

COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE PHTHALEIN DYES

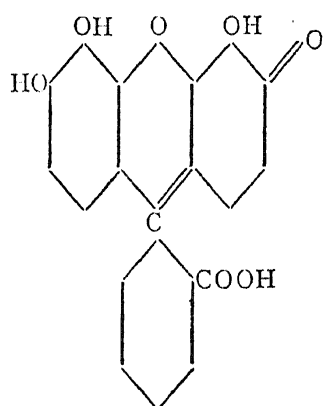
Phthaleins of the Mixed Type

BY SIKHIBHUSHAN DUTT

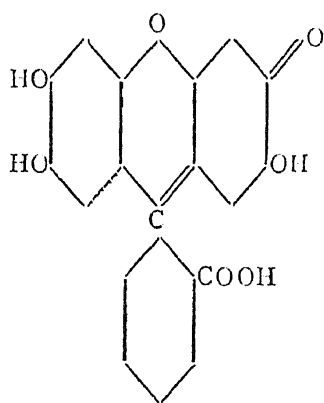
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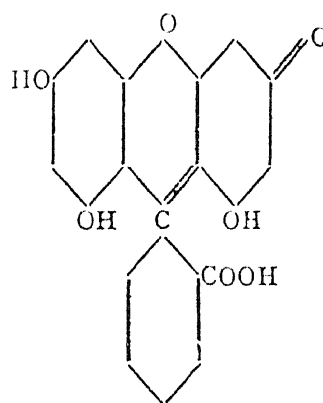
FROM the point of view of colour in relation to chemical constitution, perhaps some of the most interesting compounds in existence are the phthaleins obtained by the condensation of phthalic anhydride with aromatic phenols and amino-phenols, since they offer very great possibilities for generalisation. Dutt¹ has already pointed out in connection with the exposition of a "Theory of colour on the basis of molecular strain", that in the phthalein series, the nearer a hydroxy group is to the strained pyrone oxygen atom, the greater is the development of colour. Thus in alkaline solution, gallein is blue, hydroxyquinol-phthalein is pink and phloroglucinol-phthalein is orange, with absorption maxima at 5980 Å, 5540 Å and 4980 Å respectively :



Gallein (blue). 5980 Å

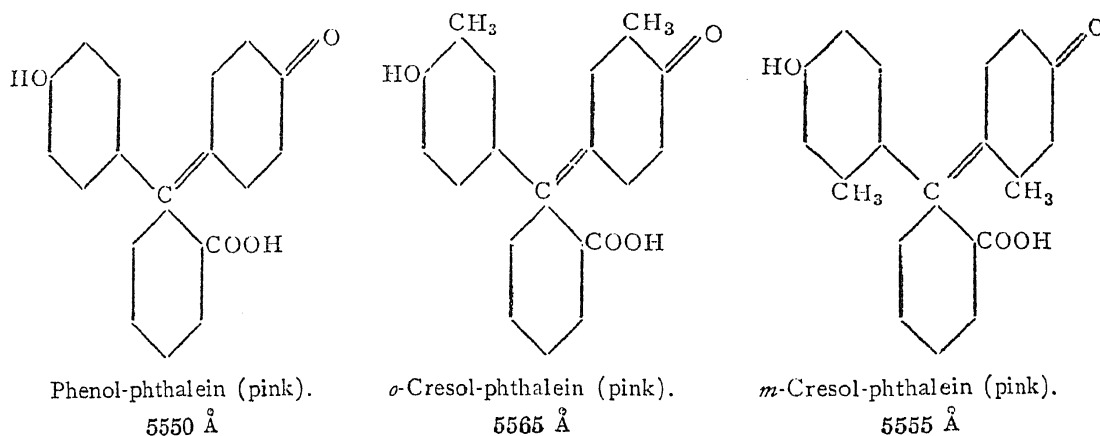


Hydroxyquinol-phthalein (pink)
5540 Å

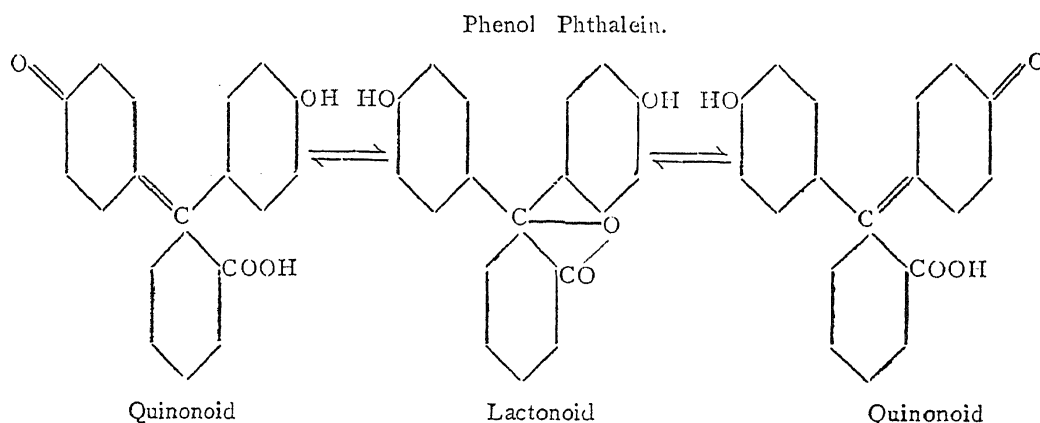


Phloroglucinol-phthalein
(orange) 4980 Å

In the simpler phthaleins like phenol-phthalein and its higher homologues and analogues which do not contain any pyrone oxygen atom bridging the two benzene nuclei, the change of colour due to difference in the load is much less marked. For example, phenol-phthalein, *o*-cresol-phthalein and *m*-cresol-phthalein are all pink with slightly different shades and very close absorption maxima. Thus :

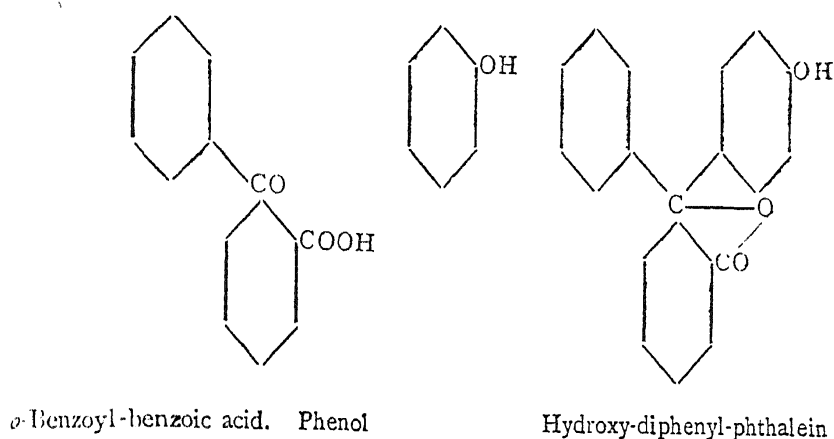


Phenol-phthalein is one of the simplest of organic compounds which passes from the colourless to the intensely coloured (pink or crimson) state by the action of alkali. This interesting and remarkable transition has been shown by the well-known and classical work of Otto Fischer, Hepp, Nietzki, Schroeter, Bernthsen and Friedlander, to be due to the conversion of the colourless lactonoid to the highly coloured quinonoid form :

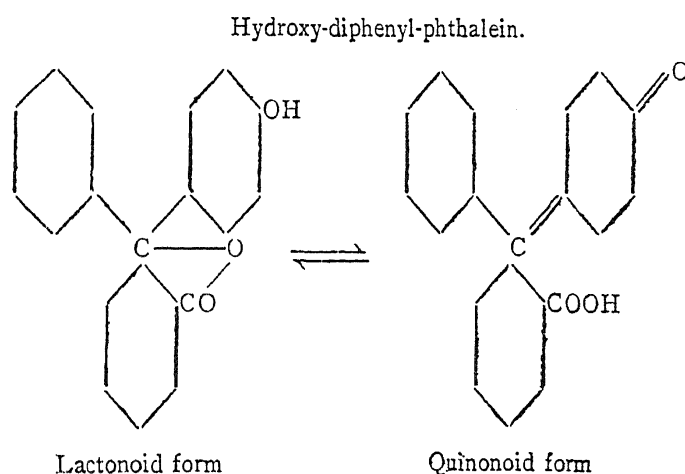


From the diagrams given above, it can be easily seen that lactonoid phenol-phthalein can tautomerise into two different and distinct quinonoid forms under the influence of alkali. Consequently it is not difficult to visualise, that under conditions in which all the three forms of phenol-phthalein are capable of existence, there will be twice as many highly strained and therefore deeply coloured quinonoid forms as comparatively unstrained and colourless lactonoid forms. It is for this reason that the alkaline solutions of phenol-phthalein are always deeply coloured, particularly in view of the fact that in alkaline solution not only the lactonoid form is difficult to exist due to extensive hydrolysis and opening up of the lactone ring, but the opportunity for the formation of the quinonoid form is also very great.

But if a condition could be created in which the tautomerism of the phenol-phthalein nucleus is rendered possible in only one of the two quinonoid forms mentioned above, the colour development of the substance is likely to be much less intense than in the case of phenol-phthalein. Such a condition exists in the case of hydroxy-diphenyl-phthalein obtained by the condensation of phenol with *o*-benzoyl-benzoic acid :



Under the influence of alkali, hydroxy-diphenyl-phthalein can tautomerise into only one possible quinonoid form :



Consequently from theoretical considerations it can be expected that hydroxy-diphenyl-phthalein will dissolve in alkali with less colour development than phenol-phthalein. From actual experimental evidence, this expectation has been realised and it has been found that hydroxy diphenyl-phthalein dissolves in alkali with only a pale yellow colour as contrasted with the intense pink colour of phenol-phthalein. In the solid state the substance is like phenol-phthalein, perfectly colourless.

Hydroxy-diphenyl-phthalein has been previously prepared in an impure state by Pechmann² by heating *o*-benzoyl-benzoic acid with phenol and

TABLE I

Mixed phthaleins derived from *o*-benzoyl-benzoic acid (*p* = phthalein)

Name of the compound	M. P. (° C.)	Appearance	Colour in solution of dilute NaOH	Absorption maxima in dilute alkaline sol. (Å)	Analyses. % Composition (Theoretical values in brackets)
Phenyl-phenol-p	92.5	Colourless glistening prismatic needles	Light yellow	4450	C = 79.1 (79.4); H = 4.9 (4.6)
Phenyl- <i>o</i> -cresol-p	133	"	"	4510	C = 79.5 (79.7); H = 5.3 (5.06)
Phenyl- <i>m</i> -cresol-p	146	"	" (hot)	4450	C = 79.4 (79.7); H = 5.4 (5.06)
Phenyl-carvacrol-p	236	"	Deep yellow (,,)	4480	C = 80.2 (80.4); H = 6.5 (6.1)
Phenyl-thymol-p	253	"	" (,,)	4480	C = 80.4 (80.4); H = 6.2 (6.1)
Phenyl-resorcinol-p	169	"	Orange yellow	4710	C = 75.2 (75.4); H = 4.7 (4.4)
Phenyl-catechol-p	86	"	red	5330	C = 75.3 (75.4); H = 4.5 (4.4)
Phenyl-quinol-p	241	"	Deep yellow	4565	C = 75.4 (75.4); H = 4.6 (4.4)
Phenyl- α -naphthol-p	229	"	"	4900	C = 81.5 (81.8); H = 4.7 (4.5)
Phenyl-phloroglucinol-p	117	"	"	4650	C = 72.0 (71.8); H = 4.4 (4.1)
Phenyl-pyrogallol-p	126	"	"	4725	C = 72.1 (71.8); H = 4.2 (4.1)
Phenyl- <i>m</i> -dimethyl-amido- pterol-p (free base)	124	Pink glistening needles	Pink (alcohol)	5550	N = 4.5 (4.4)
Ditto. (hydrochloride)	102	Pink glistening plates	" (water)	5550	N = 3.8 (3.8)

stannic chloride and he has described it as a colourless substance melting at 155° C., and dissolving in alkalis with a red colour like phenol-phthalein. This statement of Pechmann with regard to the behaviour of hydroxy-diphenyl-phthalein with alkali was rather surprising, since in accordance with the calculations of the present author from theoretical considerations, it ought to have a much weaker colour than phenol-phthalein. This led the present author to reinvestigate the problem, as the result of which it is now revealed that the *o*-benzoyl-benzoic acid used by Pechmann in 1881 for the preparation of hydroxy-diphenyl-phthalein melted at 87–94° C., which was apparently grossly contaminated with phthalic acid. Consequently the hydroxy-diphenyl-phthalein prepared by Pechmann from this material must have been largely admixed with phenol-phthalein, which accounted for the red colour given by his substance with alkali. The *o*-benzoyl-benzoic acid used in the present investigation was very carefully purified so as to make it perfectly free from phthalic acid, and the purest specimen on repeated crystallisation from xylene had a melting point of 129° C. On condensation with phenol in absence of any condensing agent or in presence of stannic chloride or a trace of concentrated sulphuric acid, hydroxy-diphenyl-phthalein is obtained which after exhaustive purification melted sharp at 92.5° C. and gave only a pale yellow coloration with dilute caustic soda. This was quite in accordance with expectations from theoretical considerations.

Encouraged by this promising result, the present author carried out further condensations of the pure *o*-benzoyl-benzoic acid with a number of phenols and amino-phenols and isolated the corresponding derivatives of diphenyl-phthalein in a state of great purity. The following substances were condensed with *o*-benzoyl-benzoic acid: phenol, *o*-cresol, *m*-cresol, carvacrol, thymol, catechol, resorcinol, quinol, pyrogallol, phloroglucinol, α -naphthol and *m*-dimethyl-amido-phenol. The absorption maxima of the condensation products have been determined and have been found to be considerably lower than those of the corresponding symmetrical phthaleins obtained from the respective phenol and phthalic anhydride (Table II).

In this connection it is interesting to note that similar reduction of the intensity of colour due to diminished tautomerism has been observed by Dutt and Agarwal³ in the case of organic salts and metallic derivatives of isonitroso-1 : 3-diphenyl-thiohydantoin as compared with the corresponding salts and derivatives of isonitroso-1 : 3-diphenylthio-barbituric acid prepared by Dharam Dass and Dutt.⁴ Whereas the first compound can tautomerise into only one strained form, the second can do this in two strained forms as shown in the diagrams given below, and as a consequence, the salts and derivatives of the former are only crimson in colour (absorption maxima between

TABLE II

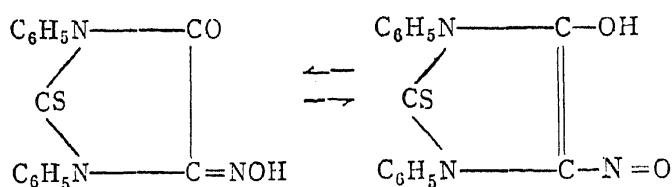
Comparison of the absorption maxima of the phthaleins derived from phthalic acid and o-benzoyl-benzoic acid

(Figures indicate wave-lengths in Angstrom units)

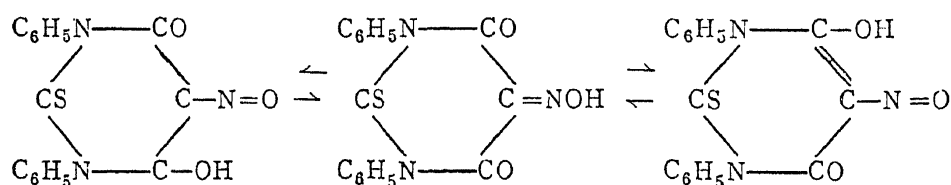
Compound derived from . . . and	Phthalic acid	<i>o</i> -Benzoyl-benzoic acid
Phenol	5550	4450
<i>o</i> -Cresol	5565	4510
<i>m</i> -Cresol	5555	4450
Carvacrol	5980	4480
Thymol	6030	4480
Resorcinol	4940	4710
Catechol	5960	5330
Quinol	5780	4565
α -Naphthol	5850	4900
Pyrogallol	5980	4725
Phloroglucinol	4980	4650
<i>m</i> -Dimethylamido-phenol ..	5550	5550

5320 Å and 5550 Å) but in the latter case they are green (absorption maxima between 5880 and 6610 Å), in spite of the fact that both the compounds possess almost identical molecular structures.

Isonitroso-1 : 3-diphenyl-thiohydantoin (crimson salts).

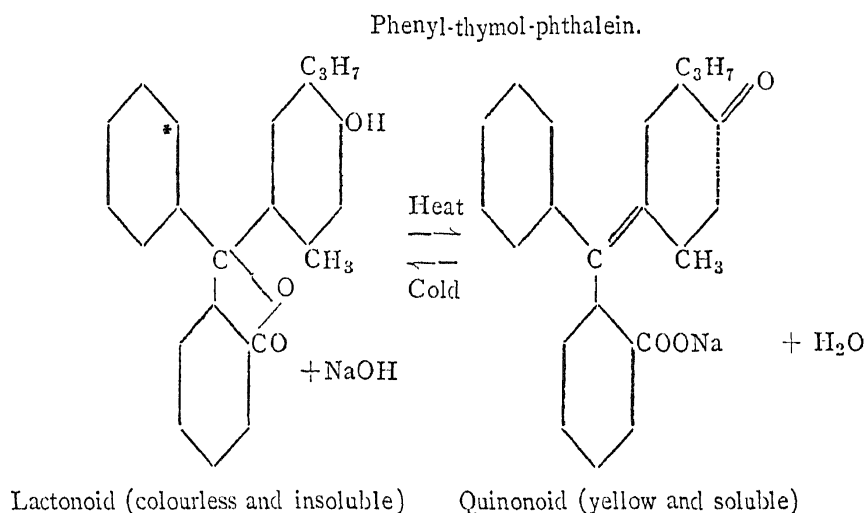


Isonitroso-1 : 3-diphenylthioarbituric acid (green salts).



A further point of interest in connection with the phthaleins of the mixed type described in this paper is that the condensation products with

the higher homologues of phenol tend to become progressively insoluble in dilute caustic soda with increasing molecular weight. But on heating them with concentrated aqueous or alcoholic caustic soda, they all dissolve with a characteristic bright yellow coloration, undoubtedly due to the fission of the lactone ring and formation of a quinonoid structure. But this colour disappears on cooling due to the reformation of the insoluble lactonoid form which gets precipitated. Thus phenyl-thymol-phthalein behaves in the following manner on treatment with concentrated caustic soda :



This behaviour is also characteristic of phenyl-carvacrol-phthalein and phenyl-*m*-cresol-phthalein.

Experimental

Preparation of o-benzoyl-benzoic acid.—This acid was prepared by a slight modification of the original method described by Pechmann.⁵ After six recrystallisations from boiling water and two from boiling xylene, the substance was obtained in glistening colourless prisms melting sharp at 129° C. The melting point did not rise any further after more crystallisations.

Condensation of o-benzoyl-benzoic acid with aromatic phenols and aminophenols.—The condensations were effected by heating an equimolecular mixture (1/10 gram-molecule) of the acid and the phenol at 150–160° C. in an oil-bath. The condensations take place without the use of any condensing agent and usually take about 5–6 hours for completion, for the quantity of materials indicated. The end of the reaction is indicated by the molten mixture becoming completely solidified. The addition of two drops of concentrated sulphuric acid or about 1 c.c. of stannic chloride greatly facilitates the reaction which becomes completed within one-fourth of the time otherwise taken in absence of any condensing agent. The condensation products

are purified by repeated extraction with boiling water so as to remove any unchanged *o*-benzoyl-benzoic acid, and the insoluble products are then crystallised from dilute alcohol, ether or benzene. The phthaleins of the mixed type obtained in this way have remarkable power of crystallisation, but are generally always obtained in the form of glistening prismatic needles. In the solid state, they are all colourless with the exception of the compound derived from *m*-dimethylamido-phenol, which is pink. For the sake of abbreviation, the properties and absorption maxima of these compounds in dilute aqueous caustic soda have been given in tabular forms (Table I).

Summary and Conclusions

1. Mixed or unsymmetrical phthaleins obtained by the condensation of pure *o*-benzoyl-benzoic acid with aromatic phenols and amino-phenols, many of which have been prepared for the first time, have been shown to have much less intense colour development on solution in alkali than pure or symmetrical phthaleins obtained by the condensation of the same phenols and amino-phenols with phthalic anhydride.

2. The cause of the above interesting phenomenon has been traced to the existence of less intense tautomerism between the lactonoid and the quinonoid forms of the unsymmetrical phthaleins as compared with those of the symmetrical phthaleins. In some cases the tautomerism only begins to make itself manifested under drastic circumstances, that is in hot solutions of concentrated alkali.

3. The colour phenomena exhibited by the unsymmetrical and symmetrical phthaleins on treatment with alkali are quite comparable with similar phenomena exhibited by isonitroso-1:3-diphenyl-thiohydantoin and isonitroso-1:3-diphenylthiobarbituric acid under identical conditions as studied by Dutt and his pupils, and due to the same cause.

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