Halogen-Containing Substituents. II. The Methoxy System. Reactivity Parameters. Charge Distribution and Conformation of the Anisoles[1]

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Received January 7, 1972

The side-chain halogenated anisoles $ArOCH_2X$, $ArOCHX_2$, and $ArOCX_3$, with Ar = Ph, *m*-FPh, and *p*-FPh and X = F and Cl, were studied in order to elucidate both the substituent parameters of the side-chain groups and their electronic distributions; the latter were calculated by the CNDO/2 method. Analysis of the results gave an estimation of the apparent conformation of the anisoles with respect to the angle by which the halogenated methyl group is twisted out of the benzene plane.

In the first paper of this series,[1] a study of the electronic properties of halogen-containing methyl groups was presented. With these results established firmly, we are now reporting a study of halogen-containing (F, Cl) methoxy groups, where the primary objective was a systematic evaluation of their electronic properties in terms of the experimental parameters, σ_I and σ_R°. In addition, it was anticipated that comparison of the data for the methyl and methoxy series would provide valuable insight into the factors controlling the electronic behavior of the oxygen linking atom.

The most highly developed method for obtaining such information is Taft's treatment[2,3] of the Hammett equation, which involves examination of the appropriately substituted phenyl system. This treatment ascribes the effect of a substituent to the sum of two independent contributions resulting from inductive and resonance interactions. Such a separation, which has been examined critically by Ehrenson,[4] has found application, among others, in studies of the electronic transmission modes,[5] of the role of π(p-d) conjugation in suitable systems,[6] and recently in the correlation between the empirical and a theoretically calculated scale of resonance.[7]

In the course of determining the ground-state charge distributions for the anisoles by Pople's CNDO/2 method,[8] the question of the precise conformation of the substrates became important. A limited amount of data is available; for example, X-ray analysis has shown that *p*-dimethoxybenzene adopts a trans-planar conformation in the crystal[9] and dipole moment and Kerr constant measurements[10] have shown that in para-substituted anisoles the methyl group is apparently twisted out of the plane of the benzene ring. However, information concerning side-chain substituted anisoles is not available; hence, we have used the CNDO/2 results in conjunction with the experimental parameters to explore new methods for determining conformations in these molecules.

Results and Discussion

The series of anisoles $ArOCH_2X$, $ArOCHX_2$, $ArOCX_3$, with X = F, Cl, and Ar = Ph, *m*-FPh, *p*-FPh (excepting $ArOCH_2F$), were prepared as described in the Experimental Section. The substituent parameters of the groups were determined using both the ^{19}F nmr and the infrared methods. Thus, chemical shifts (δ) of the meta and para fluorines in the fluorophenyl compounds[2,3] were measured and are recorded in Table I together with the σ_I and σ_R° parameters derived from the equations

$$\delta_m = -7.1\sigma_I + 0.60 \quad (1)$$

$$\delta_p - \delta_m = -29.5\sigma_R^\circ \quad (2)$$

The resonance parameters were also obtained using Katritzky's[1,11] infrared method, in which the square root of the intensities of the 1600-cm^{-1} ring-stretching vibrations, $A^{1/2}$, of the appropriate monosubstituted benzene was calculated and the corresponding σ_R° value was derived from the equation

$$\sigma_R^\circ = 0.0079A^{1/2} - 0.027 \quad (3)$$

These values are also given in Table I. Good agreement between the ^{19}F and infrared methods is noteworthy and serves to increase confidence in their application and reliability.

All attempts to prepare the α-fluoroanisoles required for this study were unsuccessful; however, the substituent constants for OCH_2F were obtained by linear interpolation of the plots (not given) of σ_I or σ_R° values *vs.* the number of fluorine atoms in $OCH_{3-n}F_n$ (n = 0–3). In similar plots for the chlorine series, a slight damping effect reminiscent of that for the halogen-containing methyl series[1] was observed and, although this effect was less pronounced here, it is ratio-

(1) Part I: E. T. McBee, I. W. Serfaty, and T. Hodgins, *J. Amer. Chem. Soc.*, **93**, 5711 (1971).

(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 (1963).

(3) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963). A refined treatment of σ_I and σ_R° parameters of substituents in the benzene system is forthcoming (see ref 14 cited in P. R. Wells, S. Ehrenson, and R. W. Taft, in "Progress in Physical Organic Chemistry," Vol. 6, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1968, p 147). These results are not expected to affect the conclusions of this study. (b) R. Pollet, R. Van Pouke, and A. De Cat, *Bull. Soc. Chim. Belg.*, **75**, 40 (1966). These authors measured substituent constants for the $OCHF_2$ group.

(4) S. Ehrenson in "Progress in Physical Organic Chemistry," Vol. 2, S. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1964, p 195, and references cited therein.

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

(6) R. W. Taft and J. W. Rakshys, *J. Amer. Chem. Soc.*, **87**, 4387 (1965).

(7) R. T. C. Brownlee and R. W. Taft, *ibid.*, **90**, 6537 (1968); **92**, 7007 (1970).

(8) (a) J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967); (b) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970; (c) J. A. Pople, *Accounts Chem. Res.*, **3**, 217 (1970).

(9) T. H. Goodwin, M. Przybylska, and J. M. Robertson, *Acta Crystallogr.*, **3**, 279 (1950).

(10) (a) M. J. Aroney, R. J. W. LeFevre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc. B*, 666 (1969); (b) M. J. Aroney, M. G. Corfield, and R. J. W. LeFevre, *J. Chem. Soc.*, 2954 (1964).

(11) (a) R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, **88**, 1413 (1966); (b) R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *ibid.*, **89**, 1757 (1967).

TABLE I
SCALES OF SUBSTITUENT EFFECTS DERIVED FROM ^{19}F NMR AND INFRARED MEASUREMENTS AND FROM MO CALCULATIONS

Substituent	^{19}F Nmr[a] δ_m	δ_p	σ_I	σ_R°	Ir[b] $A^{1/2}$	$\pm\sigma_R^\circ$	MO[c] Δq_π[4]	$\Sigma\Delta q_\pi$	m
OCH_3[d]	−1.05	11.45	0.29	−0.425	57.7	0.430	−396	−647	2
OCH_2F			0.37	−0.350		0.310	−320	−505	5
$OCHF_2$	−2.62	4.32	0.45	−0.269	32.1	0.227	−241	−403	9
OCF_3[e]	−3.20	2.21	0.53	−0.183	27.8	0.193[f]	−187	−383	12
OCH_2Cl	−2.28	7.36	0.41	−0.327	45.2	0.330	−301	−489	16
$OCHCl_2$	−2.95	3.98	0.49	−0.230	35.6	0.255	−211	−354	20
$OCCl_3$	−3.04	1.65	0.51	−0.165	27.5	0.195	−196	−309	21

[a] Shifts are given in parts per million relative to fluorobenzene (probable error ±0.07). Probable errors are ±0.01 in σ_I and ±0.004 in σ_R°. [b] σ_R° values derived from eq 3. [c] The excess π charge at the para carbon, Δq_π^4, and on the ring, $\Sigma\Delta q_\pi$, given in 10^{-4} electron, for the chosen conformation, taken from Table II. [d] ^{19}F nmr shifts from ref 2 and 3a. See also ref 3b. [e] $\sigma_I = 0.55$ (ref 2) and $\sigma_R^\circ = -0.18$ (ref 3). [f] $\pm\sigma_R^\circ = 0.250$ (ref 11b) is probably in error.

nalized as arising from important pairwise interactions[12] between the chlorine atoms.

The quantitative results given in Table I achieve the principal objective of this investigation. The general trends with increasing halogen substitution of the methoxy group, namely, a decrease in resonance donor capacity and an increase in the magnitude of the inductive effect, are observed. As it happened, the resonance and inductive parameters for this methoxy series are correlated by the simple equation

$$\sigma_I = \sigma_R^\circ + 0.72 \quad (4)$$

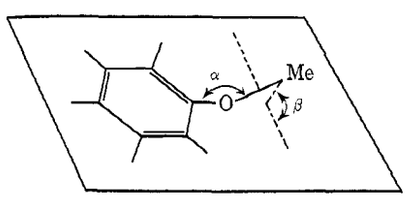
Other workers[13] have noted similar correlations for substituents containing oxygen as the linking atom. These results are analogous to those for Taft's "united-atom-like-first-row-pair donor" (UAFPD) theory[3a] and, although differing in behavior from that found for true UAFPD substituents, suggest that the oxygen atom is exerting the dominant influence in controlling the substituent parameters in the oxygen family. Both Taft[3] and Ehrenson[4] have analyzed this point in detail.

A comparison of the results for the methoxy (OY) with the corresponding methyl[1] (Y) series shows the inductive parameters to be linearly proportional according to the following equation. This result would

$$\sigma_I(OY) = 0.53\sigma_I(Y) + 0.32 \quad (5)$$

not be readily anticipated by an inductive theory based primarily on a direct electrostatic interaction between the substituent and a suitable probe (field effect[2]) but is more indicative of inductive transmission through the bonds with the oxygen atom attenuating, by a factor of approximately one-half, the effect of the halogen-containing methyl group. However, the complex nature of σ_I, as noted earlier,[1] obviates a more refined treatment at this time. No such simple relationship was found between the σ_R° values of the two series, for reasons developed in the following section.

Conformation of Halogenated Anisoles.—The position of a methoxy group relative to an attached benzene moiety is defined by the angles α (C_{Ar}–O–C_{Me}) and β (the angle by which the methyl group is twisted out of the benzene plane). For those anisoles whose geometry



has been discussed, angles of α are usually reported[9,14] around 118–120°. This value is close to that expected for an oxygen bonding *via* sp^2 hybridized orbitals to both carbon atoms, which places the oxygen p_z orbital in perfect location for resonance interaction with the ring,[15] and the degree of conjugation of this orbital with the ring is determined by β. However, molecular polarizability measurements have shown[10] that the angle β can vary within the range of possible values, from 0° in *p*-cyanoanisole to 90° in 2,4,6-tri-X-substituted anisoles (X = CH_3, Cl, Br). The twisting of the methyl group out of the benzene plane results therefore from the balance of the two opposing effects. The first is the electron demand by the aryl system, as evidenced by Figure 1, which was constructed from literature values[9a,10] and shows the approximate linear correlation between the angle β and the σ_R° of the substituent in para-substituted anisoles. This effect tends to place the OCH_3 group coplanar with the ring so as to maximize overlap of the π system with the p_z orbital of oxygen. The second and counteracting effect forces the methyl group out of the benzene plane and has been attributed[16] to steric repulsion between the ortho and side-chain substituents. Another contributing factor, not considered previously, is the repulsion between the oxygen lone pair and the benzene ring, which would be greatest and most destabilizing for an eclipsed conformation ($\beta = 0°$). The barrier to rotation for the methoxy group in anisole has been estimated[17] to be

(12) H. J. Bernstein, *J. Phys. Chem.*, **69**, 1550 (1965), and references cited therein. This model has been applied to ^{13}C nmr shifts for halogenated methanes [W. M. Litchman and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 1400 (1968)] and heats of formation of fluorocarbons [J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968)]. The precise nature of the interaction is unknown but it is probably a complex blend of various factors including steric and polarization contributions.

(13) (a) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961); (b) N. L. Bauld, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, No. 21-0.

(14) (a) C. Romers and B. Hespers, *Acta Crystallogr.*, **20**, 162 (1966); (b) J. Toussaint, *Bull. Soc. Roy. Sci. Liege*, **13**, 111 (1944).

(15) Relatively little discussion of the hybridization of oxygen appears in the literature. Ground-state oxygen $(2s)^2(2p_x)^2(2p_y)(2p_z)$ can undergo reorganization *without* electron promotion to $(sp^2)^2(p)^2(s^2p)^2$. Some justification for this type of hybridization based on MO theory is given by C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).

(16) M. Horak, E. R. Lippincott, and R. Khanna, *Spectrochim. Acta, Part A*, **23**, 1111 (1967). In addition, references in this paper support the contention that $0° < \beta < 90°$; however, others[17] have advocated a planar model, $\beta = 0°$.

(17) N. L. Owen and R. E. Hester, *ibid.*, **25**, 343 (1969).

about 6 kcal/mol and also has been detected by other methods.[18]

The resonance donor properties of the halogen-containing anisoles are clearly related to their apparent conformation, and consequently an estimation of the angle β was required for each compound. A new approach to this problem was found in the application of the CNDO/2 method,[8] which calculates the electronic distribution in the compounds from their molecular geometry. Modified versions[19] of QCPE Computer Programs No. 91 and 141 were used for molecules containing first-row and second-row elements, respectively. Unfortunately, the lack of experimental dipole moment data for these compounds generally precluded their use as evidence supporting the accuracy of the calculations. As before,[1] the benzene ring was taken as a regular hexagon with C–C = 1.397 Å and C–H = 1.08 Å. For the substituent, values of C–H = 1.09 Å, C–F = 1.32 Å, and C–Cl = 1.76 Å were used throughout. In all cases, the phenyl C–O and the methyl C–O bonds were taken equal to 1.36 and 1.37 Å, respectively, and the angle α was 118° unless otherwise noted; the angle β was varied between 0° and 90° corresponding to the conformations m, which together with the calculated charge distributions are given in Tables II, III, and IV.

TABLE II

π CHARGE DENSITY ($\times 10^4$) ON THE RING CARBONS OF HALOGENATED ANISOLES FOR VARIOUS CONFORMATIONS[a]

Substituent	m	Δq_π^1	Δq_π^2	Δq_π^3	Δq_π^4	Δq_π^5	Δq_π^6	$\Sigma\Delta q_\pi$	α	β
OCH_3	1	482	−651	266	−404	250	−619	−676	118	0
	2	486	−636	262	−396	248	−611	−647	118	18
	3	478	−509	209	−325	209	−509	−447	118	90
OCH_2F	4	435	−637	269	−365	252	−581	−627	118	18
	5	424	−551	233	−320	231	−522	−505	118	56
	6	387	−497	198	−281	211	−441	−423	118	90
$OCHF_2$	7	350	−554	267	−321	233	−561	−586	118	18
	8	302	−429	206	−246	198	−446	−415	120	75
	9	302	−432	200	−241	200	−432	−403	118	90
	10	417	−585	256	−359	252	−608	−627	160	90
OCF_3	11	261	−529	274	−268	239	−526	−549	118	18
	12	298	−403	206	−187	206	−403	−383	118	90
	13	205	−407	211	−190	206	−412	−387	115	80
	14	321	−559	255	−303	255	−559	−590	160	90
OCH_2Cl	15	394	−578	258	−348	242	−582	−609	118	0
	16	393	−536	236	−301	233	−514	−489	118	45
	17	386	−518	225	−287	227	−488	−455	118	55
	18	379	−503	214	−274	220	−463	−427	118	65
	19	363	−489	198	−259	210	−421	−398	118	90
$OCHCl_2$	20	283	−410	197	−211	197	−410	−354	118	90
$OCCl_3$	21	227	−385	195	−176	195	−385	−329	118	90

[a] The substituent is attached to the 1 position. Each conformation m is defined by the angles α (C_{Ar}-O-C) and β (angle by which the group $CH_{3-n}X_n$ is twisted out of the benzene plane). The excess π charge is $1.0000 - \Delta q_\pi$ and the sum of these values over each ring position (1-6) is given by $\Sigma\Delta q_\pi$.

Although differences within a few degrees for the angle α undoubtedly occur depending on the molecule under examination, practical considerations prohibited taking them into account and hence restricted this study primarily to the results obtained from varying only β.

The CNDO/2 method has been applied previously to a representative set of substituents attached to a phenyl ring: two linear relationships *have been established*[1,7] between the σ_R° values for these substituents and the corresponding calculated values of either the excess π charge at the para carbon, Δq_π^4, or the total excess π charge, $\Sigma\Delta q_\pi$, in the phenyl system. These two relationships are given by the lines in Figures 2 and 3, respectively. A similar analysis of the CNDO/2 calculations performed on the side-chain halogenated anisoles gave data for the varying m conformations, which are plotted also in Figures 2 and 3. The important finding was that *one* conformation for each molecule existed, the results from which fitted best *both* of the original[1,7] lines simultaneously. Consequently, these results, which are summarized in Table I, were chosen to represent the apparent conformation of the appropriate anisole. It is emphasized here that the apparent conformation of the appropriate methoxy group refers to its time-averaged position, which de-

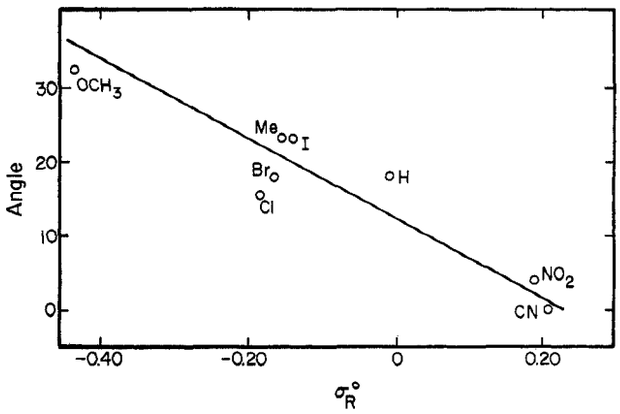


Figure 1.—Correlation between the angle β in para-substituted anisoles and the resonance parameter of the substituent.

TABLE III

σ CHARGE DENSITIES ($\times 10^4$) ON THE RING CARBONS AND HYDROGENS OF HALOGENATED ANISOLES IN VARIOUS CONFORMATIONS m[a]

Substituent Y	m	$\Delta q\sigma^1$	$\Delta q\sigma^2$	$\Delta q\sigma^3$	$\Delta q\sigma^4$	$\Delta q\sigma^5$	$\Delta q\sigma^6$	$\Sigma\Delta q\sigma^C$	$\Sigma\Delta q^H$
OCH_3	1	1396	54	11	198	21	109	1789	1
	2	1393	41	12	194	20	103	1763	4
	3	1397	10	27	159	27	10	1630	15
OCH_2F	4	1459	32	21	183	19	98	1812	64
	5	1457	−3	32	163	25	50	1724	75
	6	1509	4	41	142	26	−3	1719	115
$OCHF_2$	7	1554	−87	26	162	29	95	1779	276
	8	1622	−30	36	127	40	13	1808	217
	9	1611	−5	39	125	39	−6	1803	206
	10	1937	1	35	172	39	8	2192	199
OCF_3	11	1674	−85	31	138	32	105	1895	412
	12	1687	−19	43	107	43	−19	1842	342
	13	1663	−30	41	109	42	2	1827	346
	14	2090	−6	43	147	42	−6	2310	362
OCH_2Cl	15	1509	43	18	169	27	109	1875	238
	16	1509	22	33	158	29	70	1821	113
	17	1511	13	36	151	30	53	1794	116
	18	1513	5	40	146	32	37	1773	175
	19	1513	5	43	138	32	0	1731	169
$OCHCl_2$	20	1607	−2	45	119	44	−2	1811	287
$OCCl_3$	21	1651	−4	52	109	53	−4	1857	334

[a] See footnote *a* in Table II. The σ charge on the ring carbons is $3.0000 - \Delta q_\sigma$. The sum of the excess charge on the phenyl ring hydrogens is given by $\Sigma\Delta q^H$.

(18) (a) S. K. Garg and C. P. Smyth, *J. Chem. Phys.*, **46**, 373 (1967); (b) R. W. Creecely, K. W. McCracken, and J. H. Goldstein, *Tetrahedron*, **25**, 877 (1969). Other workers have obtained similar evidence in ortho-disubstituted anisoles [K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **44**, 2855 (1966)] and ethers [H. Kessler, A. Rieker, and W. Rundel, *Chem. Commun.*, **8**, 475 (1968)].

(19) (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.

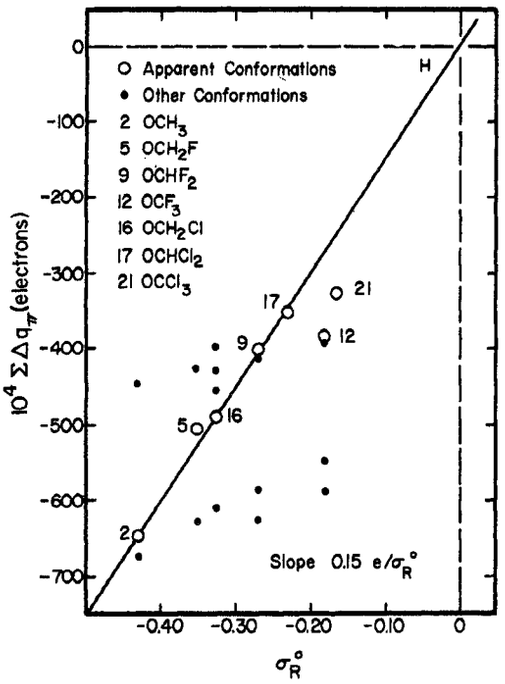


Figure 2.—Correlation between the excess π charge density on the ring of the halogen-containing anisoles and the σ_R° values of the substituents $OCH_{3-n}X_n$. Points in the same vertical correspond to various conformations (m) of the same substituent.

TABLE IV

CHARGE DENSITIES ($\times 10^4$) ON $OCH_{3-n}X_n$ OF GROUPS OF HALOGENATED ANISOLES IN VARIOUS CONFORMATIONS m[a]

Substituent	m	Δq^X	Δq^H	Δq^C	Δq^O
OCH_3	1		−173	1540	−2133
	2		−171	1534	−2144
	3		−180	1573	−2230
OCH_2F	4	−1281	−1027	4680	−2594
	5	−1272	−1040	4700	−2435
	6	−2099	−322	3767	−2647
$OCHF_2$	7	−1936	−1299	6442	−2742
	8	−2192	−328	5716	−2615
	9	−2193	−330	5713	−2604
	10	−1918	−1287	6820	−3463
OCF_3	11	−2211		7519	−2644
	12	−2210		7537	−2708
	13	−2213		7531	−2682
	14	−2204		7910	−3387
OCH_2Cl	15	−1722	80	2053	−1990
	16	−1666	99	2057	−2043
	17	−1672	97	2078	−2058
	18	−1677	95	2088	−2078
	19	−2084	88	2097	−2084
$OCHCl_2$	20	−1363	362	2585	−1965
$OCCl_3$	21	−1105		3074	−1880

[a] See footnote in Table II. Δq^X represents the average excess charge on the halogen. Analogous values for the other atom in the substituent are referenced by the element in the superscript.

pends on the energy differences of all the available conformations.

The value of $\beta = 18°$ found for anisole (conformation $m = 2$ in Table II) is precisely that derived by LeFevre[10] from dipole moment measurements.[20] The α-haloanisoles had $\beta = 56°$ (OCH_2F) and 45° (OCH_2Cl); the remaining compounds, $OCHX_2$ and OCX_3, gave $\beta = 90°$, indicating that the dihalo and

(20) The calculated dipole moment $\mu = 1.46$ D was also closest to the experimental value[19] of 1.24 D (compare 1.83 D for conformation $m = 3$).

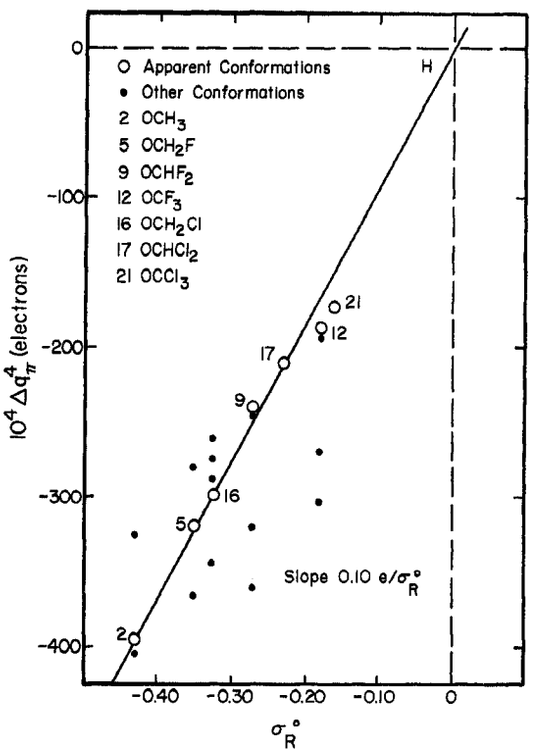


Figure 3.—Correlation between the excess π charge density at the para carbon of anisoles and the σ_R° values of the substituents $OCH_{3-n}X_n$. Points in the same vertical correspond to various conformations (m) of the same substituent.

trihalo groups are perpendicular to the benzene plane, a situation that is consistent with important steric interactions[16] with the ortho hydrogen atom and results in placing the p electrons of the oxygen orthogonal with the benzene π system where overlap is forbidden by symmetry. Rather unexpected experimental support of the latter contention for OCF_3 may be inferred from the results of molecular photoelectron spectroscopy.[21] The largest deviations were found in the case of the OCX_3 groups, which for all conformations studied gave points below the line. However, the calculations showed that even with $\beta = 90°$ ($m = 12$ and 21), resonance transfer of charge[1] to the ring π system was occurring, which is in agreement with the experimental values of σ_R°, and supports the simple model of oxygen hybridization presented herein. Incidently, the apparent conformation derived for OCF_3 differs from those proposed previously[22] and calculations on the latter ($m = 11$ and 14) disagreed with expectation values deduced from Figures 2 and 3.

Charge Distribution in the Benzene Ring.—The CNDO/2 results can be interpreted at various levels,[1,7,8a] but some caution should be exercised.[23] Our results, given in Tables II, III, and IV, are self-explanatory; however, the following trends are noteworthy. (i) The π charges alternate around the ring in a manner predicted by VB theory for ortho,para-directing donor

(21) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

(22) W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1314 (1963). The experimental dipole moment for OCF_3 reported in this paper is $\mu = 2.36$ D, which may be compared to the value of 2.06 D calculated in this work.

(23) See, for example, the results given by M. E. Schwartz, C. A. Coulson, and L. C. Allen, *ibid.*, **92**, 447 (1970). This contention was reinforced by a referee.

substituents.[24] (ii) The charge on the meta carbons (Δq_π^3, Δq_π^5) is relatively insensitive to any variation of the substituent. (iii) The electron deficiency in the σ framework of the benzene ring ($\Sigma\Delta q_\sigma$) is dominated by the large positive value of Δq_σ^1 resulting from the adjacent oxygen atom.[25] (iv) The difference in π charge at various positions, in particular $\Delta q_\pi^1 - \Delta q_\pi^2$, is larger in magnitude than the resonance transfer of charge $\Sigma\Delta q_\pi$ and results from reorganization of charge. This latter feature, which was defined previously in an operational manner[1] as a π-inductive effect, makes some contribution to the σ_I inductive parameter.

Experimental Section

Elemental analyses were performed by the staff of Dr. C. S. Yeh, Purdue University Microanalytical Laboratory. Vapor phase chromatographic (glpc) separations were carried out on a Varian Aerograph 200, using an 8 ft × 0.375 in. aluminum column packed with 20% QF-1 60/80 Chromosorb W (column I) and an 8 ft × 0.375 in. aluminum column packed with 25% SE-30 on 60/80 Chromosorb W (column II). Proton magnetic resonance (nmr) spectra were recorded on a Varian A-60A spectrophotometer using CCl_4 as a solvent and tetramethylsilane as the standard. Ir spectra were measured on a Perkin-Elmer 421.

^{19}F Nmr Calibrations.—All measurements were made as previously reported.[1-3]

Infrared Measurements.—The infrared intensities of the 1600-cm^{-1} stretching vibrations of the anisoles in CCl_4 and cyclohexane solution were measured as reported previously[1,11] and the average values of $A^{1/2}$ derived from five different measurements are recorded in Table I.

Materials.—*m*- and *p*-fluorophenols were purchased from Pierce Chemical Co.

Aryl Chloromethyl Ethers.—These compounds were prepared by a two-step synthesis as described by Barber.[26] The appropriate sodium phenolate was treated with a solution of sodium chloromethane sulfonate, prepared according to the procedure of Schoellkopf,[27] and the resulting sodium aryloxymethane sulfonate was treated further with PCl_5. The resulting oily mixture was poured into ice water, extracted with ether, washed with 1 *N* NaOH solution, dried ($MgSO_4$), and distilled to give pure products. Phenyl chloromethyl ether was obtained in 74% yield: bp 57° (0.5 mm); n^{20}D 1.5368 [lit.[26b] bp 88–90° (15 mm), n^{20}D 1.5362); nmr δ 5.60 (s, J_{CH} = 176.0 Hz).

Anal. Calcd for C_7H_7ClO: C, 59.00; H, 4.90; Cl, 24.90. Found: C, 58.85; H, 4.95; Cl, 24.77.

The *m*- and *p*-fluorophenyl chloromethyl ethers were obtained in 29 and 21% yield, respectively: bp 66° (4 mm) and 65° (4 mm), n^{20}D 1.5122 and 1.5210, and nmr δ 5.72 and 5.72 (s, CH_2), respectively.

Anal. Calcd for C_7H_6ClFO: C, 52.35; H, 3.74; Cl, 22.10; F, 11.84. Found for meta: C, 52.59; H, 3.85; Cl, 21.83; F, 11.71. Found for para: C, 52.43; H, 3.74; Cl, 22.33; F, 11.99.

Aryl Dichloromethyl Ethers.—The three ethers were prepared by a two-step synthesis adapted from that descibed by Laato and Lehtonen.[28] The appropriate phenol was converted into the aryl formate, which was further treated with PCl_5 to give the corresponding aryl dichloromethyl ether in 95–100% yield. The samples were purified by glpc at 180° using column II.

Anal. Calcd for $C_7H_6Cl_2O$: C, 47.41; H, 3.50; Cl, 40.20. Found: C, 47.41; H, 3.19; Cl, 40.22.

Phenyl dichloromethyl ether had n^{20}D 1.5362 (lit.[28] n^{20}D 1.5361) and nmr δ 7.50 (s, J_{CH} = 209.5 Hz).

Anal. Calcd for $C_7H_5Cl_2FO$: C, 43.10; H, 2.56; Cl, 36.42; F, 9.75. Found for para: C, 43.37; H, 2.67; Cl, 36.62; F, 9.74.

The *m*- and *p*-fluorophenyl dichloromethyl ethers had n^{20}D 1.5133 and 1.5132, respectively, and nmr δ 7.28 and 7.28 (s, $OCHCl_2$).

Aryl Trichloromethyl Ethers.—These ethers were prepared from their corresponding phenols by a two-step synthesis according to the procedure described by Iarovenko and Vasileva.[29] The aryl chlorothioformate,[30] prepared by the reaction of thiophosgene with the appropriate phenol, was treated with chlorine at 45–50°. Phenyl trichloromethyl ether was obtained in 90% yield: n^{20}D 1.5415 (lit.[29] n^{20}D 1.5395); bp 92° (10 mm); nmr δ 7.19 (s).

Anal. Calcd for $C_7H_5Cl_3O$: C, 39.81; H, 2.37 Cl, 50.00. Found: C, 39.64; H, 2.53; Cl, 49.20.

The *m*- and *p*-fluorophenyl trichloromethyl ethers were obtained in 96 and 82% yield, respectively: bp 70° (3 mm) and 60° (2 mm); n^{20}D 1.5191 and 1.5191 (lit.[31] n^{20}D 1.5191 for para), respectively.

Anal. Calcd for $C_7H_4Cl_3FO$: C, 36.60; H, 1.74; Cl, 46.40; F, 8.27. Found for meta: C, 36.81; H, 1.55; Cl, 46.24; F, 8.20. Found for para: C, 36.86; H, 1.96; Cl, 46.29; F, 8.50.

Aryl Difluoromethyl Ethers.—According to the procedure of Miller and Thanassi,[32] the appropriate phenols were converted into the title compounds by their reaction with chlorodifluoromethane. Purification of the products was carried out by glpc on column I at 100°. Phenyl difluoromethyl ether had n^{20}D 1.4497 (lit.[32] n^{20}D 1.4473), nmr (neat) δ 6.32 (t, J_{HF} = 75.0 Hz).

The *m*- and *p*-fluorophenyl difluoromethyl ethers were obtained in 45 and 13% yield, respectively, and had n^{20}D 1.4347 and 1.4350, nmr δ 6.40 and 6.38 (t, J_{HF} = 73.5 Hz), respectively.

Anal. Calcd for $C_7H_5F_2O$: C, 51.80; H, 3.08; F, 35.11. Found for meta: C, 51.89; H, 3.26; F, 35.22. Found for para: C, 51.76; H, 3.33; F, 34.81.

Aryl Trifluoromethyl ethers.—The reaction of the corresponding aryl trichloromethyl ether[31] with SbF_3 (mixed with 10% $SbCl_5$) followed by glpc purification at 125° on column II afforded the title compounds in *ca.* 70% yield. Phenyl trifluoromethyl ether had n^{20}D 1.4070 (lit.[31] n^{20}D 1.4073).

Anal. Calcd for $C_7H_5F_3O$: C, 51.80; H, 3.08; F, 35.11. Found: C, 52.00; H, 3.20; F, 34.89.

The *m*- and *p*-fluorophenyl trifluoromethyl ethers had n^{20}D 1.3950 and 1.3951 (lit.[33] n^{25}D 1.3914 and 1.3912).

Registry No.—Phenyl chloromethyl ether, 6707-01-3; *m*-fluorophenyl chloromethyl ether, 34888-01-2; *p*-fluorophenyl chloromethyl ether, 34888-02-3; phenyl dichloromethyl ether, 1195-43-3; *m*-fluorophenyl dichloromethyl ether, 34888-04-5; *p*-fluorophenyl dichloromethyl ether, 34917-96-9; phenyl trichloromethyl ether, 34888-05-6; *m*-fluorophenyl trichloromethyl ether, 34888-06-7; *p*-fluorophenyl trichloromethyl ether, 407-13-6; *m*-fluorophenyl difluoromethyl ether, 34888-08-9; *p*-fluorophenyl difluoromethyl ether, 34888-09-0; phenyl trifluoromethyl ether, 456-55-3; *m*-fluorophenyl trifluoromethyl ether, 1077-01-6; *p*-fluorophenyl trifluoromethyl ether, 352-67-0.

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

(25) The corresponding values found[1] in the side-chain halogenated toluenes are smaller but are more dependent on the number of halogens in the substituent.

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