The Transmission of Polar Effects: the Reversed Dipolar Substituent Effect

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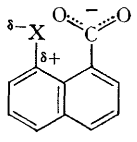
SEVERAL investigations have been made to distinguish between the inductive and the field effects for the transmission of polar substituent effects.[1] Unfortunately, the results for most model systems studied can be explained by both inductive transmission through the bonds connecting the substituent to the reaction site and by a field effect operating through the transmissive cavity. The molecular structures of these models involve the bonds that could transmit the effect inductively being contained in the low dielectric cavity which would transmit the field effect. However, the field effect of a dipolar substituent has an angular dependence[2] which is not involved for an inductive effect. If a suitable model is chosen, it should, in principle, enable the identification of the mode of transmission.[3] As part of an investigation of model systems, reversed dipolar substituent effects[4] have been observed. The dipolar substituent effect is usually characterised by that dipole end embedded in the molecule. If the substituent is sited in the molecule such that the dipole end not embedded in the molecule is very proximate to the reaction site, it can markedly reduce or even reverse the normal substituent effect. This reversal has been detected for a number of 8-substituted 1-naphthoic and *cis-ortho*-substituted α-phenylcinnamic acids.† The reactions of the acids studied were their ionisation in 80% 2-methoxyethanol–water at 25° and their esterification with diazodiphenylmethane in ethanol at 30°. In Tables 1 and 2, the ionisation constants for a number of these acids are shown.

The 8-substituted 1-napthoic acids all have the carboxylic group completely or very extensively deconjugated with the ring.‡ This results in acid-strengthening by preferentially de-stabilising the acid compared to the carboxylate anion.[7] For the 8-methyl substituted acid, the latter effect easily overcomes the small acid-weakening polar effect of the methyl group. However, all the strongly dipolar and *normally* acid-strengthening substituents are now weaker acids than the methyl acid (see Table 1). This results from the disproportionately strong influence of the "negative" end of dipolar substituent which is extremely close to the carboxylate group (I) and gives a reversal of the substituent effect. A similar effect occurs for the *cis-ortho*-substituted α-phenylcinnamic acids. Molecular models indicate that the *ortho*-substituent is very close to the carboxylate group in stable conformations of these acids. The transmission of polar effects from the *meta*- and *para*-positions is quite normal for both the *cis*- and *trans*-systems,§ *i.e.*, ρ/ρ_0 equal to between 0·4 and 0·5. The effect of the normally acid-strengthening *ortho*-substituents in the *cis*-series has been considerably modified (see Table 2), compared to the normal effects of *ortho*-substituents in the *trans*-series. This again results from a dipolar field effect in which the "negative" end of the dipole is very proximate to the carboxylate group. This effectively opposes the normal substituent effect (II). The results for the esterification reaction confirm and support these interpretations. Together with a recent report of a similar

TABLE 1

*p*K*a* *Values of 8-substituted 1-naphthoic acids in 80% 2-methoxyethanol–water at 25°*

Substituent	pK_a
H	6·40
Cl	6·04
Br	6·16
NO_2	6·00
Me	5·99

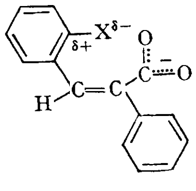


(I)

TABLE 2

*p*K*a* *Values of substituted α-phenylcinnamic acids in 80% 2-methoxyethanol–water at 25°*

Substituent	*cis*-Acids	*trans*-Acids
H	5·59	7·00
o-Cl	5·57	6·86
o-Br	5·64	6·80
o-NO_2	5·48	6·64
p-Cl	5·36	6·66
p-OMe	5·71	7·23
p-NO_2	5·08	6·33



(II)

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† The *cis*-configuration refers to the cinnamic acid structure, *i.e.*, the 3-phenyl and carboxylic groups.

‡ The deconjugation effect results in a twist of at least 60° for the carboxyl group, caused by the nitro-group, and even greater twists are caused by the other substituents (ref. 5). The resonance stabilisation will decrease by at least 75% for the nitro-group and more for the other substituents (ref. 6). This steric effect can be considered to be approximately constant for all the 8-substituents studied.

§ The large acid-strengthening effect observed for *cis*-compared to the *trans*-acids results from the deconjugation of the 3-phenyl and carboxylate groups with the olefinic link due to steric interactions.

effect,[4] these studies establish the importance of transmission by the field effect for these dipolar substituents. Other explanations have been advanced to explain related observations.[8]

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