

yield), b.p. 17–18° and was characterized as N-ethyl-difluoroazomethine.

Anal. Calcd. for C₃H₅F₂N: F, 40.8. Found: F, 40.5, 40.3.

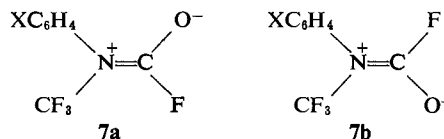
Spectral characterization was n.m.r., F¹⁹ doublets at –10.96 and –10.86 p.p.m. relative to external trifluoroacetic acid (approximately +65.6 and 65.7 relative to CCl₃F); proton, typical ethyl; mass spectrum showed pattern expected for C₂H₅N=CF₂. A total of 34% of unreacted ethyl isothiocyanate was recovered and no by-products were detected.

2. *Reaction of Isothiocyanates with Mercuric Fluoride and Carbonyl Fluoride.* A mixture of 27.0 g. (0.20 mole) of phenyl isothiocyanate, 96 g. (0.40 mole) of mercuric fluoride, and 10 g. of cesium fluoride was charged into a 240-ml. stainless steel pressure vessel. The vessel was chilled, evacuated, charged with 25 g. (0.38 mole) of carbonyl fluoride,⁵ and then heated for 2-hr. intervals successively at 60, 100, 140, 175, and 200°. The crude product (light-colored solid) was extracted with several portions of methylene chloride. The combined extracts were distilled to give 31.7 g. (77%) of N-(fluoroformyl)-N-(trifluoromethyl)aniline, b.p. 134° (180 mm.).

A series of aryl isothiocyanates was run in a similar manner and the yields, physical properties, and analytical data are given in Table I.

N-(Fluoroformyl)-N-(trifluoromethyl)-*m*-fluoroaniline, typical of the series, had the expected F¹⁹ n.m.r. pattern (10% in CCl₃F as solvent and internal calibrant) of CF₃ doublet (intensity 3) at +56.8 p.p.m. and COF quadruplet (intensity 1) at +4.04 p.p.m., *J* = 15 c.p.s. On chilling, the pattern broadened and resolved at approximately –30° into two sets of doublets and quadruplets of unequal intensity. The result is readily explained by restricted rotation¹¹ resulting from increased contributions from forms such

as 7. Correlation studies on the effect of substituent



X with barrier and chemical shifts are currently in progress with Dr. D. R. Eaton of this laboratory.

Infrared, ultraviolet, and proton n.m.r. spectra were also obtained on these anilines. The carbonyl frequency was in the region of 1835 cm.⁻¹.

3. *Reaction of N-Aryldichloroazomethines with Metal Fluorides.* A series of metal fluoride exchange reactions with N-aryldichloroazomethine was carried out. The experimental conditions and results are given in Table II. Trapping of the azomethine product directly with carbonyl fluoride was found best in these reactions.

4. *Reaction of N-(Fluoroformyl)-N-(trifluoromethyl)aniline with Diethylamine.* Excess anhydrous diethylamine was bubbled into a solution of 8.43 g. (0.0408 mole) of N-(fluoroformyl)-N-(trifluoromethyl)aniline in 150 ml. of ether. The reaction was exothermic, and a white precipitate was removed by suction filtration after the reaction was over. The filtrate was distilled to give 7.04 g. (75%) of N-phenyl-N-(trifluoromethyl)-N',N'-dimethylurea, b.p. 111° (3.2 mm.), *n*²⁰_D 1.4760.

Anal. Calcd. for C₁₀H₁₁F₃N₂O: F, 24.6; N, 12.1. Found: F, 24.2; N, 11.8.

Only a single resonance at –10.1 p.p.m. (relative to CF₃CO₂H) was seen in the F¹⁹ n.m.r. spectrum. Infrared and ultraviolet spectra were as expected.

(11) W. D. Phillips in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 441. The N-(fluoroformyl)anilines are analogous to formamides.

N-Fluoroalkylamines. II. N,N-Bis(trifluoromethyl)anilines

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Contribution No. 1094 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received May 27, 1965

N,N-Bis(trifluoromethyl)anilines, a new class of compounds, have been prepared by reaction of *N*-(fluoroformyl)-*N*-(trifluoromethyl)anilines with sulfur tetrafluoride. The physical and chemical properties of this class of compounds are described. The inductive and resonance effects of the *N,N*-bis(trifluoromethyl)amino group are reported in comparison to other fluorinated substituents and discussed in terms of current theories of origin and transmission of inductive and resonance effects.

N,N-Bis(trifluoromethyl)anilines (1) have not been reported in the literature, although a number of fluoroalkylamines are known² and recently *N*-(trifluoro-

(1) This work was presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

methyl)aniline was described.³ The electronic effects of the bis(trifluoromethyl)amino group were of particular interest for comparison to other fluorinated substituents such as CF₃, OCF₃, SCF₃, and SF₅.⁴ In the preceding paper,⁵ *N*-(fluoroformyl)-*N*-(trifluoromethyl)anilines (2) were described as precursors to anilines 1.

(2) (a) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chapters X and XI; (b) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962.

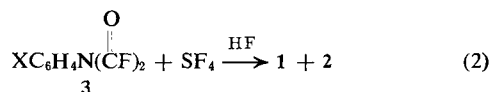
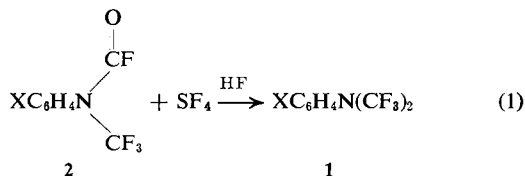
(3) (a) K. A. Petrov and A. A. Neimysheva, *J. Gen. Chem. USSR* (Eng. Transl.), **29**, 2135, 2662 (1960); (b) *N*-(difluoromethyl)-*m*-methoxyaniline and *N,N*-bis(difluoromethyl)-*m*-toluidine were reported to have been prepared from reaction of the aniline with a difluoromethyl halide (HCF₂X): J. B. Dickey, U. S. Patent 2,516,302 (1950).

(4) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963); **84**, 3072 (1962).

(5) W. A. Sheppard, *ibid.*, **87**, 4338 (1965).

Results and Discussion

Synthesis. N,N-Bis(trifluoromethyl)anilines **1** have been prepared by reaction of sulfur tetrafluoride with N-(fluoroformyl)-N-(trifluoromethyl)anilines (**2**) in the presence of anhydrous hydrogen fluoride as solvent and catalyst.^{6,7} Also N,N-bis(fluoroformyl)anilines (**3**) can



be converted with sulfur tetrafluoride in the same manner, but anilines **2** must be the intermediate since they are usually isolated as by-products, or as major products under mild conditions. Unfortunately, yields of anilines **1** by either route were generally low (2–12%, although a yield of 39% was obtained once with the *m*-nitro substituent) and not reproducible (only tar obtained in some experiments). The reaction temperature was critical, and best results were obtained in the region of 120 to 140°. The difficulty of accurate temperature control in a pressure vessel may have caused poor reproducibility. Also the formation of tars by undesirable side reactions, such as Friedel-Crafts condensations, promoted by impurities in the SF₄, HF, or stainless steel pressure vessel, is suggested since higher yields were usually obtained if the aromatic ring was deactivated with a nitro or fluoro substituent. Trichlorofluoromethane was used as an inert solvent in addition to hydrogen fluoride in a few runs. Under the best conditions, a considerable amount of starting material was recovered so that the total material accounted for ranged up to 86%.

Physical and Spectral Properties. N,N-Bis(trifluoromethyl)aniline is a stable, colorless liquid with a pleasant sweetish odor (typical aromatic character), and is soluble in the majority of organic solvents, especially non-polar hydrocarbons. As usually found, the complete replacement of aliphatic hydrogen by fluorine lowers the boiling point considerably (115° compared to 193° for N,N-dimethylaniline). The infrared and ultraviolet spectral properties are as expected (see the Experimental Section). The F¹⁹ n.m.r. spectrum is a single sharp resonance at +56.0 c.p.s. at infinite dilution in trichlorofluoromethane as solvent and internal calibrant. The change in F¹⁹ chemical shift for the trifluoromethyl group with substituent was measured and found to range from -0.16 to +0.42 p.p.m. for *p*-nitro to *p*-amino, respectively, relative to the parent. This variation is slightly less than that observed for aryl trifluoromethyl ethers⁸ but gives similar

(6) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960). One example was reported of conversion of an amide carbonyl to a difluoromethylene group.

(7) The use of hydrogen fluoride as a catalyst was described in the original report on the use of sulfur tetrafluoride as a fluorinating agent.⁶ In other work, the use of hydrogen fluoride as a catalyst and solvent has been demonstrated: see W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964).

(8) D. R. Eaton and W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1310 (1963).

correlation curves using the σ_I and σ_R plots for the *meta* and *para* substituents, respectively. The dipole moment of N,N-bis(trifluoromethyl)aniline is 2.61 D. with the negative end away from the ring (**1** with *p*-NO₂ group has $\mu = 1.80$ D.). This suggests that the N(CF₃)₂ group is electronegative to an amount similar to that found for an OCF₃ (C₆H₅OCF₃, $\mu = 2.36$ D.) or a CF₃ (C₆H₅CF₃, $\mu = 2.60$ D.). Deactivation of the ring by the (CF₃)₂N group is indicated since N,N-bis(trifluoromethyl)aniline did not give a colored complex with tetracyanoethylene as does N,N-dimethylaniline, although a weak interaction was indicated by λ_{max} 330 m μ (ϵ 30), $K = 3.90$.⁹

Chemical Reactions. The bis(trifluoromethyl)amino group, when attached to the aromatic ring, is inert to chemical transformations involving acids and bases and strong oxidizing and reducing conditions. The hydrolytic stability of these trifluoromethyl groups should be contrasted with the ease of hydrolysis of fluorinated amines of the type R₂NCF₂X where X is fluorine or fluoroalkyl.¹⁰ N,N-Bis(trifluoromethyl)aniline was nitrated in concentrated sulfuric acid to give 83 to 94% yield of *p*-nitro derivative, as characterized by infrared and proton and fluorine n.m.r. However, a few per cent total of *ortho* and *meta* isomers was detected by gas chromatography. A similar result was found for bromination. The *m*- and *p*-nitroanilines (**1**, X = *m*- and *p*-NO₂) were reduced catalytically to the corresponding phenylenediamines (**1**, X = *m*- or *p*-NH₂) which behaved normally in formylation, as well as in diazotization followed by coupling to malononitrile. The *p*-bromoaniline (**1**, X = *p*-Br) was converted to the Grignard derivative and carbonated to give 53% over-all yield of the corresponding benzoic acid (**1**, X = *p*-CO₂H). The *meta*-substituted benzoic acid (**1**, X = *m*-CO₂H) was obtained in 55% yield by free-radical dibromination of the *m*-toluidine (**1**, X = *m*-CH₃) followed by hydrolysis and oxidation with nitric acid. N,N-Bis(trifluoromethyl)aniline was thermally stable up to 475° (phenyl trifluoromethyl ether was stable under the same conditions to over 550°).¹¹

All of the anilines **1** prepared by fluorination or by chemical transformation on the ring are listed in Table I with physical and analytical data.

Electronic Properties of Bis(trifluoromethyl)amino Group. The electronic properties of the N(CF₃)₂ group were of considerable interest for comparison to other fluorinated groups.⁴ The *para*-orienting influence of this group suggested that it would behave like a normal amino group in supplying electrons to the *para* position by a resonance mechanism, particularly to stabilize the transition state from an attacking electrophilic reagent. However, the strong electron-withdrawing character of the CF₃ groups has effectively removed the unshared electron pair for normal behavior as a base since anilines **1** do not form salts with strong acids. Consequently we predicted that the (CF₃)₂N group would have a strong inductive electron withdrawal (+I effect), and a resonance donation (-R)

(9) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958). K is association constant for complex formation in methylene chloride solution.

(10) (a) D. C. England, R. L. Melby, M. Dietrich, and R. V. Lindsey, *ibid.*, **82**, 5116 (1960); (b) R. J. Harder and W. C. Smith, *ibid.*, **83**, 3422 (1961).

(11) W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964).

Table I. N,N-Bis(trifluoromethyl)anilines

X of XC ₆ H ₄ N(CF ₃) ₂	M.p., °C., and/or <i>n</i> ^{25D}	B.p., °C. (mm.)	F ¹⁹ n.m.r. chemical shift, c.p.s. ^a	Method of preparation ^b (% yield)	Formula	Anal.							
						Carbon ^c		Hydrogen		Fluorine		Other	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
H	1.3821	118	3161	A1 (5)	C ₈ H ₅ F ₆ N	41.9	42.5	2.20	2.47	49.8	49.7	N, 6.12	5.98
NO ₂ <i>meta</i>	1.4295	76 (4.8)	3165	A2 (2)	C ₈ H ₄ F ₆ N ₂ O ₂					41.6	40.7	N, 10.2	6.38
				A1 (39)									10.2
<i>para</i>	...	54-55 (1)	3152	A2 (5)								N, 10.2	10.5
				A1 (5)									10.5
NH ₂ <i>meta</i>	1.4285	71 (7.3)	3159	B1 (83-94)	C ₈ H ₆ F ₆ N ₂					46.7	47.2	N, 11.5	11.8
				B3 (67)									11.8
<i>para</i>	12.5-14.5	71-73 (9)	3185	B3 (76)		39.5	40.1	2.46	2.68	N, 11.5	11.8
CH ₃ <i>meta</i>	1.3916	95-97 (170)	3158	A2 (3)	C ₉ H ₇ F ₆ N					46.9	46.7	N, 5.76	5.66
				A2 (2)									5.30
<i>para</i>	1.3921	91-93 (145)	(3154)	A2 (2)		44.5	45.0	2.90	3.18	46.9	46.8	N, 5.76	5.30
F <i>meta</i>	1.3736	117-118	3167	A1 (12)	C ₈ H ₄ F ₇ N					53.8	54.4	N, 5.67	5.70
				A1 (12)									5.68
<i>para</i>	1.3713	118-119	3182	A1 (12)		38.9	39.2	1.63	1.79	53.8	53.6	N, 5.67	5.68
Br <i>para</i>	...	84-87 (50)	3171	B2 (66)	C ₈ H ₄ BrF ₆ N	31.2	32.0	1.31	1.94	Br, 25.9	24.6
CO ₂ H <i>meta</i>	99.8-100.6	B4a (55)	C ₉ H ₅ F ₆ NO ₂					41.7	41.2	N, 5.17	4.83
				B4b (53)									4.83
<i>para</i>	139.0-139.4	B4b (53)		39.6	39.3	1.84	2.09	Neut. equiv., 273	274
													276
NHCH <i>para</i>	65.0-65.6	...	3200 ^d	B5 (87)	C ₉ H ₅ F ₆ N ₂ O							N, 10.3	9.9
				B6 (95)									22.1
N=NCH(CN) ₂ <i>para</i>	134.8-135.8	B6 (95)	C ₁₁ H ₅ F ₆ N ₅	41.1	41.2	1.56	1.70	N, 21.9	22.1
NHC(O)N(CH ₃) ₂ <i>para</i>	121.8-124.4	B7 (95)	C ₁₁ H ₁₁ F ₆ N ₃ O					N, 13.3	13.3
													13.0

^a At infinite dilution in CCl₃F as solvent and internal calibrant at 56.4 Mc./sec. ^b Letter and number refer to procedure listed in Experimental Section. ^c Carbon analysis of highly fluorinated compounds have frequently been found 0.4 to 0.7% high although not reproducibly so. ^d Approximate value in CDCl₃ solvent.

Table II. Ionization Constants and Substituent Parameters

	Benzoic acids, 50% water-ethanol at 25°		Anilines, water at 25°		
	pK _a	σ ^a	λ _{max} (mμ)	pK _a	σ ^b
<i>meta</i>	5.08	0.40	286	3.25	0.47
<i>para</i>	4.88	0.53	282	3.10	0.53

^a Calculated using values pK_a for benzoic acid as 5.66 and ρ = 1.467. ^b Calculated using values pK_a for anilinium ion as 4.56 and ρ = +2.767.

Table III. F¹⁹ N.m.r. Chemical Shift Measurements of σ-Parameters for FC₆H₄X

X	ν, c.p.s. ^a	δ, p.p.m. ^b	σ _I	σ _R	X	ν, c.p.s. ^a	δ, p.p.m. ^b	σ _L	σ _R
H	6382	0			N[(O=)CF] ₂ <i>meta</i>	6186	-3.49	0.58	-0.01
N(CF ₃) ₂	<i>meta</i>	6221	-2.86	0.49	<i>para</i>	6202	-3.19		
	<i>para</i>	6202	-3.19		NO	...	-1.78 ^c	0.33	0.32
NCF ₃	<i>meta</i>	6194	-3.36	0.56	NO ₂	...	-3.45 ^c	0.57	0.20
	<i>para</i>	6190	-3.40		NCO	...	-9.45 ^c		
					NCS	6275	-1.92	0.36	-0.17
						6557	+3.11		
						6247	-2.39	0.42	-0.07
						6371	-0.20		

^a Relative to CCl₃F; at 56.4 Mc.; values at infinite dilution in CCl₃F. ^b Relative to C₆H₅F. ^c Value reported in ref. 12 at 5% concentration in CCl₄.

which would be considerably reduced relative to that of $N(CH_3)_2$. In other words, this group should be halogen-like, similar to an OCF_3 . The pK_a measurements on the anilines **1** with *m*- and *p*-amino and -carboxyl substituents did indeed show that the $N(CF_3)_2$ is a strong +I group of the same magnitude as CF_3 , but that it is not -R but +R (see Table II). The F^{19} n.m.r. chemical shift correlations using the *m*- and *p*-fluoroanilines (**1**) by the method of Taft¹² confirmed the electronic effects found by pK_a measurements (Table III). For comparison purposes, the σ parameters, including σ_I and σ_R which give a qualitative comparison of the inductive and resonance effects, are summarized in Table IV along with data for some other fluorinated

Table IV. Substituent Parameters for Fluorinated Groups

Substituent	Method ^a	σ_m	σ_p	σ_I	σ_R	σ_{R^o}
$N(CF_3)_2$	B	0.40	0.53	0.29	0.23	
	A	0.47	0.53	0.44	0.06	
	F	0.49	0.50	0.49		0.01
CF_3^b	B	0.42	0.53	0.33	0.18	
	A	0.49	0.65	0.44	0.18	
	F	0.44	0.49	0.39		0.10
$CF(CF_3)_2^b$	B	0.37	0.53	0.25	0.26	
	A	0.52	0.67	0.48	0.17	
	F	0.50	0.52	0.48		0.04
OCF_3^c	B	0.38	0.35	0.39	-0.04	
	A	0.47	0.27	0.50	-0.23	
	F	0.53	0.51	0.55 ^d		-0.04 ^d
SCF_3^c	B	0.40	0.50	0.31	0.17	
	A	0.46	0.64	0.40	0.22	
	F	0.60	0.63	0.57		0.06

^a B from benzoic acid pK_a ; A from anilinium ion pK_a ; F from F^{19} chemical shift measurements. ^b Reference 15. ^c Reference 4a. ^d Calculated from values given in ref. 12 at 5% concentration in CCl_4 .

substituents. The $N(CF_3)_2$ group appears somewhat similar in behavior to nitroso. However, only F^{19} n.m.r. measurements have been used for determining the σ parameters in this group,¹² and the *para*-orientation effects reported¹³ are considered questionable.¹⁴ The apparent +R effect of the NO group can, of course, be explained by the normal resonance picture, but the +R effect of the $N(CF_3)_2$ group cannot be readily explained in terms of normal resonance or by the current theories of fluoride ion hyperconjugation or of π -inductive effect. Arguments against these mechanisms have been presented in full in a recent publication.¹⁵ In any case, a fluoride ion hyperconjugation mechanism is not possible for the $(CF_3)_2N$ group, and we feel that the data are explained by an alternative proposal of a fluorine $p-\pi$ interaction.¹⁵ That is, the *p*-electrons of the fluorines of the trifluoromethyl groups interact with the π -electron system causing return of electron density to the ring and partially counteracting the strong inductive electron withdrawal. This small return of electron density is felt more strongly at the *meta* than the *para* position so that the *para* position appears more

(12) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

(13) B. G. Gowenlock and W. Luttkie, *Quart. Rev.*, (London), **12**, 321 (1958).

(14) P. W. Robertson, T. R. Hitchings, and G. M. Will, *J. Chem. Soc.*, 808 (1950). Kinetic studies on Br_2 reaction with nitrosobenzene were interpreted as bromination occurring on the HX adduct and consequently not measuring orientation effect of NO.

(15) W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).

deactivated than the *meta*. In the ground state, this effect is apparently strong enough so that the expected -R effect of the $(CF_3)_2N$ is overcome. In the transition state, however, the powerful electron demand of an attacking electrophilic reagent must overcome all other factors, and the unshared pair on nitrogen can participate in the usual manner in stabilizing the transition state.

The small variation in σ parameters determined by the different methods may result from solvation effects in pK_a measurement or disturbances of ring currents by the bulky highly fluorinated groups for the F^{19} measurements.¹⁶ The F^{19} n.m.r. chemical shift measurements on the anilines **2** and **3** with *m*- and *p*-fluoro substituents are also reported in Table III and present an additional argument for $p-\pi$ interaction. The +R effect decreases from $N(CF_3)_2$ to $N(COF)(CF_3)$ and becomes -R for $N(COF)_2$ even when the +I effect increases. This result is predicted because of the numerical decrease in possible interacting forms when a CF_3 is replaced by a COF.

Experimental Section

Materials. The *N*-(fluoroformyl)-*N*-(trifluoromethyl)anilines were described in the preceding paper.⁵ *N,N*-Bis(fluoroformyl)anilines were prepared by addition of carbonyl fluoride to aryl isocyanates.¹⁷ Sulfur tetrafluoride and Freon 11 (trichlorofluoromethane) were obtained from the Organic Chemicals Department, E. I. du Pont de Nemours and Co. Anhydrous hydrogen fluoride was obtained from Harshaw Chemical Co.

***N,N*-Bis(trifluoromethyl)anilines.** The anilines **1** prepared in this work are listed in Table I with physical properties and analytical data. The detailed procedures for preparation are listed below and, where a procedure was used for synthesis of more than one aniline, only a typical example is given. The methods of preparation with reference to the Experimental Section and yields are also summarized in Table I with footnotes describing any significant modification of reaction conditions.

A. Preparation. 1. From *N*-(Fluoroformyl)-*N*-(trifluoromethyl)anilines. As pointed out in the discussion of the results, the sulfur tetrafluoride reactions were very difficult to reproduce and in some runs very low yields or chiefly carbonaceous or tarry products were obtained.

N-(Fluoroformyl)-*N*-(trifluoromethyl)-*m*-nitroaniline (**2**, X = NO_2), 23.6 g. (0.10 mole), was charged into a 145-ml. Hastelloy-lined pressure vessel. The vessel was cooled in Dry Ice, evacuated, and charged with 5 g. of anhydrous hydrogen fluoride and 12 g. (0.11 mole) of sulfur tetrafluoride. The reactants were heated under autogeneous pressure for 2-hr. intervals successively at 75, 100, 120, and 140°. The vessel was cooled and vented, and the dark liquid product was dissolved in methylene chloride (trichlorofluoromethane or 1,1,2-trichloro-1,2,2-trifluoroethane was also found to be a convenient solvent). The solution was stirred with an excess (approximately 15 g.) of sodium fluoride powder or pellets (added portionwise to remove HF), filtered, and distilled (a small additional amount of

(16) See the discussion of these factors in ref. 15.

(17) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

sodium fluoride powder was added to the pot during distillation to remove any residual HF). A total of 6.63 g. (39%) of *N,N*-bis(trifluoromethyl)-*m*-nitroaniline, b.p. 70–73° (3.3 mm.), n_D^{25} 1.429–1.438, and 11.1 g. (47%) of recovered starting material, b.p. 85–100° (3.0 to 1.8 mm.), n_D^{25} 1.4701–1.4825, was obtained. The nitroaniline **1** was purified by refractionation through an 18-cm., spinning-band column.

2. *From N,N-Bis(fluoroformyl)anilines.* The procedure described above was used in the reaction of 35 g. (0.18 mole) of *N,N*-bis(fluoroformyl)-*m*-toluidine (**3**, X = CH₃) with 45 g. (0.42 mole) of sulfur tetrafluoride in 10 g. of hydrogen fluoride and 30 ml. of trichlorofluoromethane. A total of 1.47 g. (3.7%) of *N,N*-bis(trifluoromethyl)-*m*-toluidine, b.p. 95–107° (170 mm.), n_D^{25} 1.3924–1.4022, and 9.7 g. (22%) of *N*-(fluoroformyl)-*N*-(trifluoromethyl)-*m*-toluidine, b.p. 134° (170 mm.), n_D^{25} 1.4343–1.4352, was obtained.

B. Reactions on the Aromatic Ring. 1. Nitration. A mixture of 7.55 g. (0.033 mole) of *N,N*-bis(trifluoromethyl)aniline and 19 ml. of concentrated sulfuric acid treated with 5 ml. of 90% nitric acid at 10 to 20° (see ref. 11) gave 7.5 g. (83%) of *p*-nitro-*N,N*-bis(trifluoromethyl)aniline, b.p. 54–55° (1 mm.). The *para* substitution was proven by comparison to authentic samples of *meta* and *para* isomers prepared by fluorination method and by spectral analysis: infrared spectrum, 1940 and 852 (*para*-disubstituted aromatic), 1330 and 1530 cm.⁻¹ (NO₂); ultraviolet spectrum, $\lambda_{\max}^{\text{isooctane}}$ 247 m μ (ϵ 9260), sh. 340 m μ (ϵ 121). The proton n.m.r. was a four-line A₂B₂ pattern centered at -7.71 p.p.m. relative to tetramethylsilane with δ = 0.741 p.p.m. and J = 9.3 c.p.s., typical of a *para*-disubstituted aromatic. The F¹⁹ n.m.r. was a single sharp peak.¹⁸ Gas chromatographic analysis on a 2-m. column packed with 20% diglyceride on 60–80 firebrick (not acid washed) at 151° gave the results: per cent (retention time in min.) *meta* 1.9 (19.0), *para* 92.4 (22.7), *ortho* 5.6 (23.6); the *meta* and *para* isomers were characterized by comparison to authentic samples; the peak at 23.6 min. was assumed to be *ortho* and occurred at expected position for column conditions.

2. *Bromination.* Bromination of 8.0 g. of *N,N*-bis(trifluoromethyl)aniline using 0.3 g. of iron powder and 2.0 ml. of bromine¹¹ gave 1.3 g. (16%) of recovered starting material, b.p. 46–50° (50 mm.), and 7.1 g. (66%) of *p*-bromo-*N,N*-bis(trifluoromethyl)aniline, b.p. 84–87° (50 mm.). Again *para* substitution was shown by spectral analysis: infrared, characteristic 830-cm.⁻¹ band; proton n.m.r. A₂B₂ pattern centered at -7.30 p.p.m. relative to tetramethylsilane, δ = 0.27 p.p.m. and J = 9.2 c.p.s.; F¹⁹ n.m.r. single sharp resonance. Gas chromatographic analysis as above for nitro derivative showed *meta* 1.7% (4.6 min.), *para* 94.9% (5.4 min.), and *ortho* 0.3% (5.9 min.).

3. *Reduction of Nitro Group.* Hydrogenation of 5.33 g. (0.020 mole) of *p*-nitro-*N,N*-bis(trifluoromethyl)aniline in 100 ml. of absolute alcohol containing 0.026 mole of hydrogen chloride at approximately 3 atm. in a Parr apparatus using 0.30 g. of platinum oxide as

catalyst was rapid¹¹ and gave 3.61 g. (76% based on nitro compound) of *N,N*-bis(trifluoromethyl)-*p*-phenylenediamine, b.p. 71–73° (9 mm.).

4. *Benzoic Acids. a. By Bromination, Hydrolysis, and Oxidation.* *N,N*-Bis(trifluoromethyl)-*m*-toluidine, 0.71 g. (0.0029 mole), was brominated with 0.96 g. (0.0054 mole) of bromine in 10 ml. of carbon tetrachloride followed by hydrolysis with 25 ml. of concentrated nitric acid.¹¹ The crude *N,N*-bis(trifluoromethyl)amino-*m*-benzoic acid, m.p. 97.4–97.8°, was obtained in a yield of 0.44 g. (55%). The acid was purified by two recrystallizations from hexane followed by sublimation, m.p. 99.8–100.6°.

b. From Grignard Reaction. The Grignard reagent from 3.12 g. (0.010 mole) of *p*-bromo-*N,N*-bis(trifluoromethyl)aniline and 0.32 g. of magnesium in 13 ml. of ether was treated with dry carbon dioxide at -10° to give, after hydrolysis with 6 *N* sulfuric acid, 1.46 g. (53%) of sublimed *N,N*-bis(trifluoromethyl)amino-*p*-benzoic acid, m.p. 136.5–138.0°. The acid was purified by recrystallization from hexane and by sublimation, m.p. 139.0–139.4°.

5. *Formylation of Aniline.* *N,N*-Bis(trifluoromethyl)-*p*-phenylenediamine, from 3 g. of the hydrochloride by base treatment and ether extraction, was heated under reflux for 2 hr. with 10 ml. of 98–100% formic acid. The cooled solution was poured into 100 ml. of cold water and the mixture was extracted with methylene chloride to obtain 2.54 g. (87%) of the formamide, m.p. 65.0–65.6° after recrystallization from ethylene chloride-pentane.

6. *Diazotization and Coupling.* A slurry of 1.4 g. of *N,N*-bis(trifluoromethyl)-*p*-phenylenediamine hydrochloride in 15 ml. of water and 1.7 ml. of 6 *N* hydrochloric acid was diazotized at 0 to 5° by addition of a solution of 0.35 g. of sodium nitrite in 10 ml. of water. A solution of 0.85 g. of malononitrile in 10 ml. of water was added, and a yellow precipitate formed immediately. After 5 min., the solution was made basic with 10% sodium hydroxide, then after an additional 5 min. at 0° was acidified with 6 *N* hydrochloric acid. The yellow precipitate of carbonyl cyanide *N,N*-bis(trifluoromethyl)-*p*-aminophenylhydrazone was collected on a filter, washed with water, and air-dried, yield 1.54 g. (95%). The hydrazone was recrystallized from a mixture of chloroform and pentane, m.p. 134.8–135.8°, $\lambda_{\max}^{\text{CH}_2\text{CN}}$ 237 m μ (ϵ 8700) and 347 m μ (ϵ 24,200). The proton n.m.r. in CDCl₃ solution showed a resonance at -10.4 p.p.m. (intensity 1, NH) and a large (intensity 4) sharp resonance of half-width 1–2 c.p.s. at -7.70 p.p.m. (see section 12 below).

7. *Conversion of Amine to Isocyanate and to Urea Derivative.* Following a literature procedure,¹⁹ 2.00 g. of *N,N*-bis(trifluoromethyl)-*p*-phenylenediamine hydrochloride in 50 ml. of dioxane was treated with anhydrous hydrogen chloride, with excess phosgene, and, after distilling a portion of the solvent to remove excess of these reagents, was then treated with dimethylamine. Removal of the solvent under reduced pressure left a crystalline residue which was recrystallized from methylene chloride by addition of pentane and cooling to give 2.13 g. (95%) of 3-[*p*-*N,N*-bis-

(18) S. Andreades, J. F. Harris, and W. A. Sheppard, *J. Org. Chem.*, **29**, 895, 898 (1964). The use of F¹⁹ n.m.r. was described as a method for determination of isomer distribution for aryl trifluoromethyl sulfides.

(19) N. E. Searle and H. E. Cupery, *J. Org. Chem.*, **19**, 1622 (1954), step A-4.

(trifluoromethyl)aminophenyl]-1,1-dimethylurea, m.p. 121.8–124.4°. A portion recrystallized twice more from these solvents had m.p. 121.4–125.2°.

C. Properties. 1. Stability. Thermal stability was determined in a stainless steel pressure vessel using mass spectrometric analysis as described previously.¹¹ *N,N*-Bis(trifluoromethyl)aniline showed significant decomposition (12%) at 475°, and at 625° the decomposition was 80%.

No indication of hydrolytic instability of the bis-(trifluoromethyl)amino group was found in any of the experiments described above.

2. Physical and Spectral Measurements. a. Ionization Constants. The ionization constants of benzoic acids were determined by potentiometric titration in 50% ethanol–water, and of the anilines by spectrophotometric measurements in water as described previously.⁴ The results are reported in Table II.

b. N.m.r. Calibration. The F^{19} n.m.r. calibrations were carried out as described previously^{8,15} in trichlorofluoromethane as solvent and internal calibrant. Measurements were made at four concentrations (40, 20, 10, and 5%), and the chemical shift was obtained by extrapolation to infinite dilution. The calibrations for the trifluoromethyl group are listed in Table I. The chemical shift data for the aromatic fluorines are given in Table III.

3. Substituent Parameters. The Hammett σ constants were calculated by standard methods²⁰ from the ionization constant data. Substituent constants were calculated from the F^{19} n.m.r. chemical shift data using the procedure described by Taft and co-workers.^{12,15} The σ_I , σ_R , and σ_{R^0} parameters were calculated according to Taft.²¹ The data are reported in Table IV.

4. Dipole Moments. The dipole moments were determined by literature methods⁴ employing a Wissenschaftlich Technische Werkstätten Dipolmeter type DMOI, cell DFLI (20-ml. volume). The data are given in Table V.

5. Spectral Properties. The infrared, ultraviolet, and proton n.m.r. spectra were taken on the majority of compounds reported in Table I and were as expected, except for the proton n.m.r. spectrum for the carbonyl cyanide phenyl hydrazone. This compound showed a single sharp resonance for the aromatic pro-

(20) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(21) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

Table V

Dielectric constants, densities, and polarizations in benzene at 25°				
Compd.	F_2	ϵ	D	P_2
Benzene (solvent)	0.00000	2.2740	0.8722	(P_1 , 26.694)
$C_6H_5N(CF_3)_2$	0.00523	2.3227	0.8783	178.86
	0.01060	2.3720	0.8828	181.70
	0.02119	2.4665	0.8916	179.94
$p-O_2NC_6H_4N(CF_3)_2$	0.00520	2.2987	0.8804	114.78
	0.01030	2.3227	0.8872	118.12
	0.02038	2.3690	0.8985	121.88
Molar refraction, polarization, and dipole moments				
Compd.	MR	P_∞ (25°)	μ (Debye)	
$C_6H_5N(CF_3)_2$	40.22	179.74	2.61	
$p-O_2NC_6H_4N(CF_3)_2$	46.378	112.82	1.80	

tons (in deuterioacetone, at -7.1 p.p.m., half-width *ca.* 5 c.p.s.; in $CDCl_3$, at -7.7 p.p.m., half-width 1–2 c.p.s.) rather than the usual, four-line A_2B_2 pattern, evidently because of a close similarity in the shielding effects of the $(CF_3)_2N$ substituent compared with the $NHN=C(CN)_2$ group. Addition of triethylamine to the $CDCl_3$ solution, which presumably ionizes the hydrazone group, resulted in an A_2B_2 pattern centered at -7.3 p.p.m., $\delta = 0.217$ p.p.m., $J = 9$ c.p.s.²² In the infrared spectra, typical aromatic absorption and strong CF bands in the 1100–1400-cm.⁻¹ region were always noted. Ultraviolet spectrum for *N,N*-bis(trifluoromethyl)aniline in iso-octane, λ_{max} 265 m μ (ϵ 277), 258 (364), 253 (304), and 249 (211), is similar to that found for phenyl trifluoromethyl ethers and for toluene.

N,N-Bis(fluoroformyl)fluorobenzenes. The *m*- and *p*-fluorophenylisocyanates²³ were treated with carbonyl fluoride in the presence of cesium fluoride at 200° for 12 hr. in a pressure vessel.¹⁷ The product was extracted in methylene chloride and recrystallized several times from benzene–hexane solution. *N,N*-Bis(fluoroformyl)-*m*-fluoroaniline had m.p. 75.2–76.5°.

Anal. Calcd. for $C_8H_4F_3NO_2$: F, 28.1; N, 6.90. Found: F, 27.9; N, 6.75, 6.97.

N,N-Bis(fluoroformyl)-*p*-fluoroaniline had m.p. 95–97°.

Anal. Found: F, 26.3; N, 6.88, 6.83.

(22) Carbonyl cyanide *p*-chlorophenylhydrazone [B. Lythgoe, A. R. Todd, and A. Topham, *J. Chem. Soc.*, 315 (1944)] in deuterioacetone also showed a single aromatic resonance at -7.0 p.p.m. of half-width *ca.* 3 c.p.s. A sample of this compound was supplied by Dr. W. W. Prichard of this laboratory.

(23) C. W. Todd, U. S. Patent 2,655,445 (1953); *meta*: b.p. 87.5° (65 mm.), n_D^{25} 1.5117; *para*: b.p. 90° (56 mm.), n_D^{25} 1.5118.