ment with either experimental results or the predictions of more sophisticated models where available. The one system where the PLM prediction is incorrect is the electrocyclic interconversion of 1,3,5-hexatriene and 1,3-cyclohexadiene, where the least-motion pathway is proscribed by orbital symmetry requirements.[20]

In considering the relationship of the PLM approach to that based on the conservation of orbital symmetry[5] (COS) four particular types of situation can be visualized. In the first where, because of the lack of suitable elements of symmetry, the COS approach cannot be used the PLM approach seems to offer a useful alternative. The second situation is where both approaches are applicable and are in agreement. The third type of situation is where COS does not distinguish between two symmetry-allowed processes, but the PLM approach does, *e.g.*, cyclopropyl X solvolyses. In the fourth type of situation there is disagreement between the predictions of the two approaches, but the requirements of COS outweigh those of PLM.[20]

A useful and interesting side product of PLM calculations is the insight they give into the atomic motions that are occurring during a reaction. From a consideration of the relative geometries of the reactant and product in the configuration where the value $E_{\min}$ is generated,[1] it is apparent that many atoms probably undergo motion during reaction. In a migration, for instance, suitable motions by the rest of the molecular framework may help reduce the amount of motion undergone by the migrating moiety. For the case of an anti elimination from an olefin to produce an acetylene,[1] reactant and product geometries are related in such a way as to suggest that the acetylene will be produced with some rotational energy. For the corresponding syn elimination it appears that the acetylene produced will have some translational energy.

The results presented here also emphasize the degree of nonplanarity of the transition states involved in the electrocyclic transformations of butadiene and hexatriene, and in the Cope rearrangement.[44]

Acknowledgments. The authors wish to thank Professors Alex Nickon and Roald Hoffmann for discussions of certain aspects of this work. The study was supported by grants from the National Research Council of Canada. Acknowledgments are also made to the Institute of Computer Science of the University of Toronto and the Sir George Williams University Computer Center for the use of computer services.

(39) J. Hine, *J. Org. Chem.*, 31, 1236 (1966).

(40) (a) A. Sherman and H. Eyring, *J. Amer. Chem. Soc.*, 54, 2661 (1932); (b) G. E. Kimball and H. Eyring, *ibid.*, 54, 3876 (1932).

(41) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp 104, 144.

(42) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(43) M. J. S. Dewar, *Discuss. Faraday Soc.*, 2, 261 (1947).

(44) Some of the systems considered in this and previous papers[1,3] involve reaction proceeding from different starting conformers but no account has been taken of differences in conformer energies.[45] As long as these differences are smaller than the difference in energy of the associated transition states the predictions of the PLM approach may still be valid. If, however, they are larger the predictions would not be invalid. It is not readily apparent how the approach might be modified to take account of these differences.

(45) This point was raised by a referee.

Dissociation Constants of 8-Substituted 9,10-Ethanoanthracene-1-carboxylic Acids and Related Compounds. Evidence for the Field Model for the Polar Effect[1]

Ronald Golden[2] and Leon M. Stock*

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. Received August 28, 1971

Abstract: Several 8-substituted 9,10-ethanoanthracene-1-, 8-substituted 9,10-dihydroanthracene-1-, and 8-substituted anthracene-1-carboxylic acids have been prepared. The dissociation constants for the acids have been measured in 50% aqueous ethanol. Many traditionally acid-strengthening dipolar substituents, for example, the fluoro, chloro, and cyano groups, exhibit the opposite influence in the bridged anthracenes. Empirical tests of the results reveal that steric and hydrogen bonding interactions play no important role in the determination of acid strength. The reversed substituent effects therefore indicate that dipolar substituent effects have an angular dependence in accord with an electrostatic field model for the polar effect.

Investigations designed to assess the relative merits of the through-bond induction model and the electrostatic field model for the polar effect[3] suggest that the field model offers a better physical description of the observed influence of monopolar and dipolar substituents.[4] This conclusion is based, for the most part, upon differences in the magnitude of the substituent effects predicted by the two limiting models. For example, the reaction constant for the dissociation of 4-substituted bicyclo[2.2.1]heptane-1-carboxylic acids is 1.18-fold greater than the reaction constant for the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids.[5]

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(1) Chemistry of the Bicyclo[2.2.2]octanes. XIII. This research was supported by a grant from the National Science Foundation.

(2) National Science Foundation Fellow at the University of Chicago, 1964–1968.

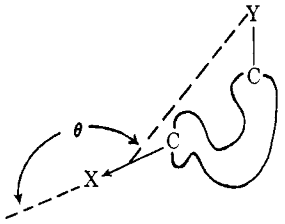
(3) The term polar effect is used to characterize the observed influence of unconjugated, sterically remote substituents on reaction processes. This designation permits the use of the terms inductive effect and field effect for the description of the transmission mechanism.

(4) L. M. Stock, *J. Chem. Educ.*, in press.

(5) C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, 90, 336 (1968).

This result is in good quantitative agreement with the predictions of an electrostatic model (1.2) but in less satisfactory agreement with the predictions of an induction model (at least 1.4).[5] Other studies have established that the polar contribution does not depend on the state of hybridization of the carbon–carbon bonds between the substituent and the reaction site,[6–8] and that the number of paths between the substituent and the reaction side is not an important factor in the propagation mechanism.[6,9] These findings and others[4] point to the greater merit of an electrostatic model.

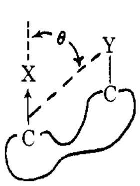
The possibility, of course, exists that a new version of the inductive model might accommodate the observed differences in magnitude. We, therefore, performed an experiment based on the angular dependence implicit for dipolar substituents in the electrostatic field model and for which the results are consistent with only one mechanism and for which the two theories clearly predict substituent effects of different sign as well as different magnitude. Thus, electrostatic analysis indicates that rotation of a bond dipole must reverse the sign of the substituent effect. In molecules with the proper geometry, for example, II, acid-strengthening, electron-withdrawing substituents should, according to this theory, oppose the ionization of an acidic hydrogen atom. Such substituents would then be acid weakening, in direct opposition to the prediction of even a sophisticated inductive model. For any inductive model, the primary consideration is the partial charge induced at the substituted carbon atom. The sign and magnitude of this charge and the anticipated substituent effect do not depend on the geometric relationship between the substituent and the reaction center.



I

$\cos\theta < 0$

$\log(K/K_{\mathrm{H}}) > 0$

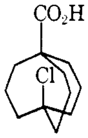


II

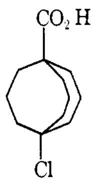
$\cos\theta > 0$

$\log(K/K_{\mathrm{H}}) < 0$

This aspect of the problem has been considered previously. Roberts and Carboni suggested that the acidity of III and IV might be compared and suggested several other U-shaped molecules in which a reversed net polar substituent effect might be observed.[10a] The ortho-substituted phenylpropiolic acids are abnormally weak relative to the meta and para derivatives.[10] The unusually small acid strengthening influences of *o*-chloro and *o*-nitro groups were attributed to opposing inductive and field contributions.[10a] Dewar and Grisdale observed that polar effects in 7-substituted 1-naphthoic acids were also unusually small.[11] Wells and Adcock pointed out that the decreased acidity of these molecules and of the 8-substituted 2-naphthoic acids was most compatible with the view that the dipolar substituent effect had an angular dependence.[12] More recently, the 8-substituted 1-naphthoic acids have been studied.[13] The results for these compounds also hint that polar effects are modified when the substituent and the reaction site have U-shaped geometry.

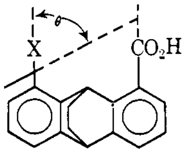


III



IV

Other factors, such as π-electron interactions or bulk steric effects, complicate the interpretation of the data for the naphthalene derivatives. We chose a different model compound, the 8-substituted 9,10-ethanoanthracene-1-carboxylic acids, in which these factors do not play a role, but for which electrostatic considerations predict a reversal of the dipolar substituent effect. This structure has the desirable features necessary to isolate the polar effect. The π system is interrupted by the ethano bridge, preventing classical resonance and π inductive effects. Resonance interactions between the two benzene nuclei are a minor factor in the chemistry of the bridged anthracenes.[14] The molecular geometry is fixed. The C_1–C_8 distance is about 4.5 Å, sufficient to make bonding and nonbonding interactions between groups in these positions unimportant.



V

Preliminary work revealed that electron-withdrawing substituents do exert an acid-weakening influence in the 8-substituted 9,10-ethanoanthracene-1-carboxylic acids.[15] We examined other compounds of this structure to verify the original observation and extended the investigation to the 8-substituted 1-anthroic acids and to the 8-substituted 9,10-dihydroanthracene-1-carboxylic acids.

Results

Synthesis. The desired carboxylic acids were synthesized from one of three commercially available anthraquinones. The sequence for the conversion of 1,8-dichloroanthraquinone to 8-chloro-1-anthroic acid and its 9,10-dihydro and 9,10-ethano derivatives is

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[6] F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967).

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

[8] C. J. Mayers and L. M. Stock, unpublished results.

[9] Recent work has revealed that dipolar substituent effects in the 4-substituted cubane-1-carboxylic acids and in the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids are very similar. Unpublished observations of T. W. Cole, Jr., E. Liu, and L. M. Stock.

[10] (a) J. D. Roberts and R. A. Carboni, *J. Amer. Chem. Soc.*, **77**, 5554 (1955); (b) M. S. Newman and S. H. Merrill, *ibid.*, 77, 5552 (1955).

[11] M. J. S. Dewar and P. J. Grisdale, *ibid.*, 84, 3539, 3548 (1962).

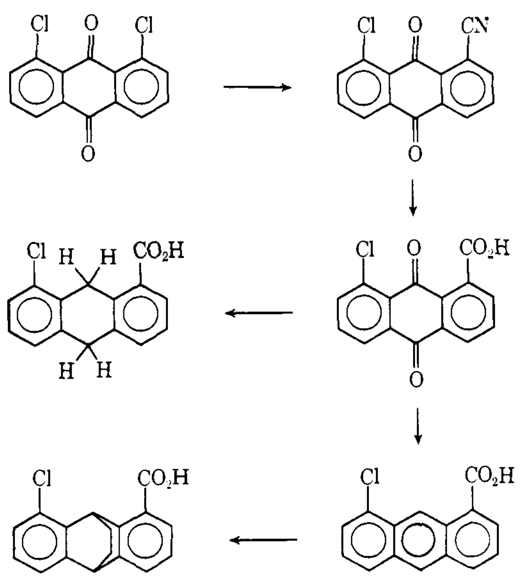
[12] P. R. Wells and W. Adcock, *Aust. J. Chem.*, **18**, 1365 (1965).

[13] (a) M. Hojo, K. Katsurakawa, and Z. Yoshida, *Tetrahedron Lett.*, 1497 (1968); (b) K. Bowden and D. C. Parkin, *J. Chem. Soc. D*, 75 (1968); *Can. J. Chem.*, 47, 185 (1969); (c) M. J. S. Dewar, *J. Chem. Soc. D*, 547 (1968).

[14] (a) C. F. Wilcox and A. C. Craig, *J. Org. Chem.*, **26**, 2491 (1961); (b) L. M. Stock and J. Suzuki, *J. Amer. Chem. Soc.*, **87**, 3909 (1965); (c) see, however, S. Clementi, V. Mancini, and G. Marino, *J. Chem. Soc. D*, 1457 (1970).

[15] R. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, **88**, 5928 (1966).

Chart I



typical (Chart I). Similar methods were employed for the preparation of many other compounds as described in the Experimental Section.

Few difficulties were encountered. The reduction of 8-hydroxyanthraquinone-1-carboxylic acid to the related hydroxyanthroic acid was unsuccessful. Similar problems have been noted for other hydroxyanthraquinones.[16] The desired 8-hydroxy-9,10-ethanoanthracene-1-carboxylic acid was prepared by the hydriodic acid cleavage of 8-methoxy-9,10-ethanoanthracene-1-carboxylic acid. This compound was prepared without difficulty by the reduction of 8-methoxyanthraquinone-1-carboxylic acid. Another problem was encountered in the attempt to substitute the chlorine atoms of 1,8-dichloroanthraquinone and 8-chloroanthraquinone-1-carboxylic acid with anhydrous potassium fluoride in aprotic solvents at 150–200°. The reactions produced intractable material and isolable residues showed little, if any, incorporation of fluorine by ^{19}F nmr. 8-Fluoro-9,10-ethanoanthracene-1-carboxylic acid was derived from 1-amino-8-chloroanthraquinone. This compound was converted to 8-fluoro-1-chloroanthraquinone, which was reduced to 8-fluoro-1-chloroanthracene prior to the addition of ethylene, and the subsequent carbonation. The product contained a small amount of unsubstituted acid, but this contaminant could be removed by recrystallization.

Dissociation Constants. The thermodynamic dissociation constants of the monobasic acids were determined by both the differential potentiometric method of Grunwald and by potentiometric titration.[17,18] Observations were made using independently prepared solutions of the acids and reagents to randomize experimental error. The dissociation constant for benzoic acid was determined frequently throughout the measurements. The average pK_A values for benzoic acid were 5.74 ± 0.01 and 5.75 ± 0.01 for the differential potentiometric and potentiometric titration methods, respectively, in good agreement with previous results.[6,19]

Table I. Thermodynamic Dissociation Constants for Carboxylic Acids in 50% (Weight) Aqueous Ethanol at 24.95°

		pK_A	
8 Substituent	Grunwald method	Speakman method	Av
8-Substituted 9,10-Ethanoanthracene-1-carboxylic Acids			
H	6.04 ± 0.03 (3)	5.96 ± 0.01 (5)	5.99 ± 0.04 (8)
F		6.01 ± 0.01 (2)	6.01 ± 0.01 (2)
Cl	6.25 ± 0.02 (4)	6.23 ± 0.03 (3)	6.24 ± 0.05 (7)
CN	6.07 ± 0.02 (3)	6.02 ± 0.01 (1)	6.05 ± 0.02 (4)
OCH_3	6.17 ± 0.01 (3)	6.08 ± 0.01 (1)	6.15 ± 0.04 (4)
OH	5.99 ± 0.02 (3)	5.95 ± 0.02 (1)	5.98 ± 0.02 (4)
CH_3		6.07 ± 0.02 (3)	6.07 ± 0.02 (3)
CO_2CH_3	6.20 ± 0.01 (4)	6.06 ± 0.01 (2)	6.16 ± 0.06 (6)
CO_2H		5.67 ± 0.03 (4)	
		5.97 ± 0.03^a	5.97 ± 0.03 (4)^a
CO_2^-		7.19 ± 0.02 (4)	
		6.89 ± 0.02^a	6.89 ± 0.02 (4)^a
8-Substituted 9,10-Dihydroanthracene-1-carboxylic Acids			
H	5.54 ± 0.02 (1)	5.57 ± 0.03 (2)	5.56 ± 0.02 (4)
Cl	5.80 ± 0.03 (1)	5.67 ± 0.01 (2)	5.71 ± 0.06 (3)
CO_2H		5.32 ± 0.01 (3)	
		5.62 ± 0.01^a	5.62 ± 0.01 (3)^a
CO_2^-		6.61 ± 0.05 (3)	
		6.31 ± 0.05^a	6.31 ± 0.05 (3)^a
8-Substituted 1-Anthroic Acids			
H	5.61 ± 0.01 (3)		5.61 ± 0.01 (3)
Cl	5.57 ± 0.01 (3)		5.57 ± 0.01 (3)
CN		5.49 ± 0.02 (2)	5.49 ± 0.02 (2)
OCH_3		5.63 ± 0.01 (1)	5.63 ± 0.01 (1)
CO_2H		5.26 ± 0.01 (2)	
		5.56 ± 0.01^a	5.56 ± 0.01 (2)^a
CO_2^-		6.55 ± 0.02 (2)	
		6.25 ± 0.02^a	6.25 ± 0.02 (2)^a

[a] Statistically corrected.

The dissociation constants for the dibasic acids were determined by the method of Speakman.[18] The results are summarized in Table I.

There are modest differences in the results obtained by the independent methods. It is very probable that thermodynamic values measured by the Grunwald method are more accurate than those measured by the Speakman method. The discrepancies may be attributed to deviations of ionic and molecular activity coefficients from the behavior predicted from the Debye–Hückel limiting theory at the higher ionic concentration used in the potentiometric titration method. At the equivalence point, the ion concentration is between 10- and 100-fold greater in the titration method. Dissociation constants measured by the Grunwald method showed no dependence on concentration. In contrast, the pK_A obtained for 8-chloro-9,10-ethanoanthracene-1-carboxylic acid by potentiometric titration depends on the concentration of the acid (pK_A observed, initial concentration: 6.22, $4.4 \times 10^{-4}M$; 6.13, $7.7 \times 10^{-4} M$; 6.08, $16.2 \times 10^{-4}M$). When the ionic strengths of the solutions employed for the potentiometric titration and for the differential method are small and equal, then both methods yield very similar results. Although the two methods gave slightly different absolute thermodynamic acidities, the values of log (K/K_H) remained constant within the experimental precision. The importance of relative free-energy changes for the interpretation of the data makes these quantities, rather than the absolute acidities, of primary interest.

Discussion

The traditional acid-strengthening, electron-withdrawing dipolar substituents are acid weakening in

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(16) J. Houben, "Das Anthracen und die Anthrachinone," G. Theime Verlag, Leipzig, 1929.

(17) A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(18) J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

(19) E. Grunwald and B. J. Berkowitz, *J. Amer. Chem. Soc.*, **73**, 4939 (1955).

both the ethanoanthracenes and the dihydroanthracenes. This finding offers cogent evidence for the angular dependence of the polar effect. The reversal is greatest for the chlorine substituent but clearly beyond the limit of experimental uncertainty for the other electronically similar substituents (Table II).

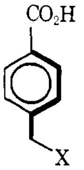
Table II. Log (K/K_H) for Bridged Anthroic Acids and Related Acids in 50% Aqueous Ethanol at 24.95°

	Log (K/K_H)		
8 Substituent	Ethanoanthracene acid[a]	Dihydroanthracene acid[a]	α-Substituted *p*-toluic acid[b]
H	0.00	0.00	0.00
F	−0.05		
Cl	−0.24 ± 0.03	−0.15 ± 0.05	0.50
CN	−0.04 ± 0.02		0.42
OCH_3	−0.12 ± 0.01		0.28
OH	+0.03 ± 0.02		
CH_3	−0.10		
CO_2CH_3	−0.13 ± 0.03		
CO_2H	+0.03 ± 0.04	−0.06 ± 0.02	
CO_2^-	−0.89 ± 0.04	−0.75 ± 0.04	

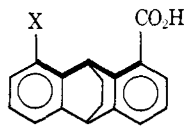
[a] This study. Weight per cent solvent. [b] Reference 23. Volume per cent solvent, 25°.

A more subtle feature, that log ($K_{CO_2^-}/K_\mathrm{H}$) is unusually negative, −0.89 for the ethano derivative and −0.75 for the dihydro derivative, also supports the conclusion that the polar effect has an angular dependence. This ratio is generally larger (less negative), since, in most molecules, the influence of the charge and the carboxylate dipole act in opposition.[20–22] However, electrostatic analysis indicates that the contribution of the dipole of the 8-carboxylate group of the ethanoanthracene is near zero. The reduction in log ($K_{CO_2^-}/K_\mathrm{H}$) thus is also predicted by the angular dependence implicit in the electrostatic model.

More quantitative comparisons of the observations are possible. From the viewpoint of the classical inductive theory the values of log (K/K_H) for the 8-substituted 9,10-ethanoanthracene-1- and the 8-substituted 9,10-dihydroanthracene-1-carboxylic acids should be similar in sign and magnitude to the values for the α-substituted *p*-toluic acids.[23] This expectation is based on the fact that the number and hybridization of the inductive transmission sites in the *p*-toluic acids are the same as those in the bridged anthracene acids.



VI



VII

The results for the toluic acids, Table II, are, however, completely dissimilar from the observations for the bridged anthracenes, indicating the inadequacy of the classical inductive model.

The Kirkwood–Westheimer electrostatic model enables a quantitative estimate of log (K/K_H) for the rigid ethano-bridged derivatives.[24] More physical insight is gained in this analysis when a two-point charge model for the dipole is employed. In brief, the work expended in the transfer of a proton from an acid, HA_1, with a dipolar substituent having two-point charges δe_+ and δe_- to an unsubstituted anion, A_2^-, located at an infinite distance from A_1^-, is given by eq 1,

$$\Delta w = e^2\delta_k[H_+ - H_-] \tag{1}$$

where the functions H_+ and H_- are determined by the positions of the charges, molecular geometry, and related factors.[24] The terms H_+ and H_- may be partitioned into contributions from the positive and negative point charges which are propagated through the high dielectric solvent (ϵ = 49 for 50% aqueous ethanol) and through the low dielectric cavity (ϵ = 2) (eq 2)

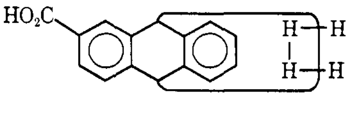
$$\begin{aligned} H_+ &= (D_{s+} + D_{l+}) \\ H_- &= (D_{s-} + D_{l-}) \end{aligned} \tag{2}$$

where D_{sk} is the fraction of the electrostatic influence transmitted through the solvent and D_{lk} is the fraction transmitted through the cavity. The contribution of each influence to log (K/K_H) is given by eq 3

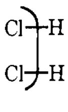
$$\Delta_k = \frac{e\mu_{CX}D_k}{2.3d_{CX}RT} \tag{3}$$

where μ_{CX}/d_{CX} defines δ_k for a CX bond, and the quantities e, R, and T have the customary meaning.

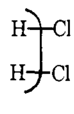
An important feature of the electrostatic model will be discussed prior to the calculation of the results for the ethanoanthracenes. In another search for a reversal of the traditional influence of substituents, Grubbs and Fitzgerald studied three bridged 2-anthroic acids.[25] These investigators observed that the acid-strengthening influence of the chlorine atoms was reduced in IX but not reversed. They noted that Tanford and Wilcox had pointed out that the numerical results achieved in a Kirkwood–Westheimer analysis may depend importantly on the position of the point charges within the cavity and in particular on the proximity of the negative point charge to the boundary of the cavity.[26] To examine this aspect of the theory, we adopted structure XIa for the 8-substituted 9,10-ethanoanthracene-1-carboxylic acids[27,28] and



VIII



IX



X

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(20) R. P. Bell and G. A. Wright, *Trans. Faraday Soc.*, **57**, 1377 (1961).

(21) C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, **30**, 777 (1965).

(22) For comparison, log ($K_{CO_2^-}/K_\mathrm{H}$) ranges between −0.47 and −0.60 for the bicyclo[2.2.2]octene, bicyclo[2.2.2]octane, and cubane acids.

(23) O. Exner and J. Jonáš, *Collect. Czech. Chem. Commun.*, **27**, 2296 (1962).

(24) (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

(25) E. J. Grubbs and R. Fitzgerald, *Tetrahedron Lett.*, 4901 (1968).

(26) (a) C. Tanford, *J. Amer. Chem. Soc.*, **79**, 5348 (1957); (b) C. F. Wilcox and C. Leung, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(27) The structural parameters are based on the work of B. A. Arbuzov and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **6**, 1004 (1964).

(28) Following the customary approach, the center of the spherical cavity was located on the C_9–C_{10} axis. The ionizable proton was located 1.45 Å beyond the carboxy carbon atom on the C–C axis.

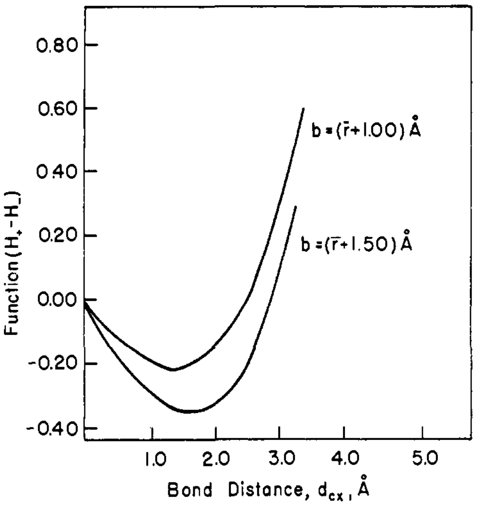
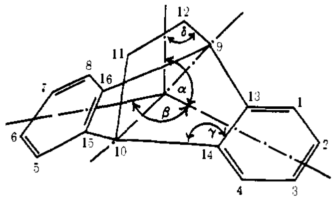


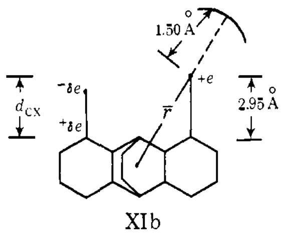
Figure 1. Variation of $(H_+ - H_-)$ as a function of d_{CX}.

located the positive pole at C_8, rendering D_{s+} and D_{i+} constant for all substituents, and calculated D_{s-} and D_{i-} for several locations of the negative pole. The results are shown in Figure 1. In this analysis, D_+ and H_+ remain constant for all substituents. As the C–X bond length increases, the magnitude of D_{i-}, at first, also increases because the distance between the negative pole and the reaction center decreases. However, the contribution of the negative pole experiences dielectric screening as the pole approaches the solvent. The latter effect becomes dominant, so that H_- reaches a maximum and then decreases. The maximum in H_- is reached at a smaller value of d_{CX} when the radius of the cavity is decreased. This result is reflected in the more positive values of H for $b = (r + 1.00)$ Å. The electrostatic model therefore suggests that substituent effect reversal should occur, but that only rather special situations will produce a large reversal for molecules with U-shaped geometry.



$\alpha = 116°$, $\beta = 128°$, $\gamma = 118°$

XIa



XIb

The acid strengths of several 8-substituted 9,10-ethanoanthracene-1-carboxylic acids were estimated by the two-point charge form of the Kirkwood–Westheimer method. The calculations were carried out only for the substituents F, Cl, and CN, for which the location of the bond moment can be defined with an element of confidence.[29] The dipole moments of the monosubstituted benzenes were used in the calculation to estimate log (K/K_H) directly. Structure XI was also adopted for these calculations. The calculations were carried out for two different cavity radii. Tanford's recommendations that the radius, b, be defined as $(r + 1.50)$ Å for dipolar substituents was used in one calculation, and a smaller radius, $(r + 1.00)$ Å, was used in a second. The results are summarized in Table III.

Table III. Calculated Acid Strength of Several 8-Substituted 9,10-Ethanoanthracene-1-carboxylic Acids in 50% Aqueous Ethanol

Group	Δ_{s+}	Δ_{i+}	Δ_{s-}	Δ_{i-}	Log (K/K_H)
			$b = (r + 1.50)$ Å		
F[a]	0.189	1.023	−0.219	−1.200	−0.21
Cl[b]	0.154	0.838	−0.187	−0.985	−0.18
CN[c]	0.260	1.413	−0.344	−1.468	−0.14
			$b = (r + 1.00)$ Å		
F[a]	0.200	0.694	−0.234	−0.792	−0.13
Cl[b]	0.163	0.567	−0.200	−0.633	−0.10
CN[c]	0.276	0.958	−0.366	−0.850	+0.02

[a] d[CF] = 1.30 Å, μ[CF] = 1.59 D. [b] d[CCl] = 1.70 Å, μ[CCl] = 1.70 D. [c] d[CCN] = 2.60 Å, μ[CCN] = 4.39 D.

Both the reversal and its order of magnitude are correctly predicted by the conventional Kirkwood–Westheimer model. The substituent effects are not ordered correctly; however, the behavior pictured in Figure 1 suggests that the net substituent effects for U-shaped geometry are sensitive to several factors not usually critical for rigid molecules.

Analysis of other features of the results reinforces the conclusion that the angular dependence of the polar effect is responsible for the reversal in the substituent effect. The bridged anthracenes were selected for study because C-1 and -8 are about 4.5 Å apart. At this distance, most substituent groups are more remote than the sum of their van der Waals radii. Bulk steric interactions, consequently, should be small. The experimental results support this view. For example, bulk steric interactions are presumably responsible for the well known acid-strengthening influence of *o*- or *peri*-methyl groups.[13,30] In contrast 8-methyl-9,10-ethanoanthracene-1-carboxylic acid is a weaker acid than the parent compound. In addition, the ratios of the dissociation constants for the acids with homomorphic substituents, (K_{Cl}/K_{CH_3}) and (K_F/K_H), are each less than unity.

We also applied several empirical tests to establish the role, if any, played by hydrogen bonding between substituents in the 8 position and the carboxylic acid proton in determining acid strength. First, we compared the dissociation constants of the 1,8 diacids and their monoesters with the constant for other representative acids for which the importance of hydrogen bonding has been established. The pertinent results are presented in Table IV.

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(29) In contrast, the group moments for the methoxy or carboalkoxy substituents are the result of several bond moment vectors. Neither free nor restricted rotation can be assumed, so that the direction and magnitude of the resultant moment depends, in an unknown way, upon the rotamer population.

(30) H. C. Brown, D. H. McDaniel, and O. Häfliger, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, Chapter 14.

Table IV. Dissociation Constants for Some Dibasic Acids and Their Monoesters[a]

Acid	pK_1	pK_2	Log $(K_1/4K_2)$	(K_1/K_α)
Maleic[b]	1.92	6.23	3.71	10.6
Fumaric[b]	3.02	4.38	0.76	2.0
1,2-*cis*-Cyclopropane[b]	3.33	6.47	2.54	
1,2-*trans*-Cyclopropane[b]	3.56	5.13	0.88	
Succinic[c]	5.52	7.43	1.31	2.1
Tetramethylsuccinic[b]	3.50	7.28	3.18	27.0
Glutaric[c]	5.83	7.16	0.73	
Adipic[d]	5.74	6.97	0.63	2.3
1,4-Bicyclo[2.2.2]octane[a]	6.10	7.47	0.77	2.1
1,4-Cubane[d]	5.13	6.53	0.80	
1,8-Anthracene[d]	5.26	6.55	0.69	
1,8-Dihydroanthracene[d]	5.32	6.61	0.69	
1,8-Ethanoanthracene[d]	5.67	7.19	0.92	2.5[d]

[a] No distinction is made between methyl and ethyl esters. [b] In water at 25°, abstracted from ref 30. [c] In 52.3 wt % aqueous ethanol at 20° (G. Schwartzenbach, *Helv. Chim. Acta*, **16**, 522 (1933)). [d] In 50 wt % aqueous ethanol, this study and ref 6.

Intramolecular hydrogen bonding interactions that lead to the stabilization of the monoanion of the dibasic acid $(O{=}CO\cdots HOC{=}O)^-$ may be detected by a large increase in (K_1/K_2) from the statistical value of 4 or, alternately, by an increase in (K_1/K_α) from the statistical value of 2.[30,31] Polar effects have only a modest influence on these ratios, as illustrated by the data for the acyclic, bicyclo[2.2.2]octane, and cubane diacids, in which hydrogen bonding is clearly unimportant. However, these ratios become large when intramolecular hydrogen bonding becomes significant, as shown by the data for *cis*-cyclopropane, maleic, and tetramethylsuccinic acids. The normal $(K_1/4K_2)$ and (K_1/K_α) for the bridged anthracenes support the view that intramolecular hydrogen bonding does not play a discernible role in the determination of acid strength.

Further support for this idea is provided by the result for 8-hydroxyethanoanthracene-1-carboxylic acid. Hydrogen bonding interactions are responsible for the increased acidity of salicylic acid ($pK = 2.98$) compared to benzoic ($pK = 4.20$) or *o*-anisic acid ($pK_A = 4.09$). In contrast, 8-hydroxy-9,10-ethanoanthracene-1-carboxylic acid is no stronger than the parent acid. This result and other observations discussed in the preceding paragraphs support the conclusion that steric interactions between groups in the 1 and 8 positions are unimportant.

Successful application of the Kirkwood–Westheimer theory for the calculation of log $(K_1/4K_2)$ for the rigid cubane and bicyclooctane diacids (for example, log $(K_1/4K_2)$ for the bicyclic acid is 0.77 compared to the theoretical value of 0.71[6]) prompted the calculation of this quantity for 9,10-ethanoanthracene-1,8-dicarboxylic acid. The logarithmic ratio is given by eq 4 where r

$$\log(K_1/4K_2) = \frac{e^2}{2.3RTrD_E} \tag{4}$$

is the distance between the removable protons, and the other quantities have been defined. D_E depends importantly in the present case on the locations adopted for the protons. The variation of this quantity as a function of the depth of the protons below the cavity surface, (r/b), and the angle, ν, between the vectors, r, joining the center of the cavity with the protons is shown in Figure 2 for diacids in which cos ν is -1 (bicyclo[2.2.2]octane 1,4-diacid), 0, and 0.60 (9,10-ethanoanthracene 1,8-diacid). The structural model XI adopted for the bridged anthracene with the two ionizable protons located, according to a convention, 1.45 Å beyond the carboxyl carbon atom defines (r/b) as 0.89 corresponding to $D_E = 25$. Log $(K_1/4K_2)$ is then 2.16, considerably larger than the experimental value, 0.92. The discrepancy between theory and experiment is much larger in this instance than for the 1,4-diacids of cubane and bicyclo[2.2.2]octane. For these molecules, similar values of log $(K_1/4K_2)$ are obtained when different conformations are adopted for the carboxyl groups. On the other hand, the calculated values of log $(K_1/4K_2)$ for 9,10-ethanoanthracene-1,8-dicarboxylic acid do depend on the conformation adopted for the carboxyl groups. Thus, log $(K_1/4K_2)$ is only 0.61 for structure XII. This result supports the viewpoint that simple conformational variations may be responsible for the discrepancy between theory and experiment. Clearly, there are other explanations. For example, the discrepancy may reflect an inadequacy of the structureless cavity model. This notion is particularly attractive because there are two carboxyl groups in close proximity to each other and to the solvent. A "structured" character for the diacid–water–ethanol interface is therefore reasonable. The feature of the results that deserves emphasis, however, is that there is nothing unusual about the result for the 1,8-diacid that would cast doubt on the interpretation of the results for the dipolar substituents.

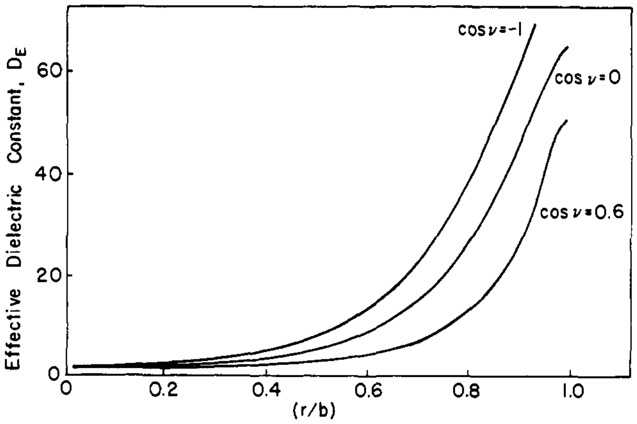
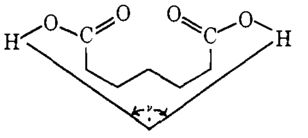


Figure 2. The relationship between D_E and (r/b) for three values of cos ν.



XII

The limited data available for the 8-substituted 1-anthroic acids are, in many ways, similar to the results for the 7- and 8-substituted 2-naphthoic acids and the 8-substituted 1-naphthoic acids.[11-13] These data have recently been analyzed by the semiempirical FMMF approach.[32] The angular dependence of the

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(31) F. H. Westheimer and O. T. Benfey, *J. Amer. Chem. Soc.*, **78**, 5309 (1956).

(32) M. J. S. Dewar, R. Golden, and J. M. Harris, *ibid.*, **93**, 4187 (1971).

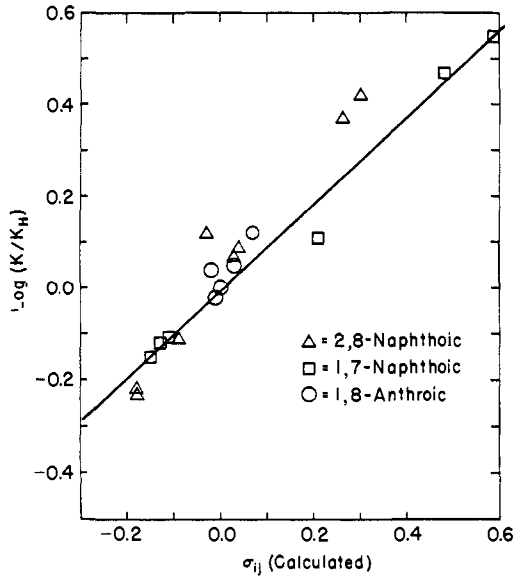

Figure 3. The relationship between the experimental values of log (K/K_H) and the calculated values of σ_{ij}.

polar effect is presumed in this reasonably successful theory for the analysis of substituent effects. The results for the 8-substituted 1-anthroic acids are accommodated with satisfactory precision as shown in Figure 3.

In summary, the results obtained in this study offer quite positive evidence for the angular dependence of the polar effect. Neither steric effects nor hydrogen bonding interactions are significant. We conclude, therefore, that an electrostatic model is much more suitable for the interpretation of polar substituent effects than is an inductive model.

Experimental Section

1-Cyanoanthraquinone. 1-Chloroanthraquinone (12.0 g, 49.5 mmol) and cuprous cyanide (6.0 g, 67 mmol) were stirred at reflux in dimethylacetamide (50 ml) for 3 hr under nitrogen. The hot solution was poured into vigorously stirred water (700 ml) to give the copper(I) complex of the product. The crude complex was decomposed with warm 3 *N* nitric acid[33] to yield 1-cyanoanthraquinone (11.1 g, 96%, mp 239–244°, lit.[34] 249°).

Anthraquinone-1-carboxylic Acid. Crude 1-cyanoanthraquinone (11.0 g, 47.2 mmol) was dissolved in aqueous sulfuric acid (32%, 900 ml). The solution was stirred and warmed to 170°. After 30 min at 170–175° the hot solution was poured onto ice. The precipitate was collected, washed with water, and then stirred with aqueous potassium hydroxide (10%). The resulting slurry was filtered. The unstirred filtrate[35] was acidified with hydrochloric acid to yield the crude product (7.3 g, 62%). Recrystallization from chlorobenzene gave pure anthraquinone-1-carboxylic acid (mp 292–293°, lit.[34] 293–294°).

1-Anthroic Acid. Anthraquinone-1-carboxylic acid (10.0 g, 39.7 mmol) was stirred at reflux in aqueous ammonia (20%, 450 ml) with zinc dust (40 g, 600 mmol) and cupric sulfate catalyst (0.5 g) until the temperature reached 70°. After 3 hr at 70° the mixture had changed from dark red to amber, and the hot aqueous solution was filtered from the insoluble residues, cooled, and acidified. The yellow precipitate (7.7 g, 87%) was recrystallized from ethyl acetate to give yellow needles of 1-anthroic acid (mp 249°, lit.[36] 245°).

9,10-Ethanoanthracene-1-carboxylic Acid. 1-Anthroic acid (4.50 g, 23 mmol) and *p-tert*-butylcatechol (0.5 g) in dry pyridine (100 ml) were treated with technical grade ethylene (900 psi of initial pressure) in a glass-lined reaction vessel at 150° for 3 days (maximum pressure 2400 psi). The solvent was removed *in vacuo* to yield a dark brown oil, which was treated with potassium hydroxide (5 g) in ethylene glycol (30 ml). The solution was washed with ethyl ether and then poured into aqueous hydrochloric acid (10%). The acid was extracted into methylene chloride (250-ml total), the organic phase was dried over sodium sulfate, and the solvent was removed to yield a brown solid (5.3 g, 92%). Three recrystallizations from benzene gave 9,10-ethanoanthracene-1-carboxylic acid (colorless prisms, mp 212.5–213.5°).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.56; H, 5.67.

8-Chloroanthraquinone-1-carboxylic Acid. 1,8-Dichloroanthraquinone (40 g, 145 mmol) and reagent grade cuprous cyanide (10.2 g, 114 mmol) were stirred at reflux in *N*,*N*-dimethylacetamide (50 ml) under nitrogen for 1 hr. The hot solution was poured into water with vigorous stirring to give a precipitate of the copper(I) complex of 8-chloro-1-cyanoanthraquinone. The complex was decomposed with warm 3 *N* aqueous nitric acid.[33] Crude 8-chloro-1-cyanoanthraquinone was hydrolyzed in hot aqueous sulfuric acid as described for anthraquinone-1-carboxylic acid to yield the product (22.9 g, 56%, mp 243–245°). Recrystallization from aqueous dioxane yielded pure 8-chloroanthraquinone-1-carboxylic acid (yellow needles, mp 245–246°, lit.[37] 243–244°).

8-Chloro-1-anthroic Acid. Crude 8-chloroanthraquinone-1-carboxylic acid (25 g, 87.3 mmol) was stirred with zinc dust (125 g, 1.9 mol) and cupric sulfate (0.5 g) at reflux in aqueous ammonia (20%, 1100 ml) until the temperature reached 70°. After 4 hr at 70° the color change from dark red to amber was complete, and the product was isolated as described for 1-anthroic acid to yield a crude product (22.3 g, 98%). Recrystallization from chlorobenzene gave 8-chloro-1-anthroic acid (mp 267–268°, lit.[37] 264.5°).

8-Chloro-9,10-ethanoanthracene-1-carboxylic Acid. Crude 8-chloro-1-anthroic acid (3.0 g, 12 mmol) was converted to 8-chloro-9,10-ethanoanthracene-1-carboxylic acid (mp 276.5–277.5°) in 95% yield by the method described for the preparation of 9,10-ethanoanthracene-1-carboxylic acid. The crude product which precipitated from the alkaline glycol solution was recrystallized from chlorobenzene.

Anal. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.61; Cl, 12.45. Found: C, 71.60; H, 4.59; Cl, 12.57.

8-Methoxyanthraquinone-1-carboxylic Acid. Crude 8-chloroanthraquinone-1-carboxylic acid (10.0 g, 34.8 mmol) was stirred at reflux with sodium methoxide (20.8 g, 520 mmol) in anhydrous methanol (300 ml) for 18 hr. The solvent was removed, the residue was dissolved in water, and the solution was acidified[35] to give yellow 8-methoxyanthraquinone-1-carboxylic acid (9.4 g, 96%, mp 288–289° after recrystallization from 80% aqueous ethanol).

Anal. Calcd for $C_{16}H_{10}O_5$: C, 68.08; H, 3.57. Found: C, 68.05; H, 3.81.

8-Methoxy-1-anthroic Acid. 8-Methoxyanthraquinone-1-carboxylic acid (1.0 g, 3.5 mmol) was reduced with zinc dust in aqueous ammonia as described for 1-anthroic acid. The crude product (0.89 g, 100%) was recrystallized from chlorobenzene to yield 8-methoxy-1-anthroic acid (mp 271–272°).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.85; H, 4.81.

8-Methoxy-9,10-ethanoanthracene-1-carboxylic Acid. Ethylene was added to 8-methoxy-1-anthroic acid (2.27 g, 9.00 mmol) as described for 1-anthroic acid. The crude product (2.45 g, 97%) was recrystallized from toluene to yield colorless plates of 8-methoxy-9,10-ethanoanthracene-1-carboxylic acid (mp 261–262°).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.20; H, 5.83.

8-Hydroxy-9,10-ethanoanthracene-1-carboxylic Acid. 8-Methoxy-9,10-ethanoanthracene-1-carboxylic acid (3.0 g, 12 mmol) was refluxed in a mixture of freshly distilled 57% hydriodic acid (36 ml) and *o*-dichlorobenzene (15 ml) for 2 hr. The mixture was diluted with water and extracted with several portions of ethyl ether (125-ml total). The organic phase was washed with aqueous potassium hydroxide (150 ml, 5%), and the aqueous layer was acidified. The resulting mixture was extracted with ethyl ether (200-ml total), the organic phase was dried over sodium sulfate, and the solvent was removed to give crude 8-hydroxy-9,10-ethanoanthra-

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(33) *Caution.* The complex is usually smoothly decomposed by aqueous nitric acid. However, the decomposition of the complex may initiate suddenly at 70–80° with a vigorous evolution of gas.

(34) F. Ullmann and W. van der Schalk, *Justus Liebigs Ann. Chem.*, **388**, 199 (1912).

(35) Stirring caused the microfine crystals to congeal into an intractable lump.

(36) C. Graebe and S. Blumenfeld, *Ber.*, **30**, 1115 (1897).

(37) H. Waldmann and R. Stengl, *Chem. Ber.*, **83**, 167 (1950).

cene-1-carboxylic acid (2.2 g, 68%, mp 202.5–204.0° after recrystallization from chlorobenzene).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.70; H, 5.37.

8-Hydroxyanthraquinone-1-carboxylic Acid. Crude 8-chloroanthraquinone-1-carboxylic acid (10.0 g, 34.8 mmol) was refluxed in aqueous potassium hydroxide (10%, 250 ml) for 2 days. The red solution was filtered and acidified[35] to yield a yellow precipitate which was recrystallized from chlorobenzene to yield 8-hydroxyanthraquinone-1-carboxylic acid (9.4 g, 100%, mp 253°).

Anal. Calcd for $C_{15}H_8O_5$: C, 67.17; H, 3.01. Found: C, 67.37; H, 3.08.

Methyl 8-Chloro-1-anthroate. 8-Chloro-1-anthroic acid (9.0 g, 35 mmol) was stirred for 3 hr in a solution of sulfuric acid (20 ml) in methanol (450 ml). The solvent was removed *in vacuo*. The residue was treated with aqueous potassium hydroxide (5%) and was extracted with three portions of chloroform (250-ml total). The organic phase was washed with saturated aqueous sodium chloride and dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was recrystallized from methanol to yield methyl 8-chloro-1-anthroate (7.05 g, 74%, mp 128.0–128.5°).

Methyl 8-Cyano-1-anthroate. Methyl 8-chloro-1-anthroate (7.23 g, 26.7 mmol) was stirred for 24 hr at reflux with reagent grade cuprous cyanide (4.7 g, 53 mmol) in *N*-methylpyrrolidinone (27 ml) under nitrogen. The hot solution was poured into water (500 ml) with vigorous stirring. The resulting precipitate was stirred overnight with a solution of ethylenediamine (25 ml) in water (300 ml). The dark blue mixture was extracted with three portions of chloroform (300-ml total). The organic phase was washed with saturated aqueous sodium chloride and dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue (4.5 g) was extracted with hot methanol (100 ml) and filtered hot, leaving an insoluble residue (2.6 g). This residue was recrystallized from benzene to yield methyl 8-cyano-1-anthroate (2.10 g, 37%, mp 171–173°, $\nu_{\mathrm{CN}}^{\mathrm{CHCl_3}}$ 2240 cm^{-1}). Unconverted methyl 8-chloro-1-anthroate (1.25 g) was recovered from the methanol extract.

8-Cyano-1-anthroic Acid. Finely powdered crude methyl 8-cyano-1-anthroate (2.50 g, 9.58 mmol) was dissolved in hot ethanol (95%, 150 ml). Water (125 ml) was added, followed by aqueous potassium hydroxide (10%, 25 ml). The mixture was stirred for 40 min at 70°. The resulting clear solution was cooled to 0° and diluted with water (200 ml). The pH was adjusted to 6 with hydrochloric acid. The ethanol was removed *in vacuo*, and the residue was acidified with hydrochloric acid to give 8-cyano-1-anthroic acid (2.35 g, 99%, mp 290–295°, $\nu_{\mathrm{CN}}^{\mathrm{KBr}}$ 2230 cm^{-1}). Recrystallization from *o*-dichlorobenzene sharpened the melting point to 294–295°.

Anal. Calcd for $C_{16}H_9O_2N$: C, 77.72; H, 3.67; N, 5.67. Found: C, 76.93; H, 3.87; N, 5.56.

8-Cyano-9,10-ethanoanthracene-1-carboxylic Acid. Ethylene was added to 8-cyano-1-anthroic acid (2.50 g, 10.0 mmol) as described for 1-anthroic acid. The crude product (2.35 g, 85%) was recrystallized from *o*-dichlorobenzene to yield 8-cyano-9,10-ethanoanthracene-1-carboxylic acid (mp 275–276°, $\nu_{\mathrm{CN}}^{\mathrm{KBr}}$ 2235 cm^{-1}).

Anal. Calcd for $C_{18}H_{13}O_2N$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.26; H, 4.92; N, 5.02.

Anthraquinone-1,8-dicarboxylic Acid. 1,8-Dichloroanthraquinone (10.0 g, 36.2 mmol) and reagent grade cuprous cyanide (9.70 g, 108 mmol) were stirred for 2 hr at reflux in *N*,*N*-dimethylacetamide (50 ml) under nitrogen. The hot solution was poured into vigorously stirred water (700 ml) and the precipitated copper(I) complex was decomposed in 3 *N* nitric acid.[33] The crude dinitrile was hydrolyzed in hot aqueous sulfuric acid as described for 1-cyanoanthraquinone, to yield anthraquinone-1,8-dicarboxylic acid (8.2 g, 77%, mp 305–311°, lit.[38] 316°, after recrystallization from water).

Anthracene-1,8-dicarboxylic Acid. Anthraquinone-1,8-dicarboxylic acid (22.5 g, 76.0 mmol) was reduced with zinc dust (75 g, 1.1 mol) in aqueous ammonia (1000 ml) as described for 8-chloro-1-anthroic acid. The crude product was recrystallized from aqueous dioxane to yield anthracene-1,8-dicarboxylic acid (12.7 g, 68%, mp 353°, lit.[38] 345°).

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 71.87; H, 3.84.

9,10-Ethanoanthracene-1,8-dicarboxylic Acid. Ethylene was added to anthracene-1,8-dicarboxylic acid (3.0 g, 11 mmol) as described for 1-anthroic acid. The crude product (1.9 g, 59%) was recrystallized from *o*-dichlorobenzene to yield colorless prisms of 9,10-ethanoanthracene-1,8-dicarboxylic acid (mp 328°).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 72.99; H, 4.97.

Methyl Hydrogen 9,10-Ethanoanthracene-1,8-dicarboxylate. 9,10-Ethanoanthracene-1,8-dicarboxylic acid (1.85 g, 6.34 mmol) was refluxed in a solution of sulfuric acid (1.5 ml) in methanol (30 ml) until a clear solution was obtained. Water was added, and the methanol was removed *in vacuo*. The mixture was made basic with dilute aqueous potassium hydroxide and extracted with ethyl ether (50-ml total). The aqueous phase was acidified to give a precipitate which was washed with water and dried. The material was dissolved in hot chlorobenzene (30 ml) and filtered. After cooling, a few crystals of unreacted starting material precipitated. These crystals were separated by filtration. The filtrate was then treated with an equal volume of cyclohexane. After standing, colorless needles of methyl hydrogen 9,10-ethanoanthracene-1,8-dicarboxylate (0.85 g, 44%, mp 215.0–215.5° after recrystallization from benzene–cyclohexane) formed.

Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.74; H, 5.40.

The combined ether washings gave a residue which was recrystallized from methanol to yield dimethyl 9,10-ethanoanthracene-1,8-dicarboxylate.

1,8-Dichloroanthracene. Zinc dust (240 g, 3.6 mol) was added to a stirred slurry of 1,8-dichloroanthraquinone (60 g, 217 mmol) in aqueous ammonia (20%, 2.4 l.) Cupric sulfate (1 g) was added and the temperature was raised to 70°. The color change was complete after 4 hr. Filtration of the hot liquid mixture yielded a solid mass containing the product. The solid was washed thoroughly with water, pressed dry, and stirred with several portions of acetone. The acetone was removed *in vacuo* to give an almost colorless residue of 1,8-dichloro-9,10-dihydro-10-hydroxyanthracene.[39] This material was dissolved in hot 1-propanol (600 ml) and a few drops of concentrated hydrochloric acid were added. Golden yellow needles rapidly separated. This material was washed with cold methanol to yield 1,8-dichloroanthracene (46.2 g, 86%, mp 155–157°, lit.[40,41] 156, 160°).

1,8-Dichloro-9,10-ethanoanthracene. 1,8-Dichloroanthracene (48 g, 190 mmol) and *p-tert*-butylcatechol (0.5 g) were dissolved in toluene (200 ml). The solution was treated with ethylene (900 psi of initial pressure) for 3 days at 150°. The resulting solution was washed with dilute aqueous potassium hydroxide and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the residue was recrystallized from heptane to give a quantitative yield of 1,8-dichloro-9,10-ethanoanthracene (mp 162°).

8-Methyl-1-chloro-9,10-ethanoanthracene. 1,8-Dichloro-9,10-ethanoanthracene (6.0 g, 21.8 mmol) was placed in a flame-dried flask under argon. Ether (250 ml)[42] was distilled into the flask from sodium benzophenone ketyl. The solution was cooled to 10°, and methyllithium (0.5 ml, 2 *M* in ethyl ether) was added as a proton scavenger. Lithium shavings (0.45 g, 65 mmol, 1.5% sodium)[43] were cut directly into the solution, and the mixture was stirred under argon for 8 hr at 10–15°. Methyl iodide (5 drops total) was added at intervals during the latter part of the reaction to clean the metal surface. The resulting slurry was cooled to −10°, and a large excess of freshly distilled methyl iodide was rapidly added. After the initial exothermic reaction had subsided, the mixture was stirred at room temperature for 1 hr. The mixture was poured into water (250 ml) and acidified, and the organic phase was separated. The aqueous layer was washed with several small portions of ether, and the combined organic phases were washed with saturated aqueous sodium chloride and dried over magnesium sulfate. When the solvent was removed a quantitative yield of a mixture of 8-methyl-1-chloro-9,10-ethanoanthracene (80%) and 1,8-dimethyl-9,10-ethanoanthracene (20%) was obtained. All attempts to separate the two alkylated products were unsuccessful.

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[38] H. Waldmann and A. Oblath, *J. Amer. Chem. Soc.*, **71**, 366 (1938).

[39] E. Bergmann and A. Weizmann, *J. Amer. Chem. Soc.*, **60**, 1801 (1938).

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[42] Attempts to carry out metallation reactions in tetrahydrofuran resulted in hydrogen abstraction by the organometallic species from the solvent to yield unsubstituted products.

[43] Excess lithium at this stage of the reaction sequence ensured the consumption of the starting material which produced unwanted byproducts in the next step.

8-Methyl-9,10-ethanoanthracene-1-carboxylic Acid. A mixture of 80% 8-methyl-1-chloro-9,10-ethanoanthracene and 20% 1,8-dimethyl-9,10-ethanoanthracene (4.4 g, 13.7 mmol) was placed in a dried flask under argon. Diethyl ether (80 ml) was distilled into the flask from sodium benzophenone ketyl and the solution was cooled to 10°. Methyllithium (0.5 ml, 2 *M* in ethyl ether) was added as a proton scavenger. Lithium shavings (0.25 g, 36 mmol, 1.5% sodium) were cut directly into the solution, and the mixture was stirred for 5 hr at 10–15° under argon. The resulting slurry was cooled to −10°, and "bone dry" carbon dioxide was passed over the mixture with cooling to keep the temperature less than 0°. Water was added to destroy the excess metal, and the mixture was acidified with hydrochloric acid. The organic phase was separated, and the aqueous layer washed with several small portions of ether. The combined organic phases were extracted with three portions of dilute aqueous potasssium hydroxide (250-ml total). Residual ether was removed from the aqueous phase *in vacuo*. The aqueous solution was then filtered, and the filtrate was acidified to precipitate 8-methyl-9,10-ethanoanthracene-1-carboxylic acid[44] (3.2 g, 88%, mp 229–230° after recrystallization from toluene).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.73; H, 6.20.

The ether layer was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. The solvent was removed, and the residue was recrystallized from methanol to yield a small amount of 1,8-dimethyl-9,10-ethanoanthracene (mp 124°).

8-Chloroanthraquinone-1-diazonium Tetrafluoroborate. A solution of sodium nitrite (15 g, 220 mmol) in cold concentrated sulfuric acid (150 ml) was added to a solution of 1-amino-8-chloroanthraquinone (20 g, 78 mmol, DuPont technical grade)[45] in an equal volume of cold concentrated sulfuric acid The dark solution was stirred for 3 hr at 10–15°, filtered through sintered glass, and poured over cracked ice (2 kg). The resulting mixture was treated with aqueous fluoroboric acid (48%, 100 ml) and stirred for 30 min. The precipitate was thoroughly washed with cold water and with acetone and dried *in vacuo* to yield the diazonium salt (20 g, 72%, mp 165° dec).

1-Chloro-8-fluoroanthraquinone, A slurry of 8-chloroanthraquinone-1-diazonium tetrafluoroborate (30 g, 84 mmol) in dry *o*-dichlorobenzene (180 ml) was stirred at 140° until boron trifluoride was no longer evolved. The cooled reaction mixture was filtered, and the solvent was removed *in vacuo*. The residue was dissolved in benzene and passed through a neutral alumina column. The yellow benzene solution was reduced in volume to 100 ml and treated with petroleum ether to yield a yellow precipitate of 1-chloro-8-fluoroanthraquinone (12.7 g, 58%, mp 175–176°).

1-Chloro-8-fluoroanthracene. 1-Chloro-8-fluoroanthraquinone (30 g, 115 mmol) was reduced with zinc dust (40 g, 610 mmol) in aqueous ammonia (450 ml, 20%) as described for 1,8-dichloroanthracene. The crude product (23 g, 87%) was recrystallized from aqueous 1-propanol to yield 1-chloro-8-fluoroanthracene (mp 99–102°).

1-Chloro-8-fluoro-9,10-ethanoanthracene. Ethylene was added to 1-chloro-8-fluoroanthracene (6.7 g, 29 mmol) as described for 1,8-dichloro-9,10-ethanoanthracene. The product was recrystallized from hexane to yield 1-chloro-8-fluoro-9,10-ethanoanthracene (4.3 g, 57%, mp 112–116°). The product was contaminated with 1,8-dichloro-9,10-ethanoanthracene.

8-Fluoro-9,10-ethanoanthracene-1-carboxylic Acid. Impure 1-chloro-8-fluoro-9,10-ethanoanthracene (5.3 g, 20 mmol) was placed in a dry flask under argon. Tetrahydrofuran (50 ml)[46] was distilled into the flask from lithium aluminum hydride. The solution was cooled to −35°, lithium shavings (0.25 g, 36 mmol, 1.5% sodium) were cut directly into the solution, and the mixture was stirred at −35° for 3 hr under argon. "Bone dry" carbon dioxide was passed over the reaction mixture with cooling to keep the temperature less than −10°. The crude product (2.7 g, 50%) was isolated by the procedure described for 8-methyl-9,10-ethanoanthracene-1-carboxylic acid. Repeated recrystallization of the initial product from benzene yielded analytically pure 8-fluoro-9,10-ethanoanthracene-1-carboxylic acid (mp 242°).

Anal. Calcd for $C_{17}H_{13}O_2F$: C, 76.11; H, 4.88; F, 7.08. Found: C, 76.22; H, 4.87; F, 7.01.

9,10-Dihydroanthracene-1-carboxylic Acid. This compound was prepared by the reduction of anthraquinone-1-carboxylic acid by the procedure of Scholl and Donat.[47] Recrystallization of the crude product provided 9,10-dihydroanthracene-1-carboxylic acid (mp 207–208°, lit.[47] 206°)

8-Chloro-9,10-dihydroanthracene-1-carboxylic Acid. 8-Chloroanthraquinone-1-carboxylic acid (2.0 g, 7.0 mmol) was reduced to the 9,10-dihydro derivative as described for the unsubstituted acid. The crude product (1.45 g, 80%) was chromatographed on acid-washed alumina with ethyl acetate to give a yellow crystalline product. This material was recrystallized from benzene to yield 8-chloro-9,10-dihydroanthracene-1-carboxylic acid (mp 213–214°).

Anal. Calcd for $C_{15}H_{11}O_2Cl$: C, 69.64; H, 4.29; Cl, 13.71. Found: C, 69.98; H, 4.41; Cl, 13.97.

9,10-Dihydroanthracene-1,8-dicarboxylic Acid. Anthraquinone-1,8-dicarboxylic acid (4.0 g, 13 mmol) was reduced to the 9,10-dihydro derivative as described in the previous cases. The crude product (3.10 g, 89%) was recrystallized from *o*-dichlorobenzene to yield 9,10-dihydroanthracene-1,8-dicarboxylic acid (mp 318–319°).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.51; H, 4.73.

The nmr spectra of the new compounds prepared in this study were recorded. The chemical shifts of the bridgehead hydrogen atoms of the ethanoanthracenes are particularly large. These observations are summarized in Table V.

Table V. Proton Nmr Spectra of 1,8-Disubstituted 9,10-Ethanoanthracenes at 60 MHz[a,b]

Substituents			Chemical shift, Hz[a]		
8	1	Solvent	H_9	H_{10}	Other
H	H	$DCCl_3$	257.4[c]	257.4[c]	
H	Cl	$DCCl_3$	289	255	
Cl	Cl	$DCCl_3$	323	252	
F[d]	Cl	$DCCl_3$	316	257	
CH_3	Cl	$DCCl_3$	307	256	CH_3 149
CO_2CH_3	Cl	$DCCl_3$	369	261	CH_3 240
CH_3	CH_3	$DCCl_3$	290	257	CH_3 147
H	CO_2H	DMSO-d_6	337	266	
F[e]	CO_2H	DMSO-d_6	358	267	
Cl	CO_2H	DMSO-d_6	366	267	
CN	CO_2H	DMSO-d_6	364	271	
OCH_3	CO_2H	DMSO-d_6	358	263	
OH	CO_2H	DMSO-d_6	355	261	
CO_2H	CO_2H	DMSO-d_6	398	267	
CO_2CH_3	CO_2H	DMSO-d_6	389	271	

[a] Chemical shifts are reported in hertz (±3 Hz) downfield from internal tetramethylsilane. [b] The ethylene bridge appeared as a broad multiplet centered from 97 to 102 Hz downfield from internal tetramethylsilane. [c] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964). [d] The ^{19}F resonance (deuteriochloroform) was a broad multiplet centered 6970-Hz upfield from fluorotrichloromethane. [e] The ^{19}F resonance (dimethyl sulfoxide) was a sharp multiplet centered 6990-Hz upfield from fluorotrichloromethane.

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(44) The presence of 1,8-dichloro-9,10-ethanoanthracene in the starting material produced 8-chloro-9,10-ethanoanthracene-1-carboxylic acid as a contaminant. The two acids proved most difficult to separate, and care was taken to exclude the dichloride from the starting material.

(45) We wish to thank the E. I. du Pont de Nemours Company for a generous gift of 1-amino-8-chloroanthraquinone.

(46) The starting material was contaminated with 1,8-dichloro-9,10-ethanoanthracene. When the lithium exchange reaction and carbonation were carried out in ether, the fluoro acid contained the chloro acid which was extremely difficult to remove. When the lithium exchange and carbonation were carried out in tetrahydrofuran, the fluoro acid contained a small, but removable, amount of 9,10-ethanoanthracene-1-carboxylic acid.

(47) R. Scholl and J. Donat, *Justus Liebigs Ann. Chem.*, **512**, 25 (1934).