The Transmission of Polar Effects: the Reversed Dipolar Substituent Effect

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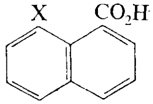
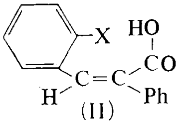
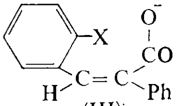
IN a communication[1] with the above title, Bowden and Parkin report measurements of the $\mathrm{p}K_a$ of 8-substituted 1-naphthoic acids, and of *cis*- and *trans*-α-phenylsuccinic acids carrying substituents in the ring *β*- to carboxyl. They interpret their results as indicating a reversed field effect of substituents when the substituent is nearer to the carboxyl group than is the ring carbon atom linked to the substituent.

While this conclusion is in principle entirely acceptable to us, in view of our own extensive work[2] on substituent effects (to which Bowden and Parkin do not refer), we must reluctantly point out that the evidence they present is unfortunately entirely inconclusive. It is well known from i.r. spectroscopic studies[3] of *o*-substituted phenols that all the substituents considered by Bowden and Parkin can form hydrogen bonds to adjacent acidic hydrogen atoms; hydrogen bonding of this type should then clearly be an important factor both in the 8-substituted 1-naphthoic acids (I) and in the *o*-substituted α-phenyl-*cis*-cinnamic acids (II). Such hydrogen bonding would of course stabilize the acids relative to their conjugate bases, and so lower their acidity; numerous examples of this kind of effect are known in the case of *o*-substituted benzoic acids. One need therefore look no further for the origin of the "anomalies" noted by Bowden and Parkin.

Their interpretation is not, in fact, self-consistent; for if the substituents in (II) acted solely by a field effect, steric interaction would greatly favour the geometry of (III) in which the effect of groups such as Cl should obviously be, if anything, more acid strengthening than in the *trans*-cinnamic acid. The sterically unfavourable orientation of X and carboxyl indicated in (II) would only be achieved if there were an *attraction* between the two groups; this of course is possible in the acid, through hydrogen bonding, but not in the conjugate base (III).


(I)


(II)


(III)

We of course were fully aware of the complications due to interactions of this kind and for this reason studied[2a] only unhindered derivatives of α-naphthoic acid where no such difficulties could arise; the same was true of the parallel studies by Wells and Adcock[4] (also ignored by Bowden and Parkin) on the substituted 2-naphthoic acids, where again care was taken to introduce substituents only into the five unhindered (4—8) positions, and of the ingenious experiments of Golden and Stock[5] who demonstrated the existence of the reversed dipolar field effect in a system where steric effects were again avoided.

Bowden and Parkin also state that previous studies had drawn no clear distinction between field and inductive effects; this is not true. The results reported by Dewar and Grisdale,[2a] and by

Wells and Adcock,[4] and by Golden and Stock,[5] are inconsistent with any interpretation in terms of inductive effects, and this conclusion has been further strengthened by recent work by Adcock and Dewar on the ^{19}F n.m.r. spectra of substituted fluoronaphthalenes in a paper[3c] which Boden and Parkin have also apparently overlooked.

This work is supported by a grant from the Robert A. Welch Foundation.

(*Received, March 25th,* 1968; *Com.* 370.)

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[1] K. Bowden and D. C. Parkin, *Chem. Comm.*, 1968, 75.

[2] (a) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539, 3541, 3546, 3548; (b) M. J. S. Dewar and A. P. Marchand, *ibid.*, 1966, **88**, 354, 3318; (c) W. Adcock and M. J. S. Dewar, *ibid.*, 1967, **89**, 379.

[3] See *e.g.* L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1959, p. 102.

[4] P. R. Wells and W. Adcock, *Austral. J. Chem.*, 1965, **18**, 1365.

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