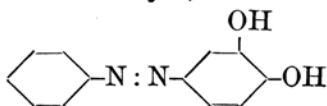


SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART II.⁽¹⁾

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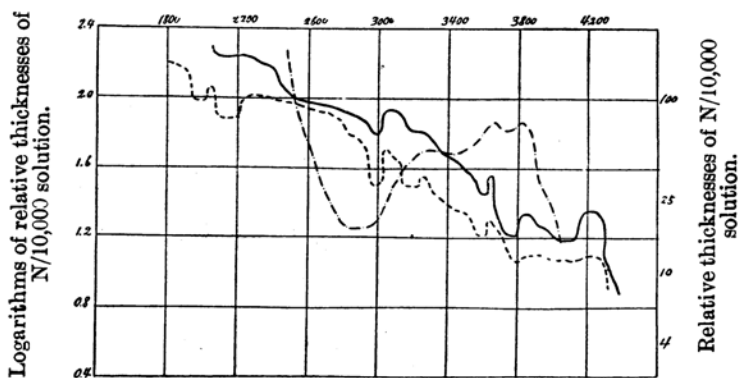
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1. Benzeneazocatechol⁽²⁾ (Benzeneazopyrocatechin),



Although the addition of KOH to this substance induces a change of colour in the solution from yellow to orange, only a slightly bathochromic influence can be observed from the absorption curve (Fig. 1). When we compare Fig. 1 with the absorption curve of No. 1 compound (Fig. 1 in Part I of this paper), we can ascertain a considerable difference between them. We think this is due to the hydroxyl-group of the meta-position with respect to the azo-group. Then,

Oscillation frequencies.



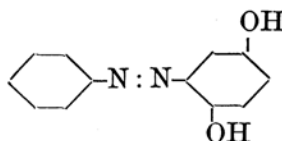
1. Benzeneazocatechol. { ——— Neutral solution.
 - - - - - 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. { - · - · - Neutral solution.

Fig. 1.

- (1) Part I of this paper has been published in this journal 1 (1926), 260. N.B. In this paper, in the 12th line from the bottom on page 261, the phrase "the bathochromic and hyperchromic influences are easily observed" should be changed to "the bathochromic influence is easily observed".
- (2) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1440.

A-form is naturally assigned to the neutral solution, but the orange alkaline solution is perhaps the mixture of A-form and R-form.

2. Benzeneazoquinol⁽¹⁾
(Benzeneazohydroquinone),



This substance is hardly affected in colour by the addition of KOH, and its absorption curves (Fig. 2) are also represented as can be expected. Only A-form exists in the solution of this compound.

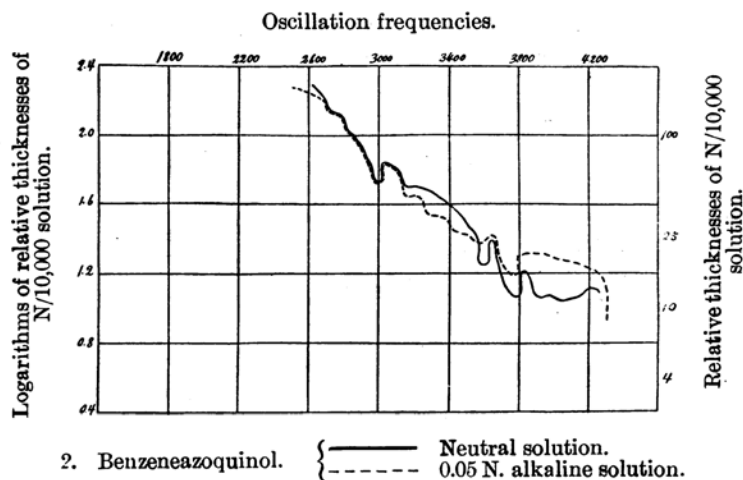
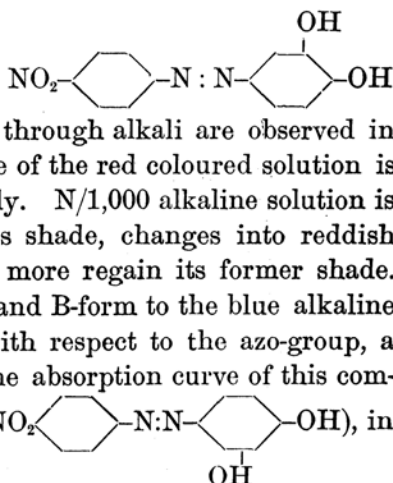


Fig. 2.

3. p-Nitrobenzeneazocatechol⁽²⁾
(p-Nitrobenzeneazopyrocatechin),



Bathochromic and hyperchromic effects through alkali are observed in the solution of this compound. As the range of the red coloured solution is quite short, it changes into blue very quickly. N/1,000 alkaline solution is already blue, but this blue solution loses its shade, changes into reddish brown after standing one day, and can no more regain its former shade. We may give A-form to the neutral solution and B-form to the blue alkaline solution. According to the meta hydroxyl with respect to the azo-group, a great difference can be observed between the absorption curve of this compound (Fig. 3) and that of No. 5 compound ($\text{NO}_2\text{-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_3(\text{OH})_2$), in Part I of this paper.

(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1447.

(2) Ibid., IV (1899), 1440.

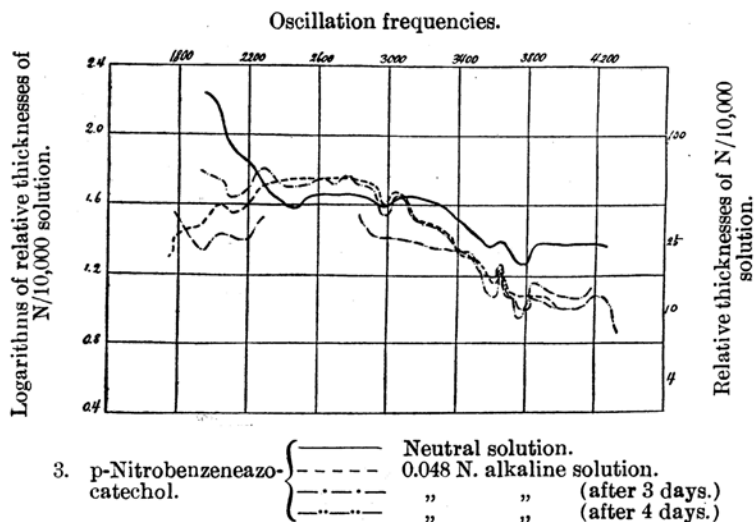
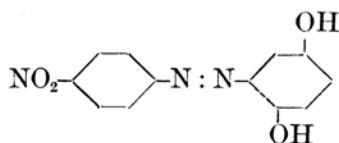


Fig. 3.

4. p-Nitrobenzeneazoquinol⁽¹⁾
(p-Nitrobenzeneazohydroquinone),



We notice a slight change in colour through KOH, that is, by the addition of an alkali, a yellowish red neutral solution becomes orange, but this orange returns to yellow after one day and does not take the former shade again. Then A-form can be assigned to the neutral solution, and probably R-form to the orange state (Fig. 4.).

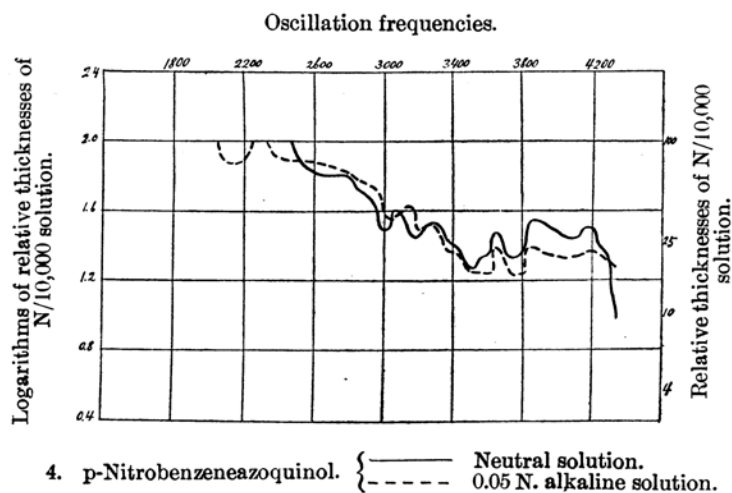
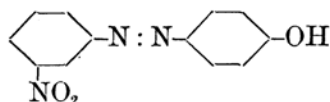


Fig. 4.

(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1447.

5. *m*-Nitrobenzeneazophenol,⁽¹⁾

The yellow neutral solution changes into red when an alkaline solution is added. The bathochromic influence due to KOH can clearly be seen in the absorption curve (Fig. 5). We can certainly give A-form to the neutral solution and R-form to the alkaline solution which cannot have B-form owing to the meta nitro-radical with respect to the azo-group.

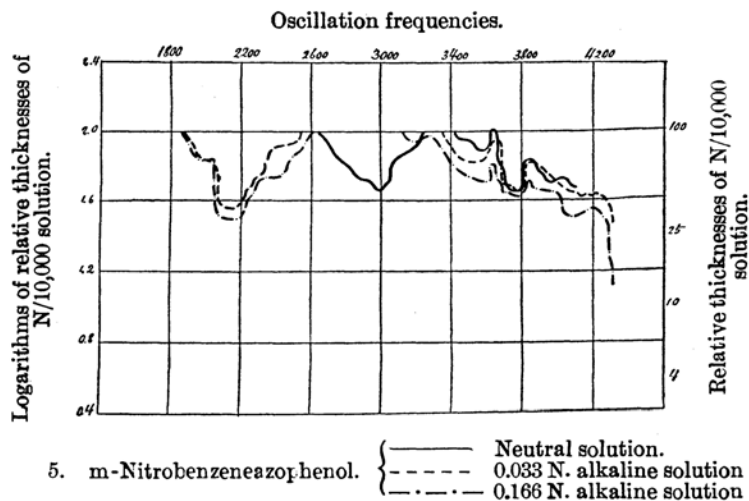
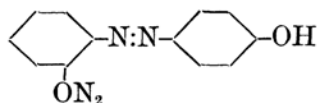


Fig. 5.

6. *o*-Nitrobenzeneazophenol⁽¹⁾

The very same colour changes in No. 5 compound can be easily observed in this case, that is, we recognise bathochromic and hyperchromic effects when the solution is alkaline, but can never get the blue solution. Therefore, A- and R-forms only exist in *o*-Nitrobenzeneazophenol solution (Fig. 6).

(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1410.

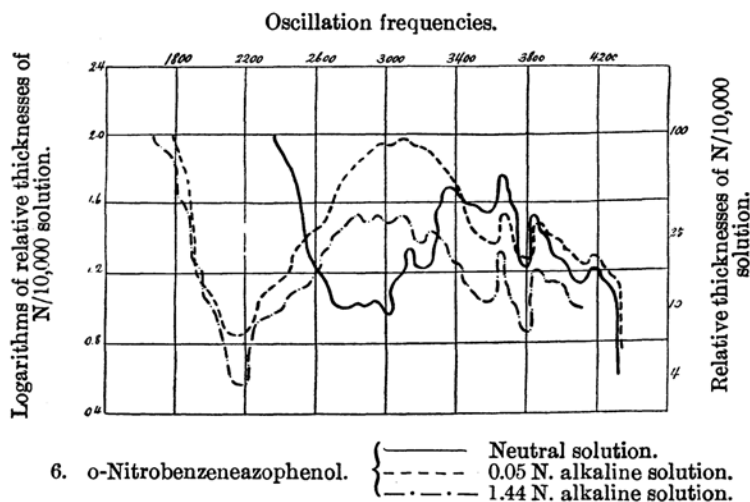
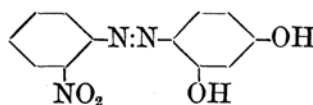


Fig. 6.

7. o-Nitrobenzeneazoresorcinol,⁽¹⁾

Only the red alkaline solution of this compound can be easily obtained, and A- and R-forms can be respectively given to the neutral and alkaline solutions (Fig. 7). It is, therefore, proved that the nitro-radical which is in the ortho-position with respect to azo-group cannot take the isonitro-structure (See No. 6 compound).

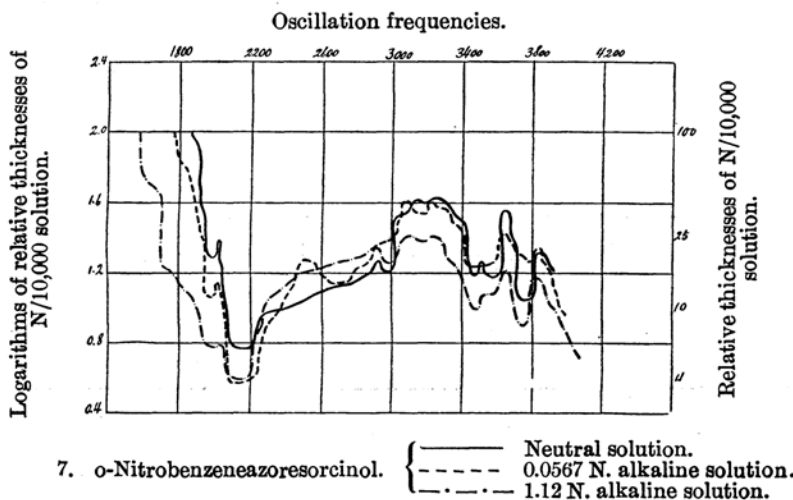
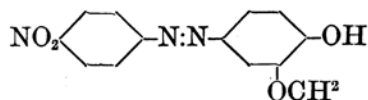


Fig. 7.

(1) Obtained from o-nitraniline and resorcinol.

8. p-Nitrobenzeneazoguaiacol,⁽¹⁾

The yellow neutral solution changes into red by the addition of alkali like many other hydroxyazo-compounds. In this case, fairly remarkable bathochromic and hyperchromic influences through alkali can be found, and of course, A- and R-forms can be respectively assigned to the two different coloured solutions. (Fig. 8).

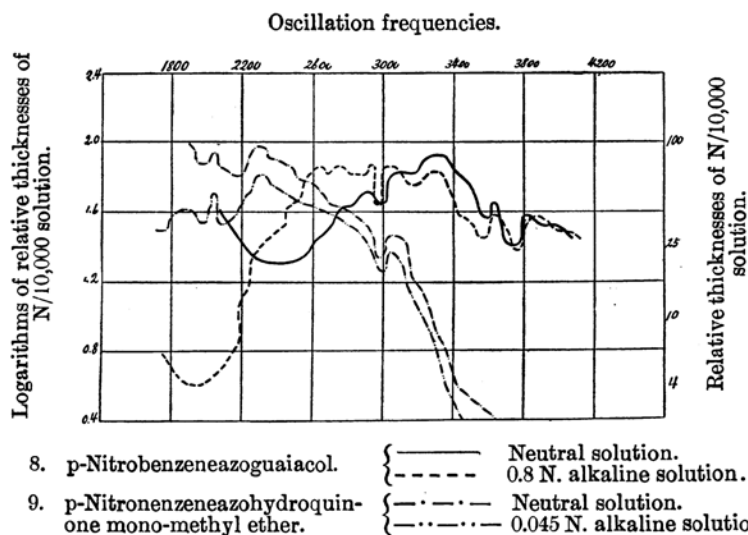
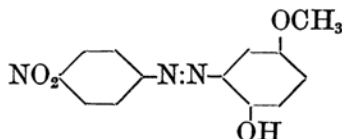


Fig. 8.

9. p-Nitrobenzeneazohydroquinone mono-methyl ether,⁽²⁾

The yellowish red neutral solution changes first into purple by the addition of alkali, and then, after one hour turns brownish yellow. Slight bathochromic and hyperchromic effects due to alkali can be observed in that case (Fig. 8). From the absorption curve, we will give A-form to the neutral solution and R-form, not B-form, to the alkaline solution.

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(1) Obtained from p-nitraniline and guaiacol.

(2) Obtained from p-nitraniline and hydroquinone mono-methyl ether, which is synthesized with hydroquinone, sodium-methylalcoholate and methyl iodide.