Transmission of Polar Effects. Part 18.[1] Ionisation and Esterification with Diazodiphenylmethane of a series of 3-(8-Substituted-1-naphthyl)propiolic and (*E*)-3-(8-Substituted-1-naphthyl)acrylic Acids and the Alkaline Hydrolysis of the Methyl Esters of the Former Series

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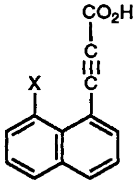
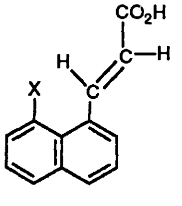
The pK_a values of 3-(1-naphthyl)propiolic acid, together with the 8-bromo- and 8-chloro-substituted derivative, and of (*E*)-3-(1-naphthyl)acrylic acid, together with the 8-bromo- and 8-chloro-substituted derivatives, have been determined in 80% (w/w) 2-methoxyethanol–water at 25 °C. The rate coefficients for the esterification of these acids with diazodiphenylmethane have been measured in 2-methoxyethanol at 30 °C. The rate coefficients for the alkaline hydrolysis of the corresponding methyl propiolates have been determined in 70% (v/v) dioxane–water at both 30.0 and 50.1 °C. In the ionisation and esterification reactions, reversed dipolar substituent effects were observed. The ΔpK_a values are quantitatively accounted for either by comparison with the results for simple model compounds or by Kirkwood–Westheimer calculations. The retardations observed for the effect of 8-halo substituents in the alkaline hydrolysis reaction are in agreement with a reversed dipolar effect and no steric 'bulk' effects are observed.

The reversal of normal dipolar substituent effects in a series of different model systems[2] has been considered to be strong evidence for the importance of field effects in the transmission of substituent polar effects. However, an alternative explanation, the steric inhibition of solvation, has been offered in other situations.[3] In an early study,[4] Roberts and Carboni studied the effects of *ortho*-substituents on the reactivity of phenylpropiolic acid. They considered that their results indicted the comparable importance of the inductive and field effects, but suggested more extreme models would be a more satisfactory test. Such a model, (8-substituted 1-naphthyl)-propiolic acid (**1**) was first suggested by them. This 'J-shaped' molecule should be close to an ideal design for the observation of dipolar substituent effects reversals, if such are real. On the other hand, the occurrence of direct primary or secondary steric effects should be absent or minimal due to the relatively distant seat of the substitution from the reaction centre.



(**1**)

In the present study, we have prepared novel systems which have both the advantages of rigidity and the lack of proximity of the substituent to the reaction site. The reactivity of (8-substituted 1-naphthyl)propiolic acids (**1**), as well as their methyl esters, and (*E*)-3-(8-substituted-1-naphthyl)acrylic (**2**) acids have been investigated.[5]



(**2**)

Table 1. pK_a Values of 3-(8-substituted-1-naphthyl)propiolic and (*E*)-3-(8-substituted-1-naphthyl)acrylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C and rate coefficients (k_2) for esterification of the acids with DDM in 2-methoxyethanol at 30 °C.[a]

Acid	Substituent	pK_a	k_2/dm^3 mol^{-1} min^{-1}
Propiolic	H	4.42	16.7
	Br	4.70	12.5
	Cl	4.90	9.30
Acrylic	H	6.71	0.729
	Br	7.05	0.427
	Cl	7.03	0.400

[a] The measurements are the mean of at least two determinations. The pK_a values are reproducible to within ±0.02 unit and the rate coefficients to within ±3%.

Results and Discussion

*p*K$_a$ *Values.*—The pK_a values of the acids were measured in 80% (w/w) 2-methoxyethanol–water at 25 °C (Table 1). The pK_a values of the unsubstituted 1-naphthylpropiolic (4.42) and (*E*)-3-(1-naphthyl)acrylic (6.71) acids are only slightly less acidic than the corresponding phenyl substituted acids (4.30 and 6.68, respectively).[6] The same substituent changes in the acids RCH_2CO_2H and $R[CH_2]_2CO_2H$ are also small but in the opposite direction.[7] Thus, it can safely be assumed that no significant steric inhibition of solvation effect is associated with the change from the phenyl to 1-naphthyl group in such systems.

The effects of the 8-halo substituents in both systems are

Table 2. Kirkwood–Westheimer calculations for the 3-(8-substituted-1-naphthyl)propiolic and (*E*)-3-(8-substituted-1-naphthyl)acrylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C.

		ΔpK_a		
	Substituent	Found	Calcd.[a]	Calcd.[b]
Propiolic	Br	-0.28	-0.74	-0.42
	Cl	-0.48	-0.75	-0.42
Acrylic	Br	-0.34	-0.80	-0.34
	Cl	-0.32	-0.77	-0.32

[a] By two-point charge approximation. [b] By point charge approximation.

Table 3. Rate coefficients (k_2) for the alkaline hydrolysis of methyl (8-substituted-1-naphthyl)propiolates in 70% (v/v) dioxane–water.[a]

	k_2/dm^3 mol^{-1} min^{-1}	
Substituent	30.0 °C	50.0 °C
H	43.8	155.3
Br	22.4	93.8
Cl	22.1	91.8

[a] Rate coefficients are reproducible to within ±3%.

Table 4. Activation parameters for the alkaline hydrolysis of methyl (8-substituted-1-naphthyl)propiolates in 70% (v/v) dioxane–water at 30.0 °C.[a]

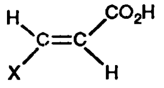
Substituent	$\Delta H^\ddagger$/kcal mol^{-1} [b]	$\Delta S^\ddagger$/cal mol^{-1} K^{-1}
H	11.7	-21
Br	13.3	-17
Cl	13.3	-17

[a] Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are considered accurate to within ±300 cal mol^{-1} and ±2 cal mol^{-1} K^{-1}, respectively. [b] 1 cal = 4.184 J.

quite consistent. The normally acid-strengthening and electron-withdrawing groups are strongly acid-weakening to the extent of about 0.3 to 0.5 pK_a units. This would appear to be a clear and unequivocal example of a reversed dipolar substituent effect which arises from the end of the dipole normally associated with the government of the effect which is now more distant from the reaction site than the other end. On the basis of an inductive transmission, the 8-halo substituent (which can be considered to be a *meta*-type substituent) can be estimated to have an effect of -0.2 pK_a unit, by the use of a reasonable transmissive factor and the ρ value for benzoic acids in this medium.[7]

$$\text{X—C}\equiv\text{C—CO}_2\text{H}$$

(3)



(4)

Two types of model calculations can be made to assess the reality of the reversal. Firstly, a semiempiric model can be used when an estimation of the polar effect of a 'non-reversed' substituent is made. The 'non-reversed' models for (1) and (2) are considered to be 3-substituted-propiolic (3) and (*E*)-3-substituted-acrylic (4) acids, respectively. There are limitations in both cases. Whereas the geometry of the systems are in reasonable agreement, the halo group in (3) is bonded to a C_{sp} atom and through conjunction in (2) is not likely to be complete. In spite of such limitations, an estimate of ΔpK_a for the effect of the 3-halo substituents can be made from studies by Charton,[8] Guilleme and Wojtkowiak,[9] and Bowden.[10] The transmission of polar effect in systems (3) and (4), as for *ortho*-substituted benzoic acids,[6] appears to be insensitive to medium.[10] For the effect of 3-halo groups, estimates of a ΔpK_a of about -0.4 pK_a unit in the propiolic system, relative to 3-phenylpropiolic acid, and of about -0.5 pK_a units for the (*E*)-acrylic system appear reasonable. This is in remarkable agreement for a complete 'reversal' of the results observed for the 8-halo-1-naphthyl systems. Secondly, the 3-(8-substituted-1-naphthyl)propiolic acid system has a simple coplanar structure not associated with the corresponding acrylic acid system. In the latter system, the planes of the naphthalene ring and acrylic acid system are considered to be orthogonal; with the ethylene group completely deconjugated with the aromatic ring by the 'bulky' 8-substituents.[11] Calculations (see the Experimental section) of the field effect of the 8-substituents in both systems have been carried out by using Kirkwood and Westheimer theory[12] for an Ehrenson ellipsoidal cavity model,[13] as shown in Table 2. The results for the point dipole approximation are in very good agreement with the ΔpK_a found. Only qualitative agreement exists for the two-point charge approximation. The present result confirms and supports the cause indicated earlier of the reversal of the normal dipolar substituent. Alternative interpretations of such reversals which arise from hydrogen bonding in the acid or steric inhibition of solvation in the anion (see below) are simply not feasible in this system because of the structural design.

Esterification with Diazodiphenylmethane (*DDM*).—The rate coefficients for the esterification of the acids with DDM in 2-methoxyethanol at 30 °C are shown in Table 1. This reaction has a rate-determining step which involves the transfer of a proton from an acid to DDM and has been used successfully in the estimation of the polar effects of substituents.[14] The same reversal of the dipolar substituent effect of all four halo-substituted acids in the esterification reaction is observed as that for the ionisation reaction. The magnitudes of the reversals for the esterification are approximately as would be expected on the basis of a comparison of Hammett reaction constants for *meta*/*para*-substituted benzoic acids in the relevant solvent systems, *i.e.* ρ for DDM esterification at 30 °C in 2-methoxyethanol is 1.18[15] and that for ionisation at 25 °C in 80% aqueous 2-methoxyethanol is 1.66.[7] This is in contrast with the diminished or even non-reversals noted in other systems for the esterification reaction.[2,16] The symmetry of the geometrical disposition of the halo group in the molecular systems under present study with regard to the transition state for esterification determines this result and further confirms the nature of the cause of the reversal.

Alkaline Hydrolysis.—The alkaline hydrolysis of the methyl 3-(8-substituted-1-naphthyl)propiolates has been studied in 70% (v/v) dioxane–water at 30.0 and 50.0 °C, as shown in Table 3. The activation parameters are shown in Table 4. The rate retardations could result from either a reversal of the normal dipolar substituent effect of the 8-halo substituents, the 'bulk' steric effect of the latter, or a combination of both.[17] However, again, the magnitudes of the retardation for the hydrolysis are as would be expected on the basis of a comparison of Hammett reaction constants for the *meta*/*para*-substituted benzoic acid systems in the relevant solvent systems, *i.e.* ρ for alkaline hydrolysis of methyl benzoates in 70% (v/v) dioxane–water at 30 °C is 2.20[18] and that for ionisation is 1.66.[7] Thus, there is no evidence or requirement for a steric 'bulk' effect in the alkaline hydrolysis of the 8-substituted esters under study, in great contrast with the same reaction of methyl 8-substituted-1-naphthoates.[19] The effects noted on the activation parameters are in agreement with this interpretation. The increased $\Delta H^\ddagger$ values are consistent with a reversed dipolar substituent effect of the 8-halo substituents, *i.e.* an 'electron-releasing' effect.[17] There are no significant changes in the $\Delta S^\ddagger$ values as would be expected in the absence of a significant steric 'bulk' effect.

Experimental

Materials.—The 3-(1-naphthyl)propiolic and (*E*)-3-(1-naphthyl)acrylic acids were prepared by the following sequence. The 1-hydroxymethylnaphthalenes were oxidised to the corresponding aldehydes. The latter gave the corresponding acrylic acids by means of the Perkin reaction. The propiolic acids were prepared by successive bromination and dehydrobromination of the acrylic acids.

8-*Bromo*-1-*naphthaldehyde.*—To pyridinium chlorochromate (21.5 g, 0.1 mol) in anhydrous methylene chloride (150 cm^3) was added 8-bromo-1-hydroxymethylnaphthalene (15.8 g, 66.6 mmol) in anhydrous methylene chloride (20 cm^3) in one portion while the reaction mixture was stirred. After 2 h, dry ether was added and the supernatant liquid was decanted from the black gum. The insoluble residue was washed thoroughly four times with 40 cm^3 portions of anhydrous ether whereupon it became a black, granular solid. The combined organic solution was passed through a silica gel column and eluted with 20 cm^3 of anhydrous ether. The pale yellow solution was then evaporated to give the crude *aldehyde*, which was recrystallised from light petroleum (b.p. 60–80 °C) to give the aldehyde as colourless needles (10.8 g, 69%), m.p. 88–89 °C (Found: C, 56.2; H, 2.7; Br, 34.1; O, 7.0. $C_{11}H_7BrO$ requires C, 56.2; H, 3.0; Br, 34.0; O, 6.8%).

8-*Chloro*-1-*naphthaldehyde.*—This was prepared by the method described above as colourless needles (8.9 g, 74%), m.p. 98.5–100 °C (Found: C, 68.8; H, 3.7; Cl, 18.8; O, 8.7. $C_{11}H_7CO$ requires C, 69.3; H, 3.7; Cl, 18.6; O, 8.4%).

(E)-3-(1-*Naphthyl*)*acrylic Acid.*—This was prepared by use of the Perkin reaction[20] to give the acid, m.p. 208–209 °C (lit.,[20] 207.5 °C).

3-(1-*Naphthyl*)*propiolic Acid.*—The acrylic acid above was esterified to form the ethyl ester, which was then brominated.[20] Dehydrobromination by alcoholic potassium hydroxide gave the required propiolic acid,[20] m.p. 134–135.5 °C (lit.,[20] 138–139 °C).

(E)-3-(8-*Bromo*-1-*naphthyl*)*acrylic Acid.*—The acid was prepared by the use of the Perkin reaction as described above as colourless plates (from acetone) (8.1 g, 29%), m.p. 227.5–229 °C (Found: C, 56.3; H, 3.2; Br, 29.5; O, 11.0. $C_{13}H_9BrO_2$ requires C, 56.3; H, 3.3; Br, 28.8; O, 11.5%).

3-(8-*Bromo*-1-*naphthyl*)*propiolic Acid.*—This was prepared as described above as pale brown needles (from chloroform) (1.6 g, 23%), m.p. 167–168.5 °C (Found: C, 56.4; H, 2.3; Br, 29.9; O, 11.4. $C_{13}H_7BrO_2$ requires C, 56.8; H, 2.6; Br, 29.1; O, 11.6%).

(E)-3-(8-*Chloro*-1-*naphthyl*)*acrylic Acid.*—The acid was prepared by use of the Perkin reaction as described above as pale yellow plates (from aqueous ethanol) (7.2 g, 30%), m.p. 219–221 °C (Found: C, 66.5; H, 3.8; Cl, 15.2; O, 14.5. $C_{13}H_9ClO_2$ requires C, 67.1; H, 3.9; Cl, 15.2; O, 13.8%).

3-(8-*Chloro*-1-*naphthyl*)*propiolic Acid.*—This was prepared as described above as pale brown needles (from aqueous ethanol) (1.1 g, 16%), m.p. 159–161 °C (Found: C, 67.4; H, 3.0; Cl, 15.2; O, 14.4. $C_{13}H_7ClO_2$ requires C, 67.7; H, 3.1; Cl, 15.4; O, 13.9%).

The propiolic acids were esterified almost quantitatively with diazomethane in ether.

Methyl 3-(1-*naphthyl*)*propiolate* was obtained as a viscous oil, b.p. 120 °C at 0.5 mmHg (Found: C, 79.5; H, 4.9; O, 15.6. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8; O, 15.2%).

Methyl 3-(8-*bromo*-1-*naphthyl*)*propiolate* was obtained as pale yellow plates, m.p. 75–76 °C (Found: C, 68.1; H, 3.0; Br, 27.4; O, 11.5. $C_{14}H_9BrO_2$ requires C, 58.2; H, 3.1; Br, 27.6; O, 11.1%).

Methyl 3-(8-*chloro*-1-*naphthyl*)*propiolate* was obtained as pale yellow plates, m.p. 80–81.5 °C (Found: C, 68.3; H, 3.7; Cl, 14.4; O, 13.6. $C_{14}H_9ClO_2$ requires C, 68.7; H, 3.7; Cl, 14.5; O, 13.1%).

General.—All products had IR, ^1H and ^{13}C NMR, and mass spectra in accord with the stated structures. The solvents and DDM were prepared as previously described.[18,21]

Measurements.—The pK_a values and the rate coefficients for esterification with DDM were determined as described previously.[21,22] The rate coefficients for the alkaline hydrolysis of the esters were measured as previously described.[23] The substrate and hydroxide anion concentrations were 2.5×10^{-4} and 5×10^{-3} to 1×10^{-1} mol dm^{-3}, respectively. The reactions were followed at the λ value showing maximum difference between substrate and product, *i.e.* 330–350 nm. The reactions were first order in both substrate and hydroxide. As the reactions were carried out in an excess of base, the resulting first-order behaviour could be observed without deviation for three 'half-lives.' The products (the anions of the corresponding acids) were obtained quantitatively from preparative-scale reactions and their identities were confirmed by spectral comparison with the acids in basic solution. This is particularly important for these esters as Fuchs[24] found significant addition to the triple bond in related esters in aqueous ethanol containing base.

Kirkwood–Westhheimer Calculations.—These were carried out in a similar way to that described previously[2] for ellipsoidal cavity[13] with both a two-point and point-charge approximation. The molecular parameters required were taken from the literature.[25] The dipole moments and dipole bond lengths were taken from the literature for substituted benzenes.[25,26] The relative permittivity* of the molecular cavity was taken as 2 and that of the solvent [80% (w/w) aqueous 2-methoxyethanol] as 32.[27] The procedure used was that of Ehrenson[13] and was in accord with that of Orttung.[28]

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Paper 0/00491J
Received 2nd *February* 1990
Accepted 7th *March* 1990