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Fluorine Nuclear Magnetic Resonance Shielding in *meta*-Substituted Fluorobenzenes. The Effect of Solvent on the Inductive Order[1]

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The F^{19} n.m.r. shielding parameters for twenty-one *m*-substituted fluorobenzenes relative to a fixed external standard and relative to fluorobenzene as an internal standard have been obtained at room temperature at high dilution in twenty widely varying pure solvents. Extensive measurements with twenty-four additional substituent groups in non-polar and in hydroxylic solvents, both pure and mixed, have also been made. In spite of a variation over 9.2 p.p.m. in shielding for a given fluorobenzene relative to the fixed external standard, the shielding parameters for seven compounds with chemically inert *m*-substituents relative to internal fluorobenzene are solvent invariant to a precision of the same order as experimental error. This result offers critical evidence that intermolecular shielding resulting from interaction of the fluorine atom with solvent makes little or no contribution to the shielding parameter of a *m*-substituted fluorobenzene relative to fluorobenzene as the internal standard. The previously reported correlation of these intramolecular substituent effects with the inductive substituent constant, σ_I, is extended over a range of 9.5 p.p.m. in shielding and the correlation is confirmed as a useful approximation. The present results obtained in solvents covering essentially two orders of magnitude in the dielectric constant compels the conclusion that the field effect of *m*-substituents either makes no practical contribution to intramolecular shielding or that it is solvent independent. It is further implied that the bond dipole moments of groups, such as —C=O ,—N=O, —C≡N and others attached to the benzene ring, are independent to good precision of wide variations in the dielectric constant and internal pressures for many non-protonic solvents at room temperatures. The effects of solvent on the shielding parameter of *m*-substituted fluorobenzenes with chemically active substituents is attributed to donor–acceptor solvent–substituent interactions. That is the fluorine atom acts as a distant but sensitive observer of solvent–substituent group interactions, being sufficiently far removed to avoid complications which may arise in the n.m.r. shielding of a nucleus directly involved in solute–solvent interactions. Effects on intramolecular shielding of solvent–substituent interaction of four types have been observed: (a) hydrogen bonding effects, (b) polarity effects on amide and ester functions, (c) effects due to formation of carbonyl addition compounds, (d) effects due to weak interactions of groups having Lewis-acidic and basic character. The latter type of interaction has been termed *Lewis-acid* bonding as an apparently useful analog of hydrogen bonding. The present results permit detailed evaluation of the effects of molecular structure on σ_I values (results for fifty substituents are tabulated). The important effects on σ_I of delocalization of charge within substituents of the general formulas COX and SO_2X is demonstrated. In addition, the trends and magnitudes of the effect of solvent–substituent interactions on σ_I values are apparently well defined by the present study. The results obtained are discussed as well as the implied applicability to chemical reactivities.

Substantial effects of solvent on F^{19} nuclear magnetic resonance shielding have been observed.[4,5] These solvent effects are a potential source of information on the nature of solute–solvent interactions. In general, however, there are substantial contributions to the solvent effects from diamagnetic susceptibility and other effects of magnetic origin, which greatly complicate evaluation of the effects of normal solute–solvent interactions.[6]

In the present work on *m*-substituted fluorobenzenes we have made use of the relatively effective transmission of electronic interactions through the benzene ring to provide information, both qualitative and quantitative, on the interaction between a large variety of organic and inorganic functional groups and solvents. The fluorine atom may be regarded as a distant but sensitive observer removed from the confusion of the "battlefield" (*i.e.*, field of interaction of solvent and substituent) by the rigid benzene ring.

The shielding of the F^{19} nucleus may be treated as the sum of intramolecular and intermolecular contributions.[7] The use of unsubstituted fluorobenzene as an internal standard of reference provides a fluorine atom which is very nearly identical with that of the *m*-substituted fluorobenzene. Shielding relative to this standard consequently may be expected (and has been shown by the present work) to measure the intramolecular shielding effect of the substituent and to contain little if any contribution from certain complicating intramolecular terms such as neighboring anisotropy effects.[7] The relatively high sensitivity of the fluorine n.m.r. shielding to intramolecular changes, however, provides information on the solute–solvent interaction which leads to a modification in the electronic character of the *m*-substituent group.

An analysis of the π-electronic shielding in *p*-substituted fluorobenzenes indicates that the π-charge density on the fluorine atom and in the carbon–fluorine bond is primarily responsible for intramolecular F^{19} shielding within a series of such molecules.[8,9] Although a satisfactory theory of F^{19} shielding in *m*-substituted fluorobenzenes has not been developed, a leading term appears to involve the ionic character of the C–F σ-bond.[8b,9] This conclusion is apparently supported by the fact that the shielding parameters are in the inductive order and a relatively precise correlation with the inductive substituent constant, σ_I, has been observed.[10]

The present investigation has had as an important objective the determination of the dependence of σ_I values on solvent as implied by the F^{19} shielding solvent effects. There is very little previous information regarding the effect of solvent on the inductive order since most reactivity investigations have been carried out in hydroxylic solvents. However, the wide variation in solvent permitted by the highly precise modified Hammett equation, $\log (k/k_0) = \sigma^0\rho$, suggests that for several well-behaved substituents there is very slight (if

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any) modification in the Ar–Y inductive order due to solute–solvent interactions.[10] On the other hand, *p*-substituent effects involving direct interaction dipolar quinoid forms show substantial dependence on solvent.[10]

A recent investigation of solvent effects on the ionization constants of a series of 4-substituted [2.2.2]bicycloöctanecarboxylic acids has indicated that solute–solvent interaction may cause appreciable variations in σ_I values for some substituent groups.[11] It is of interest to determine whether the σ_I values obtained from F^{19} shielding reproduce similar trends. Such a correspondence would be expected of characteristic specific group–solvent interactions (that is, σ_I values which are characteristic of both the substituent group and the solvent). In this endeavor, F^{19} n.m.r. shielding offers the practical advantages of a ready and systematic investigation, including substituents too reactive to be included in usual structure–reactivity investigations.

In the present work F^{19} n.m.r. shielding parameters for *m*-substituted fluorobenzenes relative to internal fluorobenzene and to a fixed external standard have been determined in 5% (vol.) solutions of 20 widely varying pure solvents at room temperature. It is demonstrated (with few exceptions) that this dilution corresponds within the experimental error to the infinitely dilute solution. Twenty-one widely varying substituent groups have been investigated under these conditions. In addition, shielding parameters for some 30 additional substituent groups have been determined largely in hydroxylic solvents, both pure and mixed. The solvent variation studied includes hydroxylic solvents of acidities varying between that of t-C_4H_9OH and CF_3CO_2H. Pyridine is included as an example of a moderately basic solvent.

Experimental

Solvents.—Eastman Kodak Co. N-methylformamide was fractionally crystallized and the purified material, m.p. −3.5 to −4.5°, was vacuum distilled, b.p. 100.5° (25 mm.), $n^{25}D$ 1.4302 (reported[12] m.p. −3.8°, $n^{25}D$ 1.4310).

Nitrobenzene from stock was fractionally distilled, b.p. 113–114 (41 mm.), $n^{25}D$ 1.5496 (reported[13] b.p. 84.9° (10 mm.), $n^{20}D$ 1.5525).

Fisher absolute methanol was refluxed for 12 hours over magnesium filings and fractionated: b.p. 64° (735 mm.), $n^{25}D$ 1.3268 (reported[13] b.p. 64.5° (760 mm.), $n^{25}D$ 1.3266).

Matheson, Coleman and Bell spectroquality cyclohexane was used. Identical n.m.r. results were obtained with a sample purified by the method of Crowe and Smyth.[14]

Eastman Kodak Co. benzonitrile was fractionally distilled over P_2O_5; b.p. 186–189° (730 mm.). The distillate was fractionally crystallized to give a purified product, b.p. 188–189° (730 mm.), $n^{25}D$ 1.5253 (reported[13] b.p. 191° (760 mm.), $n^{23}D$ 1.5272).

Fisher analytical grade nitromethane was fractionated to give a sample, b.p. 99° (735 mm.), $n^{25}D$ 1.3792 (reported[13] b.p. 101° (760 mm.), $n^{25}D$ 1.3795).

Trifluoroacetic acid obtained from Matheson, Coleman and Bell was distilled at atmospheric pressure; b.p. 70° (735 mm.) (reported[15] b.p. 70–72°).

N,N-Dimethylformamide, a Baker reagent, was fractionally distilled; b.p. 56° (23 mm.), $n^{25}D$ 1.4280 (reported[13] b.p. 153° (760 mm.), $n^{25}D$ 1.4290).

Eastman Kodak Co. diethyl maleate was fractionated and the material collected at b.p. 105–106° (13 mm.), $n^{25}D$ 1.4380 (reported[13] b.p. 99.4° (10 mm.), $n^{25}D$ 1.4383).

1,4-Dioxane obtained from stock was purified by the method of Vogel[16]; b.p. 100° (735 mm.), $n^{25}D$ 1.4154 (reported[13] b.p. 101° (760 mm.), $n^{25}D$ 1.4203).

Merck spectrograde carbon tetrachloride was used: b.p. 76.5° (740 mm.) (reported[13] b.p. 76.8° (760 mm.)).

Methylene iodide obtained from Fisher Scientific Co. was fractionally distilled giving a product, b.p. 93–94° (44 mm.) (reported[17] b.p. 88° (39 mm.)). The distillate had a pale yellow hue which turned to orange on standing. Identical n.m.r. results were obtained with the freshly distilled and with the darkened material.

3-Methylpentane of 99.9% purity was obtained from the P.S.U. petroleum refining laboratory.

Anhydrous fromic acid was kindly donated by Dr. E. Sacher who refluxed Baker reagent grade material over acetic anhydride for 24 hours, and collected the fraction boiling at 99–100° (720 mm.). This distillate was redistilled from phthalic anhydride; the fraction b.p. 100° (732 mm.) was retained (reported[18] b.p. 25° (20 mm.)).

Eastman Kodak Co. spectrograde acetone was refluxed over $KMnO_4$ for 7 hours and distilled. The distillate was refluxed over Drierite for 3 hours and then fractionally distilled: b.p. 55° (735 mm.), $n^{25}D$ 1.3561 (reported[13] b.p. 56.2° (760 mm.), $n^{25}D$ 1.3561).

Benzene obtained from stock was dried over calcium hydride for several days and fractionally distilled[19]; b.p. 80.0° (740 mm.) (reported[13] b.p. 80.1° (860 mm.)).

Diethyl ether was obtained from Mr. Evan Jensen who distilled the solvent from concentrated sulfuric acid and then dried it over sodium.

Tetrahydrofuran was obtained from Dr. Philip L. Levins who distilled a large quantity (stock) of the solvent, discarding the first 15% of the material and collecting the middle fraction; b.p. 64.0° (740 mm.) (reported[20] b.p. 65.4°).

Acetic anhydride obtained from stock was fractionally distilled[19]; b.p. 61.0–61.5° (42 mm.) (reported[13] b.p. 62.1° (40 mm.)).

Pyridine (Baker analyzed reagent) was dried over barium oxide and fractionally distilled[19]; b.p. 114.0° (740 mm.) (reported[13] b.p. 115.6° (760 mm.)).

Acetonitrile (Matheson, Coleman and Bell) was fractionally distilled[19]; b.p. 80.0° (740 mm.) (reported[13] b.p. 81.6° (760 mm.)).

Ethyl acetate obtained from stock was dried over potassium carbonate and fractionally distilled[19]; b.p. 74.0° (735 mm.) (reported[13] b.p. 77.1° (760 mm.)).

Fisher spectroanalyzed methylene chloride was used directly; Eastman Kodak Co. best grade *o*-dichlorobenzene, as supplied.

Diethylene dimethyl ether (diglyme) was obtained from Mr. Niles Gilmour and was used directly; Fisher spectroanalyzed chloroform, as supplied.

2,2,3,3-Tetrafluoropropanol (Du Pont chemical) was fractionally distilled[19]; b.p. 106.0° (740 mm.) (reported[21] b.p. 106–106.6°).

Ethanol, commercial absolute, was dried with barium oxide.

Dimethyl sulfoxide (Crown Zellerbach) was dried over barium oxide and then distilled; b.p. 39–40° (2 mm.) (reported[22] b.p. 40° (2 mm.)).

t-Butyl alcohol obtained from stock was distilled[19] discarding the first 10% and retaining the middle fraction, b.p. 82.0° (740 mm.) (reported[19] b.p. 82.4° (740 mm.)).

Glacial acetic acid was supplied by Dr. P. L. Levins who distilled[19] the material from a mixture of potassium permanganate, sulfuric acid and acetic anhydride to obtain a middle fraction, b.p. 117.0° (740 mm.) (reported[13] b.p. 117.7° (760 mm.)).

The aqueous organic solvents were prepared with distilled water. Per cent of volume (% vol.) refers to the volume of organic liquid relative to the sums of the volumes of organic liquid and of water taken.

Fluorobenzenes.—*m*-Fluorotoluene, *m*-bromofluorobenzene, *m*-chlorofluorobenzene, *m*-fluorobenzotrifluoride and *m*-fluoroacetanilide were obtained as previously reported.[23]

The following compounds were obtained from the Pierce Chemical Co., Rockford, Ill.; fluorobenzene, b.p. 84–85° (740 mm.), $n^{25}D$ 1.4646 (reported[13] b.p. 84.8° (760 mm.), $n^{30}D$ 1.4610); *m*-difluorobenzene, $n^{25}D$ 1.4353 (reported[24] $n^{18}D$ 1.4404); *m*-fluorobenzaldehyde, $n^{25}D$ 1.5141 (reported[24] $n^{24}D$ 1.5159); *m*-fluoroaniline, b.p. 82° (21 mm.) (reported[25] b.p. 185–187° (770 mm.)). Identical n.m.r. results were obtained with a sample of the latter prepared by the Schmidt reaction with *m*-fluorobenzoic acid.

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m-Fluoroanisole, $n^{25}D$ 1.4870 (reported[24] $n^{23}D$ 1.4876), and *m*-fluoro-α,α,α-trifluoroacetophenone), $n^{25}D$ = 1.4483, were obtained from L. Light and Co., Ltd., Colnbrook, England.

The following compounds were obtained from the Aldrich Chemical Co., Milwaukee, Wisc.: *m*-fluorobenzoic acid, m.p. 123–124° (reported[26] m.p. 124°); *m*-fluorophenol, b.p. 84° (20 mm.) (reported[27] b.p. 84° (20 mm.)). Dr. A. Konstam kindly provided a sample of *m*-fluorobenzyltrimethylsilane. Dr. W. A. Sheppard kindly provided a sample of *m*-fluoro-α,α,α-trifluoroanisole.

m-Fluorostyrene and *m*-fluorophenylmethyl carbinol were prepared as previously described,[28] as was *m*-fluorophenylhydrazine.[31]

m-Fluorobenzonitrile was prepared by a Sandmeyer reaction with *m*-fluoroaniline according to the method of Swartz.[29] A fraction boiling at 89° (40 mm.) was collected in 12% yield. The characteristic nitrile band at 2200 cm.$^{-1}$ was present in the infrared, $n^{25}D$ 1.5022 (reported[29] b.p. 182.6° (753 mm.)).

m-Fluoronitrobenzene was prepared from *m*-nitroaniline by the Schieman reaction[30]; 48% HBF_4 was prepared by adding 18.4 parts by weight of boric acid to 45.0 parts of HF. The latter was placed in a nickel crucible in an ice-bath and the boric acid added slowly. *m*-Fluoroaniline (34 g.) was dissolved in 110 cc. of HBF_4 solution in a 400-cc. beaker. The solution was stirred in an ice–salt-bath and a cold solution of $NaNO_2$ (17 g.) in 34 cc. of water was added keeping the temperature of the mixture at 0° by additions of small portions of Dry Ice. Subsequently, 50 ml. of cold HBF_4 solution was added and the mixture stirred for 1 hour at 0°. The diazonium salt was filtered, washed with ether, and dried on filter paper in a hood. The salt (55 g.) was decomposed in three separate batches by heating with an equal amount of sand in a round-bottom flask fitted with a condenser and receiver. The flask was heated by flame until no more BF_3 was evolved. The distillate was steam distilled, and an ether solution was washed with 5% NaOH solution with water. The product was dried over K_2CO_3, the ether evaporated and distilled. Fifteen grams of a pale yellow liquid, b.p. 52–54° (2 mm.), was obtained (reported[30] b.p. 53–54° (1–2 mm.)).

m-Fluoronitrosobenzene was prepared by the method of Oláh, *et al.*,[31] involving Zn reduction of *m*-fluoronitrobenzene. Purified material was isolated as white crystalline flakes in 30% yield. The material was stored under nitrogen at 0°; m.p. 54–55° (reported[31] m.p. 51°).

m-Fluoroacetophenone was prepared from *m*-aminoacetophenone (10.0 g., Eastman Kodak Co.) by diazotization with HBF_4 (as described in detail for *m*-fluoronitrobenzene). The dried diazonium salt was decomposed to give 2.0 g. of compound, b.p. 79° (10 mm.) (reported[32] b.p. 81° (9 mm.)).

Ethyl m-fluorobenzoate was prepared by esterification of the acid with ethanol; b.p. 100° (21 mm.) (reported[33] b.p. 94–95° (16 mm.)).

m-Fluorobenzoyl chloride was prepared from the acid by refluxing with thionyl chloride. The product was obtained by vacuum distillation; b.p. 86–87° (24 mm.) (reported[34] 91° (18 mm.)).

m-Fluorobenzamide was prepared from *m*-fluorobenzoyl chloride by addition to a cooled solution of concd. NH_4OH to obtain a product, m.p. 131–132° (reported[35] m.p. 130°).

m-Fluoro-N,N-dimethylaniline was prepared by reaction of *m*-fluoroaniline (3.4 g.) with dimethyl sulfate (4.0 g.) by the procedure reported for the preparation of the *p*-isomer.[36] The reactants were sealed in a pressure tube and heated at 200° for 1 hour in a pre-set oven. The cooled tube was opened and the oily product neutralized with excess concd. KOH. The mixture was extracted with ether and dried over $MgSO_4$. The ether was evaporated and the oily product distilled. A yield of 2.6 g. (60%) of product, b.p. 87° (20 mm.), was obtained.

m-Fluorotrimethylammonium iodide was prepared from the above amine by heating 1.0 g. with an excess of CH_3I on a steam-bath until a solid product remained. The solid was dissolved in methanol and precipitated with ether. This process was repeated to give 1.0 g. of a white crystalline solid, m.p. 199–201°.

m-Fluorophenyl acetate was prepared by acetylation of *m*-fluorophenol with acetyl chloride. Vacuum distillation gave a product, b.p. 77° (16 mm.).

m-Fluorophenyl phenyl ether was prepared by the method previously described for preparation of the *p*-isomer, *i.e.*, by heating *m*-fluorobromobenzene with sodium phenylate in the presence of a trace of Cu powder.[37] The mixture was heated to reflux in a flask placed in a sand-bath for 3.5 hours. The reaction product was poured into an alkaline solution and steam distilled. The steam distillate was extracted with ether, dried, and distilled to give a product, b.p. 120° (18 mm.).

m-Iodofluorobenzene was prepared by diazotizing *m*-fluoroaniline (5.0 g.) with HCl and $NaNO_2$ at 0°. The resulting solution was poured into a cold solution of KI and reaction allowed to take place for 1 hour. The mixture was steam distilled, extracted with ether, washed with $Na_2S_2O_3$ and Na_2CO_3 solutions, and dried over $MgSO_4$. Evaporation of ether and vacuum distillation gave 2.5 g. of product, b.p. 64–66° (13 mm.) (reported[38] b.p. 77.5° (19 mm.)).

m-Phenylfluorobenzene.—*m*-Fluoroaniline (6.8 g.) was diazotized with concd. HCl and $NaNO_3$ solution. The cold diazonium was transferred to a large flask and excess cold benzene added. The solution was stirred and sodium acetate solution added. The mixture was kept at 5–10° for 3 hours and then for 48 hours at room temperature. The benzene layer was separated, washed with water, and dried. Benzene was removed and the product distilled to give 2.5 g. of material, b.p. 117° (5 mm.).

1-(*m*-Fluorophenyl)-2-nitroethene was prepared by reaction of *m*-fluorobenzaldehyde (9.0 g.) with nitromethane (4.5 g.) in methanol solution to which aq. KOH was added dropwise to 10–15°. The solution was stirred for 15 minutes and then poured with stirring into cold 5 *M* HCl. The organic layer was extracted with a benzene–petroleum ether mixture, dried over $MgSO_4$, concentrated, and the residual oil distilled. A 73% yield of product, b.p. 131–140° (3 mm.), was obtained. Recrystallizations from CCl_4 gave m.p. 50–51°. Infrared spectra in $HCCl_3$ gave bands consistent with the *trans* isomer of the compound. *Anal.* Calcd. for $C_8H_6FNO_2$: C, 57.47; H, 3.62. Found: C, 57.70; H, 3.71.

m-Fluorothiophenol.—A Grignard reagent was prepared[39] from *m*-fluorochlorobenzene (48 g.) and Mg (11 g.) in tetrahydrofuran (125 ml.). Sulfur (8.4 g.) was added in portions over a 15-minute period and the mixture was stirred and refluxed overnight.[40] These steps were all carried out under an atmosphere of dry N_2. The mixture was hydrolyzed by dropwise addition of a cold dilute HCl solution. The aqueous layer was extracted with ether and combined with the organic layer. Dilute sodium hydroxide solution was then used to extract the product. The sodium hydroxide solution was acidified with cold HCl and extracted three times with 100-ml. portions of ether. The combined ether extracts were washed with dilute $NaHCO_3$ and with a saturated salt solution and dried over Drierite. Distillation gave a 29% yield of *m*-fluorothiophenol, b.p. 157° (740 mm.).

m-Fluorophenyl methyl sulfide was prepared by the method reported[41] for preparation of the *p*-isomer, *i.e.*, by treating *m*-fluorothiophenol (3.8 g.) in aqueous alkaline with methyl sulfate (4.4 g.) which was added dropwise with stirring over a 5-minute period. The mixture was further stirred for 2 hours and then extracted with ether. The ether solution was dried, concentrated and distilled to give an 83% yield of product, b.p. 186–187° (740 mm.). *Anal.* Calcd. for C_7H_7SF: C, 59.12; H, 4.96. Found: C, 59.90; H, 4.98.

m-Fluorophenyl methyl sulfone was prepared[41] by dissolving *m*-fluorophenyl methyl sulfide (1.4 g.) in 10 ml. of glacial acetic acid; 25 drops of 30% H_2O_2 was added and the solution boiled for 5 minutes. Another 25 drops of hydrogen peroxide was added and the solution was boiled to near dryness in a current of air. The crude sulfone was recrystallized from dilute ethanol to give *m*-fluorophenyl methyl sulfone (1.3 g.), m.p. 39–41°. *Anal.* Calcd. for $C_7H_7FSO_2$: C, 48.26; H, 4.05. Found: C, 48.04; H, 4.03. (These are average values obtained by two different analytical laboratories.)

m-Fluorophenyl methyl sulfoxide was prepared by dissolving *m*-fluorophenyl methyl sulfide (3.5 g.) in glacial acetic acid (10 ml.); 32% hydrogen peroxide (2.7 g.) was added at once and the mixture allowed to stand. Concentration and distillation of the residue gave *m*-fluorophenyl methyl sulfoxide (2.7 g.) in 68% yield, b.p. 103–106° (3 mm.).

m-Fuorobenzenesulfonyl Chloride.—*m*-Fluorothiophenol (10.7 g.) was dissolved in glacial acetic acid (50 ml.) and the solution heated to 50° while 32% H_2O_2 (29 g.) was added dropwise over a 30-minute period. The reaction mixture warmed to the boiling point after which the temperature gradually fell. The solution was concentrated and the residue heated with excess PCl_5 for 1 hour. Ice was added to hydrolyze the PCl_5 after which the mix-

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ture was extracted with an ether–benzene mixture. The organic layer was dried over $CaCl_2$, filtered, concentrated and distilled to give *m*-fluorobenzenesulfonyl chloride (7.7 g.), b.p. 112–113° (12 mm.).

***m*-Fluorobenzenesulfonic Acid.**—A few grams of *m*-fluorobenzenesulfonyl chloride was refluxed with water overnight.[40] The clear solution was then concentrated to give the crude semi-solid acid. Attempts to recrystallize were unsuccessful so the acid was used in the crude form.

***m*-Fluorobenzenesulfonamide** was prepared following the procedure reported for preparation of *p*-fluorobenzenesulfonamide from the acid chloride.[40] Crystalline material, m.p. 129–130°, was obtained. *Anal.* Calcd. for $C_6H_6FSO_2N$: C, 41.13; H, 3.45. Found: C, 41.21; H, 3.14.

Ethyl *m*-Fluorobenzenesulfonate.—*m*-Fluorobenzenesulfonyl chloride (2.4 g.) was dissolved in absolute ethanol (50 ml.). A solution of Na (0.28 g.) dissolved in absolute ethanol (20 ml.) was added to the stirred sulfonyl chloride solution over a 15-minute period. The mixture was concentrated *in vacuo* to about 30 ml., diluted to 100 ml. with cold water, and extracted with two 60-ml. portions of $HCCl_3$. The combined organic layers were washed successively with 50 ml. of cold water, saturated $NaHCO_3$ solution, and cold water. The solution was dried over Drierite, filtered, and concentrated to an oil. Distillation gave ethyl *m*-fluorobenzenesulfonate, 1.5 g., b.p. 90–91 (2 mm.).

***m*-Fluoroaniline Hydrochloride and *m*-Fluorobenzylamine Hydrochloride.**—The amines (2.0 g.) were dissolved in absolute ether (100 ml.). Dry HCl was passed into the solution for about 15 minutes. The white precipitate was filtered off and recrystallized from absolute alcohol. These operations were performed in a dry nitrogen atmosphere and the resulting hydrochlorides were dried *in vacuo* over Drierite. The *m*-fluorobenzylamine salt melted at 279–281°.

***m*-Fluoroethylbenzene.**—A Grignard reagent was prepared from *m*-fluorobromobenzene (8.8 g.) and magnesium (1.3 g.) under dry nitrogen in ether (100 ml.). Freshly distilled ethyl sulfate (14.5 g.) in ether (50 ml.) was added rapidly.[42] The mixture was stirred overnight, after which it was hydrolyzed by a dilute hydrochloric acid solution. The organic layer was separated, washed with sodium hydroxide and a saturated salt solution. Afterward, the organic layer was dried over Drierite, filtered, concentrated, and distilled to give a 46% yield (2.9 g.) of *m*-fluoroethylbenzene, b.p. 135–137° (740 mm.).

3-Fluoroazobenzene was prepared from *m*-fluoroaniline following the procedure previously reported to prepare 4-fluoroazobenzene.[37] The product, after two recrystallizations from dilute ethanol, melted at 42.5–43.0°. *Anal.* Calcd. for $C_{12}H_9FN_2$: C, 71.98; H, 4.53; N, 13.99. Found: C, 72.19; H, 4.59; N, 13.82.

Phenyl *m*-fluorobenzoate was prepared by adding 11.0 g. of *m*-fluorobenzoyl chloride to 5 ml. of phenol dissolved in 75 ml. of 10% NaOH solution. The reaction flask was stirred for 30 minutes, the solid filtered and washed with water. Recrystallization from methanol gave 8.5 g. of a white solid, m.p. 55°.

***m*-Fluorobenzyl chloride** was prepared[43] by gently refluxing *m*-fluorotoluene (55 g.) and sulfonyl chloride (34 g.) for 30 minutes. The solution was distilled at atmospheric pressure until the temperature reached 135°. Vacuum distillation of the residue gave 42 g. of product, b.p. 64° (12 mm.).

***m*-Fluorobenzyl Cyanide.**—*m*-Fluorobenzyl chloride (14 g.) in 15 cc. of ethanol was added to 7 g. of NaCN in 65 ml. of H_2O over a period of 20 minutes. The mixture was heated in a water-bath for 4 hours, cooled, and the NaCl filtered. Ethanol was evaporated and the residue was extracted with ether, dried and distilled. A colorless liquid (8.0 g.) was obtained, b.p. 109° (12 mm.).

***m*-Fluorophenylacetic Acid.**—To *m*-fluorobenzyl cyanide (10 g.) was added 10 ml. each of H_2O, concd. H_2SO_4 and glacial acetic acid. The mixture was heated for 1 hour and poured into ice. Filtration and recrystallization from petroleum ether gave a white solid (3.5 g.), m.p. 48° (reported[44] m.p. 44.5–45.5°).

***m*-Fluorobenzyl Alcohol.**—In a three-necked flask fitted with a condenser, stirrer and dropping funnel was placed $LiAlH_4$ (2.0 g.) in 100 ml. of dry ether. The mixture was stirred and refluxed to effect solution. The flask was cooled to 0° and *m*-fluorobenzoyl chloride was added dropwise over a 25-minute period.[45] The reaction was stirred for 15 minutes and the excess hydride was then decomposed with a few ml. of water. The mixture was treated with excess 10% H_2SO_4 and the ether layer was removed and dried. Distillation gave the alcohol, 10.0 g., b.p. 104–105° (22 mm.).

***m*-Fluorobenzophenone** was prepared by Dr. Y. Tsuno by the Friedel–Crafts reaction of *m*-fluorobenzoyl chloride with benzene in carbon disulfide solution.[22] A 70% yield of material, m.p. 53–54°, was obtained. Recrystallization from petroleum ether gave product, m.p. 54.5–55.0° (reported[46] m.p. 55°).

***m*-Fluorophenyl sulfur pentafluoride** was prepared by Dr. P. L. Levins, using the method of Scheimann (as described above), from *m*-pentafluorosulfur aniline hydrochloride, which was kindly provided by Dr. W. A. Sheppard. A 50% yield of product b.p. 53° (24 mm.), was obtained.

***m*-Fluorobenzoyl fluoride** was prepared from *m*-fluorobenzoic acid by the action of sulfur tetrafluoride.[47] The acid (14.2 g.) was dissolved in ether (100 ml.) in a 250–500 ml. reaction flask. The flask was provided with an inlet and outlet system. The former consisted of a glass manifold of two condensing tubes connected by a surgical rubber tubing to a cylinder of SF_4 (du Pont). From the tubes a two-way outlet was provided to an open-end mercury manometer and to the reaction flask. The outlet from the reaction flask was connected to a drying tower containing Drierite, which in turn was connected to a trap containing aqueous NaOH. The entire apparatus was enclosed in a hood. With the reaction flask inlet closed off, about 8 ml. of SF_4 was condensed in the condensing tubes by means of a Dry Ice–acetone-bath. The SF_4 was then allowed to distil into the reaction vessel. The reaction flask was cooled with a Dry Ice–acetone-bath to ensure complete transfer of the SF_4. With the inlet to the reaction vessel closed, the solution was swirled and allowed to come to room temperature. The acid dissolved with evolution of gas and the reaction mixture was allowed to stand overnight. After purging the solution with dry nitrogen, the solution was poured into an ice slush and the ether layer separated. The ethereal solution was washed with two portions of dilute $NaHCO_3$, with water, and dried over Drierite. After removal of ether, the residue was distilled giving the acid fluoride (5.0 g.), b.p. 138° (740 mm.). *m*-Fluorobenzoic acid (3.2 g.) was recovered from the bicarbonate washings.

***m*-Fluorobenzenesulfonyl fluoride** was prepared by the action of boiling aqueous potassium fluoride on *m*-fluorobenzenesulfonyl chloride as described by Davies and Dick.[48] A clear liquid, b.p. 175° (740 mm.), was obtained.

***m*-Fluorobenzoyl cyanide** was prepared according to a procedure described by Oakwood and Weisgerber.[49] *m*-Fluorobenzoyl chloride (32.5 g.) was treated with cuprous cyanide (22 g.) as described. The liquid was distilled to give 70% of crude product, b.p. 198–208° (720 mm.). This material was fractionally distilled to give 6.1 g. of final product, b.p. 199–199.5° (723 mm.). The fluorine n.m.r. shielding of this sample showed it to contain about 10% of unreacted acid chloride.

Anal. Calcd. for C_8H_4ONF: C, 64.43; H, 2.70; N, 9.39. Found: C, 64.34; H, 3.01; N, 8.81.

1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane was used as obtained from Peninsular Chemresearch, Inc., Gainsville, Fla.

Procedure.—Measurements were made at 27 ± 2°, using essentially the same procedure (B) as previously reported.[23] The following modifications are noted. Although all shielding parameters reported herein (unless otherwise stated) are referenced to the position of internal fluorobenzene, it was found convenient for actual measurements to employ 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB) as the usual experimental internal reference. This compound gives rise to a single sharp line of sufficient intensity that concentrations of 2% (volume) were used. Further, the resonance frequency of this compound is approximately the same as that of fluorobenzene[50] so that its use does not require the recording of excessively long shifts. When fluorobenzene and TCTFCB signals were found to superimpose, *p*-difluorobenzene was used as the experimental internal reference. Following the previous procedure, approximately 5% (vol.) solutions of fluorobenzenes were used. The concentration levels roughly represent the minimum amount of each material required to yield a suitably intense signal. At this concentration level the following additivity was found to hold within the experimental error.[51]

$$\int_B^A \equiv \frac{H_A - H_B}{H_B} \times 10^6 = \int_{TCTFCB}^{XC_6H_4F} = \int_{TCTFCB}^{p\text{-}FC_6H_4F} + \int_{p\text{-}FC_6H_4F}^{X\text{-}C_6H_4F}$$

where $\int_B^A$ shielding parameter for compound A relative to reference B (internal unless otherwise designated)

H = applied magnetic field strength at resonance

X = a *m*- or *p*-substituent

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The following additivity has also been demonstrated[52]

$$\int_{\text{ext. ref.}}^{\text{X-C}_6\text{H}_4\text{F}} = \int_{\text{TCTFCB}}^{\text{X-C}_6\text{H}_4\text{F}} + \int_{\text{ext. ref.}}^{\text{TCTFCB}}$$

The shielding parameter of X-C_6H_4F at infinite dilution relative to the fixed external standard was obtained by extrapolation to zero concentration of plots of $\int_{\text{ext. ref.}}^{\text{XC}_6\text{H}_4\text{F}}$ *vs.* the concentration of X-C_6H_4F (5–60% (vol.) in a given solvent). The use of 5% (vol.) solutions as a permissible approximation (to within essentially the present experimental error) of infinite dilution is therefore considered generally justified. However, *m*-fluorophenol, *m*-fluorobenzoic acid, *m*-fluorophenylacetic acid, *m*-fluorobenzyl alcohol and *m*-fluorobenzamide are substantially polymerized in 5% (vol.) solutions in carbon tetrachloride or hydrocarbon solutions,[53] so that the approximation in this case is probably not justified. The shielding parameters reported for these compounds and a few similar ones under such conditions must therefore be accepted accordingly.

Each complete spectrum was swept at least four times in both the upfield and in the downfield direction at a maximum rate of 50 c.p.s. Either a Hewlett-Packard model 200 CD wide range oscillator of a 202A low frequency function generator was used to produce a side-band of one of the reference signals at a predetermined distance from the parent peak.[54] The signal of interest was straddled by the sideband of the reference signal as closely as possible and four sweeps were made with the sideband of the reference on the high field side of the signal and then four sweeps were made on the low field side. The frequency of the output signal was monitored with a Hewlett-Packard model 5216 electronic counter. All sideband frequencies were obtained to ±0.1 c.p.s.

Spectra were recorded with a Varian model G-10 graphic recorder. Peak separations were measured from the spectra with a set of dividers and rule. Separations could be read with a reproducibility of ±0.03 cm., which corresponded to ±0.04 p.p.m. The fluorobenzene and substituted fluorobenzene signals were in every instance characterized by fine structures arising from H^1–F^{19} spin–spin couplings. The desirability of measuring the shielding parameters under conditions of highest possible dilution made complete resolution of the signals impractical. Under the conditions described, the signal consisted of an envelop of about 0.8 p.p.m. in width. The shielding parameters were measured by taking the distance between the center of this envelop and the reference peak. The average deviation of a single measurement rarely exceeded ±0.08 p.p.m. and was independent of the magnitude of the shift. The results obtained for a given compound from samples made up at different times by different investigators with few exceptions agreed within this average deviation.

Results

Shielding Parameters Relative to Fixed External Standard.—Table I lists the observed shielding parameters for tetrachlorotetrafluorocyclobutane and for fluorobenzene relative to a fixed external standard (20% (vol.) *p*-difluorobenzene in carbon tetrachloride) in twenty-five solvents at high dilution. Also listed are the corresponding values for the susceptibility corrected shielding parameters.[55]

Some of the types of solvent–fluorine atom interactions which could reasonably contribute to the observed shielding are[56]: (1) van der Waals dispersion forces,[57,58] (2) hydrogen bonding,[59] and (3) dipole interactions.[57,58] In addition, solvent magnetic anisotropy effects may contribute.[60] In an attempt to determine if one of these factors clearly predominates, the corrected shielding parameters have been plotted *vs.* the following parameters: (1) the refractive index function[57,58] $(n^2_D - 1)/(2n^2_D + 1)$, the molar polarizability of the solvent,[5] the Onsager reaction field parameter,[56,61] and the Kirkwood solvation energy.[62] All of these plots show such substantial scatter that none of the parameters individually is capable of dealing with the experimental results. The most successful parameter is the refractive index function which reproduces the largest over-all trends of the data. For example, trifluoroacetic acid has both the lowest value of the refractive index function and the lowest value of $\int_{\text{ext. ref.}}^{\text{C}_6\text{H}_6\text{F}}$, while methylene iodide has the largest values of these two quantities. Thus it appears that dispersion forces figure predominantly but not exclusively in the intermolecular shieldings.

The intermolecular shielding due to solvent variation is apparently rather specific to the fluorine atom involved. Thus, although corresponding values of the corrected shielding parameters for tetrachlorotetrafluorocyclobutane and fluorobenzene show similar trends, one obtains substantial scatter in a plot of the one shielding parameter *vs.* the other. The order of solvent effects on the shielding of either compound bears no recognizable relationship to the order of solvent effects on the shielding parameters for any *m*- or *p*-substituted fluorobenzene relative to internal fluorobenzene. This fact makes critical the evidence presented in the following section for cancellation of the fluorine atom intermolecular shielding in the latter parameters.

TABLE I

SHIELDING PARAMETERS OF TETRACHLOROTETRAFLUOROCYCLOBUTANE AND FLUOROBENZENE IN INFINITELY DILUTE SOLUTIONS RELATIVE TO A FIXED EXTERNAL STANDARD (20% (VOL.) *p*-DIFLUOROBENZENE IN CCl_4)

	Solvent	$X_v \times 10^6$	$\int_{\text{ext. ref.}}^{\text{TCTFCB}}$ p.p.m. Obsd.	Cor.	$\int_{\text{ext. ref.}}^{\text{C}_6\text{H}_6\text{F}}$ p.p.m. Obsd.	Cor.
1	Cyclohexane	0.612[b]	4.6	4.8	6.0	6.2
2	Benzene	.612[b]	5.1	5.3	5.7	5.9
3	Carbon tetrachloride	.691[b]	5.9	5.9	7.1	7.1
4	Methylene iodide	1.156[a]	9.8	8.8	11.3	10.3
5	Diethyl ether	0.526[a]	3.8	4.2	4.3	4.7
6	Tetrahydrofuran	.641[d]	4.4	4.5	4.6	4.7
7	Dioxane	.658[d]	4.7	4.8	5.1	5.2
8	Diethyl maleate	.573	4.8	5.1	4.9	5.2
9	Acetic anhydride	.439[d]	4.6	5.1	4.5	5.0
10	Acetone	.461[a]	4.0	4.5	3.9	4.4
11	Pyridine	.609	5.0	5.2	5.4	5.6
12	Dimethylformamide	.607[d]	4.7	4.9	4.4	4.6
13	Monomethylformamide	.856[d]	4.5	4.2	4.6	4.3
14	Nitrobenzene	.602[a,b]	4.8	5.0	5.3	5.5
15	Nitromethane	.391[b]	3.6	4.2	3.0	3.6
16	Acetonitrile	.522	4.5	4.9	4.0	4.4
17	Dimethyl sulfoxide	...	6.0	..	6.1	..
18	Methanol	0.530[e]	3.7	4.1	3.5	3.9
19	Formic acid	.527[a]	4.4	4.8	4.0	4.4
20	Trifluoroacetic acid	.773[d]	2.6	2.4	2.1	1.9
21	3-Methylpentane	.592[a]	4.3	4.5	5.7	5.9
22	Ethyl acetate	.549[a]	4.2	4.5	4.2	4.5
23	Benzonitrile	.635[c]	5.0	5.2	5.4	5.6
24	*o*-Dichlorobenzene	.791[d]	5.9	5.7	6.7	6.5
25	75% (vol.) aq. methanol	.578[e]	4.1	4.4	3.9	4.2

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TABLE II

SHIELDING PARAMETERS, f_H^{m-X}, FOR *m*-SUBSTITUTED FLUOROBENZENES[a]

	Solvent	*m*-Substituent —CH_3	—CH_2=CH—	—C_6H_5—	—SCH_3	—$CO_2C_2H_5$	—$COCH_3$	—OCH_3	—CHO	—NO	—OC_6H_5
1	Cyclohexane	+1.23	+0.63	+0.15	−0.23	−0.15	−0.60	−0.98	−1.30	−1.73	−1.88
2	Benzene	+1.15	+ .60	+ .08	−0.35	− .43	− .68	−1.18	−1.10	−1.73	−2.20
3	Carbon tetrachloride	+1.18	+ .65	+ .15	− .38	− .13	− .73	−1.05	−1.35	−1.78	−1.95
4	Methylene iodide	+1.18	+ .63	+ .23	− .38	− .20	− .63	−1.10	−1.28	−1.75	−1.83
5	Diethyl ether	+1.10	+ .68	+ .13	− .33	− .33	− .73	−1.05	−1.23	−1.88	−2.00
6	Tetrahydrofuran	+1.10	....	+ .05	− .35	− .40	− .58	−1.15	−1.08	−1.83	−2.05
7	Dioxane	+1.20	+0.65	+ .15	− .30	− .30	− .35	−1.13	−0.85	−1.43	−1.93
8	Diethyl maleate	+1.08	+ .50	− .13	− .53	− .65	− .80	−1.20	−1.30	−1.98	−2.20
9	Acetic anhydride	+1.13	+ .43	− .08	− .55	− .60	− .75	−1.23	−1.18	−1.85	−2.10
10	Acetone	+1.13	+ .55	− .13	− .45	− .58	− .68	−1.28	−1.13	−1.83	−2.13
11	Pyridine	+1.18	+ .60	+ .03	− .38	− .43	− .60	−1.15	−1.13	−1.68	−2.10
12	Dimethylformamide	+1.10	+ .45	− .15	− .55	− .70	− .68	−1.25	−1.13	−1.88	−2.15
13	Monomethylformamide	+1.20	....	+ .05	− .38	− .50	− .70	−1.13	−1.10	−1.78	−2.00
14	Nitrobenzene	+1.20	+0.55	.00	− .35	− .38	− .73	−1.15	−1.13	−1.70	−2.08
15	Nitromethane	+1.13	+ .43	− .10	− .53	− .58	− .73	−1.30	−1.20	−1.70	−2.18
16	Acetonitrile	+1.13	+ .30	− .23	− .53	− .65	− .73	−1.28	−1.23	−1.78	−2.20
17	Dimethyl sulfoxide	+1.05	+ .38	− .23	− .55	− .70	− .60	−1.30	−1.25	−1.88	−2.10
18	Methanol	+1.15	+ .58	.00	− .40	− .73	−1.00	−1.38	−1.50[c]	−2.03	−2.05
19	Formic acid	+1.35	R[a]	+ .15	− .53	− .90	−1.30	−1.53	−1.78	−1.78	I[a]
20	Trifluoroacetic acid	+1.05	R	− .10	−1.80	−1.88	−2.65	−3.05	−3.18	R	−2.93

	Solvent	*m*-Substituent —COF	$-CF_3$	—Br	—$COCF_3$	—CN	—COCN	—F	—$SO_2C_2H_5$	—OCF_3	—NO_2	—SF_5
1	Cyclohexane	−2.20	−2.10	−2.43	−2.48	−2.73	−3.25	−3.03	−2.83	−3.28	−3.43	−3.10
2	Benzene	−2.03	−2.28	−2.60	−2.60	−2.75	−2.78	−3.08	....	−3.25	−3.25	−3.45
3	Carbon tetrachloride	−2.15	−2.13	−2.30	−2.63	−2.75	−3.33	−3.03	−2.98	−3.33	−3.45	−3.13
4	Methylene iodide	−1.98	I	−2.40	....	−2.73	....	−2.88	−3.10	....	−3.35	I
5	Diethyl ether	−2.30	−2.38	−2.48	−2.90	−2.85	−3.15	−3.05	−3.15	−3.43	−3.55	−3.38
6	Tetrahydrofuran	....	−2.35	−2.60	....	−2.75	....	−3.23	....	....	−3.25	−3.43
7	Dioxane	−1.70	−1.95	−2.45	−2.15	−2.30	−2.23	−2.98	−2.85	−3.28	−2.78	−3.75
8	Diethyl maleate	−2.35	−2.53	−2.63	−2.88	−3.00	−2.98	−3.25	−3.60	−3.53	−3.60	−3.63
9	Acetic anhydride	−2.20	−2.40	−2.63	−2.63	−2.78	....	−3.15	−3.48	−3.43	−3.40	−3.50
10	Acetone	−2.20	−2.38	−2.65	−2.63	−2.80	−2.70	−3.20	−3.45	−3.43	−3.40	−3.50
11	Pyridine	−1.98	−2.25	−2.58	+0.65	−2.78	−2.55	−3.08	....	−3.33	−3.23	−3.43
12	Dimethylformamide	−2.08	−2.48	−2.63	−2.65[b]	−2.78	−2.45	−3.15	−3.53	−3.45	−3.35	−3.55
13	Monomethylformamide	....	−2.30	−2.60	....	−2.80	....	−3.10	−3.45	....	−3.30	−3.40
14	Nitrobenzene	−2.10	−2.20	−2.55	−2.65	−2.85	−2.90	−3.05	−3.48	−3.33	−3.40	−3.53
15	Nitromethane	−2.10	−2.25	−2.63	−2.55	−2.73	−2.80	−3.15	−3.53	−3.33	−3.38	−3.40
16	Acetonitrile	−2.08	−2.30	−2.65	−2.60[b]	−2.68	−2.78	−3.20	....	−3.33	−3.33	−3.45
17	Dimethyl sulfoxide	−1.90	−2.33	−2.63	−2.35	−2.58	−2.13	−3.13	....	−3.25	−3.15	−3.45
18	Methanol	−2.35[d]	−2.50	−2.63	+0.03	−3.10	−3.85	−3.38	−3.75	−3.50	−3.60	−3.58
19	Formic acid	−2.08	−1.98	−2.48	−2.50	−3.13	....	−3.03	−3.68	−3.05	−3.50	−3.10
20	Trifluoroacetic acid	−3.40	−2.28	−2.55	−3.75	−4.63	−4.55	−3.23	−5.68	−3.25	−5.10	−3.43

[a] I designates insufficient solubility; R designates that a fast reaction occurs. [b] A second weak signal at +0.64 p.p.m. was also observed; *cf.* Discussion. [c] Most intense signal. A second weaker signal at higher field was also observed; *cf.* Discussion. [d] Initial signal; on standing signal due to ester appears. [e] In p.p.m. relative to fluorobenzene; exptl. error = ±0.08.

Intramolecular Shielding Due to *m*-Substituents.—Table II lists the results of an essentially complete survey of the shielding effects of 21 widely varying *m*-substituents in twenty pure solvents. Among the various substituents, shielding varies over a range of 7.0 p.p.m. In general, however, closely similar shielding parameters are observed for a given substituent in any solvent. This result demonstrates that the shielding relative to fluorobenzene as an internal standard must be determined almost solely by intramolecular terms. The variations of the shielding parameters with solvent which are observed are systematic and bear definite relationships to the general chemical properties of the solvent and the substituent. Most notable of these are the shifts to lower field strength in trifluoroacetic acid for substituents having measurable base strengths.

In Table III are listed the results for seven *m*-substituents which will be generally accepted as chemically inert groups. The shielding parameters for these substituents cover a range of 4.5 p.p.m., but the value for each substituent is the same in all twenty solvents to a precision closely on the order of the experimental error. This point is illustrated by the mean value of the shielding parameter listed at the bottom of Table III. The average deviations from the mean values for all of the substituents (±0.05 to ±0.09 p.p.m.) are of essentially the same magnitude as the individual experimental errors (±0.08 p.p.m.). Although a few of the largest deviations from the mean value (note especially $-CF_3$ and $-SF_5$ in dioxane and *cf.* subsequent discussion) are apparently outside of experimental error and bear a relationship to solvent effects observed for substituents of a similar class, most deviations are not reliably outside of experimental error and clearly are of second-order character.

Since the shielding for fluorobenzene is subject to the same experimental error (or small nearly random second order solvent effects) as for any *m*-substituted fluorobenzene, the results listed in Table III are based upon fluorobenzene values adjusted slightly (as indicated) to minimize the deviations from the mean for all sub-

TABLE III

SOLVENT INSENSITIVE SHIELDING PARAMETERS, $\int_H^{m\text{-}X}$, FOR FLUOROBENZENE WITH CHEMICALLY INERT *m*-SUBSTITUENTS[a,b]

	Solvent	*m*-Substituent: CH_3	C_6H_5	H	Br	CF_3	F	OCF_3	SF_5
1	Cyclohexane	+1.15	+0.08	−0.08	−2.43	−2.18	−3.10	−3.35	−3.18
2	Benzene	+1.10	+ .03	− .05	−2.60	−2.33	−3.13	−3.30	−3.50
3	Carbon tetrachloride	+1.18	+ .15	.00	−2.30	−2.13	−3.03	−3.33	−3.13
4	Methylene iodide	+1.10	+ .15	− .08	−2.40	I[b]	−2.95	....	I
5	Diethyl ether	+1.10	+ .13	.00	−2.48	−2.38	−3.05	−3.43	−3.38
6	Tetrahydrofuran	+1.10	+ .05	.00	−2.60	−2.35	−3.23	....	−3.43
7	Dioxane	+1.08	+ .03	− .13	−2.45	−2.08	−3.10	−3.28	−3.20
8	Diethyl maleate	+1.23	+ .03	+ .15	−2.63	−2.38	−3.10	−3.38	−3.48
9	Acetic anhydride	+1.20	.00	+ .08	−2.63	−2.33	−3.08	−3.35	−3.43
10	Acetone	+1.18	− .08	+ .05	−2.65	−2.33	−3.15	−3.38	−3.45
11	Pyridine	+1.18	+ .03	.00	−2.58	−2.25	−3.08	−3.33	−3.43
12	Dimethylformamide	+1.18	− .08	+ .08	−2.63	−2.40	−3.08	−3.38	−3.48
13	Monomethylformamide	+1.20	+ .05	.00	−2.60	−2.30	−3.10	....	−3.40
14	Nitrobenzene	+1.20	.00	.00	−2.55	−2.20	−3.05	−3.33	−3.53
15	Nitromethane	+1.13	− .10	.00	−2.63	−2.25	−3.15	−3.33	−3.40
16	Acetonitrile	+1.13	− .23	.00	−2.65	−2.30	−3.20	−3.33	−3.45
17	Dimethyl sulfoxide	+1.05	− .23	.00	−2.63	−2.33	−3.13	−3.25	−3.45
18	Methanol	+1.23	+ .08	+ .08	−2.63	−2.43	−3.20	−3.43	−3.50
19	Formic acid	+1.18	.00	− .15	−2.48	−2.13	−3.18	−3.20	−3.25
20	Trifluoroacetic acid	+1.05	− .10	.00	−2.55	−2.28	−3.23	−3.25	−3.43
	Mean value	+1.15	.00	.00	−2.55	−2.30	−3.10	−3.33	−3.40
	Av. dev.	±0.05	± .08	± .05	±0.08	±0.08	±0.05	±0.05	±0.09

[a] In p.p.m. relative to fluorobenzene; exptl. error = ±0.08. [b] I designates insufficient solubility.

TABLE IV

NORMAL SHIELDING PARAMETERS, $\int_H^{m\text{-}X}$, FOR FLUOROBENZENE WITH CHEMICALLY ACTIVE *m*-SUBSTITUENTS[a,b]

	Solvent	*m*-Substituent: $-CH{=}CH_2$	$-SCH_3$	$-OCH_3$	$-OC_6H_5$	$-COCH_3$	$-CHO$	$-NO$	$-COF$	$-COCF_3$	$-CN$	$-NO_2$
1	Cyclohexane	+0.55	−0.30	−1.05	−1.95	−0.68	−1.38	−1.80	−2.28	−2.55	−2.80	−3.50
2	Benzene	+ .55	− .40	−1.23	−2.25	− .73	−1.15	−1.78	−2.08	−2.65	−2.80	−3.40
3	Carbon tetrachloride	+ .65	− .38	−1.05	−1.95	− .73	−1.35	−1.78	−2.15	−2.63	−2.75	−3.45
4	Methylene iodide	+ .55	− .45	−1.18	−1.90	− .70	−1.35	−1.83	−2.05	....	−2.80	−3.43
5	Diethyl ether	+ .68	− .33	−1.05	−2.00	− .73	−1.23	−1.88	−2.30	−2.65	−2.85	−3.55
6	Tetrahydrofuran	....	− .35	−1.15	−2.05	− .58	−1.08	−1.83	....	....	−2.75	−3.25
7	Dioxane	+ .53	− .43	−1.25	−2.05	S.E.	S.E.	S.E.	S.E.	S.E.	S.E.	S.E.
8	Diethyl maleate	+0.65	− .38	−1.05	−2.05	− .65	−1.15	−1.83	−2.20	−2.73	−2.85	−3.45
9	Acetic anhydride	+ .50	− .48	−1.15	−2.03	− .68	−1.10	−1.78	−2.13	−2.55	−2.70	−3.33
10	Acetone	+ .60	− .40	−1.23	−2.08	− .63	−1.08	−1.78	−2.15	−2.58	−2.75	−3.35
11	Pyridine	+ .60	− .38	−1.15	−2.10	− .60	−1.13	−1.68	S.E.	S.E.	−2.78	S.E.
12	Dimethylformamide	+ .53	− .48	−1.18	−2.08	− .60	−1.05	−1.80	−2.00	−2.65	−2.70	−3.28
13	Monomethylformamide	....	− .38	−1.13	−2.00	− .70	−1.10	−1.78	....	....	−2.80	−3.30
14	Nitrobenzene	+0.55	− .35	−1.15	−2.08	− .73	−1.13	−1.70	−2.10	−2.65	−2.85	−3.40
15	Nitromethane	+ .43	− .53	−1.30	−2.18	− .73	−1.20	−1.70	−2.10	−2.55	−2.73	−3.38
16	Acetonitrile	+ .30	− .53	−1.28	−2.20	− .73	−1.23	−1.78	−2.08	−2.60	−2.68	3.33
17	Dimethyl sulfoxide	+ .38	− .55	−1.30	−2.10	− .60	−1.15	−1.88	S.E.	S.E.	S.E.	S.E.
18	Methanol	+ .65	− .33	−1.30	−1.98	S.E.	S.E.	S.E.	S.E.	S.E.	S.E.	S.E.
19	Formic acid	R	S.E.	I	S.E.	S.E.	S.E.	S.E.	−2.23	−2.65	S.E.	S.E.
	Mean value	+0.53	−0.40	−1.18	−2.05	−0.68	−1.18	−1.80	−2.15	−2.62	−2.78	−3.38
	Av. dev.	±0.08	±0.06	±0.07	±0.07	±0.05	±0.08	±0.04	±0.08	±0.05	±0.05	±0.07

[a] In p.p.m. relative to fluorobenzene; exptl. error = ±0.08. [b] I designates insufficient solubility; R designates that a fast reaction occurs; S.E. effect designates that a deviation of at least 0.20 p.p.m. from the mean value occurs.

stituents. The high precision of the mean values (essentially the experimental error) as well as the consistency of the magnitude of average deviations for all of the substituents testifies to the fact that only intramolecular shielding contributes to the shielding parameters.

Eleven more substituents from Table II define mean values of the same precision as those of Table III if the results in certain acidic and certain basic solvents are excluded. This fact is illustrated in Table IV. All of the substituents of Table IV are measurably basic and for each (in contrast to the results in Table III) the trifluoroacetic acid result does not conform to the mean. Similar but smaller deviations occur in other acidic hydroxylic solvents. The solvents excluded in obtaining the mean values listed at the bottom of Table IV are indicated by the designation S.E. (or I, if insoluble; R, if a fast reaction occurs). It is significant that measurable deviations from the precise means of Tables III and IV occur for the basic solvents, *e.g.*, dioxane, dimethyl sulfoxide and pyridine, only in the case of +R substituent groups. No such deviation occurs for any of the −R substituent groups (*e.g.*, CH_3, F, SCH_3, OCH_3, etc.).

Discussion

The character of these results offers convincing evidence that such solvent effects as are observed in the substituent shielding parameters of Table II result from the alteration in intramolecular shielding produced by

certain substituent–solvent interactions. That is, to a precision on the order of the experimental error, these solvent effects result from solvent modification in the electronic character of the *m*-substituents.

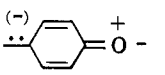
Our extensive investigation has disclosed four distinct categories of solvent effects on the substituent shielding parameters. The first involves hydrogen bonding and proton transfer interactions between acidic and basic groups (either +R or −R). The second limited category involves polarity effects on amide and ester functions. The third limited category involves the formation of methanol–carbonyl addition compounds. The fourth category involves interactions of Lewis-acidic (+R) substituents with solvents of Lewis-basic character. Each of these types of behavior, which generally may be regarded as chemical rather than physical in nature, are considered in detail in following sections.

The precision of the solvent independence of the intramolecular shieldings of Tables III and IV is of importance in connection with mode of transmission of the electron effects of the *m*-substituents to the region of detection by the fluorine nucleus. The twenty solvents investigated include non-associated, associated, polar and non-polar liquids. Dielectric constant variation of nearly two orders of magnitude has been carried out, ranging from that of the non-polar liquids, *e.g.*, cyclohexane, CCl_4 and benzene (D^{25} 2.0–2.3),[63] through highly polar liquids, *e.g.*, CH_3NO_2, $(CH_3)_2SO$ (D^{25} 36.7 and 45, resp.,[64] to that of the associated liquid, $HCONHCH_3$ (D^{25} 182).[65] In the reactivities of side-chain derivatives of benzene and similar systems, such solvent variation produces very substantial changes in the magnitude of substituent effects.[11,66]

In the latter situation, the solvent effects are attributed (at least in part) to the fact that the lines of force between the substituent dipole and the pole or dipole of the reaction center tranverse the region of the bulk solvent.[67] This results in an effective dielectric constant which will generally lie between that of the internal hydrocarbon cavity and the bulk solvent.[67] The present results show that the intramolecular shielding is (within experimental error) completely independent of the dielectric constant of the bulk solvent. Consequently field effects of *m*-substituents either make no practical contribution to the intramolecular shielding or the effective dielectric constant is independent of solvent. The Westheimer–Kirkwood model[67] does not anticipate the latter condition.

Our results appear to be understandable on the basis that the polarizing force[68] exerted on the C–F bond moment by the distant substituent dipole moment is inversely proportional to r^4 and thus is too weak to be effective in intramolecular F^{19} shielding. The observed substituent effects on shielding can therefore arise only by an intramolecular electronic transmission involving either or both the σ- and π-electrons of the benzene ring.

The results for unsaturated substituents, *e.g.*, $-COCH_3$, NO, COF, $COCF_3$, CN and NO_2 (Table IV), imply that in most aprotic media the contribution of the ionic resonance form to the resonance hybrid (and therefore the group dipole moment) is essentially invariant with the polarity or the internal pressure of the medium at room temperatures. A similar conclusion may be reached concerning resonance forms, *e.g.*, for



the $-OC_6H_5$ substituent. In both instances at least one of the charge centers of the dipolar resonance form is buried within the molecular cavity.[69]

Hydrogen Bonding Effects.—Table V presents the shielding parameters of three weakly basic substituent groups in a variety of protonic solvents. It is apparent that for all such solvents the resonance signal is shifted to lower applied field strength (implying greater inductive electron-withdrawal by the substituent) compared to the precise means established for these substituent groups in Table IV. These shifts are to be attributed to either partial or complete hydrogen bond formation between substituent and solvent. The effects are not attributable to measurable "complete" proton transfer equilibria since the strongest base *m*-fluoroacetophenone has a pK_A of ~ -7,[70] and the estimated H_0 of trifluoroacetic acid,[71] the most acidic solvent, is −4. Further, the downfield shifts on proton transfer to substrates such as these have been observed[72] to be much larger (at least 5.0 p.p.m.) than any of those given in Table V.

TABLE V

EFFECTS OF HYDROGEN BONDING ON $\int_H^{m\text{-X}}$

Solvent	*m*-Substituent CH_3CO	-CN	$-NO_2$
Normal[a]	−0.68	−2.78	−3.38
CH_3OH	−0.93	−3.03	−3.53
C_2H_5OH	....	....	−3.73
t-C_4H_9OH	−1.08	....	−3.68
$HCF_2CF_2CH_2OH$	−1.40	−3.40	−3.95
CH_2Cl_2	....	....	−3.83
$HCCl_3$	....	....	−3.98
CH_3CO_2H	....	....	−3.40
HCO_2H	−1.45	−3.28	−3.65
95% (vol.) aq. acetone	−0.80	−2.95	−3.48
80%	− .83	−3.00	−3.53
75%	− .90	−3.08	−3.63
70%	− .90	−3.08	−3.60
95% (vol.) aq. CH_3OH	− .95	−3.13	−3.60
90%	−1.00	−3.18	−3.63
80%	−1.10	−3.23	−3.70
75%	−1.38	−3.30	−3.70
83% (vol.) aq. t-C_4H_9OH	−1.08	....	−3.73
83% (vol.) aq. $HCF_2CF_2CH_2OH$	−1.33	....	−3.90
CF_3CO_2H	−2.65	−4.63	−5.10

[a] Mean value from Table IV.

The results presented in Table V give several interesting qualitative results regarding the effects of the competitive hydrogen bonding which is involved. The magnitudes of the shifts to lower field do not cor-

(63) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," N.B.S. Circ. 514 (1951).

(64) S. G. Smith, A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(65) G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

(66) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 80–87, 184–204; M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Stand.*, **60**, 569 (1958).

(67) F. H. Westheimer and J. G. Kirkwood, *J. Chem. Phys.*, **6**, 506, 513 (1938); J. N. Sarmousakis, *ibid.*, **12**, 277 (1944).

(68) *Cf.* E. A. Moelwyn-Hughes, "States of Matter," Interscience Publishers, Inc., New York, N. Y., p. 5.

(69) A detailed study, similar to the present one, on solvent effects for fluorine n.m.r. shielding of *p*-substituted fluorobenzenes has been carried out and will be reported in the near future. A preliminary communication of these results has appeared: R. W. Taft, R. E. Glick, I. C. Lewis, I. R. Fox and S. Ehrenson, *J. Am. Chem. Soc.*, **82**, 756 (1960). In general, the magnitude of solvent effects on the shielding parameters for −R *p*-substituted fluorobenzenes (relative to internal fluorobenzene) is comparable to that reported here for *m*-substituted fluorobenzenes. However, for many +R *p*-substituted fluorobenzenes the solvent effects are an order of magnitude greater.

(70) Estimated from data of R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **80**, 6355 (1958).

(71) G. V. Tiers, *ibid.*, **78**, 4165 (1956).

(72) R. W. Taft and P. L. Levins, *Anal. Chem.*, **34**, 436 (1962), and unpublished results.

TABLE VI

EFFECTS OF HYDROGEN BONDING ON $\int_H^{m\text{-X}}$

Solvent	m-Substituent —CHO	—NO	—SOCH$_3$	—CO$_2$C$_2$H$_5$	—SO$_3$C$_2$H$_5$	—COF	—COCF$_3$	—COCN	—CH=CHNO$_2$
Normal[a]	−1.18	−1.80	−2.90	−0.23[b]	−2.90	−2.13	−2.62	−3.33[b]	−1.13[c]
HCCl$_3$	....	−2.20	....	....	....	−2.53	−2.90	−3.65	....
CH$_3$OH	−1.45	−1.95	−3.48	−0.65	−3.68	−2.28	R	R	−1.35
75% (vol.) aq. CH$_3$OH	−1.53	−2.08	−3.65	−1.00	−4.00	−2.40	....	....	....
HCF$_2$CF$_2$CH$_2$OH	−1.80	−2.13	−4.23	....	....	−2.43	−2.88	−3.43	....
HCO$_2$H	−1.63	−1.93	−3.93	−1.05	−3.83	−2.23	−2.65	....	−1.35
CF$_3$CO$_2$H	−3.18	R	−6.48	−1.88	−4.68	−3.40	−3.75	−4.55	....

[a] Mean value from Table IV unless otherwise designated. [b] Mean of shielding parameters observed in carbon tetrachloride and in cyclohexane; precision of mean, 0.10 p.p.m. or less. [c] Mean of shielding parameters observed in benzene, ethyl acetate, diethyl maleate, acetone, pyridine, dimethylformamide, nitrobenzene, nitromethane and acetonitrile; average deviation from mean ±0.08 p.p.m.

TABLE VII

EFFECTS OF HYDROGEN BONDING ON $\int_H^{m\text{-X}}$

Solvent	m-Substituent —CONH$_2$	—CO$_2$C$_2$H$_5$	—SO$_2$NH$_2$	—SO$_2$CH$_3$	—SO$_2$Cl	—SO$_2$F
H.C.[a]	−0.03[b]	−0.73	I	−3.30	−5.10	−4.73
CH$_3$OH	− .73	−1.25	−2.50	−3.60	−5.43	−5.10
75% (vol.) aq. CH$_3$OH	− .98	I	−2.90	−3.95	−5.53	−5.23

[a] Mean of shielding parameters observed in carbon tetrachloride and in cyclohexane; precision of the mean, 0.10 p.p.m. or less. [b] Shielding parameter for tetrahydrofuran.

relate well with a perhaps naïvely expected trend for increasing effects of hydrogen bonding with increased acidity of the solvent. In fact, there is a notable tendency for the reverse to occur frequently. It is quite apparent from the examples provided in Table V that the effect of increased strength of hydrogen bonding to a given substrate with increased acid strength of the solvent molecule[73,74] is frequently compensated by self-association of the solvent. The very weakly acidic solvents, CH_2Cl_2 and $HCCl_3$, are unquestionably less self-associated than the more acidic solvents, *e.g.*, CH_3OH or HCO_2H. Consequently, even though a weaker hydrogen bond is formed by these less acidic solvents with a given substrate (producing potentially less downfield shift),[75] their potential for hydrogen bond formation is actually greater. Thus larger downfield shifts are frequently observed for the weaker acid solvents.

The relatively large apparent effect of hydrogen bonding by methylene chloride is perhaps surprising in view of its expected weakly acidic nature. In contrast, methylene iodide gives nearly normal shifts (*cf.* Tables II–IV). The effect on acidity of the greater electronegativity of chlorine than iodine and the relative insensitivity of the standard free energy of hydrogen bond formation to acid strength[74] are factors involved, but their relative role is not made definite by the present results.

In the mixed aqueous solvents, the methanol–water system consistently produces larger solvent shifts than acetone–water of the same water content. This effect is no doubt associated with the fact that the equilibrium[76] $CH_3OH + H_2O = CH_3O^- + H_3O^+$ effectively enhances hydrogen bonding to the substrate.

Results in protonic solvents for 15 additional +R substituent groups are given in Tables VI and VII. Similar trends are observed. Although quantitative information on base strength is not available for most of these substituents, it is apparent that there is a qualitative trend for the effects of a given acidic solvent to increase with increasing base strength. Notable in this connection are the relatively large solvent shifts in formic acid and aqueous methanol for substituents such as $-CONH_2$, $-SOCH_3$, $-CO_2C_2H_5$ and $-SO_3C_2H_5$ and the relative small shifts (from normal) observed in these solvents for the $-NO$, $-COF$ and $-COCF_3$ groups.

The results given in Table II for the SCH_3, OCH_3, OC_6H_5 substituents in formic and trifluoroacetic acids provide similar examples of shifts to lower fields due to hydrogen bonding to weakly basic −R substituents. It is apparent from the results given in Table III that the −R substituents Br, F and OCF_3 are too weakly basic to give rise to measurable H-bonding effects. Also no measurable effects of hydrogen bonding are found for the SCH_3, OCH_3 and OC_6H_5 substituents in methanol (Table IV) and in 75% (vol.) aq. methanol (unpublished results). In the more donor alcohol $HCF_2CF_2CH_2OH$, however, the $-OCH_3$ shielding is −0.57 p.p.m. to lower field than normal and the shielding of the $-NH_2$ group is −1.13 p.p.m. to lower field than that observed in hydrocarbon solvents (unpublished results). Especially interesting, however, are the results given in Tables VIII and IX which provide additional examples of effects produced in competitive hydrogen bonding.

Except for the non-protonic substituents $N(CH_3)_2$, $C_6H_5N{=}N-$, $-OCOCH_3$ of Table VIII, the substituents listed could potentially hydrogen bond by serving either as the proton donor or acceptor. The results in Table VIII fall into two characteristic patterns. The non-protonic substituents experience downfield shifts (indicative of loss of electronic charge to the solvent) in the two hydroxylic relative to hydrocarbon solvents, the effect being greater for aqueous methanol than pure methanol (consistent with the results for the +R substituents of Tables VI–VII as discussed above). In contrast, the acidic substituents $-CO_2H$ and $-OH$, for which hydrogen bonding by proton donation unquestionably predominates, experience shifts to higher field strengths (indicative of loss of positive charge to the solvent) under the same conditions. Furthermore, the shift is larger for methanol than aqueous methanol, indicating a greater effect of proton acceptor action toward uncharged substituents by methanol. These two distinct categories of behavior quite apparently can be used to distinguish the predominant mode of hydrogen bonding by amphoteric substituents.

(73) G. C. Pimentel and A. L. McClellan, ref. 53, Chapt. 3.

(74) J. R. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

(75) The fluorine shielding parameters for a series of 1–1 hydrogen bonded complexes of *p*-fluorophenol with a variety of oxygen and nitrogen bases in carbon tetrachloride solutions have been found to correlate with the standard enthalpy of complex formation, unpublished results of R. W. Taft and M. G. Schwartz.

(76) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960).

TABLE VIII: EFFECTS OF HYDROGEN BONDING ON $\int_H^{m\text{-}X}$

Solvent	m-Substituent —N(CH3)2	—CH2NH2	C5H4N=N—	—OCOCH3	—NHCOCH3	—NH2	—NHNH2
H.C.[a]	−0.08	+3.58	−3.78	−1.33	−3.80[b]	+0.50	−3.38
CH3OH	− .10	+ .33	−1.18	−1.60	−1.35	+ .78	+ .35
75% (vol.) aq. CH3OH	− .18	+ .28	I	−1.88	−1.38	+ .50	− .28
	—CO2H	—CH2CO2H	—OH	—CH2OH	—CH(CH3)OH	—B(OH)2	—SH
H.C.[a]	−0.88	−0.15	−1.43[c]	+0.18	+0.10	I	−0.78
CH3OH	− .35	+ .53	−0.43	+ .55	+ .38	+1.25	− .60
75% (vol.) aq. CH3OH	− .68	+ .43	−0.68	+ .43	+ .25	+1.13	.75

[a] Mean of shielding parameters observed in carbon tetrachloride and in cyclohexane; precision of the mean, 0.10 p.p.m. or less. [b] Shielding parameter for dimethylformamide. [c] NOTE ADDED IN PROOF.—Using the dispersion rather than the absorption mode, M. G. Schwartz has obtained the shielding parameter for 1% *m*-fluorophenol in CCl_4 of −1.20. This value apparently is attributable to largely monomeric phenol—*cf.* ref. 53.

TABLE IX: EFFECTS OF HYDROGEN BONDING ON $\int_H^{m\text{-}X}$

Solvent	m-Substituent —N(CH3)3+	—NH3+	—CH2NH3+	—SO3−	—CH2CO2−	—O−	CO2−	—B(OH)3−
CH3OH	−5.95	−3.63	−1.25	−1.03	+1.23	+1.90	+1.05	+3.33
75% (vol.) aq. CH3OH	−6.18	−3.40	−1.13	−1.30	+1.03	+1.63	+0.80	+2.93

The $-CH_2CO_2H$, $-CH_2OH$ and $-CH(CH_3)OH$ substituents show the same trends as for the functional groups (CO_2H and OH, resp.) directly attached to the aromatic ring; *i.e.*, results apparently characteristic of predominant proton donor effects are observed. These results are not completely unambiguous, however. At the concentration used ($\sim$0.5 *M*), these compounds are appreciably associated in the hydrocarbon solvents (*cf.* Experimental) and the association probably produces measurable shielding effects.

In contrast to the above behavior, the interposition of a methylene group between the ring and the $-NH_2$ group produces a rather dramatic change from one category of behavior to the other. The much more basic benzylamine shows behavior characteristic of predominant proton-acceptor action (the effect is larger than that observed for the $N(CH_3)_2$ substituent). The more-acidic and less-basic aniline, on the other hand, clearly shows in methanol the results characteristic of *predominant* proton-donor action. Additional examples of this behavior are provided by the $-NHNH_2$, $-SH$ and $-B(OH)_2$ substituents.

In Table IX are given the effects of hydrogen bonding for a series of charged substituents on change from methanol to 75% (vol.) aq. methanol. The results for all of the anions correspond to the previously discussed greater proton acceptor action of the aqueous methanol. The dramatically larger downfield shifts observed for the $N(CH_3)_3^+$ than the NH_3^+ substituent attests to the importance of delocalization of the positive charge of the latter by hydrogen bonding to the hydroxylic solvents.[77-79] It is further of interest that the shielding parameters for both the $-NH_3^+$ and $-CH_2NH_3^+$ substituents are at higher field strengths in aqueous methanol than methanol. This behavior is exceptional to that observed for uncharged proton-donating substituents. The result perhaps follows from greater ion pair association in methanol or from preferential solvation of $-NH_3^+$ by water over methanol. The origin of this effect may be either the smaller steric requirements of water and/or its greater capacity to delocalize the positive charge through hydrogen bonding to second and third solvation shells (which becomes involved with the higher solvation energy for the charged substituent).

The present qualitative survey of hydrogen bonding effects on the F^{19} shielding parameters serves as a useful preliminary investigation which will be utilized as a background to work in progress in quantitative equilibrium studies of hydrogen bonding utilizing this new analytical technique.

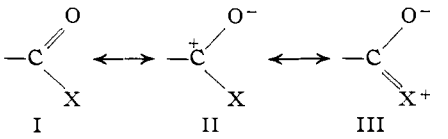
Solvent Polarity Effects on Amide and Ester Functions.—A second type of behavior was encountered with the two ester substituents $-CO_2C_2H_5$ and $SO_3C_2H_5$ and the two amide substituents $CONH_2$ and SO_2NH_2 (*cf.* Table II). In non-hydroxylic solvents, the shielding for these groups is appreciably shifted to lower field strengths (implying greater electron withdrawal) in strongly polar than in non-polar solvents. The latter solvents include cyclohexane and carbon tetrachloride, the former solvents include, for example, dimethyl sulfoxide, acetonitrile, nitromethane and dimethylformamide. Shielding in benzene, diethyl ether and methylene iodide is intermediate between that for these two groups of solvents. Table X lists some typical results illustrating this behavior.

TABLE X

EFFECTS OF SOLVENT POLARITY ON SHIELDING PARAMETERS, $\int_H^{m\text{-}X}$, FOR AMIDE GROUPS

Solvent	m-Substituent —SO2NH2	—CONH2	SO3C2H5	—CO2C2H5
Cyclohexane	I	I	−2.83	−0.15
Diethyl ether	I	I	−3.15	− .33
Diethyl maleate	−2.20	....	−3.60	− .65
Acetone	....	−0.15	−3.48	− .58
$C_6H_5NO_2$	−2.70	....	−3.48	− .38
CH_3CN	....	−0.50	....	− .65

These substituents have important resonance stabilization, *i.e.*



I II III

Apparently polar solvents increase the contributions of both the ionic forms II and III to the resonance hybrid so that the given substituent as a whole becomes more electron attracting (contrast, however, subsequent discussion).

Carbonyl-addition Compounds.—The shielding parameters for the relatively poorly resonance-stabilized electron-deficient carbonyl substituents, CHO, $COCF_3$ and COCN, are very strongly shifted to higher field strengths in methanol solution. In the case of the

(77) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 229.
(78) A. V. Willi, *Z. physik. Chem.*, **27**, 233 (1961).
(79) R. W. Taft, *J. Am. Chem. Soc.*, **82**, 2965 (1960).

benzaldehyde two signals are observed, one of which is reasonable for the normal carbonyl compound. The second weaker signal at 1.74 p.p.m. higher field strength is apparently due to the hemiacetal[80] in equilibrium with the benzaldehyde. It is probable that the shielding observed for the $COCF_3$ and COCN substituents in methanol is due to the complete formation of the methanol–carbonyl addition compounds since the shielding parameter for the single observed signal is in both instances 2.4 p.p.m. greater in methanol than cyclohexane solutions. This assignment is in reasonable agreement with the fact that the shielding parameter for the $-CH_2CN$ substituent is 2.2 p.p.m. greater than for the -COCN substituent in cyclohexane solution.

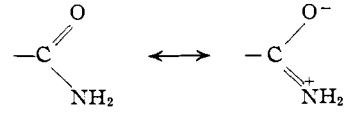
In dimethylformamide and dimethyl sulfoxide solutions of the *m*-$COCF_3$ compound, two signals were observed for both the fluorobenzene and CF_3 group fluorine atoms. The higher field signal of the former occurs at essentially the same position in these two solvents ($\int_H^{m\text{-}X} = +0.64$ p.p.m). Although molecular complexes between solute and solvent are possible, we suspect that these results and that for pyridine may be due to the hydrate–carbonyl addition compound. In 75% aq. (vol.) methanol a single fluorine signal at -0.08 p.p.m. is observed. Attempts to remove the last traces of water from dimethylformamide by heating with CaH_2, however, did not alter the result.

Effects of Interactions of Groups Having Lewis-acidic and Basic Character.—The fourth type of solvent effect encountered is a shift to higher field strengths (implying smaller inductive electron withdrawal) which is consistently found (Table XI) for substituents which may be characterized as having an atom (generally the first atom of the group) with an electronic deficiency and a partially open orbital. These Lewis-acidic substituents give rise to higher-field resonance in basic solvents, *e.g.*, dioxane and dimethyl sulfoxide. It is implied that as the result of solute–solvent interaction the electron deficiency of the first atom is partially removed. The direction of the effect is that expected by the changes in formal changes which take place on the formation of a Lewis acid–base complex, *i.e.*, $A + B: \rightleftarrows {}^{(-)}A{:}B^{(+)}$. However, the magnitude of the effect is much smaller than that expected for the formation of a stable electron pair bond between a solute and solvent molecule.[81] It is thus further implied that the interaction is weak (perhaps intermediate between chemical bonding and physical interactions) and perhaps characterizable by relatively small equilibrium constants for formation.[82]

The effect involved appears to bear the analogous relationship to Lewis-acid–base complex formation that hydrogen bonding bears to proton transfer equilibria. That is, the former involves a much weaker interaction which is very much less sensitive to variation in acid and base strength.[75] Because we believe the analogy to be useful, we shall hereafter refer to the effect as arising from a Lewis-acid bonding solute–solvent interaction. The Lewis-acid bonding interaction may be considered to mimic Lewis-acid–base coördinate covalency and potentially to prevail when the acid and base are of such nature that the chemical potential for formation of the conventional covalency is inadequate or the potential barrier for reaction sufficient to ensure slow rates of formation of the conventional complex.

Several clear trends are apparent in Table XI for the relationship between structure of the substituent and the effect on shielding of the Lewis-acid bonding. The upfield shift in dioxane compared to normal shielding increases in the order $CHO < C{\equiv}N$, $COCF_3 <$ COCN, or $-NO < -NO_2$. This is the order of decreased shielding in normal solvents and, apparently, of increased charge deficiency on the common first atom (C or N) of the substituent. Over the carbon series of substituents, the effect of Lewis-acid bonding by dioxane increases from 0.2 to 1.0 p.p.m. Thus, the larger of these solvent effects is of the same order of magnitude, for example, as the effect on intramolecular shielding produced in changing the $-CH{=}CH_2$ to the $-CH_3$ substituent.

For the substituents $-SO_3C_2H_5$, $CO_2C_2H_5$ and $CONH_2$ there is little apparent effect of Lewis-acid bonding, although the situation may be somewhat confused by the solvent polarity effect (*cf.* Table X). These substituents are all characterized as strongly resonance stabilized by interactions within the group (below) (*cf.* subsequent



discussion). Apparently, the Lewis-acid bonding interaction is not sufficiently strong to off-set resonance stabilization which is lost as the result of such an interaction, so that the effect tends to be reduced or to be absent for strongly resonance-stabilized substituents.[82] By this criterion, for example, the results in Table XI suggest that the $-SOCH_3$ substituent is less resonance stabilized than the $-SO_2CH_3$ substituent as is reasonable on other grounds (both of these substituents give approximately the same normal shifts but the former is more affected by dioxane).

The order of the effects of Lewis-acid bonding among the solvents of Table XI apparently is not the same for all substituents. For substituents showing the smaller effects the order quite generally is acetonitrile < pyridine, diglyme < dimethyl sulfoxide < dioxane. However, for COCN, the order changes to dioxane < dimethyl sulfoxide.[83] Changes in order may be associated with orientation, steric effects and other group specificities. However, the effects of Lewis-acid bonding which are apparent for the $-CF_3$ and $-SF_5$ substituents in dioxane (*cf.* Table III) suggest that the interaction is a relatively long range one and is not as susceptible to steric factors as conventional chemical equilibria.

From the variation of shielding parameters with substituent under "normal" conditions it is apparent that F^{19} intramolecular shielding is a relatively sensitive probe to changes in electron withdrawal (presumably inductively) from the *m*-position of the benzene ring. Solvent–substituent group interactions which involve acceptor–donor complexing[84] presumably would ap-

(80) G. W. Meadows and B. deB. Darwent, *Can. J. Chem.*, **30**, 501 (1952); *Trans. Faraday Soc.*, **48**, 1015 (1952).

(81) For example, the formation of a Lewis acid–base complex between *m*-fluorophenyl methyl sulfide and BCl_3 in H_2CCl_2 solution results in a downfield shift of the fluorine signal of 4.1 p.p.m.; unpublished results of J. Carten and R. W. Taft.

(82) Dr. C. D. Ritchie has kindly communicated results of a study (*J. Am. Chem. Soc.*, in press) of the integrated intensity of the infrared bands of benzonitrile in binary solutions of carbon tetrachloride and several polar solvents. The results are interpreted in terms of an equilibrium constant for the formation of a weak 1:1 complex. The apparent equilibrium constants for formation are in the order: dimethyl sulfoxide > dimethylformamide > pyridine. Further, there is no detectable effect of *m*- and *p*-substituents on the formation constant for benzonitrile–dimethyl sulfoxide complex, indicating that the apparent Lewis-acid bonding has a low sensitivity to Lewis-acidity of the nitrile. Finally, no evidence was found for a definite complex between ethyl benzoate and dimethyl sulfoxide. It is of interest to note that entirely similar trends are obtained in the solvent shielding effects of Tables II and XI.

(83) The Lewis acid bonding effect with this substituent is apparently sufficiently large to discriminate among other solvents as follows (*cf.* Table II): dimethyl sulfoxide > dioxane > dimethylformamide > pyridine > acetone, benzene, acetonitrile, nitromethane, nitrobenzene > diethyl maleate > diethyl ether.

(84) *Cf.* R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

TABLE XI

EFFECTS OF LEWIS-ACID BONDING ON $\int_H^{m\text{-X}}$

Solvent	m-Substituent —CONH₂	—CO₂C₂H₅	—SO₂C₂H₅	—COCH₃	—CHO	—NO	—COCl	—COF
Normal[a]	I	−0.25[b]	−3.00[b]	−0.68	−1.18	−1.80	−2.10[d]	−2.15
Acetonitrile	−0.50	− .65	....	− .73	−1.23	−1.78	....	−2.08
Tetrahydrofuran	− .03	− .40	−3.20	− .58	−1.08	−1.83	−2.05	....
Pyridine	− .08	− .43	R	− .60	−1.13	−1.68	−1.93	−1.98
Diglyme	....	....	−3.25	− .63	−1.03	....	−2.00	....
Dimethyl sulfoxide	−0.03	−0.70	R	− .60	−1.15	−1.88	....	−1.90
Dioxane	−0.15	−0.30	−3.03	− .48	−0.98	−1.55	−1.73	−1.83

Solvent	m-Substituent —CN	—CH=CHNO₂	—SO₂CH₃	—SOCH₃	—NO₂	—COCF₃	—COCN
Normal	−2.78	−1.13[c]	−3.28[e]	−1.90[e]	−3.38	−2.62	−3.33[b]
Acetonitrile	−2.68	−1.18	....	....	−3.33	−2.60	−2.78
Tetrahydrofuran	−2.75	....	....	....	−3.25	....	....
Pyridine	−2.78	−1.08	....	....	−3.23	....	−2.55
Diglyme	−2.63	....	....	....	−3.18	....	....
Dimethyl sulfoxide	−2.58	−0.95	....	−2.40	−3.15	−2.35	−2.13
Dioxane	−2.43	−1.00	−2.98	−2.48	−2.90	−2.28	−2.35

[a] Mean value from Table IV unless otherwise designated. [b] Mean of shielding parameters observed in carbon tetrachloride and in cyclohexane; precision of the mean, 0.10 p.p.m. or less. [c] Mean of shielding parameters observed in benzene, ethyl acetate, diethyl maleate, acetone, pyridine, dimethylformamide, nitrobenzene, nitromethane and acetonitrile; precision of the mean, ±0.08 p.p.m. [d] Mean of shielding parameters observed in cyclohexane, carbon tetrachloride, diethyl ether, tetrahydrofuran, diethyl maleate, acetic anhydride and nitrobenzene; precision of the mean, ±0.05 p.p.m. [e] Mean of shielding parameters observed in carbon tetrachloride and in nitromethane; precision of the mean, ±0.05 p.p.m.

preciably alter electron withdrawal. The effects of Lewis-acid bonding[84,85] appear to relate to the extent of net transfer of electronic charge from solvent to substituent and the extent to which this charge transfer is transmitted to the benzene ring (the transmission factor

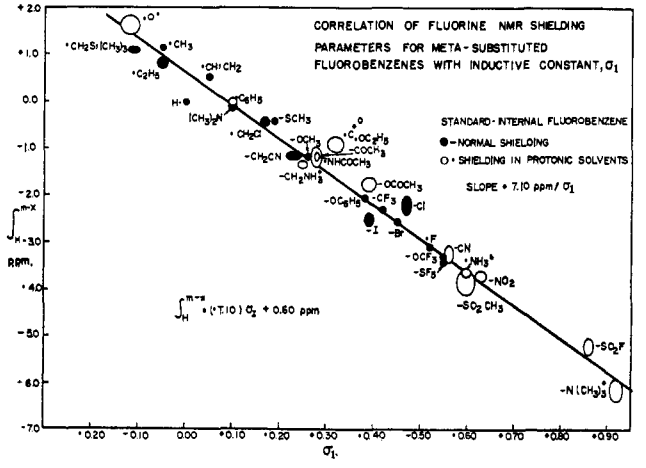


Fig. 1.—Correlation of fluorine n.m.r. shielding parameters for *m*-substituted fluorobenzenes with inductive constant, σ_I; standard of reference is internal fluorobenzene: ● designates "normal" shielding, *cf.* Tables III and IV; O designates mean shielding in protonic solvents no more acidic than formic acid.

from the *m*-position to the fluorine nucleus apparently is essentially a constant for any *m*-substituted fluorobenzene in any solvent). The smaller solvent shift in dioxane for the β-nitrovinyl than for the nitro group is reasonable in terms of attenuated transmission through the −C=C− system of the charge transfer which occurs between the similar nitro groups and dioxane.

Effects of Solvent on σ_I Values.—The empirical correlation[10] between intramolecular shielding by *m*-substituents in fluorobenzenes and the inductive substituent parameter σ_I can be examined with present results much more critically than was previously possible and the implied dependence of σ_I values on solvent can be evaluated.

The results for the chemically inert substituent groups (Table III) give plots of $\int_H^{m\text{-X}}$ *vs.* σ_I which, to a precision on the order of the experimental error, are linear and for which the slope is independent of medium. In Fig. 1, the closed circles give the mean shielding parameters (Table III) for the chemically inert *m*-substituents (and their precision measures) plotted *vs.* σ_I values. The only deviation which appears outside the combined experimental errors of $\int_H^{m\text{-X}}$ and σ_I is that for the unsubstituted fluorobenzene. The deviation for the hydrogen substituent is unexplained, although several observations may be made in this connection. The molecular symmetry of fluorobenzene differs from that of any *m*-substituted fluorobenzene which may give rise to an intramolecular shielding term.[86] In the correlations of inductive effects in aliphatic series reactivities, the hydrogen atom is a rather frequent deviator.[87] Since in aromatic series reactivities, however, the σ_I value for hydrogen has found wide applicability,[88] it appears less likely that the deviation is due to a dependence of σ_I on the type of system involved.

The important consequence of the results of Table III is the implied constancy in nearly any solvent of the σ_I values for the chemically inert substituents. Generality in ground electronic states is implied since a remarkably activating derivative of benzene would be required to convert the chemically inert *m*-substituent of the fluorobenzene to a chemically active substituent. This conclusion may also be extended to additional substituents, for example: alkyl groups; alternant hydrocarbon groups; halogens (Cl and perhaps I); $-SiX_3$ (X = halogen); $-SCX_3$ (X = halogen); $-NX_2$ (X = halogen). If solvents giving rise to either hydrogen or Lewis-acid bonding are excluded, the addi-

(85) Molecular self-association through Lewis-acid bonding can potentially affect physical properties in an analogous manner to that commonly accepted for hydrogen bonding. As possible examples, we note that aliphatic nitriles have boiling points 35–65° higher than corresponding primary amines. The lactones β-propiolactone and γ-butyrolactone have boiling points 70–120° higher than non-hydrogen bonded liquids of comparable molecular weight. (We are indebted to Prof. N. C. Deno for this observation.)

(86) W. S. Brey, Jr., and K. D. Lawson, Abstracts, Am. Chem. Soc. Natl. Meeting, Chicago, Ill., Sept., 1961, p. 4-T.

(87) R. W. Taft and I. C. Lewis, unpublished summary.

(88) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

tional substituents of Table IV (and structurally similar substituents) may be added to this category.

Inasmuch as the σ_I values for groups such as $-\overset{O}{\overset{\parallel}{C}}CH_3$, $-CN$, $-NO_2$, O^-, NH_3^+ etc., have been determined in solvents in which hydrogen-bonding effects are implied (Tables V–IX), it is not appropriate to utilize the mean shielding parameters for these substituents (Table IV) in the $\int_H^{m\text{-}X}$ *vs.* σ_I plot. Instead, the shielding parameter appropriate to the solvent conditions from which the σ_I value is derived is apparently required. Although the results of Tables V–IX imply that σ_I values for such substituents are measurably variable among different protonic solvents, mean shielding parameters for these substituents in any protonic solvent with acidity equal or less than formic acid (including various aqueous organic mixed solvents and non-hydroxylic solvents; *e.g.*, $HCCl_3$ and H_2CCl_2) can be given which apparently have useful precision. The open circles in Fig. 1 give the mean shielding parameters (and their precision measures) obtained in this manner from the results in Tables V–IX.

Since the σ_I values for the $-CH{=}CH_2$, $-SCH_3$, $-OCH_3$ and $-OC_6H_5$ substituents are apparently appropriate to the solvents on which the mean values of Table IV are based, these shielding parameters have been plotted in Fig. 1. For the substituents $-CH_2OH$, $-NHNH_2$, $-N(CH_3)_2$ and $-CH_2NH_2$ the shielding parameters plotted in Fig. 1 are mean values from the results in cyclohexane and carbon tetrachloride. For the $-NHNH_2$ and the CH_2X substituents the σ_I values have been calculated from the relationship[89]: (2) for $-AB$, $\sigma_I = (\sigma_I)_{AH} + (\sigma_I)_B/2.0$. The σ_I values plotted for the substituents $-O^-$, $-OCF_3$, SF_5 and SO_2F in Fig. 1 have been obtained from at least two aromatic series reactivities by the method of Taft and Lewis,[90] but have not been confirmed in aliphatic series reactivities. The applicability to the latter is especially questionable for the charged substituents.[11]

The correlation in Fig. 1 of the intramolecular shielding produced by *m*-substituents covers a truly remarkable range of structures with relatively good precision, according to eq. 1: $\int_H^{m\text{-}X} = (-7.10)\sigma_I + 0.60$. The fit of both closed and open circles with essentially equal precision indicates that the slope of the regression line, -7.10 p.p.m./σ_I, is within its precision completely independent of solvent, and offers confirmation of the interpretation that variation of shielding for a given substituent with solvent is due to modification in the σ_I values resulting from solvent–substituent interaction.

The fit of the shielding for $-CH_2X$ substituents to the same line as for $-X$ substituents offers confirmation of the interpretation of shielding for the latter. The interposed methylene essentially destroys any direct conjugative interactions of X with the benzene ring (leading potentially to σ_R contributions) so that the effects of CH_2X substituents must apparently be necessarily inductive. It is further significant that the fall-off factor for shielding parameters is closely the same as that observed in reactivities[89] and that there is essentially the same insensitivity of the shielding parameters for CH_2X as for X substituents to solvent dielectric constant.

The small but real deviations from eq. 1 may be caused by neighboring group anisotropies and by small σ_R contributions which are not recognizable due to the contributions from the former (and other second-order) effects. It is quite plain, however, that any σ_R contributions are of little practical consequence and this contribution, if present, is relatively unimportant, for example, compared to σ_R contributions to Hammett *meta*-σ-values ($\sigma_{(m)} = \sigma_I + 0.50\sigma_R^0$).[10]

Equation 1 may be utilized for two practical purposes: (1) for the calculation of σ_I (and σ^*) values for new substituent groups and (2) for determination of the variation of σ_I with solvent. The result may apparently be utilized with some confidence in view of the nature of Fig. 1.

Table XII lists values of σ_I calculated (column two) from the present work for 50 substituents in solvents in which no hydrogen- or Lewis-acid bonding effects are observed. Table XII also lists (column three) the σ_I values for the substituents calculated for dioxane solutions as an illustration of the effects on σ_I of Lewis-acid bonding. Further, the average σ_I values for protonic solvents which are no more acidic than formic acid are listed in column four of Table XII and the σ_I values for the acidic solvent trifluoroacetic acid are listed in column five. These results illustrate the effects of hydrogen bonding on σ_I values (in trifluoroacetic acid substantial proton transfer equilibria are probably involved with the $-CONH_2$ and $-SOCH_3$ substituents). Finally, Table XII lists the σ_I values based on chemical reactivities[87] (column 1) which have been used in Fig. 1.

The general applicability of the n.m.r. derived σ_I values in solvents which involve hydrogen and Lewis-acid bonding effects is a matter of much interest. The results in Table VIII for the $-NH_2$ and $-CH_2NH_2$ substituents clearly establish that hydrogen-bonding solvent effects will not always be the same for a given functional group, independent of its molecular environment. As noted previously, solvent effects are observed to be in opposite directions for the NH_2 group directly attached to the benzene ring as compared to that separated by an interposed methylene group. The environmental effect in this particular instance is, of course, quite severe since direct conjugation of $-NH_2$ with phenyl produces a large decrease in base strength and presumably a substantial increase in acid strength. On the other hand, the same structural change for the $-OH$ group, which produces similar effects on acid and base strength, gives results in methanol compared to hydrocarbon solvents for the $-OH$ and $-CH_2OH$ substituents which apparently imply a very nearly constant solvent effect on the σ_I value for an OH group (*i.e.*, either aliphatic or aromatic). Unfortunately, these results are not unambiguous, however, for they have not been corrected for the unknown effects of polymerization in hydrocarbon media.

The question of whether one will observe the former or the latter behavior in a given instance therefore depends not only upon the nature of the structural change in the solute but is also determined by the nature of the change involved in the hydrogen-bonding donor and acceptor capacities of the solvent. It does not appear unreasonable sometimes to utilize σ_I values which are characteristic of *a given substituent in a given solvent* (or solvent class) as a useful approximation. Such a procedure, however, must be used with appropriate caution for it is not presently possible to define the conditions under which results such as those illustrated by the $-NH_2$ group may be expected to invalidate such a treatment.

(89) Reference 77, Chapter VI. The Branch and Calvin scheme employs a fall-off factor of 1/2.8. However, J. C. McGowan, *J. Appl. Chem.*, 312 (1960), and references therein, has pointed out that the value 1/2.0 frequently better fits available data. A recent survey[87] indicates that there is no general single precise value of the fall-off factor. Values from ~1/1.8 to 1/3.0 are found dependent upon both substituent and reactivity type. In the present application the McGowan factor serves as a useful approximation.

(90) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); **81**, 5343 (1959).

TABLE XII

σ_I VALUES

	Substituent	Reactivities Weakly protonic solvents[e]	F^{19} Shielding[f] "Normal" solvents	Dioxane	Weakly protonic solvents	Trifluoroacetic acid
1	$-N(CH_3)_3^+$	+0.92	....	....	+0.93 ± 0.02	....
2	$-SO_2Cl$	....	+0.80	....	+ .86 ± .01	....
3	$-SO_2F$	+0.86[a]	+ .75	....	+ .81 ± .01	....
4	$-NO_2$	+ .63	+ .56	+0.49	+ .60 ± .02	+0.80
5	$-SF_5$	+ .55[a]	+ .56	+ .54	+ .56 ± .01	+0.57
6	$-SO_2CH_3$	+ .60	+ .55	+ .50	+ .62 ± .03	....
7	$-NH_3^+$	+ .60	....	....	+ .58 ± .02	....
8	—COCN	....	+0.55[c]	+0.42	+ .55 ± .03	+0.73
9	$-OCF_3$	+0.55[a]	+ .55	+ .55	+ .55 ± .01	+ .54
10	$-SO_3C_2H_5$	....	+ .50[c]	+ .51	+ .63 ± .02	+ .88
11	—CN	+0.56	+ .48	+ .43	+ .53 ± .02	+ .74
12	—F	+ .52	+ .52	+ .52	+ .52 ± .01	+ .54
13	$-SOCH_3$	+ .52	+ .49	+ .43	+ .62 ± .04	+1.00
14	$-COCF_3$	....	+ .45	+ .41	+ .48 ± .02	+0.61
15	$-SO_2NH_2$	....	....	+ .38	+ .46 ± .03	....
16	—Br	+0.45	+0.44	+ .43	+ .44 ± .01	+0.44
17	$-CF_3$	+0.41	+ .41	+ .38	+ .41 ± .01	+ .41
18	—COF	....	+ .39	+ .34	+ .42 ± .01	+ .56
19	$-OC_6H_5$	+0.38	+ .37	+ .37	+ .37 ± .01	+ .50
20	—NO	....	+ .34	+ .30	+ .37 ± .01	....
21	—OH	+0.25	+ .29[c,g,h]	....	+ .16 ± .04	....
22	$-OCOCH_3$	+ .39	+ .27[c]	....	+ .33 ± .02	
23	$-CH_2NH_3^+$	+ .25[b]	....	....	+ .25 ± .01	....
24	—CHO	....	+0.25	+0.22	+ .31 ± .02	+0.53
25	$-OCH_3$	+0.25	+ .25	+0.26	+ .29 ± .03	+0.51
26	$-NHCOCH_3$	+ .28	+ .20[d,g]	....	+ .24 ± .01	....
27	$-COCH_3$	+ .28	+ .18	+0.15	+ .23 ± .02	+0.46
28	$-CH{=}CHNO_2$	+ .38	+ .24	+0.23	+ .27 ± .01	....
29	$-SO_3^-$	....	....	....	+ .25 ± .02	....
30	$-CH_2CN$	+0.23[b]	+0.24[c]	....	+ .24 ± .02	....
31	$-N{=}NC_6H_5$	....	+ .19[c]	....	+ .25 ±	....
32	—SH	+0.25	+ .19[c]	....	+ .18 ± .01	....
33	$-CONH_2$	....	....	+0.11[g]	+ .21 ± .02	+0.65
34	$-SCH_3$	+0.19	+0.14	+0.15	+ .14 ± .01	+0.34
35	$-NHNH_2$	+ .15[b]	+ .14[c,g]	....	+ .10 ± .02	....
36	$-CH_2Cl$	+ .17	+ .14[c]	....	+ .14 ± .02	....
37	$-CO_2C_2H_5$	+ .30	+ .11[c]	+0.13	+ .21 ± .02	+0.35
38	$-N(CH_3)_2$	+ .10	+ .10[c]	....	+ .10 ± .01	....
39	$-C_6H_5$	+ .10	+ .08	+0.08	+ .08 ± .01	+0.10
40	$-CH_2OH$	+ .10[b]	+ .06[c,g]	....	+ .01 ± .02	....
41	$-NH_2$	+ .10	+ .01[c,g]	....	+ .05 ± .08	....
42	$-CH{=}CH_2$	+ .05	+ .01	+0.01	+ .01 ± .02	....
43	$-CH_2-NH_2$	.00[b]	.00[c,g]	....	+ .04 ± .01	....
44	$-CH_2CH_3$	− .05	− .03	....	− .03 ± .01	....
45	$-CO_2^-$	....	....	....	− .35 ± .02	....
46	$-CH_2Si(CH_3)_3$	−0.11[b]	−0.07[c]	....	− .07 ± .01	....
47	$-CH_3$	−0.05	−0.08	−0.07	− .08 ± .01	−0.06
48	$-B(OH)_2$	....	....	....	− .08 ± .01	....
49	$-O^-$	−0.12[a]	....	....	− .16 ± .01	....
50	$-B(OH)_3^-$	....	....	....	− .36 ± .03	....

[a] Calculated by the method of Taft and Lewis (ref. 90) from aromatic series reactivities. For the SO_2F substituent unpublished results of Taft and Davis on the ionization of $ArCO_2H$ and $ArNH_3^+$, H_2O, 25°, have been used. For the OCF_3 and SF_5 substituents, the results of W. A. Sheppard, *J. Am. Chem. Soc.*, **83**, 4860 (1961), and **84**, 3072 (1962), have been used. For the O^- substituent, σ-values given by J. Hine, *ibid.*, **82**, 4880 (1960), have been used. [b] Obtained by eq. 2. [c] Obtained from average shielding in carbon tetrachloride and cyclohexane solutions. [d] Measured in dimethylformamide solution only. [e] Precision ±0.03. [f] Precision ±0.01 unless otherwise indicated; $\sigma_I = (\int_H^{m\text{-}X} - 0.60)/7.10$. [g] Uncorrected for polymeric association; *cf.* Experimental. [h] The corrected value for OH is approximately +0.25, *cf.* footnote *c*, Table VIII.

The comparison of solvent effects in σ_I values obtained from the fluorine shielding effects of *m*-substituted fluorobenzenes and those obtained from the acidities of 4-substituted[2.2.2]bicycloöctanecarboxylic acids is of especial interest. Unfortunately, only one substituent, –Br, investigated by Ritchie and Lewis falls into the present category of a generally chemically inert substituent. It is implied by present results that the accurate evaluation of solvent effects on σ_I values from reactivities must be based upon reaction constants (ρ or ρ^*) which are determined from the results for chemically inert substituent groups (*i.e.*, $\rho = \log (k/k_0)/\sigma_I$ for such substituents). With ρ-values based upon the single substitution of 4-Br for H– (which therefore must be regarded as tentative and rather uncertain ρ-values), σ_I values may be calculated from the data reported by Ritchie and Lewis. Table XIII lists values of σ_I for the uncharged CO_2Et, CN and OH substituents in the pure solvents, acetone, dimethylsulfoxide and methanol, which were obtained in this manner and

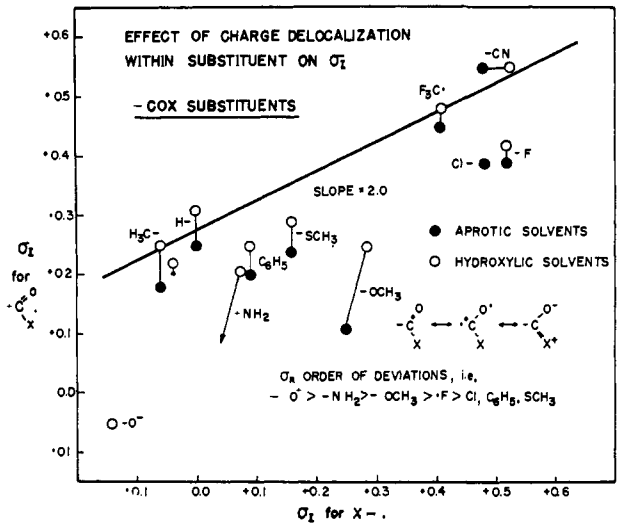


Fig. 2.—Effect of charge delocalization within substituent on σ_1; COX substituents (X is as indicated): ● designates σ_1 value for "normal" aprotic solvents; ○ designates mean σ_1 value for hydroxylic solvents. The results for the $-COC_6H_5$ and $-COSCH_3$ substituents were obtained by Dr. Y. Tsuno, unpublished results.

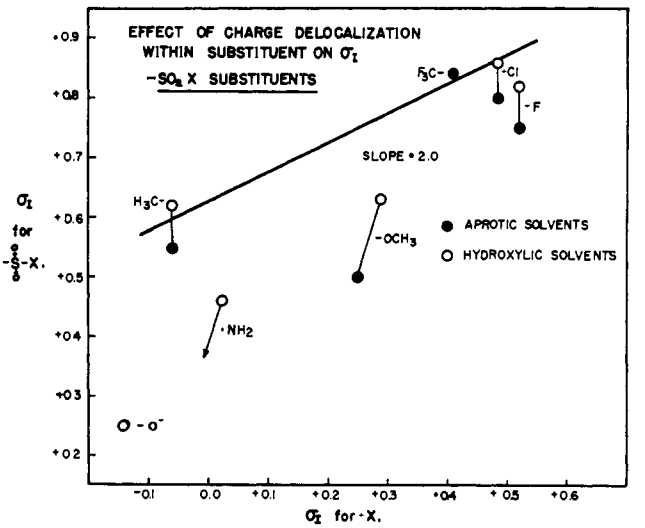


Fig. 3.—Effect of charge delocalization within substituent on σ_1; SO_2X substituents (X is as indicated): ● designates σ_1 value for "normal" aprotic solvents; ○ designates mean σ_1 value for hydroxylic solvents.

corresponding values obtained from the shielding parameters. Considering the combined uncertainties of the ρ and log (K/K_0) values, the agreement is fair (the agreement for the CN substituent is actually quite satisfactory). These results indicate that the solvent effects on shielding parameters have promising applicability to appropriate reactivity systems, but the test may not yet be regarded as critical for even the favorable examples.

TABLE XIII

COMPARISON OF SOLVENT EFFECTS ON σ_1 VALUES FROM REACTIVITIES AND SHIELDING PARAMETERS

	Acetone		CH_3OH		Dimethyl sulfoxide	
Substituent	Acidity	N.m.r.	Acidity	N.m.r.	Acidity	N.m.r
OH	+0.15	+0.16[a]	+0.24	+0.15	+0.03	+0.16[a]
$CO_2C_2H_5$	+ .21	+ .17	+ .27	+ .18	+ .36	+ .18
CN	+ .51	+ .48	+ .53	+ .51	+ .43	+ .45

[a] Based upon shielding parameters obtained by M. G. Schwartz (unpublished).

Some Comments on the Effects of Structure on σ_1 Values.—A more detailed treatment of this subject will be considered in a subsequent publication. In the present discussion several of the more important and obvious aspects of this subject deserve additional comment to that given previously.[91]

The effect of a well-localized positive charge on the first atom of the substituent group is to increase σ_1 by approximately +0.80 unit. It is clear that the effect is readily dissipated by delocalization of charge within the substituent and by interactions with the solvent. The comparable σ_1 values for $-SOCH_3$, $-SO_2CH_3$, $-NO_2$, but the much smaller value for $-COCH_3$ indicate, in accord with other evidence,[92] that the $-\overset{+}{S}-\overset{-}{O}$ bond is much more ionic than the $-\overset{|}{C}=O$ bond.

The distribution of charge within the substituent group, especially as it affects the charge of the first atom, is a primary factor determining the inductive effect of the substituent as a whole. Thus, we may estimate that the $-C\equiv N$ substituent would have a σ_1 value of perhaps 0.1–0.2 unit more positive than the $-CH_2NH_2$ substituent (*i.e.*, $\sigma_1 \cong +0.2$) if the triple bond were nearly non-polar. The estimated increase is due to the greater electronegativities of the sp than sp^3 valence states.[93] Therefore about 0.3 unit of the observed "normal" σ_1 value is due to the polarization, $-C\equiv N \leftrightarrow -\overset{+}{C}=\overset{-}{N}$. Partial neutralization of the negative charge by hydrogen bonding with trifluoroacetic acid raises this figure to about 0.45 σ_1 unit.

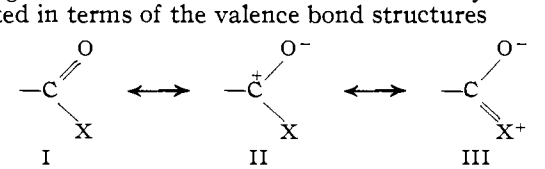
The systematic variation of structure carried out in the present work permits an especially instructive analysis of the effect on σ_1 of charge distribution within substituents of the general formulas -COX and $-SO_2X$. In the absence of any appreciable charge delocalization interactions between the X and $-C=O$ or $-SO_2$ groups, one would anticipate a relationship (eq. 2) similar to that noted earlier for $-CH_2X$ substituents, *i.e.*

$$(\sigma_1)_{-COX} = (\sigma_1)_{-CHO} + ((\sigma_1)_X/2.0) \qquad (3a)$$

and

$$(\sigma_1)_{-SO_2X} = (\sigma)_{-SO_2H} + ((\sigma_1)_X/2.0) \qquad (3b)$$

Figures 2 and 3 illustrate that these relationships do hold roughly. For COX substituents, a plot of $(\sigma_1)_{COX}$ *vs.* $(\sigma_1)_X$ gives an approximately linear relationship of slope 2.0 for the substituents X = $-CN$, $-CF_3$, $-H$ and $-CH_3$. These substituents are of such character that no appreciable delocalization interaction is anticipated (a weak hyperconjugative interaction probably occurs for the $-CH_3$ substituent). On the other hand, the relationship fails for the -R substituents, X = O^-, $-NH_2$, $-OCH_3$, $-F$, $-Cl$, $-C_6H_5$, for which there is delocalization of negative charge into the carbonyl group. These substituents give σ_1 values (for the -COX substituent as a whole) which are less than anticipated by the above relationship. The magnitude of the deviation decreases in the order of substituents given above, and corresponds to correlation with σ_R values.[10] That is, this is the qualitative order expected for decreasing delocalization of charge from X into $-C=O$. The charge distribution effect on the σ_1 value may be interpreted in terms of the valence bond structures



I II III

(91) R. W. Taft, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 13.

(92) C. C. Price, private communication.

(93) R. W. Taft, *J. Chem. Phys.*, **26**, 93 (1957).

as indicating that as structure III is increased in importance, structure II decreases in importance (*i.e.*, negative charge from X accumulates on both C and O). This result is in accord with charge density relationships obtained by HMO calculations.[94]

Similar results are obtained for $-SO_2X$ substituents. In Fig. 3 a line of slope 2.0 is drawn between the two substituents CH_3 and CF_3,[95] for which eq. 2b is expected to hold approximately. Deviations for X = -R substituents are apparent in Fig. 3. It is of interest that the magnitudes of the deviations for a given X in -COX and $-SO_2X$ are similar. A consequence is the fact that corresponding σ_I values are quite generally about +0.40 more positive in the latter series (implying the equivalent of about 0.5 electronic unit more positive charge on S than C).

The present results illustrate in an apparent unambiguous manner how a given (but arbitrary) position in the molecule must be specified in order that the terms resonance and inductive effects of substituents can have even an approximate utility.

(94) Reference 8b and unpublished results.

(95) The σ_I value of +0.84 for the $-SO_2CF_3$ substituent has been communicated to the authors by Dr. W. A. Sheppard.

[COMMUNICATION NO. 2317 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO., ROCHESTER 4, N. Y.]

The Protonation of Benzylideneaniline and its *p*- and *p'*-Dimethylamino Derivatives[1]

BY RICHARD L. REEVES AND WENDELL F. SMITH

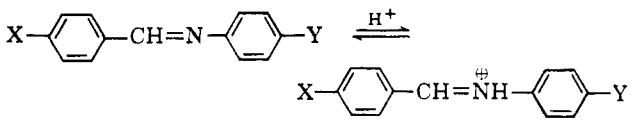
RECEIVED OCTOBER 2, 1962

The spectra of a number of substituted benzylideneanilines and their conjugate acids have been measured in either water or 50% ethanol. Protonation of the azomethine nitrogen gives a bathochromic shift of the N → V_1 absorption band, contrary to previously reported results. The mono-acid of *p*-dimethylaminobenzylideneaniline (Ib) exists almost entirely as the anilium form, whereas that of benzylidene-*p'*-dimethylaminoaniline (Ic) is a tautomeric mixture containing approximately 70–85% of the ammonium form. Hydrolysis half-times for the mono-acids are in the millisecond range, with the exception of that of Ib, which is more stable. The spectral results for the compounds studied are interpreted in the light of simple molecular orbital calculations.

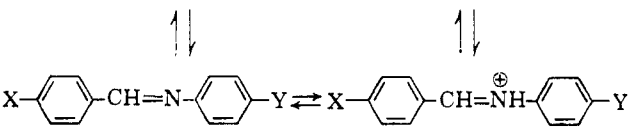
Introduction

In recent years several publications have appeared on the structure of the conjugate acid of *cis*- and *trans*-azobenzene[2,3] and on the position of protonation of 4-aminoazobenzene and its derivatives.[4] Protonation of benzylideneaniline (Ia), which is isoconjugate with azobenzene, and its two *p*-dimethylamino derivatives Ib and Ic has, however, remained a relatively unexplored subject.

The long-wave-length absorption maxima of benzylideneaniline and several of its derivatives are reported to undergo a hypsochromic shift upon conversion to the corresponding conjugate acids.[5,6] In contrast to this observation, protonation of azobenzene[7] and the Schiff base Id[8] causes a bathochromic shift of the same band. The known rapid rates of hydrolysis of Schiff bases in general[8-12] make the reported spectra obtained in highly acid solution[5,6] appear suspect. Accordingly, we have obtained spectra of the conjugate acids of benzylideneaniline and a number of its derivatives, using the flow technique described previously,[8] and have measured the hydrolysis rates in the *p*H range where the mono-acid is the predominant species. From our interpretation of the spectral results we have assigned the position of protonation in the mono-acid cations of the *p*- and *p'*-dimethylamino derivatives Ib and Ic. We also have interpreted some of the experimental results in the light of



Ia. X = Y = H; IIa. X = Y = H
b. X = $(CH_3)_2N$; Y = H; b. X = $(CH_3)_2N$; Y = H
c. X = H; Y = $(CH_3)_2N$; c. X = H; Y = $(CH_3)_2N$
d. X = $(CH_3)_3N^{\oplus}$; Y = OH
e. X = $(CH_3)_3N^{\oplus}$; Y = OCH_3
f. X = $(CH_3)_3N^{\oplus}$; Y = CH_3
g. X = $(CH_3)_3N^{\oplus}$; Y = $(CH_3)_2N$
h. X = $(CH_3)_3N^{\oplus}$; Y = H



IIIa. X = $(CH_3)_2NH^{\oplus}$; Y = H; IVa. X = $(CH_3)_2NH^{\oplus}$; Y = H
b. X = H; Y = $(CH_3)_2NH^{\oplus}$; b. X = H; Y = $(CH_3)_2NH^{\oplus}$
c. X = $(CH_3)_3N^{\oplus}$; Y = $(CH_3)_2NH^{\oplus}$; c. X = $(CH_3)_3N^{\oplus}$; Y = $(CH_3)_2NH^{\oplus}$

LCAO–MO (linear combination of atomic orbitals–molecular orbital) theory. The method has been previously applied in some detail to the interpretation of the electronic absorption spectrum of compound Ia.[7,13] The calculations have now been extended to include the alternant hydrocarbon ion isoconjugate with Ib and Ic.

The spectrum of the mono-acid cation of 4-aminoazobenzene is best interpreted in terms of an equilibrium mixture of the tautomeric azonium and ammonium ions.[4] Ricketts and Cho[14] interpret their spectral data on the mono-acid cations of benzylidene-*p'*-phenylazoaniline (I, X = H, Y = PhN=N—) and *p*-dimethylaminobenzylidene-*p'*-phenylazoaniline (I, X = $(CH_3)_2N$—, Y = PhN=N—) as involving a tautomeric mixture resulting from protonation at both the azo and the azomethine nitrogens. The results of Weinstein and McInnich[15] on hydrogen-

(1) Throughout this paper, *p*-substituents will refer to the benzylidene ring and *p'*- to the aniline ring.

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(4) For a recent review, see G. E. Lewis, *Tetrahedron*, **10**, 129 (1960).

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(13) W. F. Smith, *Tetrahedron*, in press (1963).

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