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ANGULAR DEPENDENCE OF SUBSTITUENT EFFECTS IN GEOMETRICALLY ISOMERIC 11,12-DICHLORO-9,10-ETHANOANTHRACENES (1)

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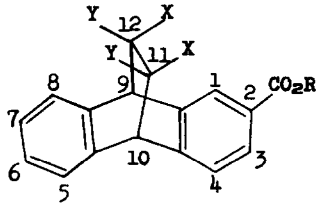
Recently we described preliminary work on some spiro [3.4] octane derivatives directed towards an experimental assessment of the importance of field effects (2). The criteria outlined previously (2) which we are using to guide us in this task have led us to explore several other systems. The bridged anthracene derivatives described below satisfy these criteria. In considering rate or equilibrium processes involving these compounds a comparison of 1 and 2 or 4 and 5 would require inductive effects to be identical since the distance through bonds is the same in each instance. Field effects, if operative, would differ because of differing distances and angular orientations between substituents and reaction sites and perhaps different effective dielectric constants.

The mixture of esters 1 and 2 was prepared by the Diels-Alder addition of cis-1,2-dichloroethylene to methyl 2-anthroate as described by Cristol for the addition of the same dihalide to anthracene (3). The two isomers were separated by a combination of column chromatography and crystallization. The syn isomer 1 shows a melting range of 160-162°. Its dipole moment in benzene is 3.80 D. The anti isomer 2 melts at 181-182.5° and has a dipole moment of 2.60 D in benzene.(4). The ethano bridged ester 3 was prepared by the addition of ethylene to methyl 2-anthroate. The corresponding acids 4,5, and 6 (6) were obtained from the esters by hydrolysis.

The apparent pK's for the three acids in 50% aqueous ethanol (v/v) were determined at 25° (7) and are as follows: acid 4, 6.07, 6.10; acid 5, 5.69, 5.67; acid 6, 6.25, 6.28. A comparison of the apparent pK's for 4 and 5 reveal a marked angular dependence of substituent effect.



	X	Y	R
1	Cl	H	CH_3
2	H	Cl	CH_3
3	H	H	CH_3
4	Cl	H	H
5	H	Cl	H
6	H	H	H

This suggests that dipolar field effects are operative in these isomers. However a comparison of values for 4 and 6 complicates any simple interpretation of these results on the basis of the Kirkwood-Westheimer field effect model exclusively. On this basis alone the syn isomer (4) would have been expected to be the weakest acid.* In agreement with this observed order of acidities is the order of rates of base hydrolyses of esters 1, 2 and 3. The second-order rate constants determined in 96% alcohol-4% water (v/v) at 25.00° are 1 - 0.265×10^{-3}, 2 - 0.682×10^{-3} and 3 - 0.148×10^{-3} (all 1 $mole^{-1}$ sec^{-1}). Although it is hazardous at best to attach too great a significance to a "three point plot" there is within this limitation an excellent linear relationship (correlation coefficient 0.997) between the logarithms of rate and apparent equilibrium constants for these two processes. This at least suggests the presence of a linear free energy relationship.

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* With reference to the Kirkwood-Westheimer equation (9), the relevant geometrical quantities associated with the bridged anthracene isomers 4 and 5 are as follows (for each C-Cl dipole, the distance r separating its midpoint from the carboxyl proton is followed by the angle θ formed by the dipole and this line): C_{12}-Cl_{syn}, 6.82 Å, -72°; C_{11}-Cl_{syn}, 7.46 Å, -84°; C_{12}-Cl_{anti}, 7.92 Å, 27°; C_{11}-Cl_{anti}, 8.47 Å, 5°. In determining these values we have assumed the geometry of ethano bridged anthracenes adopted by Arbusov and Vereshchagin (10). The carboxyl proton was placed at 1.45 Å beyond the carboxyl carbon on an extension of the line joining it to C_2.

The dibenzobicyclo [2.2.2] octadiene ring system is extremely rigid. It is impossible to construct this system with steel Dreiding models using normal tetrahedral units for carbons C_9-C_{12}. However it can be constructed with obvious strain using Fieser Plastic Dreiding models. In spite of this rigidity a small amount of relief from dipole-dipole repulsions and charge-dipole attractions or repulsions appears possible through ring deformations involving motions of C_{11} and C_{12}. The possible effect of such deformation on the geometry of the syn isomer (4) or its anion is of particular concern. It is instructive to consider the effects of ring deformation in which charge-dipole repulsion cause the C_{12}-$CO_2^{\ominus}$ distance to increase and the C_{11}-$CO_2^{\ominus}$ distance to diminish. When this is done and the original angle θ associated with the C_{12}-Cl dipole is forced to open to as large as -85°, the angle associated with the syn C_{11}-Cl dipole simultaneously decreases to about -65°. It is clear from this type of analysis that ring deformations such as these will not alter the predicted order of acidities of the three acids based upon the K & W electrostatic field model.

It is interesting that *we do not find a reversal in normal (inductive model) substituent effect* in the comparisons of reactivity between **1** and **3** and **4** and **6**. Such a reversal has been observed by Golden and Stock (11) in 8-substituted ethano-bridged anthracene-1-carboxylic acids. The reasons for the absence of a reversal in normal (inductive model) substituent effect with **1** and **4** are not completely clear. The tentative suggestion of a linear free energy relationship offers a possible argument against highly specific solvent interactions as the source of reactivity differences within the two series. One possibility is that inductive effects may be superimposed upon field effects in this system. Alternatively a field effect model which assumes a point dipole may be invalid in this system. M. J. S. Dewar and P. J. Grisdale [*J. Am. Chem. Soc*., **84**, 3539 (1962)] have criticized the point dipole model for reasonably small molecules in which the length of the dipole is comparable to the distance separating it from the reaction center. And Wilcox (12) recently discussed the importance of polarizable species contiguous with the molecular cavity in moderating the transmission of substituent effects. Accordingly in compounds **1**, **2**, **4** and **5** the C-Cl bonds may be considered as dipoles of finite length within the molecular cavity. Since the negative ends (Cl's) are closer to the edge of the cavity they would act through regions of higher effective dielectric constant than that through which the positive ends (C's) act. Thus the unexpected acid strength of **4** compared with **6** may reflect a diminished field exerted at the carboxylate center by the negative dipole ends. This could result in a dominating field originating near carbons 11 and 12 in spite of the slightly closer proximity of the chlorine atoms. The same explanation may account for differences in reactivity between **1** and **3**.

With regard to the interpretation given above, it is worth noting that Tanford's modification (13) of the Kirkwood-Westheimer model also reveals the critical dependence (of charge interactions) on the depth of the charges and dipoles within the molecular cavity.

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7. These values were determined potentiometrically using a procedure similar to that described by Wilcox and McIntyre (8).

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