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A CNDO/2 Theoretical Study of Substituent Effects on Electronic Distributions in Fluorine Molecular Orbitals. Comparison with Meta- and Para-Substituent Fluorine Nuclear Magnetic Resonance Shifts[1]

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Abstract: Calculations of charge densities (to convergence of $\pm 5 \times 10^{-4}$) by Pople's CNDO/2 method have been made for a series of ten meta- and para-substituted fluorobenzenes, trans-substituted fluoroethylenes, and substituted fluoroacetylenes, as well as for monosubstituted benzenes, ethylene, and acetylenes and for 4-substituted [2.2.2]bicyclooctyl 1-fluorides. Special attention has been directed to the calculated substituent effects upon the fluorine orbitals. The results show the following behavior. (1) In first approximation, the $2p_z$ (π) orbital charge density of the fluorine probe reflects the π-electron effects which prevail at the bonded carbon atom. In turn, the latter π-electron effects are a reflection of the delocalization of π charge by the substituent. In general, all of the calculated π-electron effects ($\Sigma\Delta q_\pi^{\mathrm{C}}$, $\Delta q_\pi^{\mathrm{C}}$, $\Delta q_\pi^{\mathrm{F}}$ for the benzene, ethylene, and acetylene systems) show substantially the same (σ_{R}^0 or σ_{R}) substituent order. (2) The substituent effect on the fluorine $2p_y$ (σ) orbital charge density of para-substituted fluorobenzenes and of 4-substituted [2.2.2]bicyclooctyl 1-fluorides (and to poorer approximation, of meta-substituted fluorobenzenes) are equal and correspond well in general to the polar effect scale, σ_{I}. These σ-electron effects are unique to the fluorine atoms of these two systems—they are not found at any intervening carbon positions, nor for the fluorines of the ethylene and acetylene systems. The fluorine σ-electron effects for the former systems arise primarily as a consequence of a direct dipolar substituent–polar fluorine electrostatic interaction. (3) At the fluorine position (in contrast with carbon positions), the calculations show no evidence of any appreciable interaction (interdependence) of σ- and π-electron effects. (4) The dominant effect of the meta substituent on the fluorine orbital densities is its effect on the σ charge density. The π effect from the meta position is apparently too small to even identify correctly its direction. (5) CNDO/2 theory appears to provide some theoretical justification for and understanding of the empirical σ_{I} and σ_{R} parameters. With the assumption that the effect of a meta or para substituent on the F nmr shift of the fluorobenzenes may be related, at least approximately, to the sum of separate effects on σ and π charge densities of the fluorine orbitals, the CNDO/2 calculations provide valuable guidelines for the interpretation of the F nmr shifts. In these terms, the unique character of the F nmr shift correlations with σ_{I} and σ_{R}^0 may be readily understood. Some areas of difficulty are pointed out and discussed briefly.

Substituent shielding effects, $\int_{\mathrm{H}}$, in the fluorine nuclear magnetic resonance (F nmr) spectra of meta- and para-substituted fluorobenzenes are among the more highly sensitive physical measures known for the effects of meta and para substituents. For neutral substituents, para shifts cover an overall range of *ca.* 40 ppm and meta shifts of *ca.* 10 ppm.[2] These parameters can be routinely measured to ±0.02 ppm.[3] There are theoretical reasons for believing that

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[1] (a) This work was supported in part by the National Science Foundation; (b) this work was presented in part at the Second Linear Free Energy Conference, Irvine, Calif., March 30, 1968.

[2] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 3146 (1963).

[3] *Cf.* D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969).

Table I. Molecular Geometry Used in CNDO/2 Calculations[a]

Substituent	Bond lengths, Å		Angles	
-H	C–H = 1.084			
-F	C–F = 1.32			
-OH	C–O = 1.36	O–H = 0.97	COH = 109° 28′, planar	
-CHO	C–C = 1.48	C–O = 1.21 C–H = 1.08	CHO = 120°, planar	CCO = 120°, planar
-CN	C–C = 1.42	C–N = 1.16	CCN = 180°	
$-NO_2$	C–N = 1.48	N–O = 1.21	CNO = 120°, planar	
$-CH_3$	C–C = 1.51	C–H = 1.10	CCH = 109° 28′	
$-CF_3$	C–C = 1.50	C–F = 1.33	CCF = 109° 28′	
$-NMe_2$	C–N = 1.42	N–C = 1.46	CCN = 101° 33′	NCN = 116°
$-BF_2$	C–B = 1.53	B–F = 1.30	CBF = 120°, planar	
$-BH_2$	C–B = 1.53	B–H = 1.19	CBH = 120°, planar	

[a] The benzene ring is a regular hexagon with C–C = 1.397 Å; C–H = 1.084 Å.

these shielding effects are related to the electronic distributions in the fluorobenzenes, particularly in certain orbitals in the immediate environment of the fluorine atom.[4–6] Support for this conclusion has been provided by empirical correlations with reactivity parameters[7] for the para position

$$\int_{H}^{p\text{-}X} = (30.4)\sigma_R^0 + (6.1)\sigma_I \qquad (1)$$
$$\lambda^p \equiv \rho_R^p/\rho_I^p = +5.0$$

and for the meta position

$$\int_{H}^{m\text{-}X} = (0.6)\sigma_R^0 + (5.3)\sigma_I \qquad (2)$$
$$\lambda^m \equiv \rho_R^m/\rho_I^m = +0.1$$

The low λ^m value, indicating correlation with σ_I only to a good approximation, has lead to the interpretation that the meta shift may be considered to be a σ-electron-effect parameter.[8] The difference, $\int_H^{p\text{-}X} - \int_H^{m\text{-}X} = \int_{m\text{-}X}^{p\text{-}X}$, depends essentially only upon σ_R^0 and, consequently, has been termed a π-electron-effect parameter.[8] The markedly different magnitudes (but same sign) of λ^p and λ^m values for these relatively precise correlations accord with the classical picture of π electronic distributions in substituted benzenes, and, in fact, have provided a bulwark in the proposed separation of σ^0 to σ_R^0 and σ_I values.[9]

The theory of the origin of substituent effects on the electronic distributions in benzene and derivatives, as well as the transmission of these effects, is uncertain and is of much current interest.[2,9–15] The Pople CNDO/2 method of calculating molecular electron densities enables a theoretical calculation for all valence electrons of atoms through fluorine in the periodic table.[11] This theory, in addition to relatively accurate calculations of the molecular dipole moment,[11] has shown notable successes in correlation of π electronic distributions in substituted benzenes[12] with the substituent parameter, σ_R^0 (or σ_R), and in correlation of polar effects of 4 substituents in [2.2.2]bicyclooctane-1-carboxylic acid ionization constants.[13] Davies[14] has reported CNDO/2 calculations for fluorobenzene, *m*- and *p*-difluorobenzene, and *m*- and *p*-nitrofluorobenzene and concluded that the general results suggest an adequate picture of the electronic structures. We have considered it useful, therefore, to carry out a theoretical CNDO/2 investigation of substituent effects on orbital electronic distributions in a number of substituted fluorohydrocarbons. We believe the substituents chosen for this study represent the widest possible choice of neutral-substituent electronic properties available within the limitations of the method.

The particular interest in this study is the comparison of the observed meta- and para-substituent F nmr shifts with the calculated effects of corresponding substituents on the orbitals of the fluorine atom (and its attached ring carbon). At present the theory of the F nmr shift is not quantitative enough to expect a theoretical calculation of the shifts from the calculated electronic distributions. However, the unique character of the observed shifts provides a basis for possible identification of dominant effects appearing in the CNDO/2 theoretical results.

In addition to meta- and para-substituted fluorobenzenes, CNDO/2 calculations were also carried out for correspondingly substituted benzenes, fluoroacetylenes, and acetylenes, *trans*-fluoroethylenes and ethylenes, and 4-substituted [2.2.2]bicyclooctyl 1-fluorides. The results for these systems provide additional insights and support for the interpretations of the results obtained with the fluorobenzenes.

Method

Pople's CNDO/2 method[11] was used without any modification to the theoretical method and parametrization. Calculations were made with an IBM 360/50 computer.

The Quantum Chemistry Exchange Program No. 91 was modified to converge using an electron density criterion of 0.5 × 10^{-3} electron in all the orbital densities (0.2 × 10^{-3} for the acetylenes and ethylenes), because of difficulty in using the energy convergence, and because the densities were the quantities of interest. We also experienced difficulty with the diagonalization routine with symmetrical molecules, as have other workers,[14] and modified it. The prediagonalization step was also removed.

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Table II. Charge Densities ($\times 10^4$) in Monosubstituted Benzenes (the Substituent Is in the 4 Position)

Substituent	H	F	OH[f]	CHO[f]	CN	NO_2	CH_3	CF_3	NMe_3	BF_2
$C_1\pi$	0[a]	−271	−425	+206	+75	+355	−151	+244	−468	+551
$C_2\pi$	0[a]	+222	+277	−28	+61	−22	+117	+10	+272	−188
$C_3\pi$	0[a]	−496	−693	+163	−14	+281	−243	+183	−690	+662
$C_4\pi$	0[a]	+330	+547	−153	+1	−669	+282	−487	+507	−293
$\Sigma C\pi$	0[b]	−489	−663	+391	+170	+203	−125	+134	−798	+1206
$C_1\sigma$	+62[c]	+141	+210	−18	+31	−91	+121	−28	+236	−141
$C_2\sigma$	+62[c]	+52	+17	+45	+8	+95	−2	+41	−7	+45
$C_3\sigma$	+62[c]	−19	+88	−4	+121	−68	+136	+98	+176	−19
$C_4\sigma$	+62[c]	+1992	+1317	+12	+386	+999	+139	−23	+85	−1039
$\Sigma C\sigma$	+372[d]	+2199	+1785	+93	+675	+963	+532	+256	+662	−1128
H_1	−62[a]	−13	−52	−26	−16	+66	−69	+17	−75	−12
H_2	−62[a]	−5	−59	−27	−7	+93	−73	+34	−80	−7
H_3	−62[a]	+174	+23	−42	+17	+275	−65	+103	+20	−58
ΣH	−310[e]	+325	−48	−52	+4	+802	−351	+252	−196	−142

[a] $1.0000 - q$. [b] $6.0000 - q$. [c] $3.0000 - q$. [d] $18.0000 - q$. [e] $5.0000 - q$. [f] In nonsymmetrical substituents the densities at the 6 (meta) and 5 (ortho) positions are not equal to the 2 (meta) and 3 (ortho) positions. The values given below are for the conformation in which the substituent hydrogen is nearer to C_3 than C_5.

Substitutent	$C_5\pi$	$C_6\pi$	$C_5\sigma$	$C_6\sigma$	H_5	H_6
OH	−640	−271	+143	+10	+87	−47
CHO	+228	−25	+6	+34	+59	−15

Table III. Charge Densities ($\times 10^4$) in Para-Substituted Fluorobenzenes (the Fluorine Is in the 1 Position and the Substituent in the 4 Position)

	H	F	OH[d]	CHO[d]	CN	NO_2	CH_3	CF_3	NMe_2	BF_2
$C_1\pi$	330[a]	+73	−79	+527	+404	+673	+183	+563	−124	+852
$C_2\pi$	−496[a]	−272	−210	−521	−431	−521	−376	−487	−213	−679
$C_3\pi$	222[a]	−272	−472	+382	+206	+501	−24	+401	−473	+870
$C_4\pi$	−271[a]	+73	+302	−405	−255	−940	+27	−759	+271	−532
$C_1\sigma$	1992[b]	+2077	+2136	+1926	+1975	+1879	+2045	+1928	+2153	+1816
$C_2\sigma$	−19[b]	−32	−71	−38	−75	+14	−86	−42	−95	−37
$C_3\sigma$	+53[b]	−32	+74	−18	−105	−77	+124	+88	+162	−29
$C_4\sigma$	+141[b]	+2077	+1393	+87	+462	+1078	+221	+60	+921	−966
H_2	+174[a]	+231	+177	+209	+229	+326	+164	+268	+155	+229
H_3	−5[a]	+231	+80	+16	+76	+329	−7	+159	+79	+3
F2s	+1721[c]	+1723	+1722	+1721	+1722	+1725	+1720	+1723	+1721	+1720
$F2p_x$	+135[c]	+139	+139	+135	+136	+136	+137	+136	+139	+133
$F2p_y$	−4368[a]	−4329	−4351	−4354	−4343	−4296	−4371	−4324	−4366	−4356
$F2p_z$	+489[c]	+471	+455	+519	+507	+540	+479	+522	+452	+544

[a] $1.0000 - q$. [b] $3.0000 - q$. [c] $2.0000 - q$. [d] For conformation in which the hydrogen of the substituent is nearer the C_3 than C_5, th following apply.

	$C_5\pi$	$C_6\pi$	$C_5\sigma$	$C_6\sigma$	H_5	H_6
OH	−420	−216	+130	−78	+145	+190
CHO	+446	−517	−6	−50	+118	+219

The atomic coordinates used for the substituted benzenes were the best values taken from the literature.[16] The values used in the benzene systems are shown in Table I. In the acetylenes, a fixed triple bond length of 1.202 Å was assumed as well as a carbon–substituent bond 0.05 Å shorter than that for the benzene case. In the bicyclooctanes the C–H bonds were taken as 1.10 Å and the C–C bonds as 1.54 Å; all angles were 109° 47′ and the substituent–carbon distance was taken as 0.06 Å longer than in the benzene case. In the ethylenes the carbon–carbon double bond length was taken as 1.337 Å and the substituent–carbon bond length was 0.01 Å shorter than in the benzene case.

The charge densities (q) and bond orders (p) are defined from the following equations.[11]

$$q_n = 2\sum_i^{\text{occ}} C_i n^2$$

$$p_{mn} = 2\sum_i^{\text{occ}} C_i m C_i n$$

Discussion

The convention has been followed which utilizes the y axis as the C–F bond axis and the z axis as perpendicular to the molecular plane. Consequently, substituent effects on the $2p_z$ orbitals of carbon and fluorine are referred to as π electronic effects and the effects on the $2p_y$ orbital of fluorine, the $\Sigma(2s, 2p_x, 2p_y)$ of sp^2 carbon or the $\Sigma(2s, 2p_y)$ of sp carbon as σ electronic effects. In the discussion of the relevant results, π electronic effects are considered first for p-XC_6H_4F (and C_6H_5X), *trans*-XC_2H_2F (and C_2H_3X), and $X{-}C_2{-}F$ (and HC_2X). Then, the σ electronic effects in these systems and in 4-substituted 1-fluoro[2.2.2]bicyclooctanes are considered. Thirdly, the relationships between π and σ electronic effects are considered, including results for meta-substituted fluorobenzenes. Finally, consideration is given to the relationship be-

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Table IV. Charge Densities in Meta-Substituted Fluorobenzene (the Fluorine Is in the 1 Position and the Substituent in the 3 Position)

	H	F	OH	OH[d]	CHO[d]	CHO	CN	NO_2	CH_3	CF_3	NMe_3	BF_2
$C_1\pi$	+330[a]	+543	+589	+595	+306	+310	+393	+313	+447	+344	+589	+149
$C_2\pi$	−496[a]	−1004	−1151	−1207	−355	−291	−535	−236	−764	−329	−1213	+156
$C_3\pi$	+222[a]	+543	+756	+757	+66	+68	+219	−441	+521	−250	+724	−101
$C_4\pi$	−271[a]	−770	−966	−911	−52	−119	−297	−1	−533	−108	−967	+391
$C_5\pi$	+222[a]	−439	+493	+486	+195	+193	+282	+198	+339	+231	+487	+27
$C_6\pi$	−496[a]	−770	−924	−924	−302	−304	+432	−153	−664	−265	−975	+51
$C_1\sigma$	+1992[b]	+2004	+1951	+1955	+1982	+1973	+1953	+2062	+1924	+1992	+1924	+1985
$C_2\sigma$	−19[b]	−100	+66	+12	−78	−68	+46	−149	+54	+18	+105	−95
$C_3\sigma$	+53[b]	2004	+1323	+1323	+7	+7	+385	+984	+129	−44	+844	−1036
$C_4\sigma$	+141[b]	+59	+164	+219	+84	+76	+199	+12	+217	+203	+256	+57
$C_5\sigma$	+53[b]	+42	+7	0	+24	+34	0	+85	−8	+33	−17	+38
$C_6\sigma$	−19[b]	+59	+129	+129	−96	−96	−47	−170	+45	−107	+157	−224
H_2	+174[a]	+411	+321	+253	−185	+283	+245	+503	+162	+330	+247	+167
H_4	−13[a]	+220	+165	+132	+10	+1	+61	+315	−29	+104	+58	−13
H_5	−5[a]	+54	−3	+10	+36	+25	+45	+147	−21	+88	−27	+45
H_6	+174[a]	+220	+180	+181	+206	+206	+216	+298	+163	+250	+155	+222
F2s	+1721[c]	+1722	+1721	+1720	+1722	+1722	+1722	+1726	+1720	+1724	+1720	+1723
$F2p_x$	+135[c]	+137	+134	+134	+136	+136	+136	+142	+134	+139	+134	+138
$F2p_y$	−4368[a]	−4337	−4368	−4376	−4346	−4339	−4335	−4264	−4383	−4307	−4393	−4327
$F2p_z$	+489[c]	+510	+510	+511	+489	+489	+497	+495	+499	+497	+509	+478

[a] $1.0000 - q$. [b] $3.0000 - q$. [c] $2.0000 - q$. [d] Refers to the conformation for which the hydrogen in the substituent is closest to fluorine.

Table V. Charge Densities ($\times 10^4$) in Monosubstituted Acetylenes (the Substituent Is at C_2)

	H	F	OH	CHO	CN	NO_2	CH_3	CF_3	NMe_2	BF_2
$C_1\pi$	0[a]	−685	−1004	+531	+92	+571	−321	+327	−1034	+1344
$C_2\pi$	0[a]	+204	+368	−228	+23	−435	+151	−258	+326	−366
$C_1\sigma$	−638[b]	−986	−816	−1050	−645	−691	−850	−356	−783	−1048
$C_2\sigma$	−638[b]	+1855	+1054	−149	+63	+557	−105	−547	+601	−1076
H	+638[a]	+914	+774	+699	+736	+942	+635	+789	+694	+652

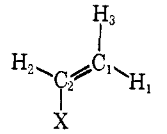
[a] $1.0000 - q$. [b] $3.0000 - q$.

Table VI. Charge Densities ($\times 10^4$) in Substituted Fluoroacetylenes (the Substituent Is at C_2 and the Fluorine at C_1)

	H	F	OH	CHO	CN	NO_2	CH_3	CF_3	NMe_2	BF_2
$C_1\pi$	+303[a]	−450	−774	+709	+259	+748	−119	+494	−814	+1448
$C_2\pi$	−680[a]	−444	−242	−872	−599	−1109	−483	−920	−271	−991
$C_1\sigma$	+1852[b]	+1573	+1714	+1445	+1864	+1848	+1638	+2149	+1717	+1438
$C_2\sigma$	−983[b]	+1579	+752	−251	−188	+243	−374	−832	+293	−1293
F2s	+1958[c]	+1964	+1961	+1959	+1960	+1963	+1958	+1961	+1960	+1957
$F2p_x$	+478[c]	+445	+459	+464	−529	+490	+471	+531	+457	+488
$F2p_y$	−4218[a]	−3985	−4089	−4200	−4177	−4025	−4216	−4138	−4153	−4271
$F2p_z$	+478[c]	+445	+417	+574	+529	+574	+471	+531	+416	+655

[a] $1.0000 - q$. [b] $3.0000 - q$. [c] $2.0000 - q$.

Table VII. Charge Densities ($\times 10^4$) in Monosubstituted Ethylenes



	H	F	OH[c]	CHO[c]	CHO	CN	NO_2	CH_3	CF_3	NMe_2	BF_2
$C_1\pi$	0[a]	−823	−1263	+436	+450	+140	+836	−447	+595	−1303	+1427
$C_2\pi$	0[a]	+298	+542	−72	−159	+11	−637	+290	−474	+455	−236
$C_1\sigma$	−309[b]	−347	−87	−461	−481	−288	−740	−120	−442	+32	−629
$C_2\sigma$	−309[b]	+1864	+1124	−326	−244	+107	+632	−83	−379	+715	−1368
H_1	+155[a]	+418	+218	+188	+292	+249	+558	+129	+351	+205	+195
H_2	+155[a]	+20	+59	+300	+152	+279	+542	+53	+503	−45	+361
H_3	+155[a]	+355	+218	+154	+146	+165	+438	+64	+253	+129	+97

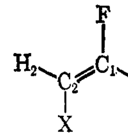
[a] $1.0000 - q$. [b] $3.0000 - q$. [c] The hydrogen of the substituent is on the H_1 side.

tween the calculated electronic distribution effects and the experimental F nmr shifts. A complete summary of the calculations of charge densities at all atomic positions is given in Tables II–IX.

All charge densities given throughout the discussion are the excess charges $\Delta q = q - q_H$, relative to the hydrogen substituent, and are given in parts per ten thousand, *i.e.*, as $10^4\Delta q$.

π-Electron Effects. Table X summarizes the results of the π electronic substituent effects of concern.

Table VIII. Charge Densities ($\times 10^4$) in Trans-Substituted Fluoroethylenes



	H	F	OH[d]	CHO[d]	CHO	CN	NO_2	CH_3	CF_3	NMe_2	BF_2
$C_1\pi$	+298[a]	−472	−903	+697	+814	+431	+1078	−145	+843	−957	+1602
$C_2\pi$	−823[a]	−472	−190	−826	−916	−752	−1447	−471	−1289	−258	−966
$C_1\sigma$	+1864[b]	+1859	+2075	+1714	+1690	+1865	+1522	+2008	+1761	+2162	+1545
$C_2\sigma$	−347[b]	+1859	+1100	−341	−264	+100	+618	−90	−377	+681	−1372
H_1	+20[a]	+267	+80	+82	+192	+143	+422	+18	+238	+77	+117
H_2	+418[a]	+267	+305	+548	+405	+537	+774	+308	+755	+195	+629
F2s	+1784[c]	+1804	+1796	+1779	+1779	+1780	+1796	+1779	+1784	+1789	+1765
$F2p_x$	+203[c]	+209	+213	+202	+198	+203	+199	+208	+202	+213	+194
$F2p_y$	−4295[a]	−4137	−4226	−4323	−4331	−4302	−4135	−4351	−4249	−4292	−4393
$F2p_z$	+525[c]	+472	+441	+620	+630	+589	+647	+512	+602	+441	+725

[a] $1.0000 - q$. [b] $3.0000 - q$. [c] $2.0000 - q$. [d] The hydrogen of the substituent is on the H_1 side.

Table IX. Densities ($\times 10^4$) in 4-Substituted [2.2.2]Bicyclooctyl 1-Fluorides[d]

	H	F	OH	NO_2	BH_2
$C_1{}^d\sigma$	+2261[a]	+2215	+2228	+2264	+2295
$C_2\sigma$	−139[a]	−114	−123	−140	−211
$C_3\sigma$	+190[a]	−114	−79	+127	+330
$C_4\sigma$	+321[a]	+2215	+1705	+620	−515
$C_{5,7}\sigma$	+190[a]	−114	−41	+157	+533
$C_{6,8}\sigma$	−139[a]	−114	−128	−136	−202
F2s	+1491[b]	+1493	+1492	+1491	+1495
$F2p_x$	+125[b]	+126	+126	+127	+124
$F2p_y$	−4165[c]	−4124	−4145	−4086	−4166
$F2p_z$	−125[b]	+126	+125	+128	+127

[a] $4.0000 - q$. [b] $2.0000 - q$. [c] $1.0000 - q$. [d] Numbering system is as follows.

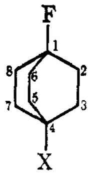


Table X. Excess π-Electron Charge Densities (in Parts per Ten Thousand Relative to the H Substituent)[a]

Substituent, X	$\sigma_R{}^0$	σ_R	XC_6H_5 $\Sigma\Delta q_{(\pi)}{}^C$	p-XC_6H_4F $\Delta q_{(\pi)}{}^C$	p-XC_6H_4F $\Delta q_{(\pi)}{}^F$	XC_2H_3 $\Sigma q_{(\pi)}{}^C$	t-XC_2H_2F $\Delta q_{(\pi)}{}^C$	t-XC_2H_2F $\Delta q_{(\pi)}{}^F$	XC_2H $\Sigma q_{(\pi)}{}^C$	XC_2F $\Delta q_{(\pi)}{}^C$	XC_2F $\Delta q_{(\pi)}{}^F$	XC_6H_4F $-\int_{m\text{-X}}{}^{p\text{-X}}$ [e]
BF_2	0.35[f]	(0.35)	1206	522	65	1191	1304	200	978	1245	177	9.50
CHO	0.26	(0.26)	391	197	30	391[b]	516[c]	105[d]	293	506	96	7.97
NO_2	0.19	0.16	203	343	51	189	780	122	136	545	96	5.75
CN	0.14	0.16	170	74	18	151	133	64	115	56	51	6.15
CF_3	0.13	0.11	134	233	33	121	545	77	69	291	53	2.85
H	0.00	0.00	0	0	0	0	0	0	0	0	0	0
CH_3	−0.11	−0.11	−125	−147	−10	−157	−443	−13	−170	−322	−7	−4.20
F	−0.34	−0.45	−489	−257	−18	−525	−770	−53	−481	−653	−33	−9.90
OH	−0.44	−0.59	−663	−409	−34	−721	−1201	−84	−636	−977	−61	−12.80
NMe_2	−0.52	−0.83	−798	−454	−37	−848	−1255	−84	−708	−1017	−62	−15.98

[a] $\Sigma\Delta q_{(\pi)}{}^C$ is the summation over all carbon atoms of the hydrocarbon cavity of the excess π charge densities at carbon; $\Delta q_{(\pi)}{}^C$ is the excess π charge density at the carbon bonded to the fluorine atom; $\Delta q_{(\pi)}{}^F$ is the excess π charge density at fluorine. [b] 364 for second conformation. [c] 399 for second conformation. [d] 95 for second conformation. [e] *Cf.* ref 2. [f] Calculated from unpublished results of Dr. Phillip Heffley.

Included for comparison in Table X are the $\sigma_R{}^0$ and σ_R π delocalization effect parameters[7,9] and the F nmr shift parameters,[3] $\int_{m\text{-X}}{}^{p\text{-X}}$ (the para–meta difference or π electronic effect parameter). The substituents are listed in Table X in descending order of σ_R or $-\int_{m\text{-X}}{}^{p\text{-X}}$ values. *It is clear from Table X that all of the calculated π electronic effects in general show substantially this same substituent order.* The only exception occurs with certain features of the results for the +R substituents. That is, although the sequences $BF_2 > NO_2 > CF_3$ or $BF_2 > CHO > CN$ are followed without exception, the positions of CHO, NO_2, CF_3, and CN in the sequences differ, in particular, between the total π electronic delocalization effects, $\Sigma\Delta q_{(\pi)}{}^C$, and the delocalization effects at atomic positions, *i.e.*, $\Delta q_{(\pi)}{}^C$ or $\Delta q_{(\pi)}{}^F$. For the acetylene, ethylene, and benzene systems the $\Sigma\Delta q_{(\pi)}{}^F$ quantities each follow the σ_R sequence $BF_2 > CHO > NO_2 > CN > CF_3$. The $\Delta q_{(\pi)}{}^C$ or $\Delta q_{(\pi)}{}^F$ quantities for these systems in general, however, give CN < CF_3 and CHO < NO_2. This situation was noted in our prior communication on the monosubstituted benzenes[12] and is confirmed by the results of Table X as having generality in CNDO/2 calculations. We have noted that the summation, $\Sigma\Delta q_{(\pi)}{}^C$, taken over all of the carbon atoms of the unsaturated hydrocarbon cavity, should provide a more correct measure of the π delocalization effect of a substituent than $\Delta q_{(\pi)}{}^C$ at a localized atomic position. The π charge at an atomic position may be influenced both by substituent polarization[15] and by charge transfer from the substituent to the π molecular orbital. However, in the summation, $\Sigma\Delta q_{(\pi)}{}^C$, polarization effects should essentially cancel, giving a theoretical scale of the power of a substituent to delocalize π charge.[12]

To first approximation, $\Sigma\Delta q_{(\pi)}{}^C$ is independent of the hydrocarbon cavity. The excellent correlation of $\Sigma\Delta q_{(\pi)}{}^C$ for the benzene system with the $\sigma_R{}^0$ or σ_R

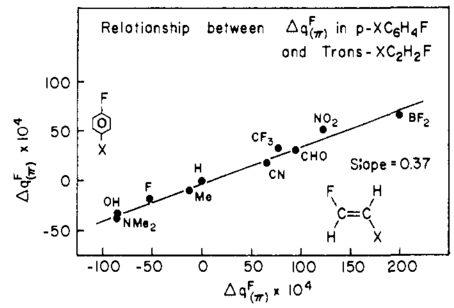


Figure 1. Relationship between $\Delta q_{(\pi)}{}^F$ in p-XC_6H_4F and *trans*-XC_2H_2F: ordinate, $10^4\Delta q_{(\pi)}{}^F$ for p-XC_6H_4F; abscissa, $10^4\Delta_{(\pi)}{}^F$ for *trans*-XC_2H_2F.

scale was noted previously.[12] In more quantitative detail, it is to be noted that the relationship of the $\Sigma\Delta q_{(\pi)}{}^C$ values to the hydrocarbon cavity appears to bear a distinction between $-R$ and $+R$ substituents, *e.g.*, for $-R$ substituents the absolute values of $\Sigma\Delta q_{(\pi)}{}^C$ increase in the order acetylene < benzene < ethylene, whereas for $+R$ substituents the order is acetylene < ethylene < benzene.

In the benzene system both NO_2 and CF_3 have excess π charges at the (para) carbon to which F is bonded (the same is true of the p-C of monosubstituted benzenes, *cf.* Table II), which are larger than the total π delocalization, $\Sigma\Delta q_{(\pi)}{}^C$. This result could be interpreted as evidence for appreciable π-polarization effects of the NO_2 and CF_3 substituents on $\Delta q_{(\pi)}{}^C$ values. However, additional considerations need to be discussed. We note here only that the $+R$ substituent effect behavior constitutes a relatively minor complication in the general accord of the CNDO/2 calculated π-electron substituent effects. Further discussion of the quantitative aspects (including potential defects) of the calculated charge density effects is postponed to the last section.

Directing attention now specifically to the π-electron effects on fluorine, plots of corresponding $\Delta q_{(\pi)}{}^F$ *vs.* $\Delta q_{(\pi)}{}^F$ values for the *trans*-fluoroethylene system *vs.* the para-substituted fluorobenzene (Figure 1) and for the fluoroacetylene *vs.* the para-substituted fluorobenzene (not shown) are satisfactorily linear. For the former, a slope of ~2.6 is obtained; for the latter the slope is ~1.7. Values greater than unity are more in accord with the smaller unsaturated hydrocarbon cavities of ethylene and acetylene than of benzene. The larger value for ethylene than acetylene is in accord with a greater π-electron mobility in the former, as expected for the less electronegative (sp^2 rather than sp) C atoms. Since $\Delta q_{(\pi)}{}^F$ values for para-substituted fluorobenzenes are very small (the average value is seven times the uncertainty of $\pm 5 \times 10^{-4}$), these linear plots add substantial confidence that the results in the benzene series are meaningful products of the CNDO/2 theory. The greatest scatter in these plots occurs for the $+R$ groups and is apparently associated with the considerations noted above.

Although no studies of a series of trans-substituent effects on F nmr shielding in fluoroethylenes have been made, it is interesting to note that a much larger upfield shift (~71.6 ppm) has been reported for the fluorine substituent of *trans*-difluoroethylene[17] than that (6.8 ppm) for the fluorine substituent of p-difluorobenzene.[12]

Two extremes in the origin of the π-electron effects at the fluorine atom may be considered: (1) a transfer of π charge between substituent and fluorine with attenuation of parallel effects at intervening carbon positions and, particularly, at the more electronegative fluorine atom; (2) a direct "field" polarization interaction between substituent and fluorine, essentially without π charge transfer. The general character of agreement of the π-electron effects of Table X clearly provides a theoretical basis (to CNDO/2 approximation) for the conclusion that the first mechanism is predominant. In first approximation, the results of Table X indicate that the $2p_z$ orbital of the fluorine probe reflects the π-electron effects which prevail at the bonded carbon atom. In turn, the π-electron effects at this carbon reflect the delocalization of π charge by the substituent.

Plots (not shown) of $\Delta q_{(\pi)}{}^F$ *vs.* corresponding values of $\Delta q_{(\pi)}{}^C$ (of the bonded carbon) for the benzene, ethylene, and acetylene systems are approximately bilinear. That is, plots are obtained with slopes of 7 for $+R$ substituents and slopes of ~14 for $-R$ substituents (indicating the much larger effects at carbon than fluorine). Earlier Hückel-type calculations for model $-R$ substituents in para-substituted fluorobenzenes gave a similar linear relationship with notably smaller slope (from 5.0 to 6.7, depending upon the computational method).[18]

It is of further interest in the interpretation of the fluorobenzene shifts to know the extent to which the fluorine probe may alter the π-electron effects at its bonded carbon. In Table XI are given $\Delta q_{(\pi)}{}^C$ values for the para carbon in monosubstituted benzenes and for corresponding para-substituted fluorobenzenes. Nearly identical values are obtained for all substituents; the ratio of the benzene to fluorobenzene values is 1.04 ± 0.01. This result and the smaller $\Delta q_{(\pi)}{}^C/\Delta q_{(\pi)}{}^F$ ratio for $+R$ (7) than $-R$ (14) substituents indicates according to CNDO/2 theory that direct conjugation, such as represented by

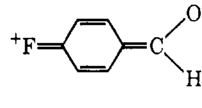


Table XI. π Electronic Effects[a]

Substituent, X	XC_6H_5	p-XC_6H_4F	
	$\Delta q_{(\pi)}{}^C$	$\Delta q_{(\pi)}{}^C$	$\Delta p_{(\pi)}{}^{C-F}$
BF_2	551	522	194
CHO	206	197	83
NO_2	355	343	142
CN	75	74	43
CF_3	244	233	93
H	0	0	0
Me	−151	−147	−41
F	−271	−257	−69
OH	−425	−409	−121
NMe_2	−468	−454	−136

[a] Δq's are in parts per ten thousand relative to H. The superscript C refers to the carbon position para to the substituent.

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[17] C. N. Banwell and N. Sheppard, *Proc. Roy. Soc., Ser., A*, **263**, 136 (1961); G. F. Flynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, 38, 2295 (1963).

[18] R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *ibid.*, 38, 380 (1963).

Table XII. σ Electronic Excess Charge Densities (in Parts per Ten Thousand Relative to H)

Substituent, X	σ_I	XC_6H_5	p-XC_6H_4F			$XC_8H_{12}F$		X-C_2H_3
		$\Sigma\Delta q_{(\sigma)}^{(H+C)}$ [a]	$\Delta q_{(\sigma)}^{C-X}$ [b]	$\Delta q_{(\sigma)}^{C-F}$ [c]	$\Delta q_{(\sigma)}^{F}$ [d]	$\Delta q_{(\sigma)}^{C-X}$ [b]	$\Delta q_{(\sigma)}^{F}$ [d]	$\Sigma\Delta q_{(\sigma)}^{(H+C)}$ [a]
NO_2	0.64	1703	937	−113	72	299	79	1583
CN	0.52	617	321	−17	25			665
F	0.51	2462	1936	85	39	1894	41	2463
CF_3	0.41	485	−81	−64	44			439
CHO	0.30	−21	−54	−66	14			2[i]
OH	0.27	1675	1252	144	17	1484	20	1685
BF_2	0.16[h]	−1332	−1107	−176	12	*e*	*f*	−1191
NMe_2	0.05	404	780	161	2			1189
H	0.00	0	0	0	0	0	0	0
Me	−0.05	125	77	53	−3			196

Substituent, X	t-XC_2H_2F			XC_2H	XC_2F			m-XC_6H_4F
	$\Delta q_{(\sigma)}^{C-X}$ [b]	$\Delta q_{(\sigma)}^{C-F}$ [c]	$\Delta q_{(\sigma)}^{F}$ [d]	$\Sigma\Delta q_{(\sigma)}^{(H+C)}$ [a]	$\Delta q_{(\sigma)}^{C-X}$ [b]	$\Delta q_{(\sigma)}^{C-F}$ [c]	$\Delta q_{(\sigma)}^{F}$ [d]	$-\int_H^{m-X}$ [g]
NO_2	965	−342	160	1446	412	121	193	3.45
CN	447	1	−7	792	−421	−44	41	2.80
F	2206	−5	158	2421	1056	374	233	3.10
CF_3	−30	−103	46	524	−374	6	80	2.20
CHO	6[j]	−150[k]	−28[l]	138	−340	−10	18	1.18
OH	1447	211	69	1650	511	80	129	1.20
BF_2	−1025	−319	−98	−834	−1200	−310	−53	0.54
NMe_2	1028	298	3	1150	144	336	65	0.08
H	0	0	0	0	0	0	0	0.00
Me	257	144	−56	318	−413	108	2	−1.20

[a] Relative excess σ charge densities summed over all carbon and hydrogen positions of the hydrocarbon cavity. The hydrogen atom of the reference H substituent is not included. [b] Relative excess σ charge densities at the carbon bearing substituent X. [c] Relative excess σ charge densities at the carbon bearing fluorine atom. [d] Relative excess $2p_y$ (σ) charge densities at fluorine. [e] For BH_2, $\Delta q_{(\sigma)}^{C-X} = -836$; for BH_2 in p-$FC_6H_4BH_2$, $\Delta q_{(\sigma)}^{C-X} = -298$. [f] For BH_2, $\Delta q_{(\sigma)}^{F} = -1$; for BH_2 in p-$FC_6H_4BH_2$, $\Delta q_{(\sigma)}^{F} = -5$. [g] From ref 2. [h] Calculated from unpublished results of Dr. Phillip Heffley. [i] For second conformation, 18. [j] For second conformation, 83. [k] For second conformation, −174. [l] For second conformation, −36.

for example, does enhance $\Delta q_{(\pi)}^{F}$ values for +R substituents. Katritzky, *et al.*,[19] have obtained experimental evidence for such effects in the F nmr shifts.

In Table XI are also listed values of the π bond order of the C–F bond in the para-substituted fluorobenzenes. The expected result is shown, namely, that decreases in π-electron densities at carbon and fluorine positions (*i.e.*, positive values of $\Delta q_{(\pi)}^{C}$ and $\Delta q_{(\pi)}^{F}$ are accompanied by an increase in π bond order (*i.e.*, increased values of $\Delta p_{(\pi)}^{C-F}$). The following relationships are followed: For −R substituents, $\Delta p_{(\pi)}^{C-F} = 3.5 \cdot \Delta q_{(\pi)}^{F}$; for +R substituents, $\Delta p_{(\pi)}^{C-F} = 2.5\Delta q_{(\pi)}^{F}$. The previous Hückel calculations for model −R substituents gave $\Delta p_{(\pi)}^{C-F} = 2.6\Delta q_{(\pi)}^{F}$, again a notably smaller slope.[18] The bilinear relationships for $\Delta q_{(\pi)}^{F}$ *vs.* $\Delta q_{(\pi)}^{C}$ and $\Delta q_{(\pi)}^{F}$ *vs.* $\Delta p_{(\pi)}^{C-F}$ also may be rationalized in terms of an enhancement of effects of +R substituents on fluorine resulting from direct conjugation.

σ Electronic Effects. These effects are summarized (except for effects on hydrogen which are listed separately in Table XIV) in Table XII. It is immediately apparent according to CNDO/2 theory that the σ-electron substituent effects (in contrast to the π effects) are not simply related between corresponding fluorine atoms of para-substituted fluorobenzenes, trans-substituted fluoroethylenes, or substituted fluoroacetylenes, or their bonded carbon atoms. Different substituent orders apply for each. In general, three completely distinct substituent scales have been recognized: (1) an electronegativity order,[20] for which the periodic electronegativity of the bonding atom of the substituent is predominant (variable hybridization or substitutional effects on this atom are of secondary importance) giving the order of electron-withdrawing effect $-B< \; < -C\leqslant$, $-H < -N< \; < -O- < -F$; (2) a polar effect scale[7] (σ_I), for which polar substitutional and hybridization effects on the bonding atom of the substituent frequency predominate over electronegativity considerations, giving the order $-CH_3 < H < -N(CH_3)_2 < -BF_2 < -OH < -C(=O)-H < -CF_3 < -F < -C\equiv N < -NO_2$; and (3) a π delocalization or resonance effect scale (σ_R), as discussed in the previous section. It is recognized, of course, that while electronegativity considerations do influence the substituent orders in the latter two scales, other considerations are of equal or greater importance.

The CNDO/2 calculations indicate that the electronegativity scale prevails at the carbon atom to which the substituent is bonded. Thus, the sequence $BF_2 < H, CH_3, CHO, CF_3, CN < N(CH_3)_2, NO_2 < OH < F$ is observed for the benzene, ethylene, and acetylene systems at the bonded carbons. For the substituted [2.2.2]bicyclooctyl 1-fluorides the same result apparently prevails, although fewer substituent effects were calculated in this series (owing to computer time limitations).

The substituent effect on the fluorine σ charge density of para-substituted fluorobenzenes corresponds in general to the polar effect scale. The correlation of these effects with the empirical σ_I scale is in fact quite satisfactory, as shown in Figure 2. The average deviation of points from the mean regression line (±6) is essentially the same as the convergence limit (±5). The largest deviations are for NO_2 (+19) and CN (−18). It may be significant that the CNDO/2 theory calculations of dipole moments of substituted benzenes are also poorest for these two substituents.[12] The dipole moment for nitrobenzene is over-calculated

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(19) J. M. Angelelli, R. T. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, **91**, 4500 (1969).

(20) (a) B. P. Dailey and J. N. Shoolery, *ibid.*, **77**, 3977 (1955); (b) P. R. Wells, *Progr. Phys. Org. Chem.*, **6**, 111 (1968).

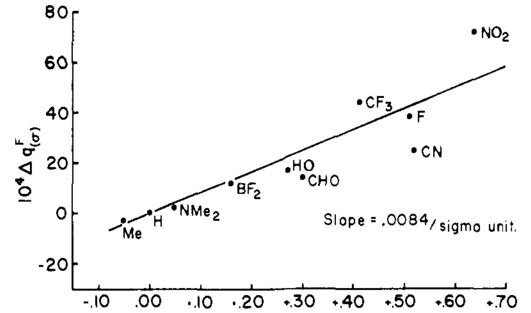

Figure 2. Correlation of substituent effects on fluorine σ charge density in para-substituted fluorobenzenes with σ_I: ordinate, $10^4\Delta q_{(\sigma)}^F$ for p-XC_6H_4F; abscissa, σ_I.

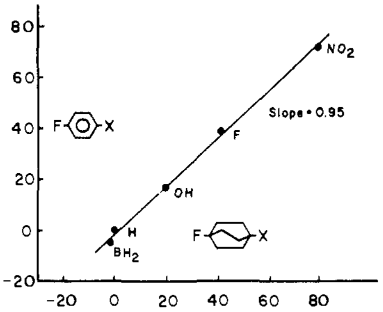

Figure 3. Linear relationship between fluorine σ-electron densities in para-substituted fluorobenzenes and 4-substituted [2.2.2]bicyclooctyl fluorides: ordinate, $10^4\Delta q_{(\sigma)}^F$ for p-XC_6H_4F; abscissa, $10^4\Delta q_{(\sigma)}^F$ for X-$C_8H_{12}F$.

(4.94 D compared to the experimental value of 4.3 D) and is under-calculated for benzonitrile (3.23 D compared to experimental value of 4.2 D).

It is of particular significance that the calculated effects of fluorine σ charge density are characterized by a dependence upon the fluorine substituent distance but no apparent dependence upon the σ charge density effects at the carbon to which the fluorine is bonded. The para-substituted fluorobenzenes and the 4-substituted [2.2.2]bicyclooctyl 1-fluorides have nearly equal corresponding fluorine–substituent distances. The substituent effects for these two systems are essentially identical. This result is of interest since it is consistent with the assumption of Roberts and Moreland[21] that the polar effects of a substituent on the ionization constant of para-substituted benzoic acid and 4-substituted benzoic acid and 4-substituted [2.2.2]bicyclooctane-1-carboxylic acids are equal. This assumption serves as the basis for the definition $\sigma_R \equiv \sigma - \sigma_I$.

Figure 3 shows a $\Delta q_{(\sigma)}^F$ *vs.* $\Delta q_{(\sigma)}^F$ plot for the fluorobenzenes *vs.* the bicyclooctyl fluorides, which is linear with slope of 0.95. The slightly smaller than unit slope of Figure 3 is in accord with the slightly longer fluorine–substituent distance for the para-substituted fluorobenzene system. It is apparent from Table XII that corresponding $\Delta q_{(\sigma)}^F$ effects in general increase with a shortening of this distance; *i.e.*, F–benzene < F–ethylene < F–acetylene. On the other hand, plots of $\Delta q_{(\sigma)}^F$ for the ethylene and acetylene systems *vs.* corresponding $\Delta q_{(\sigma)}^F$ values for the para-substituted fluorobenzenes (not shown) are not linear but show scatter patterns of at best crude linear trends. The calculated effects, $\Delta q_{(\sigma)}^F$, in the ethylene and acetylene systems are subject to considerable uncertainty, owing to assumed constant geometry, but the results do appear to lie somewhere in between the polar effect and the electronegativity effect scales.

The total (relative) σ charge transferred, $\Sigma\Delta q_{(\sigma)}^{(H+C)}$, between the substituent and the monosubstituted benzene, the ethylene, and the acetylene frameworks also follows a sequence lying between the polar and electronegativity effect scales. The complex character of the σ charge density at the carbon atom bonded to fluorine in all four systems of Table XII will be discussed further in the next section.

The point of emphasis at this stage is that the substituent effect on the fluorine σ charge densities in para-substituted fluorobenzenes and in 4-substituted [2.2.2]-bicyclooctyl 1-fluorides is unique in that the σ_I polar effect scale is followed. Further, this scale is not duplicated at the carbon bonded to fluorine or at any other carbon which intervenes between fluorine and the substituent. That is, according to CNDO/2 results, the fluorine atom σ charge density is *not* a probe of the σ charge density at either the C–F or C–X carbon. Table XIII shows additionally that the substituent σ charge density effects at the para carbon are somewhat different in para-substituted fluorobenzenes than in substituted benzenes. We conclude that the $\Delta q_{(\sigma)}^F$ effects in the fluorobenzene and bicyclooctane systems arise primarily as a consequence of a direct dipolar substituent–polar fluorine electrostatic interaction.

Table XIII. Comparison of σ Electronic Effects at Para Carbon[a]

Substituent X	p-XC_6H_4F $\Delta q_{(\sigma)}^C$	XC_6H_5 $\Delta q_{(\sigma)}^C$
NO_2	−113	−153
CN	−17	−31
F	85	79
CF_3	−64	−90
CHO	−66	−80
OH	144	148
BF_2	−176	−203
NMe_2	161	174
H	0	0
Me	53	58

[a] In parts per ten thousand.

Table XIV. σ Electronic Effects at Fluorine and Hydrogen[a]

Substituent X	p-XC_6H_4F $\Delta q_{(\sigma)}^F$	XC_6H_5 $\Delta q_{(\sigma)}^H$	XC_6H_5 $\Sigma\Delta q_{(\sigma)}^H$	$15\Delta q_{(\sigma)}^F$	$1250\sigma_I$
NO_2	72	128	1112	1080	800
CN	25	46	314	375	650
F	39	49	635	590	638
CF_3	44	79	562	660	513
CHO	14	36	258	210	375
OH	17	10	262	255	325
BF_2	12	50	168	180	200
NMe_2	2	−13	114	30	63
H	0	0	0	0	0
Me	−3	−7	−41	−45	−63

[a] Relative excess σ electronic charge densities in parts per ten thousand.

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[21] J. D. Roberts and W. T. Moreland, Jr., *J. Amer. Chem. Soc.*, 75, 2167 (1953).

Table XV. Relationship between σ Electronic Effects, $10^4\Delta_{q(\sigma)}{}^{C}$, at Corresponding Carbon Positions in $XC_8H_{12}F$ and p-XC_6H_4F

	Substituent, X: NO$_2$	NO$_2$	NO$_2$	OH	OH	OH	F	F	F
Position	$XC_8H_{12}F$	p-XC_6H_4F	p-XC_6H_4F[a]	$XC_8H_{12}F$	p-XC_6H_4F	p-XC_6H_2X[a]	$XC_8H_{12}F$	p-XC_6H_4F	p-XC_6H_4X[a]
vic-C_4	+299	+937	+669	+1384	+1252	+1481	+1894	+1938	+2076
o-C_3	−63 (−33)	−130	−18	−269 (−231)	−21 (+77)	−257 (−180)	−304	−85	−283
m-C_2	−1 (+1)	+33	+23	+16 (+11)	−52 (−59)	+62 (+20)	+25	−13	+77
p-C_1	+3	−113	+24	−33	+144	−20	−46	+85	−18

[a] Corrected.

It is of further interest to inquire into the relationship between the substituent effect of the fluorine σ charge density in para-substituted fluorobenzenes and the corresponding effects on charge density of the para hydrogen of substituted benzenes. The CNDO/2 results are shown in Table XIV. There is a rough parallel between corresponding values of $\Delta q_{(\sigma)}{}^{F}$ and $\Delta q_{(\sigma)}{}^{H}$; the latter on the average is about 80% greater. The larger substituent effects at hydrogen are presumably due to its lesser electronegativity. Table XIV also lists the total relative excess σ charge density, $\Sigma\Delta q_{(\sigma)}{}^{H}$, summed over the five hydrogen atoms of the substituted benzenes. This quantity even more closely parallels corresponding $\Delta q_{(\sigma)}{}^{F}$ values, as indicated by comparison with the quantity $15\Delta q_{(\sigma)}{}^{F}$, which is also listed. Finally, Table XIV lists the quantity $1250\sigma_I$, for which the approximate equality with $\Sigma\Delta q_{(\sigma)}{}^{H}$ indicates the correlation of the latter with the σ_I scale.[22] It will be noted that deviations for the NO_2 and CN substituents are similar to those discussed above for $\Delta q_{(\sigma)}{}^{F}$. It is of interest to note in connection with the CNDO/2 calculations of hydrogen σ-electron effects that Schmid[23] has found evidence from ir intensity measurements that the C–H bond moments of substituted benzenes follow σ_I values.

π–σ Electron Relationships. The CNDO/2 results show interactions between σ- and π-electron effects which vary in importance depending upon the kind of atomic position. At the para carbon of monosubstituted benzenes (or of para-substituted fluorobenzenes) an increase in π charge density is accompanied by a (smaller) decrease in σ charge density. The relationship is quite a precisely linear one, as shown in Figure 4. The negative slope of −3.0 apparently supports the conclusion that the σ charge density at the para carbon is predominantly controlled by the repulsion from the π electronic charge which accumulates (due to π delocalization) at this position.

Similar qualitative relationships hold for the σ and π electronic substituent effects at the 2-carbon position of 1-substituted ethylenes (or *trans*-fluoroethylenes) and 1-substituted acetylenes (or fluoro-substituted acetylenes), but the precise linear relationship of the para benzene system is not found in either of these cases.

We are indebted to Professor R. D. Topsom for pointing out to us that the approximate relationship (*cf.* Tables II–IX) $\Delta q_{(\sigma)}{}^{C}$(benzene) $\cong$ $\Delta q_{(\sigma)}{}^{C}$(bicyclooctane) − $0.4\Delta q_{(\pi)}{}^{C}$(benzene) is obeyed for the carbon positions ortho, meta, and para to the substituent of p-XC_6H_4F. That is, when the π-electron effect ($-0.4\Delta q_{(\pi)}{}^{C}$) on the $\Delta q_{(\sigma)}{}^{C}$ values for *o*-, *m*-, and *p*-C is removed, a pattern of σ-electron effects in the benzene framework emerges which is very nearly equal to that shown at the corresponding 3, 2, and 1 positions of the 4-substituted [2.2.2]bicyclooctyl 1-fluorides. This pattern is characterized by two distinct features. First, there is generally an attenuating alternation down the chain in sign of the σ-electron effect, as Pople[11] has discussed for straight-chain derivatives. Second, the corrected σ electronic effects at all carbon positions follow the electronegativity order. These relationships are illustrated in Table XV.

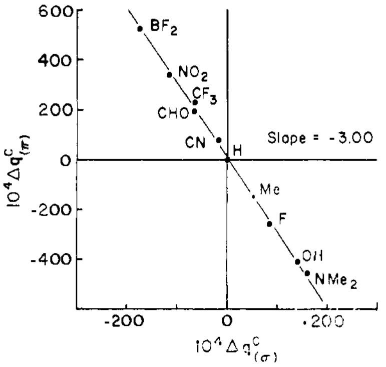

Figure 4. Correlation between substituent effects on π- and σ-electron densities at carbon para to the substituent in p-XC_6H_4F: ordinate, $10^4\Delta q_{(\pi)}{}^{C}$ for p-XC_6H_4F; abscissa, $10^4\Delta q_{(\sigma)}{}^{C}$ for p-XC_6H_4F.

Topsom's relationship (above) is of particular interest because it illustrates the importance in the CNDO/2 results of π effects on σ effects, but, perhaps surprisingly, shows (together with the results of Table X) that there is little or no apparent σ effect on the π electronic effects. It is of obvious interest to know whether these results are "real" or are instead an artifact of the CNDO/2 approximations. It may also be noted in this connection that the real existence of alternation of sign down the chain for σ electronic effects might be thought to be in conflict with the simplified but conventional interpretation of ρ_I (or ρ^*) values. These reaction parameters have been interpreted as being directly related to the change in charge density at a reaction center. Values of ρ_I (or ρ^*) do not alternate in sign down the chain for polar substituent effects or rates on equilibria. However, there appears to be no reason why attenuating alternation of the sign of σ-electron densities down a chain may not be consistent with attenuating nonalternating changes in σ-electron density at a "reaction center" which is progressively moved down a chain.

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[22] D. Blagdon, private communication, has noted a similar correlation.

[23] E. D. Schmid, *et al.*, *Spectrochim. Acta*, 22, 1615, 1621, 1633, 1645, 1659 (1966).

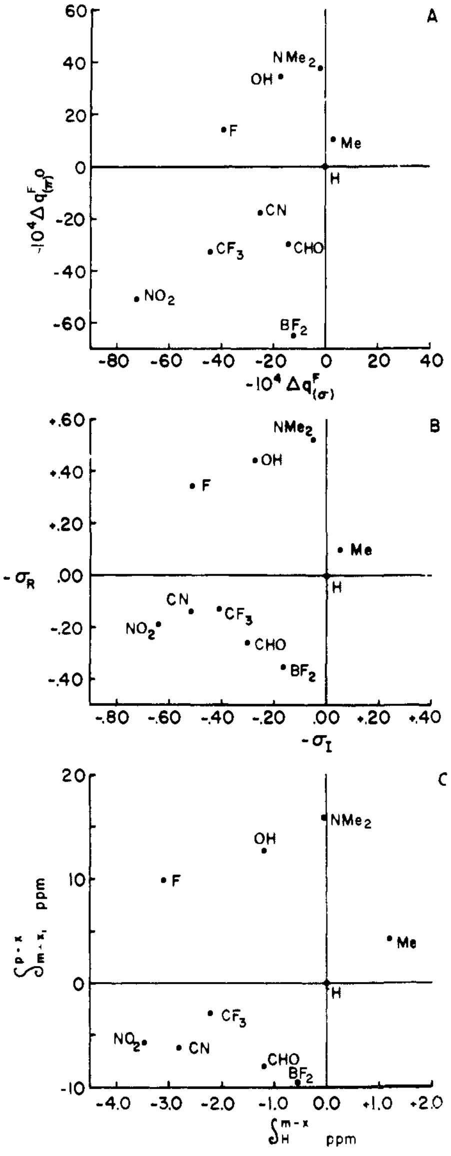

Figure 5. Corresponding quadrant scatter patterns. A: ordinate, $-10^4\Delta q_{(\pi)}{}^F$ for p-XC_6H_4F; abscissa, $-10^4\Delta q_{(\sigma)}{}^F$ for p-XC_6H_4F. B: ordinate, $-\sigma_R{}^0$; abscissa, $-\sigma_I$. C: ordinate, $\int_{m-X}{}^{p-X}$, ppm; abscissa, $\int_H{}^{m-X}$, ppm.

Returning to the fluorine atomic position of primary concern, there is no evidence in the CNDO/2 calculations of any appreciable interaction of σ- and π-electron effects. Figure 5A shows a plot for para-substituted fluorobenzenes of $\Delta q_{(\pi)}{}^F$ *vs.* corresponding $\Delta q_{(\sigma)}{}^F$ values. The scatter pattern of this plot (quadrant occupancy of substituent points) is familiar; *i.e.*, it takes the same form as plots of $-\sigma_R$ *vs.* $-\sigma_I$ (Figure 5B) or the F nmr shifts, $\int_{m-X}{}^{p-X}$ *vs.* $\int_H{}^{m-X}$ (Figure 5C). Qualitatively similar plots are observed for trans-substituted fluoroethylenes and substituted fluoroacetylenes. The distinctly nonlinear relationship between $\Delta q_{(\pi)}{}^F$ and $\Delta q_{(\sigma)}{}^F$ (Figure 5A) in contrast to the precise linear relationship between $\Delta q_{(\pi)}{}^C$ and $\Delta q_{(\sigma)}{}^C$ at the carbon to which the fluorine is bonded (Figure 4), supports the conclusion that the $\Delta q_{(\sigma)}{}^F$ effects are not transmitted from the adjacent carbon positions but rather result from a direct substituent–fluorine electrostatic interaction.

Further evidence of little or no interaction between the π and σ electronic substituent effects at fluorine is provided by Figure 3. As discussed in the first section of this paper, there are notable π electronic effects at the p-F of the fluorobenzenes. There are, however, no π electronic effects on the fluorine of the 4-substituted [2.2.2]bicyclooctyl 1-fluorides, both the $2p_z$ and $2p_x$ orbitals having constant values of charge density. Consequently, Figure 3 shows that the variable π electronic effects in the fluorobenzenes compared to the absence of such effects in the bicyclooctyl fluorides does not upset the linear relationship between the corresponding σ electronic effects, $\Delta q_{(\sigma)}{}^F$, in these two systems.

Meta-Substituted Fluorobenzenes. The effects of meta substituents on the fluorobenzene fluorine orbitals may be summarized by comparison with corresponding effects of para substituents. These results are shown in Table XVI. It is clear that corresponding σ effects from the meta and para positions ($\Delta q_{(\sigma)}{}^{m-F}$ and $\Delta q_{(\sigma)}{}^{p-F}$, respectively) are the same in sign and generally of the same magnitudes, *i.e.*, *very crudely* are equal. The small difference between $\Delta q_{(\sigma)}{}^{m-F}$ and $\Delta q_{(\sigma)}{}^{p-F}$, however, does show a σ_R dependence, being a positive quantity for +R substituents and a negative quantity for −R substituents. We are unable to offer a satisfactory explanation for this apparent π effect contribution to $\Delta q_{(\sigma)}{}^{m-F}$ values, particularly in view of the results given in the previous section. Since the differences in general are relatively small, we shall neglect them, but will regard $\Delta q_{(\sigma)}{}^{p-F}$ as a better measure than $\Delta q_{(\sigma)}{}^{m-F}$ of "pure" σ electronic effects at fluorine.

Table XVI. Comparison of Fluorine π and σ Effects in m- and p-XC_6H_4F[a]

	π effects		σ effects	
	$\Delta q_{(\pi)}{}^{m-F}$	$\Delta q_{(\pi)}{}^{p-F}$	$\Delta q_{(\sigma)}{}^{m-F}$	$\Delta q_{(\sigma)}{}^{p-F}$
BF_2	−11	65	41	12
CHO	0	30	22	14
NO_2	6	51	104	72
CN	8	18	33	25
CF_3	8	33	61	44
H	0	0	0	0
CH_3	10	−10	−15	−3
F	21	−18	31	39
OH	21	−34	0	17
$N(CH_3)_2$	20	−37	−25	2

[a] In parts per ten thousand.

On the other hand, corresponding π electronic effects from the meta and para positions cannot be characterized by a sign relationship (for NO_2, CN, and CF_3 the sign is the same; for BF_2, CH_3, F, OH, and $N(CH_3)_2$ it is opposite). Further, the calculated values of $\Delta q_{(\pi)}{}^{m-F}$ are generally very small, the largest value being only four times and the average value being only two times the convergence limit of $\pm 5 \times 10^{-4}$. Consequently, it may be concluded from CNDO/2 theory that the dominant effect of the meta substituent on the fluorine orbital densities is its effect on the σ charge density. The π effect from the meta position is apparently too small to even identify correctly its direction.

The σ and π electronic effects at the bonded (C–F) meta carbon are also of interest. Table XVII lists these values, $\Delta q_{(\sigma)}{}^{m-C}$ and $\Delta q_{(\pi)}{}^{m-C}$, in comparison with the corresponding effects on the meta

Table XVII. Comparison of π and σ Effects at Fluorine and Its Bonded Carbon in m-XC_6H_4F[a]

	π effects		σ effects	
	$\Delta q_{(\pi)}^{m-C}$	$\Delta q_{(\pi)}^{m-F}$	$\Delta q_{(\sigma)}^{m-C}$	$\Delta q_{\sigma)}^{m-F}$
BF_2	−181	−11	−7	41
CHO	−24	0	−10	22
NO_2	−17	6	72	104
CN	63	8	39	33
CF_3	14	8	0	61
H	0	0	0	0
CH_3	117	10	68	−15
F	213	21	12	31
OH	259	21	−41	0
$N(CH_3)_2$	259	30	−68	25

[a] In parts per ten thousand.

Table XVIII. Comparison of Calculated σ- and π-Electron Effects on m- and p-F Substituents

Substituent	$\Delta q_{(\sigma)}^{F}$ [a]	$\Delta q_{(\pi)}^{F}$ [a]	$\Delta q_{(\sigma)}^{F}$ [b]	$\Delta q_{(\pi)}^{F}$ [b]	$\Delta q_{(\sigma)}^{F}$ [c]	$\Delta q_{(\pi)}^{F}$ [c]
m-F	50	27	141	141	+16	21
p-F	52	−27	162	162	−13	−18

[a] Reference 24. [b] Reference 25. [c] Present results.

fluorine. Just as discussed for para substituents, the effects of meta substituents on the σ-electron densities at fluorine and its bonded carbon show no simple relationship; the signs of corresponding $\Delta q_{(\sigma)}^{m-C}$ values are sometimes the same, sometimes opposite; magnitudes are sometimes similar, sometimes dissimilar. Again, the conclusion is that the fluorine atom is *not* a probe of σ electronic effects at carbon.

Although comparison of $\Delta q_{(\pi)}^{m-C}$ values of Table XVII with corresponding $\Delta q_{(\pi)}^{p-C}$ values of Table X indicates that π electronic effects are frequently of opposite signs at the meta and para carbon positions,[10] the CNDO/2 results for both CN and CF_3 are of the same sign at these positions. Similarly, although values of $\Delta q_{(\pi)}^{m-F}$ are frequently of the same sign as $\Delta q_{(\pi)}^{m-C}$, the NO_2 substituent results do not conform to such a generalization. Consequently, it remains unclear from CNDO/2 theory as to the role of π electronic effects at meta positions.

Comparison with Other Calculations. The CNDO/2 results reported earlier by Davies[14] for the m- and p-fluoro and -nitro substituent effects in the fluorobenzenes are generally closely the same as given here. Comparison can be made for the m- and p-fluoro substituent effects in fluorobenzenes obtained in the present CNDO/2 calculations with corresponding values reported by Emsley,[24] using his modification for obtaining the elements of the Hamiltonian matrix, and by Dewar and Kelemen,[25] using their PNDO method. These comparisons are shown in Table XVIII.

The patterns displayed in each of these calculations, *e.g.*, $\Delta q_{(\sigma)}^{m-F} \cong \Delta q_{(\sigma)}^{p-F}$ and $\Delta q_{(\pi)}^{m-F} \cong -\Delta q_{(\pi)}^{p-F}$, are the same, although numerical values may differ substantially. The available comparison is much too limited, however, to draw any general conclusions.

Correlations between CNDO/2 Charge Densities and Experimental F Nmr Shifts. Conclusions. None of the existing formulations of the F nmr shift in terms of charge density and bond order terms gives satisfactory calculations of the experimental shifts using the CNDO/2 results.[4,5,14,18,26] In order to draw significant conclusions, therefore, we turn to empirical considerations. In addition to eq 1 and 2 of the introduction, the following additional correlations of nmr shifts are important.

The p-F nmr shifts of substituted fluorobenzenes are generally well correlated by corresponding ^{13}C nmr shifts at the para carbon atoms of monosubstituted benzenes[27] and of para-substituted fluorobenzenes.[28] The p-P nmr shifts of monosubstituted benzenes, although much smaller in magnitude, also are correlated by the p-F nmr shifts.[27b] The m-F nmr shifts of substituted fluorobenzenes, however, are unique. These shifts are not correlated by the corresponding ^{13}C nmr shifts at the meta carbon atom of monosubstituted benzenes or by m-P nmr shifts.[29] That is, the only meta shifts correlated satisfactorily by σ_I parameters (above) are the m-F nmr shifts of substituted fluorobenzenes (*cf.* low value of $\rho_R^m/\rho_I^m \cong 0.1$ in eq 2).

These empirical results may be compared with the following summary of theoretical results of the CNDO/2 calculations.

(1) In first approximation, the $2p_z$ (π) orbital charge density of the fluorine probe reflects the π-electron effects which prevail at the bonded carbon atom. The latter effects, in turn, are a reflection of the delocalization of π charge by the substituent. In general, all of the calculated π electronic effects ($\Sigma\Delta q_{(\pi)}$, $\Delta q_{(\pi)}^{C}$, $\Delta q_{(\pi)}^{F}$, $\Delta p_{(\pi)}^{C-F}$ for the benzene, ethylene, and acetylene systems) show substantially the same (σ_R^0 or σ_R) substituent order.

(2) The substituent effect on the fluorine $2p_y$ (σ) orbital charge density of para-substituted fluorobenzenes and of 4-substituted [2.2.2]bicyclooctyl 1-fluorides (and to poorer approximation, of meta-substituted fluorobenzenes) are equal and correspond well, in general, to the polar effect scale, σ_I. These effects are unique to the fluorine atoms of these two systems—they are not found at any intervening carbon positions. The effects arise primarily as a consequence of a direct dipolar substituent–polar fluorine electrostatic interaction.

(3) At the fluorine position, there is no evidence of any appreciable interaction (interdependence) of σ- and π-electron effects.

(4) The dominant effect of the meta substituent on the fluorine orbital densities is its effect on the σ charge density. The π effect from the meta position is apparently too small to even identify correctly its direction.

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(24) J. W. Emsley, *J. Chem. Soc. A*, 2735 (1968).

(25) M. J. S. Dewar and J. Kelemen, *J. Chem. Phys.*, **49**, 499 (1968).

(26) G. L. Caldow, *Mol. Phys.*, **11**, 71 (1966).

(27) (a) P. C. Lauterbur, *Tetrahedron Lett.*, **8**, 274 (1961); (b) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(28) G. E. Maciel and J. J. Natterstad, *ibid.*, **42**, 2427 (1965).

(29) W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 379 (1967). Because of the lack of generalized correlations of the meta shifts, Dewar concluded (incorrectly, we believe) that eq 2 for the m-F nmr shifts is "fortuitous and irrelevant."

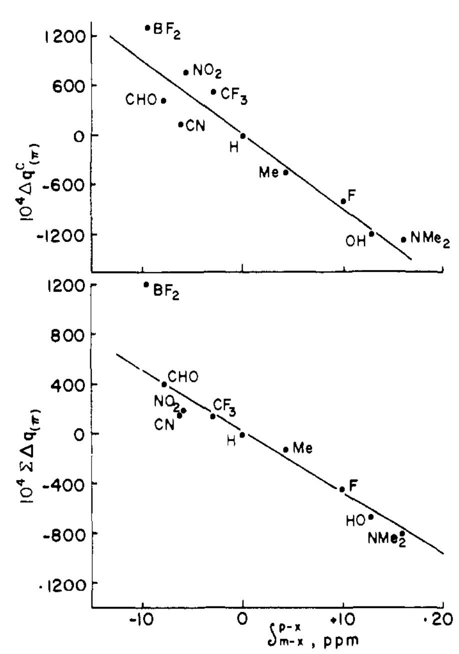

Figure 6. Correlation of π-electron effects with F nmr π electronic shielding. Upper: ordinate, $10^4\Delta q_{(\pi)}{}^{C}$ for carbon-2 of trans 1-substituted 2-fluoroethylenes; abscissa, $\int_{m-X}{}^{p-X}$, ppm. Lower: ordinate, $10^4\Sigma\Delta q_{(\pi)}{}^{C}$ for monosubstituted benzenes; abscissa, $\int_{m-X}{}^{p-X}$, ppm.

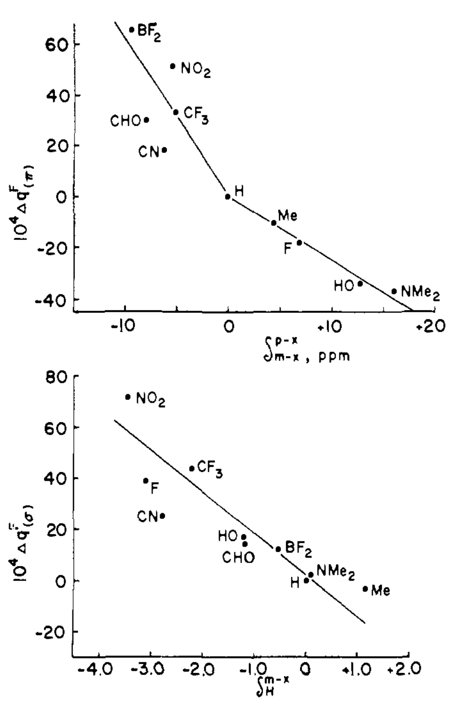

Figure 7. Upper: correlation of substituent effect on fluorine π-electron charge density in p-XC_6H_4F with F nmr π-electron shielding parameter, $\int_{m-X}{}^{p-X}$; ordinate, $10^4\Delta q_{(\pi)}{}^{F}$ for p-XC_6H_4F; abscissa, $\int_{m-X}{}^{p-X}$, ppm. Lower: correlation of substituent effect on fluorine σ-electron charge density in p-XC_6H_4F with F nmr σ-electron effect parameter, $\int_{H}{}^{m-X}$; ordinate, $10^4\Delta q_{(\sigma)}$ for p-XC_6H_4F; abscissa, $\int_{H}{}^{m-X}$, ppm.

The near 1:1 correspondence between empirical correlations and the conclusions from the CNDO/2 calculations, we believe, is impressive. This result is strongly suggestive that the F nmr shift may be directly related, at least approximately, to the sum of separate effects on σ and π charge densities of the fluorine orbitals. At least with the assumption of such a relationship, the CNDO/2 theoretical results appear to provide useful guidelines for the interpretation of the F nmr shifts. For example, the earlier conclusion[8] that the para–meta shift, $\int_{m-X}{}^{p-Y}$, is a π-electron effect parameter (at fluorine) and the meta shift, $\int_{H}{}^{m-X}$, is predominantly a σ-electron effect parameter (at fluorine) are readily understood in such terms.

Finally, the more precise quantitative character of the indicated relationships is of interest. Correlations of the various CNDO/2 calculations of the π-electron effect and of the experimental F nmr shift π-electron parameter, $\int_{m-X}{}^{p-X}$, with the empirical $\sigma_R{}^0$ parameter, of course, implies similar correlations between the first two quantities. Figure 6 illustrates two such relationships. The upper plot shows one of the largest calculated π-electron effects at atomic carbon (from Table X), namely, $\Delta q_{(\pi)}{}^{C}$ for carbon-2 of trans 1-substituted 2-fluoroethylenes plotted *vs.* corresponding $\int_{m-X}{}^{p-X}$ values. The lower plot of Figure 7 shows $\Sigma\Delta q_{(\pi)}{}^{C}$ for substituted benzenes[12] plotted *vs.* $\int_{m-X}{}^{p-X}$ values. While both plots are regarded as generally satisfactory there is scatter in both; the upper plot illustrates the nature of the "inverted orders" for certain of the +R substituents as discussed in the section on π-electron effects. Possible sources of the scatter in the plots of Figure 7 include: (i) polarization effects (as distinguished from π delocalization effects, *cf.* the discussion in the section on π effects) contributing to $\Delta q_{(\pi)}{}^{C}$ and $\Delta q_{(\pi)}{}^{F}$ values; (ii) CNDO/2 artifacts; (iii) contributions of secondary polarization effects to the F nmr shift parameter, $\int_{m-X}{}^{p-X}$. The experimental measures of the π- and σ-electron effects, *i.e.*, $\int_{m-X}{}^{p-X}$ and $\int_{H}{}^{m-X}$, respectively, are plotted in Figure 7 *vs.* the corresponding π and σ electronic effects calculated for the fluorine atom, *i.e.*, $\Delta q_{(\pi)}{}^{F}$ and $\Delta q_{(\sigma)}{}^{F}$ for p-XC_6H_4F. As discussed in a previous section, we regard the calculations of the latter two quantities for the p-XC_6H_4F system as being more reliable than for either of the corresponding quantities for the m-XC_6H_4F system.[30] The upper plot of Figure 6 shows $\Delta q_{(\pi)}{}^{F}$ plotted *vs.* corresponding $\int_{m-X}{}^{p-X}$ values. The lower plot is of corresponding $\Delta q_{(\sigma)}{}^{F}$ *vs.* $\int_{H}{}^{m-X}$ values.

In addition to points made earlier, two features of the plots of Figure 7 deserve comment. First, the separate lines indicated for +R and −R substituents in the upper (π effects) plot are certainly open to question (especially, of course, the quantitative slopes). Reasons for questioning these separate slopes are (i) there is (as noted before) a relatively high degree of scatter of points for the +R substituents; (ii) there is the possibility of a CNDO/2 artifact which tends to downgrade the π-electron effects on fluorine of −R relative to +R substituents. In Table XIX are listed estimates of "experimental" and CNDO/2 calculated π-electron densities at the para carbon of para-substituted benzenes. The former have been obtained as quoted by Wells.[31] While the agreement is generally good for +R substituents, the calculated values for −R sub-

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(30) We have noted (as suggested by earlier results and discussion) that the individual m- and p-F nmr shifts may be fitted roughly by the following empirical relationships: meta, $\int_{H}{}^{m-X} = \rho_I{}'\Delta q_{(\sigma)}{}^{p-F} + \rho_R{}'\Delta q_{(\pi)}{}^{p-F}$; para, $\int_{H(\pi)}{}^{p-X} = \rho_I{}''\Delta q_{(\sigma)}{}^{p-F} + \rho_R{}''\Delta q_{(\pi)}{}^{p-F}$. The significance of such relationships, however, is in substantial doubt.

(31) P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968, pp 103–104.

Table XIX. Approximate Experimental and Calculated π-Electron Densities at Para Carbon in p-XC_6H_5

	Exptl q_{best}[a]	CNDO/2 q_{calcd}
NMe_2	1.080	1.047
OH	1.059	1.043
F	1.045	1.027
Me	1.020	1.015
H	(1.000)	(1.000)
CF_3	0.982	0.976
CN	0.978	0.992
NO_2	0.974	0.964
CHO	0.961	0.979
BF_2	0.952	0.945

[a] Reference 31.

stituents are appreciably less than the "experimental" values in every case.

The second feature regarding Figure 7 is that the slopes of the plots are of different orders of magnitude (0.0006 and 0.0002 electron/ppm for the upper "π"-electron effect plot and 0.0016 electron/ppm for the lower "σ"-electron effect plot). This result indicates (as seems intuitively reasonable) that the F nmr shifts are more highly dependent upon charge density in the fluorine $2p_z$ (π) than in the $2p_y$ (σ) orbital. Dewar has recently reached a similar conclusion based upon correlations of F nmr shifts for aryl polyfluorides with his calculated $\Delta q_{(\pi)}^F$ values.[25] A consequence of this different dependence is that the F nmr shifts for p-XC_6H_4F compounds are not correlated by the substituent effect on the total charge density of fluorine, $\Delta q_{(tot)}^F = \Delta q_{(\pi)}^F + \Delta q_{(\sigma)}^F$. The ^{13}C nmr shifts for substituted benzenes, pyridine, and quinolines are reported[32] to be best correlated by $\Delta q_{(tot)}^C$. For the F nmr shifts, the inadequacy of the correlation with $\Delta q_{(tot)}^F$ values is readily seen by comparison of these values with corresponding para shifts, $\int_H^{p-X}$ (listed in Table XX).

Table XX. Comparison of $10^4\Delta q_{tot}^F$ and $\int_H^{p-X}$ Values for p-XC_6H_4F

Substituent, X	Δq_π^F	Δq_σ^F	Δq_{tot}^F	$-\int_H^{p-X}$, ppm
BF_2	65	12	77	10.04
CHO	30	14	44	9.15
NO_2	51	72	123	9.20
CN	18	25	43	8.95
CF_3	33	44	77	5.05
H	0	0	0	0
Me	−10	−3	−13	−5.40
F	−18	39	21	−6.80
OH	−34	17	−17	−11.60
NMe_2	−37	2	−35	−15.90

Finally, with respect to fluorine shifts in the 4-substituted [2.2.2]bicyclooctyl 1-fluorides, it is of interest that the few available substituent effects are in a qualitative σ_I order, but the direction of the shift is opposite to that of the fluorobenzene system.[33] However, Stock has presented evidence that geometrical considerations probably are the dominant factor influencing these experimental F nmr shifts.[28]

Acknowledgment. The helpful comments and suggestions of Dr. Stanton Ehrenson are gratefully acknowledged. We are also indebted to Professors R. D. Topsorn, L. M. Stock, and C. Eaborn for valuable comments in the preparation of this manuscript.

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(32) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).

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Self-Consistent-Field Wave Functions for $1,2\text{-}B_4C_2H_6$ and $1,6\text{-}B_4C_2H_6$

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Abstract: SCF molecular orbital wave functions for the two isomers of $B_4C_2H_6$ have been obtained from a minimum basis set of Slater-type atomic orbitals. Ionization potentials of 9.90 and 9.25 eV are predicted, respectively, for the 1,2 and the 1,6 isomers. The 1,6 isomer is computed to be more stable than the 1,2 isomer by about 15 kcal/mol. Charge densities are presented in certain sections of these isomers. In $1,2\text{-}B_4C_2H_6$, atom B_3 (attached to two C atoms) is expected to be sightly less reactive toward electrophiles than atom B_4 (attached to one C atom). The calculated dipole moment of 2.95 D makes the carbon side of the 1,2 isomer positive, but the value is expected to be too large by about a factor of 2, because of the minimum basis set.

The polyhedral carboranes are a series of extremely stable compounds, for which a quite extensive chemistry has grown up in recent years.[3–6] They have been the subject of much theoretical investigation by molecular orbital (MO) techniques which has provided insight into their interesting properties. Both the

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(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.