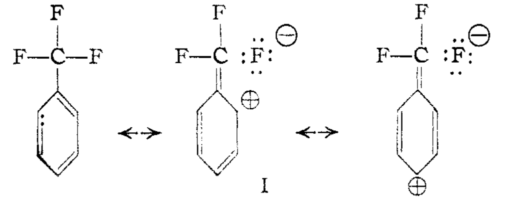
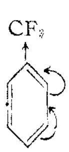
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

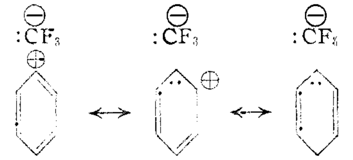
The Electrical Effect of the Trifluoromethyl Group

BY JOHN D. ROBERTS,* RICHARD L. WEBB AND ELIZABETH A. MCELHILL

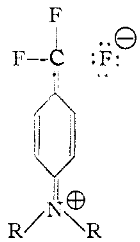
The strong meta-orienting[1] influence of the trifluoromethyl and trichloromethyl groups in electrophilic aromatic substitution reactions is usually attributed to an electron-attracting effect which is least strongly felt at the position meta to the orienting group. The preferential induction of cationic charge at the *o*- and *p*-positions may be ascribed to contributions of resonance forms of two rather different types. Type I is a variety of "no-bond" resonance analogous to that postulated for alkyl groups (hyperconjugation).[2] Resonance of type I might be expected to be considerably more effective for a trifluoromethyl group than hyperconjugation is for a methyl group because of the magnitude of the electronegativity difference between fluorine and carbon as compared to that between carbon and hydrogen.[3] A second mode (II) of preferential relay of the electron-attracting influence of the trifluoromethyl group to the *o*- and *p*-positions may be inferred from explanations[4] for the meta-directing power of $-\overset{\oplus}{N}(CH_3)_3$ and similar groups. Alternatively, II may be expressed by the resonance structures, III, which denote induction of a positive charge on C-1 by the electron-attracting group (IIIa) and distribution of the charge on C-1 over the *o*- and *p*-positions (IIIb and IIIc). Quantum mechanical treatments of resonance of type III have been made by Hückel[5] and by Wheland and Pauling.[6] Irrespective of whether I or II represents more accurately the electrical effect of the trifluoromethyl group, the possibility may be suggested of at least some degree of *conjugation* or *interaction* between the trifluoromethyl group and a strong electron-donating group, such as $-NR_2$, located at the *o*- or *p*-position. This interaction might be represented by resonance structures such as IV which are analogous to the resonance forms (V) used to symbolize the interaction between the groups of *p*-nitroanilines.

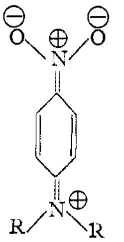

I


II


IIIa IIIb IIIc

III


IV


V

Several criteria may be used to establish resonance interaction as expressed by IV or V. For *p*-nitrodimethylaniline may be cited: (a) the large dipole moment (6.87 *D*)[7] which considerably exceeds the sum of the moments of nitrobenzene (3.95 *D*) and dimethylaniline (1.58 *D*); (b) the relatively small dipole moment of nitrodimethylaminodurene (4.11 *D*)[8]; and (c) the need for separate σ-constants to describe the influence of a nitro group on the reactivities of *p*-dimethylamino and *p*-carboxyl groups whereas a single σ-constant suffices for either *m*-dimethylamino or *m*-carboxyl groups.[9] It is the purpose of the present work to show that dipole moment and σ-constant data may be used to demonstrate resonance interaction between the substituent groups of *p*-amino- and *p*-dimethylaminobenzotrifluorides.

Experimental

Most of the trifluoromethyl derivatives used in the dipole moment determinations were prepared as described by earlier investigators. The physical properties of the materials are given in Table I. The substituted anilines and benzoic acids employed in the equilibrium and rate constant measurements were purified commercial products

---

* Harvard University National Research Fellow, 1945–1946.

[1] (a) Swarts, *Bull. sci. acad. roy. Belg.*, **6**, 389 (1920); *Chem. Zentr.*, **92**, II, 32 (1921); (b) Wertyporoch, *Ann.*, **493**, 153 (1932); (c) Simons and Ramler, THIS JOURNAL, **65**, 389 (1943); (d) Holleman, *Rec. trav. chim.*, **33**, 1 (1914).

[2] *Cf.* (a) Baker and Hemming, *J. Chem. Soc.*, 191 (1942); (b) Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41 (1941); (c) Berliner and Berliner, *ibid.*, **68**, 2355 (1946); **70**, 854 (1948); **71**, 1195 (1949); (d) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944; (e) Deasy, *Chem. Revs.*, **36**, 145 (1945); (f) Hamner and Matsen, THIS JOURNAL, **70**, 2482 (1948); (g) Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937); (h) Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 7.

[3] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, Chapter 2.

[4] (a) Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 401 (1926); (b) Ingold, *Chem. Revs.*, **15**, 225 (1934).

[5] Hückel, *Z. Physik*, **72**, 310 (1931).

[6] Wheland and Pauling, THIS JOURNAL, **57**, 2086 (1935).

[7] Marsden and Sutton, *J. Chem. Soc.*, 599 (1936).

[8] Ingham and Hampson, *ibid.*, 981 (1939).

[9] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chapter VII.

except for *m*- and *p*-trifluoromethylbenzoic acids,[10] *m*-aminobenzotrifluoride,[11] and *m*- and *p*-dimethylaminobenzotrifluorides. The physical constants of all of these substances were in close agreement with those reported in the literature.

TABLE I

PHYSICAL PROPERTIES OF TRIFLUOROMETHYL COMPOUNDS

Compound	B. p., °C.	d^{25}_4	$n^{25}D$
Benzotrifluoride[a]	103.0–103.1	1.1814	1.4114
Trifluoromethylcyclohexane[b]	105.8	1.0766	1.3739
p-Aminobenzotrifluoride[c]	57.0 (5 mm.)	1.2901	1.4815

[a] Hooker Electrochemical Co. [b] Swarts, *Bull. sci. acad. roy. Belg.*, 6, 389 (1930). [c] Ref. 11.

m- and *p*-**Dimethylaminobenzotrifluoride.**—A mixture of 34 g. of methyl iodide and 19 g. of *p*-aminobenzotrifluoride[11] was refluxed for five hours. An additional 7-g. portion of methyl iodide was run in and the mixture refluxed for two more hours. Water was added and the excess methyl iodide extracted with ether. The aqueous solution was made alkaline and extracted with ether. The ether extract was dried over potassium hydroxide, the ether was evaporated and the residue refluxed with 34 g. of methyl iodide for four hours. The excess methyl iodide was removed under reduced pressure and the residue made strongly basic with aqueous alkali. The liberated amine was extracted with ether and after distillation of the ether treated with sodium hydroxide solution and benzoyl chloride in small portions to convert any primary and secondary amines present to benzamide derivatives. The mixture was extracted with ether and the ethereal solution shaken with four 50-ml. portions of 3 *N* hydrochloric acid. The acid extract was made alkaline and the liberated amine extracted with ether. After distillation of the ether the residue of crude *p*-dimethylaminobenzotrifluoride was recrystallized from a mixture of methanol and water. The yield was 8.2 g. (37%), m. p. 70.3–70.8°.

Anal. Calcd. for $C_8H_{10}NH_3$: C, 57.14; H, 5.33. Found: C, 57.00; H, 5.60.

m-**Dimethylaminobenzotrifluoride** was prepared similarly. The yield from 40 g. of *m*-aminobenzotrifluoride was 13.5 g. (29%), b. p. 89.5–90.4° (15 mm.), $n^{25}D$ 1.4824.

Anal. Calcd. for $C_8H_{10}NF_3$: C, 57.14; H, 5.33. Found: C, 57.43; H, 5.33.

Dipole Moments.—The dipole moments were determined by the method described previously.[12] The data are given in Tables II and III.

Ionization Constants.—Apparent ionization constants of *m*- and *p*-trifluoromethylbenzoic acids were obtained at 25° in 50% water–50% ethyl alcohol (by volume) as described earlier.[13]

	Half-point scale reading	Apparent ionization constant × 10⁶
m-Trifluoromethylbenzoic acid	5.11	7.75
p-Trifluoromethylbenzoic acid	4.949	11.5

Ionization constants (pK_A) of substituted anilinium and dimethylanilinium ions were measured at 25° in aqueous sulfuric acid solutions by the procedure of Hammett.[14] A Beckman model DU spectrophotometer with a thermostatted cell holder was used as the colorimeter. For the substituted anilines, anilinium ion and *p*-nitroanilinium ions were employed as standards. The data are given in Tables IV and V.

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN BENZENE AT 25°

f_2	ε	*d*	n_D	P_2
		Trifluoromethylcyclohexane		
0.00000	2.272	0.87254		(P_1 = 26.65)
.00882	2.336	.87492		149.9
.02460	2.450	.87977		146.5
.01915	2.409	.87837		145.4
.03420	2.517	.88248		144.8
.05721	2.681	.88945		141.8
		Benzotrifluoride		
0.00000	2.272	0.87254		(P_1 = 26.65)
.00690	2.337	.87537		174.1
.01394	2.393	.87792		162.5
.02502	2.485	.88239		158.5
.04045	2.616	.88814		155.7
.07096	2.870	.90017		149.5
		p-Aminobenzotrifluoride		
0.00000	2.273	0.87244		(P_1 = 26.67)
.01005	2.508	.86856		397.3
.01929	2.729	.88315		354.5
.03353	3.068	.89122		335.7
.03982	3.220	.89455		328.9
.06248	3.732	.90657		273.9
		p-Dimethylaminobenzotrifluoride		
0.00000	2.273	0.87244	1.49713	(P_1 = 26.67)
.00396	2.390	.87446		472.1
.00820	2.513	.87682		468.0
.01692	2.743	.88111	1.49645	423.6
.02379	2.960	.88483	1.49626	421.8
.03204	3.192	.88904	1.49587	404.7

TABLE III

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞ (25°)	μ (Debye)
Trifluoromethylcyclohexane	32.33	150.0	2.40
Benzotrifluoride	30.72	168.7	2.60[a]
p-Aminobenzotrifluoride	35.90	409.7	4.28
p-Dimethylaminobenzotrifluoride	45.8[b]	481.1	4.62

[a] Freiser, Hobbs and Gross, THIS JOURNAL, **71**, 111 (1949), report 2.56 *D* in benzene solution. [b] Obtained from refractive indexes and densities of benzene solutions.

In Fig. 1, pK_A plotted against σ is compared with the line (corresponding to log k_0 = −4.569 and ρ = +2.730) obtained from a least squares fit of data on pK_A of substituted anilinium ions obtained by other investigators.[9] For the compounds studied, the median deviation, *r*, is 0.026.

The acidity constants of *m*- and *p*-nitro- and *m*- and *p*-trifluoromethyl-dimethylanilinium ions were determined using *p*-nitroanilinium ion as a standard. The data are given in Tables IV and V.

Rate Runs.—The reaction rates of *m*- and *p*-trifluoromethylbenzoic acids with diphenyldiazomethane in absolute alcohol at 30° were measured as described previously.[13]

	Concn., moles/l.	Half-life, min.	k_2, l./mole min.
m-Trifluoromethylbenzoic acid	0.0296	7.38	3.18
p-Trifluoromethylbenzoic acid	.0290	8.30	2.89

---

[10] Jones, THIS JOURNAL, **69**, 2346 (1947).

[11] Drake and co-workers, *ibid.*, **68**, 1602 (1946).

[12] Roberts, Armstrong, Trimble and Burg, *ibid.*, **71**, 843 (1949); Rogers and Roberts, *ibid.*, **68**, 843 (1946).

[13] Roberts, McElhill and Armstrong, *ibid.*, **71**, 2923 (1949).

[14] Hammett and Paul, *ibid.*, **56**, 827 (1934); ref. 9, Chap. IX.

TABLE IV

OPTICAL DENSITIES OF COMPLETELY IONIZED AND UN-IONIZED SUBSTITUTED ANILINES ($XC_6H_4NR_2$) IN AQUEOUS SOLUTION

X	R	Concn., moles/l. × 10^{-5}	λ, mμ[a]	*D* of un-ionized form at λ	*D* of ionized form at λ[b]
p-NO$_2$	H	3.58	381	0.463	0.000
p-CH$_3$	H	2.92	290	.332	.044
m-NO$_2$	H	3.84	227	.493	.103
m-CF$_3$	H	3.31	236	.257	.084
m-Cl	H	4.24	236	.304	.000
p-Cl	H	4.18	239	.440	.019
H	H	6.25	231	.480	.002
p-CH$_3$	H	4.22	233	.333	.000
p-NO$_2$	CH$_3$	2.23	424	.448	.010
m-NO$_2$	CH$_3$	3.07	248	.518	.223
p-CF$_3$	CH$_3$	2.72	274	.149	.019
m-CF$_3$	CH$_3$	3.38	252	.288	.000

[a] λ was taken usually near or at a principal absorption maximum of the un-ionized form in the region 225–425 mμ. [b] Solvent was approximately 6 *N* sulfuric acid.

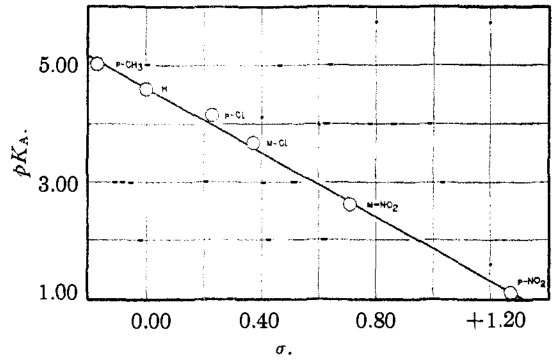


Fig. 1.—pK_A for substituted anilines in water at 25°.

Discussion

The difference in moment (0.20 *D*) between benzotrifluoride and trifluoromethylcyclohexane is quite comparable to the difference (0.24D[15]) in moment between aromatic and aliphatic cyano compounds. Differences of this sort between moments of aliphatic and aromatic compounds are usually ascribed to resonance[16] and may be taken as indicating that forms such as I or III contribute significantly to the resonance hybrid of benzotrifluoride. Resonance of type IV (or its analog derived from III) is indicated by the deviations of the observed dipole moments of *p*-amino- and *p*-dimethylaminobenzotrifluorides from the moments calculated by vector addition of the respective group moments. The moment of *p*-aminobenzotrifluoride (Table III) is 0.42 *D* larger than the value of 3.86 *D* computed from the moments of aniline (1.53 *D*) and benzotrifluoride. In this calculation the angle between the vector of the moment of the amino group and the axis of the ring was taken as 42°.[17] Similarly, the moment of *p*-dimethylaminobenzotrifluoride (Table III) exceeds by 0.44 *D*, the sum of the moments of benzotrifluoride and dimethylaniline, (1.58 *D*) indicating a substantial deviation from vector additivity even if the moment of the dimethylamino group is considered to be directed along the axis of the aromatic ring.[7] It is interesting to note by way of comparison that the moment of *p*-dimethylaminobenzonitrile is 0.35D greater than the sum of the moments of benzonitrile and dimethylaniline.[7]

TABLE V

DETERMINATION OF ACIDITY CONSTANTS OF ANILINIUM IONS ($XC_6H_5N^+HR_2$)

X	R	D at λ	C_x/C	C_{XH^+}/C	log (C_{XH^+}/C_x)	pK_A
p-NO$_2$	H	0.411	0.888	0.112	0.898	(1.11)[a]
p-CF$_3$	H	.107	.219	.781	−.553	2.57[b]
p-CF$_3$	H	.088	.153	.847	−.743	(2.57)
m-NO$_2$	H	.157	.139	.861	−.794	2.62[b]
H	H	.369	.232	.768	.520	(4.57)[a]
p-CH$_3$	H	.177	.468	.532	.056	5.03[c]
H	H	.359	.748	.252	.472	(4.57)[a]
p-Cl	H	.392	.887	.113	.895	4.15[c]
p-Cl	H	.230	.502	.498	.003	(4.15)
m-Cl	H	.229	.754	.246	.486	3.67[c]
m-Cl	H	.220	.724	.276	.418	(3.67)
m-CF$_3$	H	.222	.798	.202	.596	3.49[c]
p-NO$_2$	H	.256	.553	.447	.093	(1.11)[a]
p-NO$_2$	CH$_3$	.297	.655	.345	.279	0.92[b]
p-NO$_2$	CH$_3$	.380	.845	.155	.736	(0.92)
m-NO$_2$	CH$_3$	.262	.132	.868	−.818	2.47[b]
m-NO$_2$	CH$_3$	.419	.664	.336	.297	(2.47)
m-CF$_3$	CH$_3$	.069	.240	.760	−.501	3.27[b]
p-CF$_3$	CH$_3$	.085	.508	.492	.013	2.67[b]

[a] Reference compound, value of pK_A taken from ref. 9. [b] Reference compound was *p*-nitroaniline. [c] Reference compound was aniline.

Further evidence in favor of interaction between the groups of *p*-amino- and *p*-dimethylaminobenzotrifluorides may be inferred from the σ-constants of the trifluoromethyl groups given in Table VI. The same value of σ may be used to represent the influence of the *m*-trifluoromethyl group on the reactivities of anilines *and* benzoic acid. On the other hand, separate values differing by more than 0.2 unit are needed for the *p*-trifluoromethyl group depending on whether the effect on the reactivity of an aniline *or* benzoic acid is being considered. Similar differences in the values of σ-para for application to anilines and benzoic acid are exhibited by the *p*-nitro (0.49 unit[9]) and *p*-cyano groups (0.34 unit[18]).

If the demonstration of interaction between the trifluoromethyl group and aromatic ring is accepted, the question still remains as to whether resonance forms I or III represent more accurately the electron-attracting tendency of the trifluoromethyl group. While a final decision is not now possible, several arguments may be

---

(15) Rogers, THIS JOURNAL, **69**, 457 (1947).

(16) Sutton, *Proc. Roy. Soc. (London)*, **A133**, 668 (1931).

(17) Bergmann and Tschunowsky, *Z. physik. Chem.*, **B17**, 100 (1932).

(18) Roberts and McElhill, THIS JOURNAL, **71**, in press (1949).

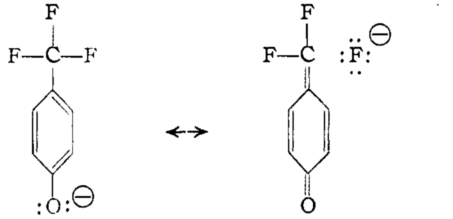
TABLE VI

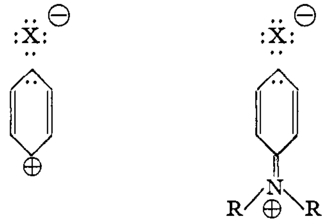
τ-CONSTANTS OF TRIFLUOROMETHYL GROUP

Reaction	Solvent	Temp., °C.	Log k^0	ρ	log k_{meta}	σ_{meta}	log k_{para}	σ_{para}
Ionization of benzoic acids	50% EtOH	25	-5.71^a	$+1.464^a$	-5.11	0.41	-4.94	0.53
Ionization of benzoic acids	H_2O	24	-4.203^b	$+1.000^b$	-3.788^c	.42	.....	...
Benzoic acids with diphenyldiazomethane	100% EtOH	30	$+0.041^a$	$+0.937^a$	$+0.502$	.53	$+0.461$	.48
Ionization of anilinium ions	H_2O	25	-4.569^b	$+2.730^b$	-3.49	.41	-2.57	.74
Ionization of dimethylanilinium ions	H_2O	25	......	$+2.77^d$	-3.27	.42	-2.67	.64
Ultraviolet absorption characteristics[e]	H_2O	..	......	......	......	(.41)[f]	....	.77[g]

[a] Ref. 13. [b] Ref. 9. [c] Swarts, *Bull. acad. roy. Belg.*, [3] **35**, 395 (1898). [d] Based on values of pK_A of p and m-nitrodimethylanilines. [e] Doub and Vandenbelt, THIS JOURNAL, 69, 2714 (1947). [f] Assumed. [g] Calculated from $\lambda_{\text{max.}}$ of p-aminobenzotrifluoride (285 mμ) assuming σ-meta to be 0.41 ($\Delta\sigma$ =0.36) by the procedure of Doub and Vandenbelt.

advanced in favor of I over III. In the first place I should probably be more important from energetic considerations since a negative charge is expected to be more favorably located on fluorine than on carbon as in III. Second, the extraordinarily facile loss of fluoride ion from *o*- and *p*- but not *m*-trifluoromethylphenolate ions[10] indicates a considerable loosening of the C–F bonds in these substances which may be expressed by resonance similar to that represented by IV. Finally, if resonance of type III is significant for the trifluoromethyl group, it might be expected to be exhibited to some degree at least by the halogens through contributions of forms such as VI. Actually, the criteria used in the present work give little if any indication of VI. Thus, the degree of interaction between the groups of p-amino- and p-dimethylaminohalobenzenes is small[7,17] and but one σ-constant is needed to express the influence of p-halogen substituents on the reactivity of either anilines or benzoic acid.[9]

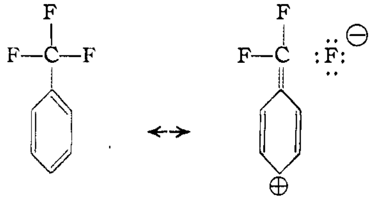




VI

Summary

Dipole moment and relative reactivity data have been used to show that an important part of the electrical effect of a trifluoromethyl group located on an aromatic ring may be represented by resonance forms of the following type



CAMBRIDGE 39, MASSACHUSETTS
RECEIVED AUGUST 16, 1949

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Copolymerization Process. I. Integration of the Rate Equations

BY EDWARD H. DEBUTTS*

The idea that many copolymerization reactions proceed by a free radical mechanism is quite well established. The acceptance of the free radical mechanism has been due in some measure to the experimental verification of predictions based on the rate equations derived assuming such a mechanism. It has been shown theoretically by several workers[1,2,3] that the composition of a copolymer should depend upon certain experimentally determinable ratios of propagation reaction rate constants (these being termed "monomer reactivity ratios") and upon the concentrations of the monomers involved. This concept has been subjected to exhaustive experimental tests[4] and has been found to be correct within rather small error. A study of the over-all rates of copolymerization has been made from the theoretical point of view by Melville, Noble and

---

* Harvard University Faculty, 1948–.

(1) Wall, THIS JOURNAL, **66**, 2050 (1944).

(2) Mayo and Lewis, *ibid.*, **66**, 1594 (1944).

(3) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

(4) Mayo, Lewis and Walling, THIS JOURNAL, **70**, 1529 (1948); other references will be found here and in (6).