# **371.** *Organic Fluorides. Part VIII.* The Ultra-violet Absorption Spectra of Some Aromatic Compounds containing Fluorine.*

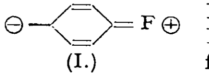
By F. Smith and Lilian M. Turton.

Measurements of the absorption of ultra-violet light by derivatives of fluorobenzene and benzotrifluoride are recorded. Some attempt is made to correlate the spectra with the chemical properties of the compounds concerned.

Although this series of papers is mainly concerned with fluorocarbons, it was thought that spectrophotometric examination of nuclear and side-chain fluorinated substances might help in devising new fluorination techniques, in interpreting results obtained by the methods already in use, and in explaining the chemical behaviour of organic compounds containing fluorine. Moreover, information regarding electronic movements obtained by ultra-violet spectrophotometric measurements may be extended to molecules which do not absorb in that region.

Comparatively few studies of ultra-violet light absorption by fluorobenzene derivatives, other than monofluorobenzene itself, have been reported. Conrad-Billroth (*Z. physikal. Chem.*, 1935, **33**, *B*, 311) discussed the theoretical significance of ultra-violet light absorption of some fluoro-halogeno-benzenes and -toluenes, as did Forster and Wagner (*ibid.*, 1937, **35**, *B*, 343) who examined also *p*-fluoroaniline and *p*-fluoronitrobenzene. A brief mention of the effect of side-chain fluorination on light absorption has been made by Ingold (*J.*, 1928, 2249). More recently, attention has been directed by Miller and Thompson to the peculiar light-absorption properties of aromatic fluoro-compounds (*J. Chem. Physics*, 1949, **17**, 845).

Fluorine is not in itself chromophoric, for simple aliphatic fluorocarbons, such as fully fluorinated paraffins and *cyclo*alkanes, do not absorb ultra-violet light selectively. Its effect on the spectra of substances into which it is introduced might thus be expected to be small, and similar to that of the other halogens, unless special influences are operative. Ingold (*loc. cit.*; *J.*, 1938, 927) has established by nitration studies that for both the inductive effect and the electromeric effect, halogens act in the order F > Cl > Br > I (cf. also Baddeley *et al.*, *J.*, 1935, 1827). The electromeric effect must be dominant in halogenobenzenes, for nuclear halogen is *ortho–para*-directing. As a general rule, monosubstitution in the benzene ring shifts the position of maximum absorption towards red, increases its intensity, and smoothes out subsidiary vibrational maxima within the bands (Morton and McGookin, *J.*, 1934, 901; Morton, " Practical Aspects of Absorption Spectrophotometry," R. Inst. Chem., 1938). The introduction of groups such as methyl or chlorine causes only small variations; other substituents such as amino or methoxyl produce approximately ten-fold increases in intensity and band displacements of the order of 100 A. The electronic transitions responsible for the bands are thought to be the same in substituted as in unsubstituted benzene, but the presence of the substituent alters the probability of the transition occurring and slightly modifies the energy it requires. The influence of substituents which cause marked changes in the spectrum (auxochromes) is believed to be connected with their ability to become conjugated with the absorbing system, thus multiplying the number of canonical structures which contribute to the ground state of the molecule and lowering the difference in energy between the ground state and the excited state, *e.g.*, $R{-}NH_2 \longrightarrow \overset{\ominus}{R}{=}\overset{\oplus}{N}H_2$. As Table I shows, substitution of fluorine in the benzene nucleus markedly increases the intensity of absorption, more nearly resembling methoxyl and amino-groups than chlorine. These findings are in agreement with the series of inequalities (quoted above) that Ingold obtained by chemical experiments and also with Pauling's postulate (" The Nature of the Chemical Bond," Cornell Univ. Press, 2nd edn., 1945, pp. 153, 235, 350) that structure (I) as a canonical form for fluorobenzene has at least twice the probability of the analogous form in chlorobenzene. This may well have an important bearing on the differences between chlorination and fluorination.



(I.)

Table II and Fig. 1 present a comparison of some nitro- and amino-toluene derivatives with corresponding monofluoro-compounds. It will be seen that introduction of fluorine at position 2

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* Part VII, *J.*, 1951, 609.

in 4-nitrotoluene lowers both the wave-length and the intensity of maximum absorption, while a similar substitution in 4-aminotoluene causes little change. As data for 4-acetamido-5-nitrotoluene are not available, values for 4-amino-5-nitrotoluene are included in Table II for comparison with those of 4-acetamido-2-fluoro-5-nitrotoluene. Since acetylation of an amino-compound usually smooths out the bands of higher wave-length into inflexions the introduction of fluorine at position 2 seems to cause slight lowering of intensity of absorption, together with considerable displacement of the 4175-A. band.

TABLE I.

| Substance. | $\lambda_{\text{max.}}$, A. | $\varepsilon$. | Solvent. | Ref. |
|---|---|---|---|---|
| Benzene | 2550 | 300 | Alcohol | 1 |
| Chlorobenzene | 2640 | 300 | Alcohol<br>Hexane | 1, 2 |
| Fluorobenzene | 2600 | 1500 | Hexane | 2 |
| Aniline | 2340; 2845 | 11,500; 1750 | Alcohol | 3 |
| Anisole | 2720 | 2,200 | Alcohol | 1 |
| Toluene | 2617—2645 | 300 | Hexane | 1, 2 |
| *o*-Fluorotoluene | 2600—2690 | 900 * | Hexane | 2 |
| *o*-Chlorotoluene | 2650 | 300 * | Hexane | 2 |

(1) Morton and Stubbs, *J.*, 1940, 1348. (2) Conrad-Billroth, *Z. physikal. Chem.*, 1934, **25**, *B*, 139. (3) Morton and McGookin, *loc. cit.*

* The *p*-halogenotoluenes have higher $\varepsilon$ values, but the relative value is the same.

TABLE II.

| Compound. | Principal $\lambda_{\text{max.}}$, A. | $\varepsilon$. | Solvent. | Ref. |
|---|---|---|---|---|
| *p*-Nitrotoluene | 2722 | 11,500 | ? | 1 |
| *p*-Aminotoluene | 2357; 2905 | 10,300; 2000 | ? | 1 |
| 4-Amino-5-nitrotoluene | 2300; 2800; 4175 | 20,000; 6300; 5700 | Alcohol | 1 |
| *m*-Phenylenediamine | 2300; 2930 | 10,000; 3000 | Alcohol | 1 |
| 2-Amino-4-nitrotoluene | $\left.\begin{matrix}2310\\2530\end{matrix}\right\}$ 2885; 3730 | 12,000; 4900; 1700 | Alcohol | 1 |
| *p*-Fluoronitrobenzene | 2570 | 8700 | Hexane | 2 |
| *p*-Fluoroaniline | 2900—3000 | 3300 | Hexane | 2 |
| *p*-Chloroaniline | 2900—2970 | 2300 | Hexane | 2 |
| *p*-Aminophenol | 2870 | 3300 | ? | 1 * |
| *p*-Nitroaniline | 2300; 3800 | 5000; 10,000 | Water | 3 |
| | 3740 | 15,350 | Alcohol | 1 |
| | 3550 | 15,000 | Hexane | 3 |
| *p*-Phenylenediamine | 2905 | 3300 | Alcohol | 1 |
| Nitrobenzene | 2570 | 10,000 | ? | 1 |
| *p*-Chloronitrobenzene | 2701 | 11,300 | Alcohol | 1 |
| | 2650 | 12,900 | Hexane | 2 |
| *p*-Nitrophenol | 2300; 3200 | 6000; 10,000 | Alcohol | 3 |
| | 2250; 2900 | 6000; 8000 | Hexane | 3 |

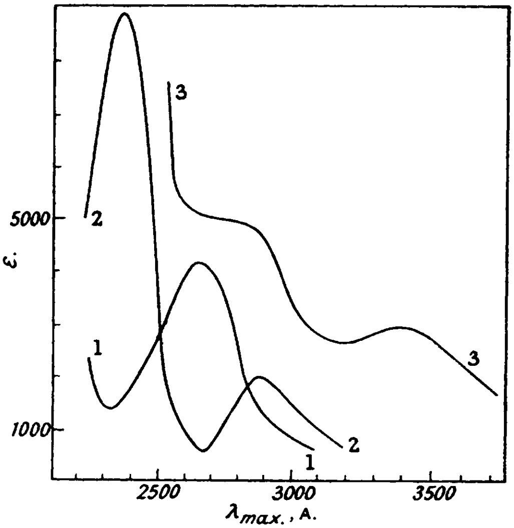
(1) Morton and McGookin, *loc. cit.* (2) Forster and Wagner, *loc. cit.* (3) Dede and Rosenberg, *Ber.*, 1934, **67**, 147.

* Ref. 1, Table I, misquotes the result given in Ref. 1 as 3015; 2700. The above figures have been calculated from the experimental curve.

The sole difference between 4-amino-2-fluorotoluene and 2-fluoro-4-nitrotoluene lies in the fact that the nitro-group is an electron acceptor and the amino-group an electron donor. The close resemblance between the spectra of aniline and *m*-phenylenediamine on the one hand, and *p*-amino- and 4-amino-2-fluoro-toluene on the other, provides some support for the conclusion that fluorine is behaving as a donor group, causing little change in the energy of the transition and a relatively small increase in its probability (intensity) when introduced into a benzene ring which already contains a donor group. Forster and Wagner's results (*loc. cit.*) for *p*-fluoroaniline, when compared with other *para*-derivatives of aniline (see Table II), also agree with the conclusion that nuclear fluorine acts strongly by the electromeric effect (cf. Sponer and Lowe, *J. Opt. Soc. Amer.*, 1949, **39**, 840; Roberts, Webb, and McElhill, *J. Amer. Chem. Soc.*, 1950. **72**, 408).

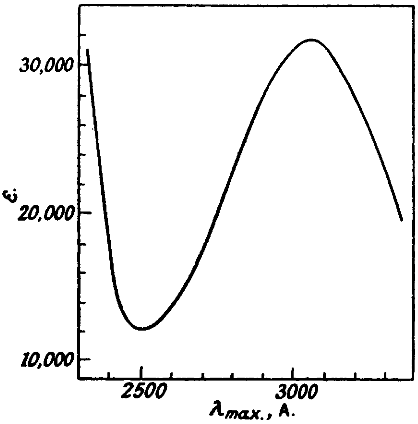
Since the nitro-group is itself a chromophore it is not easy to decide which bands of nitrobenzene derivatives should be assigned to electronic transitions associated with the ring and which to those of the nitro-group. Moreover, solvent has a marked effect upon the absorption of these compounds. If the low-wave-length bands of *p*-nitrophenol and *p*-nitroaniline are comparable with the 2570-A. band of nitrobenzene, fluorine substituted in position 4 in nitrobenzene is tending to behave similarly to hydroxyl and amino-substituents. The difference between *p*-fluoro- and *p*-chloro-nitrobenzene is rather striking, but on the other hand there is little resemblance between the spectra of 2-amino- and 2-fluoro-4-nitrotoluene ; for these the differences may be connected in part with solvent effects. It is of interest, however, that Conrad-Billroth (*loc. cit.*) and Forster and Wagner (*loc. cit.*) were unable to ascribe a generally applicable " vector length " ($Q$ value) to fluorine, as fluoro-compounds displayed inexplicable deviations from theoretical expectations.

FIG. 1.



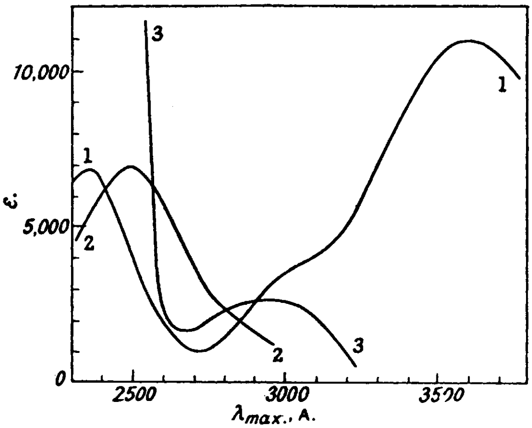
1. *2-Fluoro-4-nitrotoluene* (*in* cyclo*hexane*).
2. *4-Amino-2-fluorotoluene* (*in ethanol*).
3. *5-Fluoro-2-nitroacetanilide* (*in ethanol*).

FIG. 2.



*Azobenzotrifluoride* (*in ethanol*).

FIG. 3.

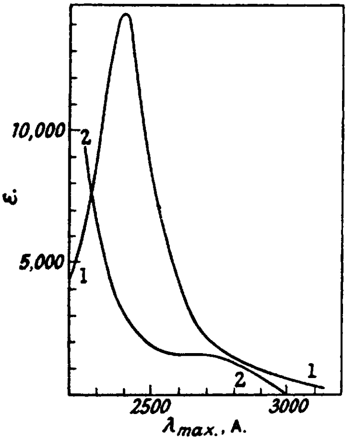


1. *5-Amino-2-nitrobenzotrifluoride* (*in ethanol*).
2. m-*Nitrobenzotrifluoride* (*in ethanol*).
3. m-*Aminobenzotrifluoride* (*in ethanol*).

The $CF_3$ group was observed by Swarts (*loc. cit.*) to have a hypsochromic effect on a dye, increasing the intensity of the absorption and the definition of diffuse absorption bands. Comparison of the spectrum of azobenzotrifluoride (Fig. 2) with that of azobenzene (Table III) shows an effect of this kind in the ultra-violet region : the weaker band (4450 A.) is completely absent in the fluorine-containing derivative. The spectra of trichloromethyl- and trifluoromethyl-benzenes without other substituents will be dealt with in a later communication.

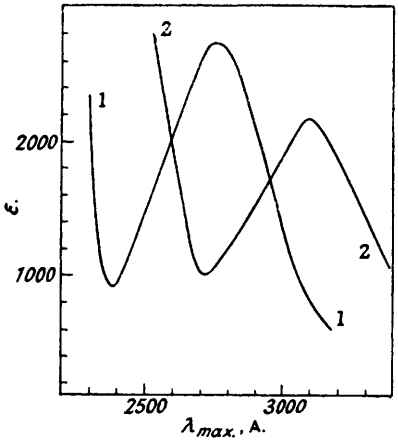
Table III contains data for some nitro-, amino- and aminonitro-toluenes for comparison with Figs. 3 and 4. 5-Amino-2-nitrotoluene and 5-amino-2-nitrobenzotrifluoride have intensities of the same order, but fluorination has caused the 3735-A. band to be displaced 100 A. towards blue. *m*-Nitrobenzotrifluoride shows a similar lowering of wave-length compared with *m*-nitrotoluene. A small change in the opposite direction for the higher-wave-length band has occurred on passing from *m*-aminotoluene to *m*-aminobenzotrifluoride while the band of lower wave-length displayed by the latter is either absent or shifted below 2300 A. The ultra-violet light-absorption curve of 3-acetamido-4-fluorobenzotrifluoride is almost identical with that of the corresponding acetamidotoluene; 2-acetamido-5-fluorobenzotrifluoride, however, does not show selective absorption at the wave-length where *o*-acetamidotoluene absorbs.

FIG. 4.



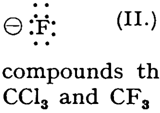
1. 3-*Acetamido*-4-*fluorobenzotrifluoride* (*in ethanol*).
2. 2-*Acetamido*-5-*fluorobenzotrifluoride* (*in ethanol*).

FIG. 5.



1. 5-*Methoxy*-2-*nitrobenzotrifluoride* (*in* cyclo*hexane*).
2. 4-*Methoxy*-3-*nitrobenzotrifluoride* (*in ethanol*).

Some comparison of the influence of $CF_3$ and $CH_3$ on the benzene ring may be made by considering the effect of their introduction on the spectra of nitrobenzene and aniline. Substitution by a methyl group at position 3 in nitrobenzene slightly lowers the energy of the transition responsible for the 2570-A. band and causes a small increase in its intensity. Substitution by $CF_3$, however, causes a small increase in the energy required, with some decrease in intensity. The band resembles that of *m*-chloronitrobenzene (Table III). The higher-wave-length bands of aniline and *m*-aminotoluene are closely similar; that of *m*-aminobenzotrifluoride is of slightly higher intensity and greater wave-length, and is not unlike that of *m*-chloroaniline. Thus a trifluoromethyl group at position 3 appears to exert much the same influence as a chloro-substituent, in accord with the view that the properties of $CF_3$ cannot be explained solely in terms of an inductive effect (cf. Miller and Thompson, *loc. cit.*; Sponer and Lowe, *loc. cit.*). The suggestion of the importance of canonical forms such as (II) to account for the chemical properties of benzotrifluoride may also explain the spectra. Hamner and Matsen's work (*J. Amer. Chem. Soc.*, 1948, **70**, 2482) on side-chain-chlorinated derivatives of benzene is of interest in this connection, although for fluoro-compounds their explanation would not be entirely satisfactory. The differences between $CCl_3$ and $CF_3$ will be discussed fully in a subsequent communication.



(II.)

5-Methoxy-2-nitro- and 4-methoxy-3-nitro-benzotrifluoride (Fig. 5) bear a relation to each other analogous to that existing between 5-amino-2-nitro- and 4-amino-3-nitro-toluene (Table III), which is not unexpected since both amino and methoxyl are donor groups. For each pair of isomers the difference in position and intensity of the high-wave-length bands is in the same direction. Comparison of 5-methoxy-2-nitro- with 5-amino-2-nitro-benzotrifluoride (Fig. 3) is complicated by the presence in the latter of the strong band at 3630 A.; if the inflexion at 3000 A. (ε 3500) is assumed to correspond to the peaks in the fluoro- and methoxy-compounds, then there is a progressive shift towards red when a donor group is substituted at position 5 in *o*-nitrobenzotrifluoride, the order of influence being $NH_2 > OMe > F$.

TABLE III.

| Substance. | $\lambda_{max.}$, A. | ε. | Solvent. | Ref. |
|---|---|---|---|---|
| Azobenzene | 3180; 4450 | 23,000; 800 | Alcohol | 1 |
| 5-Amino-2-nitrotoluene | 2330; 3735 | 13,000; 7400 | Alcohol | 2 |
| *m*-Nitrotoluene | 2637 | 12,000 | ? | 2 |
| *m*-Aminotoluene | 2369; 2872 | 11,500; 1950 | ? | 2 |
| *m*-Acetamidotoluene | 2420 | 15,000 | Alcohol | 2 |
| *o*-Acetamidotoluene | 2460 | 19,500 | Alcohol | 2 |
| *m*-Chloronitrobenzene | 2565 | 7150 | Alcohol | 2 |
| *m*-Chloroaniline | 2910 | 2690 | Hexane | 3 |
| 4-Amino-3-nitrotoluene | 2300; 2800; 4175 | 20,000; 6300; 5750 | Alcohol | 2 |

(1) Morton, *loc. cit.* (2) Morton and McGookin, *loc. cit.* (3) Forster and Wagner, *loc. cit.*

The spectra plotted in Fig. 5 may also be considered in relation to Schiemann's observation (*Ber.*, 1929, **52**, 1794) that, when a fluorine atom is situated *para*-(or to a lesser degree *ortho*-) to a nitro-group in the benzene nucleus, the replacement of F by OMe or OH is easily effected with weak alcoholic alkali (cf. Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2346). While the curves of 2 : 5-difluoro- and 5-methoxy-2-nitrobenzotrifluoride have similar absorption maxima, the peak for 5-fluoro-2-nitrobenzotrifluoride is at a much shorter wave-length. The fact that fluorine can be replaced by methoxyl must mean that the latter can better satisfy the demand of the nitro-group for electrons from positions *para*- or *ortho*- to it in the ring. Further, Gottlieb (*J. Amer. Chem. Soc.*, 1936, **58**, 532) found that chlorine is readily replaced by fluorine in 1-chloro-2 : 4-dinitrobenzene on treatment with potassium fluoride. From these data, the relative order $OMe > F > Cl$ for the electromeric effect can be deduced, in agreement with Ingold's conclusions and those indicated by the spectra herein presented.

## EXPERIMENTAL.

The absorption measurements were made with a small Hilger quartz spectrograph (No. E370) in conjunction with a Spekker photometer and a tungsten-steel spark source of ultra-violet light. In most cases Ilford " backed " Iso-Zenith plates were used. For bands below 2300 A. Ilford Type Q III Special plates or Schumann plates, often in conjunction with aluminum electrodes, were found more satisfactory. The plates were read by eye with the aid of a low-power lens.

The compounds studied were purified by the normal procedures. For the spectrographic work the ethyl alcohol was distilled over sodium. *cyclo*Hexane was purified by several treatments with oleum, each followed by washing and distillation until the substance showed no absorption. Molecular extinction coefficients (ε) were calculated from the equation $\varepsilon lc = M \log I_0/I$ where $M$ = molecular weight, $c$ = concentration (g./l.), $l$ = length of tube (cm.), and $\log I_0/I$ (optical density) = drum reading of the Spekker photometer.

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