Table VIII. Experimental and Calculated Values of k_D at 80°

Radical	Solvent	$k_D = (k_t/a) \times 10^{-8}$, M^{-1} sec^{-1}	$k_D = (8RT/3000\,\eta) \times 10^{-8}$, M^{-1} sec^{-1}
$(C_6H_5)_2\dot{C}(OH)$	C_6H_6	120	240
(IIa)	$(CH_3)_2CHOH$	58	140
$(C_6H_5)(4\text{-}BrC_6H_4)\dot{C}(OH)$	C_6H_6	13	240
(IIc)	$(CH_3)_2CHOH$	11	140

ak_D where k_D is the bulk encounter constant. This leads to eq 21. Under our conditions ΔE_a was ap-

$$\Delta E_t = \Delta E_a + \Delta_D \tag{21}$$

proximately zero. However in principle ΔE_a should be negative provided a is less than one[17] leading to $\Delta E_t \leq \Delta E_D$. Estimates of ΔE_D are 2.9 kcal/mol in benzene and 6.4 kcal/mol in isopropyl alcohol.[19-21] These values are obtained by use of the modified Debye equation, $k_D = 8RT/3000\eta$, where η is the solvent viscosity.[21] Examination of the values of ΔE_t in Table IV shows that the inequality, $\Delta E_t < \Delta E_D$, is obeyed.

One can use the relation $k_t = ak_D$ to obtain values of k_D. These values are compared with those calculated from the modified Debye equation in Table VIII. The agreement is good for $(C_6H_5)_2\dot{C}(OH)$ but the effect of the bromo substituent is much larger than what is expected on the basis of simple diffusion theory.

Summary

In isopropyl alcohol (and probably acetonitrile) the ketyl radicals are hydrogen bonded to the solvent. This hydrogen bonding accounts for the shift of the equilibrium (Ia,b,c $\rightleftarrows$ 2IIa,b,c) to the radical side on going from benzene to isopropyl alcohol solution. The order of radical stability as determined by the equilibrium constant, K_1, also appears in the rate constants for cleavage of the benzpinacols and those for termination of the ketyl radicals. This order is reflected in the ratio of recombination to disproportionation, the most stable radical being the least likely to disproportionate. While the effect of remote substituent is much smaller than that of solvent, the ketyl radical is stabilized by replacement of a para hydrogen by bromine and destabilized by replacement with a methoxy group.

Acknowledgment. I would like to thank Mr. F. C. Ferris and T. Prater for their excellent technical assistance and Dr. L. R. Mahoney for many helpful discussions in the course of this work.

---

[17] This is so because as the temperature decreases, the solution viscosity increases and it is well known that at a fixed temperature a increases with increasing viscosity.[18]

[18] Kh. S. Bagdasar'yan, *Russ. J. Phys. Chem.*, 41, 897 (1967); R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, 87, 3766 (1965).

[19] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

[20] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 499.

[21] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 14, 48 (1960).

Transmission of Substituent Effects in Anthracene. Acid Dissociation Constants of 10-Substituted-9-anthroic Acids and Substituent Chemical Shifts of 10-Substituted-9-fluoroanthracenes. Evidence for the π Inductive Effect[1]

Gloria L. Anderson, Roger C. Parish, and Leon M. Stock*

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637.

Received January 30, 1971

Abstract: The acid dissociation constants for six 10-substituted-9-anthroic acids have been determined for 50% aqueous ethanol. The substituent chemical shifts for 14 10-substituted-9-fluoroanthracenes have been determined for six solvents. The results support the view that substituent effects propagated by π electron interactions, in particular π induction, are enhanced in the meso anthracenes relative to the para benzenes.

Four component interactions are often considered in discussions of the propagation and transmission of the electronic effects of substituent groups.[2,3] These interactions are designated as the polar (inductive) effect, the π inductive (inductoelectromeric or inductomesomeric) effect, the resonance (mesomeric) effect, and the direct conjugative (electromeric) effect.[2,3] It is now well recognized that progress in the definition of the factors governing the propagation of substituent effects and in the development of satisfactory empirical and theoretical methods for the treatment of substituent effects requires the investigation of carefully selected model compounds in which the capacity for the transmission of the electronic effects may be varied systematically. Thus, the study of substituent effects in rigid bicyclic molecules, initiated by Roberts and Moreland, has enabled the definition of the magnitude of monopolar and dipolar substituent effects for selected, fixed geometries and

---

[1] This research was supported by a grant (GP 13639) from the National Science Foundation.

[2] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 84, 3539 (1962).

[3] P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 6, 147 (1968).

also provided convincing evidence that an electric field model offers a realistic picture of the propagation mechanism.[4–8]

The many data for benzene derivatives and the factors important for the transmission of substituent effects in these molecules have been carefully analyzed.[2,3,9–11] The role of substituent effects in the chemistry of naphthalene and its derivatives[12–19] has also been discussed.[3,16,20] The important idea that one polar and one π electron parameter can be widely used to describe a substituent's behavior in different substrates and in different reactions has received attention.[2,3,9,21,22] More specifically, both Taft and Dewar and their associates have suggested that a four-parameter treatment involving one polar term and one π electron effect term has considerable merit for the correlation of the results for the benzenes and naphthalenes.

Several years ago Norman and Ralph pointed out that resonance theory suggested that π electron interactions between substituents in the meso positions of anthracene should be large by comparison with π electron interactions between the same groups in the para positions of benzene.[23] Their efforts, and those of others, to demonstrate the enhancement of substituent effects propagated *via* π electron interactions through studies of 10-substituted-9-anthroic acids and their derivatives were frustrated by the steric interactions between the peri hydrogen atoms and the carboxyl group.[23,24] Indeed, the data concerning the acidity of the 10-substituted-9-anthroic acids,[23] the reactivity of these acids with diphenyldiazomethane,[24] and the carbonyl stretching frequencies of the related methyl esters[23] are approximately correlated by $\sigma_{p\text{-R}}{}^{\circ}$.[23] These parameters defined by data for phenylacetic acid and its derivatives[9,25,26] are only applicable for molecules with negligible resonance interactions between the substituent and reaction site. Other probes such as the nitrile stretching frequency of 10-substituted-9-cyanoanthracenes or the 10-proton substituent chemical shifts[27] of 9-substituted-anthracenes[28] were inconclusive.[29]

We undertook a study of ^{19}F SCS of 10-substituted-9-fluoroanthracenes to test the predictions of theory, as discussed subsequently, that π electron interactions are enhanced for the meso anthracenes and to explore the proposal that polar and resonance interactions can be described by the same parameters in the benzene, naphthalene, and anthracene series. The undesirable steric influences of the peri hydrogen atoms on the test group are avoided in these molecules. Moreover, the steric effects of the peri hydrogen atoms may be used advantageously to inhibit the resonance of certain substituents, thereby enabling an estimate of π inductive contributions. Accordingly, 15 9-fluoroanthracenes were prepared[30] and their chemical shifts determined. To complete the work, we also examined the strength of seven 9-anthroic acids available from earlier studies.[6c]

Results

The substituent chemical shifts (SCS) for the 10-substituted-9-fluoroanthracenes were determined for six solvents. The results are summarized in Table I.

The thermodynamic acid dissociation constants for the 9-anthroic acids were determined by the differential potentiometric method.[31] Observations were made on several samples of each acid employing different batches of solvent and different electrodes. The dissociation constant of benzoic acid was frequently redetermined during the study to establish the reliability of the observations. The data are summarized in Table II.

The dissociation constants determined for the acids in 50% ethanol–water are linearly related to the available data for the acids in 80% 2-methoxyethanol–water[23] and to the rate data for the esterification of the acids by diphenyldiazomethane in several solvents.[24] We conclude that the equilibrium constants for the 9-anthroic acids in 50% ethanol–water illustrate an apparently general pattern of interactions between the substituent and the carboxyl group.

Discussion

Resonance and molecular orbital theory both predict that π electron interactions between substituents in the meso positions of anthracene are enhanced. Norman

---

(4) J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, **75**, 2167 (1953).

(5) H. Stetter and J. Mayer, *Chem. Ber.*, 95, 667 (1962).

(6) (a) H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86**, 5188 (1964); (b) R. Golden and L. M. Stock, *ibid.*, **88**, 5928 (1966); (c) F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967); (d) G. L. Anderson and L. M. Stock, *ibid.*, 90, 212 (1968); (e) G. L. Anderson and L. M. Stock, *ibid.*, **91**, 6804 (1969).

(7) (a) C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, **30**, 777 (1965); (b) C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, 90, 336 (1968).

(8) K. Bowden and D. C. Parkin, *Can. J. Chem.*, **47**, 177 (1969).

(9) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

(10) K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963).

(11) (a) J. D. S. Ritter and S. I. Miller, *J. Amer. Chem. Soc.*, **86**, 1507 (1964); (b) R. A. M. O'Ferrall and S. I. Miller, *ibid.*, **86**, 4016 (1964).

(12) C. C. Price, E. C. Mertz, and J. Wilson, *ibid.*, **76**, 5131 (1954).

(13) K. C. Schreiber and M. C. Kennedy, *ibid.*, **78**, 153 (1956).

(14) (a) A. Fischer, J. D. Murdoch, J. Packer, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.*, 4358 (1957); (b) A. Fischer, W. J. Galloway, and J. Vaughan, *ibid.*, 3591 (1964).

(15) (a) A. Bryson, *J. Amer. Chem. Soc.*, **82**, 4862 (1960); (b) A. Bryson and R. W. Matthews, *Aust. J. Chem.*, **16**, 401 (1963).

(16) (a) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3546 (1962); (b) W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967).

(17) (a) P. R. Wells and W. Adcock, *Aust. J. Chem.*, **18**, 1365 (1965); (b) P. R. Wells and W. Adcock, *ibid.*, 19, 221 (1966).

(18) (a) K. Bowden and D. C. Parkin, *Chem. Commun.*, 75 (1968); (b) K. Bowden and D. C. Parkin, *Can. J. Chem.*, **47**, 186 (1969).

(19) M. Hojo, K. Katsurakawa, and Z. Yoshida, *Tetrahedron Lett.*, 1497 (1968).

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

(21) C. G. Swain and E. C. Lupton, *ibid.*, **90**, 4328 (1968).

(22) C. D. Ritchie and W. F. Sager, *Progr. Org. Chem.*, **2**, 323 (1964).

(23) R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 2221 (1961).

(24) (a) K. Bowden, N. B. Chapman, and J. Shorter, *Can. J. Chem.*, **42**, 1979 (1964); (b) K. Bowden and D. C. Parkin, *ibid.*, **47**, 185 (1969).

(25) R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959).

(26) R. O. C. Norman, G. K. Radda, D. A. Brimacombe, P. D. Ralph, and E. M. Smith, *J. Chem. Soc.*, 3247 (1961).

(27) The ^{19}F substituent chemical shift (SCS) is defined as the difference between the resonance frequency of a ^{19}F nucleus in a substituted molecule and that of the same nucleus in a molecule in which a hydrogen atom replaces the substituent. Positive values mean that the resonance signal for the substituent compound is upfield of the signal for the hydrogen bearing reference compound.

(28) K. Bowden, J. G. Irving, and M. J. Price, *Can. J. Chem.*, **46**, 3903 (1968).

(29) The CN stretching frequencies for mesitonitrile and 9-cyanoanthracene are sensibly equal (to within 1 cm^{-1}), but about 12 cm^{-1} lower than that of benzonitrile. The introduction of a bromine atom causes a 2 cm^{-1} shift to lower frequency for 4-bromobenzonitrile and a 1 cm^{-1} shift to lower frequency for 10-bromo-9-cyanoanthracene.[23] The proton SCS are quite small and, apparently, influenced by the diamagnetic anisotropy of the remote group.[28]

(30) G. L. Anderson and L. M. Stock, *J. Org. Chem.*, **36**, 1140 (1971).

(31) A. L. Bacarrela, E. Grunwald, H. P. Marshall, and E. L. Purlee, *ibid.*, **20**, 747 (1955).

Table I. ^{19}F Substituent Chemical Shifts for 10-Substituted-9-fluoroanthracenes[c]

10-Substituent	$SCS_{9,10}^{A}$, ppm CCl$_4$	1,4-Dioxane	TFP[a]	DMF	Benzene	MeOH
H	0.00	0.00	0.00	0.00	0.00	0.00
O^- [b]	Ins	+31.82	Ins	+31.00	Ins	+22.42
OCH_3	+4.03	+3.91	+3.77	+3.60	+3.86	+3.54
$OCOCH_3$	+1.17	+0.90	−0.52	+0.79	+0.92	+0.53
NH_2	+12.25	+14.68	Ins	+17.12	+12.84	+14.19
$NHCOCH_3$	Ins	Ins	Ins	+0.08	Ins	Ins
CH_3	+2.44	+2.60	Ins	Und	+2.50	+2.44
F	+4.39	+3.56	Ins	+3.26	+4.13	+3.56
Cl	−0.13	−0.57	Ins	−1.44	−0.30	−1.14
Br	−0.84	−1.31	Ins	−2.15	−0.90	−2.02
$COOCH_3$	−5.02	−4.86	−6.89	−5.69	−5.30	−5.52
COOH	Ins	Ins	Ins	−4.43	Ins	−4.90
CN	−11.15	−11.81	−14.55	−13.51	−11.47	−13.14
NO_2	−8.35	−9.13	Ins	−10.72	−8.84	Ins
$NC_5H_5^+$	Ins	Ins	Ins	−9.33	Ins	−10.74

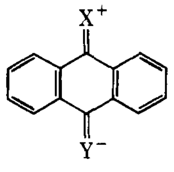
[a] Tetrafluoropropanol. [b] Solvent contained a small amount of methanolic sodium hydroxide. [c] Ins = insoluble. Und = undetermined.

Table II. Thermodynamic Dissociation Constants for 10-Substituted-9-anthroic Acids in 50 W % Ethanol–Water at 25°

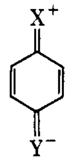
Substituent	pK_A
H	4.59 ± 0.03[a]
CH_3	4.70 ± 0.00
OCH_3	4.62 ± 0.03
F	4.42 ± 0.02
Cl	4.11 ± 0.03
Br	4.09 ± 0.02
NO_2	3.59 ± 0.05

[a] Mean experimental deviation.

and Ralph note that the contribution of structure A to the description of the anthracene is greater than the contribution of structure B to the related benzene.[23]



A



B

Molecular orbital theory measures the expected enhancement by the atom–atom polarizability which is −0.22 for the meso positions of anthracene compared to −0.10 for the para positions of benzene or, in another way, by the charge, q_{ij} at C_j resulting from the introduction of a CH_2^- group at C_i, which is 0.29 for the anthracene compared to 0.14 for the related benzene.[2] Previous experimental work, as already discussed, has not provided definitive evidence concerning the character of the conjugative interactions between meso substituents.[23,24,28,29] The steric interactions that obviate a confident interpretation of many data are absent for the fluorine atom of 9-fluoroanthracene and for ten substituents with spherical or cylindrical symmetry. Consequently, the ^{19}F chemical shift approach was adopted for this study. In the subsequent discussion, we present the evidence that substituent effects propagated by π electron interactions largely dictate the SCS for the aryl fluorides, that substituent effects propagated by π electron interactions are enhanced in the meso anthracenes, and that the π inductive effect plays a major role in the anthracene series.

For convenience, the chemical shifts for several aryl fluorides and Diels–Alder adducts of 9-fluoroanthracene are summarized in Table III.

Table III. ^{19}F SCS for Some 10-Substituted-9-fluoroanthracenes, 4-Substituted-fluorobenzenes, 4-Substituted-3,5-dimethylfluorobenzenes, and 4-Substituted-1-fluoronaphthalenes in DMF

Substituent	9,10-A[a]	1,4-B[b]	1,4-DMB[c]	1,4-N[d]	Adduct[e]
Sterically Unencumbered Substituents					
CN	−13.51	−9.80	−9.67	−11.34	−0.88[f]
O^-	+31.00				
O^-	22.42[h]	19.50[h]			
Sterically Inhibited Substituents					
NO_2	−10.72	−10.30	−5.51	−12.77	−1.83[f]
COOH	−4.43	−6.05	−1.73	−8.19	
$COOCH_3$	−5.69	−6.70	−2.80	−8.89	−1.01[g]

[a] This study. [b] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963). [c] M. J. S. Dewar and Y. Takeuchi, *ibid.*, **89**, 390 (1967). [d] Reference 16b. [e] Reference 6e. [f] Dimethyl acetylenedicarboxylate adduct. [g] Maleic anhydride adduct. [h] In methanol.

The ^{19}F SCS for the aromatic compounds are much greater in magnitude than those for the anthracene adducts.[6e] The chemical shifts for 10-cyano-9-fluoroanthracene and its adducts are typical. The SCS is −13.5 ppm for the aromatic compound compared to −0.4 ppm for the maleic anhydride adduct or to −0.9 ppm for the dimethyl acetylenedicarboxylate adduct. The SCS for 4-cyanofluorobenzene and 4-cyano-1-fluoronaphthalene are similarly much greater than the SCS for the adducts. The results for these compounds are in accord with the accepted view that substituent effects propagated by π electron interactions principally determine the SCS for conjugated substituents.[6e] The SCS of the adduct is, approximately, equal to the polar contribution[32] for the substituent in the aromatic compounds with a 1,4-substitution pattern.

The results for the cyano and oxide groups offer evidence for the enhancement of π electron interactions between meso substituents. The polar, π inductive, and resonance contributions of the cylindrically symmetrical cyano group each deshield the fluorine nucleus. The values of $SCS_{1,4}^{B}$ and $SCS_{1,4}^{3,5\text{-DMB}}$ differ by only 0.1 ppm, indicating that the behavior of the cyano

---

[32] In this instance, several interactions, *i.e.*, field effects, van der Waals contributions, etc.,[6e] constitute the polar contribution.

group is unperturbed in a sterically crowded environment. The SCS for 10-cyano-9-fluoroanthracene is 3.7 ppm smaller than that for 4-cyanofluorobenzene. For the aryl oxides, the polar and π inductive contributions are opposed by the resonance contribution. The finding that the SCS for the anthracene, 22.4 ppm, is larger than the SCS for the benzene, 19.5 ppm, suggests that resonance interactions are enhanced in the anthracene. These data do not, of course, exclude the simultaneous enhancement of π inductive interactions.

Several investigators have examined ^{19}F chemical shifts to assay the magnitude of the π inductive effect. The sensitivity of the magnetic resonance method to changes in the distribution of π electron density renders it particularly suitable for the detection of the polarization of the π electron system arising from the substituent-induced change in electronegativity of the substituted carbon atom.[2,3,33] Dewar and Takeuchi attempted to separate the polar, π inductive, and direct resonance contributions by the application of a modified FM method to the data for 4-substituted-1-fluorobenzenes and 4-substituted-3,5-dimethyl-1-fluorobenzenes.[34,35] They concluded that the π inductive contribution was not large in the para benzene series with $SCS_{1,4}{}^{B}$ for the nitro group partitioned into polar, -4.4, direct resonance, -6.0, and π induction, -1.2 ppm, respectively. The polar contribution estimated for this molecule on the basis of the data for the adducts of 10-nitro-9-fluoroanthracene is -1.8 ppm. Thus, the FM method may underestimate the π inductive effect in the fluorobenzenes. Using somewhat different theoretical and statistical methods, Wells, *et al.*, have analyzed the data for the fluorine chemical shifts and for selected reactions of benzene and naphthalene derivatives.[3] They also conclude that, barring an error in the theoretical calculations, the π inductive effect is a secondary factor.

The contribution to the chemical shift from π induction is, very nearly, isolated from other interactions in appropriately constituted meso anthracenes. The dipolar character and geometry of the nitro group make it an excellent substituent for an experimental estimate of π induction. The large dipolar ($\sigma_I = 0.63$) and modest resonance ($\sigma_R{}^\circ = 0.19$) components are well documented.[3] The crystal structure,[36] infrared spectrum, and Kerr constants are consistent with a structure for 9-nitroanthracene in which the nitro group is in a plane between 65 and 115° from the plane of the carbon atoms of anthracene.[37] A deviation of comparable magnitude for 10-nitro-9-fluoroanthracene would decrease the resonance contribution to a negligible value, while not altering the contribution from π induction. Less structural information is available for 9-anthroic acid and its derivatives. However, the homomorphic relationship between the nitro and carboxylate groups suggests that resonance contributions should be negligible for this group also. The ^{19}F chemical shifts for selected nitro and carboxyl compounds are summarized in Table III.

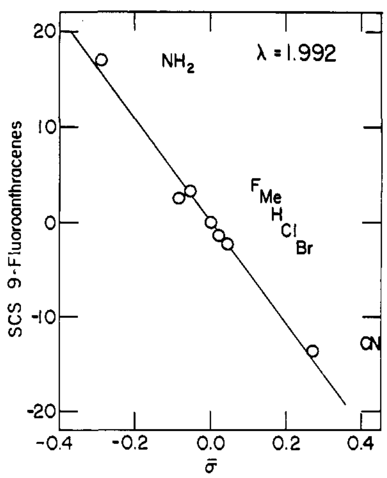


Figure 1. The relationship between the SCS for the 9-fluoroanthracenes and $\bar{\sigma}$ based on eq 1. The parameter $\bar{\sigma}$ is given by $(\sigma_I + \lambda\sigma_R{}^\circ)(1 + \lambda)^{-1}$ with $\lambda = \rho_R/\rho_I = 1.992$.

The SCS for the benzene derivatives are significantly smaller than for the corresponding 3,5-dimethylbenzenes. The decreased substituent effect on the chemical shift for the dimethylbenzenes is, as discussed by Dewar and Takeuchi,[34,35] reasonably attributed to the steric inhibition of resonance. For 10-nitro- and 10-carbomethoxy-9-fluoroanthracene, the SCS are each strikingly smaller than the values measured for the related 3,5-dimethylfluorobenzenes. If, as the results for the bridged anthracenes strongly infer, the polar contribution is small, about -1.8 ppm for the nitro derivative and -1.0 ppm for the ester, then the larger downfield shifts for the anthracenes, in the presumed absence of substantive resonance interactions, strongly suggest that π induction is a major factor.[38] The same conclusion is reached when the data for the anthracenes are analyzed by the FM method used by Dewar and Takeuchi.[34,35]

To test this proposal in another way, we employed the four-parameter equation used by Wells, *et al.*, for the study of substituent effects in the benzene and naphthalene series.[3] The data for six substituents

$$\mathrm{SCS} = \rho_I\sigma_I + \rho_R\sigma_R{}^\circ \qquad (1)$$

free of severe steric effects (NH_2, CH_3, F, Cl, Br, CN) were used in this analysis. The results are illustrated in Figure 1 and the ρ values for the related 1,4-benzenes and 1,4-naphthalenes are presented in Table IV.[39]

Table IV. Reaction Constants for 1,4-Benzene, 1,4-Naphthalene, and 9,10-Anthracene Series

Data series	ρ_I	ρ_R
1,4-Benzene[a]	-7.80	-32.1
1,4-Naphthalene[a]	-12.1	-32.1
9,10-Anthracene[b]	-18.2	-36.1

[a] Reference 3. [b] Reference 39.

---

[33] (a) H. H. Jaffé, *J. Amer. Chem. Soc.*, 77, 274 (1955); (b) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," Wiley, London, 1965, pp 307–310.

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

[35] Y. Takeuchi, *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo*, 17, 53 (1967).

[36] J. Trotter, *Acta Crystallogr.*, 12, 237 (1959).

[37] R. J. W. Le Fevre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. B*, 775 (1968).

[38] Other experiments directed toward the demonstration of π induction are underway.

[39] We are indebted to Professor Taft for the computation. The precision obtained in the correlation is improved when σ_R (benzoic acid) is used rather than $\sigma_R{}^\circ$.

Table V. Calculated σ Constants, Acid Dissociation Constants, and Substituent Chemical Shifts for Halogen Substituents

	$\sigma_{ij}{}^{a}$				Log (K/K_H)			SCS		
Substituent	$\sigma_{4.1}{}^{B}$	$\sigma_{4.1}{}^{N}$	$\sigma_{10.9}{}^{A}$	0.5F	1,4-B[b]	1,4-N[c]	9,10-A[d]	1,4-B[e]	1,4-N[c]	9,10-A[d]
F	0.06	−0.04	−0.18	0.29		0.08	0.17	6.20	3.82[f]	3.26
Cl	0.23	0.19	0.13	0.32	0.40	0.40	0.48	2.48	0.55[f]	−1.44
Br	0.23	0.19	0.12	0.34	0.40	0.46	0.50	2.00	−0.62	−2.15

[a] $\sigma_{4.1}{}^{B} = \sigma$; $\sigma_{4.1}{}^{N} = 0.5F + 0.2M$; $\sigma_{10.9}{}^{A} = 0.5F + 0.29M$. [b] Reference 9. [c] Reference 16b. [d] This study. [e] Footnote *b*, Table III. [f] Unpublished results.

The substituent chemical shifts for the groups with small steric requirements are correlated with good precision by eq 1. For the anthracene series, ρ_I is -18.2, more than twice ρ_I for the para benzenes. Several lines of evidence indicate that the trend in ρ_I for these aryl fluorides should be identified with the trend in π induction. First, the polar contribution[32] should be both small and invariant among the aromatic compounds. Second, π induction originates in the polar or dipolar substituent-induced change in electronegativity of the substituted carbon atom. The magnitude of the π inductive contribution is, therefore, related to σ_I rather than to $\sigma_R{}^{\circ}$. The SCS for the nitro- and carbomethoxyanthracenes are predicted to be -11.6 and -5.6 ppm, respectively, by the $\rho_I\sigma_I$ term of eq 1 in reasonable agreement with experiment. Third, the ρ_I parameters for the three series parallel the atom–atom polarizabilities. The chemical shifts and dissociation constants for the haloanthracene derivatives are also in accord with the view that π induction is important.

The results for the three halogen substituents present an intriguing pattern that was recognized by Norman and Ralph.[23] They pointed out that the 10-halo-9-anthroic acids were distinctly stronger acids than expected on the basis of enhanced resonance contributions.[40,41] This view is well illustrated by the available experimental data for the 9-anthroic acids and the 9-fluoroanthracenes and the σ constants estimated on the basis of the FM method, Table V.

Halogen substituents increase the strength of the 9-anthroic acids to a greater extent than expected on the basis of the resonance analysis or on the basis of the molecular orbital oriented FM analysis. Indeed, the data suggest that the 4-halo-1-naphthoic acids are also stronger acids than the FM approach predicts. These results are closely paralleled by the magnetic resonance data. The fluorine nucleus for the 4-halofluorobenzenes is more shielded than the fluorine nucleus of the 10-halo-9-fluoroanthracenes with the 4-halo-1-fluoronaphthalenes, apparently, in an intermediate position. Any pronounced enhancement of resonance interactions would, of course, lead to a reduction in acidity and an increase in shielding in magnetic resonance. On the other hand, an overcompensating enhancement of π induction would account for the observations. The results for the halogens, therefore, confirm the ideas developed in the discussion of the other substituents.

Conclusion

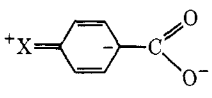
The greater shielding in the anion of 10-hydroxy-9-fluoroanthracene compared to the corresponding benzene, the small increase in ρ_R, and the chemical shifts for the halogen substituents suggest that direct resonance interactions are larger, but only moderately so, in the anthracenes. In addition, our analysis has led to the conclusion that π induction is important for the meso anthracenes. Several points deserve attention before this view may be accepted with complete confidence. First, Dewar and Squires[42] suggested that dipolar substituent effect contributions to the chemical shift should be larger for the more polarizable aryl fluorides than for alkyl fluorides. Arguments in favor of this view have recently been advanced by Adcock and his associates.[43] However, as already discussed, the trends observed in the magnetic resonance data are also discernible in the results for the carboxylic acids where polarizability is presumably not a factor. Further study will be necessary to resolve this point. Second, Dewar, *et al.*,[44] have recently advanced a new semiempirical model, the FMMF method, for the estimation of substituent constants. This model does not, except in an incidental way, include the concept of π induction. Use of this approach for the fluoroanthracenes yields a reasonable correlation of the data for most substituents. However, the datum for the hydrogen derivative deviates from the least-squares line by about 1 ppm. Dewar, *et al.*,[44] suggest that this discrepancy is the consequence of a substituent-induced structural deformation that alters the environment of the fluorine atom.[6d,e,42,45] Physical evidence to support this proposal has not yet been obtained. Finally, the magnitude of all π electron interactions between substituents should, according to simple π electron theory, be larger in the 9,10-anthracenes than in other substituted benzenes and naphthalenes. Consequently, a favorable situation for the detection of π induction has been examined in this study. We presume that π induction plays a proportionally important role in other unsaturated molecules and experiments designed to test the view are in progress.

Experimental Section

The chemical shift measurements were accomplished by the same procedures used in the previous investigation of the bridged anthracenes.[6e]

---

(40) Structure C is the important resonance form for the benzoate.



C

The contribution of this structure should be greater in the anthroate.

(41) K. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 285.

(42) M. J. S. Dewar and T. Squires, *J. Amer. Chem. Soc.*, **90**, 200 (1968).

(43) W. Adcock, P. D. Bettess, and S. Q. A. Rizvi, *Aust. J. Chem.*, **23**, 1921 (1970).

(44) M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, 93, 4187 (1971).

(45) J. B. Dence and J. D. Roberts, *ibid.*, 91, 1542 (1969).