

Infrared spectra and conformation of methyl-substituted benzoic acids[†]

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ABSTRACT: Infrared spectra of all isomers of polymethyl-substituted benzoic acids were recorded in the carbonyl and hydroxyl regions in tetrachloromethane at various concentrations and interpreted in terms of conformation. According to a plot of $\nu(\text{C}=\text{O})$ of the monomeric form vs Hammett substituent constants σ , these compounds may be classified into two classes. Derivatives with none or only one methyl group in the *ortho* position are concluded to exist in an equilibrium of two planar conformations, unless the equilibrium is degenerate. Derivatives with two *ortho*-situated methyl groups are concluded to take up one non-planar conformation. These findings are supported by the shape of the hydroxyl and carbonyl bands, which are unsymmetrical in the former class, although they could not be reliably separated into bands pertinent to the individual conformers. This conclusion is at variance with the common interpretation which has invariably ascribed to these and similar *ortho* derivatives non-planar conformations with a variable torsional angle. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: methylbenzoic acids; infrared spectra; conformation

INTRODUCTION

Methyl-substituted benzoic acids have served as classical model systems to demonstrate and evaluate steric effects.^{1,2} Most studies have identified the steric effect with the steric hindrance to resonance and its intensity has been assumed to depend on the torsional angle $\phi = \angle \text{O}=\text{C}-\text{C}=\text{C}$. For instance, the NMR chemical shifts,^{3,4} the dissociation constants in water,^{5–7} the electronic spectra^{4,7} and the dipole moments of esters⁸ were explained in terms of the value of the angle ϕ , which increases with steric hindrance. Some typical values of ϕ are given in Table 1. The torsional angle seemed to be affected not only by *ortho* methyl groups but also by those in the *meta* position: this was called the buttressing effect.⁹ The angle ϕ was also estimated¹⁰ or calculated at different levels: MM2³ or CI PPP.¹¹ Only in the cases of dissociation constants was an alternative interpretation presented in which the steric hindrance to resonance was replaced by the primary steric effect and possible steric hindrance to solvation.¹²

The theory of hindered resonance and variable torsional angle probably finds its origin in the interpretation of the electronic spectra of substituted benzaldehydes and acetophenones.¹³ When applied to benzoic

acids, it is evidently correct, at least in a qualitative sense, for compounds with a strong steric effect, e.g. 2,6-dimethylbenzoic acid (**15**) (Scheme 1) ($\phi = 53^\circ$ in the crystalline phase¹⁴) and other sterically congested molecules. However, we have challenged^{15–17} this theory in the case of 2-methylbenzoic acid and possibly other compounds with less steric hindrance. For example, 2-methyl-5-nitrobenzoic acid has a planar conformation in the crystalline state,¹⁷ and the gas-phase acidities^{15,16} and the enthalpies of formation¹⁸ are better understood in terms of an equilibrium between the two planar forms, **7a** and **7b** (Scheme 1). This view was supported by simple AM1 calculations¹⁶ (Table 1).

The present study was undertaken with the assumption that planar and non-planar conformations of benzoic acids can be distinguished by IR spectroscopy in the C=O and O—H regions, either by the occurrence of two bands in the case of equilibria like that shown previously (**7a** \rightleftharpoons **7b**) or by correlations with constants σ or similar parameters. Previous IR studies²² of these compounds in the solid state dealt only with the band assignment and did not address the conformation.

EXPERIMENTAL

Materials. A number of the methyl-substituted benzoic acids (**1–20**) (Table 2) were characterized in our previous work^{15,23} and the remaining ones were prepared and given to us by Dr P. Jiménez and co-workers.¹⁸

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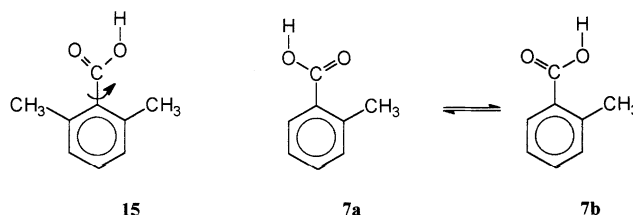
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Table 1. Torsional angles $\phi = \angle \text{O}=\text{C}-\text{C}=\text{C}$ ($^\circ$) in some methyl-substituted benzoic acids as deduced from various approaches

Compound	Methyl position	UV (Ref. 7 or 4)		^{13}C NMR (Ref. 4)	MM2 (Ref. 3)	CI-PPP (Ref. 11)	AM1 (Refs 15, 16)	X-ray (Refs 14,17,19,20)
7	2	38	36	21	29	37	0	0 ^a
8	2,3	53	42	27	29	42	0	10
15	2,6	70	62	51	55	60	33	53
17	2,4,6	—	58	—	55	53	31	48
19	2,3,5,6	76	70	51	—	65	75	73

^a Concerns 5-nitro-2-methylbenzoic acid;¹⁷ an x-ray structure of 2-methylbenzoic acid²¹ was not sufficiently precise.

**Scheme 1.** Numbering of compounds according to Table 2**Table 2.** The $\nu(\text{O}-\text{H})$ and $\nu(\text{C}=\text{O})$ monomer frequencies of methyl-substituted benzoic acids (in CCl_4)

Compound	Methyl position	$\nu(\text{O}-\text{H})$ (cm^{-1})				$\nu(\text{C}=\text{O})$ (cm^{-1})		
		Apparent	$\Delta\nu_{\frac{1}{2}}$	Asymmetry		Apparent	Asymmetry	
				AF ^a	α^b		AF ^a	α^b
1	H	3540.3	27.5	1	-2	1742.5	2	-7
2	3	3541.0	26.4	1	-2	1740.5	1	-3
3	4	3542.1	26.4	0	-2	1738.9	1	-3
4	3,4	3542.0	26.3	0	-2	1737.5	0	-3
5	3,5	3541.2	26.7	0	-2	1738.9	2	-3
6	3,4,5	3542.8	24.1	0	-2	1736.7	2	-5
7	2	3539.6	31.0	5	-7	1740.2	11	-18
8	2,3	3537.7	32.3	5	-6	1738.4	3	-11
9	2,4	3541.4	29.1	5	-9	1736.1	10	-18
10	2,5	3539.6	31.3	7	-12	1738.5	6	-20
11	2,3,4	3539.0	32.1	5	-8	1734.9	6	-11
12	2,3,5	3537.7	32.5	4	-6	1735.0	-5	+22 ^c
13	2,4,5	3540.9	33.8	4	-9	1735.0	9	-20
14	2,3,4,5	3538.7	30.5	5	-8	1732.6	-3	+2
15	2,6	3517.2	27.4	1	-2	1746.1	1	-3
16	2,3,6	3515.8	26.1	1	-1	1747.1	1	-3
17	2,4,6	3519.1	27.3	0	-2	1742.1	1	-5
18	2,3,4,6	3516.4	26.4	0	-1	1743.8	1	+2
19	2,3,5,6	3514.3	24.1	0	-1	1749.6	6	-20 ^d
20	2,3,4,5,6	3514.6	24.1	1	-1	1746.8	8	-6

^a A factor measuring the asymmetry in % (see Discussion).

^b The angle α ($^\circ$) expressing the asymmetry (see Figure 1 and Discussion).

^c Asymmetry in reverse direction, caused by an additional band at 1747cm^{-1} , not belonging to the monomer $\nu(\text{C}=\text{O})$.

^d Additional band at 1738cm^{-1} , not belonging to the monomer $\nu(\text{C}=\text{O})$.

Spectral measurements. Infrared absorption spectra were recorded on a Bruker IFS 88 FT-IR spectrometer in tetrachloromethane at concentrations of 0.003 ($d = 1\text{ mm}$), 0.0006 and 0.00012 mol l^{-1} ($d = 1\text{ cm}$). The

dimeric form prevails at the highest concentration and the monomeric form at the lowest concentration. Separation of the carbonyl bands was achieved by the standard program²⁴ which enables only the number of resulting

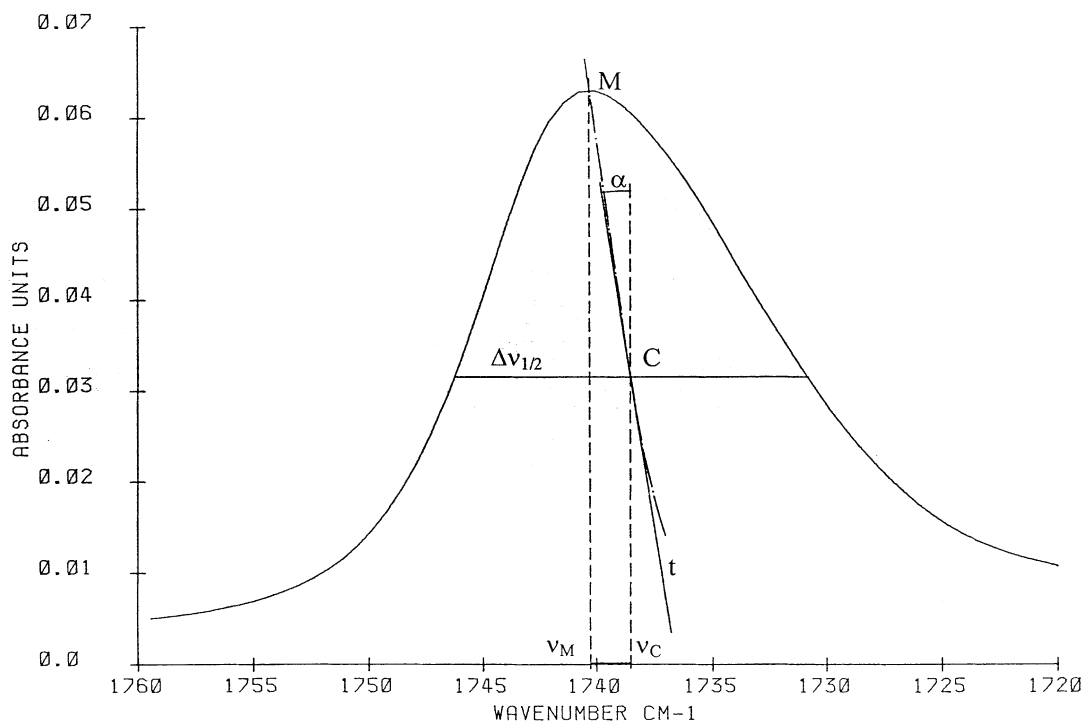


Figure 1. The carbonyl band of 2-methylbenzoic acid (**7**) and evaluation of its asymmetry according to the asymmetry factor AF and the angle α

bands to be predetermined but their position, half-width and shape (Gauss/Lorentz ratio) are obtained unambiguously and cannot be controlled. A Fourier self-deconvolution²⁴ before separation was also attempted but did not improve these results. Attempted deconvolution of asymmetric hydroxyl bands, showing no shoulder, was completely unsuccessful: satellite bands were obtained whose number and position depended only on the chosen value of the reduction factor (range 1.1–1.5).

With the resolution used (2 cm^{-1}), the ATS 89B program does not allow an interval of wavenumber reading finer than 0.64 cm^{-1} . Therefore, we used a graphical procedure and obtained the apparent maxima of the $\nu(\text{C}=\text{O})$ and $\nu(\text{O}-\text{H})$ bands as the point of intersection of the band axis with the spectral curve. With sufficient enlargement, the accuracy of the reading was better than 0.1 cm^{-1} . The two *ad hoc* measurements of asymmetry suggested here were determined from the same graph (Figure 1). One measure, called the asymmetry factor AF , is defined as the difference between the wavenumber for the maximum (ν_M) and the wavenumber corresponding to the centre of the half-width (ν_C) divided by the value of the half-width ($\Delta\nu_{1/2}$). This measurement is expressed as a percentage:

$$AF = 100(\nu_M - \nu_C)/\Delta\nu_{1/2} \quad (1)$$

The other possible measurement is the value of the angle α between the band axis and the vertical direction as depicted in Figure 1.

RESULTS AND DISCUSSION

We followed two lines of investigation. One approach (which might be called classical spectroscopy) consisted of searching bands which could be assigned to individual rotamers. In this study, we focused on the number of bands in the $\text{C}=\text{O}$ and $\text{O}-\text{H}$ regions. The other approach, correlation analysis, entailed plotting the $\text{C}=\text{O}$ or $\text{O}-\text{H}$ frequencies against various substituent constants or other physical quantities. We believed that planar and non-planar molecules should show different patterns in these plots.

Separation of carbonyl and hydroxyl bands

At the concentrations used, two bands were observed in the carbonyl region, belonging to the monomeric and dimeric forms of the acid. They were well separated and could be readily distinguished. However, no further splittings attributable to the presence of rotamers in equilibrium were observed. The bands of certain compounds were simply more or less unsymmetrical. In the case of compounds **7–14**, with one *ortho* methyl group, we assumed that they existed as two rotamers in equilibrium (e.g. **7a** \rightleftharpoons **7b**). The remaining compounds (Table 2) were expected to show only one band since they are either symmetrical (**1, 3, 5, 6**), slightly unsymmetrical with little difference between the conformers (**2, 4**) or

exist in one non-planar conformation (**15–20**). However, we were unable to resolve the C=O bands of the monomeric forms satisfactorily (Table 2). One problem that arose was additional bands not related to the carbonyl bond. In some cases, these could be revealed by their independence of concentration while true carbonyl bands are controlled by the monomer \rightleftharpoons dimer equilibrium. Two examples of these bands are given in the footnotes to Table 2. The origin of these bands was not assigned and not all such bands were discovered. However, the main problem evidently lies in the insufficient separation of the bands. Attempted resolution using the Gaussian–Lorentzian program²⁴ is described in the Experimental section. Although two bands were formally obtained in all cases where their presence was assumed, the resolution was imprecise and some parameters of the resolved bands were physically unrealistic. Moreover, similar apparent resolutions were possible even in the case of compounds which cannot exist in two conformations: real and apparent cases could not be distinguished with certainty.

For this reason, we decided to restrict further studies to distinguishing symmetrical and asymmetric bands and it was necessary to give an at least semiquantitative character to the term asymmetry. As shown in Figure 1 and described in the Experimental section, we suggested two measurements to do so. These are defined here as *ad hoc* orientation characteristics and are given no strict physical meaning. The so-called asymmetry factor AF is related to the distance of the band maximum to the wavenumber of the centre of the half-width [equation (1)]. Its value is evidently zero for asymmetrical band and the theoretically highest but not realizable value is 50%. The highest value observed is 11% (Table 2). Another measurement of the asymmetry could be the angle α (Figure 1). This is also zero for symmetrical bands and the highest observed value is 22°. Table 2 reveals that these two measurements are generally higher for **7–14**, assumed to exist as an equilibrium of two rotamers, than for the remaining compounds. When studying the $\nu(\text{C}=\text{O})$ frequency, the results for AF and of α were not always consistent and several unexplained exceptions were encountered. When we gave some arbitrary limits to AF and α (e.g. 3% and 10°, respectively), most compounds could be classified correctly with a few exceptions such as **14** (misassigned as existing in one conformation), **19** and **20** (apparently in two conformations). The case of **19** can be explained (Table 2, footnote). For **12**, the positive value of the angle α corresponds to the satellite band on the side of higher frequencies (Table 2) caused by an additional band not related to the carbonyl bond. On the other hand, assignment of the two bands of **7–14** assumed to represent the two conformers may be fairly safe. The steric effect of an *ortho*-situated methyl group raises the $\nu(\text{C}=\text{O})$ frequency, as can be proved particularly by comparison with *para* derivatives, e.g. **7** and **3**. It follows that the *sp* rotamer (**7a**) should show a higher frequency

than the *ap* rotamer (**7b**), since the steric effect on the carbonyl bond is evidently greater. An opposite assignment in the case of the corresponding ester²⁵ was only tentative and cannot be considered to be proved. According to our assignment, the side band represents the *ap* rotamer and the main band the *sp* rotamer. This statement does not agree with the reported conformation of the corresponding ester based on the intensity of the ν_{16} band.²⁶ However, it is very strongly supported by AM1 calculations^{15,16} and by the preferred conformation in the crystalline state.^{17,19} The dipole moment of the ester was also interpreted in favour of the prevailing *sp* form.²⁷ It is true that the two conformers differ little in energy and their equilibrium may be subject to the conditions of the experiment.

More significant results were obtained from the analysis of the O—H band. Although no reasonable band separation was achieved even in this case, the measurements of asymmetry are convincing and the compounds can be classified safely (Table 2). All compounds with two conformers (**7–14**) have $AF \geq 4\%$ and $\alpha \geq 6^\circ$. Compounds existing only in one conformation (**1, 3, 5, 6, 15–20**) or in two conformations differing only in the *meta* position (**2, 4**) exhibit $AF = 0$ or 1% and $\alpha \leq 2^\circ$. Interestingly, even the half-width $\Delta\nu_{1/2}$ could be sufficient for a classification: in the case of compounds with two conformers it is $>29\text{cm}^{-1}$, whereas it does not exceed 27.5cm^{-1} in other cases. Assignment of bands to the two rotamers is in agreement with that made from $\nu(\text{C}=\text{O})$. The steric effect now lowers the frequency. Hence the side band at lower frequencies (i.e. more displaced) should be assigned to **7b** in which the O—H bond is more influential. The *sp* rotamer still prevails.

Further frequencies related to the carboxyl group of compounds **1–20** are collected in Table 3. They were assigned tentatively but their pertinence to the monomer or dimer is unambiguous according to the concentration dependence. Only in the $1290\text{--}1180\text{cm}^{-1}$ region did the absorption by the solvent not allow the use of a cell thicker than 1 mm and the dependence on concentration was not followed. Assignment of the bands of the dimer of **14, 19** and **20** is tentative in this region. For other compounds, our assignment agrees with that of Arenas *et al.*²² based only on solid state spectra.

Correlation analysis

In this approach, the $\nu(\text{C}=\text{O})$ and $\nu(\text{O}—\text{H})$ or even other frequencies were used and plotted against various parameters characteristic of the structure. The Hammett constants σ , expressing the substituent polar effects,²⁸ appeared most appropriate. For *meta*- and *para*-substituted benzoic acids, with substituents more polar than the methyl group, a good linear dependence on σ was observed for both the $\text{C}=\text{O}$ ²⁹ and $\text{O}—\text{H}$ ³⁰ frequencies. One could expect that for congested derivatives, the steric

Table 3. Other carboxyl vibrational frequencies of methyl-substituted benzoic acids in the 1800–1100 cm⁻¹ region (cm⁻¹, in CCl₄)

Compound	Monomer		Dimer		
	$\beta(\text{COH})$	$\nu(\text{C—O})$	$\nu_{\text{as}}(\text{C=O})^{\text{a}}$	$\beta(\text{COH}) + \nu(\text{C—O})$	
1	1351	1172	1696	1416	1288
2	1358	1164	1696	1412	1280, 1308
3	1361, 1318	1170	1696	1419	1286
4	1365, 1331	1164, 1127	1694	1424	1273, 1308
5	1338, 1370	1158, 1170	1696	1415	1245, 1310
6	1342	1141	1692	1422	1247, 1311
7	1341	1179	1695	1407	1270
8	1325	1128, 1169	1694	1402, 1437	1299, 1274
9	1335	1184, 1147	1691	1408	1275, 1307
10	1337	1162, 1151	1694	1414	1268, 1302
11	1336	1126, 1173	1691	1412, 1399	1297, 1268
12	1341	1159, 1121	1691	1414, 1405sh	1306, 1251
13	1347, 1325	1115, 1135	1688	1412	1268, 1308
14	1338	1134	1689	1405	1303, (1254)
15	1328sh	1107, 1168	1697	1433, 1394	1289
16	1326	1124, 1167	1699	1425	1293
17	1332	1153	1698	1437, 1395	1292
18	1320	1129	1698	1410	1287
19	1323	1137	1699	1417	1310, (1258)
20	1327	1139	1698	1428	1311, (1281)

^a Apparent maximum.

effect of the substituent would be manifested by a deviation from the straight line defined for purely polar effects. For the acids **1–20**, the Hammett equation can be used in the form of the equation

$$\nu - \nu^0 = \rho \sum \sigma_i \quad (2)$$

where the summation extends over positions 2–6 on the benzene ring and the reaction constant ρ is in cm⁻¹; ν^0 relates to benzoic acid.

The additivity of substituent effects is not a necessary consequence of the Hammett equation and is valid only as an approximation. Nevertheless, for methyl derivatives this approximation is very good.³¹ More important in our case is a necessary extension of the Hammett equation, valid principally only for *meta* and *para* substituents, also to *ortho* substituents. Any chosen value for the σ_o constant of the methyl group must be of restricted validity only in a specific region, either only for some IR frequencies or for some particular compounds.²⁸ From several possibilities,³² we chose the value $\sigma_o = 0.10$, determined from IR spectroscopy, viz. from the intensities of substituted benzonitriles.³³ Figure 2 reveals that good linearity was obtained with the $\nu(\text{C=O})$ frequency for **1–14**. The remaining compounds deviated very distinctly. In our opinion, this graph is proof that all methyl-substituted benzoic acids can be divided into two classes that are structurally different. Further interpretation, in terms of conformation, is supported by the following reasoning. The higher frequency of $\nu(\text{C=O})$ for **15–20** indicates hindered conjugation with the

benzene ring, and hence a non-planar conformation as shown in structure **15**. This hindered resonance may be quantified by the deviation of these points from the straight line in Figure 2. This deviation is not constant but depends on the number of methyl groups in the 3,5-positions (buttressing effect). In energy units, it amounts to 0.1–0.2 kJ mol⁻¹, compared with the entire effect of resonance which may be estimated to be 0.5 kJ mol⁻¹ from comparison of the carbonyl frequencies of aromatic and aliphatic carboxylic acids. We previously stressed¹⁵ that the theory of hindered resonance should always be tested by comparing the energy of assumed steric hindrance with the entire resonance energy. In our case, the resonance energy observed in spectroscopy represents the difference between ground and excited states and is much less than the whole resonance energy in the ground state, estimated¹⁵ to be 15 kJ mol⁻¹. It should be pointed out that the result from Figure 2 does not depend on the somewhat problematic choice of the constant σ_o . For alternative possible values,³² a very similar graph would be obtained.

A similar plot for the hydroxyl frequency (Figure 3) supports the above conclusion but is more complex. The benzoic acids are separated into three groups: **1–6** without any *ortho* substituent are situated along a line pertinent to *meta* and *para* substituents with stronger polar substituents,³⁰ **7–14** with one *ortho* methyl group are displaced slightly downwards and **15–20** with two *ortho* methyl groups are markedly displaced. In the last case, the displacement is of the same order of magnitude

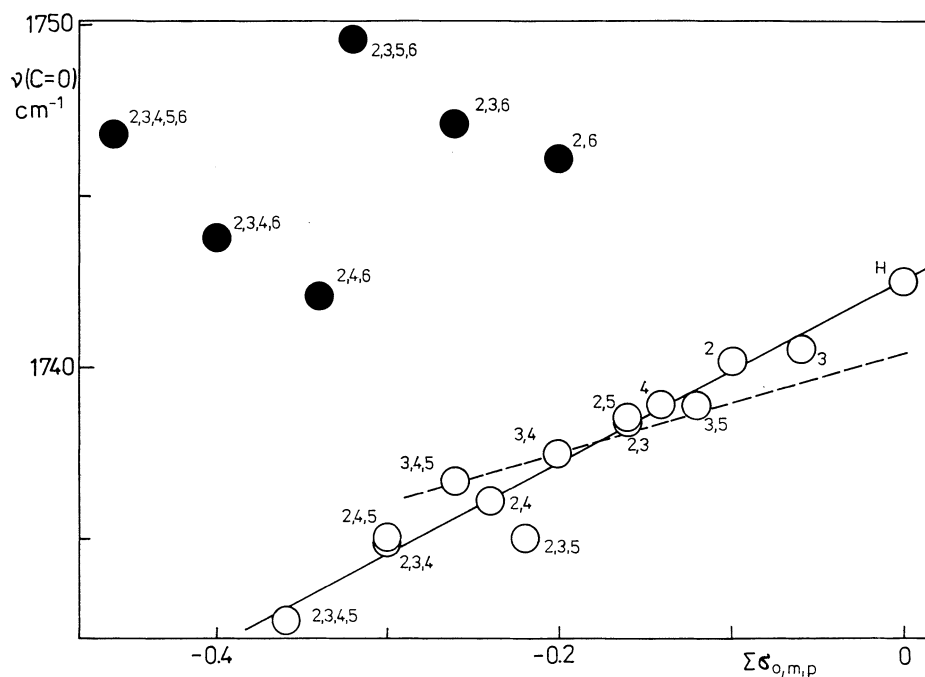


Figure 2. Hammett plot of the carbonyl stretching frequency of methyl-substituted benzoic acids vs the sum of substituent constants σ . Molecules with (○) no or one and (●) two *ortho* methyl groups. The dashed line was derived in Ref.²⁹ for *meta* and *para* substituents with stronger polar effects

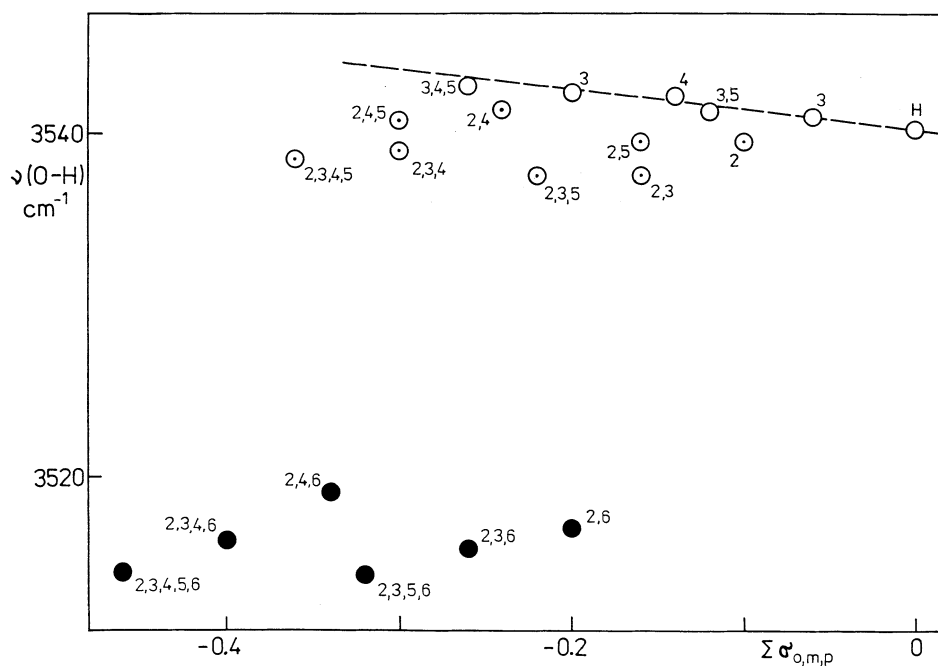


Figure 3. Hammett plot of the O—H stretching frequency of methyl-substituted benzoic acids vs the sum of substituent constants σ . Molecules with (○) no, (◐) one and (●) two *ortho* methyl groups. The dashed line has the slope derived in Ref.³⁰ for *meta* and *para* substituents with stronger polar effects

as in Figure 2 but in the opposite direction. From the slope for polar substituents,³⁰ it can be determined that conjugation with the benzene ring (an electron-releasing effect) makes the O—H bond less polar and stronger. Hence a hindrance to resonance makes this bond weaker

and the $\nu(\text{O—H})$ frequency lower. From the difference in $\nu(\text{O—H})$ between aliphatic and aromatic acids, the effect of resonance may be estimated to be 0.5 kJ mol^{-1} , equal to that of $\nu(\text{C=O})$.

We attempted many other correlations but they were

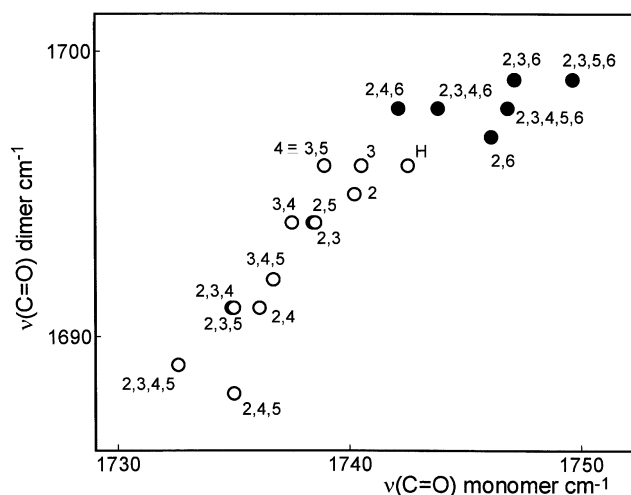


Figure 4. Plot of the C=O stretching frequencies of methyl-substituted benzoic acids, dimer vs monomer. Molecules with (○) no or one and (●) two *ortho* methyl groups

less indicative. The $\nu(\text{C}=\text{O})$ frequencies of the dimer revealed a similar dependence on σ to that of the monomer. Correlation of $\nu(\text{C}=\text{O})$, dimer vs monomer, may be of interest (Figure 4) since it is based entirely on direct spectroscopic quantities and does not refer to any empirical constant. Classification of compounds into two classes is evident but the physical meaning does not stem directly from the graph. No dependence was found between the frequencies $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ although it has been reported for a series of carbonyl derivatives more different in structure.³⁴

Using a similar procedure to the above, we can reinterpret the ^{13}C NMR shifts of the C-4 carbon atom of methyl-substituted benzoic acids. These shifts were first corrected in a complex way to obtain the reduced shifts $\Delta\delta_i$, which were then explained in terms of the variable angle ϕ .⁴ However, the derivatives with a *para*-situated methyl group could not be treated in this way since too large angles were predicted. A plot of $\Delta\delta_i$ vs σ (Figure 5) gave a different result: the compounds can be divided into the same classes as in Figures 2–4, viz. without steric hindrance, with a small steric hindrance and with a strong hindrance disturbing the coplanarity.

CONCLUSIONS

Convincing spectral proof has been presented showing that methyl-substituted benzoic acids can be divided into two different classes. We interpret this fact in terms of conformation and steric hindrance to conjugation. The acids of one class are concluded to exist as an equilibrium of two planar conformers whereas those of the second class exist as one non-planar conformation. The concept of variable conformation¹³ with a continuously increasing torsional angle ϕ was based on wrong assumptions and should be abandoned in the case of aromatic carbonyl compounds. It is not excluded that it may hold for some other compounds.

Correlation analysis using σ constants has again proved to be an efficient tool for structure investigations based on spectroscopic data. It can complement the classical spectroscopic reasoning based essentially on the

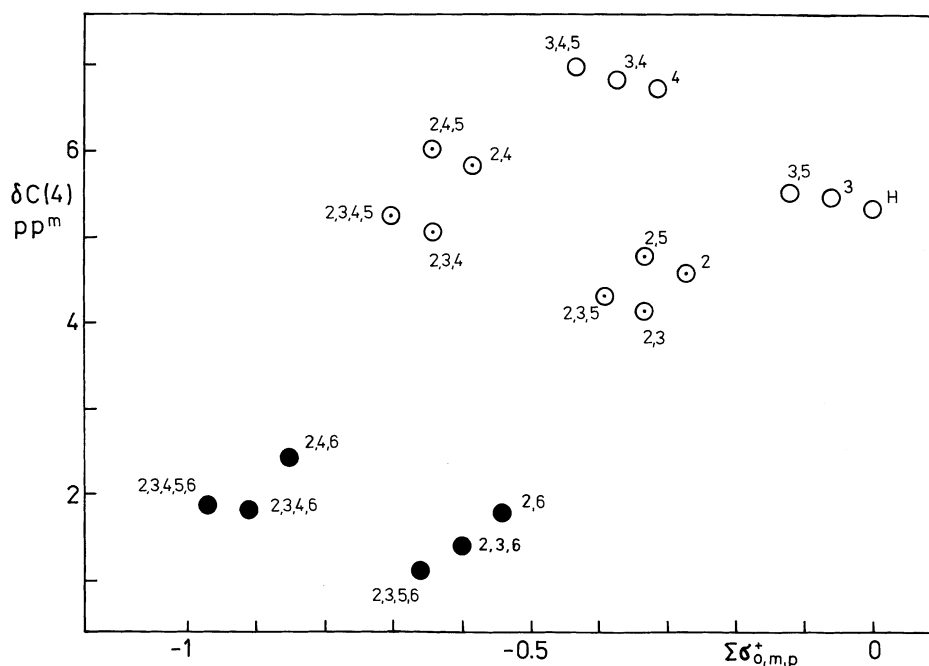


Figure 5. Plot of the corrected substituent-induced shifts of ^{13}C (4) in methyl-substituted benzoic acids (Ref.⁴) vs the sum of substituents constants σ^+ . Molecules with (○) no, (◐) one and (●) two *ortho* methyl groups

number of bands and their shifts with solvent or temperature. The necessary precondition is a sufficient number of structurally similar compounds.

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