

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Ultraviolet Absorption Spectra of Some Substituted Benzotrifluorides<sup>1</sup>

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The ultraviolet absorption spectra of four aminobenzotrifluorides in neutral and acidic solutions are described. The trifluoromethyl group is shown to have bathochromic effects on the absorption maxima of anilines and hypsochromic effects on the absorption maxima of nitrobenzenes. The difference in the spectra of 2-nitro-3-aminobenzotrifluoride and 3-amino-4-nitrobenzotrifluoride agrees with the previously recorded difference in the basicities of these two *o*-nitroanilines.

Ponderman and Girardet<sup>2</sup> noted a considerable difference in the basicity of the two isomeric trifluoromethyl-substituted *o*-nitroanilines, 2-nitro-3-aminobenzotrifluoride (I) and 3-amino-4-nitrobenzotrifluoride (II), which permitted the separation of the compounds by means of selective salt formation. Since we had an opportunity to repeat this work it was thought desirable to subject these and a few related benzotrifluorides to spectral comparisons in the hope of elucidating the effect of the trifluoromethyl group on the other substituents present.

The absorption curves of I and II are shown in Fig. 1 together with the curves for 2-nitro-5-aminobenzotrifluoride (III)<sup>3</sup> and *m*-aminobenzotrifluoride (IV). It is noted that both I and II exhibit their maximum absorptions at 232 m $\mu$  and in the 390–400 m $\mu$  range. Also III possesses two maxima, the first of which lies at 234.5 m $\mu$  and the second maximum is at 370 m $\mu$ . It is of interest to compare the spectra of I and II with that reported for *o*-nitroaniline<sup>4,5</sup> which exhibits three maxima.

The maximum at the longest wave length appears at 412 m $\mu$  and it can be attributed to the electronic transitions represented by the resonance interaction of the *o*-nitroamino groups since the related maxima also appear in certain substituted *o*-nitroanilines (425 and 418 m $\mu$  in 2-nitro-4-chloroaniline and 2-nitro-4,6-dichloroaniline, respectively).<sup>5</sup> Steric inhibition of coplanarity of the *o*-nitroamino groups, as well as the electron-withdrawing effect of the trifluoromethyl group, would explain the hypsochromic shift of this band in I and II to the 390–400 m $\mu$  range. This also explains the difference between I and II since the shift and decrease in intensity of this band is more pronounced in the former compound.<sup>6</sup>

The second maximum of *o*-nitroaniline is found at

(1) From the M.S. thesis of J. F. A., Duquesne University, June, 1950.

(2) E. Ponderman and A. Girardet, *Helv. Chim. Acta*, **30**, 107 (1947).

(3) Recently a paper by F. Smith and L. M. Turton [*J. Chem. Soc.*, 1701 (1951)] appeared in which the spectra of III and *m*-amino- and *m*-nitrobenzotrifluorides are recorded. Our results are in close agreement.

(4) L. Doub and J. M. Vandebelt, *THIS JOURNAL*, **69**, 2714 (1949); **71**, 2414 (1949).

(5) E. Heilbronner and O. Weber, *Helv. Chim. Acta*, **32**, 1513 (1949).

(6) It is likely that the trifluoromethyl group inhibits the coplanarity of the nitrophenyl system differently than the methyl group since, in the former, the fluorine atoms create a strong negative field which should repel the oxygen atoms of the nitro group. Thus, while the trifluoromethyl and the methyl groups are approximately of equal size, the effect of the former on the nitro group should be larger. The negative field around the trifluoromethyl group is of particular importance if the previously suggested "no-bond" resonance phenomenon is significant (see ref. 7).

283 m $\mu$ <sup>4,5</sup> and is also present in the 4-chloro and 4,6-dichloro derivatives (276 and 283 m $\mu$ , respectively).<sup>5</sup> This band can be attributed to the electronic transitions associated with the nitrophenyl chromophore since it occurs in *p*-chloronitrobenzene (280 m $\mu$ ),<sup>4</sup> in *p*-nitrotoluene (285 m $\mu$ ),<sup>4</sup> and at somewhat lower wave lengths in nitrobenzene (269 m $\mu$ ),<sup>4</sup> and *p*-nitroanilinium ion (258 m $\mu$ ).<sup>4</sup> In I and II this band is strongly masked and is recognizable only in II as an inflection point at approximately 270 m $\mu$ . It is not surprising that the 280 m $\mu$  band is suppressed in I and II and that, where evidence for its presence is available, it is hypsochromically displaced since the effect of the electron-withdrawing trifluoromethyl group is similar to the effect of the NH<sub>3</sub><sup>+</sup> group cited above.

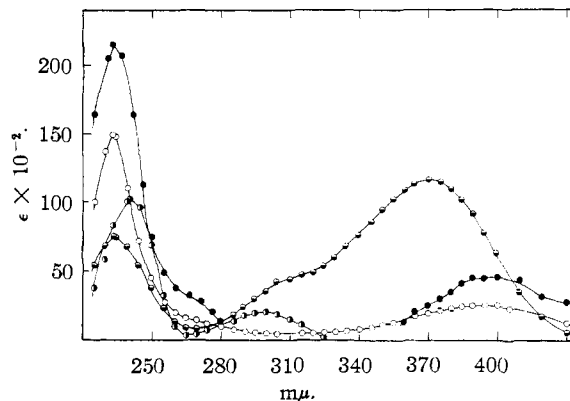


Fig. 1.—Absorption spectra in 95% ethanol: ●, 3-amino-4-nitrobenzotrifluoride; ○, 2-nitro-3-aminobenzotrifluoride; ●, 3-aminobenzotrifluoride; ○, 2-nitro-, 5-aminobenzotrifluoride.

The third band present in *o*-nitroanilines is found in the 225–239 m $\mu$  range. Thus, the band in the parent compound at 224 m $\mu$ <sup>4,5</sup> is bathochromically displaced to 233 and 235 m $\mu$  in the 4-chloro- and the 4,6-dichloro-2-nitroanilines,<sup>5</sup> and similarly it is found at 233.5 and 232.5 m $\mu$  in I and II, respectively. This band is probably related to the 231 m $\mu$  absorption maximum of aniline<sup>7</sup> and can be attributed to the electronic transitions associated with the aminophenyl chromophore. It is noteworthy that this band increases in intensity and is bathochromically displaced as electron withdrawing groups present in the aniline structure facilitate the +E effect of the amino group.

The spectra of I and II in an acidic medium are helpful in the interpretation of the origin of the various bands. Thus, we notice (Fig. 2) that the

(7) J. D. Roberts, *et al.*, *THIS JOURNAL*, **72**, 410 (1950).

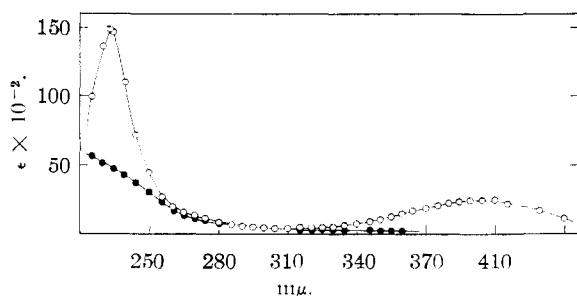


Fig. 2.—Absorption spectra of 2-nitro-3-aminobenzotrifluoride: O, in 95% ethanol; ●, in 10 *M* alcoholic hydrogen chloride.

spectrum of I is almost completely suppressed in 10 *M* hydrochloric acid and there remains only strong absorption in the 220–250  $m\mu$  range. II, on the other hand, still shows appreciable absorption in the same acidic medium (Fig. 3) and has two maxima, a strong one at 232  $m\mu$  and a weak one at approximately 410  $m\mu$ . In other *o*-nitroanilinium

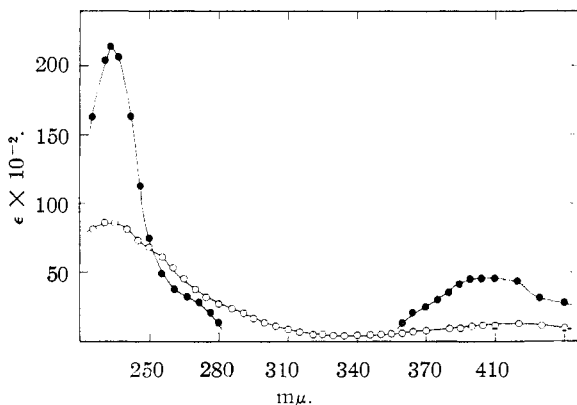


Fig. 3.—Absorption spectra of 3-amino-4-nitrobenzotrifluoride: ●, in 95% ethanol; O, in 10 *M* alcoholic hydrogen chloride.

compounds<sup>5</sup> there are observed maxima at 266–269  $m\mu$  which indicate the contribution of the nitrophenyl chromophore. The behavior of II under acidic conditions indicates a rather normal behavior (when compared to other *o*-nitroanilinium compounds) while the spectrum of I under acidic conditions points to a complete disappearance of the *o*-nitroaniline and nitrophenyl chromophores. This can be interpreted to mean that I is more basic than II and that this difference in basicity, as well as the absence of the residual nitrophenyl absorption, is a result of the absence of coplanarity of the nitro and phenyl groups. Thus, the spectral behaviors of I and II are in agreement with the observed differences in basicity.<sup>3</sup>

The spectrum of III can be compared to that of *p*-nitroaniline.<sup>4,5,8</sup> The 370  $m\mu$  band is analogous to the 375–382  $m\mu$  band observed in the parent compound and the hypsochromic shift of this band (attributed to the *p*-nitroaniline chromophore) is explained by the electron-withdrawing character of the trifluoromethyl group. Under acidic conditions (Fig. 4) the spectrum of III also resembles that

(8) W. D. Kumler, *THIS JOURNAL*, **68**, 1184 (1946).

of the *p*-nitroanilinium ion<sup>4,5</sup> except that the maximum of the latter (258–259  $m\mu$ ) is bathochromically displaced.

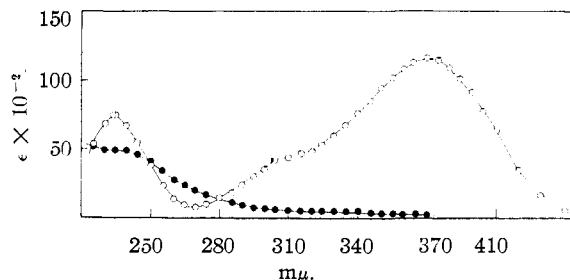


Fig. 4.—Absorption spectra of 2-nitro-5-aminobenzotrifluoride: O, in 95% ethanol; ●, in 10 *M* alcoholic hydrogen chloride.

The spectrum of IV<sup>3</sup> is shown in Fig. 5 under neutral and acidic conditions. It is observed that the maximum is present at 241.5  $m\mu$  and is probably analogous to the 246  $m\mu$  band reported for *m*-nitroaniline.<sup>4</sup> The rapid fading of the spectrum of IV

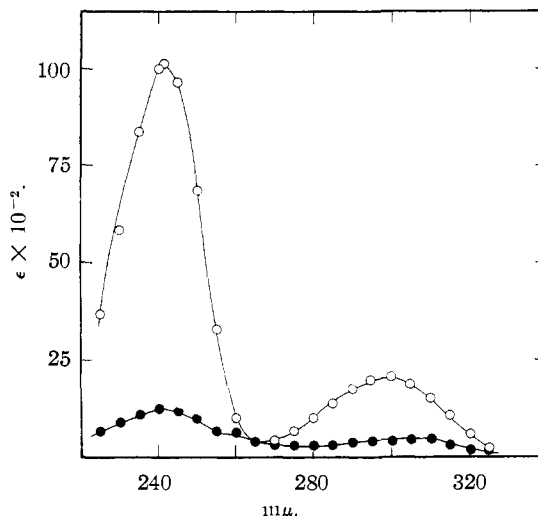


Fig. 5.—Absorption spectra of 3-aminobenzotrifluoride: O, in 95% ethanol; ●, in 0.0996 *N* alcoholic hydrogen chloride.

under even mildly acidic conditions indicates that IV is a relatively strong base<sup>7</sup> and that the *m*-trifluoromethylanilinium ion does not possess any strong chromophores. It is noteworthy that while the trifluoromethyl group has a bathochromic effect on the maximum of the amino group (compare the maximum of IV with that of aniline at 231  $m\mu$ ), it has a hypsochromic effect on the maxima of nitrobenzene derivatives. Thus, the maximum of nitrobenzene (269  $m\mu$ ) is displaced to 247  $m\mu$  in *m*-nitrobenzotrifluoride (Fig. 6) and the maximum of *p*-chloronitrobenzene (280  $m\mu$ )<sup>3</sup> is displaced to 263  $m\mu$  in 2-chloro-5-nitrobenzotrifluoride (Fig. 6). Similar observations on the bathochromic and hypsochromic effect of the trifluoromethyl group were recorded by Smith and Turton.<sup>3</sup>

#### Experimental

**Materials.**—*m*-Nitro-, *m*-amino- and 2-chloro-5-nitrobenzotrifluoride were generously supplied by the Hooker

Electrochemical Company and were purified before use by fractional distillation and crystallization. Compounds I and II were prepared by the method of Ponderman and Girardet,<sup>2</sup> and compound III was obtained by using the procedure of Rouche.<sup>9</sup>

**Procedure.**—The absorption spectra were determined in 95% ethanol solutions by means of a Beckman DU spectrophotometer. Where indicated in the accompanying figures small volumes of the stock solutions were diluted

TABLE I  
THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME BENZO-TRIFLUORIDES

Benzotrifluoride	$\lambda$ (m $\mu$ )	Absorption maxima		$\epsilon' \times 10^{-3}$
		$\epsilon \times 10^{-3}$	$\lambda' \text{ (m}\mu\text{)}$	
2-NO <sub>2</sub> , 3-NH <sub>2</sub>	233.5 <sup>a</sup>	14.9 <sup>a</sup>	395 <sup>a</sup>	2.58 <sup>a</sup>
3-NH <sub>2</sub> , 4-NO <sub>2</sub>	232.5 <sup>a</sup>	21.2 <sup>a</sup>	390-400 <sup>a</sup>	4.50
	232 <sup>b</sup>	8.70 <sup>b</sup>	410 <sup>b</sup>	1.20
2-NO <sub>2</sub> , 5-NH <sub>2</sub>	234.5 <sup>a</sup>	7.42 <sup>a</sup>	370	11.6 <sup>a</sup>
	245 <sup>b</sup>	4.94 <sup>b</sup>		
3-NH <sub>2</sub>	241.5 <sup>a</sup>	10.12 <sup>a</sup>	300 <sup>a</sup>	2.01 <sup>a</sup>
	241 <sup>c</sup>	1.20 <sup>c</sup>		
3-NO <sub>2</sub>	247 <sup>a</sup>	6.90 <sup>a</sup>		
2-Cl, 5-NO <sub>2</sub>	263 <sup>a</sup>	9.33 <sup>a</sup>		

<sup>a</sup> In 95% ethanol. <sup>b</sup> In 10 M alcoholic hydrogen chloride. <sup>c</sup> In 0.1 M alcoholic hydrogen chloride.

(9) H. Rouche, *Bull. Sci. Acad. Roy. Belg.*, **13**, 346 (1927).

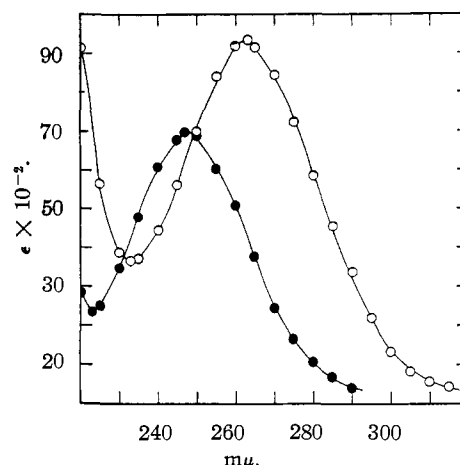


Fig. 6.—Absorption spectra in 95% ethanol: O, 2-chloro-5-aminobenzotrifluoride; ●, 3-nitrobenzotrifluoride.

with standard solutions of alcoholic hydrogen chloride and the absorption curves were then read without delay. The spectral properties of the compounds reported in this paper are summarized in Table I.

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## A Spectrophotometric Study of the Homolytic Dissociation of Tetrafluorenylhydrazine<sup>1</sup>

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Tetrafluorenylhydrazine undergoes homolytic and ionic dissociations in solution; however, only homolytic dissociation takes place in non-polar solvents. The extent of homolytic dissociation of tetrafluorenylhydrazine in benzene, dioxane, pyridine, tetrahydrofuran and toluene has been determined spectrophotometrically at several temperatures and concentrations. The dissociation constants in different solvents vary noticeably; however, the heat of dissociation appears to be nearly constant at 16.2 to 17.4  $\pm$  1.2 kcal. The heat of dissociation of the N-N bond in tetrafluorenylhydrazine is about 14 kcal. less than that in tetraphenylhydrazine. This difference is explained by the coulombic repulsion of the high charge density on the two nitrogen atoms as set forth by G. N. Lewis and D. Lipkin.

The tetraarylhydrazines resemble the hexaaryl-ethanes in their ability to dissociate yielding diarylamino free radicals. While tetraphenylhydrazine dissociates in solution only at relatively high temperatures (above 90°C),<sup>2</sup> some of its derivatives show appreciable dissociation at room temperature and have been studied qualitatively by ebulliometric and colorimetric methods.<sup>3</sup> The dissociation of tetraarylhydrazines appears to be affected by steric and resonance effects; however, Lewis and Lipkin<sup>4</sup> asserted that the coulombic repulsion of the high charge density on the two nitrogens is also an important factor in the dissociation.

Cain and Wiselogle<sup>5</sup> studied the rate of dissociation of tetraphenylhydrazine by measuring the rate of absorption of nitric oxide and obtained 30 kcal. as the heat of activation. Lewis and Lipkin<sup>4</sup> observed that diphenylamino radicals combine instantaneously at 100°K., indicating that the activation energy for association must be less than 1

kcal. Therefore, the heat of dissociation of tetraphenylhydrazine is presumably equal to the 30 kcal. found for the heat of activation. This value was confirmed by Cole and Gilbert<sup>6</sup> from heat of combustion data. The heat of dissociation of other tetraarylhydrazines has not been determined experimentally.

Goldschmidt<sup>7</sup> observed that tetrafluorenylhydrazine shows a green color in solution at room temperature due to dissociation and found colorimetrically that the degree of dissociation increases in the series of solvents: ether, acetone, toluene, benzene, pyridine.

It is the purpose of this work to study the homolytic dissociation of tetrafluorenylhydrazine in solution at several temperatures and at several concentrations in order to evaluate the equilibrium constants, the heats and the entropies of this dissociation. The solvents employed were benzene, dioxane, pyridine, tetrahydrofuran and toluene.

### Experimental

**Materials.**—Tetrafluorenylhydrazine was prepared by the oxidation of 9-aminofluorene<sup>7</sup> which was obtained from

(1) Taken in part from the M.S. thesis of T. J. Weismann, Duquesne University, 1954.

(2) H. Wieland, *Ber.*, **39**, 1500 (1906).

(3) H. Wieland, *Ann.*, **392**, 130 (1912).

(4) G. N. Lewis and D. Lipkin, *THIS JOURNAL*, **63**, 3232 (1941).

(5) C. K. Cain and F. Y. Wiselogle, *ibid.*, **62**, 1163 (1940).

(6) L. G. Cole and E. C. Gilbert, *ibid.*, **73**, 5423 (1951).

(7) S. Goldschmidt, *Ann.*, **456**, 161 (1927).