CCCXX.—The Fluorescence Spectra of the Vapours of Fluorobenzene and p-Fluorotoluene.

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Contrary to previous report (J., 1923, 123, 2155), it has been found that chlorobenzene and most chlorine-substituted derivatives of benzene having the chlorine atom in the nucleus emit characteristic spectra when their vapours are subjected to the high-tension discharge from a Tesla transformer. The spectra, in the same circumstances, of fluorobenzene and p-fluorotoluene are similar to those of the corresponding chloro-compounds but are much more completely developed. It seemed of interest, therefore, to examine the spectra, if any, emitted by these fluoro-compounds under the influence of ultra-violet light, since benzene and its simple substitution products emit identical spectra when their vapours are excited either by the high-tension discharge or by the short waves from a mercury lamp (Marsh, ibid., p. 3315, etc.). The apparatus

employed in this investigation was identical with that described by Marsh (loc. cit.).

The fluoro-compounds were prepared by Wallach's method, in which the diazopiperidide of the corresponding amine is decomposed with concentrated aqueous hydrofluoric acid; 15% of the theoretical yield of the fluoro-compound was obtained in each case and 40 g. of each compound were prepared. Before examination the purified fluoro-compound was diluted with alcohol (80 g.) that had been carefully purified and showed no absorption above λ 2200. This results in a dilution of the vapour of the compound with nonactinic alcohol vapour and so reduces absorption effects.

Both compounds that have been examined in detail give well-banded spectra in the ultra-violet, identical with their Tesla-luminescence spectra but containing fewer bands. In the spectrum of fluorobenzene, 22 sharp bands are measured in the ultra-violet; these fall into groups showing an identical arrangement with the bands in the Tesla-luminescence spectrum. Differences in the position of bands in the two cases are due to errors of measurement. The spectrum of p-fluorotoluene shows 18 bands, which again are identical with those in the Tesla spectrum. No part of the fluorescence spectrum can, however, be identified with the bands in the green region found in the Tesla spectrum.

Fluorobenzene.

Luminescence

| Fluorescence | | $\frac{3724}{3727}$ | $\frac{3720}{3721}$ | $\frac{3690}{3695}$ | $\frac{3678}{3681}$ | 3652 3651 |
|---------------------------------------|------|---------------------|---------------------|---------------------|---------------------|--------------|
| Fluorescence Luminescence | | 3599 3598 | 3590 3590 | 3534 3535 | 3511 3514 | |
| ${\bf p}\text{-}{\it Fluorotoluene}.$ | | | | | | |
| Fluorescence | 3573 | 3555 | 3536-363 | 36 35 | 16 3 | 4903390 |

3555

3573

Experimental Data.—Fluorobenzene. No relationship can be seen between the various wave-lengths, but the wave-numbers per mm. can be grouped as shown:

3638

3511

| A. | | в. | | C. | | D. |
|------|-------|------|-------|------|-------|------|
| | | | | 3599 | | |
| | | 3690 | (100) | 3590 | | |
| | | 3686 | ` ' | | | _ |
| 3778 | (100) | 3678 | | _ | | |
| 3774 | , , | | | | | |
| 3770 | (105) | 3665 | (100) | | (99) | 3466 |
| | • • | 3662 | (101) | | (102) | 3459 |
| | | 3652 | | | , , | |
| 3746 | (100) | 3646 | | | | _ |
| 3744 | (103) | 3641 | | | | |
| | • | 3635 | (101) | 3534 | | |
| 3724 | | | | | | |
| 3720 | | | | | | |
| | | | | 3511 | | |

The wave-number differences are given in brackets. Corresponding bands in adjacent groups differ by nearly v 100.

p-Fluorotoluene. No relationship can be traced between the wave-lengths of the various bands, but they can be grouped in two ways to show a simple wave-number relationship. In one case corresponding bands in the adjacent groups differ by ν 100, and in the other by ν ca. 80.

| Arrangement | (1). | | | | | |
|------------------|-------|-------------|------|------|------|------|
| Α. | | В. | | C. | | D. |
| | | 3597 | | | | - |
| | | 3594 | | | | |
| | | 3588 | (99) | | (99) | 3390 |
| 3682 | | | | | | |
| 3673 | (100) | 3573 | (99) | 3474 | | |
| | | 3569 | | | | |
| 3659 | (100) | 3555 | (95) | 3460 | | |
| 3650 | (106) | 3544 | | | | _ |
| 3638 | | | | | | |
| | | | | 3428 | | |
| | | 3511 | | | | |
| | | 3507 | | | | |
| Arrangement (2). | | | | | | |
| Α. | | в. | | С. | | D. |
| 3682 | (75) | 3597 | (84) | | (85) | 3428 |
| 3673 | (79) | 3594 | (83) | 3511 | ` ' | |
| | ` ' | 3588 | (81) | 3507 | | |
| 3659 | (86) | 3573 | ` ' | | | |
| 3650 | (81) | 3569 | | | | |
| 3638 | (83) | 3555 | (81) | 3474 | (84) | 3390 |
| | • | 3544 | (84) | 3460 | , , | |

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