenzaldehyde and the corresponding arylamides of *p*-aminophenylacetic acid; analogously, compound VI (Table 1) was synthesized from *p*-nitrobenzaldehyde and *p*-dimethylaminoanilide of *p*-aminohydrocinnamic acid. *p*-Dimethylaminoanilide of *p*-aminophenylacetic acid was obtained by reduction of *p*-dimethylaminoanilide of *p*-nitrophenyl-

acetic acid by the procedure used for the synthesis of the corresponding derivative of *o*-nitrophenylacetic acid [6]. Colorless crystals (from toluene), m.p. 149–150°.

Fig. 1. Absorption spectra of the surfaces of powders of compounds of formulas 1, 2, and 3. The curve numbers correspond to the compound numbers in Table 1

Figure 1: Fig. 1. Absorption spectra of the surfaces of powders of compounds of formulas 1, 2, and 3. The curve numbers correspond to the compound numbers in Table 1

Found, %:	N 15.84
$C_{16}H_{19}N_3O$. Calculated, %:	N 15.60

Similarly obtained were the anilide, *p*-anisidide, *p*-oxyanilide of *p*-aminophenylacetic acid, and the *p*-dimethylaminoanilide of *p*-aminocinnamic acid, used for the synthesis of azomethines without additional purification. The arylamides of *p*-nitrophenylacetic acid and the *p*-dimethylaminoanilide of *p*-nitrocinnamic acid were synthesized according to the literature data [7,8].

Fig. 1. Absorption spectra of the surfaces of powders of compounds of formulas 1, 2, and 3. The curve numbers correspond to the compound numbers in Table 1.

The absorption spectra of the surfaces of powders of the synthesized compounds were recorded on an SF-10 spectrophotometer.

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