Steric Effects and Steric Hindrance to Resonance in *tert*-Butylbenzoic Acids in the Gas Phase and in Solution

Jiří Kulhánek,[a] Michèle Decouzon,[b] Jean-François Gal,[b] Pierre-Charles Maria,[b] Pavel Fiedler,[c] Pilar Jiménez,[d] Maria-Victoria Roux,[d] and Otto Exner*[c]

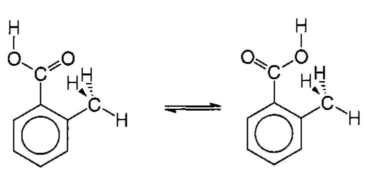
Keywords: Resonance / Hindered resonance / Steric hindrance / Conformation analysis

Substituent effects of the *tert*-butyl group in isomeric *tert*-butylbenzoic acids have been investigated on the basis of enthalpies of formation, gas-phase acidities, acidities in methanol and in dimethyl sulfoxide, and the IR spectra in tetrachloromethane. In contrast to 2-methylbenzoic acid, 2-*tert*-butylbenzoic acid must adopt a non-planar conformation, as is confirmed by its IR spectrum. Enhanced acidity in the gas phase has been found for all isomers and attributed to a pole-induced dipole interaction in the anion (polarizability effect); in the *ortho* isomer the steric inhibition of resonance is only responsible for a minor part of the observed effect. In solution, the electrostatic interaction is attenuated, but remains strong in the case of the *ortho* isomer.

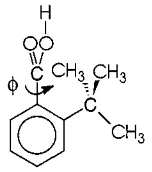
Introduction

We have previously investigated various types of steric effects in the model system of mono- and polymethylbenzoic acids.[1−5] Strong steric effects were observed even on the gas-phase acidities;[1,2] with the aid of enthalpies of formation[6] these could be separated into the effects in the acid molecule and those in the anion. The commonly accepted explanation[7] assumes a twisted non-planar conformation of the acid molecule, reducing the conjugation between the carboxy group and the benzene ring, the increased energy being manifested in an enhanced acidity. This explanation, refered to as "steric hindrance to resonance", was challenged by us because molecules of 2-methylbenzoic acid and of other benzoic acids bearing only one *ortho*-methyl group are not twisted; they exist as equilibrium mixtures of two planar conformations,[1,3] for instance **1A** ⇌ **1B**. Even in non-planar derivatives, the calculated steric hindrance to resonance represents only a minor part of the observed effect; the major contribution can be attributed to the electrostatic interaction in the anion[5] (pole-induced dipole interaction[8]). The classical interpretation, considering the hindered resonance as the main factor, was thus challenged, particularly since it attributes the gradually increasing steric effects in polymethylbenzoic acids to the increased torsion angle ϕ between the plane of the COOH group and the benzene ring[7] (see structure **2**). According to our results, this angle is close to zero in benzoic acids without *ortho* substituents or with just one *ortho*-methyl substituent.[1,3] In acids with two *ortho*-methyl groups it is close to 50° and does not vary significantly.[1,5]

The above results lead to the conclusion that the principle of steric inhibition of resonance should be used with caution; in every case the actual conformation of the molecule should be proven and the energy of the assumed resonance estimated, at least approximately. All the results were obtained on the model system of methyl-substituted benzoic acids, in which one methyl group exerts a relatively small steric effect. In the present paper, we extend this investigation to 2-, 3-, and 4-*tert*-butylbenzoic acids (formulae **2**, **3**, and **4**, respectively, see Table 1). The reasons for choosing the extremely bulky *tert*-butyl substituent were twofold. On the one hand, this substituent may force an a priori evident conformation and thus confirm the previous results on methyl derivatives, the conformations of which had to be determined for each compound. On the other hand, some additional steric effects may be observed that are not present in methyl derivatives. Thus, in 2-*tert*-butylbenzoic acid **2**, a coplanar conformation of the COOH group with the benzene ring is evidently impossible, the calculated[5a] angle ϕ being 50.2° (RHF, 6-31+G** basis). Hence, we intend to confirm here the conclusions outlined in the preceding paragraph, using **2** as a contrasting example to the planar molecule of **1**. We used the same techniques for measuring the gas-phase acidities,[1,2] the acidities in methanol and in dimethyl sulfoxide (DMSO),[4] and the IR spectra[3] as described previously. The gas-phase enthalpies of formation are known from a previous investigation.[9]



1A **1B**



2

---

[a] Department of Organic Chemistry, University of Pardubice,
CZ-53210 Pardubice, Czech Republic

[b] GRECFO, Chimie Physique Organique, Université de Nice-Sophia Antipolis,
F-06108 Nice Cedex 2, France

[c] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
CZ-16610 Praha 6, Czech Republic

[d] Instituto de Química-Física "Rocasolano", C.S.I.C.,
Serrano 119, E-28006 Madrid, Spain

1434−193X/99/0707−1589 $ 17.50+.50/0

Table 1. Physical properties of *tert*-butylbenzoic acids[a]

	Quantity	2-*tert*-butylbenzoic acid (**2**)	3-*tert*-butylbenzoic acid (**3**)	4-*tert*-butylbenzoic acid (**4**)
1	$\Delta_f H^\circ$(g) enthalpy of formation, ref.[9]	−376.1	−400.8	−398.5
2	$\Delta_1 H^\circ$(g) substituent effect in $\Delta_f H^\circ$(g)[b]	21.1	−3.6	−1.3
3	SE_4(g) steric effect in $\Delta_f H^\circ$(g)[b]	22.4	0	0
4	ΔG°_{acid}(g) gas-phase acidity	1377.8[c]	1389.5[d]	1392.7[e]
5	$\Delta_2 G^\circ$(g) substituent effect in ΔG°_{acid}(g)[b]	−14.5	−3.8	−0.6
6	$\Delta_2 H^\circ$(g) substituent effect in ΔH°_{acid}(g)[b]	−14.2	−3.8	−0.6
7	SE_6(g) steric effect in ΔH°_{acid}(g)[b]	−13.6	0	0
8	$\Delta_3 H^\circ$(g) subst. effect in $\Delta_f H^\circ$(g) of the anion[b]	6.9	−7.4	−1.9
9	SE_5(g) steric effect in $\Delta_f H^\circ$(g) of the anion[b]	8.8	0	0
10	pK(me) pK in methanol	8.83	9.50	9.59
11	$\Delta_2 G^\circ$(me) acidity in methanol[b]	−3.3	0.5	1.0
12	SE_8(me) steric effect in $\Delta_2 G^\circ$(me)[b]	−4.4	0	0
13	pK(DMSO) pK in dimethyl sulfoxide	10.82	11.05	11.25
14	$\Delta_2 G^\circ$(DMSO) acidity in dimethyl sulfoxide[b]	−1.0	0.3	1.4
15	SE_8(DMSO) steric effect in $\Delta_2 G^\circ$(DMSO)[b]	−2.4	0	0
16	ν(O−H) CCl_4 cm^{-1}	3520.5	3540.3	3541.4
17	$\Delta\nu_{1/2}$ [asymmetry factor AF] of the O−H band[f]	28.6 [0]	29.0 [0]	27.0 [0]
18	ν(C=O) (monomer) CCl_4 cm^{-1}	1748.5	1739.7	1738.4
19	$\Delta\nu_{1/2}$ [asymmetry factor AF] of the C=O band[f]	11.2 [5]	12.7 [1]	12.9 [−3][g]
20	β(COH) CCl_4 cm^{-1}	1319	1343	1344
21	γ(C−O) CCl_4 cm^{-1}	1188 1111	1167 1128	1176
22	ν(C=O) (dimer) CCl_4 cm^{-1}	1700	1695	1693

[a] 298 K, energies in kJ·mol^{-1}. − [b] These quantities are identified by a subscript corresponding to the number of the defining equation. − [c] **2** was found to be a stronger acid than the reference 4-trifluoromethylphenol [ΔG°_{acid}(g) = 1381 kJ·mol^{-1} according to ref.[13]] by −(3.25 ± 0.16) kJ·mol^{-1}. − [d] **3** was found to be a stronger acid than the reference 3-trifluoromethylphenol [ΔG°_{acid}(g) = 1391 kJ·mol^{-1} according to ref.[13]] by −(1.54 ± 0.41) kJ·mol^{-1}. − [e] **4** was found to be a weaker acid than the reference 3-trifluoromethylphenol by +(1.67 ± 0.15) kJ·mol^{-1}. − [f] The asymmetry factor AF is defined in ref.[3] − [g] The S-like shape of the band axis suggests interference from a small satellite band.

Steric hindrance in **2** has seldom been investigated.[10] Most physicochemical studies mention only pK values[11] or IR frequencies[12] of **4** within the framework of Hammett correlations.

Results and Discussion

Conformation

The conformations of the methyl-substituted benzoic acids were deduced from AM1 calculations,[1b] for some compounds from ab initio calculations,[5a] and in a few cases from X-ray data.[1,3] The most general and possibly most objective experimental proof can be obtained from infrared spectral data by means of a Hammett plot.[3] When the ν(C=O) wavelengths are plotted against the substituent constants σ, the points for the planar acids are situated close to a straight line and are controlled by the polar effect of the methyl groups. The points for the non-planar acids (bearing two *ortho*-methyl groups) deviate very strongly in the direction of higher wavelengths due to the inhibition of resonance. When we now plot the points for *tert*-butylbenzoic acids **2**−**4** (Table 1) on the same graph, Figure 1 is obtained. The points for **3** and **4** lie on the Hammett line, while that for **2** deviates by approximately the same distance as seen for the non-planar methylbenzoic acids. Since the non-planar conformation of **2** is a priori evident, Figure 1 should be considered merely as a confirmation of the previous approach rather than as a determination of the conformation of **2**. The value of ν(C=O) appears to be the quantity most sensitive to the inhibition of resonance. Ab initio calculations[5a] revealed that the angle ϕ is of the same order in **2** as that in 2,6-dimethylbenzoic acid for example (58.2° and 47.4°, respectively), but that the molecule of **2** is more deformed with C(1)−C(2) more stretched and the C_{ar}−C bonds displaced out of the ring plane. These deformations had no apparent influence on any further observations.

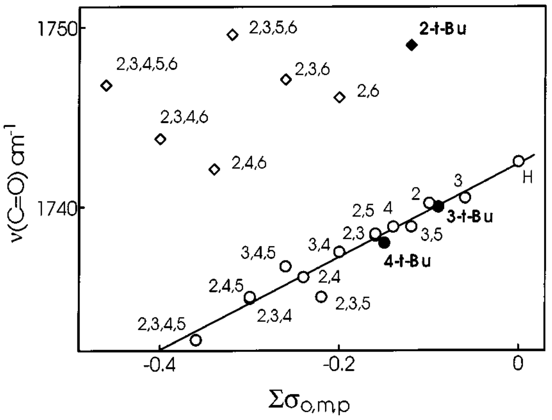


Figure 1. Hammett plot of the carbonyl stretching frequencies of substituted benzoic acids vs. the sum of substituent constants σ: ○ methyl and polymethyl derivatives (ref.[3]) without or with one *ortho*-methyl group, ◇ with two *ortho*-methyl groups; ● tert-butyl derivatives with no *ortho-tert*-butyl group, ◆ with one *ortho-tert*-butyl group; the position of substituents is given for each point; the regression line was determined for the methyl derivatives

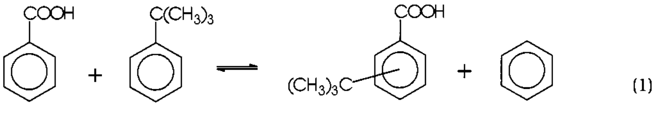
In constructing the above plot (Figure 1), there could be some problems in choosing a suitable value of σ_o for *tert*-butyl in an *ortho* position. Since the Hammett equation does not generally hold for *ortho* substituents, any such value might only be of restricted applicability: Ideally, it should be derived from spectral measurements in non-polar solvents. While we were able to find a suitable value for 2-methyl,[3] the only available value[14] for 2-*tert*-butyl, $\sigma_o = -0.08$, refers to the σ^- reactivity and is too small in absolute terms. In Figure 1, a value of $\sigma_o = -0.12$ has been used, estimated on the basis of σ_o for 2-methyl. It is important to note that the conclusion drawn from this plot does not rely on the accuracy of the σ values; one could even obtain a satisfactory graph by plotting ν(C=O) vs. the number of alkyl groups.

Similar graphs (not shown) were obtained by plotting the data for **2**−**4** in the plots ν(O−H) vs. σ (see Figure 3 of ref.[3]) or ν(C=O) monomer vs. ν(C=O) dimer (Figure 4 of ref.[3]). In all cases, 2-*tert*-butylbenzoic acid may be grouped together with 2,6-dimethylbenzoic acids. Remarkably, the amount of dimer decreases in the order **4** > **3** > **2**, so that a slight steric hindrance needs to be taken into consideration, even in the *meta* position. Such a steric effect from the *meta* position was observed in the gas phase, but was strongly attenuated in solution.[2]

The conformation of **2** can also be estimated on the basis of the asymmetry factor[3] *AF* of ν(O−H) (Table 1, line 17). The zero values obtained are consistent with the non-planar conformation of **2**, as well as with the planar symmetrical conformation of **4**, and with an equilibrium of two almost identical conformations in the case of **3**. A non-zero value would be expected only in the case of an equilibrium between markedly different forms, as in **1A** ⇌ **1B**. The *AF* of ν(C=O) is less reliable, as was found previously (Table 1, line 19).

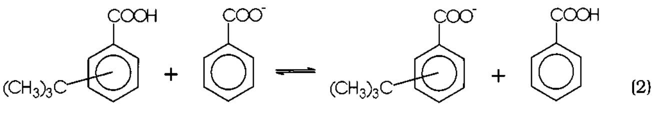
Substituent Effects in the Gas Phase

The substituent effect of the *tert*-butyl group on the carboxy group (or vice versa) can be expressed in terms of the reaction enthalpy, $\Delta_1H°$, of the isodesmic reaction according to Equation 1.[1]



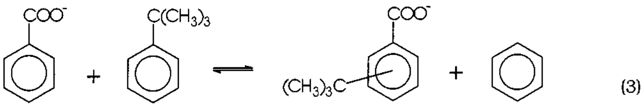
(1)

The values of $\Delta_1H°$ were calculated from the enthalpies of formation,[9,15] $\Delta_fH°$, and are given in Table 1, line 2. The substituent effect can also be estimated independently from the gas-phase acidities. Relative values of these acidities relate to proton transfer from the substituted to the unsubstituted acid in an isodesmic reaction as shown in Equation 2.



(2)

Our experimental values of $\Delta_2H°$ for this reaction are given in Table 1, line 6. By summation of Equation 1 and Equation 2 we obtain Equation 3, which expresses the substituent effect in the anion. The values of $\Delta_3H°$ are given in Table 1, line 8.



(3)

All the isodesmic reactions have previously been formulated for methyl-substituted benzoic acids;[1] here they are merely extended to *tert*-butyl derivatives. Evidently, the three measures of the substituent effect, in the acid molecule ($\Delta_1H°$), in its anion ($\Delta_3H°$), and on the acidity ($\Delta_2H°$) are not equal; they are roughly parallel for **3** and **4**, but not for **2**. Classically, this may be interpreted in terms of different contributions of inductive (and/or hyperconjugation) effects in all the isomers, with steric effects only being important in **2**. Previously, an approximate correlation between $\Delta_1H°$(g) and $\Delta_2H°$(g) was found for twenty polymethyl-substituted benzoic acids,[1b] with some expected and some unexpected deviations (see Figure 2). When we plot the three *tert*-butylbenzoic acids in the same graph, we observe systematic deviations in the direction of stronger acidities, increasing in the sequence *para* < *meta* < *ortho*. In terms of the enthalpies of formation ($\Delta_1H°$, Figure 2, *x* axis), the *tert*-butyl acids **3** and **4** are much less stabilized than the corresponding methyl acids: compare the values (in kJ·mol^{-1}) −3.6 and −1.3 in Table 1, line 2, with −6.7 and −9.3 for the methyl acids. While the stabilization itself is evidently due to interaction through the benzene ring (possible "hyperconjugation"), its reduction in **3** and **4** must be classified as steric hindrance. Steric interaction between more distant groups has been observed in isolated molecules in the gas phase[1,2] and cannot be rationalized in

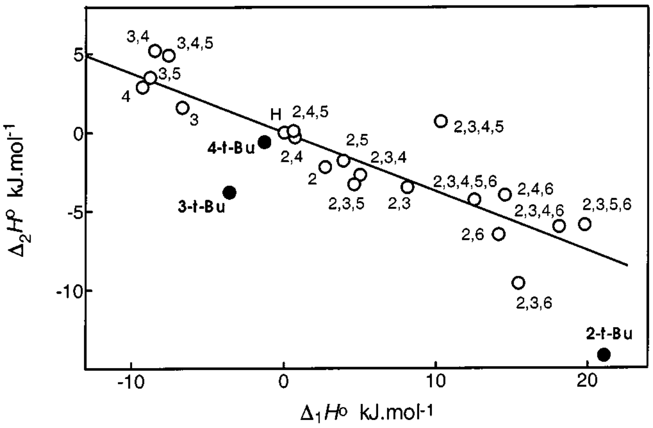


Figure 2. Plot of the cumulative substituent effects in substituted benzoic acids: *x* axis, substituent effect on the enthalpy of formation, $\Delta_1H°$(g), Equation 1; *y* axis, substituent effect on the gas-phase acidity, $\Delta_2H°$(g), Equation 2; ○ methyl derivatives (ref.[1b]), ● *tert*-butyl derivatives; the regression line was determined for the methyl derivatives

terms of Stuart−Briegleb models. Of course, the presence of steric hindrance in **2** is beyond doubt. In the acidities (Equation 2 and Figure 2, *y* axis), the same kind of deviation is even more apparent, making **3** and **4** even stronger acids than benzoic acid, while the corresponding methyl derivatives are weaker. Of course, **2** is still much stronger. Similar effects have generally been explained in terms of polarizability or, more precisely, pole-induced dipole interactions in the anion.[5,8] The strong effect even in the *meta* position is remarkable. The net overall effects of the *tert*-butyl group may thus be weaker or even reversed compared to those due to the methyl group. The slightly enhanced effects seen in the values of the standard constants σ[16] are based mainly on p*K* values in aqueous solvents; they were tested only in solution and are essentially due to steric hindrance of solvation.[17]

Separation of Polar and Steric Effects

The main reason for the somewhat irregular pattern of substituent effects (see the scatter in Figure 2) lies in the combination of polar effects present in all positions and steric effects predicted mainly for the *ortho* position. We have previously attempted a simple separation of these factors,[1,4] assuming that polar effects are equal in the *ortho* and *para* positions, and that steric effects are negligible in the *meta* and *para* positions. In spite of its simplicity, this separation yielded reasonable results, at least for the weakly polar methyl group[1,4] (steric effects at the *meta* position are not necessarily zero in the gas phase, but are certainly negligible in polar solution[2]). In the case of a single *ortho* group in **2**, the steric effect *SE* is defined as the simple difference between the *ortho* and *para* positions, i.e. Equation 4 for an acid molecule or Equation 5 for the anion. The steric effect on acidity, SE_6, is then given by the difference in the relative acidities, Equation 6.

$$SE_4 = \Delta_1H°(ortho) - \Delta_1H°(para) = \Delta_fH°(ortho) - \Delta_fH°(para) \quad (4)$$

$$SE_5 = \Delta_3H°(ortho) - \Delta_3H°(para) \quad (5)$$

$$SE_6 = \Delta_2H°(ortho) - \Delta_2H°(para) \quad (6)$$

The values of SE_4, SE_5, and SE_6 for 2-*tert*-butylbenzoic acid are given in Table 1, lines 3, 9, and 7, respectively. The data are best interpreted by comparison with those for the methyl-substituted benzoic acids. When we plotted the steric effects in their anions (SE_5) vs. the steric effects in the acids (SE_4), we obtained the pattern shown in Figure 3.[5] The straight lines with slopes of unity indicate that the actual steric effects (van der Waals interactions) are equal in the acid molecule and in the anion: The geometries of the COOH and COO$^-$ groups are very similar. The greater stability of the anions bearing *ortho*-methyl groups could be explained in terms of pole-induced dipole interactions.[5,8] This was found to be twofold higher for two *ortho*-methyl groups than for one *ortho*-methyl group. Very approximately, it can be expressed by the electrostatic equation,[8] which, in its corrected form, can be written as Equation 7.[5]

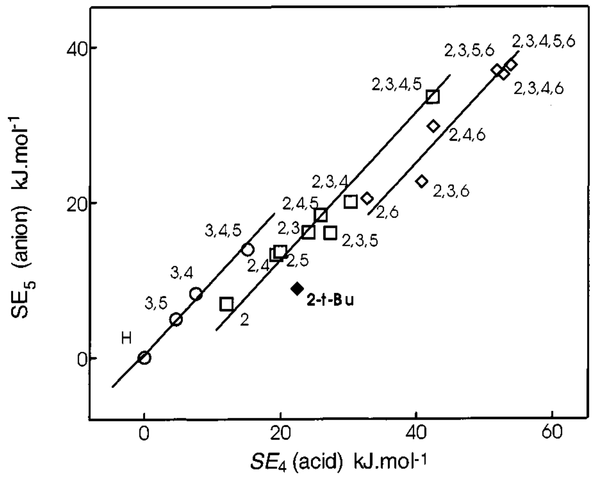


Figure 3. Dependence of steric effects in substituted benzoic acids (SE_4, Equation 4) and in their anions (SE_5, Equation 5) in the gas phase: ○ methyl and polymethyl derivatives (ref.[1b]) with no *ortho*-methyl groups, □ with one *ortho*-methyl group, ◇ with two *ortho*-methyl groups; ◆ 2-*tert*-butylbenzoic acid; the straight lines have slopes of unity

$$\Delta E = -\alpha q^2/32\pi^2\varepsilon_o{}^2\varepsilon_{ef}{}^2r^4 \quad (7)$$

This expression is very sensitive to the distance *r* as well as to the effective relative permittivity ε_{ef}: The polarizability α can be obtained from molar refraction measurements.[18] Figure 3 does not reveal any particular position of the non-planar 2,6-dimethyl derivatives, hence the steric inhibition of resonance should be approximately equal in the anion and in the acid molecule. This was corroborated by calculations.[5a]

When we plot the values for 2-*tert*-butylbenzoic acid on this graph (Figure 3), this compound is found to be grouped with the non-planar derivatives. The pole-induced dipole interaction of a *tert*-butyl group appears to be approximately equal to that of two methyl groups. This is qualitatively in accord with the electrostatic expression, Equation 7. The polarizability α of *tert*-butyl is about three times larger[18] than that for methyl, but the distance *r*, to which the result is particularly sensitive, is somewhat longer; the effective relative permittivity ε_{ef} should be little changed.

Recently, we estimated the contribution of hindered resonance in the molecule of 2,6-dimethylbenzoic acid as 18 kJ·mol^{-1},[5] representing a half of the overall steric effect. Since the total steric effect in **2** is only 22.4 kJ·mol^{-1}, the hindrance to resonance in this molecule is probably smaller.

Acidities in Solution

The relative acidities, compared to that of benzoic acid, are expressed by the isodesmic reaction according to Equation 2. For practical reasons, we previously compared the gas-phase acidities as $\Delta_2H°$, and the acidities in solution as $\Delta_2G°$.[4] Figure 4 relates to solutions in methanol. Methylbenzoic acids without *ortho* substituents produce a straight line; substituent effects are regularly attenuated in solution. Methylbenzoic acids with one *ortho*-methyl group show a moderate deviation, while non-planar derivatives with two *ortho*-methyl groups deviate strongly. This was explained in terms of better solvation of a non-planar carboxy group,[4,19] making the acids stronger. When we include *tert*-butyl derivatives in this plot, they reveal the polarization effects in the gas phase but not in solution. The *meta*- and *para*-*tert*-butylbenzoic acids are as strongly acidic in methanol as the corresponding methylbenzoic acids, while in the gas phase they are even stronger. In this way, the common values[16] of the constants σ can be explained. The non-planar acid **2** is very strong in the gas phase, but not so strong in solution; better solvation of a non-planar COOH group is compensated by steric hindrance to solvation due to the bulky *tert*-butyl group.

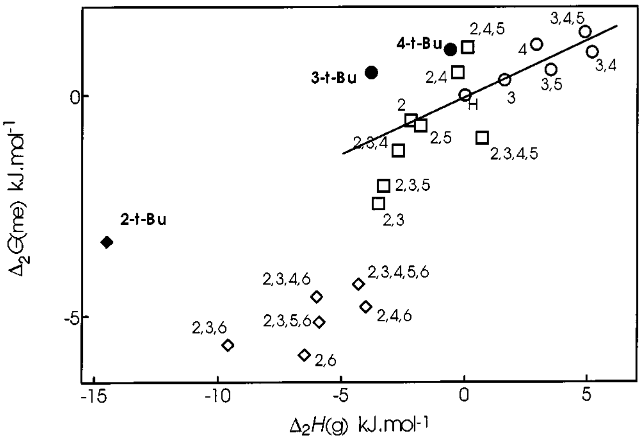


Figure 4. Plot of the acidities of substituted benzoic acids $\Delta_2H°$ (Equation 2), *x* axis in the gas phase, *y* axis in methanol: ○ methyl and polymethyl derivatives (refs.[1b,4]) with no *ortho*-methyl groups, □ with one *ortho*-methyl group, : with two *ortho*-methyl groups; ◆ 2-*tert*-butylbenzoic acid, ● *tert*-butyl derivatives with no *ortho-tert*-butyl group; the regression line was determined for the first group

Separation of the steric effect is also possible in solution: Instead of Equation 6 we use the same expression in terms of $\Delta G°_{acid}$ (Equation 8).

$$SE_8 = \Delta G°_{acid}(ortho) - \Delta G°_{acid}(para) \tag{8}$$

On plotting the steric effects in solution, SE_8, vs. those in the gas phase, SE_6, (Figure 5), we obtained separate groups of methyl-substituted benzoic acids.[4] Within each group, the smaller effects of the more remote substituent were observable in the gas phase, but this trend was not seen in solution. One can envisage the solvent penetrating between the more remote groups, or one can explain this fact in terms of Equation 7 by invoking a higher value of ε_{ef}. The acid **2** behaves similarly. Whereas in the gas phase the steric effect of one *tert*-butyl group is larger than that of the two methyl groups in 2,6-dimethylbenzoic acid, in methanol it is attenuated to a value similar to that found in 2,3-dimethylbenzoic acid.

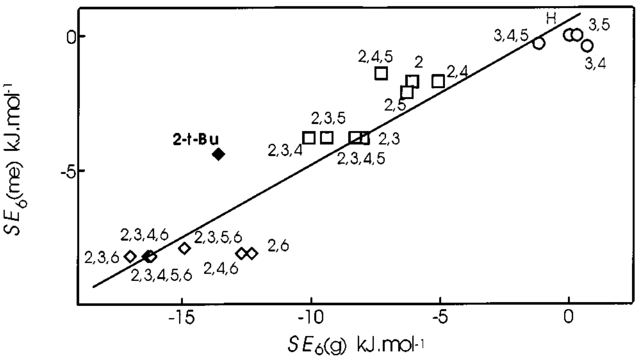


Figure 5. Plot of the steric component SE_5 (Equation 5) influencing the acidity of substituted benzoic acids, *x* axis in the gas phase, *y* axis in methanol: the points are denoted as in Figure 4

In DMSO, the dependence of $\Delta_2G°$(DMSO) and $\Delta_2H°$(g) (not shown) is found to be similar as that depicted in Figure 4, but with a higher degree of scatter; the dependence of SE_8(DMSO) and SE_6(g) is similar to that shown in Figure 5, with the deviation of **2** being even more marked. In all cases, the plots of steric effects are more significant and easier to understand than plots of the unresolved quantities, $\Delta_2G°$(solvent) vs. $\Delta_2H°$(g). This confirms once more the physical meaning of the simple separation of steric and polar effects as given by Equation 4−6.

Conclusions

In our model system of *tert*-butylbenzoic acids, the *tert*-butyl group has constituted an extremely bulky substituent with axial symmetry that exerts strong steric effects. All effects observed previously with methyl-substituted benzoic acids have been observed with higher intensity, particularly electrostatic interaction in the ions, and thus demonstrate more convincingly the steric inhibition of resonance and the attenuation of these effects in solution. In addition, interaction between distant groups in neutral molecules has been detected in the gas phase, which is not observable with smaller substituents.

Experimental Section

tert-Butylbenzoic acids **2**−**4** (Table 1) have been described previously.[9]

The gas-phase acidities were determined by Fourier-Transform Ion Cyclotron Resonance (FTICR) as described previously.[1] In previous studies, we used 3-trifluoromethylphenol as a reference acid for all measurements, with the aim of obtaining strictly comparable results; precise referencing on the acidity scale was of less importance for our purposes. In the present work, this reference compound could only be used with 3- and 4-*tert*-butylbenzoic acids; for 2-*tert*-butylbenzoic acid it was too weakly acidic and had to be replaced by the isomer 4-trifluoromethylphenol. The difference in $\Delta G°_{acid}$ values between the two isomers was determined as 10.0 kJ·mol^{-1}.[13] Values of $\Delta G°_{acid}$ were converted into $\Delta H°_{acid}$ as previously,[1] taking into account only the symmetrical part of the entropy. The final results are given in Table 1, lines 4−6, with the primary measurements of the relative acidities in footnotes[c−e].

The pK values in methanol and DMSO were measured potentiometrically with a glass electrode.[4] The results were referenced to standard values for benzoic acid and are thus strictly comparable with previous data.[4] The pK values are given in Table 1, lines 10 and 13.

Infrared absorption spectra were recorded in tetrachloromethane as described previously,[3] at concentrations of 0.00012 $\text{mol}\cdot\text{L}^{-1}$; the data can be compared directly with previous measurements made at 0.0006 $\text{mol}\cdot\text{L}^{-1}$ (O−H) or 0.00012 $\text{mol}\cdot\text{L}^{-1}$ (C=O).[3] Wavenumbers assigned to the carboxy group are given in Table 1, lines 16−22. Asymmetry of the ν(C=O) and ν(O−H) bands was expressed by the asymmetry factor AF as defined previously[3] (lines 17 and 19). The other suggested measure of asymmetry,[3] i.e. the angle α, is less suitable for comparing compounds more different in their structure since it depends on the band intensity.

Acknowledgments

The support of the Grant Agency of the Czech Republic, grant No. 203/99/1454 (to P. F. and O. E.) and of the Conseil Général des Alpes Maritimes (to M. D., J.-F. G. and P.-C. M.) is gratefully acknowledged.

---

[1] [1a] M. Decouzon, P. Ertl, O. Exner, J.-F. Gal, P.-C. Maria, *J. Am. Chem. Soc.* **1993**, *115*, 12071. − [1b] M. Decouzon, J.-F. Gal, P.-C. Maria, S. Bõhm, P. Jiménez, M. V. Roux, O. Exner, *New J. Chem.* **1997**, *21*, 561.

[2] M. Decouzon, O. Exner, J.-F. Gal, P.-C. Maria, *J. Chem. Soc., Perkin Trans. 2* **1996**, 475.

[3] P. Fiedler, O. Exner, *J. Phys. Org. Chem.* **1998**, *11*, 141.

[4] J. Kulhánek, O. Exner, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1397.

[5] [5a] S. Böhm, O. Exner, unpublished results. − [5b] O. Exner, *Chem. Listy* **1998**, *92*, 235.

[6] [6a] M. Colomina, P. Jiménez, M. V. Roux, C. Turrión, *An. Quím.* **1986**, *82*, 126. − [6b] M. Colomina, P. Jiménez, M. V. Roux, C. Turrión, *J. Chem. Thermodyn.* **1984**, *16*, 1121; **1987**, *19*, 1139. − [6c] M. Colomina, P. Jiménez, R. Pérez-Ossorio, M. V. Roux, C. Turrión, *J. Chem. Thermodyn.* **1988**, *20*, 575.

[7] [7a] A. L. Baumstark, P. Balakrishnan, M. Dotrong, C. J. McCloskey, M. G. Oakley, D. W. Boykin, *J. Am. Chem. Soc.* **1987**, *109*, 1059. − [7b] J. Guilleme, E. Diez, F. J. Bermejo, *Magn. Reson. Chem.* **1985**, *23*, 449. − [7c] J. M. Wilson, N. E. Gore, J. E. Sawbridge, F. Cardenas-Cruz, *J. Chem. Soc.* **1967**, 852. − [7d] M. Charton, *Prog. Phys. Org. Chem.* **1987**, *16*, 287. − [7e] D. Leibfritz, *Chem. Ber.* **1975**, *108*, 3014. − [7f] A. U. Acuña, A. Ceballos, M. J. Molera, *J. Phys. Chem.* **1977**, *81*, 1090. − [7g] G. S. Hammond, in *Steric Effects in Organic Chemistry* (Ed.: M. S. Newman), John Wiley & Sons, New York, **1956**, p. 425.

[8] T. B. MacMahon, P. Kebarle, *J. Am. Chem. Soc.* **1977**, *99*, 2222.

[9] M. Colomina, P. Jiménez, R. Pérez-Ossorio, C. Turrión, *J. Chem. Thermodyn.* **1979**, *11*, 1179.

[10] [10a] M. Hojo, M. Utaka, A. Yoshida, *Tetrahedron* **1971**, *27*, 5433. − [10b] P. O. Hansen, A. Berg, K. Schaumburg, *Magn. Reson. Chem.* **1987**, *25*, 508.

[11] [11a] L. L. McCoy, E. E. Riecke, *J. Am. Chem. Soc.* **1973**, *95*, 7407. − [11b] F. Van Meurs, A. J. Hoefnagel, B. M. Wepster, H. Van Bekkum, *J. Organomet. Chem.* **1977**, *142*, 299. − [11c] M. Ludwig, V. Baron, K. Kalfus, O. Pytela, M. Večeřa, *Coll. Czech. Chem. Commun.* **1986**, *51*, 2135. − [11d] A. J. Hoefnagel, B. M. Wepster, *J. Chem. Soc., Perkin Trans. 2* **1989**, 977.

[12] [12a] C. Laurence, B. Wojtkowiak, *Bull. Soc. Chim. Fr.* **1971**, 3124. − [12b] R. A. Nyquist, T. D. Clark, *Vibr. Spectrosc.* **1995**, *8*, 387.

[13] NIST Standard Reference Database 69 − March 1998 Release, *NIST Chemistry Webbook*.

[14] M. T. Tribble, J. G. Traynham, *J. Am. Chem. Soc.* **1969**, *91*, 379.

[15] M. Bureš, R. Holub, J. Leitner, P. Voňka, *Thermochemické veličiny organických sloučenin [Thermochemical Quantities of Organic Compounds]*, Institute of Chemical Technology, Prague, **1987**.

[16] O. Exner in *Correlation Analysis in Chemistry − Recent Advances* (Eds.: N. B. Chapman, J. Shorter), Plenum Press, New York, **1978**, p. 439.

[17] O. Exner, S. Böhm, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1235.

[18] A. I. Vogel, *J. Chem. Soc.* **1948**, 1833.

[19] J. Kulhánek, O. Pytela, *Coll. Czech. Chem. Commun.* **1997**, *62*, 913.

[O98563]