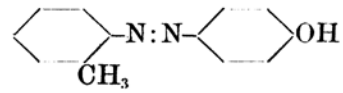
SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART V.[2]

By Taku UEMURA and Shozo TABEI.

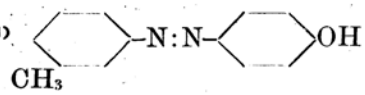
Received June 11, 1927. Published September 28, 1927.

Some influences with regard to the methyl-group in tolueneazo-cresols were mentioned in our previous paper,[3] and, in this paper, we shall continue the same subject.

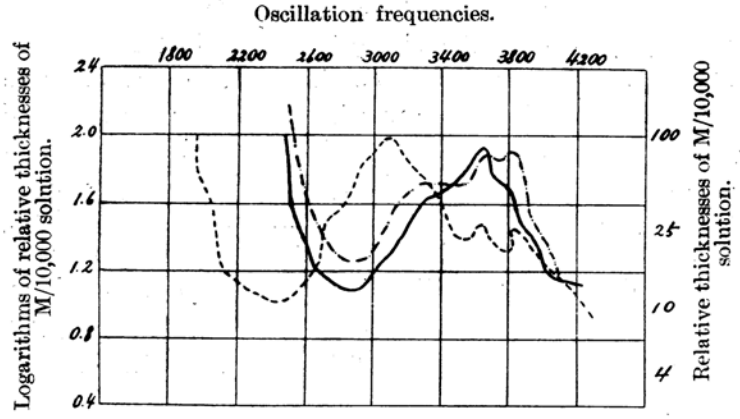
Experimental.

1. **o-Tolueneazophenol,**[4] 

(2) Read before the Chemical Society of Japan, June 11, 1927.
(3) Uemura and Tabei, This journal, **2** (1927), 229.
(4) Noelting and Werner, *Ber.*, **23** (1890), 3257; Paganini, Ibid. **24** (1891), 366.

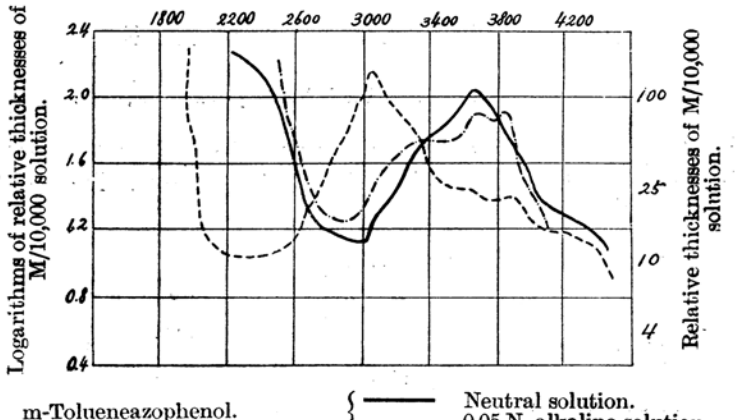
2. **m-Tolueneazophenol,**[1] 

The neutral solutions of these two compounds are yellow and give a deeper shade by adding KOH. When we compare the neutral absorption curve of p-hydroxyazobenzene[2] with the absorption curves of these compounds, the hyperchromic influence due to the methyl-group can be distinctly observed (Fig. 1 and Fig. 2).



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

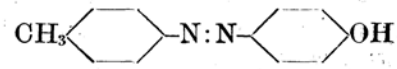
Fig. 1.



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

Fig. 2.

(1) Paganini, *Ber.*, **24** (1891), 368.
(2) This journal, **1** (1926), 262.

3. **p-Toluneazophenol,**[1] 

The absorption curves of this compound (Fig. 3) are slightly hypochromic than those of the previous two compounds. But, comparing the curve of p-hydroxyazobenzene[2] with these, we can observe an effect similar to the one we found in the cases of the two above-mentioned compounds.

The colour of this alkaline solution is orange of a somewhat deeper shade than No. 1 and No. 2. By the addition of alkali, only a bathochromic effect can be shown in the absorption curves of these three tolueneazophenols.

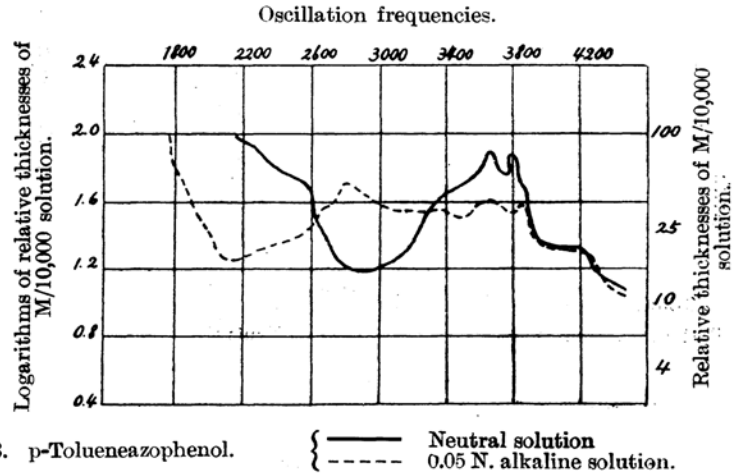
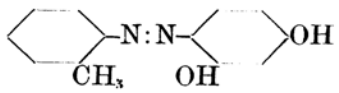
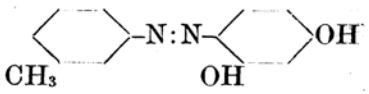
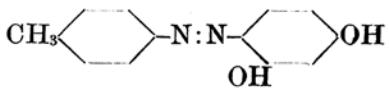


Fig. 3.

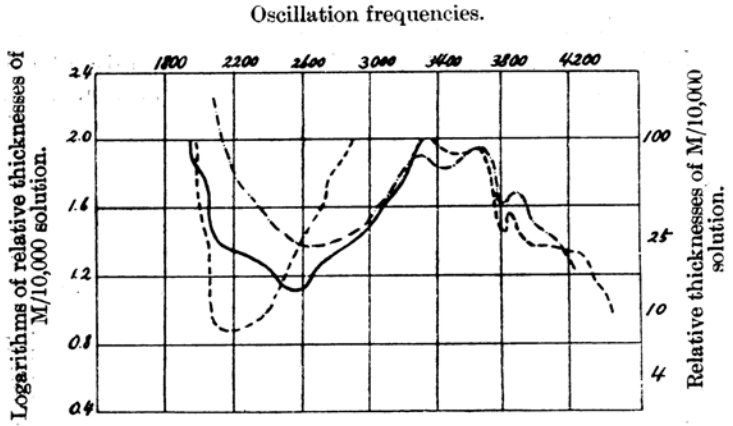
4. **o-Toluneazoresorcinol,**[3] 

5. **m-Toluneazoresorcinol,**[4] 

6. **p-Toluneazoresorcinol,**[5] 

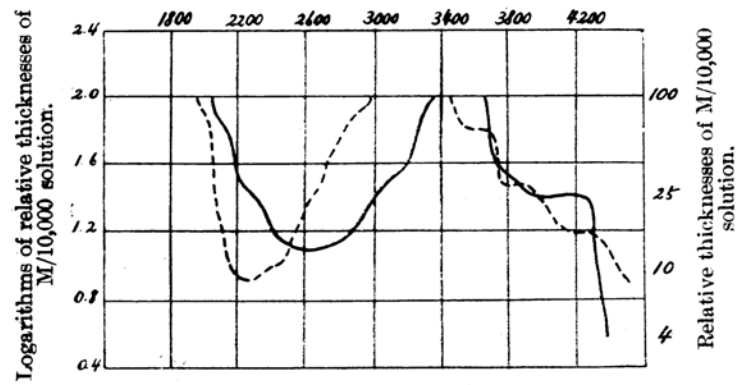
(1) Heumann and Oeconomides, *Ber.*, **20** (1887) 905; Kimich, Ibid., **8** (1875), 1030.
(2) Loc. cit.
(3) Wallach and Fischer, *Ber.* **15** (1882), 2825.
(4) Obtained from m-toluidine and resorcinol.
(5) Wallach, *Ber.*, **15** (1882), 2821.

These three compounds hardly produce any change in colour through alkali, and the hyperchromic influence can easily be recognised in their absorption curves (Fig. 4, Fig. 5 and Fig. 6). The hyperchromic effect due to the methyl-group may be detected in comparing it with benzeneazoresorcinol[1] (Fig. 4).



4. o-Tolueneazoresorcinol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.
2 (Part I). Benzeneazoresorcinol. —·—·— Neutral solution.

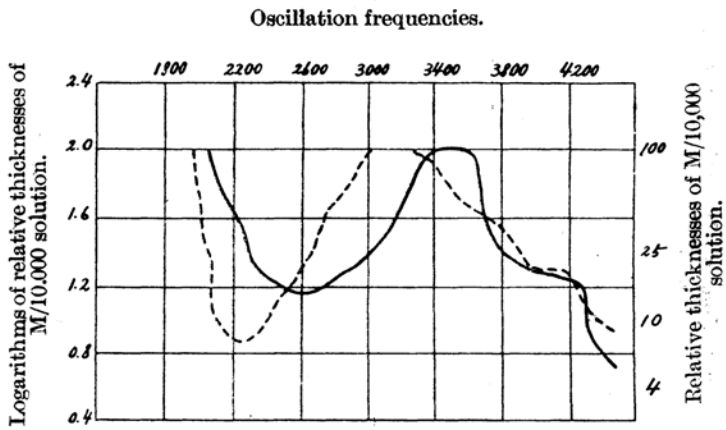
Fig. 4.



5. m-Tolueneazoresorcinol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.

Fig. 5.

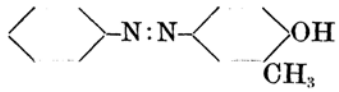
(1) This journal, 1 (1926), 262.



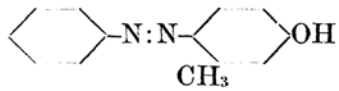
6. p-Tolueneazoresorcinol. ——— Neutral solution. - - - - - 0.05 N. alkaline solution.

Fig. 6.

7. **Benzeneazo-o-cresol,**[1]

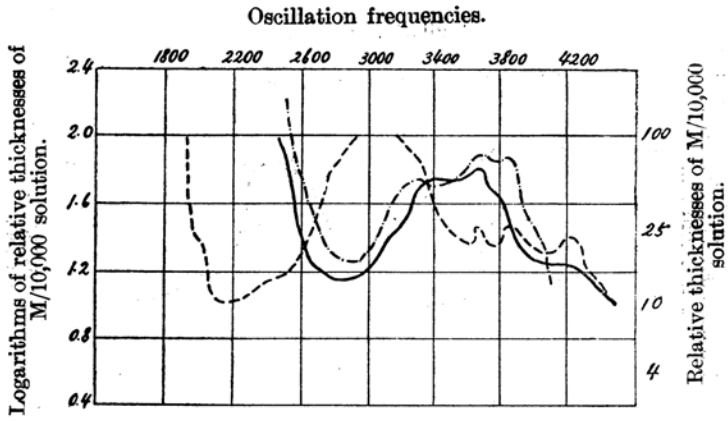


8. **Benzeneazo-m-cresol,**[2]



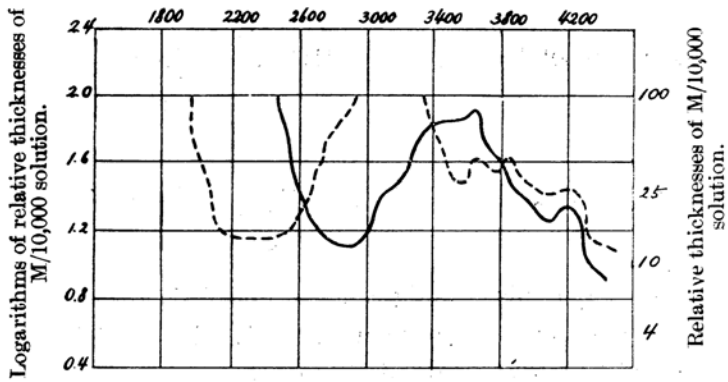
These two compounds are light yellow in their neutral solution and change into a yellowish orange when KOH is added. Their absorption curves (Fig. 7 and Fig. 8) are quite different from benzeneazo-p-cresol,[3] and this must be owing to the position of the hydroxyl-group in the cresol ring. When it takes the para-position with respect to the azo-group (these two compounds), only one absorption band can be seen, while two bands are clearly represented in the case of the ortho-position (benzeneazo-p-cresol). Comparing these absorption curves with that of p-hydroxyazobenzene[4] (Fig. 7), we are able to find the hyperchromic influence which most likely comes from the methyl-group in the cresol ring.

(1) Liebermann and Kostanecki, *Ber.*, **17** (1884), 131 & 879. Noelting and Kohn, Ibid., **17** (1884), 363.
(2) Noelting and Kohn, Ibid., **17** (1884), 366.
(3) This journal **1** (1926), 263.
(4) Loc. cit.



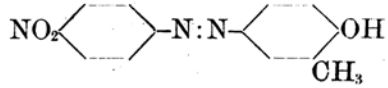
7. Benzeneazo-o-cresol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.

Fig. 7.



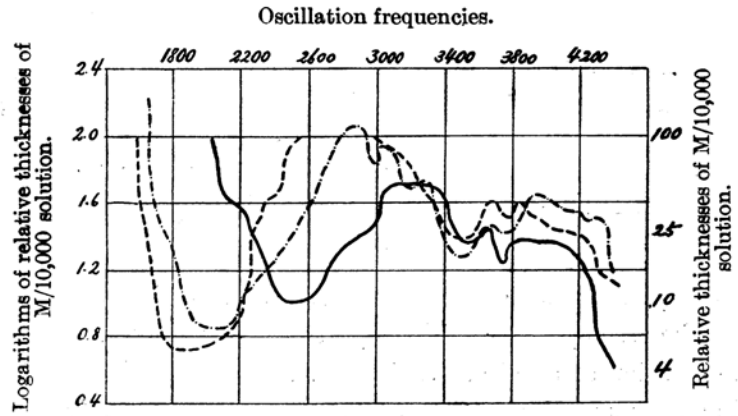
8. Benzeneazo-m-cresol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.

Fig. 8.

9. p-Nitrobenzeneazo-o-cresol,[1] 

The yellow neutral solution changes into deep red when it is alkaline, but can not turn blue. When we compare the alkaline solution curve (0.002 N. KOH) of p-nitrobenzeneazophenol[2] with the curve of this compound (Fig. 9), the hyperchromic effect due to the methyl-group can be recognised.

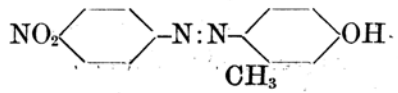
(1) Bamberger, *Ber.*, **28** (1895), 846.
(2) This journal, **1** (1926), 263.



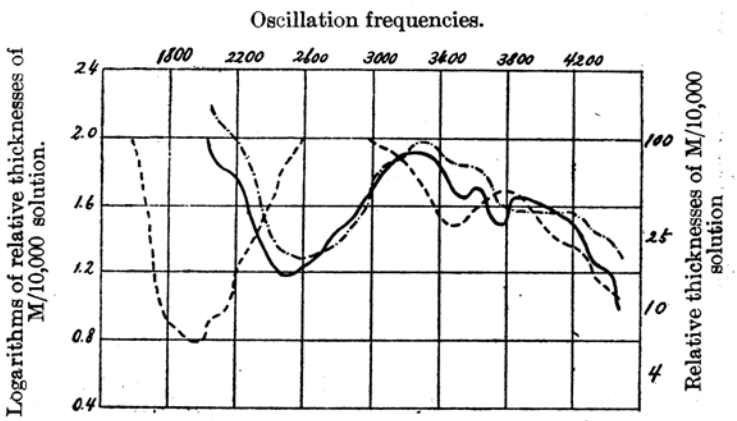
9. p-Nitrobenzeneazo-o-cresol. { ——— Neutral solution. - - - - - 0.002 N. alkaline solution.
4 (Part I). p-Nitrobenzeneazophenol. —·—·— 0.002 N. alkaline solution.

Fig. 9.

10. p-Nitrobenzeneazo-m-cresol,[1]



The colour change through alkali is just the same as No. 9 compound. This neutral curve (Fig. 10) is slightly more hyperchromic than that of p-nitrobenzeneazophenol.[2] As the nitro-radical is situated in the para-position with regard to the azo-group, hyperchromic and bathochromic influences somewhat greater than No. 7 and No. 8 compounds are observed in the absorption curves of No. 9 and No. 10 compounds.

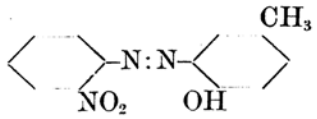


10. p-Nitrobenzeneazo-m-cresol. { ——— Neutral solution. - - - - - 0.05 N. alkaline solution.
4 (Part I). p-Nitrobenzeneazophenol. —·—·— Neutral solution.

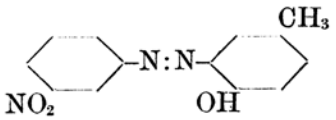
Fig. 10.

(1) Bamberger, *Ber.* 28 (1895), 847.
(2) Loc. cit.

11. **o-Nitrobenzeneazo-p-cresol,**[1]



12. **m-Nitrobenzeneazo-p-cresol,**[2]



These componnds have two absorption bands owing to the hydroxyl which takes the ortho-position with respect to the azo-group.

By the addition of alkali to their neutral solution, the colour of these compounds changes yellow into red and only the bathochromic effect can be detected in their absorption curves, not the hyperchromic, like No. 9 and No. 10 compounds. This means probably that the hydroxyl situated in ortho-position with respect to the azo-group is less effective than the one in para-position, for the same relation is also preserved in the curve of p-nitro-benzeneazo-p-cresol.[3] And as for the nitro-radical, we may obtain a greater bathochromic curve when the para-position with regard to the azo-group is occupied by that group (Fig. 11 and Fig. 12).

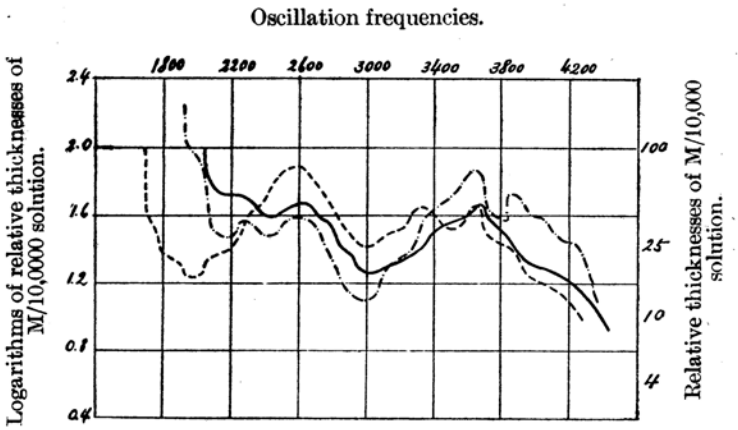


Fig. 11.

(1) Goldschmidt and Brubacher *Ber.* **24** (1891), 2308.
(2) Meldola and Hanes *J. Chem. Soc.*, **65** (1894), 838.
(3) This journal. **1** (1926), 265.

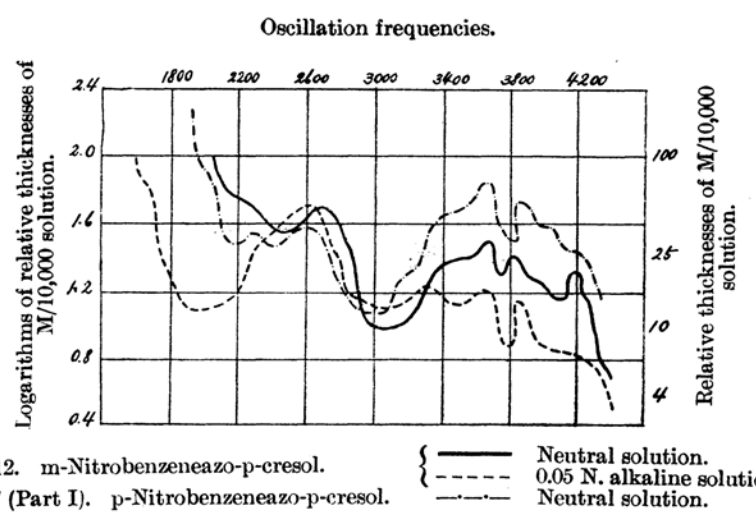


Fig. 12.

Summary.

(1) Tautomeric transformations may take place in these hydroxyazo-compounds.

(2) We may assign A (azo)-form[1] to the neutral solution and R (red)-form[1] to the alkaline.

(3) In general, one band can be shown in the absorption curves, except when the hydroxyl-group takes an ortho-position with regard to the azo-group.

(4) Hydroxyl- and nitro-radicals in para-position with respect to the azo-group are most effective in the absorption curve.

(5) The methyl-group has generally a hyperchromic influence upon the non-methylated compounds.

The writers gratefully acknowledge suggestions received from Prof. Yuji Shibata of the Tokyo Imperial University. The present investigations have been made possible through financial help from the Department of Education and from the School, for which we wish to express our sincere thanks.

Dyeing Department, Tokyo Higher Technical School.

(1) This journal, 1 (1926), 261.