ORTHO EFFECTS—VII

CONJUGATIVE AND FIELD EFFECTS OF DIMETHYLSULFONIO GROUP ON THE IONIZATION OF BENZOIC ACID[1]

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Abstract—The effect of the Me_2S^+ group on the ionization of benzoic acid has been re-examined in comparison with that of the Me_3N^+ group. The thermodynamic pKa values of *o*-, *m*-, *p*-Me_2S^+ and *o*-, *m*-, *p*-Me_3N^+ substituted benzoic acids have been determined in 65 vol% aq. dimethyl sulfoxide, 50 vol% aq. ethanol, and in water potentiometrically. The result of this work, $\sigma_{p\text{-}Me_2S^+} > \sigma_{m\text{-}Me_2S^+}$, is contrary to that previously found by others, $\sigma_{p\text{-}Me_2S^+} < \sigma_{m\text{-}Me_2S^+}$. The following relations were found to exist irrespective of the solvent used: $\sigma_{m\text{-}Me_2S^+} = \sigma_{m\text{-}Me_3N^+} + 0.06$, and $\sigma_{p\text{-}Me_2S^+} = \sigma_{p\text{-}Me_3N^+} + 0.13$. The conjugative effect of Me_2S^+ group has been found to be acid-strengthening from the *meta* or *para* positions, while it becomes acid-weakening from the "ortho" position.

In the preceding paper[1] we have reported the anomalously low acidity of *o*-dimethyl-sulfoniobenzoic acid in H_2O. Therefore it seems necessary to re-examine the effects of the *m*- and *p*-substituents in comparison with the effects of trimethylammonio substituent, although the Hammett σ-constants of these onium groups are available[2-5]

This paper presents pKa data of *o*-, *m*- and *p*-dimethylsulfonio- and trimethyl-ammoniobenzoic acids in H_2O, 50 vol% aq. EtOH, and 65 vol% aq. DMSO determined by the potentiometric titration with activity coefficient corrections. A revised set of the Hammett σ-constants and the effect of *o*-Me_2S^+ and *o*-Me_3N^{+6} groups are derived from these data and discussed with the aid of NMR spectral data.

RESULTS AND DISCUSSION

Table 1 lists the corrected pKa values of dimethylsulfonio- and trimethylammonio-benzoic acids and unsubstituted acid in H_2O, 50 vol% EtOH, and 65 vol% DMSO, together with data determined in the preceding papers[1] and found in the literature.

In 50 vol% EtOH substituent effect of the *p*-Me_3N^+ group shows somewhat large difference between ours (1·53) and the two others (1·38, 1·34). A similar situation is seen in the *m*-Me_3N^+ case, where ours is 1·72 while the value reported by Roberts is 1·58. Thus our substituent effects for these two groups in 50 vol% EtOH are 0·15–0·20 pKa units larger than those reported by others. However, difference of these two values, i.e. relative substituent effects of *m*- and *p*-Me_3N^+ groups, are 0·20 (Roberts) and 0·19 (present work), showing satisfactory agreement. This means that, so far as the relative substituent effects are concerned, both data can be used free of question.

The pKa values in 65 vol% DMSO differ considerably according to the method used, but the substituent effects agree well with each other.

TABLE 1. CORRECTED pKa VALUES OF DIMETHYLSULFONIO- AND TRIMETHYLAMMONIOBENZOIC ACIDS IN THE THREE SOLVENTS AT 25°

Acids		Water	50 vol% EtOH–water	65 vol% DMSO–water
H		4·19	5·70 (5·76[a], 5·80[b])	6·88 (7·00,[c] 5·77[d])
	o-	2·18	2·84	3·81 (2·7[d])
$Me_2S^+ OTs^-$	m-	3·09 (3·18[e])	3·90	5·23
	p-	3·06 (3·28[e])	4·01	5·35 (5·47,[c] 4·24[d])
	o-	1·16 (1·37[f])	2·40	3·6
$Me_3N^+ Cl^-$	m-	3·16	3·98 (4·18[e])	5·31
	p-	3·21	4·17 (4·38,[e] 4·46[b])	5·57

[a] Ref. 12, corrected with $- \log f_- = 0.05$.

[b] Ref. 9.

[c] Our results in ref 1b by the potentiometric titration, corrected with $- \log f_+ = - \log f_- = 0.04$ and $\log f_\bullet = 0$.

[d] Our results in ref. 1b by the indicator-spectrophotometry, corrected with $- \log f_+ = - \log f_- = 0.05$ and $\log f_\bullet = 0$.

[e] Ref. 3, corrected with $- \log f_+ = 0.08$ and $- \log f_\bullet = 0.06$. The pKa values were determined without being referred to the pKa value of benzoic acid.

[f] Ref. 6.

[g] Ref. 2, corrected with $- \log f_+ = 0.05$ and $- \log f_\bullet = 0.01$.

Effects of meta *and* para *substituents.* Table 2 summarizes the Hammett σ-constants

TABLE 2. HAMMETT σ-CONSTANTS CALCULATED FROM THE CORRECTED pKa VALUES

Substituents	Solvents	ρ	σ_m	σ_p	$\sigma_m - \sigma_p$
	H$_2$O	1·00	1·10 (1·02)[a]	1·13 (0·92)[a]	−0·03 (0·10)[a]
$Me_2S^+ OTs^-$	50 vol% EtOH	1·46[b]	1·23	1·16	0·07
	65 vol% DMSO	1·55[c]	1·07	0·99	0·08
	H$_2$O	1·00	1·03	0·98	0·05
$Me_3N^+ Cl^-$	50 vol% EtOH	1·46	1·18 (1·08)[d]	1·05 (0·94)[d]	0·13 (0·14)[d]
	65 vol% DMSO	1·55	1·01	0·86	0·15
$\sigma(Me_2S^+)$	H$_2$O		0·07	0·15	
$-\sigma(Me_3N^+)$	50 vol% EtOH		0·05	0·11	
	65 vol% DMSO		0·06	0·13	

[a] Ref. 3, corrected. *cf.* uncorrected values: $\sigma_m = 1.00$, $\sigma_p = 0.90$, $\Delta\sigma = 0.10$.

[b] Roberts *et al.*[12] reported the value 1·464 for the line drawn through the points for the m-, p-NO$_2$, m-, p-Br, H, p-Me, and p-MeO groups. We obtained 1·44 from the p-NO$_2$, p-Cl, H, p-Me, and p-MeO groups.

[c] Ref. 1a.

d Ref. 2, corrected. *cf.* uncorrected values: $\sigma_m = 1.02$, $\sigma_p = 0.88$, $\Delta\sigma = 0.14$.

calculated from the corrected pKa values in Table 1. First, the σ-constants of Me_2S^+ in H$_2$O are found to be $\sigma_{p\text{-}Me_2S^+} > \sigma_{m\text{-}Me_2S^+}$. This result is quite contrary to that reported previously by others,[3] $\sigma_{p\text{-}Me_2S^+} < \sigma_{m\text{-}Me_2S^+}$; care should be paid to the concept[4,5] which was derived on the basis of the previous values. Further inspection of Table 2 reveals that these σ-constants vary so much with change of solvent, the variations being considerably larger than those ordinarily observed.[16] As a result of

this variation. the difference $\sigma_{m\text{-Me}_2\text{S}^+} - \sigma_{p\text{-Me}_2\text{S}^+}$ is negative in H_2O while it becomes positive in aqueous organic solvents. Consequently, it seems a serious question whether this difference can be taken as a measure of the conjugative effect of Me_2S^+ group[2, 3, 5] even in a qualitative sense.

This phenomenon is surely due to the different solvent effects for the *m*- and *p*-substituents, and therefore this difference in solvent effects can reasonably be expected to be minimized by taking the difference, $\sigma(\text{Me}_2\text{S}^+) - \sigma(\text{Me}_3\text{N}^+)$ with the meta acids on one hand and the para acids on the other. The results are quite satisfactory (Table 2), the differences being substantially constant from solvent to solvent. Thus we can obtain the following equations irrespective of the solvents used.

$$\sigma_{m\text{-Me}_2\text{S}^+} = \sigma_{m\text{-Me}_3\text{N}^+} + 0.06 \pm 0.02 \tag{1}$$

$$\sigma_{p\text{-Me}_2\text{S}^+} = \sigma_{p\text{-Me}_3\text{N}^+} + 0.13 \pm 0.02 \tag{2}$$

As is well known from the ionization data of phenols,[3] anilinium ions.[2] and also from UV spectra.[3, 17] Me_3N^+ is incapable of conjugation with the benzene ring and exerts its effect mainly by field effects.[18-20] Similarly, substituent effects of Me_2S^+† group in the ionizations of benzoic acids has been considered not to involve the conjugative effect, because its σ-constants are almost equal to those of the Me_3N^+ group.[3, 4] However, in the case of the ionizations of phenols appreciable amounts of conjugation between Me_2S^+ and O^- groups is reported[3] with the aid of UV spectra.[3] These situations suggest that the solvent independent values of 0.06 and 0.13 in eqs 1 and 2 are indicating the presence of the conjugative effect of *m*- and *p*-Me_2S^+ groups even in the case of the ionizations of benzoic acids. and, if so, would possibly become a good measure of the conjugation.

This view can be checked independently by considerations based on simple electrostatic calculations. Details are given and the results summarized in Table 5. Table 5 shows as to which of the increase or the decrease in the field effects involved in the dimethylsulfoniobenzoate anions is resulted when the positive charge localized on sulfur is partly distributed over the benzene ring by conjugation. Although qualitatively. the results are in conformity with the observations; as for the *m*- and *p*-derivatives the field effect is strengthened by the conjugation, while in the case of the ortho derivative the same conjugation weakens the field effect and hence lowers its acidity.

Effects of ortho *substituents.* The effect of the *o*-Me_3N^+ group is certainly less complicated than that of *o*-Me_2S^+ since it is free from the conjugative effect as mentioned above. Namely it is composed of the steric and polar effects, which can be estimated approximately with the steric effect of *o*-t-Bu group in H_2O (0.87^{14}) and with the value derived using electrostatic calculation from the substituent effect of *p*-Me_3N^+, respectively. These data are listed in Table 3. The sum of the steric and field effects is 2.75 pKa units which is about 0.3 pKa units less than the observed.*

As for the steric effect of the *o*-Me_2S^+ group. the upper limit of its estimation might be that of *o*-i-Pr group (0.71^{14}). Because the solfonium group is tetrahedral and the preferred conformation of the *o*-Me_2S^+ group would be that in which lone pair electrons of the sulfur are close to the carboxyl group, the corresponding lower limit

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* This difference may well be attributed to the inductive effect from the *ortho* position which is not included in the estimations. and also to the lower effective dielectric constants ($D_o < D_p$).

Substituents	Steric[a]	Field[b]	Sum	Obsd[c]
o-Me$_2$S$^+$	0·23–0·71	1·85	2·08–2·56	2·01
o-Me$_3$N$^+$	0·87	1·85	2·72	3·03

[a] It is assumed that the steric effects of Me$_3$N$^+$ is equal to that of t-Bu group. As for the Me$_2$S$^+$ group, see text.
[b] The field effect is estimated to be $\sigma_{p\text{-Me}_3\text{N}^+}$ ($D_p r_p/D_o r_o$), and assumed that $D_p = D_o$. For D and r see calculations in Experimental.
[c] pKa (H) − pKa (X) in H$_2$O (Table 1).

could be that of o-Me (0·46[1a]), or more safely, a half of that of o-Me group, 0·23. The field effect of the o-Me$_2$S$^+$ group is estimable as being nearly equal to that of o-Me$_3$N$^+$. Hence, as indicated in Table 3, the sum in this case amounts to 2·08–2·56 in pKa units which, in contrast to the case of the o-Me$_3$N$^+$ group, becomes 0·07–0·55 pKa units greater than the observed. If this increment is due to the inductive effect and the lower effective dielectric constant ($D_o < D_p$), the calculated value should be smaller than the observed and this is clearly not the case. Thus the o-Me$_2$S$^+$ group is evidently less acid-strengthening than anticipated.

This anomalous effect of an o-Me$_2$S$^+$ substituent in comparison with that of o-Me$_3$N$^+$ can be explained in terms of the conjugative effect of the Me$_2$S$^+$ group. which is, as shown in Table 5, acid-strengthening from the *meta* or *para* positions but acid-weakening when it is in the *ortho* positions. To conclude, the apparent big difference in acidities (*ca.* 1 pKa unit) of o-trimethylammonio- and o-dimethylsulfonio benzoic acids in H$_2$O is mostly attributable to the difference in steric effects and partly. but still appreciably, due to the acid-weakening conjugative effect of o-Me$_2$S$^+$.

The influence of solvents on the ortho effects of the o-Me$_3$N$^+$ group seems interesting. As was shown in the preceding paper[1b] the acid strengthening ortho effect of o-Me$_2$S$^+$ increases steadily on changing solvent from H$_2$O to the less aqueous DMSO and this was explained as being due to the strong intramolecular stabilization by field effects. For instance the increase amounts to 0·66 in pKa unit from H$_2$O to 65 vol% DMSO. However, in the case of o-Me$_3$N$^+$, the *ortho* effect decreases by 0·22 pKa units (Table 1) for the same solvent change. Similar phenomenon can be seen in H$_2$O—50% aq. EtOH as solvents. Presumably, this decrease arises from the competition of the two opposing effects; one is the *ortho* effect-decreasing steric effect typically observable in the case of o-t-butyl benzoic acid[1a] and the other is the *ortho* effect-increasing polar effect just mentioned above, the former exceeding the latter in the o-Me$_3$N$^+$ case.

NMR spectra. Table 4 lists chemical shifts of Me and Ph protons of relevant acids and some other related compounds. The spectra were determined in both protonated and dissociated states in acidic and alkaline D$_2$O solutions. The signals of the Ph protons show AA'BB' pattern for the p-substituted acids, so the centers of the two half spectra are regarded as the chemical shifts of two pairs of protons. For other samples the signals are multiplets but of similar pattern for the corresponding onium compounds, therefore the chemical shifts of the main peaks are recorded and compared. It is characteristic of the compounds shown in this Table that the Ph protons

TABLE 4. CHEMICAL SHIFTS OF Me AND Ph PROTONS, δ (ppm)[a]

Protons		Substituted benzoic acids						Substituted benzenes[b]	
		o		m		p			
		Me$_2$S$^+$	Me$_3$N$^+$	Me$_2$S$^+$	Me$_3$N$^+$	Me$_2$S$^+$	Me$_3$N$^+$	Me$_2$S$^+$	Me$_3$N$^+$
Methyl[c]	Acid[d]	3·29	3·85	3·36	3·77	3·38	3·78	3·26	3·65
	Anion[e]	3·16	3·76	3·20	3·71	3·25	3·67		
Phenyl[f]	Acid	8·0	7·8	7·95–8·2	7·9–8·1	{8·052, 8·227}	{7·996, 8·203}	7·81	7·71
	Anion	7·8	7·5	8·1	7·95	{7·913, 8·078}	{7·831, 8·036}		

[a] DSS as the internal standard.
[b] In D$_2$O. Both onium salts are iodide.
[c] Sharp singlet.
[d] In 2N-DCl-D$_2$O.
[e] In slightly alkaline NaOD-D$_2$O.
[f] AA'BB' for the *para* isomers; the centers of the two half spectra are shown. Multiplet for the other compounds; the chemical shifts of the corresponding main peaks are shown.

of the sulfonium compounds always shift to lower field than those of the corresponding ammonium compounds do whereas the situation is reversed in the case of the Me protons. This fact is best explained as a result of charge-delocalization from the positive sulfur to the benzene ring and therefore gives structural support to the interpretation given for the pKa data.

TABLE 5. INCREASE OR DECREASE IN THE FIELD EFFECT OF THE Me$_2$S$^+$ GROUP DUE TO THE CONJUGATIVE EFFECT

Positions	Calcd (δ/rD)[a]			Obsd (pKa unit)
ortho	0·29 $\delta(1/D_B - 1/D_o)$	<	0[b]	− 0·38– − 0·86[c]
meta	0·10 δ/D_B	>	0	0·06[d]
para	0·14 δ/D_B	>	0	0·13[d]

[a] See calculations in Experimental.
[b] Because $D_B > D_o$.
[c] Difference in pKa in H$_2$O (1·02) of o-Me$_2$S$^+$- and o-Me$_3$N$^+$-substituted benzoic acids minus difference in steric effects (0·64 − 0·16, see Table 3) of the two acids.
[d] Equations 1 and 2.

EXPERIMENTAL

pKa *measurement*. The pKa values were obtained by the potentiometric titration using a Hitachi–Horiba M-4 Type pH-meter equipped with a glass (1026-05T) and a 3·33 N aqueous KCl calomel (2080-05T, ceramic filter type) electrodes. The meter was calibrated and checked with the standard buffer solutions (pH 6·86 and 4·01 at 25°) before and after titrations. Each measurement was ascertained to be correct within ±0·01 pKa unit. Titrants were delivered from a 10-ml buret which was graduated to 0·02 ml. Solutions were stirred magnetically under N$_2$. The waiting period[7] between stirring and pH measurement was extended to about one min. although the drifts in pH readings disappeared within ½ min in 50 vol% EtOH and 65 vol% DMSO as well as in H$_2$O. Two pairs of the glass and calomel electrodes were used in measurements in 50 vol% EtOH and checked for identical results.

The technique and calculations of Albert and Serjeant were followed,[8] but more elaborated calculations were performed to obtain the activity coefficients of charged acid molecules and zwitterions. The Debye–Hückel equation (Eq. 1) was used for charged acid molecules, and the Ingold expression (Eq. 2)[9] for zwitterions.

$$-\log f_+ \text{ or } -\log f_- = 1.823 \times 10^6 \, Z^2/(DT)^{3/2}\sqrt{I}/(1 \pm 1.6\sqrt{I}) \qquad \dots 1$$

$$-\log f_\pm = 4\pi N e^4 \, Z^2 \, dI/2303 \, k^2 \, (DT)^2 \qquad \dots 2$$

where I is the ionic strength. d the distance of two charges in a molecule and the rest of the symbols are used conventionally. The distances, d, were measured on the figures, which were drawn using the following structural parameters:[10] benzene C—C, 1.40 Å; C (benzene)—C (carboxylate), 1.51; C—O, 1.24; C (benzene)—N, 1.48; C (benzene)—S, 1.74;[11] < O—C—O, 123°; < C—C—C (ring), 120°; benzene plane–OCO plane. 0° for *meta* and *para* derivatives; 90° for *ortho* derivatives.

In water. In calculation of ionic strength, I, zwitterions were taken as two singly charged ions. Assuming an appropriate activity coefficient, $f_\pm$, stoichiometric hydrogen-ion concentration, $[H^+]$, was calculated from activity of hydrogen ion, $\{H^+\}$. Using $[H^+]$ thus obtained, I was recalculated and $f_\pm$ was obtained from Eq. 1. This calculation was repeated until the starting $f_\pm$ became essentially identical with the resulting $f_\pm$. The acid concentration was 0.01 M for *m*-, *p*-substituted and unsubstituted acids and the titrant 0.1 N KOH. The eight pKa values calculated from the data during a titration between 10% and 90% neutralization fell within a spread of ± 0.02 pKa units and the average value was reproduced within 0.01 pKa unit. Considerably higher concentrations were used in the cases of *ortho* substituted acids because of their high acidities. The o-Me$_2$S$^+$ substituted acid was titrated at 0.02 and 0.05 M concentrations with 0.2 and 0.5 N KOH. respectively, and the same precision as above. The o-Me$_3$N$^+$ substituted acid was titrated at 0.1 M concentration with N KOH and gave a pKa of 1.19 ± 0.02. This is in good agreement with a pKa of 1.14 ± 0.02 obtained by the titration of the *ortho* betaine, o-Me$_3$N$^+$ C$_6$H$_4$CO$_2^-$, at 0.1 M with N HCl, for its unfavorably high acidity and high ionic strength. The activity coefficient terms were calculated as follows: *meta* and *para* derivatives, − log f_+ = 0.05–0.06 and − log $f_\pm$ = 0.01–0.02; benzoate anion. − log f_- = 0.02–0.04; o-Me$_2$S$^+$ derivative, − log f_+ = 0.07–0.08 and − log $f_\pm$ = 0.02 at 0.02 M. − log f_+ = 0.09–0.10 and − log $f_\pm$ = 0.04–0.05 at 0.05 M; o-Me$_3$N$^+$ derivative, − log f_+ = 0.12–0.13 and − log $f_\pm$ = 0.09–0.10 (acid). − log f_+ = 0.11–0.12 and − log $f_\pm$ = 0.06–0.08 (betaine).

In 50 vol% EtOH. The acids were titrated at 0.005 M with 0.05 N KOH in this solvent. The value of 52.5 was used for the dielectric constant[9] and the ionic strength was calculated neglecting the hydrogen-ion concentration. The activity coefficient terms, − log f_+ and − log $f_\pm$, for the *meta* and *para* derivatives were calculated to be 0.07 and 0.02, and for the *ortho* derivatives 0.07–0.08 and 0.01, respectively. The term for benzoate anion. − log f_-, was 0.04. The pKa calculation was performed assuming unit activities and readings of pH-meter scale being equal to logarithm of reciprocal hydrogen-ion concentrations.[12] Precision and reproducibility were almost the same as in H$_2$O except for the cases of *ortho* derivatives, in which the eight pKa values fell within a spread of ± 0.03.

In 65 vol% DMSO. Titrations were carried out in the same way as in 50 vol% EtOH and gave the same precision and reproducibility, except that the precision for the o-Me$_3$N$^+$ derivative was ± 0.1. The activity coefficient terms were calculated using the dielectric constant of 70[13] as follows: *meta* and *para* derivatives. − log f_+ = 0.05 and − log $f_\pm$ = 0.01; *ortho* derivative. − log f_+ = 0.05 and − log $f_\pm$ = 0.00; benzoate anion. log f_- = 0.03.

NMR spectra. The NMR spectra of dimethylsulfonio- and trimethylammoniobenzoic acids, and dimethylphenylsulfonium and trimethylphenylammonium iodides were measured in both acidic and alkaline D$_2$O. using a Japan Electron Optics Laboratory JNM-3H-60 spectrometer at 60 Mc sec^{-1}. Chemical shifts are from the internal standard of sodium 2.2-dimethyl-2-silapentane-5-sulfonate (DSS). Concentrations of solutes were 0.7–1.4 × 10^{-4} mole/0.5 ml (5–10%).

Solvents and titrants. H$_2$O was deionized with ion-exchange resins, specific resistance > 10^7 Ω cm. Reagent grade EtOH was treated with Na and diethyl phthalate[14] and fractionated through a 30-cm column packed with porcelain rings. DMSO was purified as described before.[1e] KOH and HCl were of analytical grade.

Acids. Benzoic acid was recrystallized before use. The preparation and analytical data of o- and p-dimethyl-sulfoniobenzoic acids were described in the preceding paper.[1b] The same method was applied for the preparation of the *meta* isomer. All acids prepared were checked by NMR.

m-*Carboxyphenyldimethylsulfonium* p-*toluenesulfonate* (m-$Me_2S^+C_6H_4$–CO_2H . OTs^-). Recrystallized from EtOH–EtOAc. m.p. 193–194° (cor) (lit.[3] 196–197°). (Calcd for $C_{16}H_{18}O_5S_2$: C. 54·22; H. 5·10; S. 18·09. Found: C, 54·34. H, 5·25; S. 17·81%). Purity from neut. equiv., 99·5%.

o-*Carboxyphenyltrimethylammonium chloride* (o-Me_3N^+ $C_6H_4CO_2H \cdot Cl^-$). The method described by Willstätter and Kahn[15] was adopted. Commercial anthranilic acid was methylated with Me_2SO_4 to give N-methylanthranilic acid and this was esterified with CH_2N_2. The Me ester was methylated with MeI to give the trimethylammonium derivative. This was treated with Ag_2O to give the betaine. o-trimethyl-ammoniobenzoic acid anion, recrystallized from hot EtOH. m.p. 231° (cor) (lit.[15] 224°). (Calcd for $C_{10}H_{13}O_2N \cdot 1/2 H_2O$: C. 63·81; H. 7·51; N. 7·44. Found: C. 63·66; H. 7·44; N. 7·51%). The betaine was treated with HCl and the white precipitate collected. dec 173° (cor). (Calcd. for $C_{10}H_{14}O_2NCl \cdot H_2O$: C. 51·39; H. 6·90; N. 6·00; Cl. 15·17. Found: C. 51·28; H. 7·03; N. 5·95; Cl. 15·36%). Purity from neut. equiv.. 99·55%.

m- *and* p-*Carboxyphenyltrimethylammonium chlorides* (m- and p-Me_3N^+-$C_6H_4CO_2H \cdot Cl^-$). Commercial m- and p-aminobenzoic acids were methylated with MeI in MeOH containing KOH. According to the method of Willstätter and Kahn[15] the *para* isomer was collected as "perjodid" (I_3^-) and decomposed to the iodide by steam distillation. Since this method takes much time. *meta* derivative was collected by evaporation of MeOH after filtration. Both derivatives were treated successively with Ag_2O and HCl then recrystallized from EtOH.

meta isomer: dec 184° (lit.[2] dec 181·5–182°). (Calcd. for $C_{10}H_{14}O_2NCl \cdot H_2O$; C. 51·39; H. 6·90; N. 6·00; Cl. 15·17. Found: C. 51·65; H. 6·93; N. 6·03; Cl. 15·18%). Purity from neut. equiv., 100·0%.

Para isomer: m.p. 243–244° (cor) (lit.[2] 240·0–241·4°). (Calcd. for $C_{10}H_{14}O_2NCl$; C. 55·69; H. 6·54; N. 6·50; Cl. 16·44. Found: C. 55·98; H. 6·78; N. 6·47; Cl. 16·58%). Purity from neut. equiv., 99·75%.

Dimethylphenylsulfonium iodide. Commercial thiophenol was methylated with Me_2SO_4 and the iodide was obtained by treatment with KI. Recrystallization gave slightly yellow plates. dec. 90°. The perchlorate was obtained by treatment with $HClO_4$ and had sharp m.p.. 159–160° (lit.[3] 158–160°). solubility in H_2O was not enough for NMR.

Trimethylphenylammonium iodide. Commercial dimethylaniline was methylated with Me_2SO_4 and the product converted into the iodide with KI. dec 180 . perchlorate was not soluble enough in H_2O for NMR.

Calculations. For o-dimethylsulfoniobenzoate anion as an example, the change in field effects due to the conjugation becomes: $(\delta/3D_B) (1/r_1 + 2/r_3) + (1/D_or_o) (1 - \delta) - (1/D_or_o) = \delta (0·287/D_B - 0·286/D_o) = 0·29 \delta(1/D_B - 1/D_o)$. Here δ designates the delocalized charge due to the conjugation. D_B and D_o are the effective dielectric constants to be used for the charges on the benzene ring and on the sulfur of the o-Me_2S^+ group respectively, and r_1, r_3 and r_o denote the distances between the carboxylate oxygen and the C_1. C_3 carbons of the benzene ring. and the sulfur of the o-Me_2S^+ group, respectively, which were measured on a figure drawn using the structural parameters given on page 4260. δ is assumed to be distributed equally to the three o-, p-carbon atoms. Similar calculations for the *meta* and *para* derivatives give $\delta(0·273/D_B - 0·170/D_m)$ and $\delta(0·287/D_B - 0·150/D_p)$, respectively. Assuming $D_B = D_m = D_p$, simplified terms is obtained and shown in Table 5, r_o, 3·50 Å; r_m, 5·35: 6·40: r_p, 6·65: r_1, 2·37: r_2, 3·30; r_3, 4·55: r_4, 5·05.

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