Ring–Chain Tautomerism. Part 7.[1] Substituted Benzil-2-carboxylic and 2-Phenylacetylbenzoic Acids and their Methyl Esters

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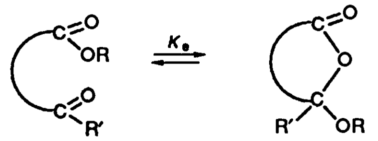
The equilibrium constants, K_e, for ring–chain tautomerism in a series of substituted benzil-2-carboxylic and 2-phenylacetylbenzoic acids, as well as for the methyl esters of the latter series, have been determined by IR and NMR spectroscopic methods. The observed pK_a values, which have been measured for solutions in 80% (w/w) 2-methoxyethanol–water, have been corrected for the tautomeric equilibria to give the true pK_a (pK_a^T). The effects of substitution on both log K_e and pK_a values have been assessed by means of the Hammett equation. The results are discussed.

Ring–chain tautomerism has been studied extensively in suitably constructed acyl carboxylic acids and their corresponding esters.[2] This behaviour has been shown to give rise to both ring (pseudo) **2** and chain (normal) **1** forms of these systems. The



(1)

1a; R = H
b; R = Me

2a; R = H
b; R = Me

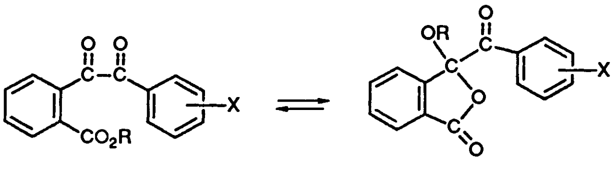
equilibrium constant, K_e, for the tautomerism equilibrium (1) is given by eqn. (2). The acidities of the tautomeric acids are

$$K_e = a_{ring}/a_{chain} \qquad (2)$$

affected by these equilibria and it has been shown[3] that the true pK_a value, pK_a^T is related to the observed value by the relation (3). If both K_e and the pK_a are known, pK_a^T can be calculated.

$$pK_a^T = pK_a - \log(K_e + 1) \qquad (3)$$

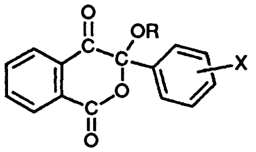
However, if a reliable estimate of pK_a^T can be made, K_e can be found by measuring pK_a. Both procedures have been employed.[4–7] Quantitative studies of these tautomeric equilibria have been made using IR, UV and ^{1}H NMR methods.[2,4–7] For certain systems, it has even been possible to isolate the tautomeric acids, **1a** and **2a**.[2] However, in solution, the interconversion is normally relatively rapid.[2] The corresponding tautomeric equilbrium has been studied for the esters using IR, UV, ^{1}H NMR and GLC methods.[1,2,8] Both the chain (normal), **1b**, and ring (pseudo) esters, **2b**, have been isolated in favourable cases.[2] The rates and mechanisms of the acid- or base-catalysed tautomerizations of the methyl esters have been investigated.[1,8] Benzil-2-carboxylic acid has been prepared in two solid modifications;[9] the yellow form is considered to have the chain (normal) structure **3a** and the colourless form the ring (pseudo) structure **4a**, confirmed by IR spectral evidence.[10]



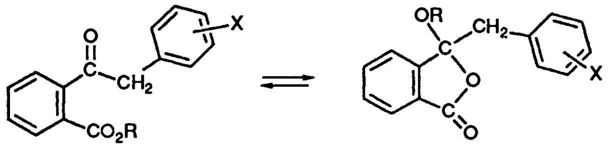
3a; R = H
b; R = Me

4a; R = H
b; R = Me

The ring (pseudo) tautomer appeared to have the five-membered ring structure **4a**, in contrast to the six-membered ring structure **5a**. A semi-quantitative estimate of the tautomeric equilibrium has been made by IR and NMR spectroscopy.[11] The ring–chain tautomerism of 2-phenylacetylbenzoic acid, **6a** and **7a**, and the corresponding methyl ester, **6b** and **7b**, has been studied by Bowden *et al.*[4,7,12] The equilibrium constants were estimated by both ^{1}H NMR and IR spectroscopic methods.



5a; R = H
b; R = Me



6a; R = H
b; R = Me

7a; R = H
b; R = Me

In this study, measurements of the tautomeric equilibrium constants for a series of 2-(substituted phenylacetyl)benzoic and substituted benzil-2-carboxylic acids and the corresponding methyl esters have been made. These results for the acids have been used to obtain pK_a^T from pK_a values 80% (w/w) 2-methoxyethanol–water. The results are discussed in terms of the polar, steric and stereochemical effects.

Experimental Results

Materials.—The preparation of both the substituted 2-phenylacetylbenzoic acids and the corresponding normal methyl esters has been described previously.[12] The corresponding pseudo methyl esters were synthesized by reaction of the appropriate 2-phenylacetylbenzoic acids or benzylidenephthalides with methanolic hydrogen chloride.[12,13] The substituted benzil-2-carboxylic acids were synthesized by dimethyl sulfoxide–aqueous hydrogen bromide oxidation[14] of the corresponding 2-phenylacetylbenzoic acids (*i.e.* the deoxybenzoins). The corresponding normal esters were prepared by esterification of the acids with diazomethane in ether.[15] We were unable to prepare the pseudo methyl esters of benzil-2-carboxylic acids,

Table 1 Physical constants of benzil-2-carboxylic acids and their methyl esters

X (Formula)	M.p./°C[a] (lit.)	Found (%) (Required) C	H	Other
Acids				
H	141–143[b] (141–141.5)[11]			
4-Me	145–147 (144–145)[19]			
3-Me	140–142	71.5	4.6	
($C_{16}H_{12}O_4$)		(71.6	4.5)	
4-OMe	171–173 (168)[19]	*c*		
3-OMe	135–137	67.4	4.4	
($C_{16}H_{12}O_5$)		(67.6	4.3)	
4-Cl	161–162 (166)[19]	*c*		
3-Cl	170–172	62.3	3.3	12.1 (Cl)
($C_{15}H_9ClO_4$)		(62.4	3.1	12.3)
4-Br	143–145	54.3	2.9	24.2 (Br)
($C_{15}H_9BrO_4$)		(54.1	2.7	24.0)
Esters				
H	117–118 (118–119)[15]			
4-Me	146–148	72.3	5.1	
($C_{17}H_{14}O_4$)		(72.3	5.0)	
3-Me	140–142	72.2	5.2	
($C_{17}H_{14}O_4$)		(72.3	5.0)	
4-OMe	75–77	68.7	4.7	
($C_{17}H_{14}O_5$)		(68.4	4.7)	
3-OMe	63–65	68.6	4.7	
($C_{17}H_{14}O_5$)		(68.4	4.7)	
4-Cl	129–131	63.1	3.6	11.5 (Cl)
($C_{16}H_{11}ClO_4$)		(63.5	3.7	11.7)
3-Cl	138–140	63.6	3.8	11.6 (Cl)
($C_{16}H_{11}ClO_4$)		(63.5	3.7	11.7)
4-Br	121–123	55.7	3.2	23.3 (Br)
($C_{16}H_{11}BrO_4$)		(55.4	3.2	23.0)

[a] Recrystallization solvent MeOH unless otherwise shown. [b] Recrystallization solvent $CHCl_3$–light petroleum. [c] Elemental analysis found was in good agreement with that required.

Table 2 Equilibrium constants (K_e) for ring–chain tautomerism in substituted benzil-2-carboxylic (**3a**, **4a**) and 2-(substituted phenylacetyl)-benzoic acids (**6a**, **7a**)[a]

X	K_e **3a**, **4a**[b]	**6a**, **7a**[b]	**6a**, **7a**[c]
H	1.4	5.7	2.5
4-Me	1.1	5.2	2.2
3-Me	1.3	5.5	2.4
4-OMe	1.0	5.0	2.2_5
3-OMe	1.5_5	6.0	2.6
4-Cl	1.8	7.8	3.1
3-Cl	2.0	8.6	3.7
4-Br	1.9	7.9	3.3

[a] The K_e values are reproducible to ± 12% in $CHCl_3$ and to ± 15% in MeOH. [b] In $CHCl_3$; 35 °C; IR method. [c] In MeOH; 25 °C, ^1H NMR method.

as reported by others[9,10] (but see below). The purity of the tautomeric methyl esters was monitored by ^1H and ^{13}C NMR spectroscopy. The solvents were purified as described previously.[16–18] The m.p.s of the acids and esters, after repeated recrystallization and drying under reduced pressure (P_2O_5), are shown in Table 1, together with the elemental analyses of new compounds.

IR Measurements.—The carbonyl stretching vibrations of the normal and pseudo methyl esters and acids were determined as previously described[4,5] for solutions (0.02 mol dm^{-3}) in chloroform at 35 (± 1) °C. The spectra of all the acids showed the presence of both ring and chain tautomers. The results for the 2-(substituted phenylacetyl)benzoic acids were comparatively simple. The absorption due to the lactone carbonyl of the ring tautomers is sharp at *ca.* 1772 cm^{-1}; while a broad absorption derives from the keto and carboxylic carbonyls of the chain tautomers at *ca.* 1702 and 1721 cm^{-1}, respectively. The latter result arises from the comparatively close frequencies of these absorptions. The area of the keto and carboxylic carbonyl absorptions was therefore calculated together. The values of K_e were then calculated as before[5] and are shown in Table 2. The values of ν_{max} of the carbonyl stretching vibrations of the normal and pseudo methyl 2-(substituted phenylacetyl)-benzoates and the corresponding acids in chloroform are shown in Table 3. The results for the substituted benzil-2-carboxylic acids were more complex. The absorption due to the lactone carbonyl of the ring tautomers is sharp at *ca.* 1783 cm^{-1}; while a broad absorption results from the α-keto and carboxylic carbonyls of the chain tautomers at *ca.* 1717 cm^{-1} and an absorption from the β-keto carbonyls of both tautomers at *ca.* 1682 cm^{-1}. The combined area of the α-keto and carboxylic carbonyl absorptions was therefore calculated. As it was not possible to prepare pseudo methyl esters of this series, the results for the corresponding pseudo methyl 2-phenylacetylbenzoates were used. The values of K_e were then calculated as before[5] using the results for normal methyl esters of this series and the pseudo methyl esters of the 2-phenylacetylbenzoate series. They are shown in Table 2. Due to the method used in their calculation the reliability of the value of K_e for these acids is less than their reproducibility (see Table 2) might suggest. The values of ν_{max} of the carbonyl stretching vibrations of the normal methyl substituted benzil-2-carboxylates and the corresponding acids in chloroform are shown in Table 4. Those of the corresponding pseudo esters were only available as normal–pseudo ester mixtures from the treatment of the acids with methanol–hydrogen chloride for the three most electron-withdrawing substituents (see below). The structure of the pseudo ring forms as the five-membered ring structures **4**, rather than the six-membered ring structures **5**, is confirmed by the carbonyl stretching frequencies observed. Thus, for a comprehensive series of related pseudo-esters, the five-membered rings give carbonyl stretching frequencies of *ca.* 1769 cm^{-1} and the six-membered rings of *ca.* 1708 cm^{-1}.[13] A Perkin Elmer model 231 spectrophotometer was used in these studies and the wavenumber measurements were reproducible to ± 1 cm^{-1} (relative to the standard, a calibration by superimposed water vapour bands).

Table 3 Carbonyl stretching frequencies of methyl 2-(substituted phenylacetyl)benzoates and the corresponding acids in $CHCl_3$[a]

X	ν_{max}/cm^{-1} Normal ester Keto[b]	Carboxylic	Pseudo ester Lactone
H	1700	1723 (1722)	1773 (1772)
4-Me	1702	1720 (1720)	1770 (1767)
3-Me	1700	1720 (1721)	1770 (1773)
4-OMe	1700	1718 (1720)	1770 (1770)
3-OMe	1705	1720 (1721)	1775 (1772)
4-Cl	1705	1720 (1720)	1773 (1773)
3-Cl	1703	1718 (1720)	1773 (1772)
4-Br	1703	1718 (1722)	1772 (1775)

[a] Values in parentheses are for the corresponding acids. [b] Estimated values for the methyl esters because of overlapping bands. For the corresponding acids these could not be estimated reliably for the same reason.

NMR Measurements.—The spectra of the compounds were measured using a JEOL EX270 spectrometer operating at 270

Table 4 Carbonyl stretching frequencies of substituted benzil-2-carboxylic acids and their corresponding methyl esters in $CHCl_3$[a]

	ν_{max}/cm^{-1}		
	Chain acid		Ring acid
X	α-Keto/Carboxylic	β-Keto	Lactone
H	1714 (1708)[b] (1730)[c]	1683 (1675)	1783
4-Me	1718 (1707)[b] (1730)[c]	1678 (1677)	1778
3-Me	1718 (1707)[b] (1733)[c]	1683 (1673)	1785
4-OMe	1720 (1707)[b] (1730)[c]	1678 (1665)	1780
3-OMe	1715 (1707)[b] (1733)[c]	1683 (1677)	1785
4-Cl	1718 (1705)[b] (1732)[c]	1683 (1685)	1785 (1783)
3-Cl	1715 (1705)[b] (1732)[c]	1685 (1682)	1785 (1784)
4-Br	1715 (1705)[b] (1734)[c]	1685 (1680)	1785 (1785)

[a] Values in parenthesis are for the corresponding methyl esters. [b] α-Keto. [c] Carboxylate.

Table 5 ^1H NMR spectral results and equilibrium constants (K_e) for ring–chain tautomerism in methyl 2-(substituted phenylacetyl)benzoates in MeOH at 25.0 °C by ^1H NMR method

	δ[a]		
X	Ring[c] (pseudo)	Chain (normal)	K_e[b]
H	3.40 (3.07_5)	4.11_5 (3.89)	2.9
4-Me	3.35 (3.06)[d]	4.07 (3.89)[d]	2.7
3-Me	3.36 (3.06_5)[d]	4.07_5 (3.90)[d]	2.5
4-OMe	3.34 (3.07)[d]	4.05 (3.89)[d]	2.3
3-OMe	3.38 (3.06)[d]	4.07_5 (3.89)[d]	3.5
4-Cl	3.36 (3.06)	4.08 (3.90_5)	4.1_5
3-Cl	3.34 (3.06_5)	4.08 (3.90)	4.6
4-Br	3.34_5 (3.06)	4.06_5 (3.90)	4.0

[a] In $CDCl_3$. Values shown are those for the methylene and in parentheses are for ester methoxy. [b] The values of K_e are considered to ± 10%. [c] Present as a quartet (see text). [d] Methyl protons also at *ca.* 2.3 and 2.2 ppm (ArMe) and at 3.8 and 3.7 ppm (ArOMe).

MHz. The ^1H NMR spectral chemical shifts were measured in ppm relative to tetramethylsilane (TMS) and the ^{13}C NMR spectral chemical shifts in ppm relative to TMS.

In the ^1H NMR spectra of the methyl 2-(substituted phenylacetyl)benzoates, the pseudo and normal ester methoxy signals are at *ca.* 3.1 and 3.9 ppm, respectively, as previously found.[8] The methylene groups in the pseudo esters have non-equivalent hydrogens, being directly bonded to an asymmetric carbon atom, and are observed as a quartet, *cf.* ref. 20. The pseudo and normal ester methylene signals are at *ca.* 3.4 and 4.1 ppm, respectively. The equilibration was conducted in methanol at 25.0 °C using hydrogen chloride (0.1 mol dm^{-3}) and isolation of the equilibrated mixture was achieved as previously described.[8,12] The values of K_e are shown in Table 5, as are the ^1H NMR spectral results in deuteriochloroform. K_e can be calculated from the ester methoxy, methylene or even other methyl present in some esters. The calculations based on the ester methoxy signals gave the most reproducible results; but all methods of calculations are in general agreement.

The solvent system used for the pK_a measurements (see below), 80% aq. 2-methoxyethanol, has spectral bands that made measurements impossible for the corresponding acids. Methanol was used for these measurements as it corresponds fairly closely to the latter solvent system in terms of polarity and solvating capacity.[21,22] Even for methanol, the measurements are difficult because of solvent spectral bands; but use of [$^2H_4$]methanol confirmed the results. In methanol separate signals were observed for the pseudo and normal acid methylene groups. Measurements in chloroform gave a time-averaged signal for the methylene group. Due to the larger values of K_e in this solvent system, very reliable values of K_e could not be determined.

The ^{13}C NMR spectra of the methyl 2-(substituted phenylacetyl)benzoates in deuteriochloroform had signals at *ca.* 203 ppm (keto carbonyl) and *ca.* 166 ppm (ester carbonyl) for the normal ester and at *ca.* 160 ppm (lactone carbonyl) and *ca.* 111 ppm (lactol carbon) for the pseudo ester. The spectra of the corresponding acids in methanol gave only a sharp signal at *ca.* 172 ppm (carbonyl), as found in related acids,[23] and a broad signal at *ca.* 152 ppm, corresponding to those described above.

The ^1H NMR spectra in deuteriochloroform or [$^2H_6$]DMSO of the normal methyl substituted 2-benzilcarboxylates have the normal ester methoxy signals at *ca.* 3.7 ppm. The equilibration of the latter esters was completed as for the methyl 2-phenylacetylbenzoates. However, no pseudo ester could be detected for any except the three esters having *m*- or *p*-chloro or *p*-bromo substituents. The latter have the pseudo ester methoxy signals at *ca.* 3.2 ppm. These three esters had very small amounts of the pseudo ester at equilibrium with K_e < 0.1. The ^1H NMR spectra of the corresponding acids could not be used to determine K_e as no suitable signals exist. However, there is some broadening of the signals due to the 6-H, as found for the 3-H in the 2-phenylacetylbenzoic acids.

The ^{13}C NMR spectra of the normal methyl 2-benzilcarboxylates in deuteriochloroform or [$^2H_6$]DMSO had signals at *ca.* 167 ppm (ester carbonyl), 188 ppm (α-keto carbonyl) and 193 ppm (β-keto carbonyl). The spectra of the corresponding acids in methanol had signals at *ca.* 169 and 170 ppm, at *ca.* 192 ppm (broad) and at *ca.* 109 ppm. These appear to correspond to the various carbonyl and lactol carbons of the normal (see above) and pseudo acid tautomers. The nature of ^{13}C NMR spectra made any quantitative conclusions impossible.

pK_a *Measurements.*—The apparent pK_a values of the acids in 80% (w/w) 2-methoxyethanol (MCS)–water at 25 (± 0.1) °C were measured as described previously[18] and are shown in Table 6. All the measurements are the results of at least two separate determinations.

Discussion

Ring–Chain Tautomerism.—The influence of remote substitution in R on the ring–chain tautomerism of the general systems [eqns. (4a–c)] has been reviewed.[2] The Hammett reaction constant, ρ, or its variants, for such substitutions are positive. It was considered that the substituents affect the electrophilicity of the carbon atom, with electron-withdrawing substituents increasing and electron-donating substituents decreasing the electrophilicity.[2] However, this is an interpretation using a rate process analogy, whereas, the process under discussion is an equilibrium. Thus, interactions between ring forms, rather than the chain forms, with electron-withdrawing substituents are relatively favourable and with electron-releasing substituents are relatively unfavourable. The likely explanation for this appears to be an effect arising from dipole–dipole interactions between the substituted phenyl group and the groups involved in the actual tautomerism.

The ring–chain tautomeric equilibrium constant, K_e, for methyl 2-phenylacetylbenzoate in methanol equal to 2.9 is very much greater than that for methyl 2-benzilcarboxylate for which K_e is $\ll$0.1. Furthermore, K_e for 2-phenylacetylbenzoic acid in methanol is equal to 2.5. However, the value for the latter acid in chloroform is equal to 5.7 which is considerably greater than the value for benzil-2-carboxylic acid of 1.4 under the same conditions. The change of R′ from $PhCH_2$ to PhCO in **1** and **2** gives a more electron-withdrawing, but more 'bulky', substituent.[24] These factors would appear to act in opposite

Table 6 Ionization of 2-(substituted phenylacetyl)benzoic and substituted benzil-2-carboxylic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C[a]

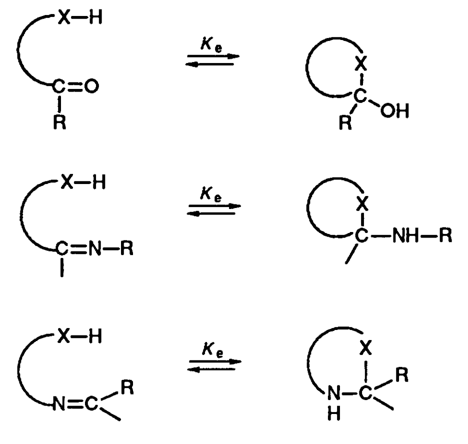
	2-Phenylacetylbenzoic acids			Benzil-2-carboxylic acids		
X	Observed pK_a	log (1 + K_e)	Calculated pK_a^T	Observed pK_a	log (1 + K_e)	Calculated pK_a^T
H	6.60	0.54_5	6.05_5	5.39	0.38	5.01
4-Me	6.64	0.50_5	6.13_5	5.41_5	0.32	5.09_5
3-Me	6.60	0.53	6.07	5.43	0.36	5.07
4-OMe	6.67_5	0.51	6.16_5	5.42	0.30	5.12
3-OMe	6.58	0.55_5	6.02_5	5.32	0.40_5	4.91_5
4-Cl	6.51	0.61_5	5.89_5	5.16_5	0.44_5	4.72
3-Cl	6.47	0.67	5.80	5.12	0.47_5	4.64_5
4-Br	6.50_5	0.63_5	5.87	5.19	0.46	4.73

[a] The pK_a values were reproducible to ± 0.02 unit.

Table 7 Hammett reaction constants for the ring–chain tautomerism and ionization of the substituted 2-phenylacetylbenzoic and benzil-2-carboxylic acids and their methyl esters[a]

System	ρ	log K_o	r	s	n
2-Phenylacetylbenzoic					
Ring–chain tautomerism of methyl esters, K_e; MeOH; 25 °C	(a) 0.357	0.41_5	0.954	0.046	8
	(b) 0.432	0.40	0.993	0.021	8
Ring–chain tautomerism of acids, K_e; MeOH; 25 °C	(a) 0.490	0.48_5	0.971	0.049	8
	(b) 0.567	0.46_5	0.966	0.062	8
Ring–chain tautomerism of acids, K_e; $CHCl_3$; 35 °C	(a) 0.400	0.78	0.956	0.050	8
	(b) 0.478	0.76_5	0.989	0.029	8
Ionization, pK_a; 80% MCS–H_2O; 25 °C	(a) 0.316	−6.59	0.982	0.025	8
	(b) 0.363	−6.60	0.971	0.036	8
Ionization, pK_a^T; 80% MCS–H_2O; 25 °C	(a) 0.580	−6.03	0.974	0.054	8
	(b) 0.683	−6.06	0.988	0.044	8
Benzil-2-carboxylic					
Ring–chain tautomerism of acids, K_e; $CHCl_3$; 35 °C	(a) 0.495	0.14	0.991	0.027	8
	(b) 0.557	0.12	0.961	0.066	8
Ionization, pK_a; 80% MCS–H_2O; 25 °C	(a) 0.539	−5.34	0.930	0.087	8
	(b) 0.661	−5.36	0.982	0.052	8
Ionization, pK_a^T; 80% MCS–H_2O; 25 °C	(a) 0.990	−4.99	0.994	0.044	8
	(b) 0.828	−4.96	0.967	0.089	8

[a] 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 $σ^n$.



(4a)

(4b)

(4c)

R = *m*/*p*-subst. phenyl

directions, with increasing steric 'bulk' favouring the chain form and increasing electron-withdrawing nature favouring the ring form.[2,4] The steric factor must therefore be more important here.

The effect of substitution in the phenyl group on the equilibrium constants for ring–chain tautomerization of the methyl 2-(substituted phenylacetyl)benzoates, **6b**, **7b**, 2-(substituted phenylacetyl)benzoic, **6a**, **7a**, and substituted benzil-2-carboxylic acids, **3a**, **3b**, has been assessed by means of the Hammett equation using both σ and $σ^n$ values.[25] The results are shown in Table 7. For the 2-phenylacetylbenzoic systems the correlations are, in general, better with $σ^n$ than with σ, whereas the converse is true for the benzil-2-carboxylic system. Unlike previous correlations for ring–chain tautomerization of acid systems,[5,7,26] there are no direct resonance interactions between the substituted phenyl and the keto-carbonyl group in the chain tautomer. The ρ values of *ca.* 0.4 found here appears to arise from the less favourable interactions of the electron-withdrawing substituents with the dipolar keto-carbonyl group in the chain tautomer, rather than the twin dipolar ketal group in the ring tautomer. Similarly substituted 2-benzoylbenzoic acids give ρ values in the range 0.5 to 1.1 for ring–chain tautomerism.[2,26] The mean reduction of ρ of a factor of *ca.* 0.5, resulting from the insertion of a methylene or carbonyl group link, is as would be expected from the decreased transmission of the polar effect.[27]

Ionization of the Acids.—As discussed in the Introduction, the acidities of acids involved in ring–chain tautomeric equilibria are affected by these interactions. The observed pK_a values are derived from two contributions, the true pK_a^T values and −log (K_e + 1), as shown in eqn. (3). Consideration of the relation between the true and observed pK_a values and the ring–chain tautomeric equilibrium constant shown in eqn. (3) indicates two limiting conditions relating to Hammett reaction constants, ρ. Firstly, if $1 \gg K_e$, the values of pK_a^T and pK_a will be identical, as will be the reaction constant, ρ. Secondly, if $1 \ll K_e$, the ρ derived for the pK_a^T values will be equal to the sum of the reaction constants derived for the pK_a and $\log K_e$ values.

The ionization of the 2-(substituted phenylacetyl)benzoic acids, **6a**, **7a**, appears to belong more closely to the second type described above as K_e in methanol varies from 2.2 to 3.7. The Hammett equation correlations for the pK_a values are shown in Table 7. The ρ value of *ca.* 0.6 for pK_a^T values approaches the sum of those for pK_a and for $\log K_e$, as would be expected. The transmission ratio of $\rho(pK_a^T)/\rho_o$ is *ca.* 0.3_5, where ρ_o is the reaction constant for the reference system, benzoic acids, under identical conditions, which is 1.69.[18] The transmission ratio would be expected to be about 0.1_5 on the basis of simple 'inductive' transmission coefficients.[27] The observed value is significantly greater than the latter, but in general agreement with a similar ratio observed for the benzil-2-carboxylic acid system (see below).

The ionization of the substituted benzil-2-carboxylic acids, **3a**, **4a**, appears to belong less closely to the second type described above, as K_e in chloroform varies from 1.0 to 2.0. The values of K_e in methanol for this system are not available. In the absence of values in any other solvent system, those in chloroform have been used and the Hammett equation correlations for the pK_a values are shown in Table 7. The transmission ratio of $\rho(pK_a^T)/\rho_o$ is *ca.* 0.5, compared to an expected value of about 0.2 on the basis of simple 'inductive' transmission coefficients.[27] As the influence of substituents is really transmitted by an electrostatic field effect,[28] the actual conformation of the molecule will be important and appears favourable for such transmission. Benzil itself has a structure in which the carbonyl groups are rotated about 110° from one another, with the phenyl rings nearly coplanar with the carbonyl groups.[29]

Benzil-2-carboxylic acid ($pK_a^T = 5.01$) is very much stronger than benzoic acid ($pK_a = 6.67$).[4] The *o*-phenyloxyacetyl group would be expected to have a secondary steric effect and be powerfully electron-withdrawing. Both effects would be acid-strengthening, as is observed. A *para*-σ value for this substituent has not been measured. However, a value of *ca.* 0.8 can be estimated from the known σ values[30] for related substituents. This estimate would give a predicted value about 0.7 pK_a units stronger than that observed using the correlation found previously for 2-substituted benzoic acids with *para*-σ values.[31] Values about 0.8 pK_a units stronger than those found were predicted for 2-acylbenzoic acids previously.[4] This appears to arise from a conformation of the α-keto carbonyl group in which the carbonyl oxygen is proximate to the carboxylic group, which reduces the effectiveness of the field effect of the carbonyl group.

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