Halogen-Containing Substituents. I. The Methyl System. Reactivity Parameters and Charge Distributions

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Abstract: A series of halogenated toluenes, ArCH$_2$X, ArCHX$_2$, ArCX$_3$, with Ar = Ph, *m*-FPh, and *p*-FPh, and X = F, Cl, and Br, was examined in order to evaluate the appropriate σ_I and $\sigma_R{}^\circ$ substituent parameters. The conclusions derived from approximate molecular orbital calculations (CNDO/2) were consistent with the experimental results and indicated charge transfer between the phenyl π system and the substituent; this resonance is rationalized in valence-bond terms as resulting from hyperconjugation. π- and σ-inductive effects, as defined here, were also found to be of considerable importance.

The electronic properties of a series of halogen-containing methyl substituents were investigated and the results obtained, together with data cited previously,[1-6] complete a comprehensive study of basic interest. Hence, the relative influence of the various halogens in these systems may be deduced, a feature which constitutes part of a continuing program designed to evaluate the changes in properties of simple substituents, as they are modified by progressive halogen substitution. The results are of value to the general understanding of the behavior of substituent interactions and more specifically provide insight into the mechanism by which halogenated methyl substituents interact with an adjacent phenyl group. This latter point is of particular concern in view of the various rationalizations that have been offered previously to account for the behavior of the trifluoromethyl group in benzotrifluoride. A detailed analysis of these factors, namely, fluoride ion hyperconjugation,[7] $I\pi$-effect,[8] field effect,[8] and fluorine p–π interaction,[3] is deferred to the Discussion.

We have applied the model developed by Taft,[9] wherein substituent effects are divided into resonance and inductive contributions.[1,2] A measure of these contributions is expressed by the σ_I and $\sigma_R{}^\circ$ parameters, respectively, which are determined quantitatively by reactivity or ^{19}F nmr measurements using appropriate benzene derivatives.

Two other approaches relevant to this problem are described in the literature. Thus, Katritzky[10] has measured $\sigma_R{}^\circ$ values by a method employing quantitative infrared spectroscopy and values have been determined in this way for some halogen-containing methyl substituents.[6] An outstanding development in the treatment of substituent effects has been the application of advanced molecular orbital (MO) calculations[11] to the problem.[12] The CNDO/2 method developed by Pople[11] has been widely applied[14] and shown to reflect satisfactorily electronic distributions in large organic molecules. Thus, Brownlee and Taft[12] have found a linear correlation between $\sigma_R{}^\circ$ and the total excess π charge for a series of monosubstituted benzenes. The CNDO/2 method was applied extensively in our investigation, and for the first time, to substituents containing second-row elements.[13b]

Results

The compounds investigated were the halogenated toluenes ArCH$_2$X, ArCHX$_2$, and ArCX$_3$, with Ar = Ph, *m*-FPh, and *p*-FPh, and X = F, Cl, and Br; they were obtained or synthesized by known methods and details are given in the Experimental Section. Taft[1,2] has shown that the aryl fluorine atom in fluorophenyl derivatives serves as a sensitive probe, whose ^{19}F chemical shift reflects the electronic properties of the substituent according to the following equations

$$\delta_m = -7.10\sigma_I + 0.60 \qquad (1)$$

$$\delta_p - \delta_m = -29.5\sigma_R{}^\circ \qquad (2)$$

where δ represents the difference in chemical shifts relative to that of fluorobenzene for each of the meta and

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[1] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963).

[2] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

[3] W. A. Sheppard, *ibid.*, **87**, 2410 (1965). Also a paper presented at the 5th International Symposium on Fluorine Chemistry, Moscow, USSR, July 1969. We are grateful to Dr. Sheppard for a copy of the latter and for a manuscript prepared for publication: W. A. Sheppard, *Tetrahedron*, 27, 945 (1971).

[4] W. A. Sheppard, *Trans. N. Y. Acad. Sci.*, **29**, 700 (1967).

[5] G. P. Syrova, Yu. N. Sheinker, V. F. Bystrov, N. V. Kondratenko, and L. M. Yagupol'skii, *Reakts. Sposobnost Org. Soedin.*, **6**, 380 (1969); *Chem. Abstr.*, 72, 2916p (1970). Unfortunately, this paper was not available to us at the time our manuscript was submitted originally. These authors report ^{19}F nmr measurements for the substituents described in Table I. In their work different solvents were used, hence small differences exist between their results and the ones we derived for σ_I and $\sigma_R{}^\circ$. However, the direction and approximate magnitude of the very small values of $\sigma_R{}^\circ$, the validity of which was queried by a reviewer, were found to be real. Both sets of data were mutually reinforcing on this point.

[6] R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1757 (1968).

[7] J. D. Roberts, R. L. Webb, and E. A. McElhill, *ibid.*, 72, 408 (1950).

[8] M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 354 (1966).

[9] (a) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959); (b) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).

[10] R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *ibid.*, **88**, 1413 (1966).

[11] J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967), and references cited therein.

[12] R. T. C. Brownlee and R. W. Taft, *ibid.*, **90**, 6537 (1968). We thank Professor Taft for providing us with a copy of his modified version of QCPE Program 91.[13a] We have used $\sigma_R{}^\circ$ as applicable to both donors and acceptors as given in this reference. In a more recent paper [*ibid.*, **92**, 7007 (1970)], these authors presented the results of CNDO/2 calculations on a series of compounds substituted by a representative set of groups containing first-row elements. Differences between their and our results arise from small variations in the choice of atomic coordinates (see text).

[13] (a) G. A. Segal, Quantum Chemistry Program Exchange, Program 91, Indiana University, 1966; (b) P. A. Dobosh, Quantum Chemistry Program Exchange, Program 141, Indiana University, 1969.

[14] Amongst others are: D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968); J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968); H. S. Tremper and D. D. Shillady, *ibid.*, **91**, 6341 (1969).

Table I. ^{19}F Nmr Chemical Shifts of *m*- and *p*-FC_6H_4Y and Derived Substituent Parameters

Subst Y	δ_m[a]	δ_p[a]	σ_I	$\sigma_R°$
CH_3	1.18[b]	5.40[c]	−0.08[b]	-0.14_6[c]
CH_2F	−0.22	0.19	0.12	-0.01_4
CHF_2	−1.44	−3.19	0.29	0.06
CF_3	−2.13[b]	−5.15[c]	0.41[b]	0.10[d]
CH_2Cl	−0.44	0.47[e]	0.15[f]	-0.03_1[g]
$CHCl_2$	−1.58	−2.20	0.31	0.02_1
CCl_3	−1.61	−2.46	0.31[h]	0.03[i]
CH_2Br	−0.56	0.13	0.16	-0.02_3
$CHBr_2$	−1.22[j]	−2.21[k]	0.26	0.03
CBr_3	−1.25[l]	−2.14[l]	0.26[m]	0.03[m]

[a] In parts per million relative to fluorobenzene. Probable error is 0.07 ppm. [b] Value from ref 1. [c] Value from ref 2. [d] Calculated from the corresponding value of δ_p and δ_m using eq 1 and 2. 0.10 reported in ref 4; 0.13 reported in ref 12. [e] 0.35 reported in ref 2. [f] 0.14 reported in ref 1. [g] 0.03 reported in ref 2. [h] 0.31 reported in ref 4. [i] 0.03 reported in ref 4. [j] Value derived from a measurement reported by M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 3318 (1966). [k] See ref 3. [l] Value derived from data reported in ref 4. [m] Value from ref 4.

the para fluoro isomers. These results are summarized in Table I.

There exists a quantitative relationship[6,10] between the infrared intensities, *A*, of the 1585- and 1600-cm^{-1} ring-stretching absorption bands of a monosubstituted benzene and the corresponding $\sigma_R°$ value of the substituent, which has the following form

$$\sigma_R° = 0.0079A^{1/2} - 0.027 \tag{3}$$

We found values of $A < 100$ for CH_2F and CHF_2 and confirmed Katritzky's data[6] for CH_3 ($\sigma_R°$ $\pm 0.10_5$) and CF_3 ($\sigma_R°$ ±0.11). In addition, Katritzky[6] has cited values of $A \leq 100$ for *all* the chlorine- and bromine-containing methyl derivatives of interest here. Such small values have limited utility because of the existence of overlapping aryl C–H out-of-plane bending fundamentals of similar magnitude. For these situations, values of $\sigma_R° = 0$ are assigned routinely.[6]

Another fruitful line of investigation proved to be the theoretical calculations of charge distribution in the halogen-containing toluenes by means of Pople's semiempirical SCF–MO treatment (the CNDO/2 method).[11] The charge densities were calculated using (i) a modified version of the QCPE Program 91,[12,13a] capable of achieving convergence of all electron densities to within $\pm 5 \times 10^{-4}$, and applicable only to compounds containing the first-row elements H–F, (ii) the QCPE Program 141 (CNINDO)[13b] for the compounds containing chlorine and which achieved convergence of the electronic energies to $\pm 1 \times 10^{-6}$ au. No similar treatment for calculations on bromine-containing compounds is generally available. All calculations were carried out using a CDC 6500 computer. Table II lists the excess π charge, relative to the unsubstituted benzene for each position in the ring, and Table III gives the excess σ charge values and excess total charges on the substituent atoms.

The symbols Δq_σ and Δq_π (in 10^{-4} electron) represent the difference in σ or π charge, respectively, at the appropriately numbered carbon atom, relative to $q_\sigma = 3.0000$ and $q_\pi = 1.0000$. Although the exact geometry of the molecules examined was not known (except for toluene), the results obtained were not particularly sensitive to reasonable variations in bond lengths and angles or to changes in substituent conformations, as seen in Tables II and III for CF_3 and CCl_3.

Table II. π-Charge Density of the Ring Carbon Atoms in Monosubstituted Benzenes[a]

Subst	$\Delta q_\pi{}^1$	$\Delta q_\pi{}^2$	$\Delta q_\pi{}^3$	$\Delta q_\pi{}^4$	$\Sigma\Delta q_\pi$	C(1)–C(7)[b]	C(7)–X[c]	μ(calcd)	μ(obsd)[d]
CH_3[e]	288	−251	117	−154	−133	1.51		0.20	0.37
CH_2F[f]	59	−88	92	−41	−65	1.50	1.34	1.79	1.77
CHF_2	−172	−16	63	76	−3	1.49	1.36	2.57	
CF_3[e]	−499	188	12	261	162	1.48	1.37	2.73[g]	2.86
CF_3[e]	−499	186	10	265	158	1.51	1.37	2.73	2.86
CF_3[h]	−627	269	3	316	234	1.48	1.37	2.95	2.86
CH_2Cl	126	−147	102	−41	−5	1.50	1.78	1.78	1.80
$CHCl_2$	31	−158	101	8	12	1.49	1.77	2.31	2.06
CCl_3	−36	−97	109	45	33	1.49	1.76	2.49	2.10
CCl_3[i]	−35	−106	109	45	34	1.49	1.76	2.25	2.10

[a] The substituent is attached to the C-1 carbon. The conformation of the substituent is staggered with respect to the benzene ring, except where noted. Total excess π charge over the 6-ring carbons is $\Sigma\Delta q_\pi$ and is given in 10^{-4} electrons as for Δq_π values. [b] Distance between the carbons C-1 and C-7, in ångströms. [c] Distance between the C-7 carbon and the halogen atoms X, in ångströms. [d] Dipole moment in the gas phase for toluene, and in benzene for the other compounds, taken from A. L. McClellan "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. [e] Similar results are reported in ref 12. [f] $\Delta q_\pi{}^5 = 82$ and $\Delta q_\pi{}^6 = -169$, due to the proximity of the fluorine atom to C-2. [g] Taken from a calculation with a C–F bond in the plane of the ring. [h] Calculation using the INDO approximation (ref 13b). See ref 32a. [i] The CCl_3 group is taken with a carbon–chlorine bond in the plane of the ring such that the chlorine atom is nearer to C-2 than to C-5; $\Delta q_\pi{}^5 = 111$ and $\Delta q_\pi{}^6 = -90$.

The nuclear coordinates needed as input for the previous programs were calculated using a Cartesian coordinates program[15] which required only the bond lengths and bond angles between adjacent nuclei in the molecule. The latter were chosen from the best literature models available;[16] the regular hexagonal geometry for the benzene ring was consistently maintained using a C–C bond length of 1.397 Å. Values of 1.080 and 1.090 Å were chosen for the aryl C–H and the methyl C–H bond lengths, respectively; the remaining bond lengths are listed in Table II. A tetrahedral geometry was adopted around the side-chain atom, except for $PhCCl_3$ for which an angle of C_{Ar}–C–Cl = 108.5° was used.

Discussion

The definitions of terms used commonly in studies of substituent effects have not been applied consistently. The following definitions are relevant to the aryl-sub-

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(15) J. H. Schachtschneider and F. S. Mortimer, Computer Program CART (SD-4063), Purdue University, Lafayette, Ind., 1966.

(16) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18**, (1965).

Table III. σ Charges of the Phenyl Carbons and Hydrogens and Charges in the Substituent[a]

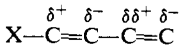
	Phenyl ring						Substituent		
Subst	$\Delta q_\sigma{}^1$	$\Delta q_\sigma{}^2$	$\Delta q_\sigma{}^3$	$\Delta q_\sigma{}^4$	$\Sigma\Delta q_\sigma{}^C$	$\Sigma\Delta q^H$	Δq^7	Δq^X	Δq^H
CH_3	145	141	5	124	561	−389	−209		53
CH_2F[b]	64	143	4	79	470	−173	2092	−2052	−130
CHF_2	−28	157	25	41	377	41	4154	−2147	−270
CF_3[c]	52	112	44	−28	336	268	5856	−2207	
CF_3	80	110	45	−29	361	257	5806	−2191	
CF_3	−159	360	191	153	1096	−665	7463	−2711	
CH_2Cl	331	111	14	82	663	−184	489	−1415	223
$CHCl_2$[d]	477	131	27	61	808	45	1125	−1200	418
CCl_3[c]	618	120	19	40	936	245	1709	−981	
CCl_3[e]	618	117	20	41	933	257	1727	−984	

[a] See footnote *a* of Table II. Total excess σ charge over the 6-ring carbons is $\Sigma\Delta q_\sigma{}^C$; total excess charge at halogen X (average) is Δq^X; total excess charge over the 5-ring hydrogens is $\Sigma\Delta q^H$; average excess charge, per methyl hydrogen, is Δq^H; total excess charge at benzyl carbon is Δq^7. [b] $\Delta q_\sigma{}^5 = 23$ and $\Delta q_\sigma{}^6 = 157$. [c] CF_3 and CCl_3 geometries are given in Table II. [d] $\Delta q_\sigma{}^5 = 9$ and $\Delta q_\sigma{}^6 = 103$. [e] $\Delta q_\sigma{}^5 = 18$ and $\Delta q_\sigma{}^6 = 119$.

stituent system, and were chosen as to best reconcile valence-bond (VB) terminology and MO calculations.

Resonance is a process that results in *net transfer* of charge between the aromatic π system and the substituent. In the classical VB model, this process controls charge distribution at the ortho and para positions,[17] a restriction that is removed here. For substituents lacking unshared electron pairs, like CH_3 and $NMe_3{}^+$, hyperconjugation[18] accounts for donor–acceptor resonance properties.

π-Inductive effect is a process that results in reorganization of the aromatic π electrons.[19] This effect had been interpreted[20] such that there arises a polarization of the contiguous π electrons exemplified by

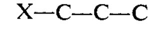


$$\mathrm{X{-}\overset{\delta^+}{C}{=}\overset{\delta^-}{C}{-}\overset{\delta\delta^+}{C}{=}\overset{\delta^-}{C}}$$

Iπ repulsion

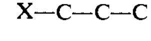
Other authors have inferred that its magnitude is proportional to inductive parameters of X.[6] For the purpose of this discussion, it is necessary only to emphasize that, in contrast to resonance, charge transfer is not occurring between the substituent and the ring.

σ-Inductive effect is a process that results in net transfer of charge between the substituent and the σ framework; this definition also accounts implicitly for reorganization of σ charge at the various positions. The classical model of inductive effects[21] leads to successive polarization of the σ electrons. However, Dewar[22] has proposed that this process terminates at the β-carbon atom



$$\mathrm{\overset{\delta^-}{X}{-}\overset{\delta^+}{C}{-}\overset{\delta\delta^+}{C}{-}\overset{\delta\delta^+}{C}}$$

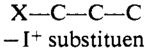
−I substituent



$$\mathrm{\overset{\delta^-}{X}{-}\overset{\delta^+}{C}{-}\overset{0}{C}{-}C}$$

and that the long-range influence of substituents results from a field effect, defined as a direct electrostatic interaction through space of the field resulting from the C–X dipole on the σ and π bonds[23] of the reaction center.

Recently, Pople[11] has suggested that substituents produce alternation of charge in the σ framework.



$$\mathrm{\overset{\delta^-}{X}{-}\overset{\delta^+}{C}{-}\overset{\delta\delta^-}{C}{-}\overset{\delta\delta^+}{C}}$$

$-I^+$ substituent

The results in Table I show the trends produced in the toluenes resulting from progressive substitution of benzylic hydrogen by the more electronegative halogens. Thus, fluorine substitution causes a regular but nonlinear increase in σ_I and $\sigma_R{}^\circ$ values, demonstrating that a simple additivity relationship is not holding. The chlorine- and bromine-containing substituents behave similarly, though the dampening, which is rather insignificant in the fluorine series, is much more prominent. In particular, σ_I values of CX_3 and CHX_2 (X = Cl, Br) are nearly identical. This phenomenon, which has been termed "saturation,"[24] has been noted previously in the chlorine series in such parameters[24,25] as σ^* and group electronegativity. Possibly, important pairwise interactions between the bulky chlorine atoms in CCl_3 counteract the normal σ-inductive effect of the individual halogens. Another point to be noted here is the order Cl > F for σ_I in CH_2X and CHX_2; though the differences are small, such behavior is contrary to that expected from an inductive transmission mechanism following the σ_I of the halogen, 0.52 and 0.47 for F and Cl, respectively. This observation is attributed to the complex nature of the σ_I parameter (see later).

Measurements of $\sigma_R{}^\circ$ values determined by Katritzky's method[10] proved to have limited use for halomethyl derivatives though the results which were valid, CH_3 and CF_3, corresponded closely with those obtained by the ^{19}F method: other values shown in the latter as $-0.03 < \sigma_R{}^\circ < 0.06$ are not measurable by this method.[6]

Charge densities (and bond orders) for the halogenated toluenes were calculated by Pople's SCF–MO theory and are summarized in Tables II and III. Agreement between the experimental and calculated dipole moments is good and provides an additional measure of confidence in the results. The principal conclusions drawn from these tables are (i) there is a net transfer of charge to the substituent; (ii) the benzylic carbon atoms become more electron deficient as the number of

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(17) G. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, p 427.

(18) A general discussion of this model is given by M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

(19) M. Godfrey, *J. Chem. Soc. B*, 751 (1968).

(20) D. T. Clark, J. N. Murrell, and J. M. Tedder, *ibid.*, 1250 (1963).

(21) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 71.

(22) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3548 (1962).

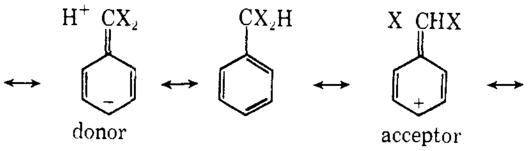
(23) M. J. S. Dewar and T. G. Squires, *ibid.*, **90**, 210 (1968).

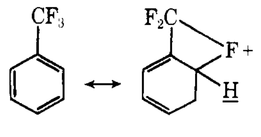
(24) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 624.

(25) M. A. Davis, *J. Org. Chem.*, **32**, 1161 (1967).

halogens increases (accompanying this change, the total excess charge progressively increases for fluorine and decreases for chlorine); (iii) the meta positions, which are always electron deficient, are unaffected by conformational changes, whereas the ortho positions are more sensitive to such changes; (iv) final π-charge distributions correspond poorly with the classical VB resonance model; (v) the variation of π charge, $\Delta q_\pi{}^C$, at the individual carbon atoms is of comparable magnitude to the total π charge transferred, $\Sigma\Delta q_\pi$; (vi) transfer of π charge is less important in magnitude than transfer of σ charge, $\Sigma\Delta q_\sigma$; in the latter, the effects of F and Cl are in *opposite* directions.

Linear correlations between $\sigma_R{}^\circ$ values and $\Sigma\Delta q_\pi$ (and $\Delta q_\pi{}^4$) for the halogenated methyl groups studied are similar to those found by Taft[12] for a series of substituents containing first-row elements. A consequence of this correlation is that all the halogen-containing methyl substituents are indeed interacting by a resonance mechanism with the aromatic π system. This result, which is readily disclosed by MO theory, must be rationalized in VB terms by hyperconjugation, which apparently escapes unequivocal experimental detection.[18] Halogen-containing methyl substituents are rare in that their influence depends on the balance of two opposing effects, namely hydrogen and halide-ion hyperconjugation (no-bond resonance). An interpretation, which explains the experimental results ($\sigma_R{}^\circ$), is derived from the values of Δq^X and Δq^H (Table III), insofar as they are reasonable probes for hyperconjugation. Acceptor behavior (halide ion hyperconjugation, F > Cl) increases with the number of halogens, while donor behavior (H$^+$ hyperconjugation) increases in the same order for the chlorine- and presumably bromine-containing compounds. In the fluorine-containing compounds, however, donor behavior *decreases* with the number of fluorines. Except for CHF_2, the opposing donor–acceptor effects are very nearly cancelling giving values $\sigma_R{}^\circ \sim 0$. This type of no-bond resonance in CF_3 was proposed two decades ago by Roberts[7] and supporting data have been offered by other workers.[26] Other interpretations for the +R effect of CF_3 ($\sigma_R{}^\circ$ 0.10) have been offered.[3,8] Hence, Sheppard[3] has proposed that it results from a p–π interaction, wherein fluorine 2p orbitals distort directly the aromatic π-electron system producing a −R effect at the meta position,





which counteracts the (strong) inductive withdrawal by CF_3. This model is not validated by the calculations,[27] and does not account for (i) the transfer of π charge *from* the phenyl system; (ii) the progressive increase in charge Δq^F on the fluorines (Table III); (iii) the large decrease of π charge at the para carbon; (iv) the consistent deficit of π charge at the meta carbons.

The large range in π charge variation at the attachment carbon, C-1 (CF_3, −499; CH_3, +288), and the meta carbon, C-3 (CF_3, +10; CH_3, +117), which are positions least likely to be affected by resonance, must result from reorganization of charge, thus indicating that important π-inductive effects are operating in the ring in all the compounds. In particular, the case for CF_3 is noteworthy because the range of values, $\Delta q_\pi{}^1$, −499, and $\Delta q_\pi{}^4$, +261, is so much larger than the value corresponding to the resonance transfer ($\Sigma\Delta q_\pi$ −161). Part of the excess charge at carbon C-1 is undoubtedly caused by the powerful $-I^+$ effect[11] of the benzylic fluorines. Other workers[28] have also emphasized the significance of π-inductive effects in their interpretations. Alternatively, it has been argued[3,6,29] that π-inductive effects cause negligible distortion to the π system. However, the basis for some of the latter arguments, for example, π-inductive effects qualitatively follow the order of resonance, and hence the $\sigma_R{}^\circ$ scale, is invalidated by Dewar's recent finding[30] that π-inductive effects are apparent in a hypothetical situation demanding *zero* resonance.

The σ_I parameter was originally shown[9a] to be a measure of inductive interactions of the substituent through σ and π bonds of the benzene ring and through space (field effect)—the latter was assumed to be minimal due to the absence of solvent effects. These inductive interactions are described by the σ- and π-inductive effects defined in this paper. Supporting evidence is given by Swain,[31] who found $\sigma_I = 100 \pm 5\%$ of $\mathfrak{F}$, where $\mathfrak{F}$ includes all substituent effects except resonance. As seen in Table III, the size of the σ-inductive redistribution $\Sigma\Delta q_\sigma{}^C$ (or better the sum $\Sigma\Delta q_\sigma{}^C + \Sigma\Delta q^H$) is large with respect to the resonance transfer, $\Sigma\Delta q_\pi$. No linear correlation of the former quantities and σ_I exists for the halogen-containing methyl substituents. Other attempts to find a meaningful correlation between σ_I and the charge distributions were foiled by the lack of a π-inductive scale, which demands that resonance distributions around the ring be known. This general problem is currently under investigation; however, initial results[32] suggest that $\Delta q_\pi{}^1$ is a probe for π-inductive effects.

Experimental Section

Elemental analyses were performed by the staff of Dr. C. S. Yeh, Purdue University, Department of Chemistry, Microanalytical Laboratory. Vapor-phase chromatography (glpc) was performed on a Varian Aerograph Model 200. Proton nmr spectra were

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[26] (a) J. Hine and R. J. Rosscup, *J. Amer. Chem. Soc.*, **82**, 6115 (1960); (b) J. Hine, *ibid.*, **85**, 3239 (1963); (c) S. Andreades, *ibid.*, **86**, 2003 (1964). An opposing viewpoint has been expressed [A. Streitwieser, Jr., and D. Holtz, *ibid.*, **89**, 692 (1967)] and although more recent arguments (private communication) have not yet been published, it appears to us that the bridgehead fluorine in 1*H*-undecafluorobicyclo-[2.2.1]heptane has a large influence, which was not given consideration in the earlier communication cited here.

[27] We examined fluorine–carbon π-bond orders to detect any important interactions. They are 0.0160, 0.0023, and 0.0138 with the ortho, meta, and para carbons, respectively. These values compare with a F–C(7) bond order of 0.1930 (*cf.* 0.6703 for C(2)–C(3)).

[28] (a) O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 65 (1966); (b) J. Burdon, *Tetrahedron*, **21**, 3373 (1965); (c) D. T. Clark, *Chem. Commun.*, 390 (1966).

[29] M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, **89**, 390 (1967).

[30] N. C. Baird and M. J. S. Dewar, *ibid.*, **91**, 352 (1969).

[31] C. G. Swain and E. C. Lupton, Jr., *ibid.*, **90**, 4328 (1968).

[32] I. Serfaty, unpublished results.

determined using a Varian A-60A nmr spectrometer with tetramethylsilane as an internal standard and CCl_4 as a solvent.

^{19}F Nmr Measurements. Fluorine nmr spectra were recorded on a Varian Model HA 56/60 operating at 56.445 MHz in the frequency sweep mode.[33] Measurements were made on approximately 5% (v/v) solutions of the substituted fluorobenzene in a 2% (w/w solution of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB) used as the standard in CCl_4, using a sealed capillary containing trifluoroacetic acid as an internal lock. These solutions are a permissible approximation for infinite dilution.[1] The chemical shifts were referenced to fluorobenzene by adding 1.2 ppm to the observed shift (relative to TCTFCB).

Infrared Measurements. The infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. Quantitative studies were done using spectroscopic grade CCl_4 and cyclohexane as solvents. The technique used was identical with that described by Katritzky; absorbance values were measured directly and by varying solution concentrations between 0.30 and 1.30 *M* appeared in the desired range of 0.05–0.60.

Materials. Spectroscopic grade CCl_4 and cyclohexane (Mallinckrodt, Inc.) were used as solvents for both infrared and nmr measurements. TCTFCB was used as obtained from Peninsular Chemresearch, Inc. Commerically available anhydrous KF was rigorously dried in a vacuum oven at 120° for at least 24 hr and was finely crushed before use. Technical grade ethylene glycol was distilled beofre use and the fraction with bp 90° (11 mm) collected.

α-Chloro-*m*- and *p*-fluorotoluenes, *m*- and *p*-fluorotoluenes, and benzotrifluoride were purchased from Pierce Chemical Co.

Benzyl bromide (British Drug Houses, Ltd.) was used without purification.

α,α-Dichloro-*m*-fluorotoluene and α,α,α-trichloro-*m*-fluorotoluene were prepared by the method of Fukui[34] by chlorination of *m*-fluorotoluene (25.0 g, 0.23 mol) in the presence of 1.0 g of PCl_3. The reaction was monitored by nmr and terminated when all the *m*-fluorotoluene had reacted. Distillation through a 45-cm spinning band column gave 10.0 g (24%) of the dichloro derivative ($n^{20}\mathrm{D}$ 1.5278; nmr δ 6.60 (s, $C\mathit{H}Cl_2$, J_{CH} = 179.0 Hz)) and 12.1 g (25%) of the trichloro derivative (bp 75° (5 mm); $n^{20}\mathrm{D}$ 1.5366).

α,α-Dichloro-*p*-fluorotoluene ($n^{20}\mathrm{D}$ 1.5282; nmr δ 6.60 (s, $C\mathit{H}Cl_2$, J_{CH} = 179.0 Hz)), and **α,α,α-trichloro-*p*-fluorotoluene** ($n^{20}\mathrm{D}$ 1.5360) were prepared as above, by chlorination of *p*-fluorotoluene.

α-Bromo-*p*-fluorotoluene and **α-bromo-*m*-fluorotoluene** were prepared by the method of Hudlicky,[35] from the corresponding *m*- and *p*-fluorotoluenes.

Benzyl fluoride was prepared according to a method adapted from the procedure of Fukui.[34] Benzyl bromide was added dropwise over a period of 2 hr to a vigorously stirred, saturated solution of anhydrous KF in ethylene glycol at 170°. Continuous distillation of any volatile material was maintained during the time of the addition. A 1:1 mixture of *toluene* and of benzyl fluoride (nmr δ 5.30 (d, J_{HF} = 48.0 Hz)), was obtained in 10% yield, and separated at 100° by preparative glpc using a column packed with QF-1 on 60–80 Chromosorb W.

α,*m*-Difluorotoluene ($n^{20}\mathrm{D}$ 1.4645; nmr δ 5.28 (d, $C\mathit{H}_2F$, J_{HF} = 47.5 Hz, J_{CH} = 152.0 Hz)), and **α,*p*-difluorotoluene** ($n^{20}\mathrm{D}$ 1.4648; nmr δ 5.28 (d, $C\mathit{H}_2F$, J_{HF} = 48.0 Hz, J_{CH} = 152.0 Hz)) were prepared as above.

Anal. Calcd for $C_7H_6F_2$: C, 65.65; H, 4.68; F, 29.70. Found for meta: C, 65.93; H, 4.92; F, 29.41.

α,α,*m*-Trifluorotoluene ($n^{20}\mathrm{D}$ 1.4420; nmr δ 6.57 (t, $C\mathit{H}F_2$, J_{HF} = 56.5 Hz)), and **α,α,*p*-trifluorotoluene** ($n^{20}\mathrm{D}$ 1.4412; nmr δ 6.57 (t, $C\mathit{H}F_2$, J_{HF} = 56.5 Hz, J_{CH} = 187.0 Hz)), were prepared by treating the corresponding α,α-dichlorofluorotoluenes with SbF_3 following procedures described for similar compounds.[36]

Anal. Calcd for $C_7H_5F_3$: C, 57.51; H, 3.42; F, 39.09. Found for meta: C, 57.23; H, 3.56; F, 39.39.

Benzal fluoride was prepared from benzal chloride using the procedure outlined above.

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(33) We acknowledge the assistance of Dr. T. W. Johnson in recording the ^{19}F nmr spectra.

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(36) A. L. Henne, *Org. React.*, 2, 49 (1944).

Vertical Stabilization of Cations by Neighboring σ Bonds. General Considerations[1-3]

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Abstract: A theory for stabilization of carbonium ions or other cations, by delocalization of neighboring σ bonds, is described. Such delocalization is available without changing the reactant geometry and is termed "vertical stabilization." The stabilizing influence is contrasted to the bridged-ion theory of neighboring group participation, in which the neighboring group moves toward the reaction center as the transition state is approached, and to frangomeric acceleration, in which the neighboring group moves away from the reaction center as the transition state is approached. The effects of structural changes on the magnitude of (vertical) σ–π conjugation are discussed. In addition, further evidence is offered against significant effects of C–H hyperconjugation on bond lengths.

Delocalization of σ bonds was first discussed in detail by Mulliken[5] in his treatment of carbon–hydrogen hyperconjugation as an explanation of certain properties of hydrocarbons.[6-8] Variations in such delocalizations with the nature of the hyperconjugated group were

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(1) Supported by the Air Force Office of Scientific Research, Grants AFOSR-69-1639 and AFOSR-69-1639A.

(2) The effects of σ–π conjugation on singlet neutral molecules, on free radicals, and on carbanions will be considered in subsequent papers.

(3) The major part of these ideas was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 39. Previous discussions of σ–π conjugation in cations are found in ref 4a–g.

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(5) (a) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); (b) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959).

(6) Ground-state properties of hydrocarbons such as bond lengths and heats of formation are better explained in terms of hybridization or repulsion effects.[7,8]

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