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SUBSTITUTED METHYL GROUPS

SUBSTITUENT EFFECTS[1]

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Abstract—The substituent parameters for the series of mono-, di- and trisubstituted Me groups, CH_2X, CHX_2, and CX_3 where X is F, Cl, Br, OMe, SCF_3, and CN, have been determined from F^{19} NMR measurements on the corresponding *meta*- and *para*-fluorotoluenes. An additive linear effect of substitution is found only for the cyano substituent. A saturation effect noted for the groups where X is F, Cl, Br and SCF_3 (particularly chloro and bromo) after disubstitution is attributed to through-space interactions of unshared p-electrons of these substituents with the π system of the ring.

THE electronic effects of halogenated substituents are of considerable interest, but the origin and mechanism of transmission of the observed effects continue to be controversial.[2] In particular, the trifluoromethyl group has been found to have a resonance withdrawal effect[3,*] which is not explained by conventional resonance pictures as normally used for nitro or cyano groups.

This +R effect was initially explained by a fluoride ion hyperconjugation or a π-inductive effect. As a result of new data, an alternative explanation of p–π interaction was proposed.[4] Like the accepted picture for resonance interaction of fluorine with an aromatic ring, a through-space return of electron density from the fluorine of the trifluoromethyl group was suggested to in part cancel the inductive electron withdrawal from the *meta* position of the ring. Thus the *para* position appeared to have an enhanced deactivation. Through-space interaction involving fluorine has also been concluded from ESR studies.[5]

This p–π interaction mechanism has been criticized[6] and was not apparent from analysis of p*Ka* data on bicyclooctane acids.[7]

This paper reports and summarizes results on a series of substituted Me's that are pertinent to the question of interaction between the unshared p-electrons of substituents on a Me group and the π system of an aromatic nucleus to which the Me group is bonded.[8]

DISCUSSION

The trisubstituted Me groups CX_3, trifluoromethyl, trichloromethyl, and tribromomethyl, are all strongly electron-withdrawing inductively since the chemical shift for the *meta* fluorine is downfield from that of fluorobenzene. The inductive effect of the CX_3 group decreases from fluorine to bromine in relative proportion to the electronegativity of the halogen. The larger downfield shift for the *para* fluorine (positive σ_R) would seem to indicate a resonance-enhanced electron widthdrawal for all trihalo-

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[*] A −R effect is reported for CF_3(σ_m 0·53, σ_p 0·48) in reaction of the benzoic acids with diazomethane.

methyls, but the trichloromethyl and tribromomethyl do not appear as effective as the trifluoromethyl. Now contrast these results to those for the tricyanomethyl where the downfield shift of the *para* fluorine is not significantly different from that of the *meta* shift even though the inductive effect of the tricyanomethyl group is much greater than the trihalomethyl. In other words, the tricyanomethyl is a much stronger electron withdrawing group inductively but does not show a significant resonance effect. Actually in benzene as solvent,[14] the *para* shift is upfield from the *meta* so that a small $-$R effect would be calculated. If the π inductive effect[17] was the major origin of apparent resonance effects, then the tricyanomethyl with the much greater inductive electron-withdrawing character should show a much larger +R effect than the trihalomethyl groups. At this point, we can definitely conclude that the transmission of the electronic effects by resonance must be different for the trihalomethyl groups than for tricyanomethyl and that a π inductive mechanisms originating simply from a polar field effect does not operate to a significant extent. We attribute this difference to the unshared p-electrons surrounding the spherical halogen which interact with the π system of the aromatic ring; in contrast the rod-like cyano group with a cylindrical π system apparently does not significantly interact with the aromatic π system.

Comparison of the F^{19} NMR data for the mono-, di-, trisubstituted Me series is also informative. As expected, the electron withdrawing character of the group increases with substitution. However, for the trihalomethyl groups, particularly in the chloro and bromo series, the effect definitely drops off so that trisubstitution is not significantly better than disubstitution. In other words, we appear to have some sort of saturation effect for halomethyl groups, particularly with bromine and chlorine, where two substituents do as well as three. This is not the case for the cyano substituent, where the inductive effect of the cyano-substituted Me group increases additively with substitution. These data are much more clearly seen in the graphs in Fig. 1. The saturation effects show up to some extent on the plot of *meta* shifts *vs* substitution but are much clearer on the plots of *para* shift *vs* extent of substitution and also on the *para-meta* difference graph. In regards to the resonance effect, the cyano substituent behaves as might be predicted and gradually reduces the apparent

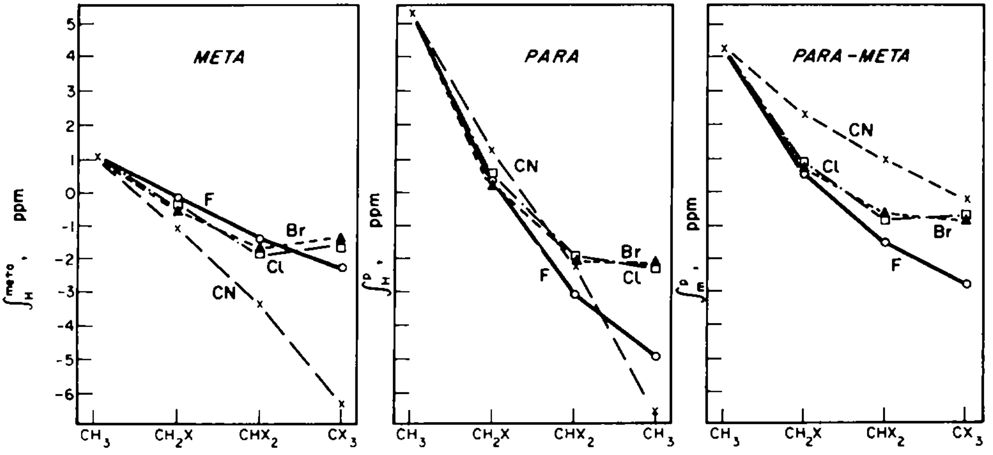

Fig 1. Plot of F^{19} NMR Shifts for $FC_6H_4CH_nX_{3-n}$ *VS* Extent Substitution of Me Group

TABLE 1. PHYSICAL AND ANALYTICAL PROPERTIES OF NEW α-SUBSTITUTED FLUOROTOLUENES

X of FC_6H_4X		bp, °C (mm)	n_D^{25}, or mp, °C and solvent recrystallization	Method of Preparation[a] (% yield)	Formula mol wt	Analysis								
						Carbon		Hydrogen		Fluorine				
						Calc	Found	Calc	Found	Calc	Found	Other	Calc	Found
CHF_2	*meta*	61° (60 mm)	—	A(62)	$C_7H_5F_3$	57·5	57·5	3·45	3·73	—	—	—	—	—
	para	61° (58 mm)		A(70)	(146·1)	—	58·1	—	4·07	—	—	—	—	—
$CHCl_2$	*para*	83 (6)	1·5255	B(53)	$C_7H_5Cl_2F$ (179·0)	—	—	—	—	10·6	10·4	Cl	39·6	39·0
$CHBr_2$	*para*	80 (2.4)	1·5849	C1(17)	$C_7H_5Br_2F$ (268·0)	31·4	31·5	1·88	2·11		—	Br	59·7	59·6
CBr_3	*meta*	85 (0·7)	1·6196	C2(57)	$C_7H_4Br_3F$	24·2	24·9	1·16	1·39	5·48	5·46	Br	69·1	69·1
	para	82 (0·7)	1·6195	C2(68)	(346·9)	—	24·5	—	1·44	—	5·48	—	—	69·2
$CClF_2$	*meta*	67·5 (76)	1·4447	B(80)	$C_7H_4ClF_3$	46·6	46·4	2·24	2·39	31·6	31·9			
	para	61 (52)	1·4450	B(68)	(180·6)	—	46·3	—	2·55	—	—	Cl	19·6	19·8
$CH(SCF_3)_2$	*meta*	71 (12)	1·4471	D(44)	$C_9H_5F_7S_2$	34·8	34·0	1·62	1·70	—	—	S	20·7	19·8
	para	74 (12)	1·4468	D(91)	(310·3)	—	34·8	—	1·74	—	—	—	—	20·6
$C(SCF_3)_3$	*meta*	62 (0·5)	1·4597	D(69)[b]	$C_{10}H_4F_{10}S_3$	29·3	29·3	0·98	1·30	46·3	46·0	S	23·4	23·4
	para	59 (0·5)	1·4601	D(80)	(410·3)	—	29·5	—	1·17	—	46·0	—	—	23·5
CH_2OCH_3	*meta*	65 (16)	1·4761	E(37)	C_8H_9FO	—	—	—	—	13·6	13·8	—	—	—
	para[c]	60 (20)	1·4750	E(59)	(140·2)	—	—	—	—	—	13·6	—	—	—
$CH(OCH_3)_2$	*meta*	84 (16)	1·4718	F(50)	$C_9H_{13}FO_2$	63·5	63·1	6·52	5·97	11·2	11·9	—	—	—
	para	84 (16)	1·4709	F(47)	(172·2)	—	63·1	—	6·34	—	11·0	—	—	—
$C(OCH_3)_3$	*meta*	64 (1·2)	1·4706	G(76)	$C_{10}H_{13}FO_3$	60·0	60·3	6·54	6·71	9·49	9·49	—	—	—
	para	64 (0·8)	1·4693	G(47)	(200·2)	—	60·4	—	6·57	—	9·44	—	—	—
$CH(CN)_2$	*meta*	—	79–80 (hexane)	H(90)	$C_9H_5FN_2$	67·5	67·7	3·15	2·84	11·9	11·9	N	17·5	17·8
	para	—	75–75·5 (hexane)	H(43)	(160·2)	—	67·4	—	2·84	—	12·1	—	—	17·8
$C(CH_3)(CN)_2$	*meta*	65 (0·35)	1·4990	I(78)	$C_{10}H_7N_2F$	—	—	—	—	10·9	10·9	N	16·1	16·3
	para	70 (0·50)	1·4905	I(87)	(174·2)	—	—	—	—	—	10·9	—	—	16·0

[a] *Letter (and numerical) designation refers to procedure listed in Experimental Section.*

[b] A purple impurity, apparent also from F^{19} NMR spectra, was removed by treatment with concentrated sulfuric acid.

[c] Reported used for solvolysis studies by A. M. Avedikian, J. Chaput, S. C. N'Ketsia, J. Dausque, A. Kergomard, J.-M. Rondier and H. Tatou. *Bull. Soc. Chim. Fr.*, 95 (1966) but no characterization given.

TABLE 2. KNOWN α-SUBSTITUTED FLUOROTOLUENES: PHYSICAL PROPERTIES AND SOURCE

X of FC_6H_4X		bp, °C (mm)	n_D^{25}		Source or Method of Preparation and Reference
CH_3	*meta*	115	1·4671	*a*	
	para	116–117	1·4663	*a*	
CH_2F	*meta*	35 (20)	1·4633	*b*	$HgF_2 + FC_6H_4CH_2Br \xrightarrow[\text{pyridine cat.}]{CHCl_3}$
	para	50 (10)	1·4673	*b, c*	$AgF + FC_6H_4CH_2Br \xrightarrow[\text{sulfone}]{\text{tetramethylene}}$
CF_3	*meta*	100	1·3980	*a*	
	para	103	1·3984	*a*	
CH_2Cl	*meta*	64 (6)	1·5109	*d*	$FC_6H_4CH_3 + Cl_2 \xrightarrow[CCl_4]{h\nu}$
	para	67 (6)	1·5109	*d*	
$CHCl_2$	*meta*	77 (6)	1·5238	*e, f*	$FC_6H_4CH_3 + 2Cl_2 \xrightarrow[CCl_4]{h\nu}$
CCl_3	*meta*	88 (7·3)	1·5325	*g*	$FC_6H_4CH_3 + \text{excess } Cl_2 \xrightarrow[100\text{–}130]{h\nu}$
	para	76 (4·3)	1·5321	*g*	
CH_2Br	*meta*	81 (7·5)	1·5443	*h*	$FC_6H_4CH_3 + Br_2 \xrightarrow[CCl_4]{h\nu}$
	para	64·5 (6)	1·5450	*h*	
$CHBr_2$	*meta*	77 (2·4)	1·5847	*e*	$FC_6H_4CH_3 + 2Br_2 \xrightarrow[CCl_4]{h\nu}$
CH_2SCF_3	*meta*	64·5 (12)	1·4582	*i*	$FC_6H_4CH_2Br + Hg(SCF_3)_2 \xrightarrow{CCl_3F}$
	para	64 (12)	1·4573	*i*	
CH_2CN	*meta*	124–126 (10)	1·4988	*a*	
	para	117–118 (18)	1·4980	*a*	
$C(CN)_3$	*meta*	92 (3·5)	1·4954	*j*	$FC_6H_4CH_2CN \xrightarrow[2ClCN]{2NaH}$
	para	91–92 (3·3)	1·4958	*j*	

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[a] Pierce Chemical Company.

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normal resonance donation of the Me group to zero. However, the halogen substituents quickly cause an apparent positive resonance withdrawal.

A possible explanation for this effect is through-space interaction between the unshared p electrons of the halogens and the π system of the ring. For the larger halogens, chlorine and bromine, the trisubstituted groups must have considerable steric interaction with possible restricted rotation. With disubstitution, the hydrogen can be located in a position such that interaction with the *ortho* hydrogen of the rings could restrict rotation of the group so that the halogens above and below

TABLE 3. NMR F^{19} CHEMICAL SHIFTS[a] OF α-SUBSTITUTED FLUOROTOLUENES, FC_6H_4X AND SUBSTITUENT PARAMETERS FOR SUBSTITUTED METHYL GROUPS

Substituent X	H $\int_{H}^{m\text{-}X}$	$\int_{H}^{p\text{-}X}$	$\int_{m\text{-}X}^{p\text{-}X}$	σ_I	$\sigma_{R^{\cdot}}$
CH_3	+1·10 (1·18)	+5·44 (5·40)	+4·34	−0·07	−0·15
CH_2CH_3	(+0·75)[b]	(+5·00)[b]	+4·25	−0·02	−0·14
$CH(CH_3)_2$		(4·75)[b]			
$C(CH_3)_3$	(+0·45)[b]	(+5·55)[b]	+5·10	+0·02	+0·17
CH_2F	−0·28	+0·25	+0·53	+0·12	−0·02
CHF_2	−1·48	−3·14	−1·66	+0·29	+0·06
CF_3	−2·20	−5·09	−2·89	+0·39	+0·10
$CClF_2$	−2·09	−4·39	−2·30	+0·38	+0·08
CH_2Cl	−0·53 (−0·45)	+0·50 (+0·45)	+1·03	+0·16	−0·04
$CHCl_2$	−1·56 (−1·53)	−2·16 (−2·25)	−0·72	+0·30	+0·02
CCl_3	−1·51	−2·31	−0·80	+0·30	+0·03
CH_2Br	−0·50	+0·22	+0·72	+0·16	−0·02
$CHBr_2$	−1·51	−2·21	−0·70	+0·30	+0·02
CBr_3	−1·26	−2·21	−0·95	+0·26	+0·03
CH_2CN	−1·28 (−1·1)	+1·07 (+1·20)	+2·35	+0·26	−0·08
$CH(CN)_2$	−3·29[c]	−2·30[c]	+0·99	+0·55	−0·03
$C(CH_3)(CN)_2$	−3·88	−2·16	+1·72	+0·63	−0·06
$C(CN)_3$	−6·46	−6·71	−0·25	+0·98	+0·01
CH_2OCH_3	+0·53	+2·41	+1·88	−0·01	−0·06
$CH(OCH_3)_2$	+0·50	+1·38	+0·88	−0·02	−0·03
$C(OCH_3)_3$	+0·41	+0·62	+0·21	−0·03	−0·01
CH_2SCF_3	−0·92	+0·73	+1·65	+0·21	−0·06
$CH(SCF_3)_2$	−2·53	−2·43	+0·10	+0·44	0
$C(SCF_3)_3$	−2·90	−3·99	−1·09	+0·49	+0·04

[a] In parts per million. Probable error is 0·04 ppm. Unless indicated otherwise all data are in $CFCl_3$ solvent at infinite dilution. Values in parenthesis are literature values in CCl_4 or a hydrocarbon solvent from ref. 15, unless indicated otherwise.

[b] Private communication from Professor R. W. Taft.

[c] Benzene solvent (insoluble in CCl_3F).

can interact to the fullest extent with the π system of the ring. These steric differences are clearly seen on space-filling molecular models. Because cyano is a rod-like substituent, the cyano group has only a small steric effect and does not appear to interact directly with the π system. However, the idea that the saturation effect results from steric interactions can also be argued for the hyperconjugation mechanism.

The chlorodifluoromethyl group is intermediate between CF_3 and CCl_3 as expected. The methyldicyanomethyl group is very close to the dicyanomethyl, and the small differences could be due to the different solvent required because of solubility problems. The slightly smaller inductive withdrawal for the dicyanomethyl could result from hyperconjugative effects derived from the strongly acidic benzylic hydrogen. Solvent effect studies on the cyano series only confirm previous observations that field effects are extremely important in transmission of electronic effects of cyanocarbon groups.[14]

'The effect of SCF_3 group substitution on the electronic properties of the methyl group is very similar to those observed for halogens including the saturation effect from two to three substituents. Again, p–π interaction from the p-electrons of both sulfur and fluorine could be significant, although the consequences of d-orbital participation, which is enhanced by the strong electron-withdrawing effect of the trifluoromethyl groups,[18] is not readily assessed.

The substitution in the Me group by OMe surprisingly results in very little apparent electronic change, almost the same as for substitution by Me. Possibly the Me groups are primarily oriented to interact with the π system, so that the unshared p-electrons of the oxygen do not. A similar result is the lack of any apparent interaction or back-bonding effects[19] in the system $(CH_3)_2N(CH_2)_nC_6H_4CO_2CH_3$ and suggests that p–π interaction may be repulsive or antibonding in nature and occurs only when forced by the configuration of the molecule.

In conclusion, this comparison of substituent effects strongly suggests that unshared p-electrons on substituents X of CX_3 group interact with the π system of the adjacent aromatic ring and may be of some importance in transmission of electronic effects. Although a through space p–π donation[4] is an attractive way to interpret this interaction, a π repulsion[20] or some other distortion of the π system is also very reasonable. However the data can also be explained by hydridization changes in bonding induced by concentration of highly electronegative halogens and can be represented as hyperconjugation.

The saturation effects noted for the chloro- and bromo-substituted methyl groups should be compared to NMR chemical shift[21] and coupling constant[22] data where halogen substitution produces anomalous effects that are not readily explained theoretically.

EXPERIMENTAL

All new compounds prepared for this study are reported in Table 1 with physical properties and analytical data. The IR, UV and proton (and F^{19}) NMR spectra were obtained on all new compounds and used to verify structures. Typical experimental procedures are given below and used for reference in Table 1. All known compounds are summarized in Table 2 with literature reference and method of preparation.

1. *Synthesis*

A. *Fluorobenzal difluoride.* Following the literature procedure,[9] 12·4 g (0·10 mole) *m*-fluorobenzaldehyde and 20 g SF_4 were heated at 150° for 6 hr in a Hasteloy autoclave. The product was distilled at reduced pressure.

B. *α-Chlorotoluenes.* A stoichiometric amount of Cl_2 (condensed in a calibrated trap) was passed into a soln of fluorotoluene in CCl_4 irradiated by a low-pressure mercury lamp.

C. *α-Bromotoluenes.* A stoichiometric amount of Br_2 was added slowly to a soln of fluorotoluene in CCl_4 irradiated with a sunlamp.

D. *α-(Trifluoromethylthio)toluenes.* Fluorobenzotribromide 8·7 g (0·025 mole) was mixed with 15·2 g (0·15 mole) bis(trifluoromethylthio)mercury[10] and heated with stirring to 100° for almost 30 min. The mixture was cooled, diluted with trichlorofluoromethane, and saturated with dry HCl gas to destroy any unreacted (trifluoromethylthio)mercury. The trichlorofluoromethane soln was filtered and distilled. For mono and di-α-bromotoluenes, molar quantities of Hg salt were used.

E. *Fluorobenzyl methyl ether.* To a soln of 9·25 g fluorobenzyl bromide in 50 ml ether was added 2·71 g NaOMe under dry N_2. The soln was refluxed for 1 hr, filtered and distilled.

F. *Fluorobenzaldehyde dimethyl acetal.* Following the literature procedure[11] a soln of 18·6 g fluorobenzaldehyde in 200 ml MeOH containing 0·3 ml conc HCl was stirred 40 hr under N_2 and then made basic with sat NaOMe in MeOH, filtered, and distilled.

G. *Methyl orthofluorobenzoate.* According to a literature procedure,[12] 10·6 g fluorobenzotrichloride was added to a cold soln of 8·42 g NaOMe in 50 ml MeOH. The soln was stirred at room temp overnight, then refluxed for 4 hr, cooled and filtered to remove NaCl. The product was distilled.

H. *Fluorophenylmalononitrile.* Adopting a literature procedure,[13] a soln of 1·7 g fluorobenzotricyanide in 30 ml acetonitrile was cooled to −40° and 0·65 g dry KCN added. After being stirred at −30 to −40° for 3 hr, the soln was filtered into 500 ml ether. A gummy ppt was added to water at 0° and acidified with 10% H_2SO_4. The fluorophenylmalononitrile was recrystallized from hexane.

I. *(Fluorophenyl)methylmalononitrile.* The potassium fluorophenylmalononitrile was prepared as above from fluorobenzotricyanide and KCN in acetonitrile. MeI, 3 g, was added and the soln warmed to room temp and stirred for 3 hr. The soln was filtered and the product distilled.

2. NMR *calibrations.* F^{19} NMR chemical shifts were measured at 25° with a Varian A56–60 spectrometer using techniques previously described. Trichlorofluoromethane was used as solvent and internal calibrant; measurements were made at 20, 10, 5% concentration and the chemical shift was obtained by extrapolation to infinite dilution. Where the compound was not sufficiently soluble in trichlorofluoromethane, the solvent was employed with 5% 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal calibrant as described previously.[14] The NMR chemical shift data are given in Table 3.

3. *Substituent parameters.* The inductive and resonance substituent parameters, σ_I and σ_R^0, were calculated for the series of substituent Me groups by the procedure described by Taft *et al.*[15] as used in earlier studies of fluorinated substituents[4, 16] and are given in Table III.

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