COLOUR AND CHEMICAL CONSTITUTION.

Part XVI.—Further Miscellaneous Observations.

By James Moir.

The main lines of the theory of the colour of "cyclic" coloured substances having been established in Parts X, XIII, and XIV, it only remains to put on record observations of the absorption wave-length of all the "monocyclic" and "dicyclic" colours which I have used in making the discovery, but have not published for fear of overloading these theoretical papers with unnecessary detail.

A. Derivatives of the Prototype Colours.

1. *Orthopara-* or (2–4′)-dioxybenzhydrol, from salicylaldehyd (see Beilstein, ii, 1114). This has λ 543 (broad) in alkali, λ 486 in HCl, and λ about 495 when in suspension in neutral water. The isomeric *p–p*-compound has λ 539 in dilute alkali, but in HCl has the same λ as the *o–p*-compound.

2. 2-oxy-4′-dimethylaminobenzhydrol, from salicylaldehyd and dimethylaniline, has λ 561 (broad) in alkali, with λ 500 in HCl. The isomeric 4–4′-compound has λ 572 in alkali and λ 504 in acid. This was predicted (as λ 571) in Part XII, top of p. 211.

3. 2–4–4′-trioxybenzhydrol, from *p*-oxybenzaldehyd and resorcin, appears to have λ 494, whereas λ 550 was expected: possibly the reaction is abnormal.

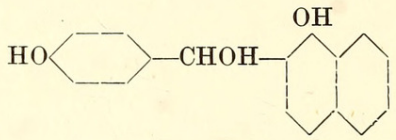
4. 2–4-dioxy-4′-methoxybenzhydrol, from anisaldehyd and resorcin, has λ about 380 in alkali. This substance appears to be monocyclic, since 2–4-dioxybenzhydrol has a similar λ.

5. 2–4-dioxy-3′–4′-dimethoxybenzhydrol-2′-carboxylic acid, from opianic acid and resorcin, has λ 390 in alkali. This is also monocyclic, being a derivative of monophenolphthalein (Part XIII, p. 38).

6. Mono-α-naphtholphthalein, from phthalaldehydic acid and α-naphthol, has λ 370, and is also monocyclic.

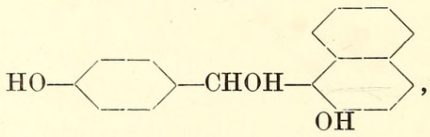
7. C-phenyl-derivative of foregoing, from benzoylbenzoic acid and α-naphthol, has λ 401 in alkali. In strong sulphuric acid, however, it has the much higher colour λ 543.

8. 1–4′-dioxybenznaphthydrol, from *p*-oxybenzaldehyd and α-naphthol, is violet with λ 590 in alkali. I have assumed the constitution to be



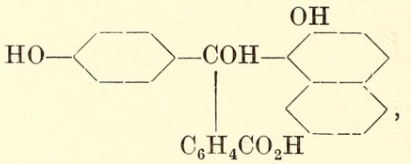
on the analogy of naphtholphthalein (Berichte, 1920, 1445).

9. The corresponding substance from β-naphthol,



or 2–4′-dioxybenznaphthydrol, has λ 556, with a *pink* colour.

10. Phenol-β-naphtholphthalein, the benzoic acid-derivative of the foregoing,



is now found to have λ 570 (broad). My statement in Part II (1918, p. 113), that it has λ 637, is erroneous.

The naphthol/phenol colour-factor from these two substances is quite different from that obtained when the C_4H_4 group of the naphthalene-ring is joined *metapara* to the benzhydrol linkage, viz. 1·026 for *orthometa-* as against 1·082 for *metapara*-attachment.

From these data I can roughly predict the wave-length of the still unknown *p–p–*α-naphtholphthalein to be about λ 628, that of the commercial *o–o–*α-naphtholphthalein being λ 662.*

B. Further Derivatives of Phenolphthalein (Part IV—*continued*).

(*a*) 3- (or 6)-oxyphenolphthalein, from 3-oxyphthalic acid, has λ 556 in NaOH and is higher in bicarbonate (λ 562).

* When, however, the hydroxyl is *para* to the benzhydrol linkage, a third naphthol/phenol factor comes into play. Its value is 1·042 (see Part XV, Naphthofluorescein). The true calculated λ of *p–p–*α-naphtholphthalein is 602. This is also the factor for safranines like Magdala-red.

(*b*) 3–6-dioxyphenolphthalein, from Thiele's dioxy-acid, gives a large difference between caustic and bicarbonate colour, viz. λ 549 and λ 563 respectively.

(*c*) 4–5-dioxyphenolphthalein, from normetahemipinic acid, gives a similar difference, viz. λ 558 in NaOH, and λ 568 in $NaHCO_3$.

(*d*) 5-methoxyphenolphthalein, from 4-methoxyphthalic acid, has λ 565.

(*e*) 3–6-dimethoxyphenolphthalein has λ 568.

(*f*) 4–5-dimethoxyphenolphthalein (" phenolmetahemipineine ") has λ 556.

(*g*) 5–6-dimethoxyphenolphthalein (" phenolhemipineine ") has λ 571.

I have to thank the Institute of Chemistry for obtaining for me small quantities of the necessary acids from unknown donors in the English universities.

(*h*) 3-nitrophenolphthalein, from 3-nitrophthalic acid, has λ 570. The value λ 559 was given in 1918, and is erroneous.

(*i*) a-nitro-fgjk-tetrabromophenolphthalein has λ 597 (blue-violet). (See Part XI, p. 130, for the nomenclature.)

(*j*) 5-nitrophenolphthalein, from 4-nitrophthalic acid, has λ 572. Its tetrabromo-compound has λ 599.

(*k*) 3–4–5–6- (or abcd)-tetrachlorophenolphthalein (" phenoltetrachlorophthalein ") has λ 581, scarcely different from that of the common (fgjk) isomer, viz. λ 583.

(*l*) Phenoldimethylalphanaphthylaminephthalein is *green*, λ 625.

C. Derivatives of Ghosh's Quinolinic Acid.

These are phthaleins with N for CH in the phthalic ring.

I. Phenolquinolineine has λ 533.
II. Orthocresolquinolineine has λ 544.
III. Thymolquinolineine has λ 593.
IV. Resorcinquinolineine has λ 490.
V. Orcinquinolineine has λ 496.

D. Derivatives of Triphenylcarbinol.

1. Ortho-oxy-malachite green (salicyl-green) has λ 627 in neutral solution, λ 572 in alkali, and λ 505 in acid.

2. 2′-oxy-4-dimethylaminofuchsone (foregoing with OH for NMe_2) has λ 490 neutral, λ 533 in alkali, and λ 479 in acid.

3. *p*-methoxy-malachite green, from anisaldehyd, has only one colour, viz. λ 605.

4. *p*-Methoxybenzaurine (=aurine methyl ether) has λ 551.

5. Dimethylaminodioxyphenyldinaphthylcarbinol, from dimethylaminobenzaldehyd and α-naphthol, has λ 730 when neutral and λ 492 when acid.

6. 2–2′–4–4′-tetraoxytriphenylcarbinol has λ 516 (non-fluorescent). On heating with zinc chloride this gives resorcin-benzein, λ 492 (very fluorescent).

7. Paranitro-malachite green has λ 642 in water. Formánek gives λ 637 in alcohol. The band is vague and not easily measured.

8. Nitro-oxy-dimethylaminotriphenylcarbinol, from 4-nitro-4′-oxybenzophenone, has apparently λ 610, whereas calculation gives λ 575. This requires reinvestigation.

9. Para-amino-malachite green (unsymm. tetramethylfuchsine), from reduction of No. 7, has λ 581 in acetic acid, λ 610 vague in stronger acid, and is yellow in HCl (λ about 420).

10. 2–2′–4–4′–4″-pentaoxytriphenylcarbinol (dioxyaurine) has λ 545.

11. Unsymm. dimethylparafuchsine, from dimethylaminobenzaldehyd and aniline hydrochloride, has λλ 547 and 493 when neutral, but when acidic shows vague bands at about λ 575 and near the red end (over λ 700), which is surprising.

E. Various Simple Coloured Substances.

(*a*) Quinonoxime. This has two vague bands at both ends of the spectrum, viz. about λλ 680 and 350.

(*b*) Sodium salt of foregoing (Na-*p*-nitrosophenol). In water λ 398. Baly gives λ 415 in alcohol.

(*c*) Nitrosodimethylaniline. The green base has λ 415+λ 725. The acetate has λ 457 alone : the chloride in HCl λ 390.

(*d*) 2–3-dicyano-quinol. This is colourless, but with a very strong fluorescence : λ about 330 neutral, λ 410 alkaline. The fluorescence of the salts of this substance is extraordinary, so that this is probably the simplest highly fluorescent substance.

(*e*) 3–6-dioxyphthalimide (from hydrolysis of above). This is yellow with λ 405 when neutral, but λ 480 in NaOH : highly fluorescent.

(*f*) 3-6-dioxyphthalic acid. When neutral this is nearly colourless with λ 370. Alkali turns it yellow (λ 437) with a marvellous fluorescence. The fluorescence must depend on the juxtaposition of ONa and COONa, since I find that sodium salicylate, when examined in presence of NaOH in sunlight, shows a fluorescence (violet).

F. Unclassifiable Observations.

I. Quinizarine : chief band λ 598.

II. 2-chloroquinizarine : chief band λ 601.

III. α-Naphthofluorane in conc. H_2SO_4 has λλ 500 and 475.
IV. Phenosafranine ("desensitol") has λλ 525+505 in water, and λλ 532+497 in alkali.
V. Quinhydrone in $AmHCO_3$: λ 480 broad.
VI. Tetrabromo-quinhydrone in NaOH: λ 510. (2-2′-6-6′ variety.)
VII. Quinhydrone of dimethylphenylenediamine: λλ 558+513.
VIII. ,, ,, tetramethylphenylenediamine: λλ 614+568.
IX. ,, ,, dihydrophenazine: λλ 701+640.

Note.—The quinhydrones obey the dicyclic colour laws, but the oxidation-factor is $\frac{2}{5}$, not $\frac{3}{5}$.