LXII.—*A Study of the Absorption Spectra of Isatin, Carbostyril, and their Alkyl Derivatives in Relation to Tautomerism.*

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Introduction.

Much uncertainty still exists with regard to the relationship between compounds described as tautomeric and desmotropic. In those cases, for example, in which a substance and two related isomeric alkyl compounds having respectively the lactam and the lactim constitution are known, it is uncertain whether the supposed parent substance has a constitution similar to that of either of the derivatives. Thus there are two methyl derivatives of isatin; the constitution of each of which has been satisfactorily determined from its chemical reactions, but there is no unquestionable evidence which proves that the constitution of isatin itself is similar to that of either of the derivatives.

It is known that the substitution of a methyl or ethyl group for an atom of hydrogen, without other alteration in the structure of the substance, merely increases the general absorption very slightly for each CH_2 added to the molecule (*Phil. Trans.*, part I., 1879, 170, 257), that is, it slightly shortens the transmitted spectrum, but makes practically no difference in the character of the absorption; for instance, it scarcely increases its intensity, nor does it convert a general absorption into one that is selective, or *vice versâ*. It has been explained elsewhere that the effect is to slightly retard the rate of vibration of the molecule. "The larger the molecule, the lower the rate of vibration" (Trans., 1881, 39, 165). It appeared to us that to ascertain and compare their absorption curves could scarcely fail to afford some information concerning the relationship of the constitution of such substances as isatin and carbostyril to that of their respective derivatives, whilst it seemed to offer a possible method of determining whether the constitution of the parent substance in each case is such as to admit of the derivatives being so simply related to them as the usually accepted formulæ represent.

By attacking the problem in this manner, there is the advantage gained over chemical methods that the question of the possibility of molecular rearrangement during the preparation of the derivative does not arise. Methylisatin is prepared from isatin by the action of methylic iodide on silver isatin. It is generally believed from accepted evidence that the atom of silver simply occupies the same position in the molecule as the atom of hydrogen which it has replaced and that

isatin and silver isatin have, therefore, a similar constitution. We shall show, however, that there is good ground for doubting whether any such conclusion can be justified. With the object of obtaining information on this point, we have examined the absorption spectra of isatin and carbostyril, and of their respective alkyl derivatives.

Our experiments had been completed, and conclusions drawn which merely awaited confirmation, before we had studied the recent attempts which have been made to solve this problem by chemical processes.

It is satisfactory to find that the conclusions arrived at by the examination of the absorption spectra are in complete accordance with those recently obtained by reasoning based upon purely chemical methods devised to obviate the sources of fallacy attaching to the earlier experiments.

It will be convenient to give a summary of this work before describing our experiments and the conclusions we have drawn from them. H. Goldschmidt and A. Meissler (*Ber.*, 1890, **23**, 253), point out that, inasmuch as some so-called tautomeric substances, such as carbostyril, when treated with alkali and alkylic haloids, give two isomeric alkyl derivatives, no conclusion as to the constitution of the parent substance can be drawn from their formation. They, likewise, hold that the action of alkylic haloids on the silver salt is untrustworthy as a guide to the solution of the problem, inasmuch as there is the possibility that the silver atom may not occupy the position of the hydrogen atom whose position is to be determined, especially as the silver derivative is usually precipitated in an alkaline solution, in which shifting of the atoms may very readily occur. Even to the method in which acid radicles are substituted for alkyl radicles, exception is taken, although it is admitted that the objections are less weighty.

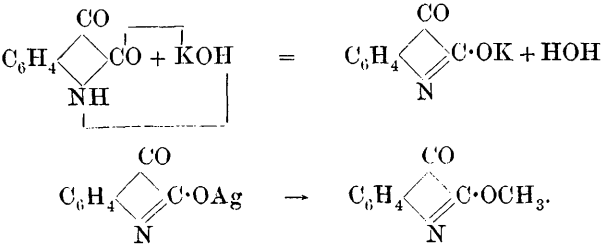
The view of these authors is that, in the reactions of tautomeric substances in which electrolytes are employed, shifting of the atoms may occur. They maintain, therefore, that, in order to obtain trustworthy results, solutions of electrolytes should be excluded and only such reactions employed as give rise to no by-products which might bring about secondary changes. In their opinion, phenylic isocyanate, the reagent which they employ, fulfils these conditions.

Methylisatin, the methyl derivative of isatin which melts at 101°, and is obtained by the action of methylic iodide on silver isatin, is a lactim, since it readily undergoes saponification; whilst its isomeride, methylpseudoisatin, melting at 134°, is a lactam. On account of the direct method of preparation of methylisatin from isatin, it is generally assumed that isatin has the lactim constitution.

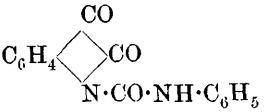
$$C_6H_4\begin{<}{}^{-N}_{CO}\end{>}C\cdot OH.$$

According to Goldschmidt and Meissler's view, the evidence of this is insufficient.*

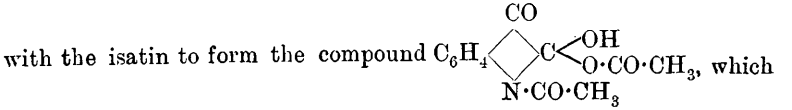
Goldschmidt and Meissler point out that, taking into account the modern views as to the nature of solutions of electrolytes, the formation of the lactim ether can be easily explained, even if we start from the lactam constitution, $C_6H_4\langle\begin{matrix}NH\\CO\end{matrix}\rangle CO$, by the formation of an intermediate potassium compound,



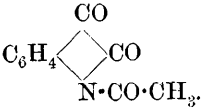
By the action of phenylic isocyanate on isatin, Gumpert (*J. pr. Chem.*, [ii], 1885, **32**, 283) obtained carbanilidoisatin, $C_{15}H_{10}N_2O_3$, which when treated with alkalis, passes into carbanilidoisatinic acid, $C_{15}H_{12}N_2O_4$; Goldschmidt and Meissler obtained similar results. Since carbanilidoisatin is converted by alkalis into a derivative of isatinic acid, it must be a derivative of pseudoisatin. The formula



has been assigned to it by Gumpert, but whilst he formulates carbanilidoisatinic acid as $C_6H_4\langle\begin{matrix}CO\cdot COOH\\NH\cdot CO\cdot NH\cdot C_6H_5\end{matrix}$, he holds to the lactim formula for isatin, explaining the formation of the carbanilido-compound by a shifting of the atoms. It is to be remembered, too, that Baeyer (*Ber.*, 1882, **15**, 2100) explains the formation of acetylpseudoisatin, on acetylating isatin, by a shifting of the atoms, assuming that a molecule of acetic anhydride first unites with the isatin to form the compound



which then, by the removal of a molecule of acetic acid, gives



Goldschmidt and Meissler, looking especially to the improbability

* See also A. Michael, *J. pr. Chem.*, [ii], 1888, **37**, 513.

of phenylic isocyanate causing any shifting of the atoms, consider that the more natural explanation is that isatin itself has the lactam constitution. This conclusion is confirmed by our results, the curve of molecular absorption derived from measurements of the absorption spectra of methylpseudoisatin being practically identical with that of isatin, whilst the curve of methylisatin differs widely from both, and differs much more widely from that of isatin than the mere substitution of a methyl group for a hydrogen atom, or the addition of CH_2 to the hydrogen atom, could possibly account for.

Goldschmidt and Meissler, in the paper already referred to, show that carbostyril and lutidone behave in a similar but unexpected manner towards phenylic isocyanate, and that both compounds give off carbonic anhydride when acted on by this reagent, yielding basic products. They draw the conclusion that the two substances are similarly constituted, but this conclusion is at variance with the commonly accepted formulæ which ascribe to lutidone a ketonic and to carbostyril a phenolic constitution. One or other of the formulæ must, therefore, be modified. Our experiments point to a very close similarity of constitution between carbostyril and methylpseudocarbostyril, and to dissimilarity between the constitution of both of these substances and that of methylcarbostyril. Methylpseudocarbostyril, from its reactions, is known to be a lactam, that is to say, the alkyl radicle is in direct union with the nitrogen; carbostyril itself must, therefore, have a constitution characteristic of the lactam class, a structure in character similar to that usually ascribed to lutidone. Here, again, our conclusions are in accord with those of Goldschmidt and Meissler in so far as they hold that the commonly received formula either of carbostyril or of lutidone must be altered. Knorr (*Annalen*, 1896, **293**, 81) also arrives at the conclusion that carbostyril is to be regarded as a lactam, and not as a lactim.

We now proceed to give a detailed account of the preparation of the various substances and of the examination of their absorption spectra. All the substances examined were prepared twice over, except methylcarbostyril, and several series of photographs of each preparation were taken and carefully compared, cadmium electrodes being used as the source of light in this case, although we usually employ lead–cadmium and tin–cadmium alloys.

Experimental.

Carbostyril.—The preparation employed, obtained from Schuchardt, of Görlitz, was recrystallised many times from alcohol until its melting point was constant. It crystallised in fine, silky needles which melted at 195—196°.

Methylpseudocarbostyril.—To prepare this, 1 part of carbostyril was dissolved in 12 times the weight of methylic alcohol, and water added to the solution until the carbostyril just remained dissolved while the solution was hot. To the cooled solution, rather more than the calculated quantity (1 mol.) of methylic iodide was added, and then a concentrated solution of sodium hydroxide (1 mol.) in small quantities at a time, and the solution boiled, using a reflux condenser, until the alkaline reaction disappeared. The solution was next made strongly alkaline with sodium hydroxide, and the methylpseudocarbostyril extracted by shaking many times with chloroform in a separating funnel; the chloroform was distilled off, and the residue repeatedly extracted with small quantities of boiling light petroleum. From the light petroleum, the methylpseudocarbostyril crystallised in tufts of beautiful, colourless needles. After being crystallised several times from light petroleum, its melting point was 71° (*Ber.*, 1887, 20, 2011).

Methylcarbostyril.—Methylcarbostyril was prepared by the action of methylic iodide on silver carbostyril; this was obtained by adding ammonia to a hot aqueous solution of carbostyril which had been mixed with the necessary quantity of silver nitrate. The white, amorphous precipitate of silver carbostyril is easily soluble in excess of ammonia, and from the ammoniacal solution it may be obtained in the crystalline form. The silver carbostyril was carefully dried over sulphuric acid, and heated in sealed tubes with excess of methylic iodide at 70—80°, the heating being continued for 6—7 hours. The methylcarbostyril, obtained on treating the product with alcohol and evaporating, was distilled over in a current of steam, separated from the water, and dried; it was then fractionated under a pressure of about 500 mm. The boiling point, at the ordinary presssure, is 247—249° (*Ber.*, 1881, 14, 1916).

Although only one preparation of methylcarbostyril was made, the corresponding ethyl derivative was prepared and the absorption spectra examined, yet it gave a practically identical absorption curve. It was, therefore, considered unnecessary to duplicate these experiments.

Isatin.—The isatin, obtained from Schuchardt, of Görlitz, was recrystallised from alcohol until the melting point was constant, namely, 203·5°; the melting point given by Baeyer is 201°.

Methylpseudoisatin.—The preparation of this substance may be conveniently divided into four stages.

I. Preparation of methylphenylhydrazinepyroracemic acid.

II. Preparation of methylindolecarboxylic acid.

III. Preparation of methyldibromoxindole.

IV. Conversion of methyldibromoxindole into methylpseudoisatin.

I. *Preparation of Methylphenylhydrazinepyroracemic Acid.*—Twenty grams of methylphenylhydrazine dissolved in very dilute hydrochloric acid was treated with the equivalent quantity of pyroracemic acid and the crystalline mass of methylphenylhydrazinepyroracemic acid which separated was collected with the aid of the pump and washed with cold water.

II. *Preparation of Methylindolecarboxylic Acid.*—The finely powdered methylphenylhydrazinepyroracemic acid was warmed on the water-bath with 5 times its weight of a 10 per cent. solution of hydrochloric acid, and the methylindolecarboxylic acid which separated in yellowish needles, was collected with the aid of the pump, washed with water, and recrystallised several times from alcohol, when it melted at 212°.

III. *Preparation of Methyldibromoxindole.*—One part of the methylindolecarboxylic acid, dissolved in a dilute solution of sodium hydroxide, was gradually added to a solution containing $4\frac{1}{2}$ parts of bromine, 200 parts of water, and the equivalent quantity of sodium hydroxide, the mixture being well stirred and cooled. The bromide, which separated in very fine, yellow crystals, was crystallised several times from alcohol, from which it always separated in yellowish needles melting at 201°. According to Fischer and Hess (*Ber.*, 1884, **17**, 559), methyldibromoxindole crystallises in "clear tabular crystals" which melt at 204°, but we never obtained it in this form.

IV. *Preparation of Methylpseudoisatin from Methyldibromoxindole.*—For the conversion of the methyldibromoxindole into methylpseudoisatin, we followed Colman's method (*Annalen*, 1888, **248**, 116) in preference to that of Fischer and Hess (*loc. cit.*). The methyldibromoxindole was boiled with 30 times its weight of water for 2—3 hours, using a reflux condenser. The hot solution, filtered from some resinous matter, deposited the methylpseudoisatin in beautiful, red needles which, after recrystallisation from water, melted constantly at 132—133° (Fischer and Hess, *loc. cit.*).

Methylisatin.—The preparation of this derivative requires special precautions on account of its instability; the method followed was that given by Baeyer (*Ber.*, 1882, **15**, 2093). Five grams of finely powdered isatin were suspended in ice-cold water containing pieces of ice, and dissolved by adding a solution of sodium hydroxide also cooled to 0°; the calculated quantity of silver nitrate was now added in an ice-cold solution, and the dark red precipitate of silver isatin rapidly collected with the aid of a pump. The silver isatin after being washed

first with water, and then with alcohol to remove any unaltered isatin, was dried over strong sulphuric acid for three days, finely powdered, and treated in a flask with excess of methylic iodide; the semi-solid mass obtained on allowing the corked flask to remain for 48 hours was repeatedly extracted with small quantities of hot benzene, and the benzene solution diluted with an equal volume of light petroleum, which caused a small quantity of tarry matter to separate. The filtered solution was then evaporated to dryness on the water-bath, and the residue dissolved in the smallest possible quantity of hot benzene; on cooling, it deposited the methylisatin in prisms of a blood red colour, which, after recrystallisation from benzene, melted at 99—101° (Baeyer, *Ber.*, 1882, **15**, 2093). Methylisatin is unstable both in the solid state and in alcoholic solution. When freshly prepared, it has a sharp melting point and a blood red colour, but after it has been kept for some time the colour changes to brick red and the melting point is no longer sharp. It was, therefore, found necessary to photograph this substance immediately after its preparation.

We now proceed to give a general description of the spectra examined. Oscillation frequencies are indicated by $1/\lambda$ and wave-lengths by λ.

Description of the Spectra of the Substances Investigated.

Carbostyril.

General description of the spectra.—There is a total absorption of all rays beyond $1/\lambda$ 2700, until the dilution is 1 milligram-mol. of the substance in 500 c.c. of liquid with 5 mm. of thickness, when the rays extend to 2770.

At a thickness of 3 mm., an absorption band becomes visible, which continues to 1 milligram-mol. in 2500 c.c. with a thickness of 1 mm.

With 2 mm. of liquid containing 1 milligram-mol. in 500 c.c., the absorption band lies between $1/\lambda$ 2900 and 3300, the rays being transmitted then as far as $1/\lambda$ 3500, after which there is total absorption.

When the absorption band has almost disappeared, the continuous spectrum extends to $1/\lambda$ 4000, and the liquid in a layer of 2 mm. then contains 1 milligram-mol. in 2500 c.c.

Methylpseudocarbostyril.

General description of the spectra.—There is a total absorption of all rays beyond $1/\lambda$ 2680 in from 25 mm. to 15 mm. of liquid; this extends as far as 2780 with 1 mm. of liquid containing 1 milligram-mol. in 100 c.c. There is an absorption band from $1/\lambda$ 2850 to 3370, with 3 mm. of liquid containing 1 milligram-mol. in 500 c.c., and a very feeble transmission of rays from 3370 to 3500. This absorption band

is distinctly seen down to a dilution of 1 milligram-mol. in 2500 c.c. with 2 mm. of liquid, the continuous rays then extend to about 4050.

It will thus be seen that the spectrum curve very closely resembles that of carbostyril, the general absorption being slightly increased, which is the usual effect when methyl takes the place of hydrogen or CH_2 is added to the molecule.

Methylcarbostyril.

General description of the spectra.—All rays are transmitted to $^1/\lambda$ 3000 by 1 milligram-mol. of substance in 500 c.c. and 5 mm. of liquid. The rays beyond are all absorbed.

Through a layer of 3 mm., the rays extend to $^1/\lambda$ 3050, and from this point to 3350 there is an absorption band, beyond which the rays are transmitted to 3500. The band is very feeble with 5 mm. of liquid containing 1 milligram-mol. in 2500 c.c., and it is only just visible with 4 mm. The absorbed rays lie between 3000 and 3050, beyond this is an imperfectly transmitted continuous spectrum to about 3800.

The chief differences between these spectra and those of the parent substance, carbostyril, is the great extent of the transmitted rays and the different position of the absorption band as well also as its less persistent character or intensity.

Isatin.

General description of the spectra.—There is a very strong absorption band extending from about $^1/\lambda$ 1920 to 2780, that is to say, from the green into the ultra-violet, red, yellow, and green rays are transmitted. This absorption continues with 10 mm. of liquid containing 1 milligram-mol. in 100 c.c. With 5 mm., there is a very feeble transmission of rays between 2780 and 3000, and with 4 mm., the transmitted rays are a little stronger, but there is total absorption beyond. With 3 mm. of liquid containing 1 milligram-mol. in 100 c.c., rays are very feebly transmitted from $^1/\lambda$ 2000 to 2170, a second absorption band occurs as far as 2780, the rays are transmitted from 2780 to 3070, beyond which there is total absorption. This second absorption band continues, although much enfeebled, with 4 mm. of liquid containing 1 milligram-mol. in 500 c.c. Beyond 3170, there is total absorption to about $^1/\lambda$ 3630. It continues between 3200 and 3630 with 2 mm. of liquid containing 1 milligram-mol. of substance in 500 c.c. There is total absorption beyond 3900.

Methylpseudoisatin.

General description of the spectra.—A very strong absorption band extends from $^1/\lambda$ 1920 in the green to the very strong rays between

$^1/\lambda$ 2740 and 2900 in all thicknesses of liquid from 25 mm. down to 5 mm. containing 1 milligram-mol. in 100 c.c. All rays beyond 2900 are totally absorbed.

With layers of 4 mm. and 3 mm., there is a strengthening of the transmitted rays between $^1/\lambda$ 2740 and 2970, but a total absorption beyond. With 2 mm. and 1 mm. of liquid, the absorption of rays less refrangible than 2740 is much diminished, that is to say, the band is weakened hereabouts. With layers of 5, 4, and 3 mm. of liquid containing 1 milligram-mol. in 500 c.c., there is nothing transmitted beyond $^1/\lambda$ 3030, except the very strong line at 3600.

There is a second very strong absorption band beyond this line until we get to a layer of 4 mm. of 1 milligram-mol. in 2500 c.c., when the rays between 3600 and 3840 are feebly transmitted, and there is only a very feeble transmission of rays beyond, lying between 4250 and 4400, and so gradually the absorption diminishes.

Methylisatin.

General description of the spectra.—With 1 milligram-mol. of substance in 100 c.c., there is a total absorption beyond 1920 in the green with 25, 20, 15, 10, and 5 mm. of liquid, with, however, in the last case, a very feeble transmission of rays commencing between $^1/\lambda$ 2000 and 2170. With 3 mm. of liquid, it is evident that a very strong absorption band lies between $^1/\lambda$ 2180 and about 3350, where the rays are very feebly transmitted, all beyond 3470 being totally absorbed. This absorption band gradually diminishes in intensity but more rapidly on the part of the rays of greater oscillation frequency than is the case with those lying between $^1/\lambda$ 2270 and 2870. For instance, 2 mm. of liquid containing 1 milligram-mol. in 500 c.c. absorb the rays between 2600 and 2770. Total absorption is seen beyond 2600.

The spectrum curves of isatin and methylpseudoisatin are very similar, but that of methylisatin is quite different. The former each show two absorption bands similar in position and intensity, whilst the latter exhibits but one.

Conclusions.

Accordingly, we conclude as regards carbostyril and its derivatives, that carbostyril and the so-called methylpseudocarbostyril are of similar constitution, the latter being the true methyl derivative of the former. The same may be said of the substance termed ethylpseudocarbostyril; it is the normal ethyl derivative. The so-called "methylcarbostyril" differs from carbostyril in constitution, and is not its true alkyl derivative.

From the similarity of the curves of molecular absorption of carbostyril and methylpseudocarbostyril, we infer that if, as is

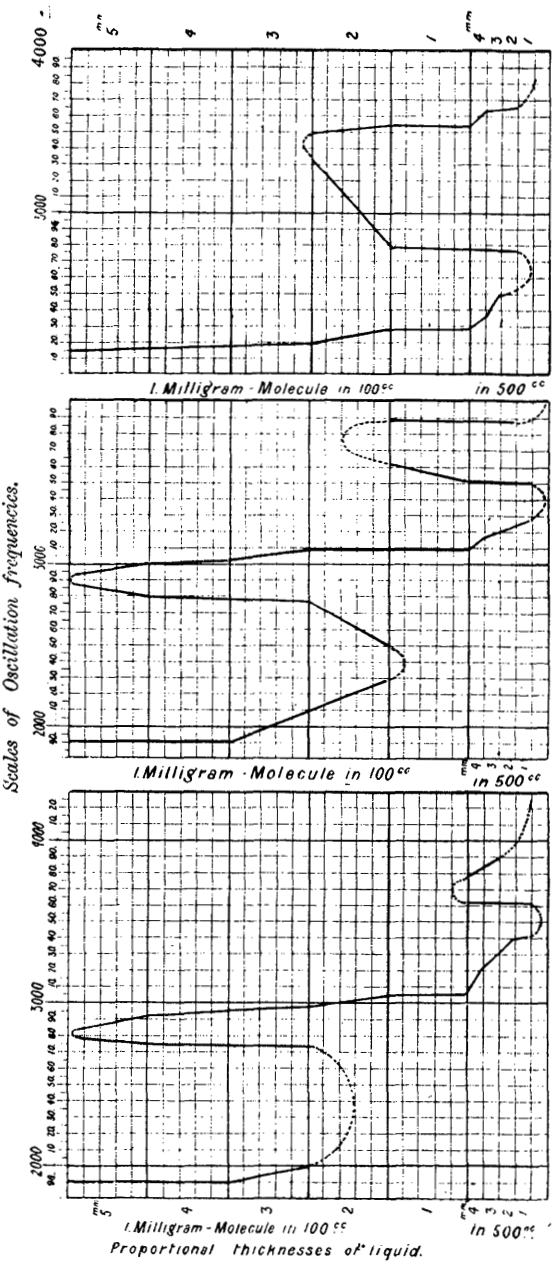
usually admitted, the latter possesses the lactam constitution, this constitution must also be assigned to carbostyril.

In the same way, isatin and the so-called methylpseudoisatin are of similar constitution, and isatin is, therefore, a lactam. The so-called methylisatin is not the true alkyl derivative of isatin, seeing that the curves of molecular absorption of the two substances are totally different.

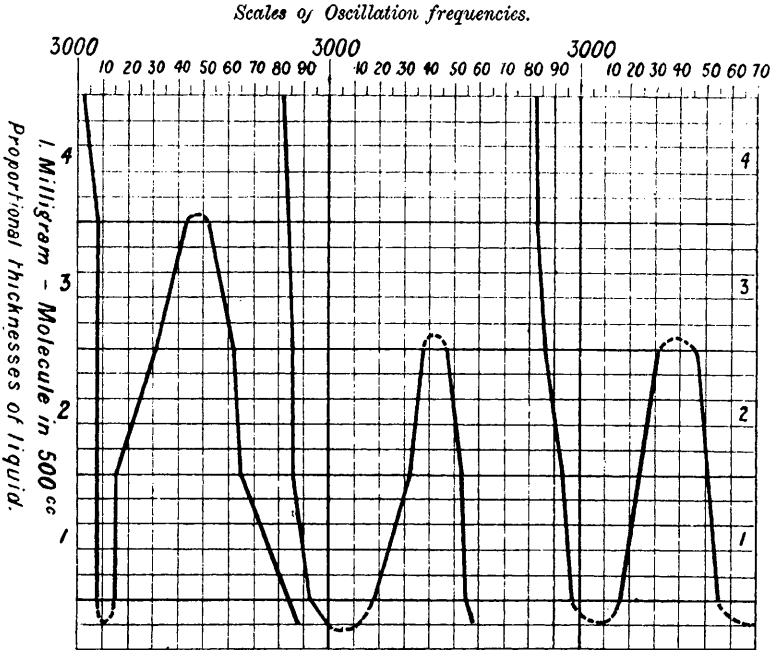
Illustrations.

As the descriptions of the spectra and the measurements afford no idea of the photographs, it became necessary to present a graphic representation of the results. The method of drawing the curves is that which was first described in 1885 (Hartley, Trans., 1885, **47**, 685; 1887, **51**, 153—201. See notes to the plates, and also Trans., 1888, **53**, 642). From ten to fifteen spectra are successively photographed on one plate, each representing the absorption spectrum of the same solution, such as contains 1 milligram-mol. in 100 c.c. placed in cells of different thicknesses, so as to give layers of liquid of 15, 10, 5, 4, 3, 2, 1 millimetres thick. The solution is then diluted to five times its volume, so that a milligram-mol. is contained in 500 c.c., and again photographed on another plate in cells 5, 4, 3, 2, 1 millimetres thick. The absorption spectrum of 5 mm. is the same as 1 mm. of the stronger solution containing 1/100th of a milligram-mol. From careful measurements of the spectra, the transmitted and absorbed rays, the oscillation frequencies $^1/\lambda$ and the wave-lengths λ are determined for each dilution and each thickness of liquid. The curves are all obtained by straight lines joining fixed points measured on the scale of oscillation frequencies, with the exception of those portions which are represented by dotted lines indicating where the rays are more or less feebly transmitted.

The range of spectrum is from the solar line E in the green, or about $^1/\lambda$ 1900, to $^1/\lambda$ 4000 in the ultra-violet, or in wave-lengths from 5263 to 2000 tenth-metres. The curve of each substance, therefore, is strictly quantitative, and represents the internal vibrations of the molecule, as was explained in the previous communications referred to above. Although, by referring to the photographs, it is easy to understand the measurements given in detail, it is not so by mere reference to the curves. Neither the termination of the absorption band in the visible region nor the red and yellow rays which are transmitted appear on the first few photographs of isatin and its derivatives. Owing to this, in the tabulated statements of the measurements, the absorption bands are not indicated at all distinctly, although in reality they are very well defined and strong.



Curves of Molecular Vibrations.



Curves of Molecular Vibrations.

Measurements.

Carbostyril, C_9H_7NO.

0·145 gram (= 1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$1/\lambda$.	λ.
25	Spectrum continuous to.....	2768	3612
20	All rays beyond completely absorbed.		
15	The same.		
	Spectrum continuous to.....	2776	3602
10	All rays beyond completely absorbed.		
5	,, ,, ,, ...	2781	3595
4	,, ,, ,, ...	2786	3589
3	,, ,, ,, ...	2796	3576
2	,, ,, ,, ...	2806	3563
1	,, ,, ,, ...	2826	3538
	The same as (2).		

Carbostyril—(continued).

0·145 gram in 500 c.c. of alcohol.

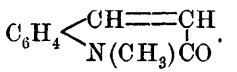
Thickness of layer of liquid in millimetres.	Description of Spectrum.	$1/\lambda$.	λ.
4	Continuous spectrum to.....	2826	3538
	Complete absorption beyond except strong line showing faintly at $1/\lambda$ 3471; line showing faintly at $1/\lambda$ 3394.		
3	Spectrum continuous to.....	2856	3501
	Strong line showing at $1/\lambda$ 2884.		
	Absorption band 2884—3394.		**3467 to 2946**
	Feeble continuous spectrum from $1/\lambda$ 3394 to $1/\lambda$ 3471.		
2	Spectrum continuous to.....	2884	3467
	Strong line showing at	2938	3403
	Absorption band 2884—3323.		**3467 to 3009**
	Spectrum continuous from $1/\lambda$ 3323—3520. Complete absorption beyond, except lines at $1/\lambda$ 3638 and $1/\lambda$ 3886.		
1	Spectrum continuous to.....	2938	3403
	Absorption band 2938—3188.		**3403 to 3136**
	Faint indication of lines at $1/\lambda$ 2949, 3064, and 3076.		
	Spectrum continuous from 3188 to 3532. Complete absorption beyond, except strong lines at $1/\lambda$ 3638 and 3886.		

Carbostyril—(continued).

0·145 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$1/\lambda$.	λ.
4	Spectrum continuous to.....	2999	3334
	Absorption band 2999—3130.		**3334 to 3194**
	Strong lines showing at 3064 and 3076. Spectrum continuous from 3130 to 3570. Complete absorption beyond, except lines at $1/\lambda$ 3638 and 3886.		
3	Spectrum continuous to.....	3638	2748
	Very faint continuation of spectrum from 3638 to 4054.		
	Complete absorption beyond.		
2	Spectrum continuous to.....	4135	2418
	Lines showing faintly between $1/\lambda$ 4036 and 4565.		
	Complete absorption beyond.		
1	Spectrum continuous to.....	4135	2418
	Strong cadmium lines showing between $1/\lambda$ 4290 and 4656.		

Methylpseudocarbostyril, $C_{10}H_9NO$. M. p. 71°.



0·159 gram (= 1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
25	Spectrum continuous to.....	2738	3652
	Complete absorption beyond.		
20	,, ,, ,, ...	2749	3637
	Strong line showing at $^1/\lambda$ 2768.		
15	Same as (20).		
10	Complete absorption beyond.....	2768	3612
5	,, ,, ,, ...	2768	3612
4	,, ,, ,, ...	2768	3612
3	,, ,, ,, ...	2775	3603
2	,, ,, ,, ...	2781	3595
1	,, ,, ,, ...	2791	3582

Methylpseudocarbostyril—(continued).

0·159 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	2826	3538
	Complete absorption beyond.		
	Faint lines at $^1/\lambda$ 3355 and 3466.		
3	Spectrum continuous to	2826	3538
	Absorption band 2826—3328.		**3538 to 3004**
	Line showing at 2884. Spectrum continuous from 3328 to 3471.		
	Complete absorption beyond, except line at...	3886	2573
2	Spectrum continuous to.....	2936	3405
	Absorption band 2936—3240.		**3405 to 3086**
	Spectrum continuous $^1/\lambda$ 3240 to 3491. Complete absorption beyond, except cadmium lines at $^1/\lambda$ 3638 and 3886.		
1	Spectrum continuous to.....	2938	3403
	Absorption band 2938—3192.		**3403 to 3133**
	Faint indication of lines at $^1/\lambda$ 3064 and 3076 Spectrum continuous from $^1/\lambda$ 3192 to 3528.		
	Complete absorption beyond, except strong cadmium lines at 3638 and 3886.		

Methylpseudocarbostyril—(continued).

0·159 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	3004	3328
	Absorption band 3004—3139		**3328 to 3185**
	Lines showing at $^1/\lambda$ 3064 and 3076.		
	Spectrum continuous to.....	3893	2536
	Complete absorption beyond, except strong lines at 3638 and 3886.		
3	Spectrum continuous to	3520	2840
	Still faint between $^1/\lambda$ 2938 and	3349	2985
	Strong lines at $^1/\lambda$ 3638 and 3886, with very faint indications of spectrum between.		
2	Spectrum continuous to.....	4132	2420
	Complete absorption beyond.		
1	Spectrum continuous to	4132	2420
	Complete absorption beyond, except lines between 4306 and 4536.		

Methylcarbostyril, $C_{10}H_9NO$. B. p. = 247°.

$$C_6H_4\begin{<}CH{:}CH \\ N{=}C{\cdot}OCH_3\end{>}.$$

0·159 gram (= 1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
25	Spectrum continuous to..	2945	3395
20	Continuous spectrum to.....	2950	3389
15	,, ,, ,, ...	2955	3384
10	,, ,, ,, ...	2965	3372
5	,, ,, ,, ...	3004	3328
4	,, ,, ,, ...	3004	3328
3	,, ,, ,, ...	3013	3318
2	,, ,, ,, ...	3018	3313
1	,, ,, ,, ...	3033	3297

Methylcarbostyril—(continued).

0·159 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	3076	3250
	Lines showing between $^1/\lambda$ 3355 and 3638.		
	Absorption band 3076—3410.		**3250 to 2932**
	Faint indication of spectrum from $^1/\lambda$ 3410 to	3520	2840
	Complete absorption beyond.		
3	Spectrum continuous to	3076	3250
	Absorption band 3076—3319.		**3250 to 3013**
	Spectrum continuous, but very faint, from 3319 to 3638. Complete absorption beyond, except line at	3886	2573
2	Spectrum continuous to.....	3076	3250
	Absorption band 3076—3135.		**3250 to 3189**
	Spectrum continuous from $^1/\lambda$ 3135 to 3638.		
	Complete absorption beyond, except strong line at	3886	2573
1	Same as (2). Spectrum very faintly continuous between $^1/\lambda$ 3638 and 3886; exceedingly faint continuation to about.....	4030	2481

Methylcarbostyril—(continued).

0·159 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	3886	2573
	Faint prolongation to	4080	2450
	Complete absorption beyond.		
3	Spectrum continuous to.....	3886	2573
	Faint prolongation to.....	4080	2450
	Complete absorption beyond.		
2	Spectrum continuous to	4135	2418
	Complete absorption beyond, except lines		
	between.....	4290	2331
	and	4423	2260
1	Same as (2); additional line at	4565	2190

Isatin, $C_8H_5NO_2$.

0·147 gram (= 1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
25	Complete absorption of all rays beyond	1900	5263
20	The same.		
15	The same, except two strong lines appearing very feebly at.....	2884	3467
	and.....	2938	3403
10	Same as preceding, but lines more distinct.		
	Line also at.....	2768	3612
	Spectrum continuous, but weak, from.....	2884	3467
	to	2997	3336
5	**Absorption band 1900—2768.**		**5263 to 3612**
	Line at	2768	3612
	Spectrum continuous, but faint, from.....	2826	3538
	to.....	3004	3320
	Lines $^1/\lambda$ 3064 and $^1/\lambda$ 3076 faintly transmitted.		
4	**Absorption band 1900—2768.**		**5263 to 3617**
3	**Absorption band 2083—2768.**		**4800 to 3612**
	Spectrum continuous $^1/\lambda$ 2768 to	3064	3263
2	Spectrum nearly continuous, but weak, to...	2768	3612
	Spectrum strong $^1/\lambda$ 2768 to	3076	3250
	Line showing at	3638	2748
1	Same as (2), with lines at ..... and $^1/\lambda$ 3886.	3638	2748
	Absorption band 3076—3638.		{3250 2748
	Complete absorption beyond.		

Isatin—(continued).

0·147 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	3188	3136
	Absorption band 3188—3638.		**3136 to 2748**
	Faint spectrum from $^1/\lambda$ 3638 to	3886	2573
	Strong line at 3886. Complete absorption beyond.		
3	Spectrum continuous to.....	3240	3086
	Absorption band 3240—3638.		**3086 to 2748**
	A few lines showing faintly.		
	Faint spectrum $^1/\lambda$ 3638 to	3886	2573
	Complete absorption beyond.		
2	Same as preceding, with lines showing more distinctly.		
	Spectrum continuous to.....	3214	3111
	also from $^1/\lambda$ 3601 to 3886.		
1	Spectrum continuous to.....	3886	2573
	but faint between $^1/\lambda$ 3528 and.....	3638	2748
	Complete absorption beyond.....	3886	2573
	except for strong line showing faintly at..	4423	2260

Isatin—(continued).

0·147 gram in 2500 c.c. of alcohol.

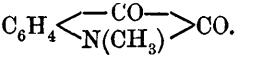
Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	3900	2564
	Still somewhat faint between.....	3284	3045
	and.....	3605	2773
	Complete absorption beyond	3900	2564
3	except for lines showing faintly between $^1/\lambda$ 4331 and 4418.		
	Spectrum continuous and fairly strong to ...	3952	2530
2	Additional lines showing at $^1/\lambda$ 4306, 4478, and 4828.		
	Spectrum continuous and strong to.....	3952	2530
1	Lines showing between $^1/\lambda$ 4290 and 4656. Same as (2).		

Isatin—(continued).

0·147 gram in 12,500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Spectrum continuous to.....	4290	2331
	Weak between $^1/\lambda$ 3965 and 4290.		
	Strong lines showing between 4290 and 4656.		
3	Spectrum continuous; weak between $^1/\lambda$ 3965 and	4290	2331
2	Spectrum continuous.		
1	,, ,,		

Methylpseudoisatin, $C_9H_7NO_2$. M. p. 133°.



0·161 gram (= 1milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ
25	Complete absorption of all rays beyond	1900	5263
20	,, ,, ,, ,,		
15	Complete absorption beyond 1900, except lines at $^1/\lambda$ 2884 and 2938.		
10	Complete absorption beyond 1900, with additional line at 2768.		
5	**Absorption band 1900—2768.**		**5263** to **3612**
	Strong line visible at 2768.		
	All lines transmitted from $^1/\lambda$ 2768 to.....	3004	3328
4	Line at $^1/\lambda$ 2083. Feeble, but not continuous, spectrum to 2768.....		
	Absorption band feeble, **1900—2768.**		**5263** to **3612**
	All lines transmitted from 2768 to	3076	3250
3	Continuous, but feeble, spectrum to	3076	3250
	Still somewhat feeble from $^1/\lambda$ 2083 to	2768	3612
2	Continuous spectrum to.....	3076	3250
	Complete absorption beyond, except for line at $^1/\lambda$ 3638.		
1	Continuous spectrum to.....	3076	3250
	Complete absorption beyond, except line at 3638.		

Methylpseudoisatin—(continued).

0·161 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Continuous spectrum to.....	3240	3086
	Absorption band 3240—3638.		**3086** to **2748**
	Complete absorption beyond.		
	A few lines showing faintly between $^1/\lambda$ 3240 and	3638	2748
3	Same as (4). Line showing very faintly at 3886.		
2	Spectrum continuous to.....	3638	2748
	but faint from $^1/\lambda$ 3240 to.....	3638	2748
1	Same as (2), with lines showing faintly at ...	4331	2308
	and	4425	2259

Methylpseudoisatin—(continued).

0·161 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Continuous spectrum to	3886	2573
	Lines showing between	4306	2322
	and	4542	2206
3	Continuous spectrum to	3886	2573
	Lines showing between	4290	2331
	and	4542	2206
2	Continuous spectrum to	3918	2552
	Lines showing between	4290	2331
	and	4656	2147

Methylpseudoisatin—(continued).

0·161 gram in 12,500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Continuous spectrum to	3965	2522
	Almost complete absorption $^1/\lambda$ 3965 to	4290	2331
	All the strong lines between $^1/\lambda$ 4290 and 4656 seen.		
3	Continuous spectrum to	4290	2331
2	,, ,, but stronger.		
1	,, ,, ,,		

Methylisatin, $C_9H_7NO_2$. M. p. 101°.

$$C_6H_4\langle\begin{matrix}CO\\ -N\end{matrix}\rangle CO\cdot CH_3.$$

0·161 gram (= 1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
25	Complete absorption of all rays beyond	1900	5263
20	,, ,, ,, ,,		
15	,, ,, ,, ,,		
10	Complete absorption except line at $^1/\lambda$ 2083.		
5	The same as 10 with lines at 2137 and 2161.		
4	Spectrum continuous from $^1/\lambda$ 2083 to	2175	4597
	Very faint line at 3471.		
3	**Absorption band 2175—3354.**		**4597 to 2981**
	Lines showing feebly at 3354 and 3471.		
2	Spectrum continuous to	2270	4405
	Absorption band 2270—2775.		**4405 to 3603**
	Faint spectrum from $^1/\lambda$ 2775 to	3528	2834
1	Same as (2), but rays stronger. Very faint line at	3644	2744

† *Methylisatin*—(continued).

0·161 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Continuous spectrum to.....	2357	4242
	Very faint indication of lines from 2443 to	2472	4045
	Absorption band 2472—2768.		**4045 to 3612**
	Rather weak spectrum from $^1/\lambda$ 2768 to.....	3638	2748
	Complete absorption beyond.		
3	Continuous spectrum to.....	2502	3996
	Feeble **Absorption band 2502—2768.**		**3996 to 3612**
	Spectrum from $^1/\lambda$ 2768 to	3638	2748
	Complete absorption beyond.		
2	Same **Absorption band** but feebler from **2502—2768.**		**3996** to **3612**
1	Same as preceding; line at ..... more strongly marked.	3886	2573

Methylisatin—(continued).

0·161 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Continuous spectrum to.....	3638	2748
	Very faint continuation to.....	3733	2678
	Complete absorption beyond, except strong line at 3886.		
3	Continuous spectrum to.....	3638	2748
	With faint continuation to	3900	2564
	Very faint indication of line at 4046.		
2	Spectrum continuous to.....	4038	
	With lines showing between 4306 and 4656.		
1	Continuous spectrum to.....	4120	2427
	Same otherwise as preceding.		

Methylisatin—(continued).

0·161 gram in 12,500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	$^1/\lambda$.	λ.
4	Continuous spectrum to.....	4135	2418
	Somewhat faint from	3886	2573
	to	4135	2418
3	Continuous spectrum.		
2	,, ,,		
1	,, ,,		

Our best thanks are due to Mr. Alexander Lauder, of the University College of North Wales, Bangor, for his assistance in the general work of the research, and especially for the great care he has taken in preparing the substances examined.

We are now engaged in a more comprehensive research on this subject, embracing the examination of the absorption spectra of derivatives of etheric succinosuccinates, phloroglucinol, and other substances which exhibit tautomeric phenomena.

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