(11) E. Buchta and K. Geibel, *Justus Liebigs. Ann. Chem.*, **648,** 36 (1961).

(12) Dielectric constants of solutions were measured using a Dipolmeter Type DM 01 (Wissenschaftlich-Technische Werkstätten GmbH, Weilheim,-Germany). The Guggenheim method[13] was employed for obtaining dipole moments.

(13) E. A. Guggenheim, *Trans. Faraday Soc.*, **74,** 2193 (1952).

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

(15) (a) See G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London, 1961, for a compendium of acid-dissociation constants and a discussion of measurement methods. (b) A reviewer has suggested that an estimate of the magnitude of an inductive effect of our carbonyl at C-6 might be made on the basis of data from appropriate 6-keto acids or from analogous chloro acids. Such data do not appear to be available, and were they available their ΔpK magnitudes would not suffice to establish the better model accounting for the transmission of the substituent's effect. The question regarding the source of the unexpected acid-strengthening effect of the carbon–carbon double bond at the 6 position may be resolved by pK_a comparisons of **4**, **5**, and *trans*-spiro[3.4]-5-octene-2-carboxylic acid (see note 22).

(16) See D. H. R. Barton, F. McCapra, P. J. May, and F. Thudium, *J. Chem. Soc.*, 1297 (1960), for evidence that a remote carbon–carbon double bond can influence rates of base-catalyzed condensations of benzaldehyde with steroidal ketones.

(17) The relationship between electronegativity and s character has been documented by H. A. Bent, *Chem. Rev.*, **61,** 275 (1961), and by J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84,** 540 (1962), among others. A wealth of data are available which demonstrate the effects of bond-angle deformation on acidities (presumably through s-character alterations). See, for example, K. B. Wiberg and B. R. Lowry, *ibid.*, **85,** 3188 (1963); F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89,** 5677 (1967); A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *ibid.*, **91,** 529 (1969); A. G. Cook and G. W. Mason, *J. Org. Chem.*, **37,** 3342 (1972); A. Streitwieser, Jr., P. H. Owens, R. A. Wolf, and J. E. Williams, Jr., *J. Am. Chem. Soc.*, **96,** 5448 (1974), and references cited therein.

(18) H. J. Geise and F. C. Mijlhoff, *Recl. Trav. Chim. Pays-Bas*, **90,** 577 (1971).

(19) C. S. Foote [*Tetrahedron Lett.*, 579 (1963)] cites a value of 103.3° for the pseudorotating cyclopentane which is an average value obtained from J. B. Hendrickson, *J. Am. Chem. Soc.*, **83,** 4537 (1961).

(20) The $C_3C_4C_5$ bond angle of cyclopentene is reported to be 104.0°; that for $C_2C_3C_4$ is 103.0°.[21]

(21) M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, **74,** 1104 (1970).

(22) A planned test for conformational transmission in these spirane systems is the determination of the pK_a's of 5-methylenespiro[3.4]octane-2-carboxylic acid or spiro[3.4]-5-octene-2-carboxylic acid. In these derivatives the bond-angle deformations conformationally transmitted to C_2 should decrease the s character of its external orbitals. ^{13}C–H coupling constants at C_2 may also reveal these effects.

(23) Because of uncertainties in the conformations of the five-membered ring and to greatly simplify calculations estimating R and $\cos\theta$, the cyclopentane ring was assumed to be planar. Consequently a 108° bond angle was employed for the five-membered ring. Calculations were performed with the cyclobutane ring either planar or bent with a dihedral angle of 152.6° [24] (moving the carboxyl group into a more equatorial position). The difference in ΔpK_a's (≤ 0.01) obtained using these two geometries were insignificant and thus only the "planar model" results are given. Other bond angles and lengths used[24-26] were 1.55 Å for the C–C bonds of the five-membered ring, 90° and 1.55 Å for the C–C–C bond angles and C–C bond lengths, respectively, for the cyclobutane, 109° for the H–C_2–CO_2H bond angle, and 1.50 Å for the C–CO_2H bond. The ketone C=O bond was assigned a length of 1.24 Å and the position of the carboxyl proton located at 1.45 Å beyond the carboxyl carbon on the extension of the C–C bond. The C=O dipole was assigned a group moment of 3.0 D from Smyth's data[27] for cyclopentanone.

The effective dielectric constants (D_E) and ΔpK's were calculated from the Kirkwood–Westheimer equations using alternately a sphere and an ellipsoid to approximate the molecular cavity. Tanford's modification was employed locating the point dipoles and charges 1.5 and 1.0 Å, respectively, below the surface of the cavity. A value of 78.5 was used for the external (solvent) dielectric constant and a value of 2.0 for the internal dielectric constant.

(24) L. A. Hulshof, A. Vos, and H. Wynberg, *J. Org. Chem.*, **37,** 1767 (1972).

(25) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Am. Chem. Soc.*, **92,** 5013 (1970).

(26) "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, Burlington House, London, 1958, and Supplement 1956–1959.

(27) C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, N.Y., 1955.

(28) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41,** 2774 (1963).

(29) Melting points were determined on a Fisher-Johns or a Hoover apparatus and are corrected. Infrared spectra were obtained on a Perkin-Elmer Model 621 recording spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian Model A-60 spectrometer. Gas–liquid chromatographic analyses and preparative-scale separations were conducted with a Varian Model 90-P or Model A-700 chromatograph. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-6E spectrometer. Calculations were performed with the aid of IBM Model 1130 and Model 360/45 computers. Analyses were performed by M-H-W Laboratories.

(30) E. Buchta and K. Geibel, *Justus Liebigs Ann. Chem.*, **648,** 36 (1961).

(31) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases", Wiley, New York, N.Y., 1962, Chapters 2 and 3.

(32) The method of A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee [*J. Org. Chem.*, **20,** 747 (1955)] was employed.

Carbon Acids. 10. Resonance Saturation of Substituent Effects in the Fluorene Series

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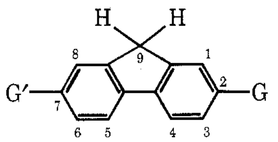
Equilibrium acidities for 14 2-substituted fluorenes were found to vary over a range of 6.1 pK units in dimethyl sulfoxide solution. A rather poor Hammett plot was obtained with σ_m ($\rho = 7.5 \pm 0.53$, $r = 0.969$). Groups capable of strong electron acceptor resonance interactions (CN, PhCO) or strong electron donor resonance interactions (MeO, F) deviated most from the line, indicating that the 2 position in the fluorene ring has considerable "para character", as well as "meta character". The effect of substituting a second CN, Et_2NSO_2, or Br atom into an equivalent position on the fluorene nucleus (the 7 position) was substantially less than additive (by 0.5–0.8 pK units). This is attributed to a resonance saturation effect. Similar resonance saturation effects were observed for $PhSO_2$, Ph, and p-MeC_6H_4S groups in 2,9-disubstituted fluorenes, but no saturation of the effects of MeO or PhS was observed in 2,7-disubstituted fluorenes. The conclusion is drawn that, in the absence of steric effects, saturation effects result from changes in electron distribution in the anion caused by resonance delocalization, and that polar saturation effects are of little or no importance.

Three distinct mechanisms for "saturation" of the electronic effects of substituents, namely, polar, resonance, and steric, were visualized in 1941 by Branch and Calvin in their classical book on theoretical organic chemistry.[1] In discussing acidities of acids without resonance, including aliphatic carboxylic acids, they remark that "there should be a tendency for polar effects of groups to increase less rapidly than the calculated values when the sum of the inductive constants of the component parts becomes very great (a saturation effect)". In addition, they suggested that two π-electron-donor groups in para positions on a benzene ring should destabilize the system by what they termed "cross-conjugation", and that the effects of the two π donors should be nonadditive.[1] (Additional evidence for a "saturation" effect of this kind was provided later.[2]) Finally, Branch and Calvin recognized that ortho groups could interfere with quinoidal resonance giving rise to steric inhibition of resonance, which causes a damping or "saturation" of substituent effects.

Experiments in the ensuing years have provided abundant examples of attenuation ("saturation") of electronic effects caused by steric inhibition of resonance, but clear-cut examples of attenuation of electronic effects by polar or resonance saturation are not common. Branch and Calvin were not able to obtain evidence for a polar saturation effect, but predicted that one should become apparent for measurements of substituent constants for weaker acids than those with which they were concerned. Taft's polar substituent constants (σ^*), derived from aliphatic carboxylic esters or acids, also failed to reveal saturation effects in aliphatic systems, i.e., "σ^* constants were generally found to be approximately additive".[3] The theoretical basis for the polar saturation effect apparently lies in the Lewis "electron-shift" hypothesis, which assumes that substitution of an electron-withdrawing group (EWG) for a hydrogen atom in an aliphatic system causes a decrease in electron density at the acidic site by successive electron displacements in the σ bond framework.[4] Analyses of substituent effects on acidities of carboxylic acids in rigid aliphatic systems during the past decade indicate, however, that transmission of electronic effects through bonds is of minor importance. The data are accommodated much more satisfactorily by assuming that the effects are primarily electrostatic in nature, and are transmitted through a dielectric cavity which includes the framework of the molecule and the solvent.[5] As has been pointed out by Ingold, the electrostatic effects of substituents should not be subject to saturation if the substituents are spaced so as to act independently.[6] According to this view, saturation of polar effects should play little or no role in most aliphatic systems, and the failure of Branch and Calvin, and of Taft, to observe such effects is understandable. We conclude that not only is there no experimental evidence for a polar saturation effect, but that there is no longer any theoretical reason to expect that an appreciable effect of this kind will be observed in aliphatic systems.

In sharp contrast to the lack of evidence for saturation of polar effects, there are theoretical reasons to expect saturation of resonance effects, and there is experimental evidence to support this view. When introduction of a substituent causes delocalization of charge from a reaction site we can expect that, because the charge density at the reaction site has been decreased thereby, the effect of introduction of a second substituent will be less than the first. Hine called attention to a resonance saturation effect of this kind on the stability of triaryl cations, $Ar_2Ar'C^+$.[7] He cited data to show that the destabilizing effect of a p-NO_2 group in Ar' is greatly decreased by the presence of p-Me_2N groups in Ar. The p-Me_2N groups in the two Ar rings delocalize the charge away from the central carbon atom thus diminishing the destabilizing effect of p-NO_2 in the third ring.[7] A similar effect was observed for triaryl anions, Ar_3C^-.[8] Here the stabilization energy of $(p\text{-}NO_2C_6H_4)_3C^-$ was found to be only about 1.2 times that of $(p\text{-}NO_2C_6H_4)(C_6H_5)_2C^-$, pointing to a marked saturation of the π-acceptor ability of the p-NO_2 group.[8] In Ar_3C^+ and Ar_3C^- ions a large part of the attenuation of multiple substituent effects must be due to steric inhibition of resonance, as the authors recognized.[7,8] Similar effects have also been obtained, however, for Ar_2CH^+ ions, where steric effects are less severe. Nonadditivity of multiple substituent effects on rates of solvolysis of benzhydryl halides, ArAr'CHX, have been reported by several investigators.[9] Similar effects have been observed for rates of bromination of diphenylethenes, ArAr'C=CH$_2$,[10] and Dubois has pointed out that, while part of the attenuation must be due to steric inhibition of resonance, there is nevertheless good reason to believe that part is also due to a resonance saturation effect.[10]

Hammett σ_m constants are believed to contain an appreciable resonance component,[11] and would therefore be expected to be subject to resonance saturation. However, careful examination of the acidities in protic solvents of benzoic acids containing substituents in 3,4, 3,5, or 3,4,5 positions has failed to reveal any evidence of nonadditivity (saturation).[12] We have observed large resonance saturation effects on equilibrium acidities in dimethyl sulfoxide (Me_2SO) solution for carbon acids of the type GCH_2EWG with various groups, G (e.g., Ph or PhS) when EWG is changed so as to increase progressively the delocalization of the negative charge in the $GCHEWG^-$ anion, as in the series where EWG is changed from CN to CH_3CO to NO_2.[13] These results led us to expect resonance saturation in aromatic systems. In view of the previous failures to observe such effects,[12] it was clear that a system more sensitive to substituent effects was needed. The fluorene system appeared to be ideal for our purpose since a good correlation with σ_m for five 2-substituted fluorenes had been reported (r = 0.997) for equilibrium acidities in Me_2SO–H_2O, and the system had been found to be highly sensitive to substituent effects (ρ = 7.5).[14] The fluorene system also has the advantage over the benzoic acid system that its "meta" positions (2 and 7) are in different rings, thus ensuring independent action of dipoles. The fluorene system is comparable in general type to the diarylmethane (anion or cation) system,[9,10] but has the advantage that steric inhibition of resonance can be eliminated, as in 2,7-disubstituted fluorenes (**1**), or minimized, as in 2,9-disubstituted fluorenes (**2**). Examination of the equilibrium acidities of **1** and **2** has revealed the presence of sizable resonance saturation effects for π-acceptor substituents, but not for π-donor substituents.



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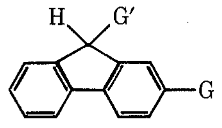


2

Experimental Section

Sources of Fluorenes. Samples of 2-bromo- and 2-nitrofluorenes were purchased from the Aldrich Chemical Co., Milwaukee, Wis. 2-Bromofluorene was purified by recrystallization from 95% ethanol. 2-Nitrofluorene was purified by repeated recrystallization from glacial acetic acid followed by recrystallization from cyclohexane. 2,7-Dimethoxyfluorene was prepared from a sample of 2,7-dihydroxyfluorenone, kindly provided by the Ash-Stevens Chemical Co. The syntheses of the 2-, 2,7-, and 2,9-substituted fluorenes will be reported in a separate publication.

p*K* Measurements. pK values for fluorene and 14 2-substituted fluorenes were measured in pure Me_2SO by the general titration method previously described.[15] All of the fluorenes discussed herein produced anions which absorbed strongly at wavelengths in the visible spectrum. Consequently, either of two methods of measurements were available. In method A the fluorene derivative was used as the indicator and measured against a standard acid.[16] In method B the fluorene derivative was used as the acid and measured against an indicator whose anion absorbed at a longer wavelength in the visible spectrum. The two methods gave results agreeing to within ±0.1 pK unit.

All of the substituted fluorenes behaved well as indicators[16] with the exception of the 2-Br, 2-Cl, 2,7-di-Br, and 2-benzoyl derivatives. Addition of a standard acid to a solution of the halofluorenyl anions (method A) resulted in immediate equilibration, followed by a very slow rise in the visible absorbance of the solution. (The cause of the rise in absorbance was not investigated.) Measurement of the halofluorenes by method B (4-chloro-2-nitroaniline as the indicator) eliminated this problem and gave the same pK values as did method A to within experimental error (±0.1 pK unit).

In the titration of potassium dimsyl (KCH_2SOCH_3) with 2-benzoylfluorene the first increment of 2-benzoylfluorene added produced slightly less of the 2-benzoylfluorenyl anion than did the second, the second produced less than did the third, etc. This became apparent when the amount of 2-benzoylfluorene added was plotted against the absorbance of the 2-benzoylfluorenyl anion formed. The simplest explanation of this behavior is that some of the potassium dimsyl added across the carbonyl group rather than effecting deprotonation. The problem was alleviated by converting $K^+CH_3SOCH_2^-$ to $K^+Ph\bar{C}HSO_2CH_3$ (presumably a less nucleophilic and more hindered

Table I. Equilibrium Acidities of 2-Substituted Fluorenes in Dimethyl Sulfoxide

Registry no.	Substituent	pK^a	$\sigma_m{}^b$
13261-62-6	2-$(CH_3)_2N$	24.2	−0.15
1430-97-3	2-CH_3	23.1	−0.07
2523-46-8	2-CH_3O	22.7_5	0.12
86-73-7	H	22.6	(0.00)
343-43-1	2-F	21.0	0.34
59014-80-1	2-CH_3S	21.6_5	0.15
59014-81-2	2-PhS	20.5	0.27^c
2523-44-6	2-Cl	20.2_5 (±0.15)	0.37
1133-80-8	2-Br	20.0 (±0.15)	0.39
59014-82-3	2-CH_3SO	19.7_5	+0.52
15860-31-8	2-PhCO	19.5_5 (±0.15)	0.36
59014-83-4	2-Et_2NSO_2	18.8	0.46^d
59014-84-5	2-CH_3SO_2	18.5	+0.60
2523-48-0	2-CN	18.2	0.56
59014-85-6	2-$PhSO_2$	18.1	0.62^e

[a] pK's are ±0.1 unit unless otherwise noted. [b] From pK's of benzoic acids unless otherwise noted (see ref 4b, p 66). [c] Based on pK's of acetophenone in Me_2SO (F. J. Cornforth, Ph.D. Dissertation, Northwestern University, August 1976). [d] σ_m for H_2NSO_2. [e] O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 65 (1966).

base) prior to titration. The titrations were then carried out with several standard acids using 2-benzoylfluorene as an indicator; the range of pK's observed was slightly larger than usual, however (±0.15 unit).

We were unable to obtain a point for 2-nitrofluorene because, in pure Me_2SO, treatment with a variety of bases generated a green-colored species absorbing strongly in the visible, but lacking the three-band pattern characteristic of 2-substituted fluorenyl anions. Dilution with water gave a red anion, apparently that observed previously.[14]

Results and Discussion

Hammett Plot Using σ_m. A plot of pK's (Table I) for the 15 fluorenes vs. Hammett σ_m constants gave a least-squares line of slope (ρ) equal to 7.5 ± 0.53, $r = 0.969$ (Figure 1). This ρ agrees with that obtained by Bowden and Cockerill for five 2-substituted fluorenes (MeO, Cl, Br, CN, and NO_2) in Me_2SO–H_2O (45–90% Me_2SO), but their correlation coefficient was much better (0.997).[14] The correspondence of ρ's is, however, fortuitous. Note that if we select a comparable group of substituents from Figure 1 (MeO, Cl, Br, and CN) the correlation coefficient would also be high ($r = 0.999$), but $\rho = 10.3$. Comparison shows that the pK's determined by the H_- method are compressed, relative to those in Me_2SO (e.g., the range for 2-MeO to 2-CN fluorene is 3.40 pK units by the H_- method,[14] as compared to 4.55 pK units in pure Me_2SO). For the more acidic fluorenes the H_- method probably gives high values, because pK's for fluorenes in water are higher than in Me_2SO.[15] As the water content of the Me_2SO–H_2O mixture is decreased to permit H_- measurements for the less acidic fluorenes, a reversal occurs, and the values become low relative to those in pure Me_2SO.[17] The overall result is a smaller ρ.

The standard deviation of the points from the line in Figure 1 is 0.467 pK units. This is far beyond the deviation expected from the experimental errors in the measurements (estimated at <0.1 pK unit) or the deviation in Hammett σ_m constants (estimated at 0.1–0.2 pK unit). A number of factors that might lead to the unexpectedly large deviations can be imagined: (1) the σ_m constants determined in water (or 50% aqueous ethanol) may not be applicable to Me_2SO since we are changing from a strongly H-bonding (donor) medium to a very weakly H-bonding (donor) medium; (2) the 2-substituted fluorenes may constitute an unusually severe test for the Hammett relationship since the data are spread over a range of 6.1 pK units, as compared to only 0.83 pK units for the corresponding meta-substituted benzoic acids; (3) the geometric relationships between the negative charge and the 2 substituent in 2-substituted fluorenyl anions may differ so markedly from that in meta-substituted benzoate ions as to give rise to the observed deviations. Surprisingly enough, factors 1 and 2 appear to be relatively unimportant, since an excellent Hammett relationship has been observed with meta-substituted acetophenones,[18] the carbon acid analogues of benzoic acids, and a reasonably good relationship has been observed with meta-substituted arylacetonitriles,[19] which have pK's of a comparable magnitude to the fluorenes and where ρ is also large (5.5).[19]

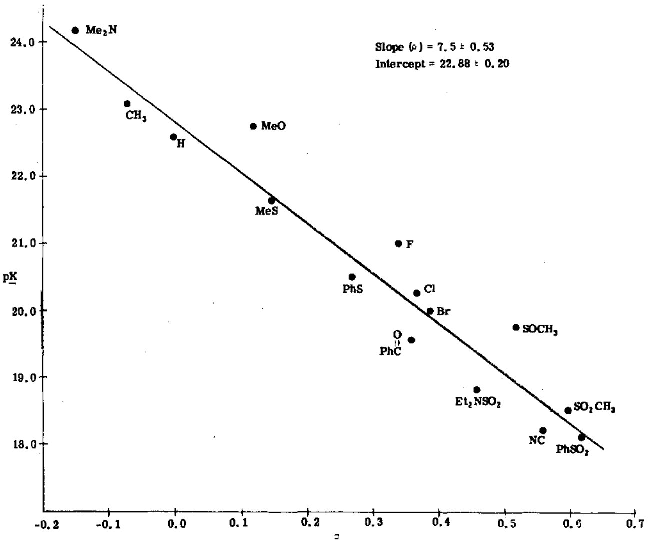
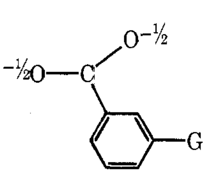


Figure 1. Hammett plot of equilibrium acidities of 15 2-substituted fluorenes in dimethyl sulfoxide solution.

Comparison of the structure of a meta-substituted benzoate ion (3) with that of a 2-substituted fluorenyl ion (4) shows that in 3 the negative charge is located on the oxygen atoms, which are one or more atoms farther removed from substituent G than are the carbon atoms bearing the charge in 4. The distribution of the negative charge in the fluorenyl anion, as judged by molecular orbital calculations,[20] is shown in formula 5. We see from 5 that about 65% of the charge is located in the cyclopentadienyl ring and about 35% is distributed over the two phenyl rings. About 49% of the charge in the five-membered ring is located at the 9 position (a "meta" benzylic position), about 17% appears at the 4b position (a "para" benzylic position), and about 17% appears at the 4a position (a "para" ring position). Although only about 3% of the charge is expected to be located in the 2 position of the fluorenyl anion itself (5), this percentage will no doubt be increased (or decreased) when the hydrogen atom in this position is replaced by a substituent, G. If G is capable of playing an electron-pair



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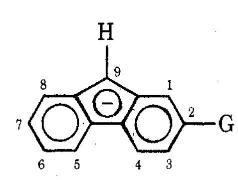

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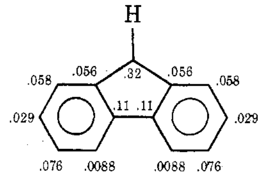

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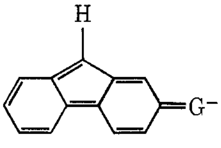
Table II. Comparison of Substituent Effects for 2- and 2,7-Substituted Fluorenes

Registry no.	Substituent(s)	pK	ΔpK_1[a]	ΔpK_2[b]
	2-CH_3O	22.7_5	−0.15	
42523-30-8	2,7-$(CH_3O)_2$	22.9_5		−0.20
	2-PhS	20.5	2.1	
59014-86-7	2,7-$(PhS)_2$	18.5		2.0
	2-Br	20.0	2.6	
16433-88-8	2,7-$(Br)_2$	17.9		2.1
	2-Et_2NSO_2	18.8	3.8	
59014-87-8	2,7-$(Et_2NSO_2)_2$	15.6		3.2
	2-CN	18.2	4.4	
39150-36-2	2,7-$(CN)_2$	14.6		3.6

[a] Relative to fluorene (pK = 22.6). [b] Relative to the corresponding 2-substituted fluorene.

acceptor role, delocalization of charge to G is possible through resonance contributor **6**, whereas if G is capable of playing an electron-pair donor role the relative distribution of charge in the two phenyl rings can be altered through resonance contributors such as **7**. The extent of contribution of **6** and **7** is in some doubt, however, since they are quinoidal forms and the resonance of both benzene rings must be destroyed therein; in addition, for **7**, there is extensive charge separation.



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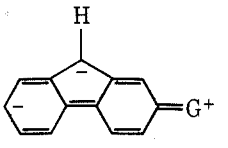

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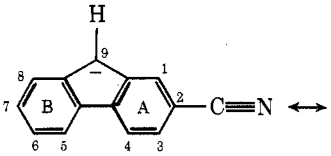
Focusing attention first on resonance electron-acceptor groups, we see by examination of Figure 1 that the points for PhCO, Et_2NSO_2, and CN deviate from the line by somewhat more than the standard deviation of 0.467 pK units, whereas the points for CH_3SO_2 and $PhSO_2$ are close to the line, and the point for CH_3SO deviates markedly and in the opposite direction. These results suggest enhanced electron-accepting ability for at least the PhCO and CN groups.[21]

The points for the resonance electron-donor substituents, F and MeO, deviate from the line by somewhat more than 0.467 pK units in a direction opposite to that observed for the resonance-acceptor groups. (It is surprising that the Me_2N group does not follow suit.) There is some indication, therefore, of electron donation for these groups beyond that observed in meta-substituted benzoic acids.[22]

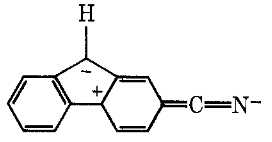
We conclude from this analysis that the much larger ρ observed for 2-substituted fluorenes in Me_2SO, as compared to meta-substituted benzoic acids in water (7.5 vs. 1.0), is due primarily to the much closer proximity of the center of charge to the substituent G in **4** than in **3**; in addition, there is a solvent effect on ρ, which is probably related principally to the change in the effective dielectric constant of the medium.[23] The behavior of groups capable of electron acceptor and electron donor resonance suggests that the poor correlation with σ_m (Figure 1) is due to the presence of appreciable "para character" in the effects of substituents located in the 2 position of the fluorene nucleus.[25]

Nonadditivity of Substituent Effects (Resonance Saturation). The additivity (or lack thereof) of substituent effects for CH_3O, PhS, Br, Et_2NSO_2, and CN groups when substituted in the 2,7 vs. the 2 position(s) on the fluorene nucleus is brought out in Table II.

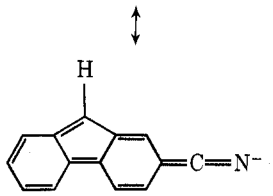
Examination of Table II shows that substitution of CN for H in the 2 position of fluorene results in an increase in acidity of 4.4 pK units (ΔpK_1), which can be attributed in part to stabilization of the 2-cyanofluorenyl anion by delocalization of the negative charge into the cyano group, as in resonance contributors **8b** and **8c**. This results in a decrease in negative charge in ring A, and to a lesser extent in the cyclopentadienyl ring and in ring B, relative to that found in the fluorenyl anion itself. Substitution of a second cyano substituent into an equivalent position of ring B (the 7 position) therefore causes an appreciably smaller acidifying effect (ΔpK_2 = 3.6). The difference of 0.8 pK units represents the size of the resonance saturation effect. Comparable results were obtained for the Et_2NSO_2 group (ΔpK_1 − ΔpK_2 = 0.6) and even Br showed a resonance saturation effect of 0.5 pK units (Table II). The effect for the PhS substituent (0.1 pK unit) is only slightly greater than experimental error, but the presence of a resonance saturation effect for an arylthio substituent is supported by evidence obtained from 2,9-disubstituted fluorenes (see below).



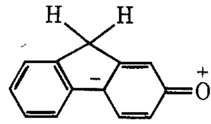
8a



8b



8c



9

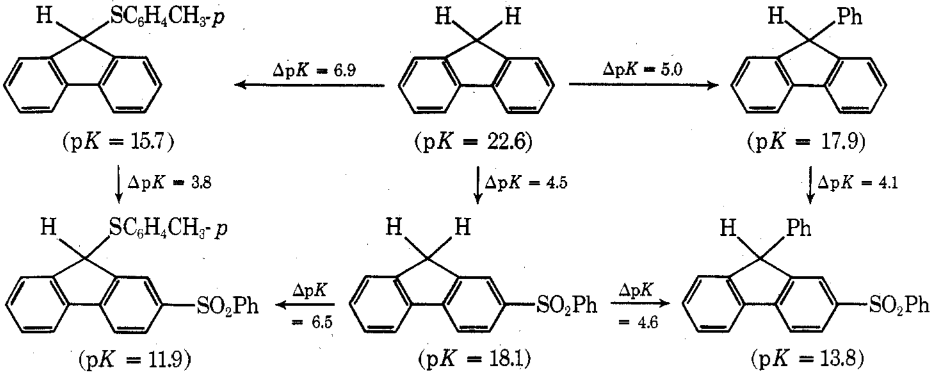
The points for the 2-MeO and 2-F substituents fall appreciably above the line in Figure 1, suggesting that their acid-strengthening polar effects are being balanced by an acid-weakening π-donor resonance effect, presumably operating mainly to stabilize the undissociated acid (e.g., contributor **9**). One might have expected the resonance effect of a second methoxyl group at the 7 position in 2,7-dimethoxyfluorene to be impeded by the buildup of charge in the cyclopentadienyl ring (as in **9**). There is no evidence, however, that such an effect occurs, since ΔpK_2 is the same as ΔpK_1, within experimental error (Table II).

Since the charge density at the 9 position is much greater than at the 2 position in the fluorenyl anion (**5**), one would expect a 9 substituent to show much the larger effect, and this is observed. For example, a 9-CN substituent increases the equilibrium acidity by 14.5 pK units,[15] whereas the effect of a 2-CN substituent is only 4.4 pK units (Table I). 9-Phenyl and 9-p-tolylthio substituents are also strongly acid strengthening (ΔpK's of 5.0 and 6.9, respectively). Scheme I shows that these effects are attenuated to 4.6 and 6.5 pK units, respectively, if a 2-$PhSO_2$ group is already present in the fluorene nucleus (a 0.4 pK unit resonance saturation of the acidifying effects of Ph or of p-$CH_3C_6H_4S$ caused by the 2-$PhSO_2$ group). Similarly, Scheme I shows that the acid-strengthening effect of the 2-$PhSO_2$ group is larger relative to fluorene (ΔpK = 4.5) than relative to 9-phenylfluorene (ΔpK = 4.1) or 9-p-tolylthiofluorene (ΔpK = 3.8). The 9-Ph and 9-p-MeC_6H_4S groups thus attenuate the effect of the 2-$PhSO_2$ group by 0.4 and 0.7 pK units, respectively.

Conclusions

We conclude that the failure of saturation of substituent effects to materialize in (saturated) aliphatic systems[1,3] is understandable because these effects are polar (electrostatic) in nature, and saturation of such effects is small or nonexistent. The additivity of Hammett σ_m constants is also understandable, since these effects are also primarily polar in nature, and the benzoic acid system is relatively insensitive to

Scheme I



substituent effects. On the other hand, we believe that the resonance saturation effect is a general phenomenon in chemistry. In fact, it often constitutes the principal basis for the physical organic chemists' "rule of thumb" that substituent effects on an equilibrium or rate involving an unstable species (anion, cation, radical, carbene, etc.) become smaller as the stability of this species increases. Unfortunately, in many instances attenuation of substituent effects due to resonance saturation is accompanied by attenuation of substituent effects by steric inhibition of resonance, and it is difficult to judge the relative magnitudes of the two effects.[10] The present results show, however, that the resonance saturation effect can be large even when the substituents are widely separated in an aromatic system. Subsequent papers will show that much larger resonance saturation effects are present when the substituents are attached directly to the acidic site, as in GCH_2EWG,[13] rather than being separated from the acidic site by a benzene ring.

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(16) The five requirements of an indicator are given in ref 15. A standard acid is any compound whose p*K* is well established and whose anion is transparent at the wavelength used for measurement.

(17) The acidities in pure Me_2SO are on an absolute scale,[15] whereas those in Me_2SO-H_2O are relative to 9-phenylfluorene, p*K* = 18.49, as an arbitrary standard. The absolute p*K* of 9-phenylfluorene in Me_2SO is 17.9.[15] Using this as a standard, comparison shows that the p*K* of 2-cyanofluorene is 0.2 unit "too high" in Me_2SO-H_2O, whereas the p*K*'s of fluorene and 2-methoxyfluorene are 1.1 and 1.0 units "too low".

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(19) J. E. Bares, unpublished results.

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(21) The result for SO_2NEt_2 is in some doubt since no σ_m for this group appears to be available, and it was necessary to use σ_m for SO_2NH_2 in the plot. Judging from the CH_3SO_2 and $PhSO_2$ points, the (tetrahedral) sulfonyl groups appear to behave differently from the PhCO and CN groups in which the functions are planar. We will not comment on the surprising behavior of the CH_3SO function until this result can be checked with other sulfinyl groups and in other carbon acid systems.

(22) The *m*-CH_3O point deviates somewhat from the line for the meta-substituted acetophenones but the *m*-Me_2N and *m*-F points do not.[18] For the arylacetonitriles the *m*-CH_3O point deviates, but *m*-F does not.[19]

(23) The ρ for benzoic acids in Me_2SO is about 2.4.[24]

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