(1973).

(26) Analogous reduction of 9-bromocamphor also proceeds well (the 70% yield reported in the Experimental Section resulted with no effort to optimize conditions), and thus reduction by tri-*n*-butyltin deuteride should be preferable to zinc-acetic acid-*d* for preparation of camphor-9-d_1; cf. K. M. Baker and B. R. Davis, *Tetrahedron*, **24**, 1655 (1968); D. R. Dimmel and W. Y. Fu, *J. Org. Chem.*, **38**, 3782 (1973).

(27) J. D. Connolly and R. McCrindle, *Chem. Ind.* (*London*), 379 (1965).

(28) A shorter sequence to 8-perdeuterated derivatives may now be derivable through D(+)-8-bromocamphor, inasmuch as the latter has recently become readily available as a result of the work of Money et al.[25]

(29) W. L. Meyer, A. P. Lobo, and E. T. Marquis, *J. Org. Chem.*, **30**, 181 (1965).

(30) This argument applies, of course, only to a symmetric ion **11**. The observed isotopic distribution *could* result from a mechanism in which C-2-methyl bond breaking and C-3-methyl bond formation are both complete prior to the start of decarboxylation or lactonization (see below), i.e., through an ion formally similar to **11**, provided that the two carboxylates are differently solvated, as could occur if some or all of the decarboxylation begins before solvent reorganization around **11** is complete. There is no evidence to exclude this as a viable alternative to the sequences proposed in the main discussion. Unequal isotope distribution could also result from an ion **11** in which there is preferential intramolecular "solvation" of the cationic C-2 by one of the carboxylates, as could occur if some or all of the decarboxylation begins before reorientation of the two carboxylates of **11** is complete. None of our evidence would distinguish this situation from the β-lactonizations which are discussed, so it is not considered separately here. Finally, unequal isotope distribution could also arise from an ion which in other respects is similar to **11**, but which is specifically monoprotonated at either the α- or γ-carboxylate, but this seems unlikely at pH 11 inasmuch as the second dissociation of the bromo diacid probably has a pK_a of about 6; cf. footnote 39 of ref 1.

(31) The three other stereoisomers of **34/35**, each of which must be examined as a pair of isotopic isomers differing in the location of methyls 8 and 10, are not considered because there is no apparent reasonable mechanism for their formation under these reaction conditions.

(32) Another hypothetical mode of decomposition of lactones **34** and **35** to laurolenic acid would be by [2 + 2] cycloreversion of the β-lactone system, but this is considered improbable because under comparable conditions simple β-lactones hydrolyze rather than expel CO_2 in such a manner. For example, at 100 °C in water *cis*-2-hydroxycyclopentanecarboxylic acid lactone affords no cyclopentene but only hydroxy acids.[33] Thermal cycloreversion of analogous β-lactones is normally observed only at higher temperatures and in the absence of a nucleophilic solvent; cf. ref 34.

(33) W. R. Vaughan, W. F. Cartwright, and B. Henzi, *J. Am. Chem. Soc.*, **94**, 4978 (1972).

(34) T. Rull and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1581 (1958); G. A. Boswell, W. G. Dauben, G. Ourisson, and T. Rull, *ibid.*, 1598 (1958); H. E. Zaugg, "Organic Reactions", Vol. VIII, R. Adams, Ed., Wiley, New York, N.Y., 1954, Chapter 7.

(35) Cf. C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Am. Chem. Soc.*, **87**, 2421 (1965).

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(37) C. F. Poe and E. M. Plein, *J. Phys. Chem.*, **38**, 883 (1934).

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(39) D. M. Bowen, "Organic Syntheses", Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N.Y., 1967, pp 555–557.

(40) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(41) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(42) R. B. Woodward, T. P. Kohman, and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941).

(43) Cf. K. Biemann, "Mass Spectrometry, Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962, Chapter 5, for method and assumptions.

A Vanished Substituent Effect Predicted by the Kirkwood–Westheimer Electrostatic Field Model

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syn- (**2b**) and *anti*- (**3b**) *cis*-11,12,dichloro-9,10-dihydro-9,10-ethanoanthracene-1-carboxylic acids have been synthesized. Geometric assignments were made on the basis of their ^{13}C chemical shifts along with those of model compounds. The apparent pK_a's of **2b** and 9,10-dihydro-9,10-ethanoanthracene-1-carboxylic acid (**9b**) (previously reported by Stock) in aqueous ethanol are identical within experimental error. This result is predicted by the Kirkwood–Westheimer equation and is a consequence of the angular orientation of the dipole with respect to the site of ionization. The apparent pK_a of **3b** is approximately 0.47 units smaller than that of **9b**. These results are briefly discussed in terms of the Kirkwood–Westheimer electrostatic field model.

The Kirkwood–Westheimer expression[1] for calculating electrostatic effects of dipolar substituents upon acidities of carboxylic acids includes the angular orientation of the dipole with respect to the site of ionization (eq 1).

$$\log \frac{K}{K_0} = \frac{eu \cos \theta}{2.30\, kTR^2 D_E} \qquad (1)$$

That both the sign and magnitude of dipolar substituent effects can be dependent upon the angular disposition of the dipole relative to the carboxylate group has been experimentally verified.[2]

An interesting consequence of this electrostatic model is the prediction that for a dipole oriented perpendicular to a line joining its midpoint to the ionizing proton, the substituent effect should vanish. That is, for $\theta = 90°$, $K = K_0$. We report here a case where the resultant dipole of a vicinal dichloride possesses this geometric characteristic.

Results

Methyl *syn*-*cis*-11,12-dichloro-9,10-dihydro-9,10-ethano-1-anthroate (**2a**) and the corresponding anti-cis dichloro isomer **3a** were prepared by the cycloaddition of *cis*-1,2-dichloroethene and 1-methyl anthroate (**1**). The isomers were separated by a combination of chromatography and crystallization. Progress in effecting the separation was followed by NMR monitoring of the relative intensities of the C_9 proton signals (peri to CO_2Me), the singlets for which lie downfield (δ 6.12 for **2a** and 5.73 for **3a**) from the remaining nonaromatic protons. The geometric assignments for **2a** and **3a** were made

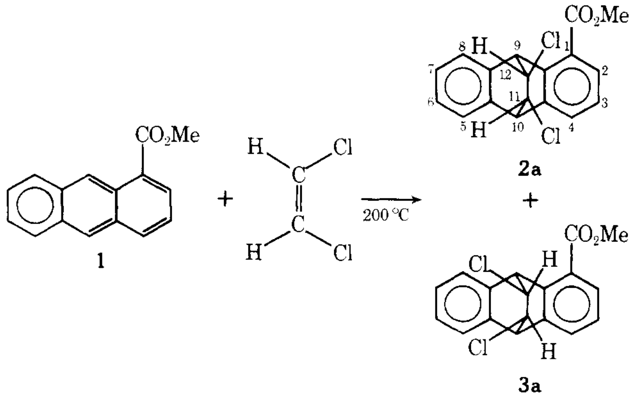


Table I. Apparent pK_a's[5] of Several Bridged Anthracene-1-carboxylic Acids in 50% Aqueous Ethanol at 25 °C

Acid	pK_a
2b	5.94, 5.94
3b	5.48, 5.50
9b[a]	5.96 ± 0.01

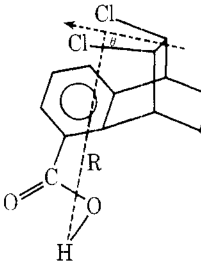
[a] Average of five runs determined potentiometrically in 50% by weight aqueous ethanol.

on the basis of the patterns of ^{13}C chemical shifts observed for the ring carbons.[3] They are consistent with the pK_a's determined for the corresponding acids **2b** and **3b** obtained by hydrolysis of the esters.

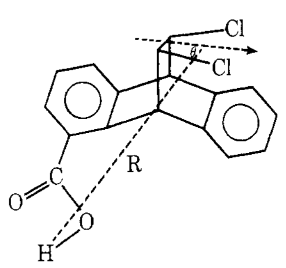
The apparent pK_a's for **2b** and **3b** were determined by potentiometric titration in 50% by volume aqueous ethanol at 25 °C. The results are summarized in Table I. Included for comparison is the apparent pK_a for 9,10-ethano-9,10-dihydro-1-anthroic acid (**9b**) reported by Stock.[4]

Discussion

An inspection of the data in Table I reveals the expected increase in acidity for the anti dichloro acid **3b** compared with the unsubstituted acid **9b.** The magnitude of this difference is comparable to the ΔpK_a (0.57) observed for the analogues bearing the carboxylate group at the 2 position.[2a] In the present case the shorter distance separating the site of ionization and the resultant dipole is compensated by a larger acute angle, θ, found in the K–W expression and perhaps by a larger effective dielectric constant. By contrast, the apparent pK_a of the syn-dichloro acid **2b** is, within experimental error, the same as that for the unsubstituted acid **9b.** This vanished substituent effect is predicted by the K–W equation. The results are not accommodated by the classical inductive model. The pertinent structural features of **2b** and **3b** are illustrated. The distances R and the angles θ were calculated assuming the geometry of ethanoanthracene adopted by Arbusov and Vereshchagen.[6,7] The distances and angles are with reference to a resultant dipole which bisects the C_{11}–C_{12} bond and lies in the plane containing the two chlorines.[8] For purposes of K–W calculations, the magnitude of the resultant dipole was estimated. Since two carbon–chlorine dipoles in close proximity are not electrically independent of one another, a vector summation of two single C–Cl bond moments cannot provide a reliable resultant.[9] Consequently the resultant dipole formed from the two C–Cl bonds in **2b** and **3b** was calculated from dipole moments experimentally determined[2a] for 9,10-dihydro-9,10-ethanoanthracene (**8**) and *cis*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene (**6**). The dipole moment found for **8** is 0.92 D; that for **6** is 2.92 D. The measured dipole moment of **6** can be attributed to two contributing dipoles. The two carbon–chlorine dipoles (forming the "resultant" dipole whose value is sought) are assumed to lie in a plane 60° off the axis which bisects the C_{11}–C_{12} bond and bisects a line joining C_9 and C_{10}. The dipole moment of **8** is collinear with this same axis with the negative end in the direction of the region flanked by the aromatic rings. Using these vector quantities, the "resultant" moment formed by the two C–Cl bonds is calculated to be 3.27 D. Table II lists the calculated values for R's and θ's, as well as for D_E[10] and log K/K_0. The Tanford modification[11] was adopted with respect to placement of charges and dipoles relative to the cavity surface. The dielectric constant of the solvent (50% by weight aqueous ethanol) is 49.[12]



2b



3b

Thus the K–W expression predicts a vanished substituent effect for **2b.**[13] This is the direct result of the value of θ, which is approximately 90° within the limits of uncertainty of the structural parameters used in its estimation.[13] The calculated ΔpK_a for the anti acid **3b** is, at best, in fair agreement with the experimental value when the Tanford ellipse cavity is employed. The Tanford spherical model leads to a major underestimation of D_E.

Experimental Section[14]

Anthraquinone-1-carboxylic Acid. Using the procedure developed by Coulson,[15] freshly recrystallized benzanthrone (20.0 g, 0.087 mol) was oxidized with 82 g of chromium trioxide. The product was obtained in 69% yield as a beige-colored solid, mp 298–300.5 °C (lit.[4] mp 292–293 °C).

1-Anthroic acid was prepared by the zinc reduction of anthraquinone-1-carboxylic acid as described by Stock.[4] Best results were obtained when the zinc was activated with 6 N HCl immediately prior to use. The product was obtained in 73% yield, mp 248–250 °C (lit.[4] mp 249 °C).

1-Methyl anthroate (1) was prepared in 93% yield by esterification with ethereal diazomethane. The ester was obtained as yellow plates, mp 100.5–103.5 °C (lit.[16] mp 104 °C), and was used without further purification in the reactions with *cis*-dichloroethylene.

Methyl *syn*- and *anti-cis*-11,12-Dichloro-9,10-dihydro-9,10-ethano-1-anthroates (2a and 3a). A sample of 5.0 g (0.021 mol) of 1-methyl anthroate, 0.1 g of 2,6-di-*tert*-butylphenol, 6.8 ml of freshly distilled *cis*-1,2-dichloroethylene, and 20 ml of toluene were combined in a heavy-walled, 25 × 200 mm tube. The mixture was degassed and the tube sealed. The tube was heated in a steel bomb at 194–203 °C for 72 h. The tube was opened and the mixture examined by NMR. The spectrum showed that over 90% of the methyl anthroate had reacted. Separation of the products and starting ester was performed by liquid chromatography in a 25 × 300 mm column packed with 100–200 mesh Florisil in hexane. The esters were eluted in the following order with partial resolution: methyl anthroate (~4/1 hexane–benzene), syn ester **2a** (~1/1 hexane–benzene), and anti ester **3a** (~pure benzene). Recrystallizations of appropriate fractions from CCl_4 afforded **2a** as a white solid, mp 156–158 °C, and **3a** as a white solid, mp 178–179 °C. Yields from several cycloadditions averaged in the range of 15–20% for each pure isomer.

The mass spectra of both isomers show a parent peak at *m/e* 332 and an intense peak at *m/e* 301 ($M^+ - OCH_3$). The infrared spectra (KBr disks) are very similar. They show the expected carbonyl stretch at approximately 1715 cm^{-1}. Small differences are observable in the 600–800-cm^{-1} region. A distinct difference in NMR spectra (taken in CCl_4) is observed. The C-9 proton of the syn (**2a**) ester appears at 6.12 ppm. The C-9 proton of the anti (**3a**) ester appears at 5.73 ppm. A similar deshielding of C-9 protons in a number of 1-substituted anthracenes has been described.[17]

Table II. Parameters and Calculated Values of Log K/K_H for *syn*- (2b) and *anti*- (3b) *cis*-11,12-dichloro-9,10-dihydro-9,10-ethano-1-carboxylic Acids

	Parameters			Tanford sphere		Tanford ellipse		Measured
	R, Å	μ, D	θ	D_E	Log K/K_H	D_E	Log K/K_H	Log K_X/K_H
2b	5.44	3.27	89	4.24	0.01	7.33	0.01	0.02 ± 0.02
3b	6.01	3.27	46.4	4.50	0.70	8.64	0.36	0.47 ± 0.02

Anal. Calcd for $C_{18}H_{14}Cl_2O_2$: C, 64.88; H, 4.20; Cl, 21.30. Found for **2a:** C, 64.95; H, 4.25; Cl, 21.18. For **3a:** C, 64.86; H, 4.28; Cl, 21.56.

***syn-cis*-11,12-Dichloro-9,10-dihydro-9,10-ethano-1-anthroic Acid (2b).** A 1.30-g (3.91 mmol) sample of **2a** was combined with 50 ml of methanolic NaOH (0.55 g NaOH in 50 ml of methanol) and boiled under reflux for 1 h. The mixtue was cooled, diluted to 200 ml with water, and filtered. The filtrate was acidified with 6 N HCl. The white solid was collected, repeatedly washed with water, and dried. The acid was thus obtained in 96.4% yield, mp 266–269 °C. Recrystallization from benzene raised the melting point to 267–270 °C.

The mass spectrum shows the parent ion at *m/e* 318. The infrared spectrum (KBr disk) shows a broad carboxylic acid O–H band centered at 3040 cm^{-1} and a carbonyl at 1680 cm^{-1}. The NMR spectrum (Me_2SO-d_6) shows (in addition to the aromatic protons) two apparent singlets at 4.78 and 6.05 ppm. The former is assigned to the protons at C-10, C-11, and C-12, and the latter to the proton at C-9.

Anal. Calcd for $C_{17}H_{12}Cl_2O_2$: C, 63.95; H, 3.76; Cl, 22.2. Found: C, 64.15; H, 3.88; Cl, 22.0.

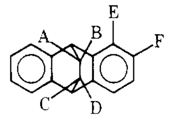
***anti-cis*-11,12-Dichloro-9,10-dihydro-9,10-ethano-1-anthroic Acid (3b).** This acid was prepared by hydrolysis of **3a** as described for the syn isomer. The acid was initially obtained in 96% yield as white crystals, mp 251–254.5 °C. Recrystallization from chloroform yielded the pure acid, mp 258–259.5 °C.

The mass spectrum shows the parent ion at *m/e* 318. The infrared spectrum is similar to that of its isomer **2b** with slight differences observable in the fingerprint region. The NMR spectrum of **3b** (Me_2SO-d_6) shows, in addition to the aromatic proton signals, the C-9 proton as a singlet at 5.85 ppm. The peaks for the C-10, C-11, and C-12 protons coincide to give an apparent singlet at 4.73 ppm.

Anal. Calcd for $C_{17}H_{12}Cl_2O_2$: C, 63.95; H, 3.76; Cl, 22.2. Found: C, 63.81; H, 4.00; Cl, 22.3.

Acknowledgments. We wish to express our appreciation to Professor G. E. Maciel and Dr. D. Miiller for their invaluable help in confirming our geometric assignments in the course of their study of the ^{13}C NMR properties of a number of these bridged anthracene derivatives.

Registry No.—1, 25308-58-1; **2a,** 60573-54-8; **2b,** 60573-55-9; **3a,** 60618-77-1; **3b,** 60618-78-2; *cis*-1,2-dichloroethylene, 156-59-2.



2a, A = C = F = H; B = D = Cl; E = CO_2Me
3a, B = D = F = H; A = C = Cl; E = CO_2Me
4, A = C = E = H; B = D = Cl; F = CO_2Me
5, B = D = E = H; A = C = Cl; F = CO_2Me
6, A = C = E = F = H; B = D = Cl
7, A = D = E = F = H; B = C = Cl
8, A–F = H
9a, A–D, F = H; E = CO_2Me
10, A–E = H; F = CO_2Me

References and Notes

(1) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(2) See (a) E. J. Grubbs, R. Fitzgerald, R. E. Phillips, and R. Petty, *Tetrahedron*, 935 (1971); (b) C. L. Liotta, W. F. Fisher, E. L. Slighton, and C. L. Harris, *J. Am. Chem. Soc.*, **94**, 2129 (1972); (c) L. M. Stock, *J. Chem. Educ.*, **49**, 400 (1972); (d) A. B. Thigpen, Jr., and R. Fuchs, *J. Org. Chem.*, **34**, 505 (1969); (e) K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963); and references cited therein.

(3) The ^{13}C study was conducted by Professor G. E. Maciel and Dr. D. Miiller at Colorado State University. The chemical shift assignments of **2a, 3a, 4,** and **5** were made largely on the basis of derived patterns of additivity relationships among the shifts of compounds **2a–10,** methyl benzoate (**11**), methyl *m*-toluate (**12**), and methyl 3,4-dimethylbenzoate (**13**). A set of shifts for all the above compounds **2a–10** was derived which was entirely self-consistent within an assumed framework of additivity of ^{13}C shifts of the ring carbons. ^{13}C–^1H splitting patterns and selective ^1H decouplings were also employed in making these assignments. The sources for several of these model compounds and a complete discussion of this investigation will be published elsewhere.

(4) R. Golden and L. M. Stock, *J. Am. Chem. Soc.*, **94**, 3080 (1972).

(5) Since Stock's value for the unsubstituted compound **9b** was reported in 50% by weight aqueous ethanol and ours were determined in 50% by volume aqueous ethanol, we repeated the titration of **2b** in 50% by weight aqueous ethanol. The value thus obtained, 5.93, is within the experimental error of that obtained in the 50% by volume aqueous ethanol shown in Table I.

(6) B. A. Arbusov and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **No. 6,** 1004 (1964).

(7) The chlorines on carbons 11 and 12 were assumed to form tetrahedral angles with the C_{11}–C_{12} bond and to lie in a plane which forms a 120° angle with the plane of carbons 9, 10, 11, and 12. The bond lengths were taken to be C–Cl (1.77 Å), C_{sp^3}–C_{sp^3} (1.54 Å), C_{sp^3}–C_{sp^2} (1.50 Å), aromatic C–C (1.39 Å), and C_1–C_{17} (carboxylate carbonyl carbon) (1.46 Å). The carboxyl proton was placed at 1.45 Å beyond the carboxyl carbon on an extension of the line joining it to C_1.

(8) The dibenzobicyclo[2.2.2]octadiene ring system is extremely rigid. The degree of molecular readjustment from dipole–dipole interactions (and possibly charge–dipole interactions in the anion) via ring deformation involving motions of C_{11} and C_{12} would appear to be minimal.

(9) See C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, N.Y., 1955, pp 237–254.

(10) The tables given by F. H. Westheimer, W. A. Jones, and R. A. Lad [*J. Chem. Phys.*, **10,** 478 (1942)] were used.

(11) C. Tanford, *J. Am. Chem. Soc.*, **79,** 5348 (1957).

(12) The dielectric constant of 50% by volume aqueous ethanol at 25 °C is 53.8 [see M-L. Le Huérou and C-R. Guérillot, *C. R. Acad. Sci.*, **258,** 2549 (1964)]. The calculation of D_E is insensitive to variations in solvent dielectric constant of this magnitude.

(13) If the dominating effect on the ionization were the C–Cl dipole at C_{12}, its angular orientation could induce a reverse substituent effect (acid weakening). However, an anticipated reversed substituent effect in a related acid (the structural isomer of **2b** possessing the carboxyl group at C_2) was not observed.[2a] A possible reason for this was discussed.

(14) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer. Nuclear magnetic resonance spectra were determined with a Varian Model A-60 or JEOL Model JNM-PS-100 spectrometer. The mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer. The pK_a measurements were made using a Beckman research pH meter equipped with a Beckman No. 39000 glass electrode and a Beckman No. 39071-A3U calomel electrode. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich.

(15) E. A. Coulson, *J. Chem. Soc.*, 1931 (1930). See also S. Akiyama and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **33,** 1291 (1960).

(16) S. Akiyama, *Bull. Chem. Soc. Jpn.*, **35,** 1826 (1962).

(17) F. Gobert, S. Combrisson, and N. Platzer, *Tetrahedron*, **30,** 2919 (1974).