Transmission of Polar Effects: Prediction by the Kirkwood–Westheimer Electrostatic Field Effect Model

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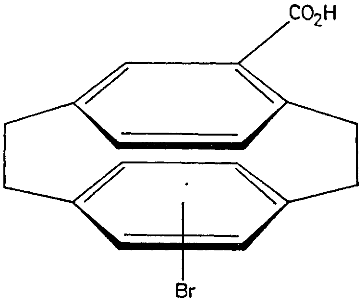
Summary The pK_a values of four pseudo-substituted bromo- and unsubstituted 4-carboxy[2.2]paracyclophanes have been measured and Kirkwood–Westheimer calculations carried out; the substituent effects observed are both normal and reversed, the electrostatic field theory accounting for them both qualitatively and, for the pseudo *ortho*-, *meta*-, and *para*-isomers, quantitatively.

Investigations of the transmission of substituent effects by either an inductive or electrostatic-field effect model suggest that the latter gives a more satisfactory description.[1,2] A study of the reactivity of isomeric pseudo substituted bromo-4-carboxy[2.2]paracyclophanes (I) has been carried out to test these models. The pK_a values of the acids in 2-methoxyethanol–water (4:1) have been measured (Table 1). The inductive model[3] would predict identical values for the pseudo *gem*- and *meta*-isomers and for the pseudo *ortho*- and *para*-isomers, as well as that the substituent effects would be very small. The field effect model used was that suggested by Kirkwood and Westheimer[4] and modified by others,[5] as shown in equation (1) for the point dipole.



(I)

Table 1. pK_a values of substituted 4-carboxy[2.2]paracyclophanes in 2-methoxyethanol–water (4:1) at 25 °C.

Substituent	pK_a
H	7·59
pseudo *gem*-Br	7·99
pseudo *ortho*-Br	7·75
pseudo *meta*-Br	7·28
pseudo *para*-Br	7·34

$$\log (K/K_0) = e\mu \cos \theta / 2.3kTR^2D_e \qquad (1)$$

Table 2 shows the observed and calculated ΔpK_a values using both the spherical point dipole and two-point dipole model approximations. While the pseudo *para*- and *meta*-isomers both show the normal and expected acid-strengthening effect, the pseudo *ortho*- and *gem*-isomers are both weaker than the unsubstituted acid. The latter

TABLE 2. Observed and calculated ΔpK_a values using the Kirkwood–Westheimer model for the ionisation of bromo-4-carboxy[2.2]paracyclophanes.

Substituent	ΔpK_a		
	Obs.	Calc.[a]	
		KW1	KW2
pseudo *gem*	0·40	0·73	1·01
pseudo *ortho*	0·16	0·06	−0·20
pseudo *meta*	−0·31	−0·33	−0·37
pseudo *para*	−0·35	−0·31	−0·39

[a] KW1 and KW2 are the spherical point dipole and two-point dipole model approximations, respectively.

reversed dipolar substituent effect has been observed previously in other systems,[2] where the 'negative end' of the dipolar bromo-substituent has a disproportionately strong influence resulting in a reversal of the normal substituent effect. These results are confirmed and/or amplified by studies of the reactivity of the acids with diazodiphenylmethane and the alkaline hydrolysis of their methyl esters.

The angular dependence and size of the substituent effects demonstrate cogently that an electrostatic field effect is in operation. The modified Kirkwood–Westheimer spherical cavity model accounts for the results relating to these 'sphere-like' molecules both qualitatively and, for the pseudo *ortho*-, *meta*- and *para*-isomers, quantitatively.

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