The Relationship between ¹⁹F Substituent Chemical Shifts and Electron Densities: *meta*and *para*-Substituted Benzoyl Fluorides

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The ¹⁹F substituent chemical shifts (SCS) of *meta*- and *para*-benzoyl fluorides are found to correlate well with substituent parameters using the dual substituent parameter (DSP) equation, indicating that they reflect electronic perturbations induced by the substituent. The direction of the SCS values is such that donating substituents cause upfield shifts whilst acceptors cause downfield shifts. STO-3G calculations indicate that substituents induce only very small changes in π -electron density about the fluorine atom, but that these changes correlate reasonably well with the observed SCS values. For the *para* series, the slope of the relationship between Δq_{π}^{F} and ¹⁹F SCS is 5000 ppm/electron, indicating the great sensitivity of the flourine atom to small changes in electron density.

INTRODUCTION

Because of the widespread use of ¹⁹F NMR as a structural probe in chemistry and biology there has been considerable interest in determining the factors which influence ¹⁹F substituent chemical shifts (SCS). In particular, there have been many attempts to rationalize ¹⁹F shifts in terms of electron distributions. The *para*-substituted fluorobenzene system was one of the earliest studied and calculations at the HMO¹, CNDO/2², and *ab initio* (STO-3G)³ levels of approximation have been made for this system.

It was found by the CNDO/2 results, and later confirmed from the *ab initio* calculations, that π rather than the total electron density gives the best correlation with fluorine SCS. For example, a plot of Δq_{π}^{F} versus ¹⁹F SCS gave a reasonably linear plot of slope 2100 ppm/electron³. The sign of the slope was in the expected direction, with donors causing upfield shifts and acceptors downfield shifts. The magnitude of the slope is approximately ten times greater than those given when ¹³C shifts are related to carbon π electron densities,³ indicating the greater sensitivity of fluorine to changes in electron density. (Plots of Δq_{π}^{C} vs δ^{C} typically have slopes of 100-300 ppm/electron.⁴) The corresponding trends in total electron density (Δq_{τ}^{F}) for the p-fluorobenzene series also predicted the correct direction for ¹⁹F SCS values, although the plot was somewhat more scattered.3 There was no apparent relationship between Δq_{σ}^{F} and SCS values for the p-fluorobenzenes.^{2,3}

In this paper we examine the relationship between electron density and ¹⁹F chemical shifts in the benzoyl fluoride system (1 and 2).

This system was chosen because it has a planar geometry and hence allows the π and σ components





of electron density to be separated. As in the fluorobenzenes (3), the fluorine atom is bonded to an sp^2 carbon. Calculations were carried out for both *meta* conformations (2a and 2b).

RESULTS AND DISCUSSION

The ¹⁹F substituent chemical shifts for the para and meta derivatives of benzoyl fluoride, measured at low concentration in CDCl₃, are shown in Tables 1 and 2. We have included substituents which cover a wide range of donor and acceptor properties so that meaningful analyses could be carried out by the dual substituent parameter (DSP) equation.⁵ However, a full basis set⁵ could not be obtained for the para series because of difficulties in synthesizing the amino and dimethylamino compounds, which tend to polymerize. Taft and co-workers have previously published data for some benzovl fluorides and our results are in agreement with their values.¹ Also shown in Tables 1 and 2 are STO-3G electron densities and, for comparison, the corresponding chemical shifts⁶ and electron densities³ for the fluorobenzene series.³

Para compounds.

The results for the *para* series in Table 1 show that the direction of ¹⁹F substituent chemical shifts is such that

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Table 1. Substituent chemical shifts (SCS) and electron densities^a $(\times 10^4)$ in *para*-benzoyl fluorides and fluorobenzenes

	p-Benzovl fluorides				p-Fluorobenzenes ^d				
	scs	$\Delta q_{\alpha}^{F} \Delta q_{\pi}^{F}$		Δq_{τ}^{F}	SCS	Δq_{σ}^{F}	Δq_{π}^{F}	Δq_{τ}^{F}	
NH ₂ (pl) ^e		38	8	46	-14.20 ^f	14	68	82	
NH ₂ (pyr)		27	5	32					
NH ₂ (tet)		24	5	29		6	52	58	
OMe ^e	-2.15	19	4	23	-11.54	-9	44	35	
F	-0.10	-2	1	-1	-6.70	-19	18	-1	
CI	0.31				-3.10				
Br	0.31				-2.50				
Me	-0.67	10	2	12	-5.46	6	15	21	
н	0.00		0	0	0.00	0	0	0	
CF₃	1.88	-21	-4	-25	5.15	27	-30	-57	
CN	2.09	-41	-4	-45	9.11	49	-54	-103	
COMe ^h	2.10	-18	-2	-20	6.60 [†]	-28	-25	-53	
COF	2.77	-32	-3	-35	11.40 ^r	-43 ⁱ	- 4 0'	-83 ⁱ	
NO ₂	3.23	-59	-6	-65	9.37	-67	-79	-146	

^aElectron densities (×10⁴), expressed relative to the unsubstituted compound. Positive values denote an increase in electron density. ^b ¹⁹F chemical shifts measured in CDCl₃, expressed (in ppm) relative to the unsubstituted compound. Benzoyl fluoride has a ¹⁹F chemical shift 17.61 ppm downfield from CFCl₃. Positive shifts are downfield. ^cChemical shifts measured in CCl₄, expressed (in ppm) relative to the unsubstituted compound. Data from Ref. 6c. ^dElectron densities for the fluorobenzenes from Ref 3. ^eCalculations were performed for planar, pyramidal²¹ and tetrahedral amino conformations. ^fRef. 6a. ^aSCS values are for OMe, calculations for OH. ^hSCS values are for COMe, calculations for CHO. ⁱThis work.

donating substituents cause upfield shifts, whilst withdrawing substituents cause downfield shifts. This trend is similar in direction to that in the fluorobenzenes, although the magnitude of the SCS values is much smaller. Clearly, the response of a fluorine nucleus to substituent effects changes from one series to another. A striking example of this can be seen for the benzyl fluoride series (4), a system which bears some similarity to the benzoyl fluorides (the fluorine is attached to a carbon adjacent to a benzene ring in both systems) where the ¹⁹F substituent chemical shifts go in the opposite direction^{7a} (i.e. donors cause downfield shifts and acceptors upfield shifts).

The various responses of a fluorine atom to substituent influences can be seen clearly by comparing DSP analyses⁵ for the three systems so far mentioned. The variation in sign and magnitude of the ρ_{I} and ρ_{R} values indicates the different susceptibility of fluorine to substituent effects in the three systems.

$$δ^{\rm F} = 3.3 \sigma_{\rm I} + 6.0 \sigma_{\rm R}^{-0} sd = 0.28;$$

 $f = 0.17 (1) p$ -benzoyl fluorides
 $δ^{\rm F} = -10.2 \sigma_{\rm I} - 17.2 \sigma_{\rm R}^{-{\rm BA}} sd = 0.37;$
 $f = 0.07 (2) p$ -benzyl fluorides⁷

$$\delta^{\rm F} = 7.0\sigma_{\rm I} + 30.6\sigma_{\rm R}^{0} \, sd = 0.56;$$

f = 0.08 (3) p-fluorobenzenes³

Equations (1–3) show that both inductive and resonance effects contribute to fluorine substituent chemical shifts (δ^F) in all these systems. The smaller ρ values in the benzoyl fluoride series reflect the smaller range in substituent-induced fluorine chemical shifts in this system. The negative ρ values for the benzyl fluorides are indicative of the reversed substituent chemical shifts in this system. As yet there has been no satisfactory explanation of this phenomenon, although it has been suggested that hyperconjugation may be important.⁸

Rationalization of the data for the benzoyl fluorides can be obtained by comparing the results with the well-known results for the fluorobenzene series. Unlike the benzyl fluorides, the fluorobenzenes and benzoyl fluorides have a well-defined (planar) geometry, and hence the results should not be complicated by uncertainties in the preferred conformation.

A comparison of the $\rho_{\rm R}$ values for these two systems shows that resonance effects are five times more important in the fluorobenzenes than the benzoyl

Table 2. Substituent chemical shifts (SCS) and electron densities^a $(\times 10^4)$ in *meta*-benzoyl fluorides and fluorobenzenes

			m-Benzoyl fluorides						m-Fluorobenzenes ^d				
		Con	formation	2a Conformation			2b						
	SCS ^b	Δq_{σ}^{F}	Δq_{π}^{F}	Δq_{τ}^{F}	Δq_{σ}^{F}	Δq_{π} F	Δq_{τ}^{F}	SCS°	$\Delta q_{\sigma}{}^{F}$	Δq_{π}^{F}	Δq_{τ}^{F}		
NH ₂ (pl) ^e	0.04 ^f	0	-2	-2	10	1	11	-0.50					
NH ₂ (pyr)		-3	-2	-5	5	0	5						
NH ₂ (tet)		-4	-2	-6	3	0	3		13	-18	-6		
ОМе ⁹	0.48	-13	0	-13	-13	-4	-17	1.05	-14	-23	-37		
F	1.25	-22	-1	-23	-18	-2	-20	3.30	-28	-20	-48		
CI	1.04												
Br	0.95							2.30					
Me	0.13	4	0	4	5	1	6	-1.18	12	-4	8		
Н	0.00	0	0	0	0	0	0	0.00	0	0	0		
CF₃	1.04	-19	-2	-21	-24	-2	-26	2.13	-42	-7	-49		
CN	1.31	-38	1	-39	40	-4	-44	2.75	-71	-12	-83		
COF	1.42	-23	-2	-25	-26	-2	-28	2.15	–48 ^h	~-5 ^h	-53 ^h		
NO ₂	2.07	-52	0	-52	-58	-8	-66	3.45	-102	-14	-116		

^aElectron densities (×10⁴), expressed relative to the unsubstituted compound. Positive values denote an increase in electron density. ^{b19}F chemical shifts measured in CDCl₃, expressed (in ppm) relative to the unsubstituted compound. Benzoyl fluoride has a ¹⁹F chemical shift 17.61 ppm downfield from CFCl₃. Positive shifts are downfield. ^cChemical shifts measured in CCl₄, expressed (in ppm) relative to the unsubstituted compound. Data from Ref. 6b. ^dElectron densities for the fluorobenzenes from Ref. 3. ^eCalculations were performed for planar, pyramidal²¹ and tetrahedral amino conformations. ^fSCS data are for the dimethylamino substituent. ^aSCS values are for OMe, calculations for OH. ^hThis work.

fluorides. The smaller resonance effects for the benzoyl fluorides indicate that conjugation of the fluorine atom with the benzene ring has been substantially reduced compared with the fluorobenzenes. In fact, the major resonance interaction in the benzoyl fluorides is between the substituent and the oxygen atom $(A \leftrightarrow B)$, rather than the fluorine atom. This is confirmed by the calculated electron densities on the oxygen atom.9 The importance of structures such as B has also been demonstrated by some data of Taft's which suggest that the COF group has a $\sigma_{\rm B}^{0}$ value of 0.31. (The $\sigma_{\rm R}^{0}$ value for COF was obtained from data in Ref. 10.) However, the fact that there is still some resonance contribution to ¹⁹F SCS values, as seen by the $\rho_{\rm R}$ value of 6.0 in Eqn (1), indicates that resonance conjugation between the para substituent and the fluorine atom has not been eliminated completely. This suggests that there may be some contribution from structures such as C which allows formal conjugation of the fluorine with the substituent X (C \leftrightarrow **B**).



The $\rho_{\rm I}$ values for the benzoyl fluorides are also smaller than those for the fluorobenzenes. Inductive effects on fluorine substituent chemical shifts have been interpreted largely in terms of two mechanisms, namely π inductive effects,^{11–13} and direct field effects.¹⁴ Although the particular blend of these effects for the benzoyl fluorides is not known, it seems certain that both mechanisms would predict smaller effects in the benzoyl fluorides compared with the fluorobenzenes.

In terms of the direct field effect, the $\rho_{\rm I}$ values should be reduced both because of an increased distance between the fluorine atom and the substituent, and also because the C—F bond has been orientated at an angle to the C—X bond. The π inductive effect is also reduced in the benzoyl fluorides because the fluorine is no longer attached directly to the benzene ring as in the fluorobenzenes. However, there is evidence that *para* substituents can polarize a distant carbonyl group¹⁵ and since the fluorine is bonded to this polarizable system then it seems likely that π inductive effects have not been completely eliminated in the benzoyl fluoride system. It should be noted that in many of the previously studied systems where the π inductive effect has been considered to contribute to ¹⁹F SCS values, the fluorine atom has been bonded to an aromatic ring and hence the π inductive effect involved polarization of the phenyl ring electrons.¹³

Since there has been a reasonably satisfactory explanation of fluorine SCS values in terms of electron density for the fluorobenzenes,^{2,3} but not for the benzyl fluorides,^{7a} we performed electron density calculations on the benzoyl fluorides to see whether a relationship existed for this series.

From the STO-3G results for the *para* compounds in Table 1 it can be seen that donating substituents increase the σ , π and total electron densities about the fluorine whilst these are decreased by the withdrawing substituents. The similarity in the direction of response for π , σ and total electron densities on the fluorine atom is not normally observed for carbon atomic positions within a molecule. The influence of substituents on the σ electron density is normally in the opposite direction to their influence on π density.^{2,3} For example, in the *p*-benzoyl fluorides we have noted that for the position *para* to X (C-1), the relationship between $\Delta q_{\sigma}^{\ C}$ and $\Delta q_{\pi}^{\ C}$ is given by Eqn (4), whilst Eqn (5) specifies the relationship for the C-alpha atom.

$$\Delta q_{\sigma}^{\ C} = -0.56 \Delta q_{\pi}^{\ C} \qquad r = 0.995 \tag{4}$$

$$\Delta q_{\sigma}^{\ C} = -1.43 \Delta q_{\pi}^{\ C} \qquad r = 0.999 \tag{5}$$

For both of these carbon atomic positions, substituents which increase π electron density cause a proportional decrease in σ electron density. The relationship between $\Delta q_{\sigma}^{\ F}$ and $\Delta q_{\pi}^{\ F}$ for the fluorine atom in *para*-benzoyl fluorides is not as precise as those for C-1 and C-alpha and, as we noted above, has a positive, rather than a negative slope. Table 1 shows that, in general, an increase in π electron density about the fluorine is associated with an increase in σ electron density. It is interesting to note that CNDO calculations² did not show any linear relationship between $\Delta q_{\sigma}^{\ F}$ and $\Delta q_{\pi}^{\ F}$ on the fluorine atom in *p*-fluorobenzenes. Recent *ab initio* calculations also show that such a relationship does not exist in the fluorobenzene series.³

Because $\Delta q_{\pi}^{\ F}$ was found to be the theoretical parameter of choice for correlating fluorine SCS values in the fluorobenzenes,³ we have plotted this parameter against the fluorine SCS values for the benzoyl fluorides in Fig. 1. It should first be noted that the fluorine atom in the benzoyl fluorides is not in a formally conjugating position and hence large changes in $\Delta q_{\pi}^{\ F}$ would not be expected. Indeed, the range in $\Delta q_{\pi}^{\ F}$ values is extremely small when compared with systems where the fluorine atom is conjugated with the substituent, e.g. fluorobenzenes, or $\beta\beta$ -difluorostyrenes.¹⁶ In this respect it can be seen that the *ab initio* calculations are a vast improvement over the simple HMO method which predicted larger changes in $\Delta q_{\pi}^{\ F}$

The slope of the relationship in Fig. 1 is 5000 ppm/electron, which is somewhat higher than that for the fluorobenzenes. This indicates that the sensitivity factor which relates the fluorine chemical shift to the local π electron density is altered when the structural environment of the fluorine atom is changed. There is considerable precedence for this



Figure 1. Plot of ¹⁹F SCS (in ppm) versus π electron density on the fluorine atom in *p*-benzoyl fluorides. Slope = 5000 ppm/electron (r = 0.993) for the correlation excluding COMe and COF (slope = 5300, r = 0.961 including all points).

type of behaviour in ¹³C chemical shifts. (We have noted that the shift charge ratio (SCR), which relates the ¹³C SCS to the local π electron density, varies in different series of disubstituted benzenes.⁴) It should also be noted that although the sensitivity factor relating fluorine SCS and π densities is an order of magnitude larger than the factor which relates ¹³C SCS and π densities, ¹⁹F SCS values are of the same magnitude as ¹³C SCS. This is because substituentinduced perturbations of π density about fluorine are generally smaller than those for carbon atomic positions. Ewing and Toyne have also recently made this observation.¹²

Although $\Delta q_{\pi}^{\ F}$ has been plotted against the fluorine SCS, either $\Delta q_{\sigma}^{\ F}$ or $\Delta q_{\tau}^{\ F}$ would give reasonable, although somewhat less precise, correlations with ¹⁹F SCS. Thus although it seems intuitively more reasonable to select $\Delta q_{\pi}^{\ F}$ as the term of choice for correlating electron density with SCS, the current results show that the σ and total electron density results cannot be ruled out altogether. For the *para* position in benzene derivatives, $\Delta q_{\sigma}^{\ C}$ has often been rejected as it predicts the wrong direction for chemical shifts. In system 1, however, $\Delta q_{\sigma}^{\ F}$ predicts the correct direction for SCS results, as do $\Delta q_{\pi}^{\ F}$ and $\Delta q_{\tau}^{\ F}$. The slopes of the relationships between ¹⁹F SCS and $\Delta q_{\sigma}^{\ F}$ or $\Delta q_{\tau}^{\ F}$ are 670 ppm/electron (r = 0.938) and 600 ppm/electron (r = 0.944), respectively.

The difficulty in deciding which electron density terms are important in determining SCS values arises because of the previously mentioned relationship between Δq_{σ}^{F} and Δq_{π}^{F} . The magnitude and sign of the proportionality constant relating the two terms changes for different atomic positions within a molecule. For the fluorine atom of the benzoyl fluorides it is especially difficult to assess the relative importance of each of the terms because of the similarity in the direction of response of $\Delta q_{\sigma}^{\rm F}$ and $\Delta q_{\pi}^{\rm F}$ (and hence $\Delta q_{\tau}^{\rm F}$) to substituent effects.

Meta compounds

The range of shifts in the *meta* series of benzoyl fluorides is smaller than for the *para* series and depends more on the inductive effect of the substituent than its resonance effect. This is illustrated by a DSP analysis [Eqn (6)]. The corresponding results for the *meta*-benzyl fluorides and fluorobenzenes are also shown.

$$\delta^{\rm F} = 2.5\sigma_{\rm I} - 0.3\sigma_{\rm R}^{0} \, sd = 0.25;$$

f = 0.23 (6) *m*-benzoyl fluorides
$$\delta^{\rm F} = -8.5\sigma_{\rm I} - 2.8\sigma_{\rm R}^{0} \, sd = 0.26;$$

f = 0.07 (7) *m*-benzyl fluorides^{7b}

$$\delta^{\rm F} = 5.3\sigma_{\rm I} + 0.8\sigma_{\rm R}^{0} \, sd = 0.50;$$

f = 0.21 (8) *m*-fluorobenzenes³

In Eqn (6) the ratio of resonance to inductive effects is 0.3/2.5 = 0.1 which is much smaller than the corresponding ratio (6.0/3.3 = 1.8) for the *para* series. Thus, a comparison of Eqns (1) and (6) shows that there is a drastic drop in the importance of resonance effects in going from the *para* to the *meta* series. A similar trend was seen in the fluorobenzene^{3.6} series [compare Eqns (3) and (8)].

The ratio of para to meta inductive effects is still a matter which is surrounded by controversy. Shorter^{1'} considers that, in general, direct field effects or through-bond effects should be larger in the meta position, whilst π inductive effects should be smaller. The overall effect could therefore be that para and meta inductive contributions may have similar magnitudes. In fact, the ratio of meta/para inductive effects depends critically on the type of measurement being made (e.g. ionization constants or chemical shifts) and on the site of measurement. Thus, whilst it has been found that $\rho_{\rm I}$ (meta) $< \rho_{\rm I}$ (para) for the fluorobenzenes $(3)^{3,6}$ (where ¹⁹F SCS values were the measured quantity) it has also been noted that $\rho_{I}(meta) > \rho_{I}(para)$, when ¹³C SCS values on the Calpha atom are measued for compounds of the general form 5.15



The fact that $K_{I} = {}_{\rho I}(meta)/{}_{\rho I}(para)$ is less than 1.0 in system 3, but greater than 1.0 in 5, indicates that different mechanisms dominate the inductive components of SCS values in the two systems. In fact, that K_{I}

is less than 1.0 in 3 is in accord with a π inductive effect mechanism being the main contributor to the inductive component of fluorine SCS values in this system. In this case the π electrons of the benzene ring are polarized by the inductive effect of the substituent X. Further support for this suggestion can be seen in the data for systems 6 and 7.^{14d-18} The results show that $\rho_{\rm I}$ (system 6)/ $\rho_{\rm I}$ (system 7) = 2.5/1.5 = 1.67, indicating that the larger $\rho_{\rm I}$ value occurs when the fluorine lies along the main axis of polarization of the phenyl ring electrons.

It has been suggested that in system 5 a field-effect mechanism is consistent with the $\rho_{\rm I}(meta)/\rho_{\rm I}(para)$ ratio being greater than unity, although, as we noted ¹⁵ in that work, the effect is independent of the total electron density on the carbon atom, and hence inconsistent with a classical direct field effect. However, the experimental data is in accord with a π inductive effect whereby the π electrons of the carbonyl are polarized by (the field effect of) the substituent. It is clear in such cases that the term 'field-induced π polarization has more merit than the often abused term π -inductive effect.

The benzoyl fluorides are structurally similar to compounds of type 5 and hence one would expect $\rho_{\rm I}(meta)$ to be greater than $\rho_{\rm I}(para)$ for the C-alpha SCS values in this system. Indeed, we have measured these carbon SCS values9 and find this to be true. This is in contrast to the fluorine SCS values, where $\rho_{I}(meta) < \rho_{I}(para)$. It is also interesting to note that the ratio $K_{I} = \rho_{I}(meta)/\rho_{I}(para)$ for the fluorine SCS values of the benzoyl fluorides is equal to the same ratio for the fluorobenzenes. As we noted above, the observed $K_{\rm I}$ values for the fluorobenzenes seem to indicate that the inductive component of the fluorine shifts is largely due to π polarization of the phenyl ring electrons. Because of the two possible conformations of the meta-benzoyl fluorides it is difficult to assess the relative importance of direct field effects, or to decide whether π polarization of the carbonyl group has a significant influence on the fluorine SCS values in this system. We do note, however, that the trend $\rho_{\rm I}(meta) < \rho_{\rm I}(para)$ also holds for the fluorine SCS values in the benzyl fluoride system, as well as in systems 6 and 7.

Rationalization of the experimental data for the *m*-benzoyl fluorides can be obtained from the theoretical results. For the *meta* series the calculations were performed for the two conformations 2a and 2b. The results in Table 2 show that the changes in $\Delta q_{\pi}^{\ F}$ for *meta* conformation 2a are almost negligibly small. On the other hand, the substituent influence on $\Delta q_{\pi}^{\ F}$ for conformation 2b is a little larger, but still smaller than for the *para* series. Correspondingly, the changes in $\Delta q_{\sigma}^{\ F}$ and $\Delta q_{\pi}^{\ F}$ for either of the two *meta* conformations are also smaller than the same terms for the *para* series. These results appear to be in accord with the generally smaller *meta* ¹⁹F SCS values.

We have found that the energy differences between the two *meta* conformations for a given substituent are extremely small, and hence believe that an average of the electron densities for the two conformations should give the most realistic picture of the actual electron density. Figure 2 shows a plot of the average



Figure 2. Plot of ¹⁹F SCS (in ppm) versus π electron density on the fluorine atom in *m*-benzoyl fluorides. Slope = 4500 ppm/electron, *r* = 0.929.

 $\Delta q_{\pi}^{\ F}$ values against ¹⁹F SCS values for the *meta* compounds. Whilst the plot is less satisfactory than that for the *para* compounds, it does indicate that a reasonable correlation exists between $\Delta q_{\pi}^{\ F}$ and $\delta^{\rm F}$ in the *meta* compounds. It is difficult to gain an accurate assessment of the slope of the relationship because of the small range in $\Delta q_{\pi}^{\ F}$ values; however, it is in the vicinity of 4500 ppm/electron. For the *m*-fluorobenzenes³ $\Delta q_{\pi}^{\ F}$ was found to be unsatisfactory for correlating $\delta^{\rm F}$, although $\Delta q_{\pi}^{\ F}$ did give a reasonable relationship. For our series we have found that $\Delta q_{\sigma}^{\ F}$ or $\Delta q_{\pi}^{\ F}$ correlate reasonably well with $\delta^{\rm F}$, with slopes of 340 (r = 0.952) and 320 ppm/electron (r = 0.951) respectively. The slope for $\Delta q_{\pi}^{\ F}$ is similar to that found for the *m*-fluorobenzenes.³

CONCLUSIONS

Our results show that the fluorine atom in *meta* or *para* substituted benzoyl fluorides is a sensitive probe for substituent effects. DSP analyses of the results indicate that resonance effects make an important contribution to the ¹⁹F SCS values in the *para* series, but not in the *meta* series. Inductive effects of the substituent X also contribute to the SCS values in both the *meta* and *para* series. In the *para* series, the small substituent induced changes in Δq_{π}^{F} are found to be related to the SCS values. Although Δq_{σ}^{F} and Δq_{τ}^{F} also give reasonable correlations for this system, we consider that changes in Δq_{π}^{F} account for the major contribution to δ^{F} . The linear relationship between Δq_{π}^{F} and Δq_{σ}^{F} or Δq_{τ}^{F} accounts for the fact that these latter terms also correlate with δ^{F} .

EXPERIMENTAL

The benzoyl fluorides were prepared from the reaction of the corresponding benzoic acid with sulphur tetrafluoride.^{6b} We are grateful to Professor R. W. Taft for providing us with further details on the synthesis. The *ab initio* calculations were performed on a DEC-10 computer using a version of the GAUSSIAN-70 program.¹⁹ Because of the size of the molecules involved we were limited to using an STO-3G basis set, with standard geometries.^{20,21} ¹⁹F spectra were run on a JEOL PFT-100 NMR spectrometer at 94 MHz using 5 mm tubes with sample concentrations of 0.2% v/w in deuterochloroform. Substituent chemical shifts were measured directly by using the unsubstituted compound as an internal reference. 8 K data points were

1. R. W. Taft, F. Prosser, L. Goodman and G. T. Davis, J. Chem. Phys. 38, 380 (1963).

- 2. R. T. C. Brownlee and R. W. Taft, J. Am. Chem. Soc. 92, 7007 (1970).
- W. J. Hehre, R. W. Taft and R. D. Topsom, Prog. Phys. Org. Chem. 12, 159 (1976).
- 4. J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sadek, V. O. Lopez, R. W. Taft, *J. Org. Chem.* in press.
- S. Ehrenson, R. T. C. Brownlee and R. W. Taft, Prog. Phys. Org. Chem. 10, 1 (1973); P. R. Wells, S. Ehrenson and R. W. Taft, Prog. Phys. Org. Chem. 6, 147 (1968).
- (a) 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); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen and G. T. Davis, J. Am. Chem. Soc. 85, 709 (1963); (c) R. T. C. Brownlee, S. K. Dayal, J. L. Lyle and R. W. Taft, J. Am. Chem. Soc. 94, 7208 (1972).
- (a) J. Bromilow, R. T. C. Brownlee and A. V. Page, *Tetrahedron Lett.* 3055 (1976); (b) A. Page, BSc. (Hons) Thesis, La Trobe University, Australia (1975).
- 8. W. Adcock and A. N. Abeywickrema, *Tetrahedron Lett.* 1809 (1979).
- 9. R. T. C. Brownlee and D. J. Craik, unpublished results.
- 10. See Refs 6 (a and b), using Eqn (4) of Ref. 6 (a).
- (a) S. K. Dayal, S. Ehrenson and R. W. Taft, J. Am. Chem. Soc. 95, 5595 (1973); (b) J. Fukunaga and R. W. Taft, J. Am. Chem. Soc. 97, 1612 (1975); (c) G. L. Anderson, R. C. Parish and L. M. Stock, J. Am. Chem. Soc. 93, 6984 (1971).

used, with a spectral width of 1000 Hz, resulting in a digital resolution of 0.003 ppm.

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REFERENCES

- 12. D. F. Ewing and K. J. Toyne, J. Chem. Soc. Perkin Trans. 2 243 (1979).
- 13. W. F. Reynolds, Tetrahedon Lett. 675 (1977).
- (a) W. Adcock and B. D. Gupta, J. Am. Chem. Soc. 97, 6871 (1975); (b) W. Adcock and T. C. Khor, Tetrahedron Lett. 3063 (1976); (c) W. Kitching, M. Bullpitt, D. Gartshore, W. Adcock, T. C. Khor, D. Doddrell and I. D. Rae, J. Org. Chem. 42, 2411 (1977); (d) W. Adcock and T. C. Khor, J. Am. Chem. Soc. 100, 7799, (1978); (e) W. Adcock and D. P. Cox, J. Org. Chem. 44, 3004 (1979).
- J. Bromilow, R. T. C. Brownlee and D. J. Craik, Aust. J. Chem. 30, 351 (1977).
- W. F. Reynolds and G. K. Hamer, J. Am. Chem. Soc. 98, 9296 (1976).
- J. Shorter, Correlation Analysis in Chemistry: Recent Advances, Chapt. 4. Plenum, New York (1978).
- 18. W. Adcock and T. C. Khor, *Tetrahedron Lett.* 3769 (1977). 19. QCPE Program 236, W. J. Hehre, R. F. Stewart and J. A.
- Pople, J. Chem. Phys. 51, 2657 (1969). 20. J. A. Pople and M. Gordon, J. Am. Chem. Soc. 89, 4253
- (1967).
 21. W. J. Hehre, L. Radom and J. A. Pople, *J. Am. Chem. Soc.*94, 1496 (1972).

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