A Fluorine Nuclear Magnetic Resonance Shielding Study of Substituent Effects on π-Charge Distributions in Benzophenone and Its Lewis Acid Adducts[1a]

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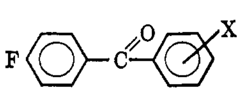
Abstract: Fluorine nuclear magnetic resonance (F nmr) shielding has been investigated for an extensive series of *p*-fluoro-*m*′- and -*p*′-substituted benzophenones and their Lewis acid complexes in methylene chloride solution. This study appears to be the first systematic study of substituent nmr shielding effects in both the reactant and the product of a chemical reaction under common conditions. The *p*-fluorophenyl label is used to measure π-charge density at the carbonyl carbon atom. It is concluded that the change in π-charge density at the carbonyl carbon induced by the *polar effect* of the *m*′- or *p*′-substituted phenyl group is directly proportional to the product of the σ value of the substituent and the carbonyl carbon atom charge density in the unsubstituted derivative. This result provides strong support for the hypothesis of Hammett.

Substituent effects on fluorine nuclear magnetic resonance shielding (F nmr) in *para*-substituted fluorobenzenes have been related to the changes in π-electron charge density at the fluorine atom and its bonded carbon atom.[2] HMO calculations further suggest approximately linear relationships in *p*-fluorobenzoyl derivatives, *p*-FC_6H_4COX, between the π-charge densities at the carbonyl carbon and *p*-fluoro-substituted carbon atom.[3] The expected consequence of these relationships is that F nmr shielding in the *p*-fluorophenyl label may be utilized to measure changes in π-electron charge density which occur at the carbonyl carbon atom.

The polar effects of *meta*- and *para*-substituted phenyl groups on chemical reactivities follow with relatively high precision the modified $\sigma\rho$ relationship.[4] Derivations are encountered when the measured effects include those of direct conjugation. Hammett supposed that the quantity $-\sigma$ measures the change in charge density produced by the substituent at the side-chain reaction center.[5] In this paper we have subjected this hypothesis to direct test in the following manner.

F nmr shielding in an extensive series of *p*-fluoro-*m*′- and '-*p*′-substituted benzophenones (structure I) and in their Lewis acid complexes has been determined.



I

Within each series, the polar effects of the *m*′- and *p*′-substituted phenyl groups on the F nmr shielding are found to follow the $\sigma^0\bar{\rho}$ relationship,[4] confirming the Hammett hypothesis. The values of $\bar{\rho}$ for the uncomplexed ketone and for several Lewis acid adducts have been determined by the procedure of Taft and Lewis.[6] A direct relationship is found between the $\bar{\rho}$ values and the π-electron density at the carbonyl carbon atom of unsubstituted *p*-fluorobenzophenone and its adducts. The relationship bears an analogy to Hine's τ relationship.[7] The results have important application to substituent effects on the thermodynamic properties for formation of the Lewis acid adducts of I. This is the subject of the following companion paper.

F nmr shielding in the formation of 1:1 adducts of BF_3, BCl_3, and BBr_3 with *p*-fluorophenyl-labeled bases has been found to be ideal for the present objectives. Thus the shielding parameters of both uncomplexed base and the 1:1 adduct are obtained in a common pure solvent (CH_2Cl_2). The shielding for the adduct is found to involve little or no medium effect. In the present work results similar to that previously obtained with *p*-fluorobenzonitrile[8] have been found for the *p*-fluorobenzophenones, I. At room temperatures the adducts are rapidly dissociated giving rise to a single time-average fluorine signal. The signal is the weighted average of the shielding parameters for complexed and uncomplexed base.[9] The observed shieldings for a series of methylene chloride solutions having an approximately constant concentration (~0.4 *M*) of the *p*-fluorobenzophenone, and increasing concentrations of Lewis acid display a limiting downfield shift at a stoichiometric acid–base ratio of unity (*cf.* Figure 2 of ref 8 as a typical result). With the weaker acids or bases employed in this study an acid–base ratio of 3–10 is required to obtain the limiting shift (the shielding parameter for the adduct).

The proton adducts of compounds such as series I ketones have F nmr shieldings which are highly medium sensitive.[10] It is, therefore, impossible to obtain the

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[1] (a) This work was performed at the Pennsylvania State University. Support in part by the Office of Naval Research is gratefully acknowledged. (b) Department of Chemistry, University of California, Irvine, Calif.

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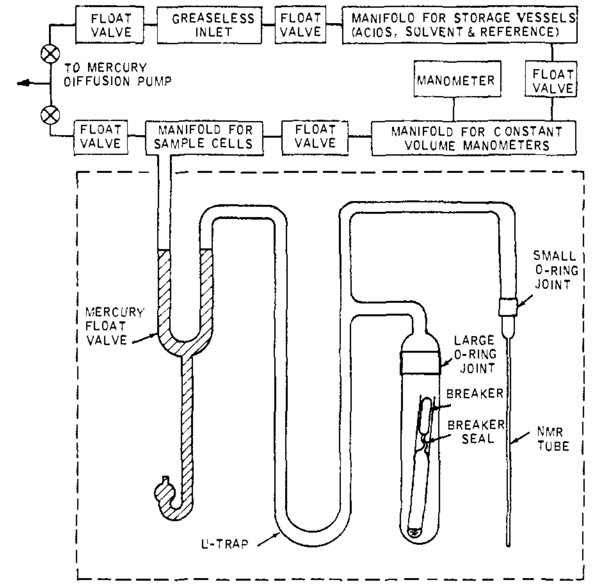

Figure 1. Vacuum line schematic.

shielding parameters for the proton adducts and the uncomplexed ketones in a common solvent. In this work we have obtained the shielding parameters of the protonated forms of I as they occur in 99.8% (wt) H_2SO_4 containing the ketone (~0.4 *M*).

Experimental Section

Preparation of *m*- and *p*-Fluorobenzophenones. *p*-Fluorobenzophenone. To a solution of 5 g of benzoyl chloride and 10 ml of fluorobenzene in 25 ml of carbon disulfide, 6 g of $AlCl_3$ was added in several portions with stirring. Stirring was continued for 3 hr and then the mixture was warmed on a steam bath for 1 hr. The solvent was removed and the residue decomposed with ice and hydrochloric acid. The oily product was extracted with ether and washed with aqueous sodium hydroxide solution and water. The ether was evaporated and the residue purified through an alumina column. Recrystallizations from petroleum ether gave 5.5 g of the ketone (mp 49–50°, lit.[11] mp 48.2–48.7°).

***m*-Fluorobenzophenone.** This ketone was obtained by the condensation of 4 g of *m*-fluorobenzoyl chloride with benzene in carbon disulfide solution in the presence of $AlCl_3$. The product was recrystallized from petroleum ether (mp 54.5–55°, lit.[12] mp 55°).

The following ketones were prepared in the same manner from fluorobenzene and the correspondingly substituted benzoyl chlorides. The products were purified by repeated recrystallizations from aqueous ethanol, ethanol, and petroleum ether: *p,p*′-difluorobenzophenone (mp 107°, lit. mp 106–107°,[11] 107.5–108.5°[13]), *m,p*′-difluorobenzophenone (mp 61.0–61.5°), *p*-fluoro-*m*′-chlorobenzophenone (mp 77.5–78°), *p*-fluoro-*m*′-trifluoromethylbenzophenone (mp 45–46°), *p*-fluoro-*p*′-trifluoromethylbenzophenone (mp 100.5–101.5°), *p*-fluoro-*p*′-nitrobenzophenone (mp 88–88.5°), *p*-fluoro-*m*′-bromobenzophenone (mp 84.5°).

***p*-Methoxy-*p*′-fluorobenzophenone.** To a solution of 18 g of anisole and 15 g of *p*-fluorobenzoyl chloride in 75 ml of carbon disulfide, 15 g of $AlCl_3$ was added dropwise under moderate refluxing. After standing for 2 hr at room temperature the solvent was removed and the residue decomposed with hydrochloric acid and ice. The resulting mixture was heated on a steam bath for 1 hr and the crystalline product collected on a filter and washed with water. The product was purified by recrystallizations from ethanol (mp 97–97.5°, lit. mp 94.5–95.5°,[14] 96.0–96.5°[15]).

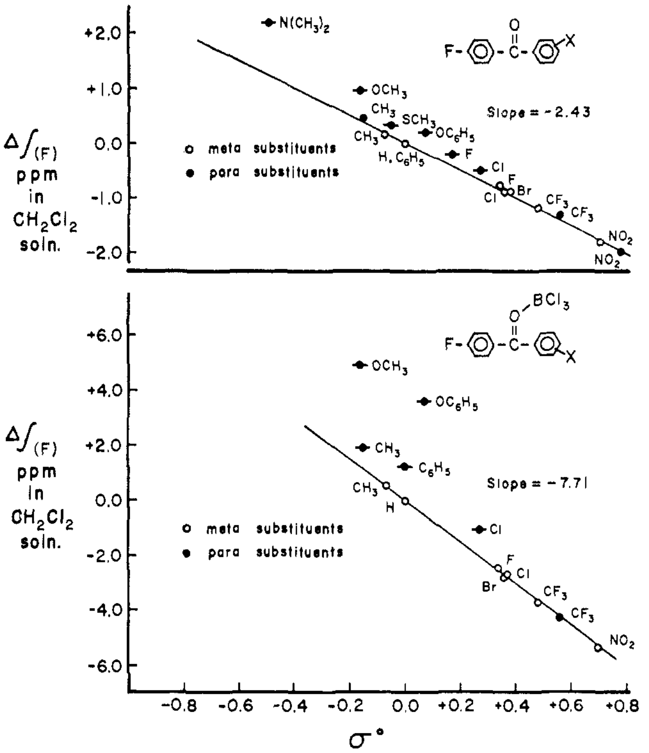

Figure 2. Polar effects of 3′ and 4′ substituents and conjugation effects of 4′ substituents in *p*-fluorobenzophenones and their BCl_3 adducts on fluorine nuclear magnetic resonance shielding.

***p*-Methoxy-*m*′-fluorobenzophenone** was obtained in the same way from *m*-fluorobenzoyl chloride and recrystallized from aqueous ethanol and ethanol (mp 69.5–70°).

The following ketones were prepared similarly by the Friedel–Crafts reaction of *m*- or *p*-fluorobenzoyl chloride with substituted benzenes in carbon disulfide solution. The products were purified by repeated recrystallizations from aqueous ethanol, ethanol, and petroleum ether: *p*-methyl-*p*′-fluorobenzophenone (mp 97.5–98°, lit.[15] mp 98–99°) and *p*-methyl-*m*′-fluorobenzophenone (mp 53–54°) were obtained from toluene; *p*-ethyl-*p*′-fluorobenzophenone (mp 69.5–70°) and *p*-ethyl-*m*′-fluorobenzophenone [bp 139–141° (2 mm)] from ethylbenzene; *p*-butyl-*p*′-fluorobenzophenone (mp 75–75.5°) and *p*-*t*-butyl-*m*′-fluorobenzophenone (mp 30–31°) from *t*-butylbenzene; *p*-chloro-*p*′-fluoro- (mp 113–114°, lit.[14] mp 115°) and *p*-chloro-*m*′-fluorobenzophenone (mp 79.5–80°) from chlorobenzene; *p*-bromo-*p*′-fluorobenzophenone (mp 108.5–109°, lit.[14] mp 107–108°) and *p*-bromo-*m*′-fluorobenzophenone (mp 87–88°) from bromobenzene in poor yields; *p*-ethoxy-*p*′-fluorobenzophenone (mp 87.5–88°, lit.[15] mp 86.5–87.5°) and *p*-ethoxy-*m*′-fluorobenzophenone [bp 176° (4 mm)] from phenyl ethyl ether; *p*-phenoxy-*p*′-fluorobenzophenone (mp 101.5–102°) and *p*-phenoxy-*m*′-fluorobenzophenone (mp 61–62°) from diphenyl ether; *p*-thiomethyl-*p*′-fluorobenzophenone (mp 105–106°, lit.[14] mp 105.5–106.5°) and *p*-thiomethyl-*m*′-fluorobenzophenone (mp 78–79°) from thioanisole; *p*-phenyl-*p*′-fluorobenzophenone (mp 148.5–149°) and *p*-phenyl-*m*′-fluorobenzophenone (mp 104–105°) from biphenyl.

***m*-Methyl-*m*′-fluorobenzophenone.** To a Grignard solution prepared from 14 g of *m*-fluorobromobenzene and 2.2 g of magnesium, 9 g of *m*-methylbenzonitrile diluted with an equal amount of ether was added dropwise under cooling in ice–salt bath. The reaction mixture was allowed to stand overnight, warmed under gentle reflux for 1 hr and decomposed with ice and hydrochloric acid. The aqueous mixture was heated on a steam bath for 1 hr and left overnight. The organic material was dissolved in ether, washed with aqueous sodium hydroxide solution, dilute hydrochloric acid, and water, and dried over calcium chloride. Distillation yielded 12 g of the ketone [bp 130–130.5° at (2 mm)].

***m*-Methyl-*p*′-fluorobenzophenone** was prepared in the same way. A center fraction, 137–139° (2 mm), was recrystallized from petroleum ether (mp 46.5–47°).

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m-Trifluoromethyl-*m*′-fluorobenzophenone (mp 37–38°) and *m*-trifluoromethyl-*p*′-fluorobenzophenone (mp 45–46°) were obtained by the reaction of *m*-trifluoromethylbenzonitrile with the Grignard reagents of the corresponding fluorobromobenzenes.

***m*-Chloro-*m*′-fluorobenzophenone.** A Grignard solution prepared from 15 g of *m*-fluorobromobenzene in 30 ml of ether was added slowly (1 hr) to a cold solution of *m*-chlorobenzoyl chloride, 14 g, in 25 ml of ether. After addition of the reagent, the mixture was allowed to stand overnight at room temperature. The mixture was refluxed for 0.5 hr and decomposed with ice and hydrochloric acid and the aqueous mixture heated on a steam bath for 1 hr. The organic layer was taken up with ether and washed with water, aqueous sodium hydroxide, and water. After drying over calcium chloride, the ether was removed, and the resulting product was dissolved in alcohol and precipitated by adding water. Three recrystallizations from light petroleum gave 11 g of the ketone (mp 61.5–62°).

The same procedure was applied for the preparations of *m*,*m*′-difluorobenzophenone (mp 58.5–59°, recrystallization from petroleum ether), *m*-bromo-*m*′-fluorobenzophenone from *m*-bromobenzoyl chloride (67–67.5°, recrystallization from aqueous ethanol, ethanol–petroleum ether mixture), and *p*-trifluoromethyl-*m*-fluorobenzophenone from *p*-trifluoromethylbenzoyl chloride (mp 56° from aqueous ethanol and petroleum ether).

Samples of the ketones which were used to prepare the Lewis acid adducts were sublimed and stored in a desiccator.

Acids. Commercial samples of BF_3, BCl_3, and BBr_3 were purified by trap-to-trap distillation on the vacuum line. Appropriate baths were used in the traps until a fraction was obtained with the following vapor pressure: BF_3, 290 mm (−112°); BCl_3, 470 mm (0°); BBr_3, 54 mm (20°). $AlCl(C_2H_5)_2$ and $AlCl_2(C_2H_5)$ were purchased from Texas Alkyls Inc. and were distilled before use. Purified samples of of $AlCl_3$ and BI_3 were kindly supplied by Mr. J. W. Carten.

Preparation of Nmr Samples. All solutions were prepared on a vacuum line at 10^{-5} mm in the general manner indicated earlier.[8] Figure 1 pictures the vacuum line scheme. The essentially nonvolatile benzophenones were weighed into a small capillary tube which was placed in the nmr tube and evacuated to $\sim 10^{-6}$ mm. The acid (BF_3, BCl_3, or BBr_3), the nmr reference (TCTFCB),[16] and the solvent (CH_2Cl_2) were measured quantitatively as vapors from calibrated constant volume manometers. Transfer from the manometer was made through appropriate Hg float valves in to the U trap and subsequently into the nmr tube by means of a liquid N_2 bath. The slightly volatile acids [BI_3, $AlCl_3$, $AlCl(C_2H_5)_2$, and $AlCl_2(C_2H_5)$] were protected from contact with air and moisture by the use of magnetic breaker seals. The breakers were filled with the approximate amount of acid required in a separate operation and placed in a tube and attached to the line. After evacuation, the seal was broken and the acid transferred from the breaker seal to the U trap and finally into the nmr tube with the benzophenone. The weight of acid was determined by weighing the breaker seal before and after the sample preparation. Solvent and nmr reference were transferred subsequently as described above. In every case the prepared nmr tube was sealed off under vacuum and stored in liquid N_2 until its spectra were obtained at 25 ± 1°. In each case the solution displayed a single *p*-fluorophenyl signal.

The procedure used in preparing the samples of uncomplexed bases[16] and the H_2SO_4 solutions[17] is that described earlier. The procedure followed in obtaining the shielding parameters also has been previously described.[16]

Results

In Table I are listed the shielding parameters (relative to internal fluorobenzene), $\int_{\text{H}}^{p\text{-X}_0}$, for a series of Lewis acid adducts of *p*-fluorobenzophenone in methylene chloride solution at 25°. The shielding parameters have been obtained from at least three separate experiments with stoichiometric acid to base ratio (a/b) of 1 to 5. The limiting shifts from these experiments are precise to ±0.08 ppm. For the uncomplexed ketone the precision is ±0.03 ppm. The BF_3 and $AlCl(C_2H_5)_2$ results are about 0.3 ppm upfield from the limiting value at $a/b = 1$, presumably because of a small amount of dissociation. For these, the limiting shift was obtained at $a/b = 3\text{–}5$. A titration curve for BF_3 ($a/b = 0.17\text{–}5.3$) gave results similar to those reported with *p*-fluorobenzonitrile.[8] Analysis by the Ehrenson computer program[18] gave the limiting shift indicated and a dissociation equilibrium constant (in *M* units) $K_\text{D} = 0.004 \pm 0.002$.

Table I. Fluorine Nmr Shielding Parameters for Lewis Acid Adducts of *p*-Fluorobenzophenone

Acid	$\int_{\text{H}}^{p\text{-X}_0}$, ppm	Acid	$\int_{\text{H}}^{p\text{-X}_0}$, ppm
None (uncomplexed)	6.69	$AlCl_2(C_2H_5)$	21.77
$AlCl(C_2H_5)_2$	17.20	$AlCl_3$	22.40
BF_3	17.62	BBr_3	22.85
BCl_3	21.20	BI_3	23.62

Table II lists the 3′- and 4′-polar substituent shielding effects for the *p*-fluorobenzophenone and its BF_3, BCl_3, BBr_3, and H_2SO_4 adducts. All except the latter were obtained in methylene chloride solution at 25°. The latter are from measurements in 99.8% H_2SO_4. The symbol $\Delta\delta$ represents the shielding relative to the unsubstituted *p*-fluorobenzophenone derivative. For the methylene chloride solutions, the shielding parameter relative to internal fluorobenzene may be obtained, of course, by combining $\left(\int_{\text{H}}^{p\text{-X}} = \int_{\text{H}}^{p\text{-X}_0} + \Delta\int\right)$ the results of Tables I and II.

The shielding parameters for the BF_3 adducts given in Table II were obtained utilizing the Ehrenson computer program to analyze for each ketone the results of five to seven experiments with $a/b = 0.3$ to 8.0. For the p'-CF_3 substituent, for example, this analysis gave $\Delta\delta = -3.60$ ppm and $K_\text{D} = 0.018 \pm 0.008$. This may be compared with $\Delta\delta = -3.52$ ppm observed in an experiment with $a/b = 7.71$. The values for K_D obtained for the other BF_3 adducts of Table II were within the range 0.002–0.02.

The shielding parameters for the BCl_3 and BBr_3 adducts given in Table II are the limiting shifts obtained from two or three experiments with $a/b = 3\text{–}7$. The precision is approximately ±0.08 ppm for each. The precision of the H_2SO_4 results is comparable.

Table III lists the shielding effects of conjugating p' substituents for *p*-fluorobenzophenone and its BF_3, BCl_3, BBr_3, and H_2SO_4 adducts under the same conditions as for the corresponding results in Table II. The shielding parameters for the BF_3, BCl_3, and BBr_3 adducts were obtained as the limiting shifts for two or three experiments with $a/b = 1$ to 4. The precision is ±0.08 ppm.

Table IV lists the shielding effects of m' and p' substituents for *m*-fluorobenzophenone in benzene and H_2SO_4 solutions. For comparison the corresponding *p*-fluorobenzophenone shielding effects are also shown. It is apparent from Table IV that *p*-F shielding effects in the uncomplexed ketone are uniformly about threefold greater than for corresponding *m*-F shielding effects. A substantial number of similar results were

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Table II. Polar Effects of 3′ and 4′ Substituents on Fluorine Nmr Shielding (ppm) in *p*-Fluorobenzophenone and Its BF_3, BCl_3, BBr_3, and H_2SO_4 Adducts

Subst	σ^0	Uncomplexed ketone		BF_3 adduct		BCl_3 adduct		BBr_3 adduct		H_2SO_4 adduct	
		$\Delta\int^{\text{exptl}}$	$\Delta\int^{a}$	$\Delta\int^{\text{exptl}}$	$\Delta\int^{a}$	$\Delta\int^{\text{exptl}}$	$\Delta\int^{a}$	$\Delta\int^{\text{exptl}}$	$\Delta\int^{a}$	$\Delta\int^{\text{exptl}}$	$\Delta\int^{a}$
m′-CH_3	−0.07	+0.15	+0.17	+0.57	+0.45	+0.53	+0.54	...	+0.54	+0.53	+0.49
H	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)	(0.00)
m′-F	0.34	−0.75	−0.82	−1.96	−2.18	−2.44	−2.62	−2.25	−2.81	−2.25	−2.39
m′-Cl	0.37	−0.88	−0.89	...	−2.37	−2.66	−2.85	...	−3.07	−2.62	−2.59
m′-Br	0.36	−0.89	−0.86	−2.15	−2.30	−2.80	−2.77	−2.58	−2.98	−2.70	−2.52
m′-CF_3	0.48	−1.17	−1.17	...	−3.07	−3.70	−3.70	−3.67	−3.97	−3.20	−3.36
p′-CF_3	0.54	−1.32	−1.31	−3.60	−3.46	−4.25	−4.16	−4.20	−4.47	−3.80	−3.78
m′-NO_2	0.70	−1.79	−1.72	...	−4.48	−5.33	−5.40	−5.61	−5.79	−5.65	(+0.81)[b]
p′-NO_2	0.82	−2.01	−1.99	...	−5.25	...	−6.31	...	−6.80	−6.78	(+0.97)[b]
$\bar{\rho} = \int_{\text{H}}^{p\text{-X}_0} \Big/ 2.75$			−2.43		−6.40		−7.71		−8.27		(−7.00)[c]

[a] $\Delta\int^{\text{calcd}} = \sigma^0\bar{\rho} = \int^{p\text{-X}_0}(1 + \sigma^0/2.75)$; *cf.* eq 9 and Discussion. [b] Calculated values of σ^0 in H_2SO_4. It is noteworthy that these values meet the usual relationship,[4] $(\sigma^0_{(m)} - \sigma_I)/(\sigma^0_{(p)} - \sigma_I) \cong 0.5$. [c] Observed value of $\bar{\rho}$.

Table III. Effects of Conjugating *p*′ Substituents on the Fluorine Nmr Shielding of *p*-Fluorobenzophenone and Its BF_3, BCl_3, BBr_3, and H_2SO_4 Adducts[a]

Subst	σ^+	Uncomplexed ketone		BF_3 adduct		BCl_3 adduct		BBr_3 adduct		H_2SO_4 adduct	
		$\Delta\int^{\text{exptl}}$	$\bar{\sigma}^+$	$\Delta\int^{\text{exptl}}$	$\bar{\sigma}^+$	$\Delta\int^{\text{exptl}}$	$\bar{\sigma}^+$	$\Delta\int^{\text{exptl}}$	$\bar{\sigma}^+$	$\Delta\int^{\text{exptl}}$	$^+\sigma$
p′-$N(CH_3)_2$	−1.7	+2.19	−0.90	...	...	...	...	...	...	...	...
p′-OCH_3	−0.78	+0.91	−0.38	+4.38	−0.68	+5.05	−0.66	+5.41	−0.65	+6.10	−0.87
p′-OC_2H_5	...	+1.01	−0.42	...	...	...	...	...	...	+7.00	−1.00
p′-OC_6H_5	−0.5	+0.45	−0.19	+3.26	−0.51	+3.66	−0.48	...	...	+3.30	−0.49
p′-CH_3	−0.31	+0.45	−0.19	+1.79	−0.28	+1.88	−0.24	+2.21	−0.27	+2.38	−0.34
p′-C_2H_5	−0.29	+0.44	−0.18	+1.89	−0.30	+1.90	−0.25	...	...	+2.38	−0.34
p′-*t*-C_4H_9	−0.26	+0.41	−0.17	+1.70	−0.27	+1.85	−0.24	+2.04	−0.25	+2.05	−0.29
p′-SCH_3	−0.65	+0.34	−0.14	...	...	...	...	...	...	+5.75	−0.82
p′-C_6H_5	−0.22	+0.02	−0.01	+1.12	−0.18	+1.25	−0.16	+1.48	−0.18	−0.30	+0.04
p′-F	−0.07	−0.19	+0.08	...	...	...	...	...	...	+0.83	−0.12
p-Cl	+0.11	−0.52	+0.21	−0.54	+0.08	−1.05	+0.14	−0.85	+0.10	−0.45	+0.07

[a] $\bar{\sigma}^+ = \Delta\int^{\text{exptl}} \Big/ \bar{\rho}$; $\bar{\rho}$ value is given in Table II. Values in ppm.

Table IV. Comparison of Shielding Effects of 3′ and 4′ Substituents in *m*-Fluorobenzophenones and *p*-Fluorobenzophenones in Benzene and Sulfuric Acid Solutions

Subst	C_6H_6 soln, ppm		H_2SO_4 soln, ppm	
	$\Delta\int^{m\text{-F}}$	$\Delta\int^{p\text{-F}}$	$\Delta\int^{m\text{-F}}$	$\Delta\int^{p\text{-F}}$
p′-OCH_3	...	+0.86	+0.70	+6.10
p′-CH_3	+0.18	+0.42	+0.23	+2.38
p′-SCH_3	+0.08	+0.26	+0.70	+5.75
m′-CH_3	+0.06	+0.10	+0.16	+0.53
H	(0.00)[a]	(0.00)[b]	(0.00)	(0.00)
p′-Cl	−0.21	−0.56	0.00	−0.50
m′-Cl	−0.36	−0.90	−0.63	−2.62
m′-Br	−0.39	−0.90	−0.55	−2.70
m′-CF_3	...	...	−0.70	−3.20
p′-CF_3	−0.42	−1.36	−0.70	−3.80

[a] $\int_{\text{H}}^{m\text{-}C_6H_5CO} = -0.99$ ppm. [b] $\int_{\text{H}}^{p\text{-}C_6H_5CO} = -6.13$ ppm.

obtained previously.[19] In the proton adducts in H_2SO_4 it is also apparent that this factor increases to about 5.5 for polar substituent effects. For conjugating *p*′ substituents the factor increases further to approximately ninefold (*cf.* following discussion, in particular concerning eq 5).

Discussion

Theoretical treatments of substituent effects on fluorine shielding in *meta*- and *para*-substituted fluorobenzene have given the relationship[20]

$$\int_{\text{H}}^{p\text{-X}} = C_1\Delta q_{\text{F}} + C_2\Delta p_{\text{C-F}} + C_3\Delta I \qquad (1)$$

where $\int_{\text{H}}^{p\text{-X}}$ is the shielding parameter for the *para*-substituted fluorobenzene relative to internal fluorobenzene, Δq_{F} is the change (relative to C_6H_5F) in π-electron charge density at the fluorine atom, $\Delta p_{\text{C-F}}$ is the change in the C–F π-bond order, ΔI is the change in ionic character of the C–F σ bond which is induced by the polar substituent, and C_1, C_2, and C_3 are constants. By using the shielding of the *para*-substituted fluorobenzene relative to that of its *meta* isomer, $\int_{m\text{-X}}^{p\text{-X}}$,

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

[20] (a) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961); (b) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963).

the ΔI term very generally vanishes for most practical purposes. Further, HMO theory anticipates linear relationships between corresponding values of Δq_F, Δp_{C-F}, and Δq_{C-F}, where the latter is the change (relative to C_6H_5F) in π-electron density at the carbon atom to which the fluorine is bonded,[3] *i.e.*

$$\int_{m\text{-X}}^{p\text{-X}} = C_4 \Delta q_{C-F} \qquad (2)$$

The constant C_4 is estimated from experimental results to be 220 ppm/e.[19]

In simple model HMO calculations for *p*-fluorobenzoyl derivatives, *p*-FC_6H_4COX, where X is a carbon-like atom of Coulomb integral -0.5 to $+2.0\ \beta$ relative to benzene carbon, the substituent effect of X is found to produce uniformly a sevenfold greater change in the π-charge density at the carbonyl carbon than that at the *para* carbon atom.[3] This result suggests quite generally for *p*-fluorobenzoyl derivatives that

$$\Delta q_{C-F} = C_5 q_{C-O} + C_6 \qquad (3)$$

where q_{C-O} is the π-charge density at the carbonyl carbon and C_5 and C_6 are constants. Combination of eq 2 and 3 indicates that the *p*-fluorophenyl label may be used to study the π-electron density changes at the carbonyl carbon, *i.e.*

$$\Delta \int_{m\text{-X}}^{p\text{-X}} = C_7 \Delta q_{C-O} \qquad (4)$$

where $C_7 \cong 40$ ppm/e. Equation 4 may be simplified for the present experimental investigation. It has been shown[19] experimentally that for restricted families of similar substituents, such as the ketone series I or their Lewis acid adducts (*cf.* Table IV and comments), the following relationships hold.

$$\Delta \int_{H}^{p\text{-X}} = C_8 \Delta \int_{H}^{m\text{-X}} \qquad (5)$$

or

$$\Delta \int_{m\text{-X}}^{p\text{-X}} = [(C_8 - 1)/C_8] \Delta \int_{H}^{p\text{-X}}$$

where C_8 is a constant. Combining eq 4 and 5 gives

$$\Delta \int_{H}^{p\text{-X}} = C_9 \Delta q_{C-O} \qquad (6)$$

where $\Delta \int_{H}^{p\text{-X}}$ refers to the shielding of a *p*′-substituted *p*-fluorobenzophenone (or acid adduct) relative to the unsubstituted *p*-fluorobenzophenone (or adduct), Δq_{C-O} is the corresponding change in the π-charge density at the carbonyl carbon, and C_9 $[= C_8C_7/(C_8 - 1)]$ is a constant.

In interpretation of the *meta*- and *para*-substituent effects on rates and equilibria for side-chain derivatives of benzene which are described by the $\sigma\rho$ relationship, Hammett[5] supposed that the quantity $-\sigma$ measures the change in charge density produced by the substituent at the side-chain reaction center, *i.e.*, for example, for series I ketones $\Delta q_{CO} \propto (-\sigma)$. By the application of eq 6 to F nmr shielding in series I ketones and their Lewis acid adducts, it follows that the Hammett hypothesis is satisfied by the relationship

$$\Delta \int_{H}^{p\text{-X}} = -\bar{\rho}\sigma \qquad (7)$$

where ρ is used to distinguish the shielding series constant for a given series of ketone derivatives from the usual reactivity series constant, ρ.

In Figure 2 are plotted $\Delta \int_{H}^{p\text{-X}}$ values from Tables III and IV for *m*′- and *p*′-substituted *p*-fluorobenzophenones and their BCl_3 adducts *vs.* σ^0 values.[4] In general, a linear trend is clearly discernible. Linear relationships of excellent precision, however, encompass only the *m*′ and nonconjugating *p*′ substituents. The crossed-circle points for *p*′ substituents represent significant deviations from eq 7 according to the criterion of Taft and Lewis.[6] The results in Figure 2 have the same characteristics, for example, as a plot of Brown's σ^+ values[21] *vs.* σ^0. We conclude that Hammett's hypothesis is confirmed for the *polar effects* of *m*′ and *p*′ substituents.

The *additional* effects of direct conjugation between -R *p*′ substituents and the carbonyl group lead to deviations from eq 7 as might be expected by Brown's σ^+ treatment.[21] The latter parameters, however, do not generally suffice quantitatively to describe the observed combination of polar and conjugative effects. This result is seen by comparison of corresponding σ^+ values and the "effective" $\bar{\sigma}^+$ $\left(\equiv \Delta \int_{H}^{p\text{-X}} \Big/ \bar{\rho}\right)$ values which are listed in Table III for conjugating *p*′ substituents. For *p*′-OCH_3 and *p*′-SCH_3, the $\bar{\sigma}^+$ values for uncomplexed ketone and for the BF_3, BCl_3, and BBr_3 adducts are significantly less negative than Brown's σ^+ values. In H_2SO_4, however, the $\bar{\sigma}^+$ for these two substituents are significantly more negative than Brown's σ^+ values. For all of the *p*′ substituents of Table III the $\bar{\sigma}^+$ value of the uncomplexed ketone is substantially less than Brown's σ^+ value. On the other hand, Brown's σ^+ values for *p*-OC_6H_5, *p*-CH_3, *p*-C_2H_5, *p*-*t*-C_4H_9, and *p*-Cl apply quite satisfactorily for all of the Lewis acid adducts of Table III.

In Hine's τ relationship[7] the reaction constant, ρ, for polar reactivity effects of *meta* and *para* substituents is directly related to the change in the σ value of the side-chain reaction center. Thus the Hammett and the Hine hypotheses suggest that the π-charge density of the carbonyl carbon of the unsubstituted ketone derivative determines the susceptibility of this center to changes in charge density produced by substituent polar effects. This condition and eq 2, 3, and 5 lead to the relationship

$$\bar{\ } = \int_{H}^{p\text{-X}_0} \Big/ k \qquad (8)$$

where $\int_{H}^{p\text{-X}}$ is the shielding of the unsubstituted *p*-fluorobenzophenone derivative relative to internal fluorobenzenes (Table I) and k is a constant for a series of carbonyl derivatives.

Equation 8 is confirmed by the excellent agreement between $\Delta \int^{\text{exptl}}$ and $\Delta \int^{\text{calcd}}$ values given in Table II

[21] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 79, 1913 (1957); **80**, 4979 (1958).

for the uncomplexed ketones and their BF_3, BCl_3, and BBr_3 adducts; $\Delta\int^{\text{calcd}}$ is obtained as $\left(\int_{\text{H}}^{p\text{-X}_0}\Big/2.75\right)\cdot(-\sigma^0)$, *i.e.*, $k = 2.75$. The generality and precision of eq 8 (which is illustrated in Table II) indicates that this relationship may be used reliably to predict $\int_{\text{H}}^{p\text{-X}}$ values for the other Lewis acid adducts of Table I with additional well-behaved polar substituents of known σ^0 value. For these, the shielding of *m′*- and *p′*-substituted *p*-fluorobenzophenone derivatives relative to fluorobenzene is given by

$$\int_{\text{H(calcd)}}^{p\text{-X}} = \int_{\text{H(obsd)}}^{p\text{-X}_0} + \sigma^0\rho = \int_{\text{H}}^{p\text{-X}_0}\left(1 + \frac{\sigma^0}{2.75}\right) \quad (9)$$

The corresponding relationship for π-charge density given by eq 4 is

$$q_{\text{CO}} = q^0_{\text{CO}}[1 + (\sigma^0/2.75)] \quad (10)$$

where q^0_{CO} is the carbonyl carbon π-charge density in unsubstituted *p*-fluorobenzophenone.

Using the relationships established previously between σ values and F nmr substituent shielding effects in *meta*- and *para*-substituted fluorobenzenes, the present results may be used to calculate the σ values for the COC_6H_5, $CO(BF_3)C_6H_5$, and $CO(BCl_3)C_6H_5$ substituents.[16,19]

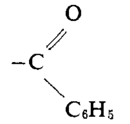
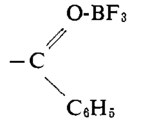
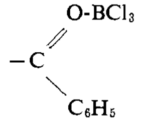
$$\sigma_{(p)} = \sigma_{\text{I}} + \sigma_{\text{R}} \quad (11)$$

$$\int_{m\text{-X}}^{p\text{-X}} = -29.5\sigma_{\text{R}} \quad (12)$$

$$\int_{\text{H}}^{m\text{-X}} = -7.1\sigma_{\text{I}} + 0.6 \quad (13)$$

In methylene chloride solutions, the additional shielding parameters have been obtained for *m*-fluorobenzophenone $\left(\int_{\text{H}}^{m\text{-X}} = -0.81 \text{ ppm}\right)$, its BF_3 adduct $\left(\int_{\text{H}}^{m\text{-X}} = -2.88 \text{ ppm}\right)$, and its BCl_3 adduct $\left(\int_{\text{H}}^{m\text{-X}} = -3.81 \text{ ppm}\right)$. These shieldings and the corresponding *p*-fluorobenzophenone results (Table I) yield the σ values listed in Table V. It is further illustrated by the $\bar{\rho}/6.3$ values given in Table V that the $\bar{\rho}$ values of Table II are essentially directly proportional to the $\sigma_{(p)}$ values as required by the discussion above.

Table V. σ Values from F Nmr Shielding Results

Substituent	σ_{I}	σ_{R}	$\sigma_{(p)}$	$\bar{\rho}/6.3$	$\Delta\sigma_{(p)}$
	+0.20	+0.20	0.40	0.39	. . .
	+0.49	+0.50	0.99	1.02	0.59
	+0.62	+0.59	1.21	1.22	0.81

It is clear from these results, eq 6, and $\Delta\int^{p\text{-X}}$ values for uncomplexed and complexed ketones (Tables II and III) that the change in σ value or charge density for the carbonyl functional group on formation of a Lewis acid adduct *is not* independent of the 3′ or 4′ substituent. However, by consideration of eq 10: for the carbonyl carbon of the uncomplexed ketone, $q_{(\text{u})} = q^0_{(\text{u})}[(1 + \sigma^0/2.75)]$; for the carbonyl carbon of the complex, $q_{(\text{c})} = q^0_{(\text{c})}[1 + (\sigma^0/2.75)]$. Therefore, for formation of the complex, $\Delta q = q_{(\text{c})} - q_{(\text{u})} = \Delta q^0[(1 + (\sigma^0/2.75)]$. Thus, for the substituent effect on formation of the complex, $\Delta q - \Delta q_0 = \Delta q_0(\sigma^0/2.75) \propto (\Delta\sigma_{\text{f0}})\sigma^0_{\text{X}}$, where $\Delta\sigma_{\text{f0}}$ = the change in $\sigma_{(p)}$ value for the unsubstituted functional group (*cf.* Table V) and σ^0_{X} is the σ value for the 3′- or 4′-polar substituent. Further consideration of matters relevant to complex formation is given in the following companion paper.