

# XXI. Chemical symmetry, or the influence of atomic arrangement on the physical properties of compounds

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XXI. *Chemical Symmetry, or the Influence of Atomic Arrangement on the Physical Properties of Compounds.* By THOMAS CARNELLEY, D.Sc., Professor of Chemistry in Firth College, Sheffield.

[Concluded from p. 130.]

## II. INFLUENCE OF ATOMIC ARRANGEMENT ON THE SOLUBILITY.

WE have seen that those compounds whose atoms are symmetrically arranged melt higher than those in which the arrangement is asymmetrical. Now let us see if there are not other physical properties which vary in this respect in the same way as the melting-point.

All bodies are acted on by at least two forces; one of which is the attraction between the molecules, and the other (viz. heat) tends to drive them apart. When the first force is in excess of the second, the body is solid; when the second is in excess, the body is a gas; when the two are about equally balanced, the body is liquid. Therefore the greater the attraction between the molecules the greater the temperature required to melt the body, and consequently the higher the melting-point. Having come to this conclusion, let us see if there are not other physical properties which depend on the attraction between the molecules, and which hence ought to be affected by symmetry of arrangement of the atoms in the molecule in the same way as the melting-point.

The first of such properties which suggests itself is solubility. In order that a solid may dissolve in any liquid, it is necessary that its molecules should undergo a sort of unloosening process; and we should therefore conclude that, of two isomeric compounds, that would dissolve the most easily in which the attraction between the molecules was the least, and which would therefore, as shown above, have the lowest melting-point. This argument shows, then, *that of two isomeric bodies that dissolves the most easily which has the lower melting-point, and in which therefore the atomic arrangement is less symmetrical.*

Let us now apply this rule in a few cases, and see whether symmetrical compounds are less soluble than their asymmetrical isomers. The following instances were taken quite promiscuously from Watts's 'Dictionary,' and are all that were tried, whether agreeing or not with the rule. The numbers in the third column represent the *order* of solubility; whilst the melting-point is taken as a measure of the symmetry:—

	Melting-point.	Order of solubility.	Remarks.
Diphenyl ben- } (1.2 or 1.3) zene, $C_6H_4Ph_2$ } (1.4)	85 205	1 2	} In alcohol, ether, $CS_2$ or $C_6H_6$ .
Phthalic acid, } $C_6H_4(COOH)_2$ } ..... { 1.2 1.3 1.4	175 $\alpha$ 300 does not melt.	? 1 2	
Dinitrobenzene, } ..... { 1.3 1.2 1.4	89 118 171	1 2 3 (?)	} In alcohol, benzene, or chloroform.
Dichlorobenzoic acid, } { 1.3.4 1.2.3 or 1.2.5 1.2.4	126 156 201	1 2 3	
Chlorobenzoic acid, } ... { 1.2 1.3 1.4	137 152 234	1 2 3	} In water.
Bromobenzoic acid, } ... { 1.2 1.3 1.4	147 155 250	1 2 3	
Nitrobenzoic acid, } ... { 1.2 1.3 1.4	143* 142 240	1 2 3	} In water.
Nitrobromobenzoic acid, { 1.2.5 $C_6H_3BrO_2$ } { 1.2.3	140 250	1 2	
Amidobenzoic acid, { 1.2 $C_6H_4NH_2COOH$ } { 1.3 1.4	144 173 186	1 2 3	} In water.
*Oxybenzoic acid, } ... { 1.2 $C_6H_4OHCOOH$ } { 1.3 1.4	156 200 210	2 ? 1	
Methoxybenzoic acid, { 1.2 $C_6H_4OCH_3COOH$ } { 1.3 1.4	99 106 175	1 1 3	} In water.
*Oxybromobenzoic acid, { 1.2.5 $C_6H_3BrOHCOOH$ } { 1.2.3	164 219	2 1	
Pyridine monocarboxylic acids:— Picolinic acid ..... Nicotinic acid .....	135 228	1 2	} In water.
Pyridine dicarboxylic acids ..... { $\gamma$ $\beta$ $\alpha$	237 243 245	1 2 3	

Table (continued).

	Melting-point.	Order of solubility.	Remarks.	
			Ba salt.	Pb salt.
†Toluene sulphonic acids, $C_6H_4.CH_3.SO_3H$ $\left\{ \begin{array}{l} 1.3 \\ 1.4 \\ 1.2 \end{array} \right.$	<div>Amide.</div> <div>108 136 154</div>	<div>1 2 3</div>	1	1
			2	2
			3	3
			} In water.	
Isostilbene, $CH_3 = C(C_6H_5)_2$ ..	Liquid.	1	} In alcohol.	
Stilbene, $C_6H_5.CH = CH.C_6H_5$	120	2		
Ditolyl, $CH_3.C_6H_4.C_6H_4.CH_3$ $\left\{ \begin{array}{l} 1.2; 1.4 \\ 1.4; 1.4 \end{array} \right.$	Liquid.	1	} In alcohol.	
		2		
Dinaphthyl ..... $\left\{ \begin{array}{l} (\alpha-\beta-) \\ (\alpha-\alpha-) \\ (\beta-\beta-) \end{array} \right.$	75	1	} In alcohol.	
	154	2		
	187	3		
Phenanthrene .....	100	1	} In alcohol.	
Anthracene .....	213	2		
Dinitrophenyl ... $\left\{ \begin{array}{l} (?) \\ 1.4; 1.4 \end{array} \right.$	93	1	} In alcohol.	
	213	2		

### III. INFLUENCE OF ATOMIC ARRANGEMENT ON THE HEATS OF FORMATION AND COMBUSTION.

We may compare the union of two or more atoms in the formation of a compound to the falling of a stone to the earth. The further the stone falls, the greater the amount of heat evolved on its being suddenly stopped; and the nearer the stone gets to the centre of the earth, the greater the attraction between the stone and the earth, and therefore the greater the force required to raise the stone—*i. e.* to separate it from the earth. In an analogous manner, the greater the heat produced in the formation of a compound from its elements, the greater its stability, and the greater therefore the force required to separate the atoms.

Again, if a stone falls halfway towards the earth's centre and afterwards falls the remaining half, then the heat given out at the second half of its journey would be less than in the

† The solubilities of the amides, Ba salts, and Pb salts of the three toluene-sulphonic acids obey the rule as regards the melting-point of the amides, the 1.4 amide, however, melts lower than the 1.2. It therefore seems probable that the orientation of the toluene sulphonic acids is incorrect.

second part of the journey of a stone which had first fallen only one quarter of the way towards the earth and afterwards fell the remaining three quarters. For a stone falling from a given height to the centre of the earth can only produce one given quantity of heat; and if it divides its fall into two parts, then the greater the amount of heat produced at the end of the first portion of its fall the less will be the amount produced in the second part of the fall.

And so it is in the formation of chemical compounds. Suppose we have a compound of carbon and hydrogen; this, on complete combustion, gives out a fixed and definite quantity of heat, say  $3x$ . If now, instead of being completely burnt to carbonic acid and water, the process stops at an intervening point with the formation of two isomeric compounds A and B, and if  $x$  units have been evolved in the formation of A and  $2x$  units in the formation of B, then the heat evolved by the further complete combustion of A and B will be  $2x$  and  $x$  respectively; i. e. of two isomeric compounds, the one which has the greatest heat of formation will have the least heat of combustion, and *vice versa*. We have also seen, that the greater the heat evolved in the formation of a compound from its elements the greater is the attraction between its atoms, and therefore the higher the melting-point. So that, of two isomeric compounds, that which has the highest melting-point will also have the greatest heat of formation and least heat of combustion.

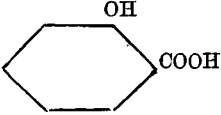
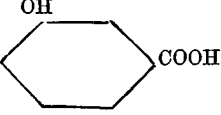
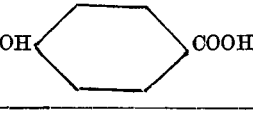
Now though isomeric compounds, as a rule, have *nearly* the same heat of formation, and therefore of combustion, yet they are not exactly the same in this respect. This being so, what is it that causes the difference, small though it may be? The cause can be nothing but the difference in the arrangement of the atoms in the two compounds. And from a comparison of all available data, which in this respect are very meagre, I venture to conclude

(1) *That the stability, and therefore the heat of formation, of symmetrical compounds (and therefore those with highest melting-points) is greater than that of asymmetrical compounds isomeric with them.*

If this be true, it will follow

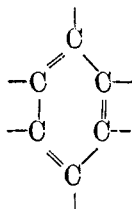
(2) *That the heats of combustion of the former compounds are less than those of the latter.*

The following table contains all the examples to which the above hypothesis can at present be applied:—

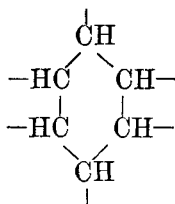
	Formula.	Melting-point.	Heat of formation.	Heat of combustion.
Salicylic acid ..... (1.2)		155	106	759
Metoxybenzoic acid (1.3)		200	111	754
Paraoxybenzoic acid (1.4)		210	115	750
Isopropylene glycol .....	$\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$	?	.....	436
Methylal .....	$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_3$	?	.....	434
Normal propylene glycol..	$\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	?	.....	431
Allyl alcohol .....	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$	?	?	443
Propyl aldehyde .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COH}$	?	69*	426
Acetone .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$	?	65	424
Mannite .....	$\text{CH}_2(\text{OH}) \cdot (\text{CH} \cdot \text{OH})_4 \cdot \text{CH}_2(\text{OH})$	166	287	760
Dulcite .....	?	185	294	753
Methyl formate .....	$\text{H} \cdot \text{COOCH}_3$	Liquid.	.....	252
Acetic acid .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{OH}$	17	.....	210
Ethyl acetate .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{OCH}_2 \cdot \text{CH}_3$	Liquid.	.....	554
Butyric acid .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	0	.....	497
*Methyl acetate .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{OCH}_3$	.....	.....	395
*Ethyl formate .....	$\text{H} \cdot \text{COOCH}_2 \cdot \text{CH}_3$	.....	.....	391
Methyl valerate .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOCH}_3$	.....	.....	856
Ethyl butyrate .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOCH}_2 \cdot \text{CH}_3$	.....	.....	823
Amyl acetate .....	$\text{CH}_3 \cdot \text{COOCH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	.....	.....	1036
Ethyl valerate .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO} \cdot \text{CH}_2 \cdot \text{CH}_3$	.....	.....	1019
Normal propyl alcohol ...	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	.....	.....	480
Isopropyl alcohol .....	$\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$	.....	.....	478
Isoamyl alcohol .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	Liquid.	.....	794
Dimethylethyl carbinol ...	$\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_3$	12	.....	788
Ethylvinyl carbinol .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} = \text{CH}_2$	.....	.....	753
Valeraldehyde .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$	.....	.....	742

These relations as regards the heats of formation and combustion of isomeric compounds are thrown out merely as suggestions; for the data are so extremely few in number that I should not be justified in doing more.

I may here mention that Julius Thomsen has shown that the determination of the heat of combustion will in many cases enable us to say whether two or more carbon atoms are united by single, double, or more linkings. Thus, he has shown that ethane is  $\text{CH}_3\text{—CH}_3$ , and propane  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$ , *i. e.* that their carbon atoms are united by single links only; whilst in ethylene and propylene two carbon atoms are connected by double linkings, thus,  $\text{CH}_2=\text{CH}_2$ , and  $\text{CH}_2=\text{CH}\cdot\text{CH}_3$ ; whereas in acetylene the two carbon atoms are bound by treble linkings,  $\text{CH}\equiv\text{CH}$ . Thomsen also concluded, from the heat of combustion, that the six carbon atoms in benzene are not bound by three double and three single linkings, thus,



but by nine single linkings, thus:—



Bruhl, however, as we shall see presently, concludes from the specific refraction of benzene that the old view is the correct one.

#### IV. INFLUENCE OF ATOMIC ARRANGEMENT ON OPTICAL ROTATION.

According to Pasteur (*Researches*, p. 27), molecules are divisible into two classes:—(1) those in which the atoms are symmetrically arranged, (2) those in which the arrangement is asymmetrical. The property of optical activity belongs to the latter class only; and Le Bel has proposed the hypothesis that when a carbon atom is united directly with four different

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elements or radicals, an asymmetrical form of molecule is produced, which must therefore be optically active. This view is supported by Van t'Hoff (*Bull. Soc. Chim.* [2] xxiii. p. 295), who finds, from the comparison of the chemical composition of all known active and many inactive bodies:—(1) *That every organic combination which rotates the plane of polarized light contains an atom of asymmetrical carbon.* The converse of this law, however, does not hold good. This may be attributed either to the presence of two isomerides of opposite rotatory power, or to the fact that asymmetrical carbon is not of itself sufficient to produce optical activity, which may also depend on the nature, as well as on the mutual diversity, of the atoms attached to the asymmetrical carbon atom. The following compounds are all optically active, and all contain an asymmetrical carbon atom, which for distinction is printed in black type:—

Lactic acid .....	$\text{CH}_3.\text{CH}(\text{OH}).\text{COOH}.$
Malic acid.....	$\text{COOH}.\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}.$
Malamide .....	$(\text{CONH}_2).\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}.$
Aspartic acid .....	$\text{COOH}.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}.$
Asparagine .....	$(\text{CONH}_2).\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}.$
Tartaric acid.....	$\text{COOH}.\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{COOH}.$
Tartaramide .....	$(\text{CONH}_2).\text{CH}(\text{OH}).\text{CH}(\text{OH}).(\text{CONH}_2).$
Secondary butyl carbinol...	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{CH}_2(\text{OH}).$
Methylethylacetic acid ...	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{COOH}.$
Hydroxyglutanic acid .....	$\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}.$
Glutamic acid .....	$\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}.$
Secondary butyl acetic acid.	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{CH}_2.\text{COOH}.$
Mannitol .....	$\text{CH}_2(\text{OH}).(\text{CH}.\text{OH})_4.\text{CH}_2(\text{OH}).$
Glucose.....	$\text{CH}_2(\text{OH}).(\text{CH}.\text{OH})_4.\text{COH}.$
Saccharic acid .....	$\text{COOH}.\text{CH}(\text{OH})_4.\text{COOH}.$
Phenylhydroxyacetic acid..	$\text{C}_6\text{H}_5.\text{CH}(\text{OH}).\text{COOH}.$

(2) *Derivatives of optically active combinations lose their rotatory power when the asymmetry of their carbon atoms disappears. When the contrary happens they do not generally lose it.*

These facts will in the future, no doubt, render great service in determining the constitution of optically active chemical compounds.



# V. INFLUENCE OF ATOMIC ARRANGEMENT ON MOLECULAR REFRACTION.

The molecular refraction of an element  $= \frac{A-1}{d} \times M$ ; where  $A$  = the index of refraction,  $d$  = specific gravity, and  $M$  = molecular weight.

Now Bruhl has recently shown, in a most important series of papers, that the molecular refraction of a compound containing polyatomic atoms is dependent on the manner in which these atoms are combined in the compound, whilst that of monatomic elements is quite independent of this.

The atom of a given element has a definite refractive equivalent, which it retains in all those compounds in which there are no double linkings; so that the refraction-equivalent of such a compound is equal to the sum of the refraction-equivalents of its constituent atoms; consequently, if we know the refraction-equivalents of each of the constituent atoms, we can readily calculate that of the compound. Thus, the refraction-equivalents of the following elements are:—

$$H=1.29; \quad O=2.71; \quad C=4.86;$$

and therefore the refraction-equivalent of alcohol,  $CH_3.CH_2.OH$ , which contains only single linkings, is

$$(2 \times 4.86) + (6 \times 1.29) + 2.71 = 20.17.$$

But we find that, in the case of those compounds containing double linkings between carbon atoms, the observed refraction-equivalent is always in excess of the calculated quantity, as shown in the table, p. 188.

Here we see that, for every double linking of carbon atoms, the refraction-equivalent is raised by two units.

Bruhl has also shown that a similar thing holds good in the case of other polyatomic elements besides carbon. Thus, oxygen, when combined with carbon by a double linking, as in acetic acid,  $CH_3.C=O$ , has a higher refraction-equiva-



lent (3.29) than when combined with only a single link, as in alcohol,  $CH_3.CH_2.OH$ , viz. 2.71.

Monatomic elements, on the other hand, possess refractive equivalents which are constant in all their compounds. The above will show at once what an important influence the double or single linking of atoms has on the refractive equiva-

	Structure.	Formula.	Molecular refraction-equivalent.		Difference.	No. of double linkings $\times 2$ = difference.
			Found.	Calculated.		
Propyl alcohol.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{C}_3\text{H}_8\text{O}$	28.00	27.61	0.39	$\left\{ \begin{array}{l} \text{No double linkings.} \\ = 1 \times 2 = 2 \\ = 2 \times 2 = 4 \\ = 2 \times 2 = 4 \end{array} \right.$
Amylene .....	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	$\text{C}_5\text{H}_{10}$	39.29	37.20	2.09	
Diallyl .....	$\text{CH}_2=\text{CH}\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_{10}$	45.99	42.06	3.93	
Valerylene .....	$\text{CH}_2=\text{CH}\text{CH}_2\text{CH}=\text{CH}_2$	$\text{C}_5\text{H}_8$	38.65	34.62	4.03	
Benzene .....	$\left\{ \begin{array}{c} \text{HC}-\text{CH} \\ \text{HC} \quad \text{CH} \\ \text{CH}=\text{CH} \\ \text{HC}-\text{CH} \end{array} \right\}$	$\text{C}_6\text{H}_6$	42.16	36.90	5.26	$= 3 \times 2 = 6$
Toluene .....	$\left\{ \begin{array}{c} \text{HC} \quad \text{C}-\text{CH}_3 \\ \text{CH}=\text{CH} \end{array} \right\}$	$\text{C}_7\text{H}_8$	50.06	44.34	5.72	$= 3 \times 2 = 6$
Mesitylene .....	$\left\{ \begin{array}{c} \text{CH}_3 \\ \text{C}-\text{C} \\ \text{C} \quad \text{C}-\text{CH}_3 \\ \text{C}=\text{CH}_3 \end{array} \right\}$	$\text{C}_9\text{H}_{12}$	65.22	59.22	6.00	$= 3 \times 2 = 6$

lents of compounds, and also what great service the knowledge of refraction-equivalents is capable of rendering in the determination of the constitution of compounds.

## VI. INFLUENCE OF ATOMIC ARRANGEMENT ON FLUORESCENCE.

Till within a few years ago, the number of bodies known which possessed fluorescing properties was very small. And it is only with the advance of the manufacture of coal-tar colours, and the investigations to which this advance has given rise, that a large number of fluorescing compounds has become known to us; so that the phenomenon of fluorescence has nowadays ceased to be a rarity. Up to the present, however, but little has been done in tracing any connexion between this property and the chemical constitution of the bodies exhibiting it. There can nevertheless be no doubt that it is dependent on a certain grouping of atoms—just as the tinctorial properties are dependent on special atomic groupings, as pointed out by O. N. Witt, to which I shall shortly refer.

Quite recently, Liebermann (*Ber.* xiii. p. 913) has made

an attempt to refer the fluorescent phenomena of the anthracene series to the chemical constitution of the members of this series. According to him, those derivatives fluoresce in which the two carbon groups binding together the two benzene rings possess the constitution  $C_6H_4 \begin{smallmatrix} \diagup CM \\ | \\ \diagdown CM \end{smallmatrix} C_6H_4$  (where M = a mono-atomic element or group); whilst those derivatives which contain the double ketone group  $C_6H_4 \begin{smallmatrix} \diagup CO \\ | \\ \diagdown CO \end{smallmatrix} C_6H_4$ , or the group corresponding to it in phenylanthracene,  $C_6H_4 \begin{smallmatrix} \diagup C(OH)(C_6H_5) \\ | \\ \diagdown CO \end{smallmatrix} C_6H_4$ , do not fluoresce. This rule he finds to hold good in the case of all the 60 to 70 compounds to which it can at present be applied; thus:—

*Fluorescent.*

Anthracene .....	$C_6H_4 \begin{smallmatrix} \diagup CH \\   \\ \diagdown CH \end{smallmatrix} C_6H_4$ .
Dichloranthracene .....	$C_6H_3Cl \begin{smallmatrix} \diagup CH \\   \\ \diagdown CH \end{smallmatrix} C_6H_3Cl$ .
Trichloranthracene .....	$X_1 \begin{smallmatrix} \diagup CH \\   \\ \diagdown CH \end{smallmatrix} X^*$ .
Dibromanthracene .....	„
Tetrachloranthracene .....	„
Anthracene sulphonic acid ...	$C_6H_4 \begin{smallmatrix} \diagup CH \\   \\ \diagdown CH \end{smallmatrix} C_6H_3.SO_3H$ .
$\alpha$ -anthracene disulphonic acid	$X_1 \begin{smallmatrix} \diagup CH \\   \\ \diagdown CH \end{smallmatrix} X^*$ .
$\beta$ -anthracene disulphonic acid	„
&c.	&c.

*Non-fluorescent.*

Anthraquinone .....	$C_6H_4 \begin{smallmatrix} \diagup CO \\   \\ \diagdown CO \end{smallmatrix} C_6H_4$ .
Anthraquinone sulphonic acid ...	$C_6H_4 \begin{smallmatrix} \diagup CO \\   \\ \diagdown CO \end{smallmatrix} C_6H_3.SO_3H$ .
Oxyanthraquinone .....	$C_6H_4 \begin{smallmatrix} \diagup CO \\   \\ \diagdown CO \end{smallmatrix} C_6H_3.OH$ .
Alizarine.....	$C_6H_3.OH \begin{smallmatrix} \diagup CO \\   \\ \diagdown CO \end{smallmatrix} C_6H_3.OH$ .
&c.	

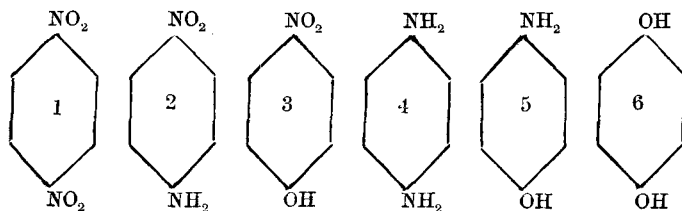
\* Constitution of X and  $X_1$  unknown.

The strength of the fluorescence is very different for different members of the fluorescing series. Thus,  $\beta$ -anthracene disulphonic acid is strongly fluorescent, whilst the  $\alpha$ -acid is but slightly so.

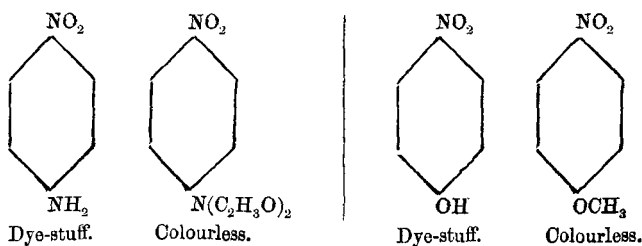
## VII. INFLUENCE OF ATOMIC ARRANGEMENT ON THE TINCTORIAL PROPERTIES.

The influence of chemical constitution on the tinctorial properties of compounds has been studied more especially by Otto Witt (*Ber.* ix. p. 522), whose more important conclusions may be briefly stated as follows :—

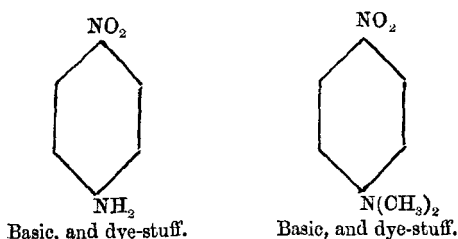
Since benzene is not a dye-stuff, it follows that colouring-properties are conditioned by the side chains. Of the three side chains,  $\text{NO}_2$ ,  $\text{NH}_2$ ,  $\text{OH}$ , not one of them alone is capable of producing a compound possessing tinctorial properties; for  $\text{C}_6\text{H}_5.\text{NO}_2$ ,  $\text{C}_6\text{H}_5.\text{NH}_2$ ,  $\text{C}_6\text{H}_5.\text{OH}$  are all colourless bodies. It is possible, however, that certain combinations of two or more of these groups will produce the necessary result; thus, of the six possible compounds,



only 2 and 3 are dye-stuffs. We therefore see that the combination of the nitro-group with the amido-, or hydroxyl groups, produces a colouring compound; or, in other words, the presence of a  $\text{NO}_2$  and a salt-forming group conditions the dyeing properties. The nitro-derivatives of benzene are to a certain extent coloured; but it is only on the introduction of a salt-forming radical that we get a true dye-stuff. That to obtain a dye-stuff the presence of a  $\text{NO}_2$  group and a salt-forming radical is necessary, is shown by the fact that if we destroy the basicity of an amido-group by the introduction of an acetyl group, or if we destroy the acidity of a hydroxyl group by introducing a methyl group, the compound entirely loses its colouring-properties, though by these changes no alteration has been produced in the general constitution of the compound. Thus



If, however, we methylate the NH<sub>2</sub> group of nitro-aniline, we do not destroy its tinctorial properties, because we do not at the same time destroy its basicity. Thus



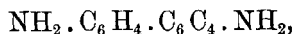
From such considerations as these Witt has enunciated the following laws:—

(1) *The tinctorial properties of aromatic compounds are conditioned by the simultaneous presence of a colour-imparting group (such as a nitro-group) and of a salt-forming group (such as NH<sub>2</sub> or OH group).*

The colouring group he terms the *chromophor*; and a compound containing a chromophor, and in which a salt-forming radical is still wanting for the formation of a dye-stuff, he calls a *chromogen*: thus NO<sub>2</sub> is the chromophor of C<sub>6</sub>H<sub>4</sub>.NO<sub>2</sub>.NH<sub>2</sub> and C<sub>6</sub>H<sub>4</sub>.NO<sub>2</sub>.OH, whilst C<sub>6</sub>H<sub>5</sub>.NO<sub>2</sub> is the chromogen of both compounds.

Further, the tinctorial properties increase with the number of NO<sub>2</sub> groups present; thus, the nitrodiphenylamines are all acids and dye-stuffs, and their dyeing-power increases with the number of NO<sub>2</sub> groups.

Again, azobenzene, C<sub>6</sub>H<sub>5</sub>.N=N.C<sub>6</sub>H<sub>5</sub>, though of a dark yellow colour, is not a dye-stuff; nor is benzidine,



though it is a strong base; but as soon as we combine the properties of the two, by introducing into the latter compound the chromophor —N=N—, or a salt-forming group into the former, we get a series of beautiful dye-stuffs.

Another point observed by Witt is

(2) *The chromophor exerts its tinctorial influence much more in the SALTS of a dye-stuff than when the latter is in the free state.*

Thus, nitraniline, nitrophenol, and picric acid, when pure, are pale yellow, whilst their salts are dark orange and sometimes red.

Again,

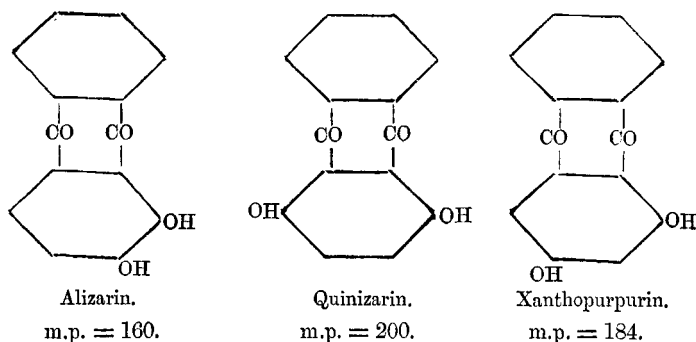
(3) *Of two dye-stuffs, both possessing in other respects a similar constitution, that has the highest tinctorial power whose salts are the most stable.*

Since most dye-stuffs owe their basicity or acidity to the presence of the  $\text{NH}_2$  or  $\text{OH}$  group, each chromogen may give rise to two colouring compounds. All dye-stuffs, therefore, may be arranged in pairs; and it is worthy of notice that corresponding dye-stuffs always have a similar colour. Thus,

Nitrophenol .....	$\text{C}_6\text{H}_4.\text{NO}_2.\text{OH}$	} bright yellow.
Nitroaniline .....	$\text{C}_6\text{H}_4.\text{NO}_2.\text{NH}_2$	
Picric acid .....	$\text{C}_6\text{H}_2.(\text{NO}_2)_3.\text{OH}$	} dark yellow.
Trinitraniline ...	$\text{C}_6\text{H}_2.(\text{NO}_2)_3.\text{NH}_2$	
Amidoazobenzene	$\text{NH}_2.\text{C}_6\text{H}_4.\text{N}=\text{N}.\text{C}_6\text{H}_5$	} yellow.
Oxyazobenzene...	$\text{OH}.\text{C}_6\text{H}_4.\text{N}=\text{N}.\text{C}_6\text{H}_5$	
Tetramidotetrazotriphenyl .....		} brown.
Tetroxytetrazotriphenyl .....		
Rosaniline .....		} red.
Rosolic acid .....		
Dioxyanthraquinone or alizarin .....		} red or violet.
Diamidoanthraquinone .....		

All the compounds referred to above (except the two anthraquinone derivatives) contain a nitrogenous chromophor. The dye-stuffs of anthraquinone, however, show that a carbon group may be a chromophor. Neither anthraquinone nor dioxyanthracene are dye-stuffs; whilst a combination of both, viz. alizarin or dioxyanthraquinone, is a powerful colouring agent. The double ( $-\text{CO}-$ ) group is therefore the chromophor of alizarin and the related dye-stuffs. These compounds also lose their colouring-properties on the introduction of methyl into the hydroxyl groups. If we increase the salt-forming power of alizarin by introducing more hydroxyl groups, or by nitration or amidation, we also increase the tinctorial properties. Further, in alizarin and the related

dye-stuffs, one of the hydroxyl groups must be in the ortho-position as regards the ( $\text{—CO—}$ ) group in order that the compound may be a dye-stuff. For there are numerous isomers of alizarin, but most of them are colourless, only quinizarin and xanthopurpurin possessing tinctorial properties; and in these, as well as in alizarin, one of the HO groups is in the ortho-position, thus :—



In the above sketch I have endeavoured to give a brief account of the more important facts which have come to light during late years in reference to the influence of chemical constitution on the physical properties of organic compounds.

I had intended saying something of this influence of atomic arrangement on the specific volume of compounds and also on the chemical activity, or the susceptibility of certain elements or groups of elements in a compound being replaced by other elements or groups of elements; but my remarks have already attained more than sufficient length, and to do these latter subjects full justice would require the space of another paper.

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XXII. *Apparatus for calculating Efficiency.* By C. VERNON BOYS, A.R.S.M., *Demonstrator of Physics at the Normal School of Science, South Kensington*.\*

[Plate V.].

IN a previous paper I have shown how work done in an engine or transmitted by shafting or belting, or expended by an electric current, or how the quantity of electricity which has passed in a conductor during any time, may be automatically measured and integrated or recorded. The present paper refers to apparatus for dividing rates of growth

\* Communicated by the Physical Society, having been read at the Meeting on January 28, 1882.