When heated above their melting points or with pyridine at 65°, both IIa and IIb were converted to the corresponding imides, as previously reported.[4]

N-Tolyl Phthalimides (IIIa and IIIb). Acid-Catalyzed Hydrolysis of Ia and Ib.—Hydrolysis of either Ia or Ib (3.44 g., 0.01 mole) with 5 *N* hydrochloric acid (10 ml., 0.05 mole) at reflux for 3 hr. resulted in high yields (2.0 g., 84%, from Ia; 1.9 g., 80%, from Ib) of the corresponding phthalimides, IIIa and IIIb. IIIa had a melting point of 182.5–183.0° (lit.[3] 182°), undepressed by admixture with an authentic sample prepared by a usual method[3a]; IIIb melted at 201–202° (lit.[4] 201–202°).

As previously reported,[4] IIIa and IIIb were converted to IIa and IIb, respectively, when heated on a steam cone for 1 hr. with 10% sodium hydroxide.

Acid-Catalyzed Hydrolysis of IIa and IIb.—Hydrolysis of IIa or IIb (2.55 g., 0.01 mole) with excess 5 *N* hydrochloric acid on a steam bath for 15 min. resulted in formation of *o*-phthalic acid (1.4 g., 84% in both cases). The product was identified by its infrared spectrum which was identical with that of an authentic sample.

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F^{19} Nuclear Magnetic Resonance Spectra of Some Benzotrifluorides

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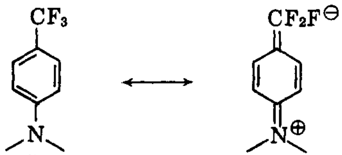
The electronic effect of the trifluoromethyl group attached to an aromatic ring and the dipole moment of *p*-dimethylaminobenzotrifluoride have been discussed in terms of resonance forms Ia,b.[1] If forms such as Ib are important, this effect might be reflected in the F^{19} n.m.r. spectrum. Taft, *et al.*,[2] have interpreted the F^{19} chemical shifts in various substituted fluorobenzenes as evidence for contributing forms IIa,b.



Ia Ib

IIa IIb

To see if n.m.r. spectroscopy could be used to detect interactions exemplified by form Ib (negative hyperconjugation), we examined the benzotrifluorides collected in Table I.

Table I shows clearly that n.m.r. spectroscopy does distinguish between the *p*-aminobenzotrifluorides and all other compounds listed. In the same solvent there is little change in the spectra until the *p*-aminobenzotrifluorides are encountered. In methanol, for example, the ϕ^* values of *p*-nitrobenzotrifluoride and *m*-dimethylaminobenzotrifluoride differ by only 0.6 unit, whereas those of *m*-dimethylaminobenzotrifluoride and *p*-aminobenzotrifluoride differ by 1.4 units. The difference between *m*-dimethylaminobenzotrifluoride and *p*-dimethylaminobenzotrifluoride is even greater (1.8 units). A similar trend is shown by the values obtained in cyclohexane.

TABLE I

F^{19} N.M.R. SPECTRA OF BENZOTRIFLUORIDES

	Cyclohexane[a] ϕ^{*b}	Methanol[a] ϕ^{*b}
Benzotrifluoride	64.1	62.7
m-Nitrobenzotrifluoride	64.2	63.1
p-Nitrobenzotrifluoride	64.5	63.2
m-Aminobenzotrifluoride	63.9	62.9
m-Dimethylaminobenzotrifluoride	63.7	62.6
p-Aminobenzotrifluoride	62.2	61.2
p-Dimethylaminobenzotrifluoride	62.0	60.8

[a] Approximately 5% solutions by volume. [b] B. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

Resonance exemplified by Ia,b, which has been invoked to account for the high dipole moment of *p*-dimethylaminobenzotrifluoride,[1] also may be responsible for the unusual F^{19} n.m.r. spectra displayed by *p*-amino and *p*-dimethylaminobenzotrifluoride. Interestingly, Gutowsky, *et al.*,[3] who have compared the F^{19} n.m.r. spectra of several substituted benzotrifluorides and fluorobenzenes, observed that substituents affect the aromatic fluorine and trifluoromethyl fluorine resonances in an opposite manner.

Experimental

The *para* substituted benzotrifluorides in Table I and *m*-dimethylaminobenzotrifluoride were prepared according to directions given in ref. 1. The remaining compounds were purchased from Columbia Organic Chemicals Company, Columbia, South Carolina, or from Aldrich Chemical Company, Milwaukee, Wisconsin. N.m.r. spectra were obtained with a Varian Associates, Model V-3000-B, high resolution spectrometer using a 40-Mc. probe at 28°. Samples were measured with trichlorofluoromethane as internal standard by counting sideband frequencies. The CF_3 peaks were sharp and symmetrical in all cases.

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Proton Nuclear Magnetic Resonance Analysis of Some Acylmetallocenes

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A gradual deshielding of the cyclopentadienyl ring protons in the metallocene series proceeding from ferrocene to ruthenocene to osmocene has been noted by