The Effect of Fluorine Substitution on the Electronic Properties of Alkoxy, Alkylthio and Alkylsulfonyl Groups[1]

BY WILLIAM A. SHEPPARD

RECEIVED OCTOBER 18, 1962

The effect of fluorine substitution on the properties of alkoxy, alkylthio and alkylsulfonyl groups has been determined quantitatively from pK_a measurements on anilines, phenols and benzoic acids containing the substituents: OCF_3, OCF_2CF_3, OCF_2CF_2H, SCF_3, SCF_2CF_2H and SO_2CF_3. The OR_f groups are like halogen and strongly deactivate by inductive electron withdrawal (σ_m, 0.34 to 0.48) but donate electrons by resonance (σ_p, 0.21 to 0.35). The SR_f groups deactivate by both inductive and resonance mechanisms (σ_m, 0.38 to 0.46; σ_p, 0.47 to 0.64). The origin of the +R character of the SR_f groups is discussed in terms of d-orbital participation by sulfur. The SO_2CF_3 group was found to be the strongest neutral electron-withdrawing group known with σ_m 1.00 and σ_p 1.65 (from pK_a's of anilinium ions). Dipole moment data for the OCF_3 group are presented and discussed.

Unusual properties result from accumulation of fluorine in organic molecules. However, no significant amount of quantitative data useful for explanation, prediction and development of theories has been collected for simple fluorinated substituents. One approach to this problem is determination, by classical methods, of substituent constants and dipole moments of fluorinated groups in aromatic systems. Such studies have been reported for the trifluoromethyl and, recently, the sulfur pentafluoride groups.[2,3]

As part of a study of fluorinated systems, synthetic routes to aryl perfluoroalkyl ethers and sulfides have been examined and the new, improved syntheses developed.[1,4,5] As a consequence, the preparation of

literature.[1,4,5,7] All compounds used for measurements were purified by distillation (center-cut from constant refractive index fractions) and/or recrystallized and sublimed to constant melting point. The compounds were shown to contain no detectable amount of impurities by analysis, spectral studies (infrared, ultraviolet and F^{19} and H^1 n.m.r.), and, where possible, vapor phase chromatography.

Ionization Constant Measurements.—Apparent ionization constants of m- and p-substituted benzoic acids were obtained at 25° in 50% water–50% ethyl alcohol (by volume) as described by Roberts and co-workers[2,8] using a Beckman pH meter, model G, with glass electrodes. The measured pK_a's are reported in Table I and are the average of two to five separate determinations that agreed within ±0.02 unit (generally within ±0.01).

Ionization constants of anilinium ions (pK_a of the reaction $RNH_3^+ \rightleftarrows RNH_2 + H^+$) were determined at 25° in aqueous solution by spectrophotometric measurements in the ultraviolet

TABLE I
pK_a MEASUREMENTS

Substituent X	(a) Benzoic acids, 50% water-ethanol, 25.0° $XC_6H_4CO_2H \rightleftarrows XC_6H_4CO_2^\ominus + H^\oplus$ pK_a	(b) Anilines, water, 25° $XC_6H_4NH_3^\oplus \rightleftarrows XC_6H_4NH_2 + H^\oplus$ λ_{max}, mμ	pK_a	(c) Phenols, water, 25° $XC_6H_4OH \rightleftarrows XC_6H_4O^\ominus + H^\oplus$ λ_{max}, mμ	pK_a
H[d]	5.71[d]	. .	4.56[d]	. .	9.919[d]
OCF₃ ortho	. .	280	2.44	. .	. .
meta	5.15 (5.19)[c]	282	3.25	287	9.02
para	5.19 (5.26)[c]	285	3.83, 3.80[f]	282	9.35
OCF₂CF₃ meta	. .	281	3.24	287	8.95
para	. .	284	3.78	292	9.32
OCF₂CF₂H meta	5.22	282	3.38	. .	. .
para	5.34	285	3.98	. .	. .
SCF₃ meta	5.13 (5.21)[c]	294	3.30	303	8.97
para	4.98 (5.17)[c]	255	2.80, 2.76[f]	260	8.66
SCF₂CF₂H meta	5.15	295	3.39	. .	. .
para	4.98	255	2.87	. .	. .
SO₂CF₃ meta	. . (4.54)[e]	314	1.79	325[h]	7.87
para	4.35 (4.17)[e]	287	−0.01[g]	287	6.79

[a] $\rho = +1.467$ (ref. 2). [b] $\rho = +2.767$ (ref. 9). [c] $\rho = 2.229$ (ref. 10). [d] Literature value; see respective footnotes a, b, c. [e] Values in parentheses reported in literature (ref. 6). [f] Duplicate measurement. [g] Anilinium ion too acidic for standard buffers, value by extrapolation from series of HCl buffered solutions; see ref. 10. [h] m-Hydroxyphenyl trifluoromethyl sulfone was prepared by diazotization and hydrolysis of corresponding aniline (ref. 7a); m.p. 74.5–76.2°. Anal. Calcd. for $C_7H_5F_3O_3S$: C, 37.2; H, 2.04; F, 25.2. Found: C, 37.3; H, 2.04; F, 25.1, 25.2.

the compounds needed for measurements was greatly facilitated. When this work was essentially complete, pK_a measurements on benzoic acids containing the OCF_3, SCF_3 and SO_2CF_3 groups were published,[6] but no analysis or discussion of these results was presented.

Experimental

Materials.—The compounds employed in this study are described in other publications from this Laboratory or in the

region employing a Cary recording spectrophotometer with thermostated cell holder. A detailed description of this procedure, which employs a series of buffered solutions, was recently given by Bryson.[9] In making these measurements at least three results, using buffer solutions within 0.4 pK_a unit of the anilinium ion, were averaged, and this average value is given in Table I. Agreement of determinations in repeat experiments and of the pK_a's of reference anilines were within the ±0.03 pK_a unit precision ascribed to the method.[9]

The ionization constants of the phenols in aqueous solution at 25° were determined by the spectrophotometric method[10] using

(1) This work was presented, in part, in a communication: W. A. Sheppard, J. Am. Chem. Soc., **83**, 4860 (1961).

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

(3) W. A. Sheppard, ibid., **84**, 3072 (1962).

(4) W. A. Sheppard, publications in preparation.

(5) D. C. England, L. R. Melby, M. A. Dietrich and R. V. Lindsey, Jr., J. Am. Chem. Soc., **82**, 5116 (1960).

(6) L. M. Yagupolskii and L. M. Yagupolskaya, Proc. Acad. Sci. USSR (Engl. Transl.), **134**, 1207 (1960).

(7) (a) L. M. Yagupolskii and M. S. Marenets, J. Gen. Chem. USSR (Engl. Transl.), **24**, 885 (1954); (b) L. M. Yagupolskii and M. S. Marenets, ibid., **26**, 99 (1956); (c) L. M. Yagupolskii and B. E. Gruz, ibid., **31**, 1219 (1961).

(8) J. D. Roberts, E. A. McElhill and R. Armstrong, J. Am. Chem. Soc., **71**, 2923 (1949).

(9) A. Bryson, ibid., **82**, 4858 (1960).

(10) A. E. Biggs and R. A. Robinson, J. Chem. Soc., 388 (1961).

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN
BENZENE AT 25°

F_2	ϵ	D.	P_2

Phenyl trifluoromethyl ether ($D^{25}{}_{25}$ 1.2218, n^{25}D 1.4038)

0.00000	2.2740	0.8722	$(P_1\ 26.743)^a$
.020448	2.4316	.8851	143.7
.041031	2.5813	.8950	141.5
.60363	2.7193	.9041	139.0

p-Nitrophenyl trifluoromethyl ether ($D^{25}{}_{25}$ 1.4458, n^{25}D 1.4652)

0.021065	2.4156	0.8937	133.6
.041019	2.5399	.9100	132.6
.061675	2.6683	.9271	131.0

p-Aminophenyl trifluoromethyl ether ($D^{25}{}_{25}$ 1.3212, n^{25}D 1.4609)

0.020243	2.6954	0.8880	317.23
.040753	3.1064	.9010	294.48
.059891	3.5184	.9125	282.66

p-Bromophenyl trifluoromethyl ether

0.019501	2.3000	0.8985	60.37
.040803	2.3255	.9237	61.58
.061026	2.3482	.9469	61.71

1,4-Bis-(trifluoromethoxy)-benzene

0.020333	2.2779	0.8951	51.95
0.042181	2.2796	0.9151	53.80

^{a} Benzene standardization liquid; literature values, used for each determination.

TABLE III

MOLAR REFRACTION, POLARIZATION AND DIPOLE MOMENTS

Compound	MR_D	P_0 (25°)	$b\mu$, (Debye)
Phenyl trifluoromethyl ether	32.42	146.0	2.36
p-Nitrophenyl trifluoromethyl ether	39.60	135.2	2.16
p-Aminophenyl trifluoromethyl ether	36.77	331.0	3.79
p-Bromophenyl trifluoromethyl ether	40.70	61.22	1.00
1,4-Bis-(trifluoromethoxy)-benzene	39.57	52.87	0.87

borax-buffered solutions. The results are reported in Table I. A precision of ±0.01 pK_a unit is ascribed to this method,[10] and in duplicate to quadruplicate measurements on the phenols this precision was in general attained. However, the measurements on the phenols with p-CF₃S and p-CF₃SO₂ groups were only precise to ±0.03 pK_a unit, possibly because of relatively poor hydrolytic stability of these phenols in the basic medium.[22]

Dipole Moments.—The dipole moments were determined by literature methods[3] employing a Wissenshaftlick Technische Werkestatten Dipolmeter type DM 01, Cell DFL1 (20-ml. volume). The data are given in Tables II and III. A precision of ±0.02 D. is ascribed to the dipole moment results given in Table III.

Results and Discussion

The Hammett σ-constants for the perfluoroalkoxy, perfluoroalkylthio and trifluoromethylsulfonyl groups, as calculated from the ionization constant data, are given in Table IVa. To assist in analyzing the results, the ionization constant data were also used to calculate the inductive and resonance parameters, σ_I and σ_R, as proposed by Taft[11,12] and the F and M parameters described by Dewar.[13] For comparison, the substituent parameters from literature values[11-16] of selected well-known substituents and hydrocarbon analogs of the fluorinated groups are presented in Table IVb.

(11) R. W. Taft, Jr., "Separation of Polar, Steric and Resonance Effect in Reactions," in M. S. Newman (Editor), "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

(12) R. W. Taft, Jr., and I. C. Lewis, J. Am. Chem. Soc., 81, 5343 (1959); R. W. Taft, Jr., J. Phys. Chem., 64, 1805 (1960).

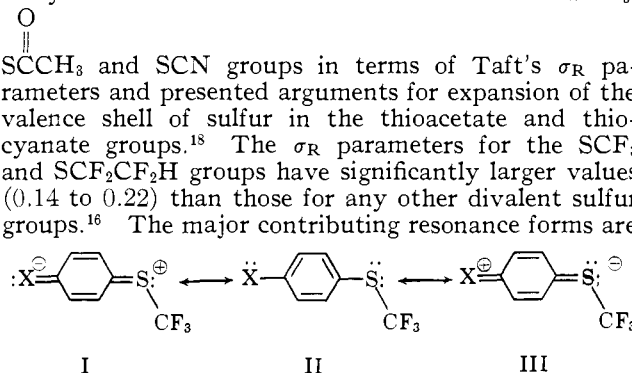(13) M. J. S. Dewar and P. J. Grisdale, J. Am. Chem. Soc., 84, 3539 and 3548 (1962).

(14) H. H. Jaffé, Chem. Rev., 53, 222 (1953).

(15) F. G. Bordwell and P. J. Barton, J. Am. Chem. Soc., 78, 854 (1956); F. G. Bordwell and G. C. Copper, ibid., 74, 1058 (1952).

(16) R. R. Beishline, J. Org. Chem., 26, 2533 (1961).

From an examination of the σ-parameters in Table IV, it is immediately apparent that the perfluoroalkoxy groups behave like alkoxy groups and withdraw electrons inductively but supply them by resonance.[17] However, the perfluoroalkyl group enhances the inductive withdrawal of electrons by oxygen to the extent that deactivation of the aromatic system occurs to the same, or greater, extent than for the halogens. Also, electron release by the resonance mechanism is diminished over that for an alkoxy group, again to an extent comparable to that for the halogens. On this basis the perfluoroalkoxy groups may be classed as halogen-like (or even as "super-halogen" since over-all they deactivate to a greater extent than halogens). It is also noted, from comparison of the σ-parameters for the OCF₃, OCF₂CF₃ and OCF₂CF₂H groups, that the inductive effects of F and CF₃ are almost the same but, as expected, significantly greater than that of a CF₂H group. This result is predicted from the similar σ_I values for the F and CF₃ groups.

The perfluoroalkylthio groups have σ_m values essentially the same as the corresponding perfluoroalkoxy groups, but unexpectedly the σ_p parameters have larger positive values with an added positive increment of 0.14 for the σ_p calculated from the anilinium ions over that from the benzoic acids. This result is indicative of a +R substituent. Recently, Beishline[16] analyzed the ionization constant data for the SCH₃,

$$\overset{O}{\underset{\parallel}{S}}CCH_3$$ and SCN groups in terms of Taft's σ_R parameters and presented arguments for expansion of the valence shell of sulfur in the thioacetate and thiocyanate groups.[18] The σ_R parameters for the SCF₃ and SCF₂CF₂H groups have significantly larger values (0.14 to 0.22) than those for any other divalent sulfur groups.[16] The major contributing resonance forms are

| I | II | III |

and the σ-parameter data provide strong evidence for large contribution of form III in the equilibrium acidity constant measurements. The contribution of resonance form I must be minor but becomes significant in the transition state for substitution of the ring by an electrophilic reagent since orientation is ortho–para and not meta.[19] For the SCH₃ group, like OCH₃, the major contribution must be from form I rather than form III. Another possible series of contributing resonance forms is represented by IV which involves fluoride ion "no-bond" structures analogous to the

IV
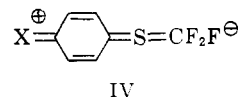
(17) This result is predicted from the ortho–para directing influence of the OCF₃ group in electrophilic substitution; see ref. 4 and L. M. Yagupolskii and V. I. Troitskaya, J. Gen. Chem. USSR, Engl. Transl., 31, 845 (1961). Dr. H. K. Hall, Jr., suggested that there is no positive evidence for electron donation by OR₁ groups in the ground states and that σ_{In} is greater than σ_p because of a direct field effect which falls off with distance. Complete lack of ortho substitution in nitration and bromination[4] could be cited as evidence to support this argument.

(18) The evidence for outer shell expansion in sulfur was recently summarized: G. Cilento, Chem. Rev., 60, 146 (1960).

(19) Nitration was reported to give only ortho–para substitution as determined by classical methods of chemical analysis.[7b] This result was checked in this Laboratory using spectral (infrared and F¹⁹ n.m.r.) methods, and no meta substitution product could be detected. Gas chromatographic analysis was not successful since synthetic mixtures of m- and p-nitrophenyl trifluoromethyl sulfides could not be separated on a wide range of columns normally useful for separating aromatic substituent isomers or fluorocarbons.

TABLE IVa

SUBSTITUENT PARAMETERS FOR FLUORINATED ALKOXY, ALKYLTHIO AND METHYLSULFONYL GROUPS

		Hammett[a]		Taft[b]			Dewar[c]		
		σ_m	σ_p	σ_I	σ_R	F	M	F'	M'
OCF$_3$	B[d]	0.40	0.35	0.51	−0.13	0.69	0.00	0.70	0.00
	A	.47	.27	.50	− .23				
	P	.40	.26	.39	− .15				
OCF$_2$CF$_3$	B	..	..	..	....	..	....	..	....
	A	.48	.28	.52	− .25				
	P	.43	.27	.42	− .17				
OCF$_2$CF$_2$H	B	.34	.25	.39	− .14	.59	−0.31	.58	−0.40
	A	.43	.21	.45	− .25				
	P	..	..	..	....				
SCF$_3$	B	.40	.50	.31	.17	.69	1.09	.71	1.42
	A	.46	.64	.40	.22				
	P	.43	.57	.39	.14				
SCF$_2$CF$_2$H	B	.38	.47	.29	.20	.66	0.98	.68	1.26
	A	.42	.61	.37	.21				
	P	..	..	..	....				
SO$_2$CF$_3$	B	(.79)	.93	.69	.22	1.37	2.45	1.42	3.15
	A	1.00	1.65	.84	.73				
	P	0.92	1.36	.84	.49				

[a] Calculated using Hammett equation from ionization constant data and ρ-values given in Table 1. [b] Calculated as described in ref. 12 using values of ρ_I +1.50, α 0.42 for ionization of benzoic acids; ρ_I +2.90, α 0.15 for ionization of anilinium ions; and ρ_I +2.36, α 0.07 for ionization of phenols. [c] Calculated as reported in ref. 13 using values of $r_{13}\sqrt{3}$, r_{14} 2; q_{13} 0, q_{14} $^1/_7$; π_{13} +0.009, π_{14} −0.102. [d] Data calculated from ionization constants of B benzoic acids, A anilinium ions, P phenols.

TABLE IVb

LITERATURE VALUES OF SUBSTITUENT CONSTANTS FROM pK_a OF BENZOIC ACIDS AND ANILINIUM IONS[a]

	σ_m	σ_p	σ_I	σ_R	F	M	F'	M'
CF$_3$	0.43	0.54 (0.65)[b]	0.39	0.12 (0.18)[b]	0.74	1.12	0.77	1.46
SF$_5$	.61	.68 (0.86)	.55	.11 (0.27)	1.05	1.07	1.08	1.39
OSF$_5$[c]	..	.44	..	....	..	....	..	....
F	.34	.06	.45	− .40	0.58	−1.61	0.56	−2.10
Cl	.37	.23	.42	− .25	.65	−0.70	.63	−0.91
OCH$_3$	.11	− .27	.21	− .47	.20	−2.58	.13	−3.36
SCH$_3$	.14	− .01	.22	− .28	.26	−0.91	.24	−1.19
O‖OCCH$_3$	.38	.29	..	....	.68	−4.55	.56	−5.93
O‖SCCH$_3$	.37	.42	.32	.10	.68	0.70	.70	0.91
SO$_2$CH$_3$	.65	.73 (1.05)	.62	.16 (0.51)	1.04	1.40	1.08	1.83
NO$_2$	.71	0.78 (1.27)	.68	.14 (0.67)	1.23	1.14	1.26	1.48

[a] Values taken from ref. 3, 11 to 16; see also footnote c. [b] Values in parentheses are from data on ionization of anilinium ions; all other values are calculated from the ionization of benzoic acids. [c] J. R. Case, R. Price, N. H. Ray, H. L. Roberts and J. Wright, *J. Chem. Soc.*, 2107 (1962). This group was shown to be *para* directing to electrophilic substitution. The value of σ_m was not measured but would be predicted to be about 0.50.

proposal advanced to explain the resonance effect of a CF$_3$ group.[2] However, the almost identical σ-parameters of the SCF$_3$ and CF$_3$ groups serve as evidence against any major contribution from form IV since appreciable diminution of the effect for the CF$_3$ would be expected on transmittal through sulfur. (It is possible, but unlikely, that the resonance effect of the CF$_3$ group may be enhanced if steric interactions with hydrogens are removed when a sulfur separates the group from the ring.) Another argument is that the small decrease in the deactivating effect of a SCF$_2$-CF$_2$H over the SCF$_3$ group resides chiefly in the inductive but not in the resonance portion (as noted from comparison of σ-parameters of SCF$_3$ and SCF$_2$-CF$_2$H with those of OCF$_3$ and OCF$_2$CF$_2$H and σ_R values for SCF$_2$CF$_2$H compared to SCF$_3$). It is expected that this type of resonance would be decreased by loss of one contributing resonance form through substitution of a CF$_2$H group for F.

As a final point in discussion of the d-orbital participation by sulfur, the theoretical aspect should be reviewed. Craig and Magnusson[20] have shown from a

study of overlap integrals that the d-orbitals of sulfur and phosphorus in the free atoms are too weakly bound and diffuse to contribute significantly to bond energy. However, polarization resulting from substitution of the sulfur with electron-withdrawing groups contracts these orbitals and adapts them for better bonding. In particular, the bonding in SF$_6$, where two d-orbitals are involved in hybrid bonds, was discussed. On the basis of these arguments it is reasonable to conclude that the strong electron-withdrawing character of the CF$_3$ group induces polarization of the sulfur atom and contracts the d-orbitals so that d-π overlap can make a significant contribution to the bonding of sulfur in the molecule.

The σ-parameters determined for the SO$_2$CF$_3$ group indicate that it is the strongest, neutral electron-withdrawing group that has been measured.[21] The

(20) D. P. Craig and L. A. Magnusson, *J. Chem. Soc.*, 4895 (1956); see also D. W. J. Cruikshank, *ibid.*, 5486 (1961), for a recent discussion of the role of 3 d-orbitals in bonding of sulfur to oxygen or nitrogen.

(21) The diazonium group, N$_2$⊕, is the only one reported to have larger positive σ parameters, σ_p = 1.8 ± 0.5 and σ_m = 1.6 from ionization of the benzoic acid derivative; a σ value of approximately 3 was determined from

calculated values of σ_I and σ_R for this group suggest that, like the nitro group, the strong electron-withdrawing power originates from a significant resonance interaction as well as by the inductive mechanism. The SO_2CF_3 group should be a useful addition to the series of strong electron-withdrawing substituents; a possible advantage of this group is improved solubility in organic solvents compared to the corresponding nitroaromatics. On the other hand, it is anticipated that $CF_3SO_2^\ominus$ will be an excellent leaving group, although no indication of loss of $CF_3SO_2^\ominus$ was observed in the aromatic series under a range of oxidizing and reducing conditions or in strong bases or acids.[22]

The F and M parameters were recently proposed by Dewar and Grisdale[13] as a measure of the modes of transmission of the primary effects of a substituent to the reaction center. The F parameter is a measure of the primary inductive effect, which is attributed chiefly to a field effect operating through space, while the σ- and π-inductive effects operating through the molecule make only minor contributions. The M parameter is a measure of the combined π-inductive-mesomeric effect of the substituent. These parameters may be calculated from σ-constants by use of the equations

$$\sigma_{ij} = F/r_{ij} + Mq_{ij}$$
$$\sigma_{ij} = F'/r_{ij} + M'\pi_{ij}$$

where

r_{ij} is the distance between atoms i and j in a molecule
q_{ij} is the formal charge at position j produced by attaching the group $-CH_2^\ominus$ at position i
π_{ij} is the atom–atom polarizability of atoms i and j

In this treatment, the electromeric effect from resonance interaction is not considered. This effect is unimportant unless there is mutual conjugation between the substituent and the reaction center. Since this factor does not affect the properties of aromatic carboxylic acids but can be very important with a NH_2 group, the F and M parameters are calculated only from the benzoic acid data.

As expected, all of the fluorinated substituents exhibit a strong field effect and have large positive values of F (0.6 to 1.4). In particular, it should be noted that the field effect for the OR_f and SR_f groups are essentially the same and are also of similar magnitude to that for CF_3, the halogens, acetoxy and thioacetoxy groups. A significantly larger value of F is calculated for the SF_5 group (1.05) and is similar to that for cyano (0.97) and methylsulfonyl (1.04). The F-value of 1.37 for the SO_2CF_3 group is much greater than that for nitro and, according to the compilation of F-values given by Dewar and Grisdale,[13] is exceeded only by groups bearing a formal positive charge, $(CH_3)_3N^\oplus$ (1.52) and $(CH_3)_2S^\oplus$ (1.73).

For the simple fluorinated substituents, the F-value per fluorine is relatively constant: CF_3, 0.24; SF_5, 0.21; OCF_3, 0.22; SCF_3, 0.22. This proportionality of F-values with number of fluorines is expected if the F parameter is chiefly a measure of field effect provided that the distances and electronegativity of the substituent atoms (carbon or sulfur) do not differ grossly.

The M-values for the OR_f groups are close to zero or slightly negative indicating that the inductive and resonance effects operating through the π-system are in opposition and effectively counterbalance one another.

However, the M parameters for the SR_f groups have relatively large positive values approaching those of the NO_2, CF_3 and SF_5 groups, again indicating that the resonance and inductive effects in the π-system operate in the same direction and reinforce the field effect. The M parameter for the SO_2CF_3 groups has a larger positive value than that of any other substituent tabulated,[13] indicating the very strong electron-withdrawing effect that this substituent exerts on the π-system in conjunction with the large field effect.

Another method of quantitatively comparing substituents is by electrophilic (σ^+) substituent constants as proposed by Brown and Okamoto.[23] Although σ^+ values have not been determined for the perfluorinated groups, agreement between σ^+ and σ is expected for the OR_f groups, but large discrepancies must occur between these parameters for the SR_f groups (see ref. 19).

The dipole moment of phenyl trifluoromethyl ether is 2.36 with the negative end of the dipole directed toward the OCF_3 groups as determined for the moments of the bromo-, nitro- and aminophenyl trifluoromethyl ethers (see Table V). This moment is almost double that for anisole and very closely approaches that for benzotrifluoride.

<div align="center">TABLE V</div>
<div align="center">DIPOLE MOMENTS AT 25.0° (IN DEBYE)</div>

Compound	Measured value	Algebraic sum	Calculated values — Vector sums with correction for angular position of OCX_3 group (angle in parentheses)[a]
$C_6H_5OCF_3$	2.36		
$C_6H_5CF_3$[b]	2.60		
C_6H_5Br[c]	1.52		
p-$BrC_6H_4OCF_3$	1.00	0.84	1.00 (163°)
$C_6H_5NH_2$[c]	1.53		
p-$H_2NC_6H_4OCF_3$	3.79	3.88	
$C_6H_5NO_2$[c]	3.95		
p-$O_2NC_6H_4OCF_3$	2.16	1.62	2.15 (153°)
p-$(CF_3O)_2C_6H_4$	0.81	0	0.80 (160°)
$C_6H_5OCH_3$[c]	1.2		
p-$O_2NC_6H_4OCH_3$[c]	4.75	2.10	4.35 (90°)
p-$(CH_3O)_2C_6H_4$[c]	1.73	0	

[a] Calculated assuming restricted rotation so that the OCX_3 group lies in the plane of the ring; see discussion. [b] Ref. 2. [c] Ref. 24.

From the dipole moments of the dimethyl ether of hydroquinone and other substituted anisoles and phenols it has been shown that the OCH_3 and OH groups lie at approximately 90° from the axis through the plane of the ring (C–O–C or C–O–H angle).[24] Since the angles must be taken into account, the OCH_3 group cannot rotate freely and must lie in the plane of the ring. The coplanarity of the OCH_3 group with the aromatic ring arises from resonance contribution by the quinoidal forms.
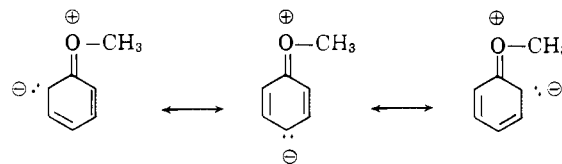
The moment of 0.81 D. for p-bis-(trifluoromethoxy)-benzene shows that the C–O–C angle for the OCF_3 group is also less than 180°. The smaller dipole value

ionization of the p-phenol and p-aniline derivatives; E. S. Lewis and M. D. Johnson, J. Am. Chem. Soc., 81, 2070 (1959). The trinitromethyl group, $C(NO_2)_3$, was previously reported to have the largest σ_p value (0.82) measured for any electrically neutral group. J. Hine and W. C. Bailey, Jr., J. Org. Chem., 26, 2098 (1961).

(22) p-Hydroxyphenyl trifluoromethyl sulfone is reported to be hydrolyzed on treatment with warm dilute base.[7b] In contrast, p-hydroxyphenyl perfluoroalkyl sulfides and ethers are more stable under these conditions.

(23) H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 79, 1913 (1957); Y. Okamoto and H. C. Brown, J. Org. Chem., 22, 485 (1957).

(24) (a) W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. 2, Elsevier Press, New York, N. Y., 1958, Chapter XII, pp. 127 and 137; (b) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Chapter 5, pp. 238–243.

compared to that for the dimethyl ether of hydroquinone and also the size of the moments for p-bromophenyl and p-nitrophenyl trifluoromethyl ethers (compared to the values for vector sum and to those of the corresponding anisoles) can be explained in one of two ways: (1) The angle for the OCF_3 group with the axis in the plane of the ring is closer to 180° than to 90°; or (2) the angle is still near 90° but the OCF_3 group rotates almost freely so that it is restricted to only a small extent to a coplanar position with the aromatic ring. This latter explanation is considered most reasonable since the resonance contribution by the quinoidal forms is grossly reduced by the electron-withdrawing

effect of the CF_3 group (note that for OCF_3 σ_R ranges from -0.13 to -0.23 while for OCH_3, σ_R is -0.47). With the precision of the data in mind, a tenuous conclusion can be drawn that the p-nitro group behaves as expected and helps to stabilize the quinoidal form compared to the p-bromo group. A more quantitative analysis of the dipole moment results is not appropriate in view of the problems discussed in ref. 24b.

Photodecomposition of p-Benzoquinone Diazides: Copolymerization with Tetrahydrofuran[1,2]

By J. K. Stille, P. Cassidy and L. Plummer

p-Benzoquinone diazide and 2,6-dimethyl-p-benzoquinone diazide decompose in various solvents in the presence of heat or light with the loss of nitrogen to give different products. Whereas the light-catalyzed decomposition in many solvents affords substituted phenols, in tetrahydrofuran nearly a 1:1 copolymer with solvent is obtained. The polymer, which contains the polyether structure, is probably an alternating copolymer and is formed through a cationic ring opening of tetrahydrofuran.

Introduction

The potential thermal stability of polymers containing the poly-(phenylene oxide) chain have made them the object of recent investigation with respect to the methods of formation of such a polymer.[3–10] Compounds containing the p-benzoquinone diazide structure decompose readily in the presence of light or heat and should lend themselves readily to the preparation of poly-(phenylene oxides). However, decomposition in the solvents benzene, anisole, and N,N-dimethylaniline provides the substituted hydroxybiphenyl derivatives,[3,11,12] while the photodecomposition of solid p-benzoquinone gives insoluble polymer.[11] The thermal decomposition of 2,6-dibromo-p-benzoquinone diazide in chlorobenzene affords a polymer containing the expected recurring unit as well as incorporated solvent.[3] In this decomposition, a mildly electrophilic diradical has been proposed as the reactive intermediate.[3,13]

Results

The monomers p-benzoquinone diazide (I) and 2,6-dimethyl-p-benzoquinone diazide (II) were prepared in anhydrous (red) and tetrahydrated (yellow) forms which could not be distinguished spectrally except for the fact that the anhydrous forms have lower molar extinction coefficients (Table I). The anhydrous form of p-benzoquinone diazide and the tetrahydrate form of

2,6-dimethyl-p-benzoquinone diazide have not been previously described. The preparation and polymerization of 2,6-dibromo-p-benzoquinone diazide (III) was undertaken for comparison purposes. All the monomers are very difficultly soluble in non-polar solvents, but are very soluble in such solvents as ethanol or water. Decomposition of the monomers by either heat or light in benzene produced the expected hydroxybiphenyl. The photodecomposition of p-benzoquinone diazide in nitrobenzene afforded nitrosobenzene and p-benzoquinone. Photolysis of 2,6-dimethyl- and 2,6-dibromo-p-benzoquinone diazides in nitrobenzene gave nitrosobenzene and presumably the corresponding quinones.
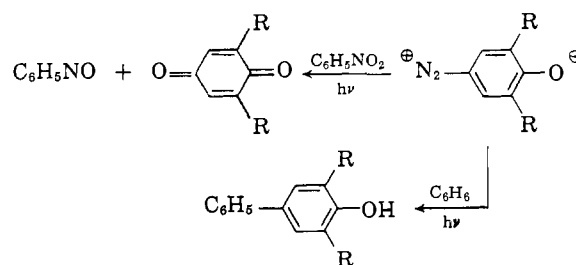
I, R = H; II, R = CH_3; III, R = Br

Decomposition of the p-benzoquinone diazides in tetrahydrofuran gave good yields of polymer. However, decomposition in 2,2,5,5-tetramethyltetrahydrofuran afforded little or no polymeric product. As shown in Table II the greatest percentage conversion and highest viscosities were obtained using light catalysis and the anhydrous forms of the monomers.

Polymerizations were also attempted using catalysts such as boron trifluoride etherate,[14,15] copper salts,[16,17] auric chloride[18] and trimethyl borate[15] which have been

(1) This article was to have been published prior to that of Kunitake and Price (ref. 19), but publication was delayed due to unforseen circumstances.

(2) (a) Presented in part at a symposium in honor of C. S. Marvel at the University of Arizona, December 27–28, 1961; (b) This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) M. J. S. Dewar and A. N. James, J. Chem. Soc., 917 (1958).

(4) G. D. Staffin and C. C. Price, J. Am. Chem. Soc., 82, 3632 (1960).

(5) C. J. Kurian and C. C. Price, J. Polymer Sci., 49, 267 (1961).

(6) H. S. Blanchard, H. L. Finkbeiner and G. A. Russell, ibid., 58, 469 (1962).

(7) A. S. Hay, ibid., 58, 581 (1962).

(8) B. O. Lindgren, Acta Chem. Scand., 14, 1203 (1960).

(9) C. G. Haynes, A. H. Turner and W. A. Waters, J. Chem. Soc., 2823 (1956).

(10) E. Adler and R. Magnusson, Acta Chem. Scand., 13, 505 (1959).

(11) O. Sus, K. Moller and H. Heiss, Ann., 598, 123 (1956).

(12) Chi-Hua Wang, Proc. Chem. Soc., 309 (1961).

(13) M. J. S. Dewar and A. N. James, J. Chem. Soc., 4265 (1958).

(14) C. E. H. Bawn, S. Ledwith and P. Matthies, J. Polymer Sci., 33, 21 (1958).

(15) J. Feltzin, A. J. Restaino and R. B. Mesrobian, J. Am. Chem. Soc., 77, 206 (1955).

(16) G. D. Buckley, L. H. Cross and N. H. Ray, J. Chem. Soc., 2714 (1950).

(17) C. E. H. Bawn and A. Ledwith, Chem. Ind. (London), 1180 (1957).

(18) A. C. Nasini, L. Trossarelli and G. Saini, Makromol. Chem., 44–46, 550 (1961).