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Some Remarks on the Structure of Aniline Black, on the Basis of Ultraviolet Absorption Spectra

by

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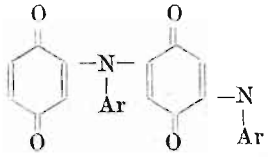
Two types of structural formulae of products of oxidation of aniline to aniline black — those of quinoneimine or phenazine — are generally accepted [1]. According to Willstätter [2] emeraldine, nigraniline, and pernigraniline possess structures consisting essentially of *p-quinoneimine rings* which are combined with benzene rings to form chains. The number of benzene rings decreases while that of quinoneimine rings increases with the progress of oxidation and deepening of colour of the product. Evidently the formation of the quinoneimine chains is the result of oxidation and condensation in *para* position.

This view of Willstätter has been criticised by Bucherer [3], who suggested another structure with *phenazine* rings. It has been supported by Green [4] who prepared "ungreenable" aniline black by oxidising pernigraniline of Willstätter in presence of aniline. The oxidation (in *ortho* position) leads to the formation of phenazine rings. This view has been critisised by Joffe and Metrikina [5]. According to them, "ungreenable" aniline black is simply pernigraniline.

It has been pointed out by a number of authors that the oxidation of aniline leads sometimes to the formation of red or brown anilinoquinone derivatives, i. e. the condensation occurs in *ortho* position. Thus, Schunck and Marchlewski [6] obtained a product, which they described as dianilino-quinone-monoanil, when oxidising aniline with hydrogen peroxide or ozone in a weakly acid medium. Similar results of the oxidation of aniline have been described by Bamberger and Tschirner [7], Szarvasy [8] and others [9].

Willstätter and Majima [10] pointed out that *para* condensation occurs when oxidation is carried out in a weakly acid medium in presence of some catalysts, such as vanadium chloride or ferric sulphate. Without catalysts an additional condensation can occur in the *ortho* position, and branched molecules can be formed.

Suida [11], in his well-known work on reaction of benzoquinone and aniline, pointed out that benzoquinone and aniline may lead to the formation of dark coloured derivatives of anilinoquinone similar to aniline black in an oxidising medium. The products are polimeric derivatives of triphenylamine (A).



(A)

In the present work the authors made a number of experiments on ultraviolet absorption spectra of emeraldine (I), aniline black (pernigraniline) (II), and "ungreenable" aniline black of Green (III) [4]— all in solution in sulphuric acid.

In order to compare with the spectra of the known compounds the spectra of solutions of model-compounds: anilinoquinone (IV), dianilinoquinone (V), phenazine (VI), saphranine (VII) and phenol blue (VIII) have been examined in sulphuric acid. Saphranine was taken as a typical phenazine dye. Phenol blue (N-dimethylindoaniline) has a structure composed of an indoaniline unit, similar to that of Willstätter's formula of aniline black.

(VIII)

Emeraldine and pernigraniline were prepared by oxidising aniline sulphate in $20^0/_0$ sulphuric acid solution, by means of chromic acid. The samples were purified by boiling with chloroform, washed with alcohol, then water; next, boiling with $10^0/_0$ sulphuric acid and finally washed with water, aqueous ammonia, and water.

Ungreenable aniline black was prepared according to Green [4], by oxidising pernigraniline with chromic acid in presence of aniline.

Anilinoquinone and dianilinoquinone were prepared according to Suida [11]. Phenazine and saphranine were commercial grade products purified by crystallisation from the appropriate solvents. Phenol blue was prepared by condensation of p-nitrosodimethylaniline with phenol. It was isolated and purified in the form of a complex salt with zinc chloride.

The results of spectrophotometric analysis are collected in Table I and on diagrams, Figs. 1-8. To calculate the extinction coefficients of emeraldine and pernigraniline the molecular weights were taken according to the formulae of Willstätter. In the case of "ungreenable" black — the molecular weight according to Green.

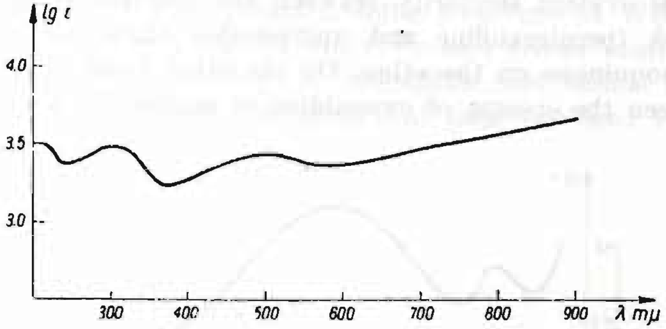


Fig. 1

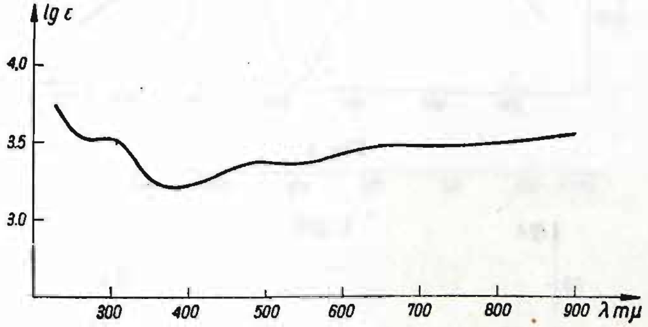


Fig. 2

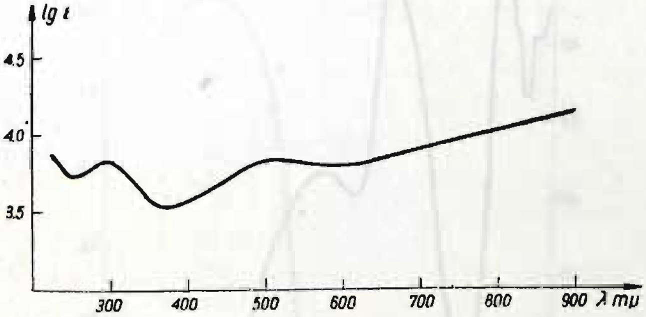


Fig. 3

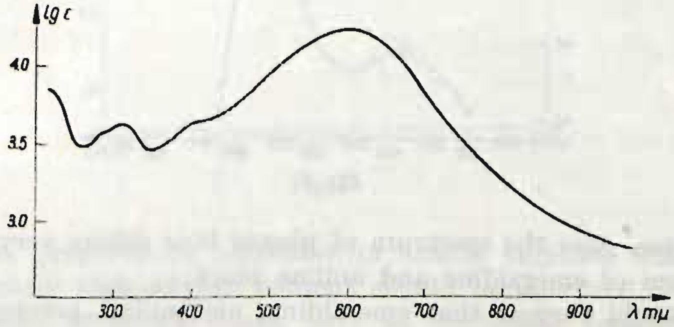


Fig. 4

There is evident similarity between the spectra of emeraldine and aniline black (pernigraniline and ungreenable black) on the one side, and dianilinoquinone on the other. On the other hand, a clear difference exists between the spectra of emeraldine or aniline black and phenazine

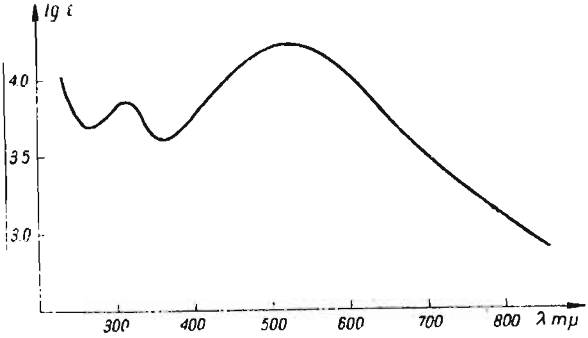


Fig. 5

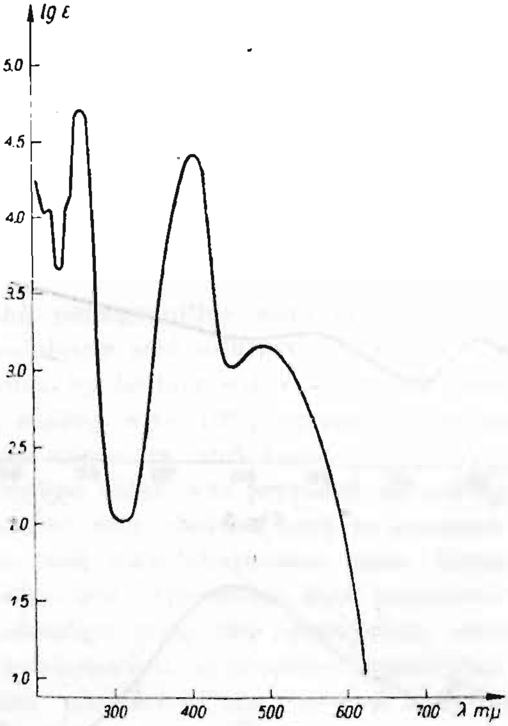


Fig. 6

or saphranine. Also the spectrum of phenol blue differs very much from the spectrum of emeraldine and aniline black.

This would suggest that emeraldine, nigraniline, pernigraniline and ungreenable aniline black may all possess a structure similar to that of dianilinoquinone. The *p*-quinoneiminine structure of Willstätter, or the phenazine structure given by Bucherer and Green cannot be confirmed by the absorption spectra of emeraldine and aniline black.

On the basis of preliminary analytical data obtained for purified pernigraniline, prepared by oxidation of aniline sulphate with chromic acid, a relatively high oxygen content should be admitted.

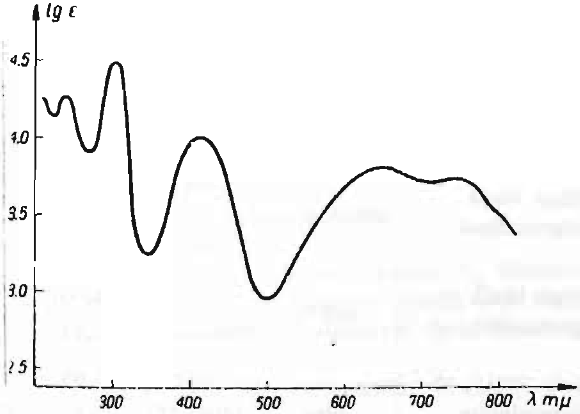


Fig. 7

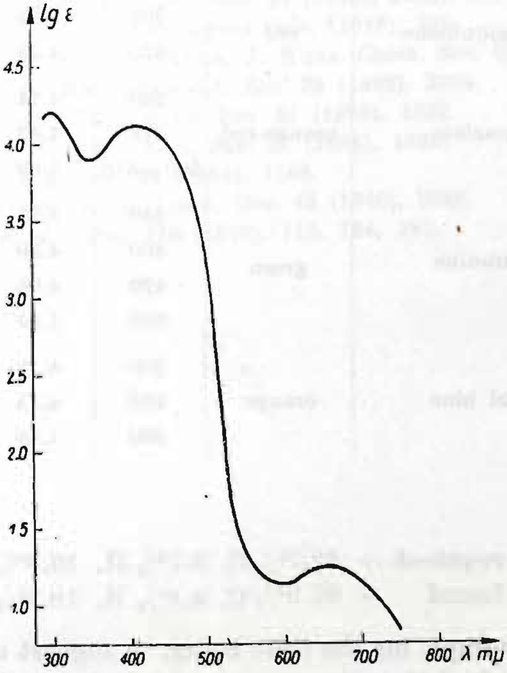


Fig. 8

One sample of aniline black gave an empirical formula near to $C_{30}H_{20}O_6N_4$.

TABLE I

No. of curve	Substance	Colour of the solution in sulphuric acid	Absorption curve			
			max.		min.	
			mμ	log ε	mμ	log ε
1	Emeraldine	magenta	300	3.83	245	3.72
			510	3.83	370	3.50
					570	1.78
2	Aniline black (pernigraniline)	bluish-green	290	3.52	275	3.51
			520	3.41	375	3.23
			670	3.50	740	3.48
3	Aniline black (ungreenable)	red *)	300	4.00	340	3.86
			500—510	3.94	370	3.72
4	Anilinoquinone	blue	312	3.63	345	3.48
			(405) **)	(3.67)	(365) **)	(3.47)
			590	4.23	425	3.61
5	Dianilinoquinone	red	308	3.89	270	3.68
			520	4.23	345	3.61
6	Phenazine	orange-red	260	4.74	240	3.75
			418	4.42	318	2.00
			500—510	3.09	450	2.99
7	Saphranine	green	240	4.28	220	4.13
			300	4.50	264	3.90
			420	4.05	344	3.20
			640	3.84	510	2.95
8	Phenol blue	orange	300	4.15	350	3.90
			415	4.13	585	1.08
			650	1.18		

Analysis:

$C_{30}H_{20}O_6N_4$ required — 67.7% C, 3.7% H, 10.5% N
found — 67.9% C, 4.4% H, 10.9% N, 0.1% Cr.

We do not attempt, for the time being, to suggest any definite structure of aniline black, but a structure in principle similar to (A) appears to be probable.

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*) The solution contained a considerable quantity of undissolved suspended particles.

**) A bend, without a definite maximum.

Further experiments are being carried out. The results, which include infra-red absorption spectra of emeraldine, aniline black, anilinoquinones, and phenazine as well as analytical data will be reported in due course.

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