

COLOUR AND CHEMICAL CONSTITUTION.

PART XV.—A SYSTEMATIC STUDY OF FLUORESCEIN AND
RESORCIN-BENZEINE.

By JAMES MOIR.

In Part XI of this work (These T., Vol. IX, part 2, p. 129) a systematic study of phenolphthalein was undertaken, as a result of which the colour-value of substitution (by bromine taken as a standard substituent) of every one of the twelve hydrogen atoms in this compound was approximately determined.

As the nature of this investigation does not seem to have been fully understood overseas, *e.g.* by the abstractor of the London Chemical Society, I think it desirable to reprint the results in another form, viz. that of the "dicyclic colour-factors" explained in Parts X and XIV.

Table of Colour-factors for Bromine in Phenolphthalein.

				Colour-factor.	
Bromine substituted for hydrogen in the <i>a</i> position					=1·0180
"	"	"	"	<i>b</i>	" =1·0020
"	"	"	"	<i>c</i>	" =1·0145
"	"	"	"	<i>d</i>	" =1·0180
"	"	"	"	<i>e</i>	" =1·0270
"	"	"	"	<i>f</i>	" =1·0145
"	"	"	"	<i>g</i>	" =1·0145
"	"	"	"	<i>h</i>	" =1·0270
"	"	"	"	<i>i</i>	" =1·0235
"	"	"	"	<i>j</i>	" =1·0125
"	"	"	"	<i>k</i>	" =1·0125
"	"	"	"	<i>l</i>	" =1·0235

Note.—The numeration of the positions is that given on p. 130 of Part XI, and is also repeated here under fluorescein.

Thus to calculate the colour of phenol-tetrabromophthalein (which is

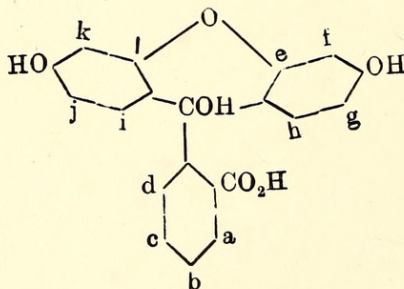
phenolphthalein with bromine for hydrogen in the *a*, *b*, *c*, and *d* positions), we have $\lambda_x = \lambda_0(554) \times 1.018 \times 1.002 \times 1.0145 \times 1.0180 = 583.6$.

Again, it was shown in Part IX, p. 225, that the factors for chlorine and iodine are almost the same as those for bromine. Putting in the numerical values into the algebraical formula given on that page, we find that the colour-factor for chlorine differs from that of bromine by 18×0.000037 , or 1 part in 1500, and that the colour-factor for iodine is greater than that of bromine by a like amount. Hence, for example, the calculated colour of phenol-tetrachlorophthalein is 583.6 (that of phenol-tetrabromophthalein just calculated) multiplied by $\left(\frac{1499}{1500}\right)^4$, chlorine having replaced bromine four times. This is 582.1. This agrees with observation, viz. $\lambda 581$ and $\lambda 582$ from two specimens. I am greatly indebted to Professors Partington of London and Mackenzie of Dundee for specimens of tetrachlorophthalic acid which they sent me after I had vainly tried to purchase it all over the world for three years.

Similarly, phenol-tetraiodophthalein should have $\lambda = 583.6 \times \left(\frac{1500}{1499}\right)^4 = 585.2$, but I have not been able to make (or obtain from its discoverer) this compound.

In the same way, the calculated colour of ordinary (*fgjk*) tetrabromophenolphthalein is $554 \times (1.0145)^2 \times (1.0125)^2 = \lambda 584.0$, and the calculated colours of tetrachloro- and tetriodophenolphthalein are $\lambda 584.0 \times \left(\frac{1499}{1500}\right)^4$ and $\lambda 584.0 \times \left(\frac{1500}{1499}\right)^4$ respectively. These agree with observation.

A.—Derivatives of Fluorescein.



Employing the same numeration of the positions as was used for phenolphthalein in Part XI, *i.e.* assuming that fluorescein is *e-l*-oxophenolphthalein, it is to be expected that the same colour-factors will hold good.

Unfortunately, the experimental difficulties have in some cases proved

too much for me, particularly as regards substitution in the h and i positions.

The following table contains my observations (note: λ fluorescein = 493 $\frac{1}{2}$):—

Substitution-products of Fluorescein.

	λ		λ
<i>a</i> -monobromo-	501	<i>a</i> -nitro-	500
<i>a</i> - <i>d</i> -dibromo-	509	<i>c</i> -nitro-	498
<i>c</i> -monobromo-	499	<i>a</i> -oxy-	{ 489 neutral 494 alkali
<i>a</i> - <i>c</i> -dibromo-	506	<i>b</i> - or <i>c</i> -oxy-	492
<i>a</i> - <i>c</i> - <i>d</i> -tribromo-	511*	<i>a</i> - <i>d</i> -dioxy-	493
<i>a</i> - <i>b</i> - <i>c</i> - <i>d</i> -tetrabromo-	514	<i>ad</i> -dimethoxy-	499
<i>a</i> -methoxy-	497	<i>b</i> - <i>c</i> -dimethoxy-	496
<i>b</i> - or <i>c</i> -methoxy-	492	<i>abc</i> -trimethoxy-	499
<i>a</i> - <i>b</i> - <i>c</i> -trichloro-	505	<i>a</i> - <i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -pentabromo-	529
<i>a</i> - <i>b</i> - <i>c</i> - <i>d</i> -tetrachloro-	513	<i>c</i> - <i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> - "	526
<i>g</i> - <i>j</i> -dibromo-	509	<i>a</i> - <i>c</i> - <i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -hexabromo-	535
<i>f</i> - <i>g</i> - <i>j</i> -tribromo-	515	<i>a</i> - <i>d</i> - <i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> - "	539
<i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -tetrabromo- } (eosine) }	521	<i>a</i> -nitro- <i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -tetrabromo-	530
<i>g</i> - <i>j</i> -dimethyl- } (cresorcin) }	500	<i>c</i> - " " "	529
<i>f</i> - <i>k</i> -dibromo- <i>g</i> - <i>j</i> -dimethyl-	516	<i>f</i> - <i>k</i> -dinitro- <i>g</i> - <i>j</i> -dibromo- } (" methyleosine ") }	522
<i>h</i> - <i>i</i> -dimethyl- } (" γ -orcinphthalein ") }	489½	<i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -tetrachloro-	518
<i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -tetrabromo-, der. of above	521	<i>abcdfgjk</i> -octochloro-	537
<i>h</i> - <i>i</i> -dioxy- (phloroglucin- phthalein) { 489 neutral 494 alkali		" -octobromo-	544
<i>h</i> - <i>i</i> -dimethyl- <i>abcd</i> -tetrachloro-	511½	<i>f</i> - <i>g</i> - <i>j</i> - <i>k</i> -tetriodo- } (erythrosine) }	525
<i>a</i> - <i>c</i> -dichloro- <i>fgjk</i> -tetrabromo-	538	<i>acdfgjk</i> -heptabromo-	540
<i>b</i> - <i>c</i> - " " " } (Phloxin M) }	529	<i>abc</i> -trichloro- <i>fgjk</i> -tetrabromo-	536
<i>abcd</i> -tetrachloro- <i>fgjk</i> -tetrabromo- } (Phloxin proper) }	544	<i>abcd</i> -tetrachloro- <i>g</i> -iodo-	520
<i>abcd</i> -tetrachloro- <i>fgjk</i> -tetraiodo- } (Rose bengale) }	548	" " <i>g</i> -iodo- <i>fkj</i> -tribromo-	543
[" α -orcinphthalein "	520 vague]	[" β -orcinphthalein "	440]†
Oxyquinolphthalein	550+527+509	[" Tribromo- β -orcinphthalein "	463]
		[" Quinolphthalein "	{ 494 neutral 499 alkali]
		Oxyquinoltetrachlorphthalein	577+530

* This may be *abd*: there is no means of deciding.

† The substances in brackets are related to fluorescein but are not direct derivatives.

It is probably unnecessary to describe the method of preparation of any of these substances, the information in Part XI about derivatives of phenolphthalein sufficing by analogy. It may be noted also that positions f and g are radically different in fluorescein, although they are almost the same in phenolphthalein. I have assumed, in assigning constitutions to these substances, that a substituent will enter the g and j positions first, since the other two *ortho*-positions, f and k, are "protected" by the oxo-linkage.

Deductions from the Observations.

A. The observations become consistent for the four "phthalic" positions, a, b, c, and d, if we assume *a*-monobromo- = *d*-monobromo- = +8, and also assume *b*-monobromo- to have no effect, and *c*-monobromo- = +4½.

Hence *a*-monobromo colour-factor in fluorescein = 1.0162

<i>b</i> -	„	„	„	=1.0000
<i>c</i> -	„	„	„	=1.0091
<i>d</i> -	„	„	„	=1.0162

These four factors therefore are smaller than those obtained for phenolphthalein, but their mutual variations resemble those of the phenolphthalein series, and the actual discrepancy is not much more than 1 part in 500, or than the error of observation. It follows therefore that the phthalic part of the fluorescein molecule does not differ much spatially from the phthalic part of the phenolphthalein molecule.

B. It has been impossible to make monobromo-compounds of the fgjk class, but by difference I estimate that f-bromo = k-bromo = +6, and that g-bromo = j-bromo = 7¼.

Hence f-monobromo colour-factor in fluorescein = 1.0122

<i>g</i> -	„	„	„	=1.0157
<i>j</i> -	„	„	„	=1.0157
<i>k</i> -	„	„	„	=1.0122

These four factors are not smaller than those obtained for phenolphthalein, and vary irregularly like an experimental error: nevertheless I think the small differences are real, and are due to the presence of the oxo-linkage.

As already stated, the *h* and *i* bromo colour-factors could not be ascertained by direct experiment. By inference from γ -orcinphthalein and phloroglucin-phthalein, however, I find them to be less than unity, viz. both the *h*-monobromo and the *i*-monobromo colour-factors are

about 0.990. This is completely discrepant with the phenolphthalein figures.

C. The chloro-derivatives follow as before from the bromo-derivatives by multiplying by $\frac{1499}{1500}$ as often as the change from bromine to chlorine is made.

D. The nitro-derivatives are not materially different from the bromo-derivatives. The a-, d-, g-, and j-nitro colour-factors are all about 1.016, and the c-, f-, and k-nitro colour-factors are all about 1.012.

E. The methyl colour-factors are considerably smaller than the bromo ones, the methoxyl colour-factors are smaller still, say 1.006 for the biggest of them, viz. the *a*-methoxyl, and the hydroxy colour-factors are smallest of all, practically unity. Indeed, when caustic alkali is employed all the oxy-derivatives of fluorescein have their absorption band in the same place as that of fluorescein. Gallein and oxyquinolphthalein constitute exceptions to this rule.

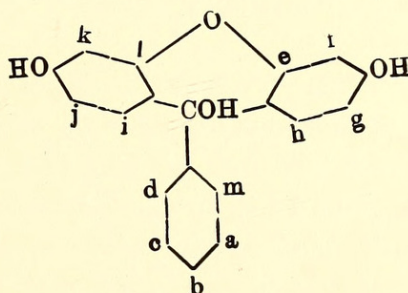
Two examples of the method of calculation may be given :—

1. *Octobromofluorescein* : $\lambda_x = 493.5 \times 1.0162 \times 1.0091 \times 1.0162 \times 1.0122 \times 1.0157 \times 1.0122 \times 1.0157 = 543.0$. The observed value was 544.

2. *Octochlorofluorescein* : $\lambda_x = \lambda \text{ for octobromofluorescein} \times \left(\frac{1499}{1500}\right)^8$.

This is 540.0. The observed value was 537. Further experiment may show that the ratio Cl/Br is not so near to unity, the error only showing in this extreme case.

B.—Derivatives of Resorcin-benzeine.



Resorcin-benzeine is phenyl-2-7-dihydroxy-xanthohydrol and is fluorescein minus the CO_2H group. The same numeration is therefore used, with *m* for the position occupied by the new hydrogen. Resorcin-benzeine in alkaline solution appears identical with fluorescein in colour and intensity of fluorescence. The absorption-band is at λ 492.

Substitution-products of Resorcin-benzeine.

	λ		λ
<i>a</i> - or <i>c</i> -oxy- . . .	{ 494 neutral 492 alkaline	<i>b</i> -bromo-	493
<i>b</i> -oxy-	{ 484 neutral 492 just alkaline 544 alkaline	<i>a</i> - or <i>c</i> -bromo-	497
<i>b</i> -methoxy-	493	<i>a</i> - or <i>c</i> -bromo- <i>b</i> -oxy-	{ 490 neutral 550 alkaline
<i>d</i> - or <i>m</i> -oxy-	430+492	<i>d</i> - or <i>m</i> -bromo-	505
<i>d</i> - or <i>m</i> -sulphonic acid	} 498	<i>b</i> -nitro-	500
“resorcin sulphophthalein”		<i>fgjk</i> -tetrabromo-	519
<i>fgjk</i> -tetrabromo- <i>m</i> -sulphonic acid	527	<i>fgjk</i> -tetrabromo- <i>b</i> -nitro-	527
		<i>b</i> -nitro- <i>d</i> - or <i>m</i> -sulphonic acid	506

It is to be noted that the list is limited from the fact that sulphuric acid cannot be used as condensing agent in making derivatives of resorcin-benzeine, because at an elevated temperature resorcin itself condenses to a coloured fluorescent compound “resorcin-ether,” the nature of which is at present unknown. It has a dirty rose colour in alkali with $\lambda\lambda$ 490 and 550 and a bluish-green fluorescence. Phosphorus oxychloride, if not overheated, forms a suitable condensing agent.

The conclusions to be drawn in the case of resorcin-benzeine are:—

A. The *f*, *g*, *j*, and *k* colour-factors are the same as those of phenolphthalein and fluorescein, viz. about 1.0135 on the average for bromine taken as standard. Further experiment is necessary to decide whether the *g*-factor is greater than the *f*-factor, and whether the *g*- and *j*-factors are identical, as they should be by symmetry.

B. In the phenyl ring the effect diminishes in the order *d*, *c*, *b*, but in this case the effect is still positive at *b*, although it appears to be *nil* in fluorescein and is sometimes negative in benzaurine. Much further work is necessary to clear up these small anomalies.

Addendum, 12th June 1922.—Professor G. T. Morgan kindly sent me a sufficient specimen of 1-3-dioxynaphthalene to enable naphthofluorescein to be made and examined. It has $\lambda\lambda$ 535 and 496. The ortho-meta naphthol/phenol factor is thus 1.042 in the dicyclic series. This could not be ascertained from naphtholphthalein, because the latter is a diortho-compound and therefore cannot be compared with phenolphthalein. This naphthalene factor can be employed to calculate the naphthosafranines and naphthacridines.

The effect of the naphthalene ring in the dicyclic series is practically the same as that of two bromine atoms substituted in the *gh* or *ij* positions: *i.e.* the *outer* carbons of the naphthalene ring have almost no effect. This is of great theoretical importance.



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