Ring–Chain Tautomerism. Part V.[1] 8-Aroyl- and 8-Acyl-1-naphthoic Acids

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The equilibrium constants for ring–chain tautomerism in a series of 8-aroyl-1-naphthoic acids in dioxan have been determined by an i.r. spectroscopic method and have been correlated with the substituent constants σ_I and $\sigma_R{}^0$ using a modified Hammett equation. The observed pK_a values, which have been measured in 80% (w/w) 2-methoxyethanol–water, have been corrected for these tautomeric equilibria to give the true $pK_a{}^T$ value. The effect of substitution on the latter values have been assessed using the Hammett equation. The equilibrium constants for ring–chain tautomerism in a series of 8-acyl-1-naphthoic acids have been determined by using the observed pK_a and estimated true $pK_a{}^T$ values in 80% (w/w) 2-methoxyethanol–water. These equilibria constants have been correlated with steric substituent constants E_s. The ' cis ' and ' trans ' conformers of methyl 8-aroyl- and 8-acyl-1-naphthoates has been detected by i.r. spectroscopy and the carbonyl stretching frequencies of the ester carbonyl groups have been assigned. The results are related to the polar, resonance, and steric effects of the substituents.

IT has been suggested by Lansbury [2] that all 8-aroyl- and 8-acyl-1-naphthoic acids may exist in solution as ring–chain tautomeric equilibria, in which the ring form predominates. An early study [3] investigated the structure of 8-benzoyl-1-naphthoic acid and deduced that in solution the acid was very largely, if not completely, in the ring form. Examinations [4,5] of the reactions of 8-formyl- and 8-acetyl-1-naphthoic acids (as well as for 5-formyl-4-phenanthroic acid [6,7]) found their reactivity

could be explained by the ring structure (I). Lansbury and Bieron [8] have prepared the two tautomeric methyl

(II) (Chain) (I) (Ring) (1)

(IV) (III)
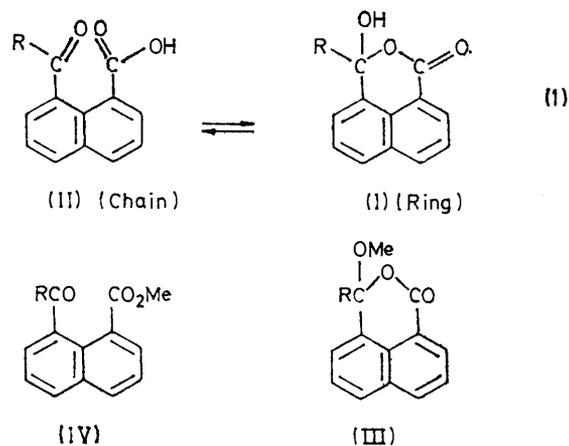
esters of 8-acetyl-1-naphthoic acid (III) and (IV) and examination of the acid itself in solution by i.r. and [1]H n.m.r. spectroscopy indicates a ring–chain tautomeric equilibria in which the ring tautomer predominates.

[1] Part IV, K. Bowden and M. P. Henry, *J.C.S. Perkin II*, 1972, 206.

[2] P. T. Lansbury, unpublished studies (see p. 609, ref. 361, in V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567); *cf.* L. Christiaens and M. Renson, *Bull. Soc. chim. belges*, 1969, **78**, 359.

[3] H. E. French and J. E. Kircher, *J. Amer. Chem. Soc.*, 1944, **66**, 298.

[4] P. R. Jones and A. A. Lavigne, *J. Org. Chem.*, 1960, **25**, 2020.

[5] V. M. Rodionov and A. M. Fedorova, *Izvest. Akad. Nauk. S.S.S.R., Otdel khim. Nauk.*, 1950, 247 (*Chem. Abs.*, 1950, **44**, 9395).

[6] M. S. Newman and H. S. Whitehouse, *J. Amer. Chem. Soc.*, 1949, **71**, 3664.

[7] G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, 1950, 2326.

[8] P. T. Lansbury and J. F. Bieron, *J. Org. Chem.*, 1963, **28**, 3564.

The ring–chain equilibria for the latter acids is shown in equation (1). Both tautomeric methyl esters have been prepared for 5-formyl-4-phenanthroic acid [6,7] and the ring–chain equilibria for the acid is shown in equation (2).

(2)
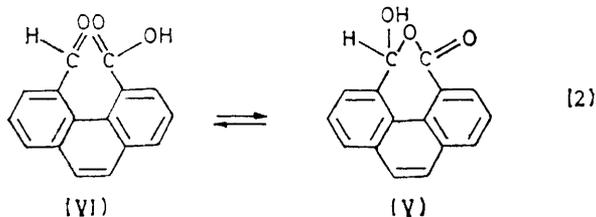
The equilibrium constants K_e are given by equation (3)

$$K_e = a_{Ring}/a_{Chain} \qquad (3)$$

and the observed pK_a can be related to the true pK_a^T by the relation (4).[9] If a reliable estimate of pK_a^T can be made, K_e can be found by measuring the observed

$$pK_a^T = pK_a - \log (K_a + 1) \qquad (4)$$

pK_a. Conversely, pK_a^T can be calculated more precisely if both the pK_a and K_e can be measured directly.

In this study, measurements of the tautomeric equilibrium constants for a series of 8-(3- or 4-substituted benzoyl)-1-naphthoic acids have been made and are used to obtain pK_a^T from pK_a values in 80% (w/w) 2-methoxy-ethanol–water. The observed pK_a and estimated pK_a^T values are used to investigate the ring–chain tautomerism in a series of 8-acyl-1-naphthoic acids, as well as 5-formyl-4-phenanthroic acid. The results are discussed in terms of polar, steric, and resonance effects.

EXPERIMENTAL AND RESULTS

The 8-(3- and 4-substituted benzoyl)-1-naphthoic acids were prepared by two standard methods. The first (Method A) was the reaction of 1,8-naphthalic anhydride with arylmagnesium bromides or iodides.[10] The second (Method B) and more successful was the reaction of the anhydride with diarylcadmium.[10,11] The 8-acyl-1-naphthoic acids, with the exception of the 8-formyl acid, were prepared similarly from 1,8-naphthalic anhydride with alkylmagnesium halides by a modification of Jones and Lavigne's method [4] (Method C). For the preparation of the 8-pivaloyl acid, the Grignard reagent was cooled in an acetone–solid CO_2 bath before the addition of the anhydride. Modifications of the methods of Fuson and Munn [12] and of Carson and Wordie [13] were used to prepare 8-formyl-1-naphthoic acid by the fusion of acenaphthenequinone in aqueous potassium hydroxide. 5-Formyl-4-phenanthroic

acid was prepared by the oxidative and basic hydrolysis of pyrene.[14] 1-Naphthoic acid was available commercially, while 4-phenanthroic acid was prepared by oxidation of 4-acetylphenanthrene.[15] After repeated recrystallisation to constant m.p. and drying in a vacuum desiccator (P_2O_5), the acids had m.p.s in good agreement with literature values [4,10-12,14,16-19] or, if previously unreported, satisfactory elemental analyses. The physical constants of the acids are listed in Table 1 with their recrystallisation solvent and

TABLE 1

Physical constants of 8-acyl- and 8-benzoyl-1-naphthoic and related acids

Substnt. [R in (I)/(II)]	M.p./°C	Lit. m.p. °C	Ref.	Method (see Experimental section)
H	167 [a]	167	12	
Me	171—172 [a]	173—174	4	C
CD₃	168—169 [a]			C
Et	147·5 [a]	147·5—148·5	10	A
Prⁱ	154—156 [a]	158·5—159·5 [e]	16	C
Buᵗ	160 [a]			C
Benzoyl substnt.				
H	129—130 [a]	128—129	10	B
4-Me	134 [a]	134—136, 135—137	10, 17	A
3-Me	161—162 [a]			A
4-OMe	197 [b]			B
4-Br	167—168 [c]	165—167	11	A
4-Cl	161 [a]			A
3-Cl	155 [a]			A
3-CF₃	182—185 [a]			A
1-Napthoic acid	161 [b]	160·5—161	18	
5-Formyl-4-phenanthroic acid	272—274 [d]	272—276	14	
4-Phenanthroic acid	172—173 [c]	173·5—174·5	19	

[a] From toluene. [b] From methanol. [c] From aqueous ethanol. [d] From aqueous dimethylformamide–acetic acid. [e] Decomposes from 154 °C.

the elemental analyses of previously unreported acids are given in Table 2. The neutralisation equivalents of the acids were determined by titration to be within $\pm 1\%$ of the calculated values. The ^1H n.m.r. and i.r. spectra of all the acids confirmed their structure and indicated them to be pure.

The normal and pseudo methyl esters were prepared and purified as previously described.[20-22] Solvents were purified as previously described.[23-25]

I.r. Measurements.—The carbonyl stretching vibrations of the normal and pseudo methyl esters, together with related model compounds, were determined as previously described [25] for 0·02M solutions in carbon tetrachloride. The spectra of the acids and methyl esters were measured

[9] C. Pascual, D. Wegman, U. Graf, R. Scheffold, P. F. Sommer, and W. Simon, *Helv. Chim. Acta*, 1964, **47**, 213.

[10] D. V. Nightingale, W. S. Wagner, and R. H. Wise, *J. Amer. Chem. Soc.*, 1953, **75**, 4701.

[11] D. P. Weeks and G. W. Zuorick, *J. Amer. Chem. Soc.*, 1969, **91**, 477.

[12] R. C. Fuson and G. Munn, *J. Amer. Chem. Soc.*, 1949, **71**, 1870.

[13] J. Cason and J. D. Wordie, *J. Org. Chem.*, 1950, **15**, 608.

[14] R. E. Dessy and M. S. Newman, *Org. Synth.*, 1958, **38**, 32.

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[17] F. A. Mason, *J. Chem. Soc.*, 1924, 2119.

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[19] K. G. Rutherford and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 213.

[20] K. Bowden and A. M. Last, *J.C.S. Perkin II*, 1973, 345.

[21] K. Bowden and A. M. Last, *J.C.S. Perkin II*, 1973, 351.

[22] K. Bowden and A. M. Last, *J.C.S. Perkin II*, 1973, 358.

[23] K. Bowden, M. J. Hanson, and G. R. Taylor, *J. Chem. Soc. (B)*, 1968, 174.

[24] K. Bowden, M. Hardy, and D. C. Parkin, *Canad. J. Chem.*, 1968, **46**, 2929.

[25] K. Bowden and G. R. Taylor, *J. Chem. Soc. (B)*, 1971, 145, 149.

as previously described [26] for 0·02M solutions in dioxan at 35(±1) °C. The spectra of all the 8-aroyl acids showed the presence of both ring and chain tautomers; whereas, the spectra of the 8-acyl-1-naphthoic acids, as well as 5-formyl-4-phenanthroic acid, indicated the absence of any detectable

tautomer is sharp, while a broad absorption results from the lactone carbonyl of the ring and the carboxylic carbonyl of the chain tautomer. The latter arises from the very close frequencies of the latter absorptions. The area of the lactone carbonyl absorption was therefore calculated by

TABLE 2

Elemental analysis of previously unreported 8-acyl-1-naphthoic acids

Substnt. [R in (I)/(II)]	Molecular formula	Calc. (%)				Found (%)			
		C	H *	O	Other	C	H *	O	Other
CD_3	$C_{13}{}^1H_7{}^2H_3O_3$	71·9	6·0	22·1		71·8	6·1	22·3	
Bu^t	$C_{16}H_{16}O_3$	75·0	6·3	18·7		75·1	6·3	18·8	
Benzoyl substnt.									
3-Me	$C_{19}H_{14}O_3$	78·6	4·9	16·5		78·6	5·2	16·3	
4-OMe	$C_{19}H_{14}O_4$	74·4	4·7	20·9		74·6	4·7	20·8	
4-Cl	$C_{18}H_{11}ClO_3$	69·6	3·6	15·4$_5$	11·4 (Cl)	69·6	3·6	15·6	11·5 (Cl)
3-Cl	$C_{18}H_{11}ClO_3$	69·6	3·6	15·4$_5$	11·4 (Cl)	69·6	3·7	15·4	11·4 (Cl)
3-CF_3	$C_{19}H_{11}F_3O_3$	66·2	3·2	13·9	16·5 (F)	66·4	3·3		16·4 (F)

* % is for $^1H + {}^2H$.

chain tautomer. Measurements of the equilibrium constants K_e were made by a modification of our previous

TABLE 3

Carbonyl stretching frequencies of methyl 8-acyl- and 8-benzoyl-naphthoates in carbon tetrachloride

Substnt. [R in (III)/(IV)]	$\nu_{max.}/cm^{-1}$		
	Normal ester CO		Pseudo ester CO
	Keto	Carboxylic	Lactone
H	1704 [a]	1734 [a]	1742
Me	1693	1722	1730
CD_3	1691	1722	
Et	1695	1723	1732
Pr^i	1686	1725	1730
Bu^t	1681	1723	
Benzoyl substnt.			
H	1669	1739, 1726	⎫
4-Me	1665·$_5$	1737	⎪
3-Me	1667	1738, 1727	⎪
4-OMe	1661·$_5$	1730	⎬ 1737(±1)
4-Cl	1669	1739, 1721	⎪
3-Cl	1672	1739, 1722	⎪
4-Br	1670	1739, 1722	⎪
3-CF_3	1674·$_5$	1739, 1721	⎭
Methyl 1-naphthoate		1725 [b]	
Methyl 5-formyl-4-phenanthroate	1693	1725	1718
Methyl 4-phenanthroate		1722	

[a] Lit.[27] values are 1701 (formyl) and 1737 cm^{-1} (carboxylic). [b] Lit.[27] value is 1724 cm^{-1}.

TABLE 4

Equilibrium constants, K_e, for the ring–chain tautomerism in 8-(3- and 4-substituted benzoyl)-1-naphthoic acids in dioxan

Substnt.	K_e *	Substnt.	K_e *
H	1·41(±0·02)	4-Cl	1·66(±0·06)
4-Me	0·43(±0·01)	3-Cl	2·63(±0·02)
3-Me	0·84(±0·02)	4-Br	1·60(±0·12)
4-OMe	0·14(±0·03)	3-CF_3	3·06(±0·14)

* The reproducibility of the K_e values are shown in parentheses.

method.[26] The i.r. spectra of the 8-(substituted benzoyl)-1-naphthoic acids showed only two distinct carbonyl absorptions. The absorption due to the keto carbonyl of the chain

assuming that the ratio of the area of the keto carbonyl to that of the carboxylic carbonyl is the same in both the normal ester and chain tautomer of acid. The latter calculated area was then deducted from the total area observed. K_e Was then calculated as before.[26] The values of $\nu_{max.}$ of the carbonyl stretching vibrations of the methyl esters in carbon tetrachloride are shown in Table 3, while the values in dioxan were 2—4 cm^{-1} smaller. The values of K_e in dioxan are given in Table 4. A Perkin-Elmer model 231 spectrophotometer and a Dupont model 301 curve resolver were used in these studies. The wavenumber measurements were reproducible to ±1 cm^{-1} (relative to the standard, a calibration by superimposed water vapour bands).[27]

^{1}H N.m.r. Measurements.—The spectra of the compounds studied were measured using a Varian A60-A spectrometer operating at 60 MHz, as in our previous study.[28] The chemical shifts were measured in p.p.m. relative to tetramethylsilane (TMS), and are quoted as τ values. The structure of the acids and methyl esters were confirmed and these compounds were shown to be >98% pure by this spectral method.

TABLE 5

^{1}H N.m.r. spectral results for the methyl esters of the 8-acyl-1-naphthoic acids in carbon tetrachloride

Substnt. [R in (III)/(IV)]	Pseudo		Normal		τ
	Methoxy	R in (III)	Methoxy	R in (IV)	
H	6·35	3·68	6·13	−0·21	
Me	6·80	8·13	6·17	7·38	
Et	6·80	7·90, 9·18	6·15	6·95, 8·77	
Pr^i	6·84	7·70, 9·12	6·20	6·74, 8·75	
Bu^t			6·17	8·55	
Ph	6·72		6·68		
5-Formyl-4-phenanthroic acid	6·22	3·87	6·23	−0·33	

Lansbury and Bieron [8] have shown that this method can be used to distinguish between the normal and pseudo

[26] K. Bowden and M. P. Henry, J.C.S. Perkin II, 1972, 201.
[27] K. Bowden, M. J. Price, and G. R. Taylor, J. Chem. Soc. (B), 1970, 1022.
[28] K. Bowden and G. R. Taylor, J. Chem. Soc. (B), 1971, 1390.

methyl esters of 8-acetyl-1-naphthoic acid and this has been confirmed for several other esters in the present study, as shown in Table 5. The methoxy methyl chemical shifts for the normal methyl esters of the 8-acetyl, -propionyl, -isobutyryl, and -pivaloyl-1-naphthoic acids occur in the range τ 6·15—6·20 and for the corresponding pseudo methyl esters in the range τ 6·80—6·84. However, the methoxy methyl chemical shifts for the two methyl esters of 8-formyl-1-naphthoic and 5-formyl-4-phenanthroic acids are very close, whereas the chemical shifts of the formyl and acetal hydrogens are distinctly separated. Furthermore the methoxy methyl chemical shifts of the normal and pseudo methyl esters of the 8-benzoyl-1-naphthoic acids are very close, but the tautomers can be distinguished in mixtures. The asymmetry of the ring carbon in the pseudo methyl 8-isopropyl-1-naphthoate causes the non-equivalence of the two isopropyl methyl groups, as previously observed in related systems.[29]

The spectra of the 8-acyl-1-naphthoic acids, as well as 5-formyl-4-phenanthroic acid, correspond closely to those of the relevant pseudo methyl esters (less the methoxy

TABLE 6

Ionisation of 8-acyl- and 8-benzoyl-1-naphthoic and related acids in 80% (w/w) 2-methoxyethanol–water at 25 °C *

Substnt. [R in (I)/(II)]	Observed pK_a		Estimated pK_a^T
H	9·11$_5$		6·05($\pm$0·05)
Me	8·31		6·2$_0$($\pm$0·1)
CD$_3$	8·30$_5$		6·2$_0$($\pm$0·1)
Et	8·52$_5$		6·2$_0$($\pm$0·1)
Pr^i	8·82$_5$		6·2$_0$($\pm$0·1)
Bu^t	9·73		6·6($\pm$0·1)
Benzoyl substnt.		log $(1 + K_e)$	Calculated pK_a^T
H	7·00	0·38($\pm$0·01)	6·62($\pm$0·04)
4-Me	7·00$_5$	0·15$_5$($\pm$0·01)	6·85($\pm$0·04)
3-Me	7·06$_5$	0·26$_5$($\pm$0·01)	6·80($\pm$0·04)
4-OMe	6·84	0·05$_5$($\pm$0·01$_5$)	6·78$_5$($\pm$0·04$_5$)
4-Cl	6·90$_5$	0·42$_5$($\pm$0·01)	6·48($\pm$0·04)
3-Cl	7·07$_5$	0·56($\pm$0·01)	6·51$_5$($\pm$0·04)
4-Br	6·90$_5$	0·41$_5$($\pm$0·02)	6·49($\pm$0·05)
3-CF$_3$	7·05	0·61($\pm$0·01$_5$)	6·44($\pm$0·04$_5$)
1-Naphthoic acid	6·45$_5$ †		
5-Formyl-4-phenanthroic acid	8·51		
4-Phenanthroic acid	5·83		
8-Methoxy-1-naphthoic acid	6·38		

* The observed pK_a values were reproducible to $\pm$0·03. The uncertainties shown for the other values are those derived either from the reproducibility (K_e and calculated pK_a^T) or the estimation (estimated pK_a^T). The values of the calculated pK_a^T are made using relation (4) and estimated pK_a^T are described in the text. † Lit.[30,31] values are 6·45, 6·40.

methyl), again indicating no detectable chain tautomer in the acids. No significant differences in spectra would be expected for the ring–chain tautomers of the 8-benzoyl acids and the spectra observed confirmed this.

[29] K. Bowden and G. R. Taylor, *J. Chem. Soc.* (*B*), 1971, 1395.
[30] K. Bowden and D. C. Parkin, *Canad. J. Chem.*, 1969, **47**, 185.
[31] W. Simon *et al.*, ' Zusammen stellung von scheinbaren Dissoziationkonstanten in Losungsmittelsystem Methylcellosolve-Wasser,' Juris-Verlag, Zurich, 1959, vol. 1.
[32] R. E. Lutz and H. Moncure, *J. Org. Chem.*, 1961, **26**, 746.

pK_a *Measurements.*—The pK_a values of the acids in 80% (w/w) 2-methoxyethanol–water at 25($\pm$0·1) °C were measured as described previously [25] and are shown in Table 6.

All our measurements are the results of at least two separate determinations.

DISCUSSION

Ring–Chain Tautomerism in 8-Aroyl-1-naphthoic Acids. —The equilibrium constants K_e for the series of 8-(3- and 4-substituted benzoyl)-1-naphthoic acids in dioxan have been determined by an i.r. spectroscopic method as shown in Table 4. As observed previously for related systems,[26,32,33] K_e increases as the ring substituent becomes more electron withdrawing and *vice versa*. However, the relation between log K_e and the substituent σ values is distinctly curved, as has been also noted by Bowden and Henry [26] for both the substituted *cis*-3-benzoyl-3-methylacrylic and 2-benzoylbenzoic acids. A modified Hammett equation (5) can be used to correlate the equilibrium constants, where σ_I and σ_R^0 are the

$$\log (K/K_0) = \rho_I\sigma_I + \rho_R\sigma_R^0 \qquad (5)$$

' inductive ' and resonance substituent constants,[34,35] respectively. The present series comprises both *meta*- and *para*-substituents. These can only be combined in a single correlation series by assigning a differential resonance contribution for the two positions. The original separation [34] of σ values into ' inductive ' and resonance effects used $\tfrac{1}{3}\sigma_R^0$ and σ_R^0 for the *meta*- and *para*-position, respectively. This has been followed in the correlation series 1, Table 7. Series 2, Table 7, only contains the

TABLE 7

Reaction constants for the ring–chain tautomeric equilibria of 8-(substituted benzoyl)-1-naphthoic acids in dioxan using the modified Hammett equation *

Series †	ρ_I	ρ_R	log K^0_e	s	r	n
1	1·286 (5·98)	2·918 (8·06)	0·058	0·073	0·970	8
2	1·782 (23·47)	3·713 (30·19)	0·122	0·023	0·999	5

* s Is the standard deviation, r the correlation coefficient, and n the number of substituents studied. The quantity in parentheses is the student's t test for the significance of the regression variable. † Series 1 comprises all substituents, while series 2 only *para*-substituents.

para-substituted acids. While both correlations result in similar relations and conclusions, the series containing only *para*-substituents is more successful. This very probably results from the absence of the arbitrary assignment of the extent of the resonance contribution from the *meta*-position. The substituent effect is found to be mainly derived from the resonance contribution and, according to Bowden and Henry,[26] arises from the stabilisation of the chain tautomer by interactions such as

[33] M. V. Bhatt and K. M. Kamath, *J. Chem. Soc.* (*B*), 1968, 1036.
[34] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436.
[35] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, p. 5352.

(VII). The reaction constants found for the 8-benzoyl-1-naphthoic acids are of the same sign but are very much greater than those previously found [26] for the cis-3-benzoyl-2-methylacrylic acid system. However the
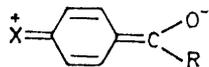
(VII)

8-benzoyl group will exist in a plane perpendicular to that of the naphthalene nucleus and be fully conjugated *internally*, whereas the cis-3-benzoyl group will suffer partial *internal* deconjugation arising from steric interactions with the total acrylic system. Thus the greater ρ_R value observed for the 8-benzoyl system arises from the full conjugation possible within this system.

Ionisation of 8-Aroyl-1-naphthoic Acids.—The observed pK_a values of these acids in 80% (w/w) 2-methoxyethanol-water at 25 °C are affected by the existence of the ring–chain tautomeric equilibria. Equation (4) relates the true pK_a^T to the observed value.[9] However the values of K_e are for solution in dioxan. Previous studies [26,28,33] indicate that these tautomeric equilibria are relatively insensitive to changes in comparatively polar media. The true pK_a^T values have been calculated as shown in Table 6. Despite the larger uncertainties and relatively small range of values in these pK_a^T values, the Hammett correlations, shown in Table 8, are fairly successful and

TABLE 8

Reaction constants using Taft or Hammett equation *

Reaction in 80% (w/w) 2-methoxyethanol-water	Reaction constant	$\log K_0$	s	r	n
pK_a^T Values of 8-(substituted benzoyl)-1-naphthoic acids at 25 °C †	(a) 0·677 (ρ)	−6·70	0·099	0·942	8
	(b) 0·677 (ρ)	−6·70	0·091	0·950	8
Ring–chain tautomerism in 8-acyl-1-naphthoic acids	−0·60 (δ)	2·24	0·12	0·977	4
ν_{max} for keto carbonyl stretching frequencies of methyl 8-(substituted benzoyl)-1-naphthoates in carbon tetrachloride	13·5 (a)	1667·5 (ν_0)	2·2	0·928	8

* See Table 7. † Correlations (a) are those using σ [36] and (b) those using σ⁰.[37]

the reaction constant ρ is *ca.* 0·7. The reaction constant ratio, ρ/ρ_0, for the 8-(substituted benzoyl) system compared with that of substituted benzoic acids under the same conditions ($\rho = 1·69$),[25] is *ca.* 0·4. Transmission of the substituent polar effects from 8-benzoyl group through the bonds by an inductive mechanism, using transmission factors found previously,[38] would give a very small value for ρ/ρ_0 of *ca.* 0·1—0·2. A model for the field effect path for transmission is more difficult.

[36] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[37] R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

[38] K. Bowden, *Canad. J. Chem.*, 1963, **41**, 2781.

However, the phenylacetic acid system can be considered to be a reasonable stereochemical analogy regarding both the reaction site–substituent dispositions and the cavity. The reaction constant ratio for the latter system is 0·46(±0·07).[38] The agreement of the latter value with that found in this study further confirms the reality of the field effect transmissive model for substituent polar effects.

Ionisation of 8-Acyl-1-naphthoic Acids.—The observed pK_a values of these acids in 80% (w/w) 2-methoxyethanol-water at 25 °C are also affected by ring–chain tautomeric equilibria as shown in equation (4). Estimates of the true pK_a^T values for these acids have been made (Table 6) from previous studies of 8-substituted acids,[30,39] as well as from the present investigation. The values of K_e obtained for these 8-acyl acids are shown in Table 9. In these acids resonance effects for the 8-acyl

TABLE 9

Equilibrium constants K_e for the ring–chain tautomerism in 8-acyl-1-naphthoic acids in 80% (w/w) 2-methoxyethanol-water at 25 °C

Substnt. [R in (I)/(II)]	K_e	Substnt. [R in (I)/(II)]	K_e
H	1200(±100)	Et	210(±140)
Me	130(±50)	Pr^i	420(±80)
CD₃	130(±80)	Bu^t	1300(±500)

groups are unimportant as all these groups are completely or *very* extensively deconjugated with the naphthalene nucleus. The equilibrium constants for the 8-acetyl, -propionyl, -isobutyryl, and -pivaloyl acids can be correlated by the Taft steric linear free energy relation

$$\log (K_e/K^0_e) = \delta E_s \qquad (6)$$

(6) with the steric substituent constants, E_s,[40] as shown in Table 8. Both the 8-formyl and -benzoyl acids are excluded as the importance of polar and resonance effects in the tautomeric equilibria of these two acids clearly separates them from the latter series. The correlation, while not highly successful, still clearly indicates the destabilising effect of steric ' bulk ' in the substituent R in (I) and (II) for the chain tautomer. This appears to arise from the severe crowding between the 1,8-substituents in the chain tautomer which is partially relieved on formation of the relatively stable six-membered peri-ring tautomer.[41]

The same order of substituent effects was observed by Bowden and Taylor [28] for tautomerism in 2-acylbenzoic acids. In both systems the benzoyl group favours the chain tautomer, relative to the other acyl groups, due to the loss of the important resonance interactions in the chain tautomer when forming the ring tautomer. The formyl groups favour the ring form more than any other acyl substituent. This cannot arise from steric effects as the steric ' bulk ' of the substituent on the formyl

[39] M. Hojo, K. Katsurakawa, and Z. Yoshida, *Tetrahedron Letters*, 1968, 1497.

[40] R. W. Taft, in ' Steric Effects in Organic Chemistry,' M. S. Newman, Wiley, New York, 1956, ch. 13.

[41] *Cf.* V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567.

group is *much* less than that of the acetyl group. However the hydrogen substituent is strongly electron-with-drawing compared with the other alkyl groups,[40] and this would appear to stabilise the chain tautomer.[26]

The equilibrium constant for ring–chain tautomerism for 5-formyl-4-phenanthroic acid is difficult to estimate. A *very* approximate estimate of the true pK_a^T would be 5·0. This results in an estimate of **3000** for K_e of this acid.

It is now possible to make some general conclusions regarding ring–chain tautomerism in acylcarboxylic acids from this and previous studies.[1,26,28] The order of inclination to form the chain tautomer is, for the acyl substituent, $Ph > Me > CH_2Me > CHMe_2 > CMe_3 > H$, and, for the link system, 1,2-benzene $> cis$-ethylene $>$ 1,8-naphthalene $>$ 4,5-phenanthrene. These orders result from a combination of polar, resonance, and steric (*both* 'bulk' and ring-size) factors.

Carbonyl Stretching Frequencies of the Methyl Esters.— The carbonyl stretching frequencies of the normal esters in carbon tetrachloride are shown in Table 3. The methyl 8-(substituted benzoyl)-1-naphthoates show one absorption band corresponding to the keto carbonyl group, and in most cases, *two* corresponding to the ester carbonyl group. The carbonyl stretching frequencies

(VIII)   (IX)

of the keto-carbonyl group vary with the substituent in the 8-benzoyl group and can be correlated using the modified Hammett equation (7) and the substituent

$$\nu = a\sigma + \nu_0 \qquad (7)$$

parameters σ.[36] The regression analysis is shown in Table 8 and the constant a is 13·5. This corresponds closely to similar correlations of ν_{max} in carbon tetrachloride; *e.g.* $a = 14·9$ (methyl 2-benzoylbenzoates).[25]

The stretching frequencies of the ester carbonyl group do not vary with the substituent in a similar manner. Two absorptions at 1738—1739 and 1721—1727 cm⁻¹ are observed for all substituents except p-methyl and -methoxy. These could correspond to the two possible conformers (VIII) '*trans*', and (IX) '*cis*', arising from the two possible geometric arrangements of the de-conjugated acyl and the methoxycarbonyl groups. The existence of two conformers would depend on the steric and polar interactions between the acyl and methoxycarbonyl groups. As the methoxy-group is more 'bulky' than the carbonyl oxygen, the conformer having least steric interaction will be that having the least 'bulky' acyl substituent and the methoxy-group on the same side of the plane of the naphthalene ring. The existence of the two conformers for the 8-benzoyl esters appears possible as the benzoyl group is completely or *very* extensively deconjugated with the naphthalene

ring. This results in the 'lateral-bulk' requirements for the phenyl group being comparable with those of the oxygen atom. The four 8-acyl groups having alkyl sub-stituents are all similarly deconjugated, but have relatively 'bulky' substituents. Consequently the '*trans*' conformers (VIII) will be strongly favoured by steric factors for these four esters and their ester carbonyl frequencies are in the range 1722—1725 cm⁻¹. Conversely for the 8-formyl ester, the 'bulk' of the hydrogen is *very* small and the more stable conformer would be the '*cis*' (IX). The latter ester has an ester carbonyl frequency of 1734 cm⁻¹. This suggests that for the 8-benzoyl esters, the high frequency absorption refers to the '*cis*' conformer (IX) and the low frequency absorption to the '*trans*' conformer. The carbonyl frequency may be considered to be determined by the relative contributions of canonical structures (X)—(XIII).[42] In
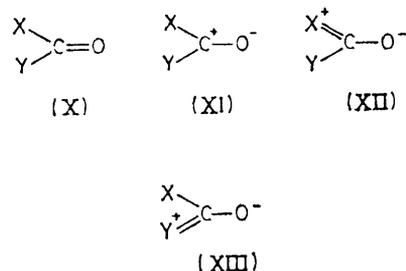
(X)   (XI)   (XII)

(XIII)

the '*cis*' conformer (IX) the contributions from canonical structures (XI)—(XIII) will be greatly reduced by un-favourable dipolar interactions with the parallel carb-onyl group and this will result in a higher ν_{max} compared to the '*trans*' conformer in which no such interaction can occur. Canonical structures such as (XI)—(XIII) would be favoured by electron-releasing groups such as p-methoxy and -methyl and this apparently results in the failure to observe the '*trans*' conformer in the latter cases. When two conformers are present, two absorp-tions would be expected for *both* the keto and ester carbonyl absorptions. However, the two absorptions are not observed for the keto carbonyl. This probably results from the keto carbonyl absorptions being broad. The frequency differences are comparatively small and are likely to give unresolved absorption bands. The conformers observed are summarised in Table 10.

TABLE 10

Conformers of methyl 8-aroyl and -acyl-1-naphthoates in carbon tetrachloride

R in (IV)	Observed conformer
H	'*cis*'
Me, Et, Pr^i, Bu^t	'*trans*'
Benzoyl substnt.	
H, 3-Me, 4-Cl, 3-Cl, 4-Br, 3-CF₃	'*cis*' and '*trans*'
4-Me, 4-OMe	'*cis*'

The variations in the carbonyl stretching frequencies of methyl pseudo-8-formyl-1-naphthoate (1742 cm⁻¹),

⁴² E. J. Hartwell, P. E. Richards, and H. W. Thompson, *J. Chem. Soc.*, 1948, 1436.

pseudo-5-formyl-4-phenanthroate (1718 cm^{-1}), and pseudo-2-formylbenzoate (1785 cm^{-1}) [43] in carbon tetrachloride clearly arise from the ring size of the pseudo ester, *i.e.* six-, seven-, and five-membered, respectively. The carbonyl stretching frequencies are strongly affected by the X–C–Y angle of a compound X–CO–Y,[44] which depends on the ring size in cyclic compounds,[45] and increase with decreasing ring size.

[43] K. Bowden, unpublished studies.
[44] J. O. Halford, *J. Chem. Phys.*, 1956, **24**, 830.
[45] R. N. Jones and C. Sandorfy, in ' Chemical Applications of Spectroscopy,' ed. W. West, Interscience, New York, 1956, ch. IV.