Ring–Chain Tautomerism. Part III.[1] Substituted *cis*-3-Benzoylacrylic Acids

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The equilibrium constants for ring-chain tautomerism in a series of substituted *cis*-3-benzoylacrylic acids have been determined using an i.r. spectroscopic method, in dioxan, and using a ^{1}H n.m.r. spectroscopic method, in dioxan and 80% (w/w) 2-methoxyethanol–water. The equilibrium constants for the *cis*-3-(substituted benzoyl)-3-methylacrylic acids have been correlated with the substituent constants σ_I and σ_R° using a modified Hammett equation. The results are related to the factors determining the position of the equilibria. 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. The effects of substitution on the latter values have been assessed by means of the Hammett equation. The reaction constants for the *cis*-acids indicated comparable transmission of the substituent polar effect to that observed in the related series of *trans*-acids.

RING–CHAIN tautomerism has been reviewed recently by Jones.[2] This type of tautomerism has been detected in a number of keto and formyl carboxylic acids.[2-5] The two tautomeric forms are the ring and chain forms, (I) and (II) respectively. Several *quantitative* studies of

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[1] Part II, K. Bowden and G. R. Taylor, *J. Chem. Soc.* (*B*), 1971, 1395.

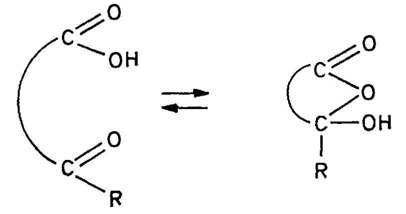
[2] P. R. Jones, *Chem. Rev.*, 1963, **63**, 461.

[3] P. R. Jones and P. J. Desio, *J. Org. Chem.*, 1965, **30**, 4293; J. Finkelstein, T. Williams, V. Toome, and S. Traiman, *J. Org. Chem.*, 1967, **32**, 3229.

[4] M. V. Bhatt and K. M. Kamath, *Tetrahedron Letters*, 1966, 3885; M. V. Bhatt and K. M. Kamath, *J. Chem. Soc.* (*B*), 1968, 1036.

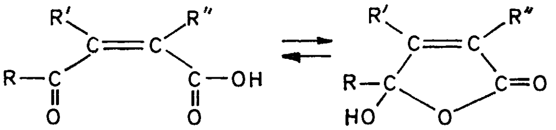
[5] K. Bowden and G. R. Taylor, *J. Chem. Soc.* (*B*), 1971, 1390.

these equilibria (1) have been made for 2-acyl- and 2-aroyl-benzoic acids.[3-5] Early investigations [6-8] clearly indicated the occurrence of ring-chain tautomerism in *cis*-3-aroylacrylic acids, (III) and (IV), as shown (2).



(1)

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



(2)

(III) (IV)

The equilibrium constant, K_e, is given by the relation (3) shown. The observed pK_a can be related [9] to the true pK_a^T by the relation (4).

$$K_e = a_{\text{ring}}/a_{\text{chain}} \qquad (3)$$

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

Lutz,[8] using an i.r. method, investigated the equilibrium for the *cis*-3-bromo-3-(4′-substituted benzoyl)-acrylic acids in chloroform. These preliminary observations indicated that the formation of the ring tautomer was, in the main, favoured by electron-withdrawing 4-substituents; as also found for 2-(substituted benzoyl)-benzoic acids.[4]

In the present study, we have investigated ring-chain tautomerism in a series of substituted *cis*-3-benzoylacrylic acids, together with their ionisation. These results have been discussed in terms of polar, steric, and resonance effects.

EXPERIMENTAL AND RESULTS

The substituted *cis*-3-benzoyl-3-methylacrylic acids were prepared by Friedel–Crafts acylation of substituted benzenes with citraconic anhydride, with the exception of the nitro-acid. The *cis*-3-methyl acids were the major products of this synthetic method; whereas, the corresponding substituted *trans*-3-benzoyl-2-methylacrylic acids were the minor and only other products. Modifications of the methods of Lutz and his co-workers [6,10] were used and the isomers separated by fractional recrystallisation. The *cis*-3-benzoyl-2-methylacrylic acids were obtained by exposing the corresponding *trans*-acids in ether to sunlight in a Pyrex vessel.[11] 3-(4′-Nitrobenzoyl)-3-methylacrylic acid was prepared by the nitration of the unsubstituted acid using a similar method to Bogert and Ritter.[12] A mixture of the *meta*- and *para*-isomers resulted which were separated by fractional recrystallisation from benzene. We were not able to purify the *meta*-isomer sufficiently for further study. The structure of the isomers was confirmed by ^1H n.m.r. spectroscopy (see below). The substituted *cis*-3-benzoylacrylic acids could not be prepared directly as they are unstable and isomerised to the *trans*-isomers; this confirmed earlier studies.[7,13] The methyl esters of the latter acids were available from our previous study.[14] After repeated recrystallisation to constant m.p. and drying in a vacuum desiccator (P_2O_5), the acids had either m.p.s in good agreement with literature values [6,10,11,15,16] or, if previously unreported, satisfactory elemental analyses (see also Table 1, footnote *h*,[17] and spectral studies below). The physical constants of the acids are listed in Table 1, together with their appearance and recrystallisation solvent.

TABLE 1

Physical constants of substituted *cis*-3-benzoylacrylic acids

Substituent	M.p./°C	Lit. m.p./°C	Ref.
H (3-Me)	79—80 [a]	79—80	6
4′-Cl (3-Me)	134—135 [b]	135—136	15
4′-Br (3-Me)	138—141 [b]	142·5	10
4′-Me (3-Me)	92—94 [a]	94—95	16
4′-OMe (3-Me)	139—141 [c]	93—95 [h]	17
4′-NO_2 (3-Me)	188—189 [d]		
4′-Cl (2-Me)	104—106 [e]		
4′-Br (2-Me)	96—99 [e]	97	11
4′-Me (2-Me)	113—114 [f]		
4′-OMe (2-Me)	117—120 [g]		

[a] Colourless prisms from benzene–light petroleum (b.p. 60—80 °C). [b] Colourless prisms from chloroform. [c] Colourless prisms from acetone–benzene. [d] Colourless prisms from benzene. [e] Colourless needles from benzene–light petroleum (b.p. 60—80 °C). [f] Colourless needles from light petroleum (b.p. 60—80 °C). [g] Colourless prisms from light petroleum (b.p. 60—80 °C). [h] Fleifel [17] has reported this compound to have m.p. 93—95 °C. Even on repeating his synthetic method, we obtained only the same *cis*-isomer (m.p. 139—141 °C) as isolated from the standard preparation used in this study. The elemental analysis (see Table 2), ^1H n.m.r. and i.r. spectra (see Tables 3 and 7), neutralisation equivalent and pK_a were all in agreement with structure given.

The elemental analyses of the previously unreported acids are given in Table 2. The neutralisation equivalents of the acids were determined by titration to be within ±1% of the calculated values. The normal methyl esters were prepared and purified as previously described,[14] while the pseudo methyl esters were synthesised either by methanolysis of the acid chloride or by a modified Fischer–Speier esterification.[18-20] Solvents were purified as previously described.[21]

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[6] R. E. Lutz, P. S. Bailey, C-K. Dien, and J. W. Rinker, *J. Amer. Chem. Soc.*, 1953, **75**, 5039, and references therein.

[7] R. E. Lutz and G. W. Scott, *J. Org. Chem.*, 1948, **13**, 284.

[8] R. E. Lutz and H. Moncure, *J. Org. Chem.*, 1960, **26**, 746.

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

[10] R. E. Lutz and R. J. Taylor, *J. Amer. Chem. Soc.*, 1933, **55**, 1168.

[11] R. E. Lutz, D. T. Merritt, and M. Couper, *J. Org. Chem.*, 1939, **4**, 95.

[12] M. T. Bogert and J. J. Ritter, *J. Amer. Chem. Soc.*, 1925, **47**, 526.

[13] G. P. Rice, *J. Amer. Chem. Soc.*, 1923, **45**, 222.

[14] K. Bowden and M. P. Henry, *J. Chem. Soc.* (*B*), 1971, 156.

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[17] A. Fleifel, *J. Org. Chem.*, 1959, **24**, 1343.

[18] R. E. Lutz and A. W. Winne, *J. Amer. Chem. Soc.*, 1934, **56**, 1168.

[19] M. S. Newman and C. D. McCleary, *J. Amer. Chem. Soc.*, 1941, **63**, 1537; M. S. Newman and L. K. Lala, *Tetrahedron Letters*, 1967, 3267.

[20] K. Bowden and M. P. Henry, unpublished studies.

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

I.r. Measurements.—The spectra of the compounds in solution were measured by use of matched 0·05-cm fixed path-length cells with sodium chloride windows and a Perkin-Elmer model 231 spectrophotometer. The spectra were scanned at slow speed, and were calibrated by superimposed water vapour bands at $\nu_{max.}$ 1670 and 1718 cm^{-1}. The wavenumber measurements were reproducible to ± 1 cm^{-1} (relative to the standard).

TABLE 2

Elemental analysis of previously unreported substituted *cis*-3-benzoylacrylic acids

Substituent	Molecular formula	Calc. (%) C	H	O	Other	Found (%) C	H	O	Other
4′-NO_2 (3-Me)	$C_{11}H_9NO_5$	56·1	3·9	34·0	6·0 (N)	56·4	3·9		5·9 (N)
4′-OMe (3-Me) *	$C_{12}H_{12}O_4$	65·4	5·5	29·1		65·7	5·4	28·8	
4′-Cl (2-Me)	$C_{11}H_9ClO_3$	58·8	4·0	21·4	15·8 (Cl)	58·6	4·2		15·8 (Cl)
4′-Me (2-Me)	$C_{12}H_{12}O_3$	70·6	5·9	23·5		70·8	6·0	23·4	
4′-OMe (2-Me)	$C_{12}H_{12}O_4$	65·4	5·5	29·1		65·7	5·6	28·9	

* See footnote *h* to Table 1.

The procedure for the determination of the equilibrium constants was an improved version of that used previously.[4,5] In this study, the apparent integrated intensity of each carbonyl bond was measured by using a Dupont Model 301 curve resolver, relative to a standard triangle of known area. When necessary, overlapping absorptions were resolved into their component bands. Calibration curves were drawn for the carbonyl absorptions of the normal and pseudo methyl esters at three different ester concentrations. Linear relations between absorption areas and concentrations were obtained and the apparent integrated intensities, A^a, were calculated. The spectra of all the *cis*-acids, approximately 0·02M in dioxan at 35 ($\pm$ 1) °C, showed the presence of both ring and chain tautomers. The absorption ' areas ', a', of the component lactone, carboxylic, and keto carbonyl bands were resolved and measured. The lactone and keto carbonyl absorptions were used in the determination of K_e, as those determinations using the carboxylic carbonyl absorption were less reproducible. From equation (3), the tautomeric equilibrium constant, K_e, can be evaluated from the measurements of the absorptions as shown in equation (5), using the same assumptions as made previously.[4,5] The reproducibility is mainly dependent on the error in measuring the smaller keto carbonyl absorption and the latter error, mainly, results in the uncertainties quoted. The values of $\nu_{max.}$ of the carbonyl-stretching vibrations of the *cis*-acids and esters in dioxan are given in Table 3 and the values of K_e in Table 4.

$$K_e = a'_{ring}A^a_{normal}/a'_{chain}A^a_{pseudo} \qquad (5)$$

^{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.[5] The chemical shifts were measured in p.p.m. relative to tetramethylsilane (TMS), and are quoted as τ values.

The procedure for determination of the equilibrium constants, K_e, has been described previously.[5] The comparatively large differences in the chemical shifts of the 3-methyl protons in the tautomers of the *cis*-3-(substituted benzoyl)-3-methylacrylic acids, due to the change from a proximate keto (chain) to ' hemi-ketal ' (ring) group, enabled these measurements to be made. Even then the experimental errors in the chemical-shift measurements made these determinations of K_e much less certain than those using the i.r. method. The 2-methyl series did not have suitable proton shifts for this method to be used. The ^{1}H n.m.r. spectral results and the equilibrium constants, K_e, for the *cis*-3-(substituted benzoyl)-3-methylacrylic acids are shown in Tables 5 and 6.

The structure of the acids were confirmed and the acids were shown to be >98% pure by this spectral method. The results are shown in Table 7. The aromatic protons were also observed and the *para*-substituted aromatic systems had a coupling constant, *J*, of 9·0 $\pm$ 0·5 Hz.

TABLE 3

I.r. spectral results for *cis*-3-(substituted benzoyl)acrylic acids and their methyl esters in dioxan

	$\nu_{max.}$ (cm^{-1})					
	Acid CO			Methyl ester CO		
	Chain			Normal (chain)		
Substituent	Ketone	Carboxylic	Ring lactone	Ketone	Carboxylic	Pseudo (ring) lactone
H (3-Me)	1676	1713	1769	1676	1727	1777
4′-Cl (3-Me)	1677	1714	1765	1677	1726	1778
4′-Br (3-Me)	1678	1714	1765	1677	1726	1779
4′-Me (3-Me)	1675	1713	1767	1674	1727	1777
4′-OMe (3-Me)	1680	1713	1765	1676	1727	1777
4′-NO_2 (3-Me)	1683	1716	1768	1681	1728	1779

TABLE 4

Equilibrium constants (K_e) for ring-chain tautomerism in *cis*-3-(substituted benzoyl)acrylic acids in dioxan by i.r. method

Substituent	K_e
H (3-Me)	10·$_6$ ($\pm$2)
4′-Cl (3-Me)	6·$_6$ ($\pm$2)
4′-Br (3-Me)	7·$_6$ ($\pm$2)
4′-Me (3-Me)	4·5 ($\pm$0·6)
4′-OMe (3-Me)	1·7 ($\pm$0·2)
4′-NO_2 (3-Me)	26 ($\pm$8)
4′-Cl (2-Me)	4·$_3$ ($\pm$1)
4′-Br (2-Me)	4·$_3$ ($\pm$1)
4′-Me (2-Me)	3·0 ($\pm$0·2)
4′-OMe (2-Me)	1·0 ($\pm$0·1)

pK_a *Measurements*.—The observed pK_a values of the acids were measured in 80% (w/w) 2-methoxyethanol–water at 25 ($\pm$0·1) °C, as described previously,[21] and are shown in Table 8. However, the substituted *cis*-3-benzoylacrylic acids were not directly available (see above). A variant procedure for the potentiometric titration was followed using the methyl esters of these acids. After following the same method as previously [21] using a sample of the ester instead of the acid, 1·10 equivalents of the 0·1M-aqueous sodium hydroxide were *rapidly* added from the microsyringe to the titration vessel. After completion of the ester hydrolysis, *i.e.* reaction 99·8% complete after up to 3 h with 'pH' approximately equal to 10·5, the microsyringe was replaced by one containing 0·1M-aqueous hydrochloric acid. The titration curve was then constructed and the pK_a obtained graphically as before.[21]

TABLE 5

Equilibrium constants (K_e) for ring-chain tautomerism in *cis*-3-(substituted benzoyl)acrylic acids in 80% (w/w) 2-methoxyethanol–water by ^{1}H n.m.r. method

	τ (3-CH_3)			
Substituent	Pseudo (ring)	Normal (chain)	Averaged	K_e
H (3-Me)	8·08	7·83	8·06	11 (±4)
4′-Cl (3-Me)	8·06	7·81	8·03	8 (±2)
4′-Br (3-Me)	8·06	7·81	8·02	6 (±1)
4′-Me (3-Me)	8·10	7·85	8·03	2·9 (±0·5)
4′-OMe (3-Me)	8·11	7·87	7·99	1·1 (±0·1)
4′-NO$_2$ (3-Me)	8·06	7·82	8·07	*

* K_e too large for measurement by this method.

TABLE 6

Equilibrium constants (K_e) for ring-chain tautomerism in *cis*-3-(substituted benzoyl)acrylic acids in dioxan by ^{1}H n.m.r. method

	τ (3-CH_3)			
Substituent	Pseudo (ring)	Normal (chain)	Averaged	K_a
H (3-Me)	8·16	7·89	8·13	8 (±3)
4′-Cl (3-Me)	8·14	7·87	8·12	*
4′-Br (3-Me)	8·14	7·87	8·13	*
4′-Me (3-Me)	8·18	7·91	8·10	2·5 (±0·3)
4′-OMe (3-Me)	8·19	7·92	8·06	1·1 (±0·2)
4′-NO$_2$ (3-Me)	8·14	7·88	8·14	*

* See Table 5.

TABLE 7

^{1}H N.m.r. spectral results for the *cis*-3-benzoylacrylic acids in [$^2H_6$]acetone

	τ *	
Substituent	2-*H*	3-CH_3
H (3-Me)	3·95	8·06
4′-Cl (3-Me)	3·94	8·05
4′-Br (3-Me)	3·94	8·04
4′-Me (3-Me)	4·06	8·06
4′-OMe (3-Me)	3·94	8·00
4′-NO$_2$ (3-Me)	3·85	8·04
	2-CH_3	3-*H*
4′-Cl (2-Me)	8·04	2·75
4′-Br (2-Me)	8·05	2·73
4′-Me (2-Me)	8·02	2·78
4′-OMe (2-Me)	8·00	2·81

* Coupling constants, *J*, were equal to 1·7 ± 0·3 Hz.

The variant method was evaluated by measuring the pK_a values of *trans*-3-(substituted benzoyl)acrylic acids available both as the acid and as the methyl ester. A correction of +0·20 pK_a unit was necessary to the value obtained by the ester method, probably due to changed content of the medium caused by using the latter procedure, to give agreement between the two methods. As in our studies of the alkaline hydrolysis of these *cis*-esters,[14] no isomerisation could be detected by u.v. or ^{1}H n.m.r. spectroscopy during the course of a titration and the corresponding carboxylate anions have been found to be stable under similar conditions to the titration studies.[20] All our pK_a measurements are the result of at least two separate determinations.

TABLE 8

Ionisation of substituted *cis*-3-benzoylacrylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C

Substituent	Observed pK_a *	log (1 + K_a)	Corrected pK_a^T
H	5·78		
4′-F	5·64		
4′-Br	5·66		
4′-I	5·70		
4′-Me	5·88		
4′-OMe	5·85		
H (3-Me)	7·60	1·06 (±0·07)	6·54 (±0·09)
4′-Cl (3-Me)	7·46	0·88 (±0·09)	6·58 (±0·11)
4′-Br (3-Me)	7·51	0·93 (±0·09)	6·58 (±0·11)
4′-Me (3-Me)	7·45	0·74 (±0·05)	6·71 (±0·07)
4′-OMe (3-Me)	7·11	0·43 (±0·03)	6·68 (±0·05)
4′-NO$_2$ (3-Me)	7·65	1·43 (±0·13)	6·22 (±0·15)
4′-Cl (2-Me)	6·61	0·72 (±0·10)	5·89 (±0·12)
4′-Br (2-Me)	6·58	0·72 (±0·10)	5·86 (±0·12)
4′-Me (2-Me)	6·61	0·60 (±0·02)	6·01 (±0·04)
4′-OMe (2-Me)	6·30	0·30 (±0·02)	6·00 (±0·04)

* The observed pK_a values were reproducible to ±0·02 (2-H, 3-Me; 2-Me, 3-H) and to ±0·05 unit (2,3-H_2).

DISCUSSION

The equilibrium constants for ring–chain tautomerism in *cis*-3-benzoylacrylic acids in dioxan and/or 80% (w/w) 2-methoxyethanol–water determined by i.r. and ^{1}H n.m.r. spectroscopic methods are shown in Tables 4 to 6. There appears to be no substantial difference between the values of K_e in these two solvents, as was also observed by Bowden and Taylor[5] for the 2-acylbenzoic acids. For substituted 2-benzoylbenzoic acids, Bhatt and Kamath[4] found a similar effect for dioxan, nitromethane, and acetonitrile; unlike chloroform as solvent. Bhatt and Kamath[4] indicated a relation between log K_e and the substituent constant, σ, for substitution in the 2-benzoyl ring. However, their relations do appear to be distinctly curved; whereas, the Hammett relation[22] (6) requires linear dependence on the substituent

$$\log (K_e/K_e^{\circ}) = \rho\sigma \qquad (6)$$

constant. A similarly curved relation between log K_e and σ for the *cis*-3-(substituted benzoyl)acrylic acids has been found in this study. Previously, the importance of resonance effects in determining the position of the tautomeric equilibria of these types have been noted.[1-3,5,23] The polar substituent effect can be separated into 'inductive' and resonance contributions, σ_I and σ_R° respectively.[24] Thus, the *para*-substituent polar effect, σ_P, can be divided into these factors, as shown in equation (7). A modified Hammett relation

$$\sigma_P = \sigma_I + \sigma_R^{\circ} \qquad (7)$$

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[22] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[23] M. S. Newman and C. W. Muth, *J. Amer. Chem. Soc.*, 1951, **73**, 4627; M. S. Newman and C. Corduvelis, *ibid.*, 1964, **86**, 1893; M. S. Newman and C. Corduvelis, *J. Org. Chem.*, 1965, **30**, 1795.

[24] 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, *J. Amer. Chem. Soc.*, 1959, **81**, 5352.

(8) can be used to correlate the equilibrium constants

$$\log (K/K_0) = \rho_{\mathrm{I}}\sigma_{\mathrm{I}} + \rho_{\mathrm{R}}\sigma_{\mathrm{R}}^{\circ} \qquad (8)$$

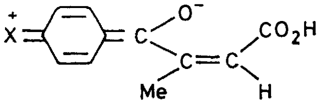
and was very successful, as shown in Table 9. The reaction constants, ρ_{I} and ρ_{R}, indicate the susceptibility of the reaction to ' inductive ' and resonance effects, respectively. The prime importance of resonance effects is shown by the large value of ρ_{R} equal to 1·9. This arises from the contribution of structures such as (V) to the stabilisation of the chain tautomer. The much smaller ' inductive ' contribution, with ρ_{I} equal to 0·4, probably arises from the more favourable interaction between an ' electron-withdrawing ' substituent dipole with the ' dipolar ' keto-carbonyl group in the chain tautomer, rather than with the ' hemi-ketal ' group in the ring tautomer.

TABLE 9

Reaction constants for the ring-chain tautomeric equilibria of *cis*-3-(substituted benzoyl)-3-methylacrylic acids in dioxan using the modified Hammett equation *

ρ_{I}	ρ_{R}	$\log K_{\mathrm{e}}^{\circ}$	s	r	n
0·374	1·885	0·957	0·072	0·990	6

* r is the correlation coefficient, s the standard deviation, and n the number of substituents studied.



(V)

The equilibrium constants for ring-chain tautomerism in the three series decrease in the order; 2-H, 3-Me; 2-Me, 3-H; 2,3-H_2; *i.e.* K_{e} values for the parent unsubstituted acids are *ca.* 11 (2-H, 3-Me), 7 (estimated; * 2-Me, 3-H), and 0·3 (ref. 25) (2,3-H_2). This appears to be caused by the steric effect of the methyl groups. The latter groups will cause some deconjugation of the carbonyl groups and the unsaturated and/or aromatic systems when twisting occurs to relieve steric ' bulk ' interactions. This will de-stabilise the chain tautomer, relative to the ring tautomer. Further, it seems likely that the ring tautomer, which has a ' strained ' unsaturated five-membered lactone ring, is favoured over the chain tautomer when ' bulky ' substituents are present.[26] The internal steric interactions are relieved on formation of this ring tautomer.

As stated in the Introduction, the acidities of these *cis*-acids are affected by the ring-chain tautomeric equilibria. The observed pK_{a} values are derived from two contributions, the true p$K_{\mathrm{a}}^{\mathrm{T}}$ and $-\log (K_{\mathrm{e}} + 1)$ [see equation (4)]. Possible correlations of the observed pK_{a} values using the Hammett equation are therefore dependent on these two factors. Thus, if $K_{\mathrm{e}} \ll 1$, the reaction constant found, ρ_{obs}, is equal to that for p$K_{\mathrm{a}}^{\mathrm{T}}$ values, ρ_{true}; whereas, if $K_{\mathrm{e}} \gg 1$, the reaction constant found is the sum of those for p$K_{\mathrm{a}}^{\mathrm{T}}$ values, ρ_{true}, and values of $\log K_{\mathrm{e}}$, ρ_{equil}; as shown in equation (9). As

$$\rho_{\mathrm{obs}} = \rho_{\mathrm{true}} - \rho_{\mathrm{equil}} \qquad (9)$$

both ρ_{true} and ρ_{equil} can be expected to be positive (this study above, ref. 4 and 27), the value of ρ_{obs} could be either positive or negative, depending on the contribution of K_{e} and the relative magnitudes of ρ_{true} and ρ_{equil}. Correlations of observed pK_{a} values of *cis*-3-(substituted benzoyl)acrylic and *cis*-3-(substituted benzoyl)-3-methylacrylic acids with σ [28] and σ° [29] values are shown in Table 10. Very poor correlations for the latter acids, with *negative* reaction constants, indicate the important contributions of K_{e} for this series (see above). However, the correlations for the former acids are moderately successful and have a *positive* reaction constant in the expected range for ρ_{true}, *i.e.* ρ/ρ_0 is equal to *ca.* 0·2 to 0·3, where ρ_0 is the reaction constant for the reference system, benzoic acids, under identical conditions, which is 1·69.[21] This ratio, ρ/ρ_0, would be expected to be *ca.* 0·2 to 0·4 (refs. 14, 27, 30) (see also below). This shows that, for this 2,3-H_2 series, K_{e} is small compared to 1. Early studies by Lutz [7] indicated that these acids were present predominantly as the chain tautomer. Our further studies [27] indicate that K_{e} for the parent *cis*-3-benzoylacrylic acid is 0·3 (±0·2), using an indirect method of estimation. Thus this confirms these conclusions.

TABLE 10

Hammett reaction constants for the ionisation of the substituted *cis*-3-benzoylacrylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C *

Series		ρ	$\log K_0$	r	s	n
2,3-H_2	(*a*)	0·391	−5·76	0·834	0·061	6
(pK_{a} values)	(*b*)	0·500	−5·79	0·933	0·040	6
2-H, 3-Me	(*a*)	−0·386	−7·42	0·715	0·149	6
(pK_{a} values)	(*b*)	−0·359	−7·41	0·611	0·168	6
2-H, 3-Me	(*a*)	0·443	−6·64	0·957	0·054	6
(p$K_{\mathrm{a}}^{\mathrm{T}}$ values)	(*b*)	0·423	−6·62	0·950	0·059	6
2-Me, 3-H	(*a*)	0·281	−5·94	0·965	0·052	4
(p$K_{\mathrm{a}}^{\mathrm{T}}$ values)	(*b*)	0·324	−5·96	0·982	0·041	4

* r is the correlation coefficient, s the standard deviation, and n the number of substituents studied. Correlations (*a*) are those using σ and (*b*) those using σ°.

The true p$K_{\mathrm{a}}^{\mathrm{T}}$ values have been calculated for the 2-H, 3-Me and 2-Me, 3-H series as shown in Table 8, using the values of K_{e} found previously. Despite the larger uncertainties in these p$K_{\mathrm{a}}^{\mathrm{T}}$ values, the Hammett correlations are successful and are shown in Table 10. The ratio, ρ/ρ_0, for all these three series in their ionisation are *ca.* 0·2 to 0·3. These values are closely comparable with the ionisation of both the corresponding *trans*-systems (*ca.* 0·2 to 0·4) [27] and the 2-(substituted benzoyl)benzoic acids (0·33).[21] The latter is a *cis*-type system itself.

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* Estimated from the linear relation between K_{e} values for 2-H, 3-Me and 2-Me, 3-H series.

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Like the systems studied by Hogeveen,[31] the *cis*- and *trans*-3-benzoylacrylic acids have comparable transmissive capabilities for substituent polar effects. The latter systems have a carbonyl group link, while those of Hogeveen have a thio, sulphinyl, or sulphonyl group link. However, the alkaline hydrolysis of the methyl esters of the *cis*-3-benzoylacrylic acids have a ratio, ρ/ρ_0, equal to *ca.* 1.[14] This is quite unlike that found for the *trans*-series with ρ/ρ_0 equal to 0·32.[14] As previously discussed, the ratio for the *cis*-esters does not arise from normal transmission to the carboxylate ester group, but from a mechanistic change to a path having neighbouring-group participation by the keto-carbonyl group.

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