LXVIII.—*The Absorption Spectra of the Vapours and Solutions of Anisole, Phenetole, and Various Derivatives.*

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IN previous communications the author has shown that the physical conditions and the nature and type of the atoms or atomic groups introduced in an oscillatory centre like benzene exercise a powerful influence on the absorption. It was proved, for example, that the vapour bands of the chlorine and bromine derivatives of benzene, and of other substances like phenol and aniline, were not so sharply defined, and were slightly more diffuse than the bands of the simple molecules themselves, and that there was a gradual decrease in the number of bands as the number of such side-chains increased, so that, finally, all the fine bands disappeared, and the absorption was then comparable with the solution phenomena. It was further proved that there was a complete absence of the fine vapour bands in the iodo- and nitro-derivatives of all these substances.

It has been shown (Purvis and McClelland, T., 1912, **101**, 1514) that whereas anisole exhibited a considerable number of vapour bands, the vapour of diphenyl ether had only two diffuse bands which were comparable with the solution bands, and that the vapour bands in *m*-aminophenol were considerably diminished, and in *m*-dimethylaminophenol and azoxybenzene they were completely eliminated, although benzene, aniline, and phenol possessed a large number of such bands (Purvis, T., 1913, **103**, 1088, 1638; 1914, **105**, 590).

The author has continued the investigation with anisole and phenetole and various derivatives of these substances to see how far and in what directions the absorption is influenced by the introduction of different groups in the vibrating nucleus. The substances investigated were: *p*-bromoanisole, phenetole, *p*-fluorophenetole, *p*-bromophenetole, *o*- and *p*-anisidines, *o*- and *p*-phenetidines, *p*-azoxyanisole, and *p*-azoxyphenetole.

The experimental conditions have been described before.

Anisole and p-Bromoanisole.—The vapour bands and the solution bands of anisole have already been described (*loc. cit.*). It was shown that the number of narrow vapour bands was forty-one, whereas there were only two rather wide and diffuse solution bands; but when the vapour was subjected to higher temperatures and pressures the bands became wider and more diffuse, and finally attained the appearance of the solution phenomena. The two solution bands may be considered to correspond with two groups of

well-marked vapour bands, and the following numbers give the positions of the heads of these bands. It was not possible to measure the edges of the diffuse solution bands, and therefore the middle of the strongest part, which was towards the more refrangible edge, was measured, and the strongest constituent of the vapour bands on its more refrangible edge was also measured:

Solution bands of anisole.	Vapour bands of anisole.
λ	λ
2800	2749, a group of 10 bands, fairly strong.
2725	2681, a group of 8 bands, fairly strong.

The more refrangible vapour bands between λ 2680 and λ 2516 do not appear in the solutions; but the rapid absorption to λ 2560 probably represents these bands weakened and widened by the solvent. It may be mentioned that the vapour bands of anisole are like those of phenol (*loc. cit.*), except that several of the weaker, more refrangible bands of the former are absent.

In *p*-bromoanisole, solutions varying from $M/100$, $M/1000$, and $M/10,000$ were examined, and at thicknesses from 2 mm. to 30 mm. The absorption was not unlike that of the corresponding solutions of anisole, but the two bands were much weaker and wider and more diffuse than the corresponding bands of the latter.

The vapour of *p*-bromoanisole was examined at temperatures and pressures varying from 16° and 770 mm. to 90° and 930 mm., and eight bands were observed between λ 2898 and λ 2700. These bands were wider and more diffuse than the corresponding bands of anisole, even at the lowest temperatures and pressures, and were shifted more towards the red end. The narrower bands of anisole had not only decreased in number, but were very diffuse; they were also more diffuse and fewer than the vapour bands of *p*-bromophenol (*loc. cit.*). The position of the corresponding solution and vapour bands are:

Solution bands of <i>p</i> -bromoanisole.	Vapour bands of <i>p</i> -bromoanisole.
λ	λ
2910	2869, a strong wide band ranging to λ 2880, which showed doubtful signs of division.
2820	2790, a moderately strong band ranging to λ 2778, which also showed doubtful signs of division.

Phenetole, *p*-*Fluorophenetole*, and *p*-*Bromophenetole*.—The absorption phenomena of the phenetole solutions were very like those of anisole. There were two well-marked bands (Fig. 1, I, upper curves), and these gradually widened into each other to produce

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one large band at greater thicknesses, with a rapid extension of the absorption on the more refrangible side.

The vapour of phenetole was examined at temperatures ranging from 16° and 757 mm. to 90° and 917 mm., and forty bands were observed which were measured and classified. The bands were very like those of anisole (*loc. cit.*), except that they were shifted slightly more towards the red, and they were a shade more diffuse. Two of the stronger groups of the vapour bands correspond with the two solution bands, and the following numbers give the heads of these bands, together with two corresponding groups of anisole vapour bands:

Solution bands of phenetole.	Vapour bands of phenetole.	Vapour bands of anisole
λ	λ	λ
2800	2750, a strong group of 8 bands.	2749, a strong group of 9 bands.
2720	2682, a strong group of 9 bands.	2681, a strong group of 8 bands.

There were other much weaker bands beyond λ 2682, which would probably correspond with the rapid absorption in the solution between $1/\lambda$ 3715 and $1/\lambda$ 4080.

In *p*-fluorophenetole the solution phenomena were not unlike those of phenetole, except that the bands were not so well defined. The two bands were weaker and more diffuse; but, like the others, they widened into each other, and formed one large band at greater thicknesses.

The vapour of *p*-fluorophenetole was examined at temperatures ranging from 10° and 763 mm. to 90° and 923 mm., and thirty-one bands were observed between λ 2860 and λ 2684. These bands were clear and well defined, and were fewer in number than in phenetole; the bands on the more refrangible side of the latter were eliminated in *p*-fluorophenetole. The bands were measured and classified. There are several well-defined groups amongst them, two of which can be compared with the two solution bands:

Solution bands of <i>p</i> -fluorophenetole.	Vapour bands of <i>p</i> -fluorophenetole.
λ	λ
2900	2852, a group of 5 bands moderately strong.
2830	2780, a group of 5 bands, fairly strong.

In *p*-bromophenetole the solutions showed two bands not unlike those of phenetole itself, but they were much weaker and wider and more diffuse (Fig 1, III, upper curves). The vapour of *p*-bromophenetole exhibited eight bands between λ 2924 and λ 2792 at temperatures and pressures ranging from 16° and 750 mm. to 100° and 926 mm. As compared with the vapour bands of *p*-bromoanisole, the bands were more diffuse and weaker; and, as compared

with the vapour bands of phenetole and *p*-fluorophenetole, they were wider and more diffuse and fewer in number. Two of the stronger groups of the vapour bands are comparable with the two weak diffuse solution bands:

Solution bands of *p*-bromophenetole.

λ
2910

2810

Vapour bands of *p*-bromophenetole.

λ
2894—2861, a strong band, stronger on the more refrangible edge, which shows doubtful signs of division.
2802—2791, a very weak diffuse band.

FIG. 1.

o- and *p*-Anisidines.—The solution curves of these substances have been drawn (Fig. 1, I and II, lower curves). It will be noticed that both show two well-defined bands, and that those of the para-compound are shifted considerably more towards the red.

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The vapour of *o*-anisidine was examined at temperatures and pressures varying from 13° and 760 mm. to 100° and 936 mm., and the following phenomena were observed:

<i>t</i> °.	Pressure in mm.	
50	840	The rays were feebly absorbed between λ 2920 and λ 2780, and then transmitted to λ 2410; they were then completely absorbed to the Cd line λ 2329; and from here the series of Cd lines to λ 2144 were fairly well marked.
55	850	The rays were fairly well absorbed between λ 2940 and λ 2780; then transmitted to about λ 2420; also the Cd lines 2265, 2194, 2144 were fairly well marked.
65	870	The rays were almost completely absorbed between λ 2970 and λ 2750, and then transmitted to λ 2450.
75	890	The rays were completely absorbed between λ 2990 and λ 2710, and then transmitted to λ 2480.
85	910	The rays were completely absorbed from λ 3010, except that the Cd line 2573 was fairly well marked.
95	920	The rays were completely absorbed from about λ 3020

The vapour of *p*-anisidine was examined at temperatures and pressures varying from 14° and 760 mm. to 100° and 936 mm., and the following phenomena were observed:

<i>t</i> °.	Pressure in mm.	
65	870	The rays were transmitted to Cd 2144, but they showed signs of weakening between λ 2400 and λ 2340.
70	880	The rays were transmitted to λ 2440, and then absorbed to Cd 2329; from here the Cd lines 2329 to 2144 were quite strong.
75	890	The rays were feebly absorbed between λ 3100 and λ 2960, and then transmitted to λ 2450; the Cd lines 2329 to 2265 were fairly well marked.
80	900	The rays were fairly well absorbed between λ 3130 and λ 2900, and then transmitted to λ 2480.
85	910	The rays were almost completely absorbed between λ 3140 and λ 2850, and then transmitted to λ 2510.
95	920	The rays were completely absorbed between λ 3150 and λ 2780, and then transmitted to λ 2580.
100	936	The rays were absorbed from λ 3200, except that between λ 2700 and λ 2580, there was a very weak transmission.

o- and *p*-Phenetidines.—The alcoholic solutions and the vapours of these two substances were also examined under similar conditions of temperature and pressure, and similar phenomena were observed, except that the two bands of the heavier molecules were shifted more towards the red. The results are therefore not described in detail. It is, therefore, clear from the observations that neither the anisidines nor the phenetidines exhibited any of the numerous vapour bands shown by aniline or phenol (*loc. cit.*), and that the few bands found in the halogen derivatives of anisole and phenetole have also completely disappeared.

p-Azoxyanisole and *p*-Azoxyphenetole.—Solutions of these two

FIG. 2.

The absorption spectra of the vapours of phenol and benzene.

The wave-lengths of the heads of the chief series of bands of benzene vapour are marked below, and the wave-lengths of phenol above, the photograph. The series of sharply-defined bands of phenol between 2644 and 2520 are well marked.

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substances showed similar absorption to that of azoxybenzene (*loc. cit.*). The absorption curve of *p*-azoxyanisole has been drawn (Fig. 1, II, upper curves) to show the great differences between its type of absorption and that of several of the other substances. The positions of the heads of the solution bands of the azoxy-compounds compared with azoxybenzene are:

	λ
Azoxybenzene	3225
<i>p</i> -Azoxyanisole	3550
<i>p</i> -Azoxyphenetole	3600

The vapours of the two substances were not examined because of their comparatively high melting points; but, as in azoxybenzene which has been examined (*loc. cit.*), it is scarcely likely that the vapours would exhibit any narrow bands. The great shift of the solution bands of *p*-azoxyanisole and *p*-azoxyphenetole as compared with azoxybenzene is worthy of note, because a similar great shift takes place in the vapour and solution bands of phenol as compared with benzene.

Witte ("Zur Struktur der ultravioletten absorptionspektren des Benzols und seiner monoderivate," *Diss.*, Leipzig, 1914) demurs to the statement (Purvis and McClelland, T., 1913, **103**, 1088) that the absorption spectrum of phenol does not show any resemblance to that of benzene described by Hartley (*Phil. Trans.*, 1907, [A], **208**, 475). At the time of the observations the photographs of phenol were compared with the reproductions of the photographs of benzene as published in Hartley's memoir. In order to test this further, the author has photographed the spectra of approximately equal quantities of benzene and phenol in a 200 mm. tube. The photographs were originally enlarged to twice the size, and even in the smaller reproductions (Fig. 2) it will be noticed that there is a striking difference between the two spectra. The phenol bands are shifted very considerably towards the red as compared with those of benzene, and the heads of the various groups are clear and well defined. When the plates are arranged so that the heads of the strongest bands of both substances lie just below one another, there does not appear to be any close resemblance between the various groups of bands, except that some groups in both are stronger than others.

General Results.

The outstanding results of the observations are:

- (1) The smaller number of vapour bands of *p*-bromoanisole, and their more diffuse appearance, as compared with the vapour bands of anisole.
- (2) The considerable number of vapour bands of phenetole,

which are comparable with those of anisole; the decreased number of vapour bands of *p*-fluorophenetole, and still more of *p*-bromophenetole; and the more diffuse appearance of the bands of the latter compound.

(3) The absence of the numerous vapour bands when the substances are in solution, and the more diffuse appearance of the solution bands of *p*-bromoanisole, *p*-fluorophenetole, and *p*-bromophenetole as compared with the solution bands of anisole and phenetole.

(4) The complete absence of any narrow vapour bands in the anisidines and phenetidines, and the close similarity of their solution and vapour bands.

(5) The similarity of the large solution bands of *p*-azoxyanisole and *p*-azoxyphenetole with that of azoxybenzene.

(6) The substitution in all the substances at higher temperatures and pressures of all the fine vapour bands by wide and diffuse bands which are comparable with the solution bands.

The introduction of an aliphatic group in phenol, as in anisole and phenetole, does not alter fundamentally the type of absorption in phenol itself, although the bands are not so sharp; but when fluorine or bromine is introduced in the nucleus there is a considerable decrease in the number of the finer bands, and they are much wider and more diffuse, particularly in the bromine compounds. Such changes may be caused by the introduced atoms or atomic groups damping and neutralising the fundamental electronic oscillations of the nucleus, whereby the period and amplitude are considerably altered; when the amino-group is introduced, as in the anisidines and phenetidines, the complex oscillations are completely neutralised, and a single large absorption band takes the place of the numerous bands found in aniline and phenol.

The comparatively wide and diffuse solution bands may indicate that the solvent produces an association of the molecules whereby the oscillations are partly mutually neutralised and partly exercised against this constraining force. Such a close association may also be produced when the molecules of the vapour are forced closer together by the constraining influence of increased pressures, for, as the author has also shown in previous communications, the absorption bands of the vapours are, under such conditions, similar to those of the solutions, and also to those of very thin films where the molecules are definitely in closer association. This intimate connexion of the vibrating centres is more obvious when there are two benzene radicles in the molecule, as in the azoxy-compounds, or as in diphenyl (Purvis, T., 1914, 105, 590), and the result is apparent in a simpler type of absorption band than that found in

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anisole or phenetole or benzene. Moreover, the incomplete neutralisation of the valencies of the nitrogen atoms, which act as oscillatory centres, is another powerful influence, particularly in the production of the colour of the azoxy-compounds.

I desire to thank the Chemical Society for a grant in aid of the expenses of this investigation.

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[*Received, April 8th, 1915.*]