

LXX.—*The Absorption Spectra of Substances containing Conjugated and Unconjugated Systems of Triple Bonds.*

By ALEXANDER KILLEN MACBETH and ALFRED WALTER STEWART.

It has long been known that saturated substances possess an absorptive power much lower than that shown by the corresponding ethylenic derivatives; and further investigations have proved that of two isomeric diethylene derivatives, that which contains a conjugated system of double linkings has a greater absorptive power than the isomeride in which the ethylenic bonds are isolated from each other (Crymble, Stewart, Wright, and Glendinning, T., 1911, **99**, 451; Crymble, Stewart, Wright, and Miss Rea, *ibid.*, 1262). The present investigation was undertaken with the idea of testing whether or not a similar rule could be established in the case of acetylenic derivatives, but the results show that no such generalisation can be looked for in this series. The data, however, are of some interest from other points of view.

It was decided to examine acetylenic compounds belonging to both aliphatic and aromatic series. Some of the latter class had already been investigated by Stobbe (*Ber.*, 1911, **44**, 1289), but no general rule could be deduced from his results, as the phenyl nucleus might be expected to interfere with the influence of the acetylenic linking to some extent.

It will probably render the data clearer if the discussion of each group of compounds be taken separately, final conclusions being reserved until the whole facts have been reviewed.

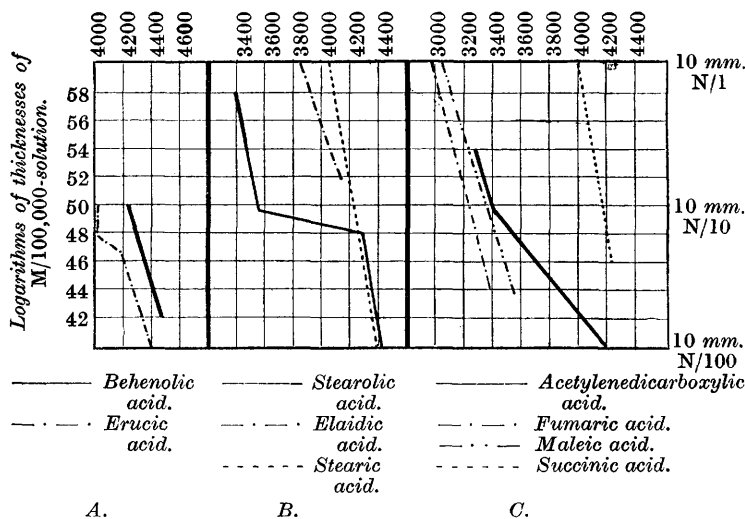
*Series I. Behenolic Acid and Erucic Acid (Fig. 1, A).—Here*

the ethylenic derivative is much more absorbent than the acetylenic analogue. In this case, the effect of the double and triple linkings may be taken as being unaffected by the presence of the carboxyl radicle, from which they are separated by eleven methylene groups.

*Series II. Stearolic Acid, Elaidic Acid, and Stearic Acid* (Fig. 1, *B*).—In this case, the acetylenic derivative is the most strongly absorbent, the ethylenic next, and the saturated substance least of all. The only factor that might account for this marked absorptive power of the acetylenic substance is to be found in the fact that the carbonyl radicle of the carboxyl group is

FIG. 1.

Oscillation frequencies.

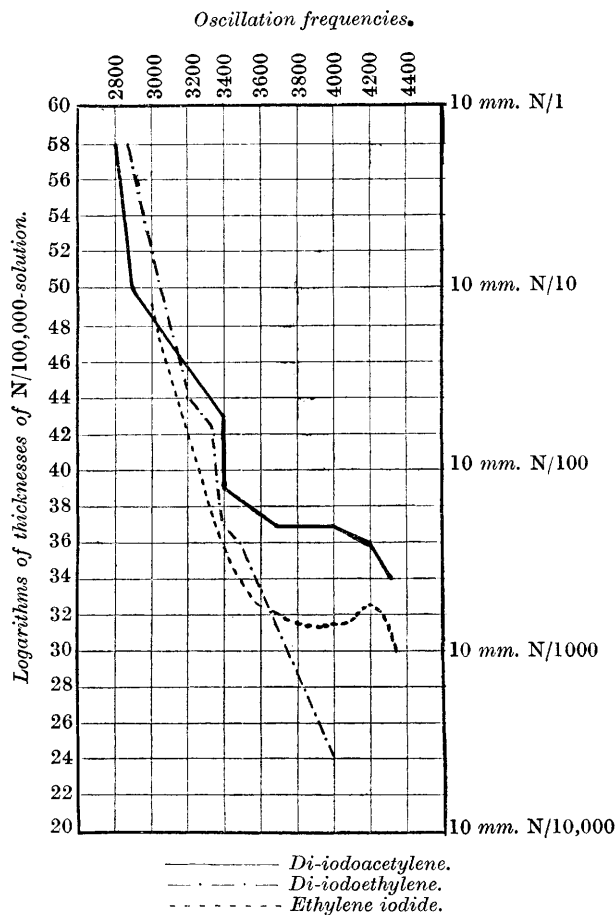


situated at the ninth carbon atom from both the triple and double linkings, which would imply, under the usual assumptions as to the arrangements of carbon chains in space, that the unsaturated centres were spatially conjugated with two turns of the spiral between them. It is sufficient to indicate this and leave the matter without further elaboration.

*Series III. Acetylenedicarboxylic Acid, Fumaric Acid, Maleic Acid, and Succinic Acid* (Fig. 1, *C*).—As can be seen from the graph, the two ethylenic isomerides are more absorbent than the acetylenic compound—fumaric acid being markedly so—and succinic acid is least absorbent of all.

*Series IV. Di-iodoacetylene, Di-iodoethylene, and Ethylene iodide* (Fig. 2).—This case presents a fresh problem. The saturated compound, ethylene iodide, possesses a distinct absorption band having its head at a frequency of 3900, and this band is directly attributable to the presence of the two iodine atoms

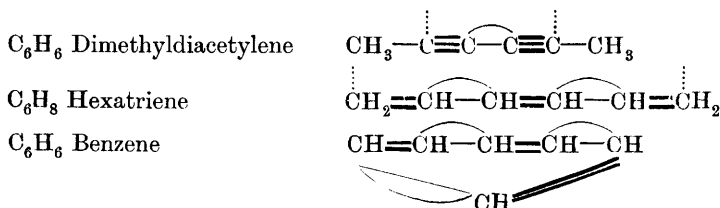
FIG. 2.



in the molecule. Now the introduction of fresh unsaturated centres in the molecule might have either of two effects, since there may be an enhancement of the band due to stimulation of the process which produces it, or, conversely, a cancellation of affinity leading to a decrease in absorptive power. An inspection of the

curves shows that the second process is in operation to some extent, for the acetylenic compound is much less absorptive than the saturated substance. The absorption of di-iodoacetylene is limited to a frequency of 4200 at a logarithmic thickness of 36, whereas the corresponding ethylenic compound continues to absorb to the same extent in a logarithmic thickness of 32. Further, the absorptive power of the acetylenic compound is, except for a portion in the visible region of the curve, actually less than that of the aliphatic analogue, from which it must be deduced that the introduction of the triple bond into the molecule has considerably influenced the absorptive power of the iodine atoms. On the other hand, by the same reasoning, the ethylenic linking has an effect opposite to that of the triple bond, whether this be attributable to a stimulation of the iodine vibration by the affinity of the residual affinity of the carbon atoms or merely to the increase in absorptive power usually noted when passing from the paraffin to the olefine derivatives.

*Series V. Dimethyldiacetylene, Hexatriene,\* Benzene †* (Fig. 3).—This case is one of the most interesting of all those which have yet been examined. A comparison of the structural formulæ of the three compounds must first be made :



It will be noticed that dimethyldiacetylene and benzene are isomeric, whilst hexatriene contains an extra pair of hydrogen atoms, and from this it might be expected that the first two substances would show greater absorptive power than hexatriene. An examination of the curves in Fig. 3 shows that this deduction is unwarranted; contrary to the usual rule, the more saturated substance is the most strongly absorbent, except just at the very top of the curve.

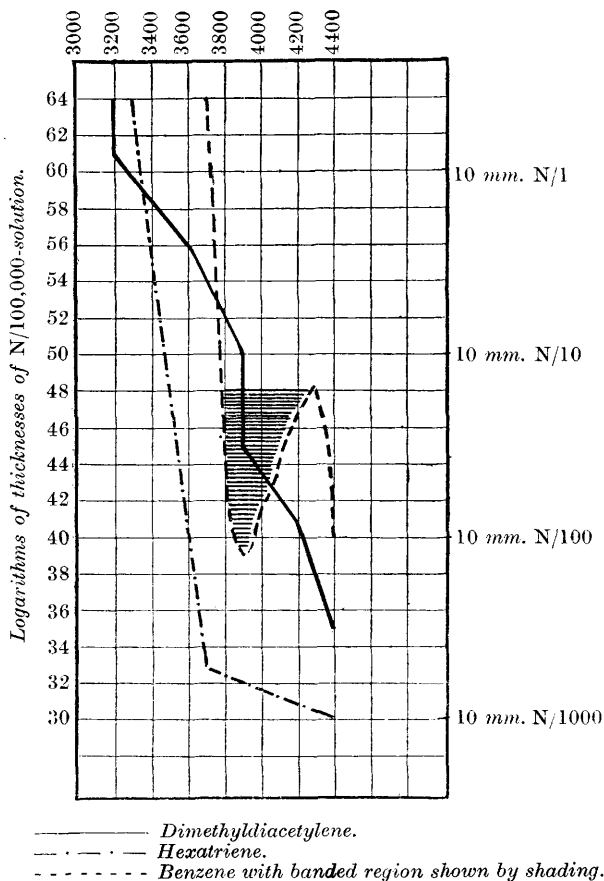
In order to explain this apparent anomaly, it is necessary to bear in mind what has already been said with respect to the influence of conjugation. Take, first, the case of benzene and hexatriene. In the benzene nucleus there are three double linkings, but these

\* This curve is taken from Baly and Tuck, T., 1908, **93**, 1909.

† This curve is taken from Baly and Collie, *ibid.*, 1905, **87**, 1332, the banded region being indicated by shading.

three linkings saturate each other and form a completely linked system with no free partial valencies. In the case of hexatriene, on the other hand, although in its molecule there are also three conjugated double linkings, these double linkings do not completely saturate each other, for there is a considerable amount of

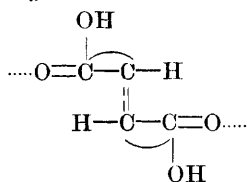
FIG. 3.  
*Oscillation frequencies.*



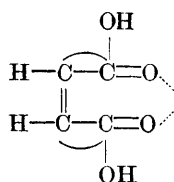
residual affinity left untouched at each end of the chain. From this it may be deduced that the presence of free affinity (or partial valencies) tends to increase absorptive power, which is borne out by the well-known fact that the introduction of any unsaturated centre into a molecule enhances the power of absorption.

A further step in advance is found when the case of dimethyldiacetylene is considered in conjunction with the foregoing. Dimethyldiacetylene contains two conjugated double linkings, and it is reasonable to assume that to some extent these will behave like two conjugated double bonds, saturating each other to a certain degree, but leaving a considerable amount of residual affinity at either end of the chain. In the case of the acetylene derivative, however, there is not the same long chain of conjugation which is present in the case of the hexatriene molecule. The whole residual affinity of the acetylenic compound is concentrated in two centres in close proximity to one another. Thus in hexatriene we find two active centres far removed from each other; dimethyldiacetylene contains two centres of residual affinity sufficiently near one another to interfere with each other, and hence reduce the amount of free affinity present, whilst benzene contains no independent centres of partial valency under normal conditions. Further, the absorptive powers of the three compounds stand in this order also.

It may reasonably be suggested that absorptive power is greatest when a molecule contains more than one centre of residual affinity and when such centres are so situated as to be incapable of mutual interference. Under such an assumption, it would be expected that of two stereoisomerides, for example, the fumaroid form would exhibit most absorptive power, a conclusion which is borne out by facts. For instance, an examination of Fig. 1, *C*, shows that maleic acid is much less absorptive than fumaric acid. An examination of their spatial formulæ indicates that in the case of fumaric acid the two accumulations of residual affinity at the ends of the chain are sufficiently far removed from one another to preclude mutual interference, whereas in the case of maleic acid they are near together.



Fumaric acid.



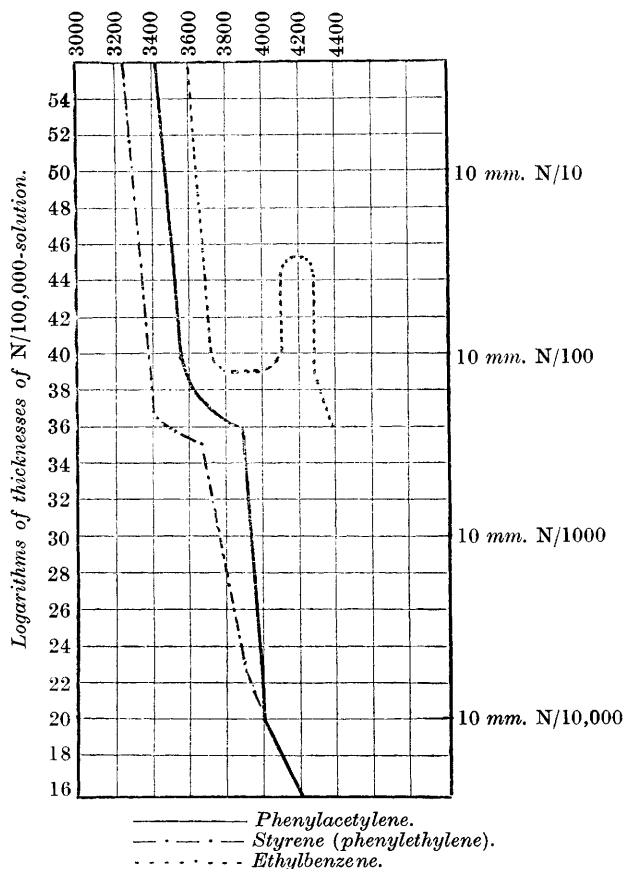
Maleic acid.

Further support of this view will be found in the facts described in Series IX.

*Series VI. Phenylacetylene, Styrene (Phenylethylene), and Ethylbenzene* (Fig. 4).—In this case the ethylenic derivative exhibits the greatest power of absorption; the acetylenic compound stands next in order, and the ethane derivative has least absorptive

power. These data hold good whether the absorptive power be judged by the wave-length absorbed by a given thickness of solution or by the dilution to which absorption persists. As regards the manner of absorption, in the case of ethylbenzene the region of banded absorption in benzene itself is occupied by a broader

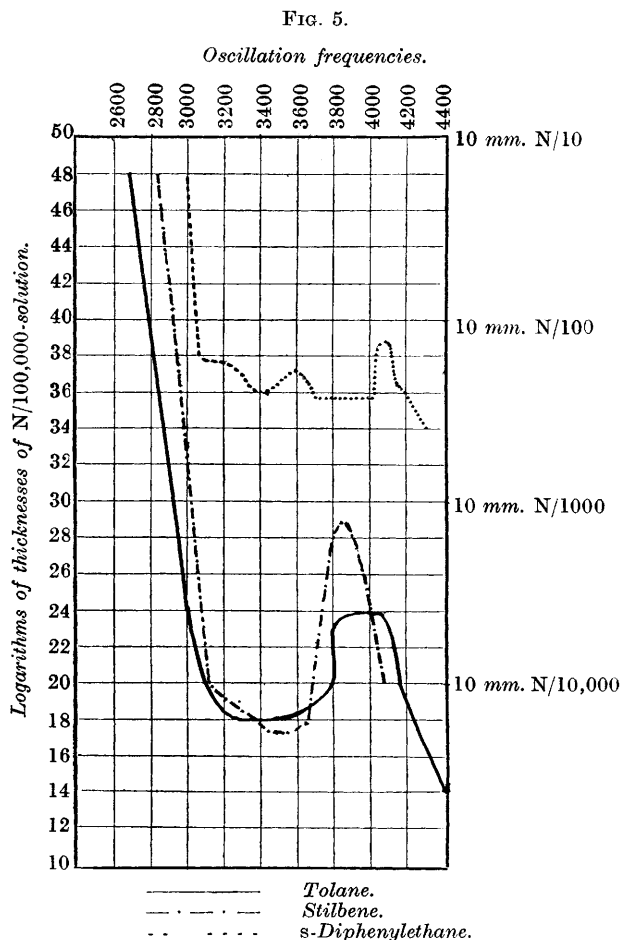
FIG. 4.  
*Oscillation frequencies.*



single band, and it appears that the introduction of the ethyl radicle into the benzene nucleus has no marked effect on the character of the absorptive power. There is no increase in the persistence of the band. With styrene (phenylethylene) and phenylacetylene, on the other hand, there is an increase in general absorptive power as compared with benzene itself, which increase

can be attributed only to the effect of introducing the new unsaturated centre into the molecule.

*Series VII. Tolane, Stilbene, and s-Diphenylethane* (Fig. 5).—The introduction of a second phenyl nucleus into the molecules mentioned in the last section leads to somewhat peculiar results.



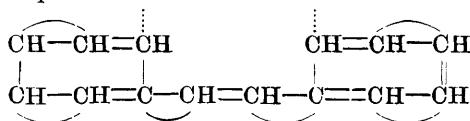
In the case of *s*-diphenylethane, the graph shows that banded absorption still persists, but that it is completely modified in character. In the first place, the absorptive power is increased, as the band appears at a greater dilution in the *s*-diphenylethane spectrum than was found to be the case in phenylethylene. Further, instead of a single narrow band, *s*-diphenylethane shows



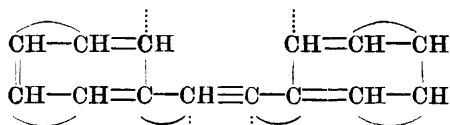
a band extending roughly from 3100 to 4100, although it is much shallower than the band of ethylbenzene and shows a tendency to split up into two smaller bands. One of these narrow bands extends from 3600 to 4100, and thus corresponds roughly with the characteristic band of ethylbenzene; the other band has its head at 3400, and does not occur at all in the spectrum of ethylbenzene. Its appearance must therefore be attributed to the introduction of the second phenyl radicle into the molecule.

Turning to the ethylene derivative, stilbene, it will be observed that it possesses an absorptive power markedly greater than that exhibited by the ethane analogue. Further, there is no sign whatever of the band characteristic of ethylbenzene; in fact, at this point of the spectrum there is especially good transmission. On the other hand, the band at 3400 traceable in the spectrum of *s*-diphenylethane is here broadened and deepened to a very remarkable extent. It seems probable that the two bands arise from a common cause, but that in the case of stilbene the absorptive power is reinforced by the presence of the long chain of conjugated linkings, seven in number, which exists in the molecule of the ethylenic compound.

In their banded absorption, the ethylenic and acetylenic analogues are approximately similar, but it will be seen from the graph that the band in stilbene extends over a much greater range of dilution than that exhibited by tolane. This fact reinforces the idea that the band of stilbene is in some way influenced by the conjugated chain, for in the case of tolane the conjugation is imperfect as compared with that of stilbene. In stilbene, the conjugated chain is made up completely of double and single bonds, whereas in tolane it contains single bonds alternating with double and triple linkings. Thus, instead of having the whole of the free affinity of the molecule concentrated at two points far removed from each other, as in stilbene, the tolane molecule has two main concentrations plus some excesses of affinity at the ends of the triple bonds.



Stilbene.

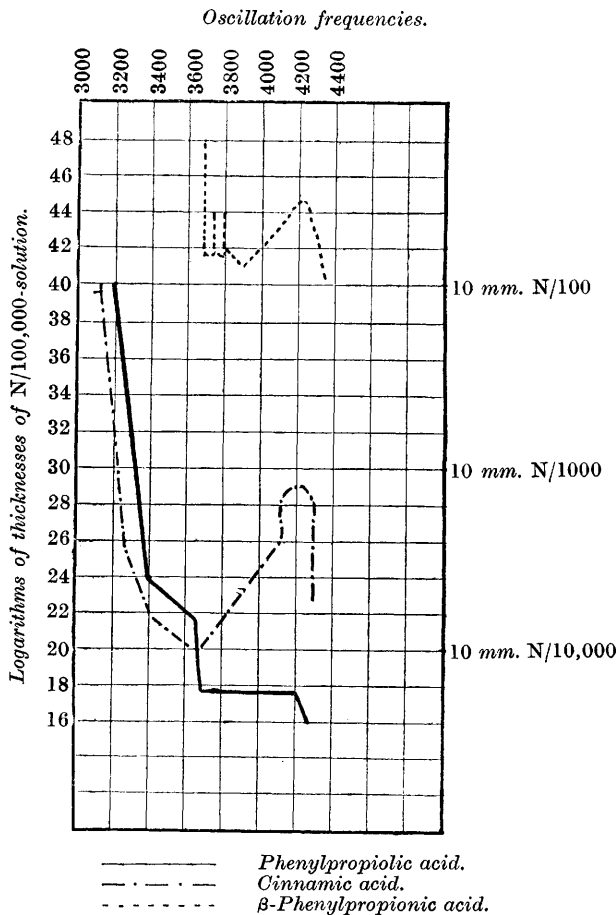


Tolane.

In this way, the contentions put forward in connexion with Series V. receive further support.

*Series VIII. Phenylpropionic Acid, Cinnamic Acid, and  $\beta$ -Phenylpropionic Acid* (Fig. 6).—In this series, the saturated member of the group shows very much less absorptive power than

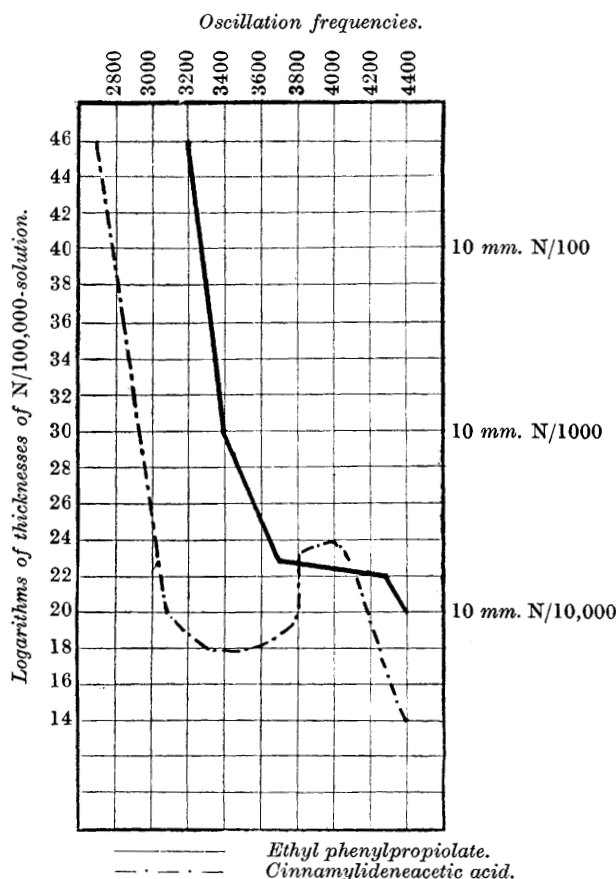
FIG. 6.



either of the other two. Traces of a modified benzenoid vibration are to be found in the one broad and two narrow bands which extend from 3700 to 4200; the dilution at which these bands occur is approximately the same as that at which the benzene bands make their appearance.

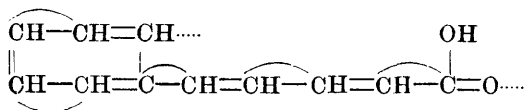
Cinnamic acid and phenylpropionic acid show a somewhat similar power of absorption through a certain range of the graph, although cinnamic acid absorbs slightly longer wave-lengths, whilst phenylpropionic acid shows an absorptive power at a dilution much higher than that at which cinnamic acid ceases to absorb markedly. Further, cinnamic acid shows a well-defined band of considerable

FIG. 7.

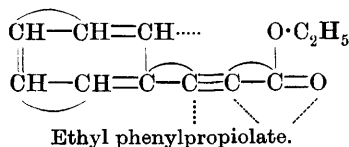


persistence in the region 3300—4200, whereas phenylpropionic acid exhibits a "step-out" at a higher dilution. Testing the absorptive power by the length of the light-waves absorbed, the order is: ethylenic, acetylenic, and saturated, but as regards the power of absorbing at greatest dilution, they stand in the order of saturation, the acetylenic derivative having most absorptive capacity.

*Series IX. Ethyl Phenylpropiolate and Cinnamylideneacetic Acid* (Fig. 7).—This case furnishes another example of the phenomenon which was discussed in Series V. The two compounds, ester and acid, are isomerides, so that, as far as additive factors go, they should exhibit the same absorptive power. An examination of their structural formulæ shows that in the one case there is a long chain of conjugated double bonds in the molecule, so that the residual affinity is concentrated at two distant points, whereas in the other case the affinity centres are nearer together and are more likely to disturb one another:



Cinnamylideneacetic acid.



Ethyl phenylpropiolate.

From what has already been said on this matter, it may be deduced that cinnamylideneacetic acid will show the greatest absorption, whilst the absorptive power of ethyl phenylpropiolate will be considerably less. An examination of the graphs shows that this prophecy is justified. The absorptive power of the ester is less than that of its isomeride, both from the point of view of the wave-length absorbed by a fixed concentration and also from the point of view of the dilution at which the substance continues to show absorption.

Thus, although the examination of acetylenic derivatives has not brought to light any close parallel between them and the ethylenic analogues so far as light-absorbing power is concerned, it has elicited new facts with regard to the influence exerted by the distribution of residual affinity in the molecule on the absorptive power of the substance. At the present time our knowledge of the subject in its broadest outlines may be summarised as follows: The introduction of a centre of residual affinity into a saturated molecule increases that molecule's power of absorbing light. The introduction of a second centre of residual affinity into the molecule normally increases the absorptive power, although in some cases (such as the iodine compounds) it may act in a converse manner. If the two centres of residual affinity are placed so far apart in the molecule, either spatially or structurally, that

they fail to exert any mutual influence on one another, then the absorptive power of the molecule is greater than is found to be the case when the same amount of residual affinity is concentrated in two adjacent points of the molecule.

THE SIR DONALD CURRIE LABORATORIES,

THE QUEEN'S UNIVERSITY OF BELFAST.

PHYSICAL CHEMISTRY DEPARTMENT,

THE UNIVERSITY OF GLASGOW.

[*Received, July 18th, 1917.*]

---