Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part XIII. Some Alkylbenzoic Acids exhibiting Steric Effects.*

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The thermodynamic dissociation constants of eleven alkylbenzoic acids have been determined conductimetrically (as well as those of 1- and 2-naphthoic acids). Nine of the benzoic acids possess substituents in the *ortho*-position, and the resultant enhancements of acid strength are capable of an interpretation in harmony with the theory of steric inhibition of mesomerism. Striking regularities in the increments in strength have been recorded for the introduction of methyl groups at the 2- and at the 6-positions of alkylbenzoic acids. The method employed for the determination of acid strengths is a refinement of that described in earlier parts of this series.

Although the literature contains the classical dissociation constants of a number of alkylbenzoic acids, the need has arisen for more dependable and extensive data for the strengths of these acids. The thermodynamic dissociation constants recorded here relate to benzoic acid substituted with (i) two or three methyl groups and, (ii) one higher alkyl group (ethyl, *iso*propyl or *tert.*-butyl) at the *ortho*-position. The strengths of 1- and 2-naphthoic acids have been redetermined.

Table 1 sets out the thermodynamic dissociation constants of these acids (in aqueous solution at 25°) and the values of $\Lambda_{0(\text{acid})}$. The methods of calculating these data from the conductivity measurements in acid and in sodium salt solution, respectively, were those described earlier in this series, although refinements in the experimental technique have been introduced. All dissociation constants previously recorded for the above acids are classical values, and these are shown in Table 1 with our values of the classical constants for comparison.

The anion mobilities (as given by Λ_0) are all remarkably consistent with molecular size,

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* Two earlier papers (*J.*, 1941, 550; 1944, 411), which appeared under specific titles, are regarded as Parts XI and XII of this series.

as illustrated by the three *o*-alkylbenzoic acids (cf. Λ_0 for *o*-, *m*-, and *p*-toluic acids = 381·2, 379·3, and 397·7, respectively). The naphthoic acids have mobilities comparable to those of the dimethylbenzoic acids.

TABLE 1.

Acid	Mean Λ_0 (acid)	10^5K therm.	10^5K classical	Earlier values of 10^5K
o-Ethylbenzoic	379·2	16·1	16·3	17 [1]
o-*iso*Propylbenzoic	378·1	23·1$_5$	23·5	—
o-*tert*.-Butylbenzoic	376·0	29·2	29·8	35·1 [4]
2 : 3-Dimethylbenzoic	379·7	18·3	18·7	—
2 : 4-Dimethylbenzoic	379·9	6·57	6·69	9·0 [1]
2 : 5-Dimethylbenzoic	379·9	10·5$_5$	10·8	12·0 [1]
2 : 6-Dimethylbenzoic	379·4	56·8	58·1	62 [3]
3 : 4-Dimethylbenzoic	379·5	3·91	3·97	—
3 : 5-Dimethylbenzoic	379·0	5·00	5·07	4·8,[1] 7·3 [2]
2 : 4 : 6-Trimethylbenzoic	376·9	36·6	37·4	38 [1, 3]
4-*tert*.-Butyl-2 : 6-dimethylbenzoic	376·5	36·1	36·4	—
1-Naphthoic	379·4	20·2	20·3	20·4 [1]
2-Naphthoic	379·2	6·90	6·96	6·78,[1] 5·23 [5]

[1] Bethmann, *Z. physikal. Chem.*, 1890, **5**, 385. [2] Pfaff, Diss., Heidelberg (1897). [3] Breed, Diss., Bryn Mawr (1901). [4] Shoesmith and Mackie, *J.*, 1936, 300. [5] Bader, *Z. physikal. Chem.*, 1890, **6**, 289.

Values of $10^5K_{\text{therm.}}$ for comparison : benzoic acid, 6·27; *o*-, *m*- and *p*-toluic acids, 12·3$_5$, 5·35, and 4·24, respectively; 4-*tert*.-butylbenzoic acid, 3·98.

EXPERIMENTAL

Measurement of Conductivity.—The bridge network (based essentially on that of Jones and Josephs, *J. Amer. Chem. Soc.*, 1928, **50**, 1049), oscillator, and amplifier were similar to those described by Dippy and Hughes (*J.*, 1954, 953). A six-decade resistance box (max. resistance 111,111 ohms) was used in series with a single-decade megohm box.

The cells, capped and of symmetrical bottle design, were of Pyrex glass and had capacities of 60—90 ml. (that of the lowest cell-constant having the greatest capacity). The stout greyed-platinum electrodes (Jones and Bollinger, *J. Amer. Chem. Soc.*, 1931, **53**, 411) were mounted rigidly by means of small Pyrex struts at distances of approx. 0·5, 1·0, and 1·5 cm. apart in the acid cells and 1·0 cm. apart in the sodium salt cell. The interiors of the cells were first treated with pure acetone and alcohol, and then allowed to stand for several weeks filled with conductivity water which was changed frequently. The cell leads were of amalgamated copper wire dipping into mercury cups immersed in the water-thermostat regulated to 25° (±0·005°).

TABLE 2.

Acid	M. p. (corr.)	Acid	M. p. (corr.)
o-Ethylbenzoic	65·6°	3 : 4-Dimethylbenzoic	168·0—168·5
o-*iso*Propylbenzoic	59·4—59·9	3 : 5-Dimethylbenzoic	171·2—171·7
o-*tert*.-Butylbenzoic	68·5	2 : 4 : 6-Trimethylbenzoic	156·6—157·1
2 : 3-Dimethylbenzoic	144·5—145·0	4-*tert*.-Butyl-2 : 6-dimethylbenzoic	168·0—169·0
2 : 4-Dimethylbenzoic	125·0—126·0	1-Naphthoic	160·3
2 : 5-Dimethylbenzoic	134·0—134·4	2-Naphthoic	184·2
2 : 6-Dimethylbenzoic	116·3—116·7		

For the basic cell-constant determination, the specific conductance given by Jones and Prendergast (*ibid.*, 1937, **59**, 731) for a pure 0·01D-potassium chloride solution was employed. The calibration cell had a constant of 0·25926 ± 0·00006 and had a 5-figure numerical resistance when filled with 0·01D-potassium chloride. The other cells were calibrated against this using approximately 0·002N-, 0·001N-, and 0·0002N-potassium chloride solutions, by the method of intermediate cell. The agreement obtained when different cells were used to determine the specific conductance of a given solution (Table 3) confirms the validity of the calibration and, moreover, demonstrates the freedom of greyed electrodes from serious deviations due to adsorption (Jones and Bollinger, *loc. cit.*).

The conductivity water (κ = 0·7—0·9 gemmho) was supplied by an improved form of the still described in earlier work in this series.

Stock solutions of acids of molality ranging from 0·01 to 0·0001 were prepared, either by dilution of stock solutions (of. earlier papers in this series) or directly from small quantities of

TABLE 3.

Cell const.	10^3C (equiv./l.)	Λ	10^5K class.	10^5K therm.	Cell const.	10^3C (equiv./l.)	Λ	10^5K class.	10^5K therm.
o-*Ethylbenzoic acid*									
0·03764	0·6883	145·5	16·5	16·1	0·03764	0·1651	233·5	16·3	16·1
	0·5349	160·0	16·5	16·1$_5$		0·1400	243·5	16·1	16·0
	0·3907	178·5	16·4	16·1		0·1010	264·3	16·2	16·0$_5$
	0·1704	231·0	16·2	16·0		0·08304	276·2	16·2	16·1
o-iso*Propylbenzoic acid*									
0·03759	0·7134	164·2	23·8	23·2$_5$	0·03759	0·2774	222·3	(23·3)	(23·0)
	0·4791	188·0	23·5	23·1		0·2708	224·4	23·5	23·2
	0·3639	205·6	23·6	23·1$_5$		0·2534	227·9	23·2	(22·8)
	0·3349	210·9	23·6	23·2		0·1702	253·8	23·3	23·1
o-tert.-*Butylbenzoic acid*									
0·03759	1·035	155·4	30·1	29·3	0·03759	0·5301	195·3	29·8	29·1$_5$
	0·8596	165·8	29·9	29·2		0·4203	209·9	29·6	29·1$_5$
	0·7976	170·2	29·9	29·2$_5$		0·3512	221·3	29·5	29·1
	0·7455	174·2	29·8	29·2		0·3209	227·0	29·5	29·2$_5$
	0·5791	189·8	29·8	29·2		0·2903	233·3	29·4	29·1$_5$
2 : 3-*Dimethylbenzoic acid*									
0·09146	2·167	96·59	18·8	18·2	0·03764	0·3729	190·0	18·7	18·4
	1·512	112·7	19·0	18·4		0·3082	201·9	18·6	18·3$_5$
	1·091	128·2	18·8	18·3$_5$	0·09146	0·2644	211·1	18·4	18·2
	0·8608	140·6	18·7	18·3	0·03764		210·9	18·3	18·2
	0·6878	153·1	18·7	18·3					
2 : 4-*Dimethylbenzoic acid*									
0·09146	1·056	84·54	6·73	6·57	0·03764	0·6760	102·3	6·71	6·58$_5$
	0·8845	91·10	6·69	6·55$_5$		0·5463	111·5	(6·66)	(6·53)
	0·8336	93·63	6·72	6·58		0·3676	130·9	6·66	6·56
	0·8000	94·87	(6·65)	(6·51)		0·3220	137·8	6·65	6·55$_5$
2 : 5-*Dimethylbenzoic acid*									
0·09146	1·443	91·19	10·9	10·6$_5$	0·03764	0·6316	127·2	10·7	10·4$_5$
	1·073	101·1	10·9	10·6$_5$	0·09146	0·5749	132·2	10·7	10·4$_5$
	1·034	104·9	10·9	10·6	0·03764		132·2	10·7	10·4$_5$
	0·6562	125·8	10·8	10·5$_5$	0·03764	0·4652	144·1	10·8	10·6
	0·6316	127·2	10·7	10·4$_5$		0·2078	191·0	(10·6)	(10·4)
2 : 6-*Dimethylbenzoic acid*									
0·03764	1·257	185·3	58·6	56·8	0·03764	0·5643	236·0	57·8	56·7$_5$
	1·173	189·5	58·5	56·7		0·5034	243·5	57·9	56·8$_5$
	0·9860	200·2	(58·1)	(56·6)		0·4267	254·0	57·9	56·7$_5$
	0·9699	201·5	58·3	56·8		0·3864	259·7	57·4	56·7
	0·8449	210·4	58·3	56·8$_5$		0·2968	275·3	(57·0)	(56·4)
	0·6024	231·9	57·9	56·8$_5$					
3 : 4-*Dimethylbenzoic acid*									
0·09146	0·7315	78·80	3·98	3·91	0·03764	0·4546	96·40	(3·93)	(3·87)
	0·7225	79·12	3·97	3·90		0·4883	93·97	3·98	3·91$_5$
	0·6492	82·92	3·96	3·90		0·4524	97·05	3·98	3·91$_5$
	0·6476	83·26	3·99	3·92		0·3689	105·8	3·97	3·91
0·03764	0·6182	84·92	3·99	3·92		0·2360	126·6	3·94	3·89
3 : 5-*Dimethylbenzoic acid*									
0·03764	0·5644	97·63	5·04	4·96	0·03764	0·3370	121·2	5·08	4·99$_5$
	0·4684	105·9	5·08	5·00		0·3308	122·2	5·08	5·00
	0·4359	108·9	5·05	4·96		0·2589	134·6	5·07	5·00
	0·3951	113·6	5·07	4·99$_5$		0·2185	143·7	5·06	5·00
	0·3882	114·7	5·10	5·02		0·1716	157·4	5·06	5·01
2 : 4 : 6-*Trimethylbenzoic acid*									
0·03764	1·347	153·5	37·7	36·6	0·03764	0·7779	186·0	37·4	36·6$_5$
	1·103	165·0	37·6	36·6		0·7382	189·2	37·4	36·6
	1·065	167·2	37·7	36·6		0·5491	207·9	37·3	36·6
	0·9304	175·2	37·6	36·6$_5$		0·4515	220·3	37·1	36·6
	0·8036	184·1	37·5	36·6		0·2142	267·1	36·9	36·6

TABLE 3. (*Continued.*)

Cell const.	10^3C (equiv./l.)	Λ	10^5K class.	10^5K therm.	Cell const.	10^3C (equiv./l.)	Λ	10^5K class.	10^5K therm.
				4-tert.-*Butyl-2 : 6-dimethylbenzoic acid*					
0·09146	0·9133	174·4	36·3	35·6	0·03764	0·2329	258·8	35·3	35·1
	0·5864	204·1	37·6	36·8	0·09146		259·0	35·3	35·1
	0·5550	206·3	36·9	36·1	0·03764	0·2135	265·3	35·9	35·7
	0·3431	238·7	37·6	$37{\cdot}1_5$	0·09146		265·4	35·9	35·7
	0·2951	242·8	(34·5)	(34·1)					
				1-*Naphthoic acid*					
0·07322	0·2076	233·5	20·5	20·2	0·07322	0·1336	260·9	20·2	20·1
	0·2038	234·1	20·3	20·1		0·1309	261·6	20·0	20·0
	0·1686	246·6	20·4	20·2		0·1308	261·4	(20·0)	(19·9)
	0·1578	251·0	20·4	20·2		0·1292	263·5	20·4	20·3
	0·1582	250·7	20·4	20·2		0·1060	275·1	20·3	20·3
	0·1338	260·6	20·2	20·0		0·09419	281·2	20·3	20·3
				2-*Naphthoic acid*					
0·07322	0·1857	171·4	(6·92)	(6·84)	0·07322	0·1453	186·7	6·94	6·88
	0·1645	179·1	6·96	6·89		0·1368	190·6	6·95	6·92
	0·1637	179·8	7·00	6·92		0·1184	199·7	6·94	6·89
	0·1534	183·7	7·00	6·92		0·1157	201·4	6·96	6·90

solid acid weighed on a micro-balance [subsequent determination of density (25°) gave the concentration (w./v.)]. The latter method was adopted where enough material was available; capped Pyrex conical flasks used for preparing the solutions had capacities from 250 to 2000 ml., and were initially cleaned with chromic acid and subsequently " seasoned " for 3 months with conductivity water.

The sodium salts were prepared in solution by the addition of a calculated weight of standard aqueous sodium hydroxide (*ca.* 0·01N), made by dissolving washed " AnalaR " sodium hydroxide pellets in water of known low conductance in a 2-litre flask fitted with a siphon and a soda-lime tube, to a known weight of the solid acid. The alkaline solution was standardised with hydrochloric acid (prepared from constant-boiling hydrochloric acid by weight dilution), phenol red being used as indicator. Capped 1-litre flasks were employed in the making of these salt solutions, and the amount of alkali employed was approximately 0·2% less than that required for equivalence (solution density of alkali relates to room temperature). It was thus ensured that the solution remained slightly acidic throughout the dilution range; the presence of a minute excess of the weak acid (unlike a trace of alkali) has no appreciable effect on the conductance of the solution. The salt solution was then diluted (by weight) to about 0·0025 g.-equiv./l., and the precise concentration calculated from the weight of sodium hydroxide added. The subsequent procedure was that described in earlier papers for the determination of $\Lambda_{0(\text{acid})}$.

The cells were filled by the method recommended by Ives and Riley (*J.*, 1931, 1998). No water correction was applied to acid conductance measurements. All weighings were corrected to *vacuo.*

Preparation and Purification of Materials.—*o*-Ethylbenzoic acid was obtained in 60% yield from *o*-bromoethylbenzene by a Grignard synthesis. Ethylbenzene was nitrated (Cline and Emmet, *J. Amer. Chem. Soc.*, 1927, **49**, 3150), and fractionation of the product yielded *o*-nitroethylbenzene (50%), b. p. 132—134°/36—37 mm. Reduction of this with iron and hydrochloric acid gave *o*-ethylaniline quantitatively which was converted by a Gattermann reaction into *o*-bromoethylbenzene, b. p. 88—89°/15 mm.

o-*iso*Propyl-, *o*-*tert.*-butyl-, 2 : 6-dimethyl-, and 2 : 4 : 6-trimethyl-benzoic acids were kindly supplied by Prof. M. Crawford and Dr. F. H. C. Stewart, whom we thank.

2 : 3-Dimethyl-, 2 : 4-dimethyl-, 2 : 5-dimethyl-, 3 : 4-dimethyl-, and 3 : 5-dimethyl-benzoic acids were provided by Professor H. A. Smith and Dr. J. A. Stansfield to whom grateful acknowledgment is made.

4-*tert.*-Butyl-2 : 6-dimethylbenzoic acid was obtained from 1-bromo-4-*tert.*-butyl-2 : 6-dimethylbenzene (Nightingale and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 101) by a Grignard synthesis (Crawford and Stewart, *J.*, 1952, 4443). The naphthoic acids were purchased.

All the acids were repeatedly recrystallised from conductivity water and finally stored for at least two weeks in desiccators. All specimens were well authenticated by both m. p. and determination of the equivalent. The m. p.s recorded in Table 2 were those of the final specimens, before measurement; they are in close agreement with the best values in the literature (Crawford and Stewart, *loc. cit.*, and Smith and Stansfield, *J. Amer. Chem. Soc.*, 1949, **71**, 81, for the alkylbenzoic acids, and Bethmann, *loc. cit.*, for the naphthoic acids).

DISCUSSION

The literature shows that the substituents so far examined enhance the strength of benzoic acid (in water) inordinately when introduced into the *ortho*-position, and a similar observation is made when such substituents occupy the β-position in ethylenic acids of *cis*-configuration. The principal factors responsible for this have been discussed by Ingold (" Structure and Mechanism in Organic Chemistry," B. Bell and Son Ltd., London, 1953). That diverse steric factors operate in *o*-substituted benzoic acids becomes manifest by examination of their behaviour in solvents of widely differing ionising capacities (*i.e.* varying in dielectric constant and in solvating character). The linear plot of log K/K_u against $1/\text{D}$ (K/K_u being the ratio of acid strength to that of the parent acid) gives a positive slope with *m*- and *p*-methoxy-, -chloro-, -bromo-, -iodo-, and -nitro-benzoic acids, and a negative slope with the *o*-isomers, whereas the converse holds for hydroxybenzoic acids (Elliott and Kilpatrick *J. Phys. Chem.*, 1941, **45**, 3). This is noteworthy in view of the general belief that the abnormally high dissociation constant of salicylic acid is due to the specific hydrogen bonding between the two substituents in the anion in that instance, whereas the abnormality of the other *o*-substituted benzoic acids mentioned above has been attributed to steric inhibition of mesomerism (Ingold, *loc. cit.*; cf. Baddeley, *Nature*, 1939, **144**, 444), an influence expected by Birtles and Hampson (*J.*, 1937, 10) and first demonstrated by them in a study of the dipole moments of substituted durenes. It should also be noted that to account for the relatively high K_1 value and relatively low K_2 value for maleic acid compared with fumaric acid both kinds of group interaction have been invoked, *i.e.* hydrogen bonding (Hunter, *Chem. and Ind.*, 1953, 155) and steric inhibition of mesomerism (Crawford, *ibid.*, p. 797) (see also, the first and second dissociation constants of phthalic acid.

It is less certain whether there is a special hydrogen bonding between methyl and carboxyl groups (despite hyperconjugation) although this suggestion was advanced by Dippy *et al.* (*J.*, 1937, 1421) to account for the abnormal dissociation constant of *o*-toluic acid in water. Such a tendency might well be contributory but it is now considered not to be dominant. The strengths of the benzoic acids substituted at the *o*-position by methyl, ethyl, *iso*propyl, and *tert.*-butyl progressively increase (see Table 1), and the fact that the abnormality is most marked with *tert.*-butyl seems to render the original hydrogen bond suggestion unacceptable as a principal factor here. Moreover, *o*-phenyl and *o*-phenoxyl groups have a comparable effect upon the strength of benzoic acid, referred to as unity in the following table of K/K_u values :

	Me *	Et	Pr^{i}	Bu^{t}	PhO *	Ph *
o-	1·97	2·57	3·69	4·65	4·74	5·53
p-	0·676	0·707	0·707	0·635	0·478	—

* Dippy, *Chem. Reviews*, 1939, **25**, 181.

It is satisfactory also to note that whereas the strengths of 2-naphthoic and benzoic acids are closely alike, that for 1-naphthoic acid lies between the values for *o*-ethyl- and *o*-*iso*-propyl-benzoic acids (see Table 1).

These observations are consistent with the theory of steric inhibition of mesomerism. The conjugation existing between carboxyl and the benzene ring, to be fully functional, demands the favoured position provided by co-planarity. If obstruction is exerted by a sufficiently bulky group in the *ortho*-position there will be a twisting of the carboxyl group out of the plane of the ring, so that the effective conjugation of carboxyl with the aromatic nucleus becomes weaker. In other words, the $-M$ effect of carboxyl, responsible for the relative weakness of benzoic acid (Dippy, *loc. cit.*), is hampered in its operation; conseqently, the greater the obstruction, as with increasing size of alkyl group, the stronger the acid.

The strengths of the benzoic acids containing two *o*-methyl substituents (see Table 1) may be interpreted along similar lines. The conjugation of carboxyl and aromatic nucleus is stronger in *p*-toluic acid and *p*-*tert.*-butylbenzoic acid than in benzoic acid. In short, there will be a greater multiplicity (electron content) of the bond between carboxyl-carbon and aryl-carbon in the *p*-alkyl-substituted acids. Thus the twisting, even if occurring to the same extent, will creat different constraints in the three different systems, and consequently it is necessary to trace the inhibition by relating the increase in dissociation constant to the appropriate parent acid in each case. Such an analysis reveals a striking reproduction of the effect as the following table of K/K_u values shows (where the K of each parent acid is referred to as unity).

Substituents	Benzoic	*p*-Toluic	*p*-*tert.*-Butylbenzoic acid
2-Methyl	1·97	1·55	—
2 : 6-Dimethyl	9·06	8·63	9·20

There is in effect a case for less easy twisting of carboxyl out of the plane of the ring in *p*-toluic acid (relative to benzoic acid), and it is noteworthy that the introduction of methyl to an *ortho*-position here increases K by a factor of about 1·6, whereas similar substitution in benzoic acid increases K by a factor of 2. Similarly, a second *o*-methyl group is responsible for an overall increase by a factor 8·6 in the former system and by 9·1 in the latter.

A further analysis is to trace the influence of the substitution of methyl and of *tert.*-butyl groups in the 4-positions of benzoic acid and 2 : 6-dimethylbenzoic acid, respectively. A remarkable similarity in the increments in free energy of ionisation is noted from the following table. Introduction of methyl into the 4-position of *o*-toluic acid has a qualitatively similar, if greater, effect. The current theory offers no satisfactory explanation of this regularity, although we consider that the feature is more than fortuitous.

Parent acid	4-Substituent	$\Delta G°$ subst. $-$ $\Delta G°$ parent (cals. mole^{-1})
Benzoic	Methyl	232
Benzoic	*tert.*-Butyl	269
2 : 6-Dimethylbenzoic	Methyl	260
2 : 6-Dimethylbenzoic	*tert.*-Butyl	269

The absence of considerations of steric orientation in phenol (Baddeley, *loc. cit.*) makes the values of the acid strengths of methyl substituted phenols, published by Sprengling and Lewis (*J. Amer. Chem. Soc.*, 1953, **75**, 5709), particularly interesting. The steady diminution of strength shown below (H representing parent phenol) makes an impressive contrast to the benzoic acid series. Doubtless the controlling factors here are simply the. formal $+I$, $+M$ effects of the methyl group.

	H	*p*-Methyl	*o*-Methyl	2 : 4-Dimethyl	2 : 4 : 6-Trimethyl
pK	9·85	10·10	10·19	10·49	10·80

An interesting result is that for 2 : 3-dimethylbenzoic acid; the enhancement factor here is approximately 3 as distinct from the factor of <2 shown by 2 : 5-dimethylbenzoic acid (related to benzoic acid as parent). This might be connected with the fact that in the 2 : 3-disubstituted acid there are two steric interactions between the three vicinal groups. The repulsion between the adjacent electropositive methyl groups would cause the 2-methyl group to obstruct carboxyl more than in the usual model, and the measured strength shows it to be about as effective as 2-ethyl. An interesting observation having a bearing on this feature can be made by examination of the acid strengths listed by Shorter and Stubbs (*J.*, 1949, 1180); although these data are inaccurate, they serve to reveal that isomeric 2 : 3- and 2 : 5-disubstituted benzoic acids almost always have widely different strengths.

Observations by Crawford and Stewart (*J.*, 1953, 288) on the solubilities of the copper salts of some of the acids discussed here may be correlated with this work. These authors ascribe the unusually high solubilities in benzene–ethanol of copper salts of *o*-methylbenzoic acids to steric inhibition of mesomerism which is responsible for a weakening of the crystal structure.

There remain the 3 : 4- and 3 : 5-dimethylbenzoic acids whose strengths are less than that of benzoic acid, and fall below that for *m*-toluic acid by amounts expected from the operation of formal electron disturbances. It is relevant to point out here, however, that in the di- and tri-substituted benzoic acids, the only system in which steric interaction of groups cannot intervene is the 3 : 5-disubstituted benzoic acid. It is for this reason that the additivity principle for benzoic acids containing more than one substituent, explored by Shorter and Stubbs (*loc. cit.*), appeared to apply well to the 3 : 5-disubstituted acids. In a 3 : 4-disubstituted benzoic acid the group in the 3-position might inhibit the operation of the *M* effect of the group in the 4-position and this would be reflected in *K*; with some substituents (other than methyl) this effect could be pronounced.

The changes in the characteristics observed by Moser and Kohlenburgh (*J.*, 1951, 805) in the ultra-violet absorption spectra of certain methylbenzoic acids are relevant. They ascribe the changes in intensity of the so-called *B* band ($\lambda_{max.}$ 2280—2320 Å) to steric interference with resonance. It was shown that absorption in this region was strong in the cases of benzoic acid and *m*- and *p*-toluic acids (being most marked in the last), whilst the intensity fell with *o*-toluic acid, and the characteristic disappeared in 2 : 6-dimethylbenzoic acid. We have confirmed these findings, and have examined (over the appropriate, if narrow, range) the ultra-violet absorption spectra of some of the other acids whose strengths are recorded here. We find that 2 : 4 : 6-trimethylbenzoic acid compares with 2 : 6-dimethylbenzoic acid, but that 2 : 4-dimethylbenzoic acid is like *o*-toluic acid in showing a noticeable *B* band. 2 : 3-Dimethylbenzoic acid occupies an intermediate position in that here the *B* band appears only as a weak inflexion. There is thus an apparent correspondence between the conclusions arising from these spectral measurements and those derived from acid dissociation constant data.

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