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Abstract

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On Color Phenomena in N-Phenylglycyl Derivatives of α-Aminoanthraquinone

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The derivatives of α-aminoanthraquinone considered in the present communication may be assigned to compounds with two electron-donor systems, i.e., to those in which, in addition to an electrophilic chromophoric system, there are two electron-donor systems not conjugated with one another. These compounds correspond to the general formula I, where A = H, CH_3, OCH_3 in the *o*-, *m*-, and *p*-positions relative to NH.

Anthraquinone derivatives with one substituent in the α- or β-position have been studied in detail by a number of investigators ($^{1-8}$); however, compounds constructed according to type I have not been described in the literature.

In contrast to the compounds with two electron-donor systems that we studied previously, in which the electrophilic system was the acyl of nitrobenzoic (*m*- or *p*-) acid (^{9}), or the acyl of 3,5-dinitrobenzoic acid (^{10}), in compounds of the present type the electrophilic system (BK) is the anthraquinone molecule. The latter represents a stronger

Table 1

Color of compounds of the type

[structural formula]

Electron-donor system A′K		Color of the substance in crystals	Color of the substance in powder
$-NHC_6H_6$	(II)	Light red	Orange-red
$-NHC_6H_4CH_3$-*o*	(III)	Orange	Yellow-orange
$-NHC_6H_4CH_3$-*m*	(IV)	Red	Brownish-red
$-NHC_6H_4CH_3$-*p*	(V)	Cherry-red	Brown-red
$-NHC_6H_4OCH_3$-*o*	(VI)	Red	Brick-red

Electron-donor system A′K		Color of the substance	Color of the substance
$-NHC_6H_4OCH_3$-*m*	(VII)	”	”
$-NHC_6H_4OCH_3$-*p*	(VIII)	Bordeaux-red	Red-brown
$-NHC_{10}H_7$-α	(IX)	Violet-red	Bordeaux-red
$-NHC_{10}H_7$-β	(X)	Dark red	Cherry-red

chromophoric system than the acyls of nitrobenzoic acids; this is evident at least from the fact that anthraquinone already has a visible color (yellow), whereas nitrobenzoic acids are colorless. As the first electron-donor system (AK) here one may regard the acylamino group together with the double bonds of one of the anthraquinone nuclei with which it is connected. True, this nucleus simultaneously also enters into the composition of the electrophilic system, so that, in essence, the CO and NHAc groups in the present case are parts of one and the same chromophoric system. Conventionally, however, such compounds may be regarded as “compounds with superimposed chromophoric systems” (^{11}). The second electron-donor system (A′K)

separated from the electrophilic system by a number of groups that disrupt the conjugation of double bonds, and is thus a “separate chromophoric system.” In their electron-donor properties the systems AK and A′K differ greatly from one another. The AK system exhibits only very weak electron-donor properties, since the donor capacity of the amino group included in it is suppressed to a considerable extent by the acyl group attached to it. Therefore α-chloroacetaminoanthraquinone (I)—the starting product for the synthesis of the compounds under consideration, which has only one electron-donor system, AK—is colored only yellow.

The A′K system is a considerably stronger electron-donor system, since it contains an amino group whose donor capacity has not been weakened by acylation; moreover, this system is strengthened by the second electron-donor group, CH_3 or OCH_3. As can be seen from Table 1, all compounds containing the A′K system are colored much more deeply than the initial compound (I), which contains only the AK system. From this one may draw the following basic conclusion: the comparatively deep color of the compounds considered is due to the interaction of the A′K and BK systems. But since these systems are not conjugated with one another, their interaction can occur only by means of exomolecular forces (^{12}). The presence of the NHAc group in the anthraquinone nucleus is in this case an unfavorable factor for color, since it lowers to some extent the electrophilic properties of the BK system and thereby leads to a rise in the color of the compounds. It should therefore be expected that, for example, compounds constructed according to type II (analogous to the nitrobenzyl derivatives we considered earlier (13)), which contain the same electron-donor system A′K but do not have an acylamino group, will have a deeper color than the present compounds.

II [[structure: anthraquinone skeleton with substituent $C_6H_5NHC_6H_4A$]]

It is further of interest to note that none of the compounds under consideration could be obtained in the form of a less deeply colored modification, the color of which could be explained by interaction of the BK and AK systems with disruption of the interaction of the BK and A′K systems. In other series of compounds with two electron-donor systems such forms were isolated by us (9,10). The explanation for this apparently should be sought in the fact that the electrophilic system of anthraquinone derivatives is considerably stronger, and therefore its interaction with the A′K system, which occurs in substances in the solid state, is more difficult to disrupt.

As for the absorption spectra of anthraquinone derivatives containing different substituents in the α- and β-positions, they have been studied in detail by a number of investigators (4–8); we therefore confine ourselves to presenting only three absorption curves. A characteristic feature of the compounds under consideration is the presence, in the substituent they contain (the acylamino group), of a second electron-donor system (a separate one). Figure 3 gives the absorption curves of two compounds containing both electron-donor systems (AK and A′K), and of one compound having only the AK system. On examining these curves, what first attracts attention is their great similarity to one another, despite the fact that the corresponding compounds differ quite markedly from one another in their color in the solid state. Thus, for example, the compound not containing the A′K system (I) is yellow, while the compound with a *p*-CH_3 group (V) is cherry-red. In this respect the absorption curves differ substantially from the light-reflection curves, which indicate differences in the coloration of the three compounds shown (Fig. 1). This similarity among the absorption curves presented, which is manifested both in their form and in the position of the maxima, may be regarded as evidence that the principal factor responsible for the comparatively deep color of the compounds under consideration

in the solid state, namely the interaction of the electron-donor system $A'K$ with the electrophilic system BK by means of extramolecular forces (12), is absent in strongly dilute solutions. However, in more concentrated solutions ($0.5 \cdot 10^{-2}$ M, in pyridine) this interaction already begins to manifest itself, and in the corresponding curves (Fig. 2) a new absorption band appears in the visible part of the spectrum. As is seen from the curves presented, in solutions ten times less concentrated this band is not yet observed at all.

In conclusion it should be noted that all the compounds synthesized by us possess the properties of vat dyes: they are reduced by sodium hydrosulfite,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

giving an intensely red vat, in which cotton fiber is dyed, however, only a faint cream color (of various shades). This indicates the low substantivity of these dyes.

Experimental part

The starting product for obtaining the compounds under consideration is α-chloroacetaminoanthraquinone (I), synthesized by us according to (^{14}). M.p. 220.5—220.8° (not indicated in the literature).

N-(n-tolylglycyl)-1-aminoanthraquinone (V). A mixture of (I) and n-toluidine (1 : 2 mol) was heated for one hour on an oil bath at

Fig. 1. Light-absorption curves of derivatives of α-aminoanthraquinone of the type:

$$\mathrm{C_6H_4}\overset{\mathrm{CO}}{\underset{\mathrm{CO}}{}}\mathrm{C_6H_3NHCOCH_2NHC_6H_4A}$$

1—α-chloroacetaminoanthraquinone, 2—$A'K = \mathrm{NHC_6H_5}$,

3—$A'K = \mathrm{NHC_6H_4CH_3}$-$n$ (in dichloroethane)

Fig. 2. Light-absorption curves of derivatives of α-aminoanthraquinone of the type:

$$\mathrm{C_6H_4}\overset{\mathrm{CO}}{\underset{\mathrm{CO}}{}}\mathrm{C_6H_3NHCOCH_2NHC_6H_4A}$$

(in pyridine, $l = 0.1$ cm). 1—$A = \mathrm{H}$, $C = 0.5 \cdot 10^{-3}\ M$,

2—$A = \mathrm{H}$, $C = 0.5 \cdot 10^{-2}\ M$, 3—$A = \mathrm{OCH_3}$-n, $C = 0.5 \cdot 10^{-3}\ M$, 4—$A = \mathrm{OCH_3}$-n,

$$C = 0.5 \cdot 10^{-2}\ M$$

a temperature of 110—115°. The cooled mass was treated with dilute HCl and then washed with water, with a soda solution, and again with water. After recrystallization from chlorobenzene, the product was obtained in the form of cherry-red prisms with m.p. 250.5—251.0°.

$C_{23}H_{18}O_3N_2$. Found %: N 7.53
Calculated %: N 7.57

All subsequent preparations were obtained analogously to the one described. Only the temperature and heating time were sometimes varied; this will be indicated in each individual case.

N-(*m*-tolylglycyl)-1-aminoanthraquinone (IV). Recrystallized from toluene. Red prismatic crystals, m.p. 172–173°.

$C_{23}H_{18}O_3N_2$. Found, %: N 7.71
Calculated, %: N 7.57

N-(*o*-tolylglycyl)-1-aminoanthraquinone (III). The bath temperature was raised to 125–127°. Heating was continued for 1 h 15 min. Recrystallized from isoamyl alcohol. Orange rectangular prisms, m.p. 185–186°.

$C_{23}H_{18}O_3N_2$. Found, %: N 7.81
Calculated, %: N 7.57

N-(*p*-methoxyphenylglycyl)-1-aminoanthraquinone (VIII). Recrystallized from aniline. Claret-red prismatic crystals, m.p. 207–208°.

$C_{23}H_{18}O_4N_2$. Found, %: N 7.46
Calculated, %: N 7.25

N-(*m*-methoxyphenylglycyl)-1-aminoanthraquinone (VII). Recrystallized from toluene. Red hexagonal prisms, m.p. 146.5–147.0°.

$C_{23}H_{18}O_4N_2$. Found, %: N 7.39
Calculated, %: N 7.25

N-(*o*-methoxyphenylglycyl)-1-aminoanthraquinone (VI). Recrystallized twice from toluene. Elongated rectangular red plates, m.p. 196–197°.

$C_{23}H_{18}O_4N_2$. Found, %: N 7.43
Calculated, %: N 7.25

N-(phenylglycyl)-1-aminoanthraquinone (II). After recrystallization from aniline—light-red prismatic crystals, m.p. 116–117°.

$C_{22}H_{16}O_3N_2$. Found, %: N 7.91
Calculated, %: N 7.87

N-(α-naphthylglycyl)-1-aminoanthraquinone (IV). Recrystallized from toluene. Wedge-shaped violet-red crystals, m.p. 239–240°.

$C_{26}H_{18}O_3N_2$. Found, %: N 6.27
Calculated, %: N 6.09

N-(β-naphthylglycyl)-1-aminoanthraquinone (X). Recrystallized from pyridine. Prismatic crystals of dark-red color, m.p. 234.5–235.0°.

$C_{26}H_{18}O_3N_2$. Found, %: N 6.21
Calculated, %: N 6.09

The synthesized compounds, as a rule, dissolve rather readily in pyridine, less readily in toluene, chlorobenzene, and dichloroethane, still less readily in acetone and benzene, and with difficulty in alcohol.

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named after M. I. Gubkin

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CITED LITERATURE

1. R. E. Schmidt, *Zs. angew. Chem.*, **41**, 41 (1928).
2. J. Houben, *Das Antracen und die Anthrachinone*, Leipzig, 1929.
3. E. Barnett, *Antracene and Antraquinone*, London, 1921.
4. J. Formaneck, *Untersuchung und Nachweisorgan. Farbstoffe auf spektroskopischen Wege*, 1908, p. 203.
5. R. A. Morton, W. T. Earlam, *J. Chem. Soc.*, **1941**, 159.
6. C. J. P. Spruit, *Rec. trav. chim.*, **68**, 325 (1949).
7. R. H. Peters, H. H. Sumner, *J. Chem. Soc.*, **1953**, 2101.
8. K. Lauer, M. Horio, *J. prakt. Chem.*, **145**, 273 (1936).
9. E. A. Smirnov, Collection of Articles on General Chemistry, **2**, Publishing House of the Academy of Sciences of the USSR, 1953, p. 1934; *ZhOKh*, **27**, 2682 (1957).

10. E. A. Smirnov, *DAN*, **20**, No. 3 (1958).
11. V. A. Izmail' skii, Proceedings of the 8th Conference on Aniline-Dye Chemistry and Technology, 1950, p. 91.
12. V. A. Izmail' skii, P. A. Solodkov, *DAN*, **60**, 587 (1948).
13. V. A. Izmail' skii, E. A. Smirnov, *ZhOKh*, **25**, 1400 (1955).
14. Bauer, German Patent 213960; *Chem. Zbl.*, **2**, 1286 (1909).

Note: Figure translations are in progress. See original paper for figures.