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The Reactivity of *p*-Nitrophenyl Esters with Surfactants in Apolar Solvents. VII* Substituent Effects on the Reactivity of 4′-Nitrophenyl 4-Substituted Benzoates in Benzene Solutions of Dodecylammonium Propionate and Butane-1,4-diamine Bis(dodecanoate)

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Abstract

The rate of decomposition of a series of 4′-nitrophenyl 4-substituted benzoates has been measured at 341 K in benzene solutions of dodecylammonium propionate and butane-1,4-diamine bis(dodecanoate). The bimolecular rate constant due to general acid–general base catalysis from the head-group components of the surfactants is dependent on the nature of the substituents, and the rate data have been correlated by Hammett σ and σ^+, Tsuno–Yukawa, and Taft dual substituent parameter linear free energy relationships. The reactivity of the esters has also been compared with the ^{13}C n.m.r. chemical shift of their carbonyl carbon atoms. The results are consistent with a mechanism involving a general-acid-catalysed aminolysis of the unprotonated ester.

Extensive studies have been made on the effects of lengthening the carbon chain, in both the amine and carboxylate head groups, of alkylammonium carboxylate surfactants,[1] and the alkanediamine chain in a homologous series of alkane-α,ω-diamine bis(dodecanoate) surfactants,[2] on the reactivity of *p*-nitrophenyl acetate (pnpa) in benzene solutions. However, no investigation has been made on changes in reactivity in these detergent systems effected by substituents on the substrate ester.

Nearly 60 years ago, Brönsted and Pedersen[3] reported that a series of rate constants, k_B, which they had measured for the base-catalysed decomposition of nitramide, bore a simple relationship to the basicity constants, K_B, of the catalysts. They then suggested that similar correlations might be found for other proton-transfer reactions. It is now generally accepted that all reactions showing general acid or general base catalysis will give relationships of the Brönsted type, namely equation (*1*) for general acid catalysis and equation (*2*) for general base catalysis:

$$\log k_A = \alpha \log K_A + c \qquad (1)$$

$$\log k_B = \beta \log K_B + c' \qquad (2)$$

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* Part VI, *Aust. J. Chem.*, 1983, **36**, 907.

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A decade later, Hammett[4] was able to generalize the regularities in the reactivity of benzene derivatives and formulated a linear free energy relationship

$$\log(k_X/k_H) = \rho\sigma \quad (3)$$

between the rate constant, k_X, for reaction of a monosubstituted benzene and k_H, that for the corresponding reaction of the unsubstituted compound, through a reaction constant, ρ, which is independent of the substituent, and a substituent constant, σ, which is independent of the reaction. Soon, a single substituent parameter scale was found to be insufficient and different σ scales have arisen, e.g., σ^+ for systems where an enhanced mesomeric interaction exists, to account for the different mechanistic requirements of various reactions. These have been extensively reviewed by Jaffé.[5]

The use of the Hammett relationship (*3*) has the disadvantage of giving discontinuities in the allowed extent of resonance between the reaction centre and the substituent. As a solution, Yukawa and Tsuno[6] proposed a scale of enhanced resonance effects based on $(\sigma^+ - \sigma)$, and incorporated this into the Hammett equation by using a new parameter, r, thus allowing for a continuous variation in the amount of resonance between substituent and reaction centre:

$$\log(k_X/k_H) = \rho[\sigma + r(\sigma^+ - \sigma)] \quad (4)$$

Taft *et al.*[7-12] refined this linear free energy relationship further by completely separating inductive and resonance effects into two individual components. Their dual substituent parameter (d.s.p.) treatment

$$\log(k_X/k_H) = \rho_I\sigma_I + \rho_R\sigma_R \quad (5)$$

allows for contributions to be made to the reaction constant by both inductive, ρ_I, and resonance, ρ_R, effects. All reactions were divided into four categories, and a different set of substituent constants was used for each category.

We have already shown[2] that the Brönsted plots [equation (*1*)] for the pseudo-first-order rate constant k_ψ for the decomposition of pnpa in the alkanediamine bis(dodecanoate) surfactants are linear, and that the slopes increase with increasing detergent concentration. These results indicated that there was a small but significant amount of proton transfer from the ammonium head group to the ester in the transition state.

We have also shown,[13] from carbon-13 product analysis of the reaction of *p*-nitrophenyl propionate with dodecylammonium propionate, that the only attacking nucleophile in this amine carboxylate salt system is the amine, and that, even in the presence of small quantities of cosolubilized water, the only identifiable products

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are *p*-nitrophenol and the appropriate amide. However, the concentration of free amine in solution is very small, for the ^1H n.m.r. spectra of alkylamine salts of carboxylic acids in benzene are consistent[14–16] with the formulation of the surfactants as $RNH_3^+ \ {}^-O_2CR'$, not $RNH_2.HO_2CR'$. Such a result supports a mechanism in which the amine attacks the ester carbonyl carbon atom in an uncatalysed pathway and/or additional pathways involving general-acid- or general-base-catalysed decomposition of the tetrahedral intermediate by alkylammonium or carboxylate ions. It does not exclude pre-equilibrium protonation of the substrate.

Application of the various linear free energy relationships to the rate data in the systems may help confirm or distinguish between details of the mechanism, because the various mechanistic pathways should lead to ρ values which vary according to both the nucleophile and the extent of acid/base catalysis. For formation of the tetrahedral intermediate, the following considerations apply. Firstly, if the rate-determining step is nucleophilic attack of the protonated ester, then the ρ value will be a combination of those due to the protonation equilibrium (expected to be negative) and to nucleophilic attack. Secondly, attack by amine is expected to have a more negative ρ value than would attack by carboxylate anion.

Thus, attack by amine upon protonated ester is expected to give a relatively large negative value of ρ; attack by amine upon ester or by carboxylate anion upon protonated ester is expected to give a small negative or relatively small positive value, and attack by carboxylate ion upon ester a larger positive value. (If the rate-determining step is a catalysed decomposition of the tetrahedral intermediate, then there is an additional ρ value to be considered.)

Results and Discussion

Rate Data

A series of *p*-nitrophenyl 4-substituted benzoates has been prepared and their decomposition to *p*-nitrophenol has been studied in benzene solutions of dodecylammonium propionate (dap) and butane-1,4-diamine bis(dodecanoate) (budb) at 341 K. The values of k_ψ, observed in solutions of dap and budb, are given in Table 1. Plots of k_ψ against detergent concentration were precisely linear for all substrates over the detergent concentrations used and the rate data were consistent with the rate equation (*6*)[13] which consists of two terms, namely

$$\text{rate} = k_M[\text{ester}] + k_2[\text{ester}]C_D \qquad (6)$$

where C_D is the concentration of surfactant in mol kg^{-1}, k_M is the rate constant for micellar catalysis, and k_2 is the second-order rate constant for the bimolecular reaction between the ester and the head groups of the surfactants. The values of k_M and k_2 are given in Table 2, and these data were treated by the Hammett, Tsuno–Yukawa, and Taft d.s.p. linear free energy relationships. Although the values of k_M are affected by the nature of the substituent, the correlation coefficients were not good ($<0 \cdot 95$) and are not discussed further herein. We think that this lack of correlation supports our belief that esterolysis reactions in surfactants in non-polar solvents are not due to a phenomenon arising from reaction in one micellar pseudo-phase

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Table 1. Rate constants, k_ψ (s^{-1}), for the reactions of *p*-nitrophenyl 4-X-substituted benzoates in benzene solutions of dodecylammonium propionate and butane-1,4-diamine bis(dodecanoate) at 341 K at various concentrations, C_D (mol kg^{-1}), of the detergent

Reactions in the presence of dodecylammonium propionate								Reactions in the presence of butane-1,4-diamine bis(dodecanoate)							
C_D	10^3k_ψ	C_D	10^3k_ψ	C_D	10^3k_ψ	C_D	10^3k_ψ	C_D	10^3k_ψ	C_D	10^3k_ψ	C_D	10^3k_ψ	C_D	10^3k_ψ
X = NO_2		X = CN		X = Br		X = Cl		X = NO_2		X = CN		X = Br		X = Cl	
0·0778	8·12	0·131	8·07	0·258	5·11	0·153	3·48	0·0394	15·2	0·0731	20·7	0·0656	4·99	0·0354	3·17
0·120	10·2	0·204	11·7	0·289	5·47	0·219	4·40	0·0467	19·1	0·0841	19·6	0·0690	4·82	0·0440	3·49
0·144	10·8	0·313	16·3	0·427	7·58	0·361	6·28	0·0663	25·4	0·157	32·2	0·104	7·16	0·115	6·76
0·209	15·5	0·355	18·1	0·434	8·03	0·447	7·30	0·0961	34·0	0·214	36·8	0·111	7·70	0·125	7·39
0·313	20·8	0·549	27·4	0·521	8·86	0·483	7·89	0·135	43·9			0·122	7·30	9·132	8·09
0·399	27·4	0·644	34·0	0·627	11·0	0·506	8·79					0·247	13·4	0·157	8·81
						0·641	11·0							0·198	10·3
X = F		X = H		X = AcNH		X = Ph		X = F		X = H		X = AcNH		X = Ph	
0·107	1·65	0·114	1·80	0·312	1·54	0·257	2·58	0·0667	2·82	0·0307	1·59	0·115	2·17	0·0512	2·11
0·205	2·39	0·165	2·32	0·485	1·93	0·389	3·62	0·0856	3·55	0·0485	2·20	0·133	2·21	0·0513	2·10
0·362	3·65	0·182	2·28	0·486	2·11	0·402	3·60	0·0911	3·48	0·0823	3·30	0·200	4·01	0·0855	2·85
0·372	3·85	0·189	2·17	0·625	2·72	0·468	4·18	0·120	4·62	0·0857	3·40	0·242	5·28	0·0956	3·16
0·530	5·20	0·251	2·87	0·799	3·37	0·499	4·30	0·150	4·99	0·0983	3·51	0·314	5·53	0·0995	3·15
0·619	6·16	0·289	3·20			0·576	5·22	0·155	5·64	0·112	4·08	0·372	6·89	0·273	6·10
								0·157	5·33	0·118	4·64				
								0·170	5·63	0·179	6·00				
								0·256	8·51	0·186	5·92				
										0·267	7·76				
										0·296	8·82				
		X = Bu		X = MeO				X = Me		X = Bu^t		X = MeO			
		0·163	1·52	0·0691	0·36			0·0368	1·18	0·148	2·91	0·0585	0·700		
		0·164	1·52	0·0934	0·38			0·0970	2·23	0·181	3·72	0·0599	0·824		
		0·389	2·76	0·198	0·66			0·154	3·08	0·282	4·40	0·117	1·36		
		0·425	3·03	0·221	0·92			0·178	3·57	0·327	5·52	0·125	1·35		
		0·522	3·67	0·286	0·85			0·191	3·69	0·467	6·66	0·135	1·17		
								0·256	4·59			0·148	1·20		
								0·273	5·18			0·187	1·81		
												0·197	1·92		
												0·240	2·29		

Table 2. Reaction of *p*-nitrophenyl 4-X-substituted benzoates with dodecylammonium propionate (dap) and with butane-1,4-diamine bis(dodecanoate) (budb) in benzene at 341 K: micellar rate constants, k_M, and second-order rate constants, k_2, derived from plots of k_ψ against C_D, and ^{13}C n.m.r. chemical shifts for the carbonyl carbon atoms

Sub-	dap		budb		^{13}C=O	Sub-	dap		budb		^{13}C=O
stituent X	10^3k_M (s^{-1})	10^3k_2 (kg mol^{-1} s^{-1})	10^3k_M (s^{-1})	10^3k_2 (kg mol^{-1} s^{-1})	chemical shift (ppm)	stituent X	10^3k_M (s^{-1})	10^3k_2 (kg mol^{-1} s^{-1})	10^3k_M (s^{-1})	10^3k_2 (kg mol^{-1} s^{-1})	chemical shift (ppm)
NO_2	2·90	59·7	4·97	294	162·42	AcNH	0·22	3·91	0·12	18·5	163·30
CN	1·26	49·2	10·6	127	162·65	Ph	0·46	8·00	1·30	17·8	163·59
Br	1·00	16·2	1·99	46·6		Me			0·61	16·2	163·76
Cl	1·02	15·0	1·62	45·4	163·01	Bu^t	0·54	5·89	1·42	11·5	163·69
F	0·61	8·76	0·89	29·2	162·88	MeO	0·17	2·66	0·26	8·33	163·91
H	0·87	5·35	1·19	25·6	163·79						

Table 3. Application of the Hammett, Tsuno–Yukawa, and Taft dual substituent parameter (d.s.p.) equations to the second-order rate constants, k_2, for reaction of *p*-nitrophenyl 4-substituted benzoates with benzene solutions of dap and budb at 341 K

Detergent	Analysis	ρ	r	Correl. coeff.	f	Analysis	ρ_R	ρ_I	f
dap	Hammett σ_p	1·195		0·987		d.s.p. $\sigma^-_{R(A)}$	0·9±0·2	1·0±0·3	0·065
	Hammett σ^+_p	0·903		0·988		d.s.p. σ°_R	1·5±0·2	1·1±0·35	0·038
	Tsuno–Yukawa	1·066	0·440	0·997	0·018	d.s.p. $\sigma_{R(BA)}$	1·1±0·2	1·3±0·3	0·038
						d.s.p. σ^+_R	0·8±0·2	1·1±0·2	0·027
budb	Hammett σ_p	1·333		0·988		d.s.p. $\sigma^-_{R(A)}$	0·9±0·2	1·1±0·2	0·088
	Hammett σ^+_p	1·003		0·969		d.s.p. σ°_R	1·5±0·2	1·2±0·3	0·056
	Tsuno–Yukawa	1·273	0·185	0·990	0·044	d.s.p. $\sigma_{R(BA)}$	1·1±0·2	1·4±0·3	0·088
						d.s.p. σ^+_R	0·9±0·2	1·2±0·1	0·048

and that the values of k_M, calculated from equation (*6*), are not a true representation of the micellar phenomenon which must take into account a reaction mechanism which includes contributions from monomeric surfactant and all small oligomers. The application of the sequential self-association model to these esterolysis reactions will be the subject of the next paper in this series.

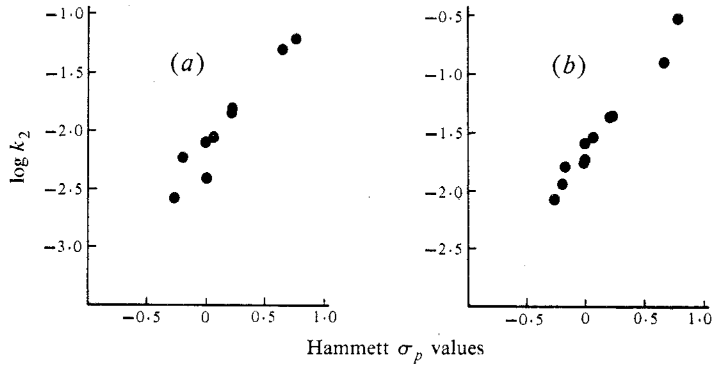
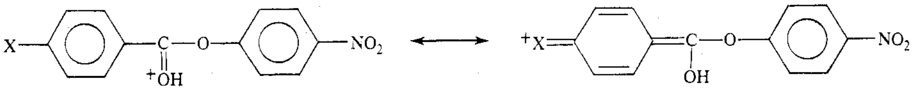


Fig. 1. The logarithm of the second-order rate constants, for reaction of *p*-nitrophenyl 4-substituted benzoates in benzene solutions of dodecylammonium propionate (dap) and butane-1,4-diamine bis(dodecanoate) (budb) at 341 K, plotted against Hammett σ_p values: (*a*) dap; (*b*) budb.

Plots of $\log k_2$ against σ_p are given in Figs 1*a* and 1*b* for dap and budb, respectively. Table 3 lists the values of ρ and the correlation coefficients for the Hammett plots [equation (*3*)] against σ_p and $\sigma^+{}_p$, together with values of ρ, r, correlation coefficients and f parameters arising from application of the Tsuno–Yukawa equation (*4*) to these reactions. (The parameter f is an indication of best fit to linearity, and is defined as the standard deviation divided by the root mean square of the distance of the data points from the line of best fit. This normalized parameter can therefore be used to compare results from different data sets.)

Analysis of k_2 values by Taft's d.s.p. treatment [equation (*5*)] gives values of ρ_I, ρ_R and f which are also shown in Table 3.

The reasonable correlation of the rate data by use of Hammett $\sigma^+{}_p$ and the contribution of $\sigma^+{}_p$ (as evidenced by r values) to the Tsuno–Yukawa correlation indicate a reaction series in which the reaction centre is capable of withdrawing electrons strongly from the ring by a resonance effect. A possibility which would lead to this present correlation is protonation of the ester on the carbonyl oxygen to give the resonance pair (1) and (2).



(1) (2)

The best fit with the d.s.p. analysis arises from use of $\sigma^+{}_R$, the values of which were derived from the same reactions as those used for derivation of $\sigma^+{}_p$ values. $\sigma^+{}_R$ series are those in which there is a strong resonance electron-withdrawing reaction centre conjugated with the aromatic ring. Thus these results also support a mechanism in which there is a significant amount of protonation of the carbonyl oxygen in the transition state.

The magnitude and sign of the ρ values (*c.* $+1$) suggest that the reaction proceeds by aminolysis of the unprotonated ester or by carboxylate ion attack upon the protonated ester (however, our ^{13}C n.m.r. product analysis[13] negates this latter pathway). The results are consistent with a pathway catalysed by general acid because there is a significant correlation of $\log k_2$ values with $\sigma^+{}_p$ and $\sigma^+{}_R$ for both the dap/benzene and the budb/benzene systems.

A ^{13}C N.M.R. Correlation

Hammett correlations and other similar approaches which use linear free energy relationships depend upon derived empirical parameters. Although these parameters are useful for correlational analysis and subsequent prediction based upon such analysis,[17] the errors inherent in the determination of these 'constants' require that relationships between different chemical measurements be analysed by direct comparison rather than through such correlations.

Comparison of n.m.r. data with rate data and equilibria has previously shown that correlations exist between the fundamental measurements (which depend largely on electronic influences about the observed nuclei) and equilibria or rates of chemical reactions.[18] We have now compared the ^{13}C n.m.r. chemical shift of the carbonyl carbon of a series of 4′-nitrophenyl 4-substituted benzoates with the second-order rate constant for aminolysis of these esters in benzene solutions of dap and budb. Provided that the mechanism of the aminolysis reaction does not change within the substituent series, the ^{13}C n.m.r. chemical shift (which is predominantly affected by the π-electrons at this carbon centre) should give a measure of the reactivity of the carbonyl carbon.

Previous studies of ^{13}C n.m.r. chemical shifts of esters,[19] substituted benzenes[19,20] and acetanilides[19] have used $(CD_3)_2SO$ as solvent, and we have used 0·044 mol dm^{-3} solutions of ester in this solvent. The values of $\delta(^{13}C{=}O)$ are given in Table 2; Fig. 2 shows plots of $\log k_2$, for the reaction of the esters in the benzene solutions of dap and budb, against the ^{13}C n.m.r. chemical shift of the carbonyl carbon of these esters. These plots have correlation coefficients of 0·951 and 0·959 for the data in solutions of dap and budb, respectively.

In Fig. 2, the data points for the 4-acetamido- and 4-fluoro-benzoates are not well fitted and they have not been used in the calculation of the least-squares-fitted lines. The Hammett plots (Fig. 1) also showed the rate constant for the 4-acetamido-substituted ester to be anomalous, presumably because of hydrogen bonding between the acetamido group and the detergent. However, a plot of $\delta(^{13}C{=}O)$ against σ_p (Fig. 3) shows that the only anomalous point occurs with the 4-fluoro substituent. This effect is probably due to the $-I, +M$ nature of the fluoro substituent. The π-electron donation of fluorine affects the ^{13}C n.m.r. chemical shifts more than does

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[18] Breitmaier, E., and Voelter, W., in '^{13}C N.M.R. Spectroscopy' 2nd Edn, pp. 68, 70 (Verlag Chemie: Weinheim 1978).

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the inductive withdrawal because of the dominance of π-electron structure on the shielding of the nucleus.[18] This influence does not appear to affect the rate parameter k_2.

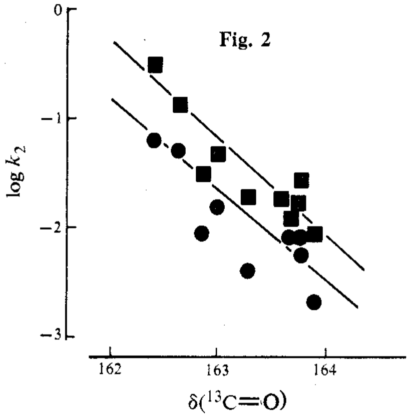

Fig. 2

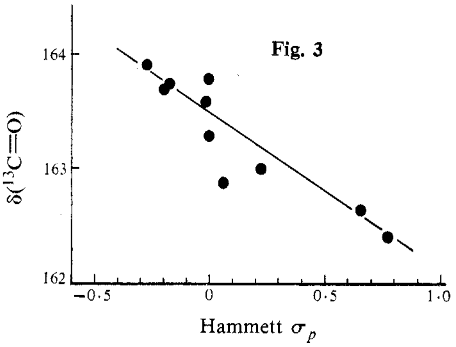

Fig. 3

Fig. 2. The logarithm of the second-order rate constants, for decomposition of *p*-nitrophenyl 4-substituted benzoates in benzene solutions of dodecylammonium propionate (dap) and butane-1,4-diamine bis(dodecanoate) (budb) at 341 K, plotted against the ^{13}C n.m.r. chemical shift of the carbonyl carbon of these esters: ● dap; ■ budb.

Fig. 3. The ^{13}C n.m.r. chemical shifts for the carbonyl carbon atoms of *p*-nitrophenyl 4-substituted benzoates plotted against the Hammett σ_p value of the 4-substituent on the benzoyl ring.

Experimental

Surfactants and Solvent

The preparation of the surfactants and purification of the solvent have been described.[13]

4′-Nitrophenyl 4-Substituted Benzoates

The substrate *p*-nitrophenyl esters were prepared by the same general method. *p*-Nitrophenol (10 mmol) and the appropriate 4-substituted benzoic acid (10 mmol) were dissolved in a minimum quantity of pyridine (*c*. 10 ml) and cooled on ice. Thionyl chloride (1 ml) was added slowly with stirring. The solidified mass was broken up by the addition of pyridine (*c*. 3 ml), and poured into ice/water (*c*. 100 ml). The precipitate was recrystallized from ethanol or ethanol/benzene. If a literature melting point was available, then the melting point and the i.r. spectrum were considered to be sufficient for characterization. This was true for the following esters, identified by the 4-substituent: H, m.p. 417–417·5 K (lit.[21,22] 415–416 K); NO_2, m.p. 433–433·5 K (lit.[21,22] 431·5–432·5 K); CN, m.p. 467·5–468·5 K (lit.[23] 468–469); Br, m.p. 433–434·5 K (lit.[24] 426–427 K); Cl, m.p. 412·3–412·8 K (lit.[21,22] 411–412 K); F, m.p. 402–402·9 K (lit.[25] 400–401 K); Me, m.p. 393·6–394 K (lit.[21,26] 397 K, 393–394·3 K); Bu, m.p. 398·5–399 K (lit.[23] 397·5–398 K); MeO, m.p. 436·3–437 K (lit.[21,24,27] 440 K, 433 K, 439 K).

Good analytical data for carbon, hydrogen and nitrogen were obtained for the other esters: Ph, m.p. 343·5–344·5 K; AcNH, m.p. 494·5–496·5 K.

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The 4-hydroxy derivative was not obtained in a crystalline form and thus could not be used in this study. Its preparation as a glass of 61% purity has been reported.[26]

Measurements

The rates of reaction were measured under pseudo-first-order conditions as already described.[13] Note that the solutions were made up by weight, so concentrations of detergent are expressed in mol kg^{-1}. All spectrophotometric measurements were made on a Cary 14 spectrophotometer in cells of pathlength 1 cm.

Analyses were performed on a Burroughs B6700 computer.

N.m.r. measurements were recorded on a Jeol FX-60 spectrometer; 8×2^{10} data points were collected for the *p*-nitrophenyl 4-substituted benzoate solutions [0·044 mol dm^{-3} in $(CD_3)_2SO$] in 10-mm sample tubes at 300 K (except for the 4-phenyl-substituted ester for which the temperature was 325 K). Tetramethylsilane was used as internal standard.

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