44. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part XVI.* Some Acylbenzoic Acids.*

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The monoacetylbenzoic acids display the order of strengths *p*- > *m*- > *o*- > H (in water at 25°) and the fact that the *o*-isomer is only a little stronger than the parent benzoic acid is interpreted in terms of the view that the acetyl group is less strongly conjugated with the benzene ring than is the carboxyl group. The greater bulks of benzoyl and toluoyl groups, and their stronger conjugative capacities, account for the relatively large enhancements in strength exhibited when these groups enter the *ortho*-position.

The dissociation constants of five acylbenzoic acids have been determined in water at 25° by the conductivity method (Table 1). The expectation that the groups Ac, Bz, and *p*-$C_6H_4Me\cdot CO$ would enhance the strength of benzoic acid when substituted in the benzene ring has been realised although the small enhancement in strength brought about by *o*-acetyl is a striking observation in view of the $-I$ and $-M$ effects normally associated with it. Hitherto dissociation constants for monosubstituted benzoic acids have not only revealed that the *ortho*-isomer is always stronger than the parent acid but that it is generally the strongest of the three isomers; this is even true of the methyl- and methoxy-substituted acids. The explanation now generally adopted (except in the special case of salicylic acid) is that the *ortho*-substituent displaces the carboxyl group from the plane of the ring, and so inhibits the functional conjugation of that group ($-M$) with the benzene ring. The magnitude of this steric obstruction to uniplanarity varies with the size of the substituent, and largely because of this the resultant relative enhancement in strength of the benzoic acid also varies considerably; cf., for instance, the effect of introducing the *o*-methyl, *o*-*tert*.-butyl and *o*-phenyl groups into benzoic acid (K/K_u 1·97, 4·66, and 5·53, respectively).

Table 1.

R in $C_6H_4R\cdot CO_2H$ [a]	*o*-Ac	*m*-Ac	*p*-Ac	*o*-Bz	*o*-*p*′-$C_6H_4Me\cdot CO$
10^5K	7·49	$14{\cdot}9_5$	$19{\cdot}9_5$	29·1 [b]	22·7
M. p.	117—118°	162°	209—210°	127° [c]	240—241°

[a] Ph·CO_2H has 10^5K = 6·27. [b] Lit.,[4] 38. [c] Monohydrate, m. p. 93—94°.

The rather massive benzoyl and *p*-toluoyl groups, unlike the acetyl group, show the customary large enhancement, serving to emphasise the singularity of the relative strengths of the acetylbenzoic acid series *p*- > *m*- > *o*- > H, an explanation of which seems to lie in a modified conjugative capacity of acetyl in the *ortho*-position. The result certainly seems to suggest that the steric interaction of the acetyl and the carboxyl group (both of $-I$ $-M$ characteristics) in the *ortho*-substituted acid is such as to lead to a preferential twisting of the acetyl group with inhibition of its mesomeric effect, and consequently the acid-strengthening influence of the substituent in these circumstances is at a discount. This implies, of course, that the conjugative capacity of acetyl is substantially weaker than that of carboxyl, a feature which should be manifested in data for mesomeric moments, but unfortunately complications arise in the interpretation of the dielectric polarisation of carboxylic acids and no direct comparison of mesomeric moments is possible.

It is noteworthy that the nitro-group (a branched substituent like acetyl, possessing similar polar characteristics) also interferes when in the *ortho*-position with respect to carboxyl but leads, on the other hand, to a large enhancement of strength (K/K_u 107). Steric inhibition of resonance here clearly must be experienced in the main by the carboxyl group, implying that this substituent is more weakly conjugated than the nitro-group.

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* Part XV, *J.*, 1956, 2995.

There is yet another consideration that bears on the relative mesomeric effects of the three groups in question, that is, the inhibition of resonance experienced by nitro- and acetyl groups when introduced independently into mesitylene and durene, as shown by dipole-moment measurements.[1] It is to be noted that a much larger depression of μ occurs with the nitro-compounds. This, coupled with the evaluated mesomeric moments (vector quantities) of nitro- and acetyl groups attached to benzene (—0·76 and —0·46 D respectively),[2] leaves no doubt as to the relative magnitude of the conjugative capacities of these two groups.

In fact, having regard to all the evidence cited in this paper it is reasonable to conclude that the sequence of the magnitude of mesomeric effects of the three groups is $NO_2 > CO_2H >$ Ac, which is also consistent with theoretical considerations.

Such a consequence would certainly account for the recorded strengths of the corresponding substituted benzoic acids, and is consistent with observations on nitration of the monosubstituted benzenes bearing these groups (all of *—I —M* type). Consider, for instance, the following percentages of isomerides formed on mononitration of monosubstituted benzenes recorded by Ingold : [3]

	Ph·COMe	Ph·CO_2H	Ph·NO_2
o-	30	18·5	6·4
m-	68	80·2	93·3
p-	—	1·3	0·3

The increasing proportion of *meta*-substitution product in passing from left to right unmistakably gives the mesomeric order shown above for the three substituent groups.

It can be understood, however, that the extent to which the uniplanarity of sterically unsymmetrical groups becomes disturbed will depend not only upon their relative conjugative capacities but also upon the steric interference caused by their bulks. Thus, although it is reasonable to assume that aroyl groups exert larger inductive and mesomeric effects than the acetyl group, the enhancement of strength shown by *o*-benzoyl- and *o*-*p'*-toluoylbenzoic acids is not due to this alone but probably also to interference with the mesomeric effect of carboxyl, *i.e.*, some effective twisting of the latter. The strengths of the aroylbenzoic acids recorded here are therefore regarded as consistent with those for the monoacetylbenzoic acids.

EXPERIMENTAL

Preparations.—*o*-Acetylbenzoic acid was synthesised from phthalic anhydride and malonic acid by Yale's method.[5] The identity of this acid is of special interest in view of the somewhat remarkable value obtained for *K*. The m. p. obtained by us, after purification, was 117° (cf. 114—115° given by Yale,[5] Gabriel and Michael,[6] and Davies and Poole [7]), and analysis provided corroboration (Found : C, 65·7; H, 5·1%; equiv., 164·1. Calc. for $C_8H_7O{\cdot}CO_2H$: C, 65·9; H, 4·9%; equiv., 164·1). The oxime had the m. p. (156—157°) described by Davies and Poole,[7] who obtained *o*-acetylbenzoic acid by a different route.

m-Acetylbenzoic acid was obtained from *m*-nitroacetophenone (84 g.) which was reduced in alcohol with iron filings and hydrochloric acid to crude *m*-aminoacetophenone (60·5 g.); 25 g. of this, after purification, were converted (Sandmeyer) into *m*-cyanoacetophenone (11·4 g.) which, in refluxing concentrated hydrochloric acid (6 hr.), yielded crude *m*-acetylbenzoic acid (9 g.).

A similar route afforded *p*-acetylbenzoic acid from *p*-nitroacetophenone.

o-Benzoyl- and *o*-toluoyl-benzoic acid were purchased.

Purification.—All acids were repeatedly recrystallised from conductivity water or from

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[1] Collected by J. W. Smith, " Electric Dipole Moments," Butterworths, London, 1955, p. 215.

[2] See Sutton in Braude and Nachod's " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, p. 395.

[3] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 262.

[4] Meyer, *Monatsh.*, 1907, **28**, 1231.

[5] Yale, *J. Amer. Chem. Soc.*, 1947, **69**, 1547.

[6] Gabriel and Michael, *Ber.*, 1877, **10**, 1554.

[7] Davies and Poole, *J.*, 1927, 2662.

aqueous acetone, and the purified materials were then dried in vacuum-desiccators over silica gel for 3—4 weeks. *o*-Benzoylbenzoic acid recrystallised as a monohydrate which was dehydrated to constant weight at 80—90°. Equivalent weights of all acids were determined by alkalimetry.

Measurement of Conductivities.—Conductivities of aqueous solutions of the acids were determined by the method and equipment previously described.[8] Evaluation of Λ_0 was carried out for each acid by the extrapolation method of Ives,[9] and values of $K_{\text{therm.}}$ (Table 2) were calculated in the usual way.

TABLE 2.

10^3c	Λ (mho cm.^{2})	10^5K	10^3c	Λ (mho cm.^{2})	10^5K	10^3c	Λ (mho cm.^{2})	10^5K
	o-*Acetylbenzoic acid.*			m-*Acetylbenzoic acid.*			p-*Acetylbenzoic acid.*	
	(Λ_0 = 379·2)			(Λ_0 = 375·8)			(Λ_0 = 377·8)	
2·138	65·99	7·52	1·455	104·0	14·9$_5$	1·740	109·3	19·8$_5$
1·770	71·21	7·48	1·156	114·2	14·9$_5$	1·234	125·8	19·9$_5$
1·585	74·82	7·49	0·9997	121·2	14·9$_5$	1·100	131·6	19·9$_5$
1·222	83·91	7·50	0·8989	126·4	14·9$_5$	0·7450	152·8	20·0
0·8851	95·92	7·42	0·7256	137·2	14·9	0·5368	172·0	20·0$_5$
0·8539	97·65	7·47	0·5134	156·5	14·9$_5$	0·1707	243·7	19·8$_5$
0·6491	109·9	7·52	0·4386	165·6	14·9$_5$			
0·5465	117·6	7·49	0·2301	205·3	14·9$_5$			
0·3532	141·3	(7·70)						
0·2178	166·4	(7·39)						
	o-*Benzoylbenzoic acid.*			o-p′-*Toluoylbenzoic acid.*				
	(Λ_0 = 366·0)			(Λ_0 = 377·1)				
1·130	145·8	28·9$_5$	0·7461	158·0	(22·0$_5$)			
1·080	148·4	29·0$_5$	0·5235	180·1	22·4			
0·8783	160·2	29·2	0·4254	190·4	(21·5$_5$)			
0·7211	171·2	28·9$_5$	0·3846	201·7	(23·2$_5$)			
0·6469	177·6	29·0	0·3231	211·6	22·8$_5$			
0·6203	180·8	29·3	0·2420	229·7	22·7			
0·5223	190·8	29·1	0·2248	234·5	22·7$_5$			
0·4580	199·1	29·2	0·2239	235·1	22·8$_5$			
0·3699	212·8	(29·4)	0·1779	249·0	22·6$_5$			
0·2814	229·1	29·0$_5$	0·1330	263·0	(21·2$_5$)			
0·2030	249·2	29·2$_5$						
0·1493	265·9	(28·6$_5$)						

It is difficult to assess the absolute significance of Λ_0 values determined by this method. They are internally consistent parameters which permit each set of $\Lambda - c$ data to give a thermodynamic dissociation constant, and as such, have a mean deviation of 1—2 units. The *p*-toluoylbenzoic acid (which provides aqueous solutions with difficulty) gave data with a correlation parameter of about twice this range.

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[8] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.

[9] Ives, *J.*, 1933, 731.