

## Autocomplexes of Anthraquinone Derivatives with a One-Membered NH Bridge

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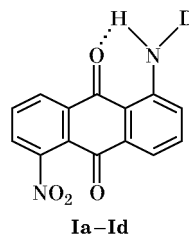
**Abstract**—A number of aminonitroanthraquinone autocomplexes with a one-membered NH bridge were synthesized from 1,5-dinitroanthraquinone and substituted aromatic amines. Intramolecular charge transfer in the products was studied by spectral methods.

Growing interest in light-sensitive organic media for high-capacity optical recording systems is concerned mainly with search for new photoluminescence materials [1]. The known photochromic materials which can be used for photoluminescence reading of optical information are few in number and are based mainly on dyes with donor–acceptor groups [2] or some derivatives of the quinone series [3, 4]. Therefore, organic compounds with intramolecular donor–acceptor (D–A) interaction (so-called *autocomplexes*), specifically those containing quinone-like acceptor fragments, are expected to be promising for the above application. It is also essential that directional change of the degree of intramolecular charge transfer in such compounds provides the possibility for controlling their electronic properties which considerably (unless predominantly) determine their unusual electro-physical and optical properties.

In the preceding communication we described the synthesis and the results of physicochemical study of D–A interactions in autocomplexes of the quinone series having a one-membered NH bridge. These compounds were obtained from quinonimines [5], where charge transfer occurs mainly through direct polar conjugation between donor and acceptor fragments of the autocomplex through the bridging nitrogen atom. The occurrence of contact charge transfer, which was revealed by us previously for the series of analogous picryl derivatives [6], was found in a few cases.

While developing studies in this line, we have synthesized a series of anthraquinone autocomplexes with a one-membered NH bridge and examined their spectral properties. The obtained compounds possessed a definite set of donor components which were studied previously. As starting compound we selected

1,5-dinitroanthraquinone (which was synthesized by the procedure described in [7]) with a view to obtain a series of autocomplexes having an enhanced acceptor moiety due to combination of a quinone-like fragment and nitro group in a single molecule.



D = 4-MeC<sub>6</sub>H<sub>4</sub> (a), 3,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (b), 4-MeOC<sub>6</sub>H<sub>4</sub> (c), 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> (d).

Compounds **Ia–Id** were synthesized by heating of equimolar amounts of 1,5-dinitroanthraquinone and the corresponding aromatic amine in diethylene glycol dimethyl ether under reflux in the presence of 4 equiv of calcined sodium carbonate. Autocomplexes like **I** were not described previously, but the possibility for replacement of nitro group in position 1 of the anthraquinone system by alkyl- or arylamino group is well known [8]. It should be noted that in the recent years analogous anthraquinone derivatives have found new applications in a number of rapidly developing fields of industry, e.g., electronics (they are promising for manufacture of liquid-crystal displays for lasers and solar batteries [9]).

The structure of compounds **Ia–Id** was confirmed by elemental analyses and physical data (see table). The IR spectra of **Ia–Id** in mineral oil contain absorption bands at about 1600 (stretching vibrations of the aromatic rings), 1630, and 1680 cm<sup>-1</sup> (carbonyl

Yields, melting points, electron absorption spectra in  $\text{CHCl}_3$ , and elemental analyses of compounds **Ia–Id** and model ionization energies ( $E_i$ , eV) of the donor fragments [19]

Comp. no.	Yield, %	mp, °C	Electron absorption spectrum, $\lambda_{\text{max}}$ , nm ( $\epsilon$ )				$E_i$ , eV [19]
			$\text{CT}_r^{\text{NO}_2} + \text{CT}_r^{m-A}$	$\text{CT}_{\text{NHD}}^{m-A}$	$\text{CT}_{\text{NHD}}^{o-A}$	ICT	
<b>Ia</b>	35	134	252 (12 145)	316 (3785)	365 (1970)	532 (3450)	8.82
<b>Ib</b>	32	149	252 (11 500)	316 (3411)	360–370 (2000)	535 (3120)	8.27
<b>Ic</b>	37	211	252 (12 360)	316 (3890)	360 (2200)	538 (4040)	8.22
<b>Id</b>		>200	255 (13 470)	320 (5810)	370 (2300)	545 (4100)	7.14

Comp. no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
<b>Ia</b>	70.55	3.86	7.62	$\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_4$	70.39	3.94	7.82
<b>Ib</b>	69.62	4.01	7.33	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4$	70.96	4.33	7.52
<b>Ic</b>	67.39	3.51	7.58	$\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_5$	67.38	3.77	7.48
<b>Id</b> <sup>a</sup>				$\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_4$			

<sup>a</sup> Found *M*: 387 (by mass spectrometry). Calculated *M*: 387.

stretching vibrations). The band at  $1680 \pm 2 \text{ cm}^{-1}$  belongs to the free  $\text{C}^{10}=\text{O}$  carbonyl group, and the low-frequency band at  $1630 \text{ cm}^{-1}$  corresponds to  $\text{C}^9=\text{O}$  which is involved in intramolecular hydrogen bond. The latter band does not change its position in going to dilute solutions in  $\text{CCl}_4$  ( $c \approx 10^{-3} \text{ M}$ ) [10]. The IR spectra of such solutions also contain a band at  $\sim 3260 \text{ cm}^{-1}$  due to associated N–H group. More concentrated solutions of **Ia–Id** ( $c \approx 10^{-2} \text{ M}$ ) are characterized by diffuse absorption in the region  $3250\text{--}3500 \text{ cm}^{-1}$ , which may be attributed to N–H groups involved in intermolecular hydrogen bond.

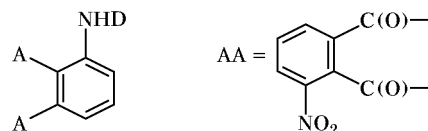
In the IR spectra of crystalline samples of **Ia–Id** (in mineral oil) we observed a sharp increase in the background absorption throughout the low-frequency region with its center at  $\sim 1480 \text{ cm}^{-1}$ , while no bands at all were present above  $1800 \text{ cm}^{-1}$ , i.e., in the region corresponding to intermolecular interactions. It is generally accepted [11, 12] that the absence of XH (OH, NH) absorption and the presence of a considerable low-frequency diffuse absorption which increases the overall background level indicate the existence of very strong hydrogen bonds (symmetric or quasisymmetric) with one minimum on the potential energy curve. Such displacement of the NH absorption band corresponds to an enthalpy  $\Delta H$  of  $-58.6 \text{ kJ/mol}$  (calculated according to Iogansen [13]).

Important results were obtained by studying the electron absorption spectra of anthraquinones **Ia–Id** in chloroform at a concentration of  $10^{-3}$  to  $10^{-4} \text{ M}$ .

The absorption bands were assigned following the empirical approach described in [14], according to which a molecule is divided into polar chromophore components. This procedure makes it possible to determine the number of bands in the electron spectra of polysubstituted benzenes with donor and acceptor groups and assign them without resorting to quantum-chemical calculations. We have already applied this method to interpret electron absorption spectra of autocomplex-like compounds [15–18].

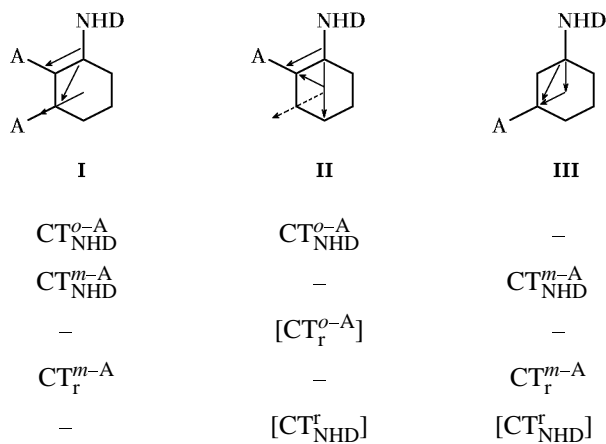
Table contains the experimental absorption maxima  $\lambda_{\text{max}}$  and molar absorption coefficients  $\epsilon$  of charge-transfer (CT) bands in the spectra of **Ia–Id**, the results of their identification by the procedure described in [14], and also ionization energies ( $E_i$ , eV) of model donor fragments, which were taken from [19].

Compounds **Ia–Id** display in the electron spectra four maxima of different intensities in the range from 250 to 550 nm. In order to identify these maxima, compounds **Ia–Id** were arbitrarily represented as the following model system:



In keeping with the quasiautonomous system approach [20], the above model system is regarded as 2,3-AA-1-NHD which should give rise to charge-

transfer bands typical of initial disubstituted compounds **II** and **III**: 2-A-1-NHD and 3-A-1-NHD, respectively. Therefore, first of all we should analyze possible transitions for compounds **II** and **III**. For this purpose, the molecules are arbitrarily divided into composite *ortho*- and *meta*-donor-acceptor systems, and theoretically possible CT bands and polarization directions are established for each system. CT bands of composite systems are summed up. Here, we do not take into account only those bands which arise from more complex transitions with the same excitation vector. In the scheme given below, such bands are placed in brackets.



The short-wave absorption bands ( $\lambda_{\max} \sim 250$  nm) are almost similar for all the autocomplexes under study. It should be assigned to charge transfer from the aromatic ring to the *meta*-acceptor group (CT<sub>r</sub><sup>m-A</sup>) with a contribution of an analogous nitrobenzene band corresponding to charge transfer from the aromatic ring to the nitro group (CT<sub>r</sub><sup>NO<sub>2</sub></sup>). This follows from a small red shift and considerably increased intensity of the above band, as compared to that typical of free nitrobenzene,  $\lambda_{\max}$  250 nm ( $\epsilon$  8900) [21]. Next follow CT bands arising from *meta* and *ortho* transitions. The long-wave maximum in the region 520–540 nm suffers a red shift as the electron-donor power of the donor fragment increases; it belongs to intramolecular charge transfer occurring in a contact mode, i.e., via through-space donor-acceptor interactions between functional groups, namely between the donor aryl-amino and acceptor anthraquinone fragments which appear spatially close to each other.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil or dissolved in CCl<sub>4</sub> at a concentration of 10<sup>-3</sup> to 10<sup>-2</sup> M.

The electron absorption spectra were measured on a Cary-219 spectrophotometer in CHCl<sub>3</sub> ( $c = 10^{-3}$  M). The mass spectra (70 eV) were obtained on a MAT-212 mass spectrometer with direct sample admission into the ion source which was heated to 200°C. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; spots were visualized by UV light. Compounds **Ia–Id** were isolated and purified by preparative thin-layer chromatography on silica gel L 40/100  $\mu$ m which was applied to glass plates; a 3:1 mixture of benzene and petroleum ether (bp 70–100°C) was used as eluent.

**Aminonitroanthraquinones Ia–Id.** A mixture of 0.15 g (0.0005 mol) of 1,5-dinitroanthraquinone, 0.0005 mol of appropriate aromatic amine (or its salt with sulfuric acid), and 0.212 g (0.002 mol) of freshly calcined sodium carbonate in diethylene glycol dimethyl ether was heated for 24 h under reflux with stirring. The heating bath was removed, and the mixture was stirred until it cooled to room temperature and was dissolved in 50 ml of a 4:1 mixture of diethyl ether and ethyl acetate. The solution was shaken with 5% hydrochloric acid, the organic phase was separated, washed with several portions of water, and dried over Na<sub>2</sub>CO<sub>3</sub>, and the solvent was distilled off. The solid residue (overall yield of the crude product 70–75%) was subjected to preparative thin-layer chromatography using 3:1 benzene-petroleum ether (bp 70–100°C) as eluent (compounds **Ia–Ic**); compound **Id** was isolated using toluene-petroleum ether-diethyl ether (3:1:0.25) as eluent.

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