LV.—*The Influence of Conjugated Linkings on General Absorptive Power. Part I. The Absorption Spectra of Some Benzene Derivatives.*

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WHEN an attempt is made to classify the various types of absorption spectra, the first distinction which is drawn is between what is termed general absorption and selective absorption: that is, compounds are divided into those which show a banded absorption spectrum and those which, showing no banded absorption, merely allow more and more of the spectrum to pass through their solutions as the latter are diluted. At the first glance, these two types appear to be quite distinct from one another, but further consideration will show that general absorption may be merely a

H H 2

special case of selective absorption in which the apparatus devised up to the present is not sufficiently sensitive to detect the other side of the band. For instance, the ordinary photographic plate is sensitive up to a frequency of between four and five thousand; but if the head of a band in any substance lay beyond this region, we should have no means of determining its position, and consequently we should assume that the substance in question gave merely general absorption. The only method which seems likely to throw light on the problem is to study the influences which affect general and selective absorption with a view to correlate the two types. The present paper represents an attempt to determine the influence of unsaturated groupings in the molecule on general absorption.

It was shown by Thiele (*Annalen*, 1899, **306**, 87) that the grouping (I), on reduction, yielded a grouping (II), and not, as was expected, the grouping (III):

and to explain this he put forward his "partial valency" hypothesis, in which he assumed that the affinities of the carbon atoms on either side of the double bonds are not completely saturated, but that there remain partial valencies which, remaining free, are ready to attach themselves to fresh atoms outside the system. The two partial valencies on either side of the central single bond are supposed mutually to saturate each other and thus become temporarily inactive.

It has been shown by Brühl (*Ber.*, 1907, **40**, 878) that such a grouping has a strong influence on refractive power, producing higher values than the calculated refractivity. Hilditch (*Trans.*, 1909, **95**, 331, 1570, 1578; 1910, **97**, 1091; Edminson and Hilditch, *ibid.*, 1910, **97**, 223) has traced the same influence in the case of optically active substances. Analogous results were observed by Pascal (*Compt. rend.*, 1909, **149**, 342) in the case of diamagnetic power. Sir W. H. Perkin (*Trans.*, 1896, **69**, 1141) proved that a similar effect was noticeable in the case of magnetic rotation. One of the present authors, in conjunction with Professor Baly, drew attention to the fact that two conjugated carbonyl groups had a very marked influence on absorption spectra, an absorption band being developed in the spectra of compounds which contain such a grouping.

Bearing the foregoing in mind, it seemed desirable to turn to the question of general absorption and examine the spectra of various isomerides which contained systems of one or more conjugated double bonds, with a view to determine the effect which

the presence of the conjugation produced on the absorptive power of the substances. The present paper contains an account of the investigation of some benzene derivatives.

It is clear that comparisons can only be made between two sets

of isomeric substances; since the carbon atom in itself appears to exert a certain absorptive power, it would not be proper to compare the general absorptions of two substances one of which contained more atoms than the other.

In the first place, we may consider a group of six compounds

which are closely allied to one another, namely, eugenol, safrole, and apiole, with the corresponding *iso*-compounds (see Figs. 1, 2, and 3):

An examination of the six formulæ above will show that in the case of eugenol and its analogues the double bonds in the side chains are not conjugated with the benzene nuclei; in the case of *isoeugenol* and its congeners, on the other hand, an extra conjugation is introduced, for the double bond in the side chain has been brought nearer to the benzene nucleus, and is now part of the conjugated system.

Turning now to the curves, we must make a selection of the particular region of the spectrum which we propose to examine. As we are dealing with general absorption, it is quite evident that we should not examine the portion of the spectrum which forms part of an absorption band, but that we must deal with some section which lies sufficiently far away from the banded region to be secure from interference on the part of factors which exert influence on selective absorption. If we choose the region lying between 10 mm. of $N/10$ and 10 mm. of $N/100$, we shall avoid the bands which appear in these thicknesses of $N/1000$ and more dilute solutions.

Inspection of the six curves will show that in every case the compound containing the system of four conjugated double bonds has a greater absorptive power than that which only contains three. This assumes that the benzene nucleus contains a system of three conjugated double bonds, but the conclusion is equally true if we consider the benzene system simply as a reservoir of residual affinity, for in that case we have the two unsaturated systems (nucleus and double bond) separated in eugenol and its

Fig. 2.

Fig. 3.

analogues, but conjugated together in *isoeugenol*, *isosafrole*, and *isoapiole*.

Let us next turn to the case of the two substances, acetophenone-oxime and acetanilide (see Fig. 4). Here again we have the benzenoid nucleus in each case, but in acetophenoneoxime we have an extra-nuclear conjugation provided by the group $\cdot\text{C}:\text{NOH}\cdot$ which is absent in acetanilide, the carbonyl group in the latter substance being separated from the nucleus by the interposition of the imino-group:

As can be seen from the curves, the rule holds in this case also, for the absorptive power of acetophenoneoxime is much greater than that of acetanilide.

Another example of the same rule is to be found in the cases of phenyl acetate and methyl benzoate:

In the first substance, we have no conjugation apart from that comprised within the benzene system, but in methyl benzoate we have the carbonyl group conjugated with the nucleus. An inspection of the curves in Fig. 5 will show that methyl benzoate has an absorptive power greater than that of the isomeric substance.

We now come to two pairs of isomerides which form a crucial test of this hypothesis. It will be remembered that in his original paper on the partial valency hypothesis (*Annalen*, 1899, **306**, 111) Thiele considered the case of what he termed "crossed double bonds," and showed that in a system of the following type:

one end of the double bond between the atoms 3 and 4 is conjugated with both the other double bonds. Now, if this be so, it is clear that such a system cannot be regarded as conjugated to the same extent as a system of double bonds, such as:

in which the partial valencies neutralise one another in the ordinary manner, leaving only one partial valency free at each end of the system.

In system (A) the partial valency of the atom (4) would have to neutralise not only the partial valency of the atom (2), but also that of the atom (5), and it is clear that in such a case as this we have incomplete conjugation. Such an instance is provided

Fig. 4.

Fig. 5.

by atropic acid, for in it the double bond of the group $\cdot\text{CH}_2$ is conjugated with the double bond of the carbonyl group, and also with the nucleus. Compare this with the isomeric cinnamic acid:

In cinnamic acid, the whole five double bonds form a single conjugated system, whereas in atropic acid, if we regard the first four as a conjugated system, it is clear that the fifth double bond will act as a disturbing influence, tending to absorb some of the partial valency of the atom marked with an asterisk, all of which ought to be devoted to saturating the partial valency of the atom of the benzene ring to which it is attached. It is clear therefore that in cinnamic acid we have a complete system of conjugation, including within itself all the double bonds of the molecule, whereas in atropic acid we have two conflicting systems, and we should therefore expect to find that the absorption of cinnamic acid was more powerful than that of atropic acid. A glance at Fig. 6 will show that this view is correct.

An analogous case is to be found in benzophenoneoxime and benzanilide:

Here the double bond of the group $\cdot\text{C}(\text{NOH})\cdot$ is conjugated with one double bond in each of the nuclei, whilst in benzanilide no such system of crossed double bonds exists, but, instead, we have two separate systems of conjugation. In both substances we have the same number of double bonds, namely, seven, but whilst in benzanilide we have the double bonds 1, 2, 3, and 4 forming a complete and self-contained conjugated system uninterfered with by the bonds 5, 6, and 7 of the second nucleus, in benzophenoneoxime we have the conjugated system of 1, 2, 3, and 4 disturbed by the intrusion of the bond 5. Thus, in benzophenoneoxime, although we have the same number of double bonds as in benzanilide, their distribution is such as to prevent the complete neutralisation of the partial valencies which is found in true conjugated systems except at their ends. From this, we should expect to find that benzanilide, having most true conjugation in its molecule, had the greater absorptive power, and an inspection of Fig. 7 will show that this is the case.

FIG. 6.

FIG. 7.

In a set of curves published by Baly and Tuck (Trans., 1906, **89**, 982) we have noticed half-a-dozen other examples of this general rule. It is known that when the phenylhydrazones of aldehydes or ketones are exposed to light, they tend to change into azo-compounds. Taking the case of acetaldehydephenylhydrazone as an example, the structures of the two substances are:

It will be seen that in the first compound the double bond $\cdot\text{N}\cdot\text{CH}\cdot$ is not conjugated with the nucleus, whereas after exposure to light the nucleus is conjugated with the double bond $\cdot\text{N}\cdot\text{N}\cdot$. An examination of the curves given by Baly and Tuck shows that the "conjugated isomeride" has greater absorptive power than the unconjugated hydrazone.

A final instance may be adduced in favour of our views. It has been shown by Hartley and Dobbie (Trans., 1900, **77**, 498) that the general absorptive power of the enolic form of ethyl dibenzoyl-succinate is much greater than that of the ketonic modifications. A layer of 25 mm. thick of a solution containing one milligram-molecule of the enolic variety in 100 c.c. of alcohol cuts off all rays beyond a frequency of 2171, whereas a corresponding experiment with the ketonic isomeride showed that light is transmitted up to a frequency of 2795. Thus the absorptive powers of the two substances differ by no less than six hundred units under these conditions:

Inspection of the two formulæ will show that in the ketonic form the only conjugation is that between the nuclei and the adjacent carbonyl radicles; the two carbonyl groups of the carboxyl radicles are not in conjugation with any double bonds. In the enolic form, on the other hand, the carbonyl radicles of the carboxyl groups are drawn into the general system of conjugation. Thus, in the ketonic form, we have the conjugation of nucleus and $\cdot\text{CO}\cdot$ group occurring twice, whilst in the enolic form we have the conjugation of nucleus, ethylenic bonds and carbonyl radicle occurring twice. The latter system is probably weakened by the cross-conjugation of the two ethylenic bonds with each other, but even after deducting a considerable amount for this, we are left with a marked preponderance of conjugation in the enolic and more absorptive form of the substance.

Results similar to those which we have described above have been obtained by us in the alicyclic and open-chain compounds also, and these will furnish the basis of a future paper. The data in the present paper include fourteen pairs of isomerides of the most different types; and we believe that it is established that if we examine two isomeric substances, that which contains the greater number of true conjugated bonds within the molecule will show the greater power of general absorption. These results seem likely to be of interest in the case of terpenes containing two double bonds the relative positions of which have not been definitely established, as a comparison of their general absorptive power with that of isomeric substances of known constitution would enable us to decide whether or not the terpenes in question contained conjugated or unconjugated linkings. We might also mention that in the course of this work we have observed another relation which appears to be general. If the absorptive power of two isomeric substances, one of which is capable of conversion into the other, be examined, we have found that the stable isomeride shows greater absorptive power than the labile form, for example, *n*-propyl bromide has less absorptive power than *isopropyl* bromide, into which it can be converted by heating. This rule holds in those cases where there is no conjugated system in the molecule.

EXPERIMENTAL.

Eugenol.—This substance was obtained from Kahlbaum, and was purified by fractionation under diminished pressure.

isoEugenol.—This was obtained from Kahlbaum, and was twice distilled, the fraction boiling at 167–168° being finally taken.

Safrole.—This was obtained from Kahlbaum, and was re-distilled until it had the correct boiling point.

isoSafrole.—Obtained from Kahlbaum. On re-distillation, the middle fraction boiled absolutely constant at 251°/760 mm.

Apiole.—This was purchased from Schuchardt. It had the correct melting point.

isoApiole.—This also was obtained from Schuchardt. It was re-crystallised from aqueous alcohol until it melted at 56°.

Acetophenoneoxime.—This was prepared by one of us, and re-crystallised from light petroleum until it melted sharply at 59°.

Acetanilide.—This was a Kahlbaum specimen, purified in the usual way (m. p. 113°). Two separate specimens of the oxime and the anilide were prepared and photographed, the spectra being found to be identical.

Methyl Benzoate.—This substance was prepared by one of us by the action of benzoyl chloride on methyl alcohol. It was

462 ABSORPTION SPECTRA OF SOME BENZENE DERIVATIVES.

fractionally distilled several times, and the fraction boiling constantly at $199^{\circ}/756$ mm. was used.

Phenyl Acetate.—This was prepared by one of us from acetyl chloride and phenol. It was purified until it boiled constantly at $195.8^{\circ}/756$ mm.

Cinnamic Acid.—Part of the curve of this substance had already been published by one of us (Stewart, Trans., 1907, **91**, 202). The compound was re-photographed at higher concentrations, and the two curves were found to be coincident.

Atropic Acid.—A specimen obtained from Schuchardt (m. p. 106.5°).

Benzophenoneoxime.—Prepared in the usual manner. Recrystallised from aqueous alcohol until it had the correct melting point.

Benzanilide.—This was obtained from Kahlbaum, and purified by recrystallisation from alcohol.

Conclusions.

1. The following rule regarding general absorption has been established. Of two isomeric substances containing two or more double bonds, the compound the molecule of which contains the longest chain of conjugations will have the greater absorptive power in the region of the spectrum above that in which any absorption bands make their appearance.

2. In the case where two isomeric substances contain the same number of double bonds, it appears that the compound containing three conjugated groups in a single system :

will have an absorptive power greater than one containing a system of so-called "crossed double bonds":

3. As this rule has been found to hold good in the case of alicyclic substances as well as in the benzene and aliphatic series, it furnishes a possibility of obtaining additional evidence of the structure of terpenes containing two double bonds the relative positions of which are not established.

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