

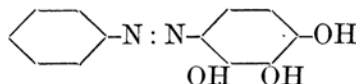
# SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART III.<sup>(1)</sup>

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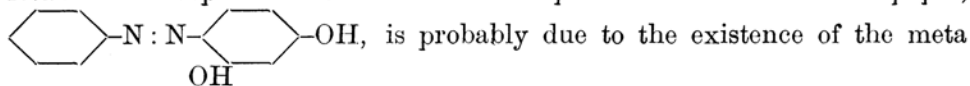
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## 1. Benzeneazopyrogallol,<sup>(2)</sup>

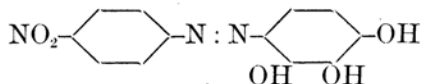


We can find very slight bathochromic and hyperchromic influences by the addition of alkali in the absorption curve (Fig. 1), and can hardly detect the change of colour in the solution. The marked difference from the absorption curves of No. 2 compound in Part I of this paper,



hydroxyl-group with respect to the azo-group in this compound. We can assign A-form to the neutral state, but the alkaline state is perhaps the mixture of A- and R-forms.

## 2. p-Nitrobenzeneazopyrogallol,<sup>(3)</sup>



KOH changes the colour of the solution from yellowish red into brown

(1) Part I and Part II of this paper were published in this journal, 1 (1926), 260 and 2 (1927), 10 respectively.

(2) Beilstein "Handbuch der Organischen Chemie," IV (1899), 1450.

(3) Obtained from p-nitraniline and pyrogallol.

and soon into orange. A-form can be assigned to the neutral solution as usual, and R-form to the alkaline solution, but we think that on account of the meta hydroxyl with regard to the azo-group, B-form cannot be assigned in this case (Fig. 1).

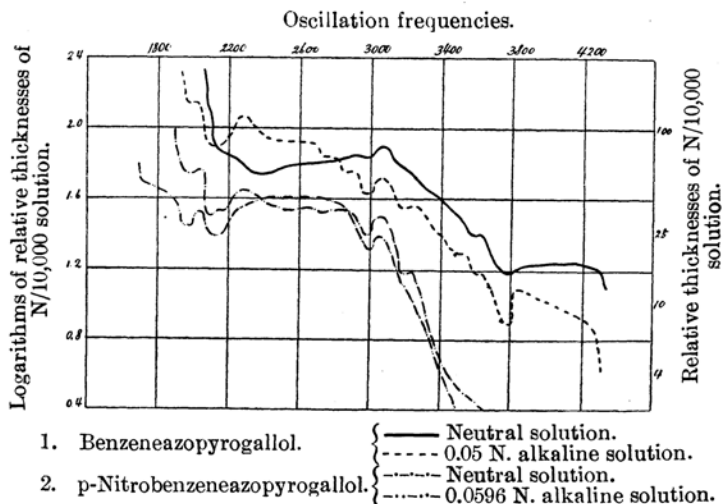
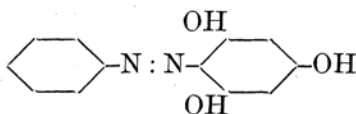


Fig. 1.

### 3. Benzeneazophloroglucinol,<sup>(1)</sup>



The yellow neutral solution does not change colour by the addition of potassium hydroxide solution. The hypochromic effect due to an alkali is rather exceptional (Fig. 2), but this is perhaps owing to a kind of destruction which has occurred in the molecule by the mutual hindrance of three movable hydrogen atoms in hydroxyl groups.

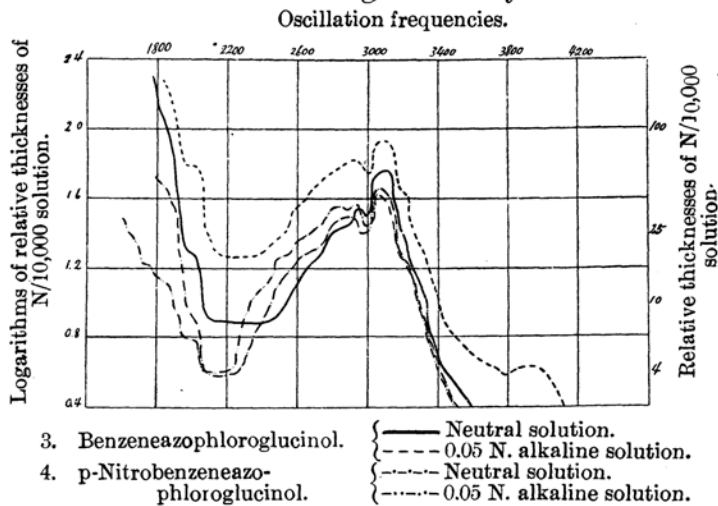
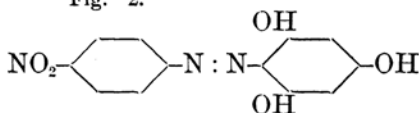


Fig. 2.

### 4. p-Nitrobenzeneazophloroglucinol,<sup>(2)</sup>



By the addition of an alkali, only a slightly bathochromic effect can be

(1) Obtained from aniline and phloroglucinol.

(2) Obtained from p-nitraniline and phloroglucinol.

seen in the absorption curve of this substance (Fig. 2), and this case, the yellowish red neutral solution changes into the orange red alkaline solution. Although we can give A- and R-forms to the two kinds of coloured solutions of this compound, it is almost safe to say that B-form is not represented owing to the mutual hindrance of labile hydrogen atoms.

All of the experimental results (Parts I, II, and III) may be summarized as follows :

No.	Compounds.	Colour of		Form to be assigned.
		Neutral solution.	Alkaline solution.	
Part I.	1 p-Hydroxyazobenzene.	y.	deep y.	A;R.
	2 Benzeneazoresorcinol.	y.	deep y.	A;R.
	3 Benzeneazo-p-cresol.	y.	r.	A;R.
	4 p-Nitrobenzeneazophenol.	y.r.	r.	A;R.
	5 p-Nitrobenzeneazoresorcinol.	r.y.	b.v.	A;R;B.
	6 m-Nitrobenzeneazoresorcinol.	y.	r.	A;R.
	7 p-Nitrobenzeneazo-p-cresol.	y.	v.	A;B.
Part II.	1 Benzeneazocatechol.	y.	o.	A;(A+R).
	2 Benzeneazoquinol.	light y.	{ nearly no change.	A.
	3 p-Nitrobenzeneazocatechol.	y.r.	b. (changeable).	A;B.
	4 p-Nitrobenzeneazoquinol.	y.r.	o. (changeable).	A;R.
	5 m-Nitrobenzeneazophenol.	y.	r.	A;R.
	6 o-Nitrobenzeneazophenol.	y.	r.	A;R.
	7 o-Nitrobenzeneazoresorcinol.	y.	r.	A;R.
	8 p-Nitrobenzeneazoguaiacol.	y.	r.	A;R.
	{ p-Nitrobenzeneazohydroquinone mono-methyl ether.	y.r.	p. (changeable).	A;R.
Part III.	1 Benzeneazopyrogallol.	y.	no change.	A;(A+R).
	2 p-Nitrobenzeneazopyrogallol.	y.r.	br. (changeable).	A;R.
	3 Benzeneazophloroglucinol.	y.	no change.	A.
	4 p-Nitrobenzeneazophloroglucinol.	y.r.	o.r.	A;R.

y.=yellow, r.=red, o.=orange, b.=blue, br.=brown, p.=purple, v.=violet.

y.r.=yellowish red, r.y.=reddish yellow, b.v.=bluish violet, o.r.=orange red.

### Summary (Parts I, II, and III).

1. Tautomeric transpositions may take place in these hydroxyazo-compounds by the addition of a potassium hydroxide solution, with an accompanying change in colour.

2. We can respectively assign A(azo)-, R(red)-, and B(blue)-forms to these tautomers. (Sometimes we recognise more readily the mixture of these forms.)

3. Tautomerism is due to the labile hydrogen atoms in hydroxyl-groups which take the ortho- or para-position with respect to the azo-group.

4. The hydrogen atom which is in the meta hydroxyl-group with regard to the azo-group does not only move by itself, but moreover hinders the transposition of the other hydrogen atoms.

5. When there are many labile hydrogen atoms, mutual hindrance may occur.

6. B-form is sometimes produced only when there is a para nitroradical with regard to the azo-group.

7. Nitro-groups which take the ortho- or meta-position with respect to the azo-group do not change into the isonitro-structure.

8. The nitro-group has considerable bathochromic influence upon these hydroxyazo-compounds.

9. Generally only one absorption band exists in the solutions of these substances, but there are two bands when methyl-group is included.

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