

ANTHRAQUINONE DYESTUFFS. XIII.*

ELECTRONIC SPECTRA OF AMINOANTHRAQUINONE DERIVATIVES
IN CONCENTRATED SULPHURIC ACID MEDIUM

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An intensive blue colouration was observed after dissolving some anthraquinone derivatives in concentrated sulphuric acid. On the basis of experimental and the theoretical results obtained by HMO and PPP methods, it was proved that this colouration is connected with the basicity ratio of the amino nitrogen and quinone oxygen and depends on the sequence of the protonation of the both centres. In addition to it, this ratio is influenced by steric effect in the case of isomeric dianthrimides.

Within our studies on kinetics and mechanism of reactions in the anthraquinone series, we have studied the spectral behaviour of some anthraquinone derivatives in concentrated sulphuric acid.

It is known that the unsubstituted aminoanthraquinones and N-alkylaminoanthraquinones are gradually protonated which causes a decolourization of the originally yellow to red neutral solutions due to the free electron pair on the nitrogen atom being no longer in conjugation with anthraquinone system. In concentrated sulphuric acid the second protonation takes place *viz.* at the oxygen atom, and an intensive yellow colouration appears. When determining the pK_a of 1-phenylaminoanthraquinone and 2-phenylaminoanthraquinone, however, we have observed that the originally intensive yellow solution of these compounds in concentrated sulphuric acid turns green to deep blue with time, an absorption band at $17\,000\text{ cm}^{-1}$ being formed and the velocity of the change being dependent on the temperature and sulphuric acid concentration. The formation of a deep blue-green colouration (absorption band at $15\,000\text{ cm}^{-1}$) has been observed in the case of dissolving 1,2'- and 2,2'-dianthrimides in concentrated sulphuric acid, too. In contrast to 1- and 2-phenylaminoanthraquinones, however, the colouration appears immediately and does not change with time. 1,1'-Dianthrimide behaves, however, as *e.g.* 1-aminoanthraquinone, *i.e.* it dissolves in concentrated sulphuric acid to give a deep yellow solution.

In the present paper the abovementioned spectral behaviour of several aminoanthraquinone derivatives in concentrated sulphuric acid is explained on the basis of theoretical and experimental results.

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EXPERIMENTAL

The absorption spectra were measured by means of recording spectrophotometers Unicam SP 700 and Specord UV VIS (Zeiss). pK_a of 2,2'-dianthrimide was determined in a standard way^{1,2}. The 1,1'-dianthrimide used was a commercial sample which was purified by repeated crystallization. The other anthrimides were synthesized according to Bradley and Leete³. The sulfo derivatives of phenylaminoanthraquinone were isolated from the mixture after sulphonation by means of thin-layer chromatography. The sulphuric acid used was of p.a. purity grade, and its concentration for spectra and pK_a measurements was determined acidimetrically.

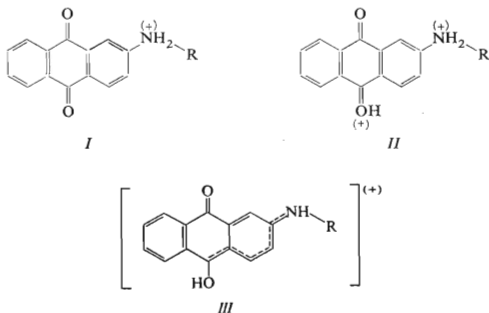
CALCULATIONS

The parameters given in Table I were used for calculations according to simple LCAO MO (HMO) method. The usual version of the Pariser-Parr-Pople method^{4,5} was used for calculation of theoretical transitions; the parameters used are given in Table II; the bond length values used were C—C 1.4 Å, C=O 1.2 Å, C—OH 1.4 Å, C—N 1.4 Å, $\beta_{UV}^{core} = -2.318$ eV.

RESULTS AND DISCUSSION

Fig. 1 represents the absorption spectra of 2-phenylaminoanthraquinone dissolved in 98% sulphuric acid measured at various time intervals after dissolution. In the range of 17000 cm^{-1} a new band is being formed which results in the solution turning blue. The velocity of this colour change increases with temperature and sulphuric acid concentration. The reaction was carried out on a laboratory scale, and sulfo-2-phenylaminoanthraquinone and disulfo-2-phenylaminoanthraquinone were isolated after dilution with water. The monosulfo derivative dissolves in 98% sulphuric acid immediately giving a blue-green solution, whereas disulfo derivative gives a deep blue solution (Fig. 1, curve 5), the colouration being not changed with time. It is obvious that the formation of blue colouration is connected with sulphonation of phenylaminoanthraquinone at its phenyl group. We suppose the following to be the reason of such a marked colour change during sulphonation: 2-phenylaminoanthraquinone is gradually protonated first at the nitrogen atom (I), which is accompanied by the decolorization of the originally orange solution, and then, to the second degree, at one of the quinone oxygen atoms, which results in formation of a deep yellow colouration (II); it thus behaves as the other amino- or N-alkylaminoanthraquinones⁶. The sulphonation at the phenyl group, however, causes a lowering of basicity of amino nitrogen atom to such an extent that the protonation takes place at quinone oxygen atom only, which results in formation of the form III accompanied by a marked deepening of colouration (development of the absorption band at 17000 cm^{-1}). From the absorption spectra of mono- and disulfo derivatives in 98% sulphuric acid it follows that only two sulfonic acid groups at the phenyl group can lower basicity of the nitrogen atom to such an extent that the equilibrium is shifted towards the form protonated at oxygen atom only (III). An analogous situation is encountered with 1-phenylaminoanthraquinone, the only difference

being that the development of the blue colouration takes substantially longer time (slower sulphonation), and that one sulfonic acid group at the phenyl group does not suffice for formation of the spectroscopically measurable amount of the form protonated at oxygen atom.



R phenyl, sulfophenyl, disulfophenyl, anthraquinonyl

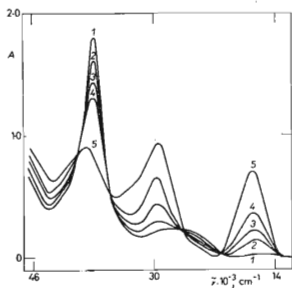


FIG. 1

Absorption Spectrum of 2-Phenylaminoanthraquinone in 98% Sulphuric Acid at Various Time Intervals

1 After 15 min, 2 3 h, 3 10 h, 4 22 h, 5 di-sulfo-2-phenylaminoanthraquinone in 98% sulphuric acid.

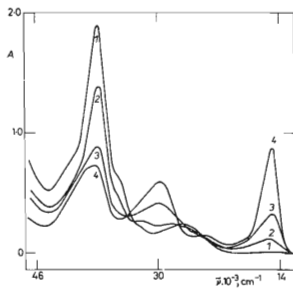
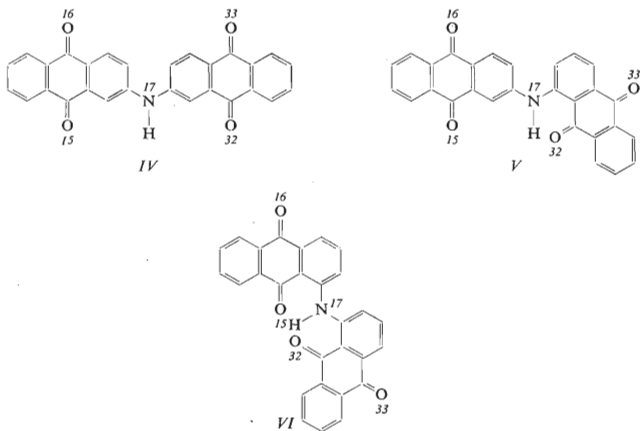


FIG. 2

Absorption Spectrum of 1,1'-Dianthrimide (1), 1,2'-Dianthrimide (2), N-Methyl-2,2'-dianthrimide (3), and 2,2'-Dianthrimide (4) in 98% Sulphuric Acid

This explanation is supported by the behaviour of isomeric dianthrimides in 98% sulphuric acid, too. 2,2'-Dianthrimide (IV) dissolves in this acid to give a deep blue solution the colour intensity of which does not change with time. The absorption spectrum (Fig. 2, curve 4) is very similar to that of disulphophenylaminoanthraquinone (Fig. 1, curve 5). Obviously, the second anthraquinone nucleus has the same effect as a twice sulphonated phenyl group. On the contrary, 1,2'-dianthrimide (V) (Fig. 2, curve 2) forms a yellow-green solution in 98% sulphuric acid (a weak band at 15000 cm^{-1}), and 1,1'-dianthrimide (VI) forms a greenish yellow solution only (it does not practically absorb in the region of 15000 cm^{-1} (Fig. 2, curve 1), the spectrum being similar to that of partially diprotonated 1-aminoanthraquinone in 98% sulphuric acid⁶.



From the HMO model it follows that the ratio of electron densities at nitrogen and oxygen atoms is practically the same for all the three isomers, and that their behaviour in sulphuric acid should be the same, too. On the basis of Stuart models resp. drawing of the planar configuration of the molecules taking into account the respective van der Waals radii, we have, however, found that, of the dianthrimide isomers, 2,2'-isomer only forms a practically planar system. Therefore, we have simulated the rotation of the anthraquinone nucleus round the C—N bond by changing the resonance integral β_{CN} within the limits 0.8–0.0 in our further calculations. This made it possible to obtain series of π -electron density values and π -electron localization energies at the electronegative and hence protonated centres of isomeric dianthrimides. From the dependences in Fig. 3 it follows that, in the case

of 1,1'-dianthrimide, the decreasing of the value of β_{CN} integral (decrease of planarity) results in a large relative decrease of electronic localization energy at the nitrogen atom (centre 17), the value identical with that of 1-aminoanthraquinone being reached for completely non-planar system ($\beta_{CN} = 0$). The localization energy change of the oxygen atoms is substantially smaller. The planar system ($\beta_{CN} = 0.8$) has two pairs of identical oxygen atoms, one oxygen atom of each anthraquinone nucleus constituting a pair, whereas, in the non-planar system, the oxygen atoms of the anthraquinone nucleus lying outside the plane have the same localization energy, and the localization energy of the oxygen atoms of 1-aminoanthraquinonyl (the atoms 15 and 16) does not practically change. A similar situation is encountered with the dependence of π -electron density on β_{CN} (Fig. 4), the only difference being that the electron density at the nitrogen atom substantially increases with decreasing β_{CN} , whereas it does not change or decreases only slightly at oxygen atoms. The corresponding dependences of 1,2'- and 2,2'-dianthrimides show the same character, the difference being in that 2-aminoanthraquinone results from rotation of one of the anthraquinone nuclei of 2,2'-isomer whereas in the case of non-symmetrical 1,2'-isomer, the result depends on which of the anthraquinone nuclei is rotated.

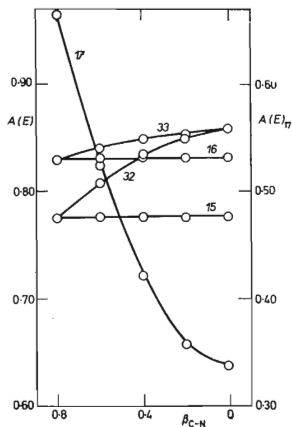


FIG. 3

Dependence of π -Electron Localization Energy of Nitrogen and Oxygen Atoms of 1,1'-Dianthrimide on β_{CN}

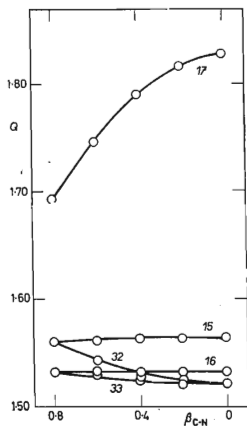


FIG. 4

Dependence of π -Electron Density of Nitrogen and Oxygen Atoms of 1,1'-Dianthrimide on β_{CN}

From the above discussion it follows generally that the decrease of planarity of the system will facilitate the protonation at the nitrogen atom and will cause the intensity decrease of blue colouration of the solutions in concentrated sulphuric acid (an intensity decrease of absorption band at 15000 cm^{-1} ; Fig. 2). From this point of view, the influence of a methyl group at nitrogen atom on the spectrum of the respective N-methyldianthrimides in concentrated sulphuric acid is quite understandable. N-Methyl group will increase the basicity of nitrogen atom by hyperconjugation effect and, being substantially bulkier than hydrogen atom, prevent the coplanarity of dianthrimides. The both effects will contribute to protonation preference nitrogen - oxygen in the case of N-methyl derivatives of dianthrimides. This is quite consistent with experimental results. Whereas 2,2'-dianthrimide gives a deep-blue solution in 98% sulphuric acid, N-methyl-2,2'-dianthrimide is greenish yellow in that medium (decrease of absorption at 15000 cm^{-1} ; compare the curves 3 and 4 in Fig. 2), and N-methyl-1,2'-dianthrimide does not absorb in the range of 15000 cm^{-1} .

TABLE I

The Parameters Used in LCAO MO (HMO) Calculations

Atomic core (X)	δ_x^a	Bond (X-Y)	k_{xy}^a
C ⁺	0	C=C	1.0
O ⁺	1.0	C=O	1.0
N ⁺²	1.0	C-NH ₂	0.8

^a δ_x and k_{xy} are the characteristic constants of the expressions for Coulombic and resonance integrals $\alpha_x = \alpha + \delta_x\beta$, $\beta_{xy} = k_{xy}\beta$.

TABLE II

The Parameters Used for Calculations according to PPP Method

Atomic core (X)	I.P., eV	E.A., eV	Z
C ⁺	11.22	0.69	1
O ⁺ (C=O)	13.60	2.30	1
O ⁺² (O-H)	32.90	10.00	2
N ⁺	14.10	1.80	1

Fig. 5 represents the absorption curves of 2,2'-dianthrimide in sulphuric acid of various concentrations. From the spectra it can be concluded that, in the given sulphuric acid concentration range, one equilibrium exists even though the isosbestic points are not clear-cut due to a strong "medium effect" characteristic for anthraquinone derivatives⁷. Colouration of the solution changes from orange in diluted sulphuric acid (non-protonated form; curve 1) through violet to blue in concentrated sulphuric acid (curve 6), and it is obvious that this blue colouration with intensive absorption band at 15000 cm^{-1} is due to monoprotonated form. pK_a of this protonation (halfprotonation $H_0 = -8.57$, $m = 0.85$) was determined in the usual way^{1,2} from the intensity change of the band at 15000 cm^{-1} ($\lambda = 662\text{ nm}$) and H_0 of the medium. This means that, if the first protonation takes place at oxygen atom to give

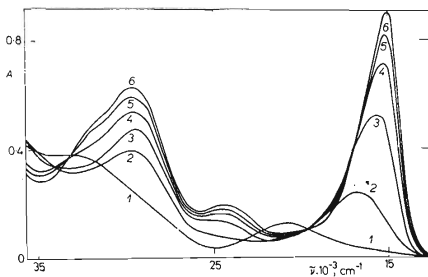


FIG. 5

Absorption Spectrum of 2,2'-Dianthrimide in Sulphuric Acid of Various Concentrations
 $\% \text{H}_2\text{SO}_4$: 1 73.3, 2 77.6, 3 86.6, 4 90.8, 5 94.1, 6 98.6.

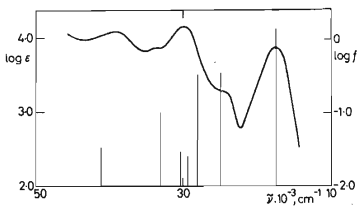


FIG. 6

Absorption Spectrum of Disulfo-2-phenylaminoanthraquinone in 98% Sulphuric Acid

the structure *III*, no further protonation occurs in 98% sulphuric acid medium. On the contrary, if the first protonation takes place at nitrogen atom (*e.g.* in the case of 1,1'-dianthrime), the situation is analogous to that of unsubstituted 1-aminoanthraquinone, a partial protonation to the second degree (*i.e.* at oxygen atom, too) taking place in 98% sulphuric acid medium, whereupon the form *II* results (Fig. 2, curve 1).

There is still one question left whether the structure *III* corresponds to the compound giving blue solution in 98% sulphuric acid. In Fig. 6 there is the absorption spectrum of disulfo-2-phenylaminoanthraquinone in 98% sulphuric acid together with the data obtained for the structure *III* by the PPP method with the parameters given in the section "Calculations" (Table II). The agreement with experiment is good. The first two bands were predicted very precisely by the theory. There is a broad band in the region 26000–35000 cm^{-1} of the spectrum which is obviously a superposition of several absorption bands. The theory predicts five electronic transitions in this region, three of them being relatively intensive. The relatively worst agreement between theory and experiment is encountered with the band at 39000 cm^{-1} ; in this region, the theory predicts one transition only of low intensity at 41000 cm^{-1} . Detailed theoretic study of spectra of compounds of this type will be published in some other work.

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