Steric effects and steric inhibition of resonance: structure and ionization of 2-*tert*-butylbenzoic acid

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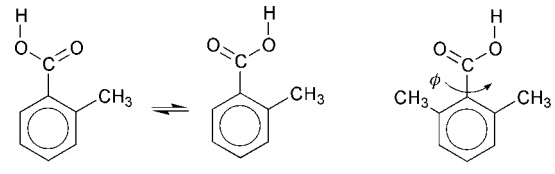
Enhanced acidity of sterically hindered carboxylic acids has been explained by steric inhibition to resonance (SIR) and van der Waals (vdW) tension. These two terms have been quantitatively evaluated on a model comparing two isomers, 2-*tert*-butylbenzoic acid (**3**) and 4-*tert*-butylbenzoic acid (**4**). Energies and geometries of **3** and **4** and their anions have been calculated using the B3LYP model at a 6-31+G(d,p) or 6-311+G(3df,2pd) basis, both in minimum-energy conformations and with a constrained dihedral angle ϕ between the ring plane and carboxyl plane. From comparison of the two isomers it follows that SIR contributes significantly to the higher energy of **3**, but also raises similarly the energy of its anion **3A**. Stronger acidity of **3** compared to **4** (both in the gas phase and in solution) cannot be explained by SIR and must be attributed to a stabilizing interaction in the anion **3A**; approximately it might be modelled as a pole/induced dipole interaction. The explanation by SIR must be used with more caution, particularly for solution acidities.

Introduction

Classic concepts of resonance, steric effect and steric inhibition of resonance (SIR) have been widely used when interpreting reactivities of crowded conjugated molecules,[1] particularly the acidities of carboxylic acids. Typical model compounds have been aromatic *ortho* derivatives: alkyl groups were used as substituents with defined steric effects and negligible polarity. For instance, the acidity of benzoic acid, only slightly stronger than that of aliphatic acids, has been interpreted by antagonistic action of the inductive effect on the one hand and of resonance of the carboxyl group with the benzene ring on the other.[2] The stronger acidity of 2-methylbenzoic acid (1) and 2,6-dimethylbenzoic acid (2) has been explained by SIR.[2,3]

The weakness of this reasoning is in attributing changes of the acid strength only to the energy of the acid molecule and neglecting the structure of the anion and its energy. Explanations referring to the resonance in the acid molecule assume tacitly that resonance in the anion is negligible or at least much weaker. While resonance can be calculated only with many problems with its exact definition, its inhibition (SIR) can be tested in a simple way. It must meet the condition that the conformation of a molecule with SIR is non-planar while that of the reference compound without SIR (in our case benzoic acid) is planar. We investigated along these lines mono- and poly-methylbenzoic acids,[4,5] mono-*tert*-butylbenzoic acids,[6] monoisopropylbenzoic acids[7] and mono- and bis-methoxybenzoic acids.[8] In these studies, the energies of the acid molecules and of their anions were evaluated separately in terms of isodesmic reactions[9] on the basis of either experimental enthalpies of formation or of calculated energies. It turned out that SIR does not exist in all molecules in which it has been assumed[3,10] since in some of them the functional group is coplanar with the benzene ring. For instance, 2-methylbenzoic acid and some polymethylbenzoic acids with only one *ortho* methyl group exist in an equilibrium involving two planar conformations[4,11] as in **1a** ⇄ **1b**, at variance with both older[2,3] and more recent[10] reports. On the other hand, 2,6-dimethylbenzoic (**2**) and higher methylated benzoic acids are in non-planar conformations. Even in the non-planar molecules SIR may comprise only a lesser part of the observable effect on the acidity as follows from calculations on fixed conformations:[5] SIR is of similar magnitude in the acid molecule and in the anion and the so-called "steric" effect on acidity is better explained in terms of pole/induced dipole interaction.[5,12] 2-*tert*-Butylbenzoic acid (**3**, Scheme 1) was included into our investigations[6] as an example of a molecule which may *a priori* be assumed as non-planar; besides its conformation was confirmed by correlations of its ν(C=O) vibrational frequency.[6] Note that all results were obtained by calculations on isolated molecules or from gas-phase experiments. They are thus directly comparable to any theoretical concept developed likewise for isolated molecules. Solvent effects were evaluated (not explained) by comparison with solvent acidities.[4a,e,6,7]



1a **1b** **1c**

In this paper we return once more to 2-*tert*-butylbenzoic acid (**3**) and use it as a model for separating and classifying various kinds of "steric" effects: previous experimental study[6] was now completed by calculations. Our purpose was twofold. First, we wanted to quantitatively estimate SIR and other effects by the same method as applied previously[5] to compounds **1** and **2**: it is based on fixed conformations with a constrained angle ϕ and on comparison of **3** with the isomeric 4-*tert*-butylbenzoic acid (**4**, Scheme 1). In particular, the effect of SIR on the acidity is not *a priori* evident since it may be present also in the anion. Secondly, the *tert*-butyl group in **3**

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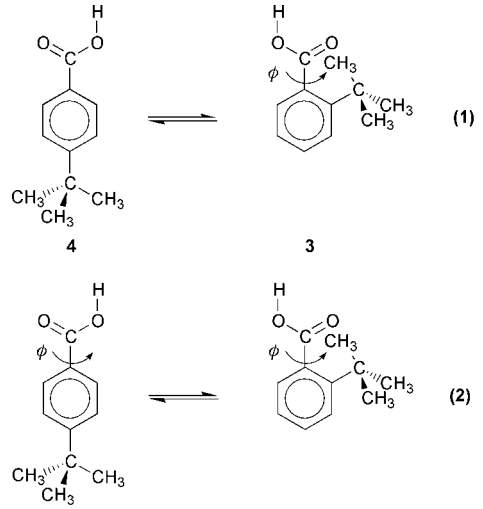


Scheme 1

may appear as too bulky and produce not only rotation of the CO_2H group but also further deformations. This effect was observed when the *tert*-butyl group was used for fixing the conformation of cyclohexane derivatives.[13]

In previous calculations we determined the geometry at an RHF (restricted Hartree–Fock) level: subsequent single-point DFT calculations, even using a very large basis, did not improve the results.[5] In this paper we deal with molecules with a strong steric hindrance, hence we have preferred geometry optimization at the DFT level.

Calculations

The B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) and B3LYP/6-311+G(3df,2pd)// B3LYP/6-31+G(d,p) calculations were performed according to the original proposal[14] exploiting the GAUSSIAN 94 program.[15] When calculating molecules in their minimum-energy conformations full geometry optimization was carried out using redundant internal coordinates. Vibrational analysis was carried out in all such cases: all structures belonged to the energy minimum. Calculations of enthalpies of atomization, $\Delta_a H^\circ_{298}$, by statistical thermodynamics proceeded according to the same program.[15]

In the case of conformations with frozen rotation (a fixed torsion angle ϕ) all remaining geometry parameters were optimized using internal coordinates.

The calculated energies are listed in Table 1, some important geometrical parameters in Table 2.

Results and discussion

Conformation and geometry

Table 1 reveals that the minimum-energy conformation of compound **3** is nonplanar with $\phi = 45°$, although the rotational barrier (*vs.* $\phi = 0°$) is only 4.1 kJ mol^{-1}. This is lower than for instance for **2** (6.7 kJ mol^{-1}, ref. 5). From the common feeling or from space-filling models, one would guess that the *tert*-butyl group is so bulky that it must enforce nonplanarity. This idea is not so obvious as it appears. Our previous experimental proofs[6] were based on empirical relationships of ν(C=O) vibrational frequencies with the substituent parameters σ: the correlations were not sensitive to

Table 1 Calculated energies of *tert*-butylbenzoic acids **3** and **4**

Molecule	DFT energy at the fixed dihedral angle ϕ[a]				
	0°	45°	70°	90°	180°
3 2-*tert*-Butylbenzoic acid	−578.106 777 6	**−578.108 353 5** (**−578.270 096 2**)[b]	−578.107 166 9	−578.104 901 5	−578.103 005 8
4 4-*tert*-Butylbenzoic acid	**−578.124 539 3** (**−578.285 917 8**)[b]	−578.119 367 2	−578.114 512 6	−578.112 901 4	[c]
	0°	35°	66°	90°	180°
3A 2-*tert*-Butylbenzoate anion	−577.557 741 4	−577.560 345 8	**−577.562 202 2**	−577.561 854 6	[c]
4A 4-*tert*-Butylbenzoate anion	**−577.571 353 0**	−577.569 124 0	−577.565 533 5	−577.564 385 6	[c]

[a] In au, at the B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level unless otherwise noted; the lowest energies for each species are printed in bold. [b] At the B3LYP/6-311+G(3df,2pd)//B3LYP/6-31+G(d,p) level. [c] Equal to that at $\phi = 0°$.

Table 2 Some calculated geometrical parameters of *tert*-butylbenzoic acids **3**, **4** and their anions **3A**, **4A**[a]

	3	**4**	**3A**	**4A**
C1–C2	**1.424**	1.399 1.403	**1.422**	1.398 1.402
C1–C(O)	**1.497**	1.484	1.547	1.551
C_{ar}–C_{al}	**1.552**	1.539	**1.551**	1.542
C=O	1.216	1.218	1.257	1.260
C–O	1.361	1.361	1.261	1.260
O–C=O	120.9	121.5	128.9	129.2
O=C–C	**127.1**	125.2	116.2 114.9	115.4
C(O)–C–C	**125.4**	118.6 122.4	**126.6**	121.2 121.3
C_{al}–C–C	**125.1**	122.8	123.1	123.1
In-plane deformation	**10.5**	1.4	**9.7**	4.3
C(O)–C–C–C_{al}	**7.1**	—	0.3	—
ϕ = O–C–C–C	**45.2**	0	**65.0**	0

[a] At the B3LYP/6-31+G(d,p) level; bond lengths in Å, angles in degrees; parameters appreciably deformed by steric effects are printed in bold.

the values of σ. In all cases they were referenced to a set of methyl-substituted benzoic acids whose conformation was determined by several methods: **3** ranged always into the subset of non-planar molecules. With respect to the low rotational barrier, it is even understandable, based on $^2J(^{13}C{=}O, ^{13}C)$ coupling constants, that the molecule of **3** is not twisted.[16] It follows that simple estimations of the lowest-energy conformation based on the presence of bulky groups are not quite reliable: even the *tert*-butyl group need not be sufficient.

On the other hand the presence of the *tert*-butyl group in compound **3** causes structure deformations which are not present in the planar molecule **1** nor in the non-planar molecule **2**. We have drawn attention[4d,11] to the somewhat surprising stretching of the C1–C2 bond in **1**: within the framework of common conformation analysis or of the Dreiding models one would predict merely distortion of a dihedral angle rather than a significant stretching of a bond. This stretching is still greater in **3** than in **1**. A second important relief of steric strain in **1** was the in-plane deformation of bond angles.[11] It can be defined as the sum of angles C1–C2–C_{a1} and C2–C1–C(O) minus 240° and is 5.3° in **1**[4d] but 10.5° in **3**. A third possible relief is out-of-plane deformation defined as the dihedral angle C(O)–C1–C2–C_{a1}; it was virtually absent in **1**[11] but is 9.4° in **3**. In the anion **3A** essentially the same deformations are observed as in **3** except the out-of-plane deformation which is reduced to 2.8°. The torsion angle ϕ is larger but the energy minimum is more flat: the rotational barrier in the direction toward $\phi = 90°$ is only 0.9 kJ mol^{-1}. In conclusion, deformations caused by the *tert*-butyl group are significant, much greater than in molecule **2** with a similar distortion of planarity. However, these deformations can have only a minute effect on acidity since they are similar even in the anion.

Comparison with experimental results

Possibilities of checking our results by comparing with experimental results are restricted. The difference in the total energies of compounds **3** and **4** represents the enthalpy of the isomerization reaction, eqn. (1), Scheme 1. Since eqn. (1) is isodesmic,[9] even also homodesmotic,[17] a reasonable agreement with the reaction enthalpy ΔH°_{298} may be expected.[9b] The latter was derived from the experimental[18] enthalpies of formation $\Delta_f H^\circ_{298}$. The disagreement (footnote b to Table 3) is considerable, exceeding the experimental uncertainty in $\Delta_f H^\circ_{298}$, estimated[18] to be 1.4 kJ mol^{-1} for one compound. It is not improved in the calculations using a larger basis, nor by calculating the reaction enthalpy $\delta\Delta H^\circ_{298}$. A second possible test is comparing energy differences between the acid and its anion with the experimental gas-phase acidities.[6] Comparison of relative values is preferable to eliminate the uncertain contribution of the enthalpy of the free proton.[19] In this case the agreement is much better (footnote c to Table 3) and completely sufficient for further calculations. However, it also exceeds the experimental uncertainty, estimated[6] to be 0.15 kJ mol^{-1} for one compound. As previously with methylbenzoic acids,[5] we also decided here to base further conclusions only on calculated energies and not to correct them on an experimental basis.

Table 3 Calculated steric effects in 2-*tert*-butylbenzoic acid **3** and during its ionization (kJ mol^{-1})[a]

	Total steric effect	SIR	vdW
Acid	42.5[b]	13.6	28.9
Anion	24.0	15.3	8.7
Acidity	−18.5[c]	1.7	−20.2
Acidity in water[d]	−4.45	∼0	−4.4
Acidity in methanol[d]	−4.4	∼0	−4.4

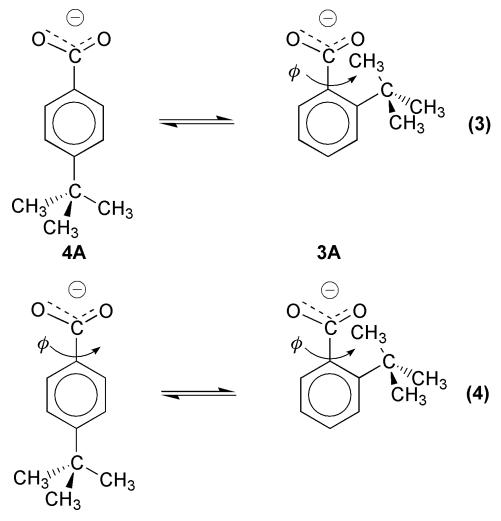
[a] At the B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level. [b] Calculated at a B3LYP/6-311+G(3df,2,pd)//B3LYP/6-31+G(d,p) level as 41.5 kJ mol^{-1}, with a correction from statistical thermodynamics calculated as $\delta\Delta H^\circ_{298}$ 42.7 or 41.7 kJ mol^{-1} at the two levels; experimental value from the enthalpies of formation $\delta\Delta H^\circ_{298}$ 22.4 kJ mol^{-1}, ref. 6. [c] Experimental value of $\delta\Delta H^\circ_{298}$ −14.9 kJ mol^{-1}, ref. 6. [d] Based on pK values in water from ref. 21 and in methanol from ref. 6.

Separation of steric and polar effects

A simple separation attempted in our previous work[4] assumes that polar effects are equal in the positions *ortho* and *para*, and steric effects are negligible in the positions *meta* and *para*. These simple assumptions may be criticized: for instance the relation between *ortho* and *para* isomers was analysed in detail.[20] Nevertheless, our separation yielded reasonable results at least for the weakly polar alkyl groups.[4–7] In the case of the *tert*-butyl group the assumption of zero steric effects in the *meta* position was not exact but comparison of *ortho* and *para* derivatives was possible.[6]

According to the above assumption, steric effects in compound **3** are defined as the enthalpy, $\Delta_1 H^\circ$, of the isomerization reaction, eqn. (1) (Scheme 1), in which the two molecules are in their real, minimum-energy conformations. Separation of the steric effects into tentative components is now based on fixed conformations. Eqn. (2) lies at the heart of the analysis. In this, both molecules are in the same conformation with equal angles ϕ; therefore no SIR is possible. The pertinent reaction enthalpy, $\Delta_2 H^\circ$, can be called the van der Waals (vdW) interaction or in older terms the primary steric effect. Subsequently, SIR can be estimated as the difference $\Delta_1 H^\circ - \Delta_2 H^\circ$. The values obtained are given in Table 3, first line. With respect to the accuracy and reliability of the approach, we can state that SIR raises the energy of **3** to a demonstrable amount but it comprises only one third of the total steric effect.

Similarly, as SIR and vdW were estimated for the minimum-energy conformation of compound **3**, they can be defined for any other conformation in the dependence on the variable torsion angle ϕ. Fig. 1 yields a picture that could qualitatively be expected. SIR increases with ϕ along a curve not very different from the function $\cos^2\phi$ as originally anticipated;[3a] vdW decreases in a similar way. The two effects compensate largely and their sum exhibits only a flat minimum. A rather similar picture was obtained previously[5] for 2,6-dimethylbenzoic acid **2**, particularly in the total effect. The main difference was near to $\phi = 90°$: the steric effect of one



Scheme 2

tert-butyl group reaches to a greater distance than that of two methyl groups.

Steric effects on the acidity

Since the acidity is controlled both by the energy of the acid molecule and of the anion, isodesmic reactions must also be formulated for the anion. In Scheme 2 eqn. (3) represents the total substituent effect while in eqn. (4) SIR is excluded. Reaction enthalpies of these reactions, Δ_3H° and Δ_4H°, were calculated from the data of Table 1 and are given in Table 3, line 2. The total substituent effect is smaller in the anion than in the acid but SIR is virtually equal. The dependence on the torsion angle ϕ is shown in Fig. 1 (broken lines). All effects are weaker in the anion; the total effect shows a very shallow minimum. The steric effect on acidity is given by the vertical distance between the two minima (Fig. 1, arrow). The whole picture is again in principle similar to that with 2,6-dimethylbenzoic acid[5] **2**.

It is evident both from Fig. 1 and from Table 3, line 3, that SIR has virtually zero effect on the acidity: the stronger acidity of compound **3** is not given by SIR increasing the energy of the acid molecule but by a lowered energy of the anion. Within the framework of separation used here, the stabilizing effect in the anion must be classified as a van der Waals interaction. We considered a more specified electrostatic model[6] which describes the *tert*-butyl group as a bulky polarizable unit and the charge of the anion as more or less localized. The model is called pole/induced dipole interaction[12] and the pertinent equation has the form[5] (5).

$$\Delta E = -\alpha q^2/32\pi^2\varepsilon_0^2\,\varepsilon_{\text{eff}}^2\,r^4 \qquad (5)$$

This expression is very sensitive to the distance r and also to the effective relative permittivity ε_{eff}; the polarizability α can be obtained from molar refraction.[22] Most important in the case of carboxylic acids is the assumed distribution of charge on the two oxygen atoms or also to the carbon atom. We obtained[5] with this equation some values of ΔE in good agreement with experiments for acids **1** and **2**. Similarly one could obtain a reasonable agreement for **3** since the polarizability of *tert*-butyl is almost four times greater[22] than for methyl. However, the model is too dependent on the choice of parameters and other models could meet the experimental values with a similar accuracy. One could imagine for instance electrostatic attraction between the negative charge on the oxygen atoms and positive charge on the hydrogens which are nearer than the alkyl carbon atoms. In our opinion, such a model contributes little to understanding the problem; in any case an explanation in terms of SIR must be rejected.

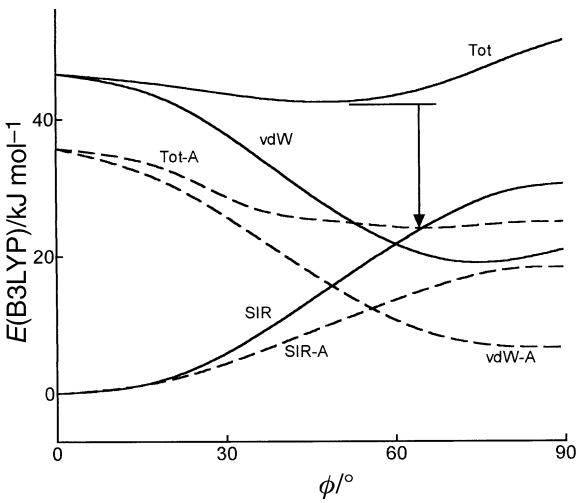


Fig. 1 Components of the steric effect (SIR, vdW, total) in 2-*tert*-butylbenzoic acid **3** (full lines) and in its anion **3A** (broken lines), as a dependence of the torsion angle ϕ; the effect on acidity is shown by the arrow between the lowest energy of the acid molecule and the lowest energy of the anion.

In solution, compound **3** shows equal acid strength in water[21] and in methanol:[6] approximately four times less than in the gas phase. In mixed solvents the results are similar.[21,23] Attenuation by a factor of four is strong compared even to structurally similar methylbenzoic acids:[5] steric hindrance to solvation must be of importance in decreasing the acidity of **3**. In any case, SIR is not possible even in solution. In our simplified scheme, we attributed the acid strengthening simply to vdW interaction (Table 3, lines 4 and 5); any hindrance to solvation is included in this term.

Conclusion

tert-Butylbenzoic acids have served as a useful model for separating and evaluating various kinds of steric effects. The effects on energy and on geometry are not quite parallel and must be estimated separately. Concerning SIR, it is better observable in the enthalpies of formation than in the acidities as was found in the case of other substituent effects.[4e,5] In our model compound **3** the effect of SIR on acidity is virtually zero. Note that our calculations of acidities are probably more reliable than those of the enthalpies of formation: agreement with experiment is better and even the experimental data themselves are more dependable. We are of the opinion that the effect of SIR has been overestimated in many other compounds. Each such case should be reexamined separately from two points of view: conformation and energy. We believe that calculation of structures with a fixed conformation could be helpful in this investigation.

Acknowledgements

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