

Non-classical buttressing effect: gas-phase ionization of some methyl-substituted benzoic acids

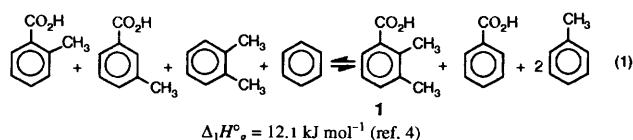
Michèle Decouzon, Otto Exner,*† Jean-François Gal* and Pierre-Charles Maria

Laboratoire de Chimie Physique Organique, Université de Nice - Sophia Antipolis, 06108 Nice Cédex 2, France

The classical concept of the buttressing effect (BE) was recently redefined by us in a general way as the excess energy of a trisubstituted benzene (or another derivative) with respect to the value anticipated from pair-wise interaction energies. This new non-classical definition is applied here to methyl-substituted benzoic acids without *ortho* substitution: on these compounds BE would be undisturbed by other effects but could not be detected until now. Acidities of the benzoic acids and basicities of their methyl esters were measured in the gas phase by the equilibrium method using Fourier transform ion cyclotron resonance (FT-ICR). By combining these quantities with the enthalpies of formation, it was possible to calculate BE separately for the neutral acid molecules, and for their deprotonated and protonated forms. In the case of uncharged molecules, BE is positive even for non-adjointing substituents, so a kind of steric interaction between distant groups must be accepted as an experimental fact. However, BE is also of comparable magnitude in the deprotonated and protonated forms. As a consequence, the relative Δ BE is strongly reduced in the acidity or basicity values, and is observable only for adjacent substituents. In aqueous solution, it is further attenuated. For this reason, BE has not been revealed previously beyond the classical definition: in all other cases, BE was effectively zero, and the substituent effects in solution were found to be additive.

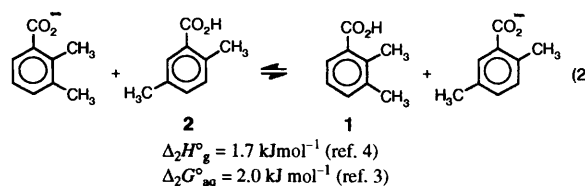
Introduction

The term buttressing effect¹ (BE) was coined to denote a composite steric interaction: the effect of a substituent adjacent to the functional group is strengthened by the presence of another, more distant substituent. The term is still in current use.² In spite of the word 'buttressing', the common interpretation of BE is not so much in terms of van der Waals interaction and angular deflections, but in terms of the restriction of movement, for instance, the restricted rotation of the first group caused by the presence of the second group. Among benzene derivatives, a classical example is 2,3-dimethylbenzoic acid **1**: the acidity strengthening effect of the 3-methyl group is mediated through the methyl group in the 2-position.³ The effect is observed clearly by comparison with a reference compound, 2,5-dimethylbenzoic acid **2**, in which BE is assumed to be absent but other interactions (denoted as inductive, electrostatic or hyperconjugative) are supposed to be equal. In our study of the gas-phase acidities of these acids⁴ we had attempted to redefine BE in a more rigorous and more general way as the excess interaction energy in a trisubstituted derivative with respect to the sum of the interaction energies of all pairs of substituents as estimated from the pertinent disubstituted derivatives. According to this definition, BE may be expressed by the enthalpy (or Gibbs energy) of a proper isodesmic reaction, for example eqn. (1) in the case of **1**.



A similar reaction can be written for **2**. When the concept is extended to the acidity (or basicity), the respective buttressing effect is the difference between BE in the neutral molecule and BE in the deprotonated (or protonated) form and may be denoted as Δ BE(acid) or Δ BE(base). The sign of the difference was chosen so that a positive Δ BE means strengthened acidity or weakened basicity.

In this conception, BE is a strictly experimental quantity, independent of any *a priori* principle: it may or may not be interpreted theoretically. One can object that the pertinent isodesmic reaction may sometimes be complex and/or unusual, but the reaction in eqn. (1) is in principle possible. The original definition¹ of BE can also be expressed using isodesmic reactions. In the mentioned example of Δ BE(acid) of **1** and **2**, the isodesmic reaction is eqn. (2) which is experimentally accessible.



As compared to the earlier definition, the new one differs in three points:

1. It may rely on a fundamental molecular property, the enthalpy of formation in the gas phase: in this case it does not depend on specific features of some particular rate or equilibrium process in a solvent.

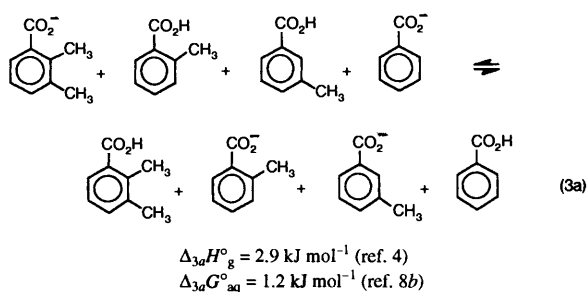
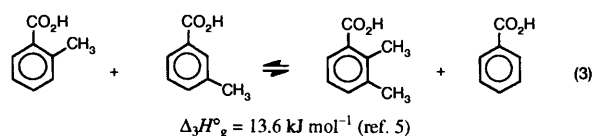
2. In the case of acid/base equilibria, it can be applied separately to acids and anions (bases and cations) as BE, or to acid–base equilibria as Δ BE: this all can be done in the gas phase or in solution. For acid–base equilibria in solution, our definition is identical with the earlier definition.

3. Most importantly, it is not restricted to a particular steric

† Permanent address: Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 16610 Praha 6, Czech Republic.

arrangement but applies to any compound with three arbitrary substituents. Actually we have found⁴ that even in 2,5-dimethylbenzoic acid, BE is positive and not negligible (7.5 kJ mol⁻¹). This result may seem inexplicable in terms of common steric effects and space-filling models, but we accept it simply as an experimental fact. BE was also evidenced⁴ for the corresponding deprotonated acid (with a reduced intensity) and for the protonated form of its ester (with a similar intensity); this piece of evidence was obtained by combining the thermochemical data⁵ with the gas-phase acidities and basicities.⁴

Our conception of BE may be related to the common notion of additivity of substituent effects. When BE is calculated equal to zero, the effects of two substituents are simply additive. This behaviour was observed, *e.g.*, with ionization in solution of many substituted benzoic acids,⁶ even with *ortho* substituents.⁷⁻⁹ In terms of isodesmic reactions, the additive character can be appreciated using eqn. (3) for the enthalpies of formation, or eqn. (3a) for the acidities.



If ΔH° or ΔG° of these reactions equals zero, the substituent effects are said to be additive. A deviation from additivity is generally not numerically equal to BE or ΔBE since in eqn. (1) the interaction of the two 'true' substituents (say the methyls in 2,3-dimethylbenzene) is taken into account, while in eqn. (3) it is not. Nevertheless, the deviation from additivity in eqn. (3a) is equal to $\Delta BE(\text{acid})$.

There is still the question of whether the term BE can be used for any interaction of three groups in any structure. Before more examples are investigated, we shall reserve this term for predominantly steric effects. In particular, those compounds with mutually conjugated substituents (*e.g.* 3-methyl-2-nitroaniline) should be excluded from this treatment. For this reason, we focused attention first on polymethyl derivatives. Our previous paper⁴ dealt with various methyl-substituted benzoic acids. The discussion was complicated since BE was observed in addition to the steric hindrance to resonance and to other steric effects: it then appeared as an effect of secondary importance. Therefore, we have decided to investigate BE as an isolated feature in a separate study.

In this paper, we have extended the above studies to methyl-substituted benzoic acids without *ortho* substituents, *viz* 3,4-dimethyl- **3**, 3,5-dimethyl- **4** and 3,4,5-trimethyl-benzoic acids **5**. Early studies of the acidities of these acids in water^{3,8} as well as in mixed aqueous solvents^{6,9} did not reveal any significant ΔBE : the substituent effects were additive within experimental error, and this was adopted as a typical behaviour. However, the experimental enthalpies of formation of **3-5** do not exhibit strict additive behaviour since they cannot be calculated from group contributions without additional correction terms.⁵ BE calculated according to our definition is positive (see later, Table 3). In order to establish whether the effect is present (probably partially compensated) also in the deprotonated or in

the protonated forms, we have now measured the gas-phase acidities of the acids **3-5** and the basicities of their methyl esters **3E-5E** whose relative basicities are assumed⁴ to be equal to those of the acids. Since we have to deal with small differences, we investigated again the reference compounds 3-methyl- **6** and 4-methyl-benzoic acid **7**, and their methyl esters **6E**, **7E**. In our previous paper we used the values reported by Taft and Topsom,¹⁰ which originate from earlier work.^{11,12} Here we have measured all the derivatives under the same conditions, against the same reference compounds.

Experimental

Materials

Compounds **3**, **4**, **6** and **7** (Table 1) were of commercial origin and **5** was provided by Dr C. Turrión. The methyl esters **3E-7E** were prepared from pure samples of the acids by the reaction with diazomethane and purified only by a simple distillation *in vacuo*.

Physical measurements

These were carried out in the same way as in the preceding paper.⁴ Proton transfer equilibria were monitored by Fourier transform ion cyclotron resonance (FT-ICR). Details of our experimental technique were described separately for gas-phase measurement of acidity¹³ and basicity.¹⁴ Gibbs energies of proton transfer between a reference acid (reference base) and the acid (base) under consideration were thus obtained at 338 K.

In the case of acidity measurements, all samples **3-7** could be compared against the same reference, 3-(trifluoromethyl)-phenol (Table 1), as used in our previous paper.⁴ The values of $\Delta \Delta_{\text{acid}} G^\circ$ at 338 K were transformed into $\delta \Delta_{\text{acid}} H^\circ$ and $\delta \Delta_{\text{acid}} G^\circ$ as previously.⁴ The temperature correction is negligible. Since the molecules of **4**, **5**, **7** are symmetrical and, in **3** and **6**, practically equal populations of the rotamers can be assumed, the relative values $\delta \Delta H^\circ$ are taken to be equal to the relative values $\delta \Delta G^\circ$ (Table 1). It follows that all gas-phase acidities of methyl-substituted benzoic acids, measured here and in our previous paper,⁴ are strictly comparable. The relative values $\delta \Delta_{\text{acid}} G^\circ$ in Table 1 should be reliable within $\pm 0.4 \text{ kJ mol}^{-1}$.

In the case of basicities, the methyl esters **3E-7E** could not be measured against one common reference compound. Nevertheless, we used a small set of reference compounds, three in every case, and calculated the average values of gas-phase basicities, GBs (Table 2). Again, the symmetry conditions are identical for all the compounds. Hence, the relative proton affinities PA (enthalpies) equal the relative gas-phase basicities GB (Gibbs energies), Table 2. Lack of common reference compound is partly compensated by the greater number of measurements, so that the relative values have the same uncertainty as for the acids, $\pm 0.4 \text{ kJ mol}^{-1}$.

Results and discussion

Let us start with the substituent effects on the enthalpies of formation of **1-5**. These substituent effects can be expressed either in terms of the deviation from additivity, eqn. (3), or of BE as defined here, eqn. (1). In the case of compound **5**, the concepts must be extended to a tetrasubstituted benzene (with one functional group and three substituents). The extension of eqn. (3) is evident; but extension of eqn. (1) may proceed in several ways. As previously,⁴ we prefer here the definition in which the three methyl groups are taken together as one block as shown by eqn. (1a) (reference to 1,2,3-trimethylbenzene, not to the dimethylbenzenes).

In Table 3, the results on compounds **3-5** are compared to the classical model system involving **1** and **2**. The experimental uncertainty deserves some comments. In the gas phase, it is

Table 1 Gas-phase acidities (in kJ mol⁻¹) of methyl-substituted benzoic Acids (AH)

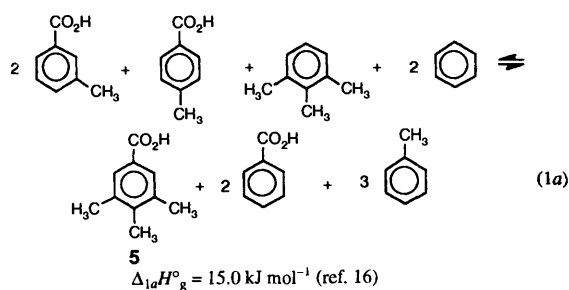
AH No.	AH Substituent	$\Delta\Delta_{\text{acid}}G^\circ(338\text{ K})^a$	$\delta\Delta_{\text{acid}}G^\circ(338\text{ K})^b$	$\Delta_{\text{acid}}G^\circ(\text{AH})^c$
3	3,4-Me ₂	+7.5 ± 0.1	+5.2	1398.5
4	3,5-Me ₂	+5.8 ± 0.1	+3.5	1396.8
5	3,4,5-Me ₃	+7.2 ± 0.4	+4.9	1398.2
6	3-Me	+3.9 ± 0.2	+1.6 (+2.9) ^d	1394.9
7	4-Me	+5.2 ± 0.3	+2.9 (+4.6) ^d	1396.2

^a Gibbs energies for the reactions $\text{AH} + 3\text{-CF}_3\text{C}_6\text{H}_4\text{O}^- = 3\text{-CF}_3\text{C}_6\text{H}_4\text{OH} + \text{A}^-$; quoted uncertainties correspond to the standard deviation for 3–4 measurements. ^b Gas-phase acidities relative to the unsubstituted compound. ^c Absolute Gibbs energies of acidity ($\text{AH} \rightarrow \text{A}^- + \text{H}^+$) (at 298 K) anchored to $\Delta_{\text{acid}}G^\circ(3\text{-CF}_3\text{C}_6\text{H}_4\text{OH}) = 1391 \pm 8\text{ kJ mol}^{-1}$ (ref. 15). The value obtained for benzoic acid as reference corresponds exactly to the value reported by J. Bartmess (333.0 kcal mol⁻¹) in the unpublished '1987 gas-phase acidity scale' prefiguring the GIANT table (ref. 15). ^d In parentheses, values from the literature (ref. 10).

Table 2 Gas-phase basicities (in kJ mol⁻¹) of methyl-substituted methyl benzoates

B Formula or No.	B Substituent	Ref.	$\Delta\text{GB}(338\text{ K})^a$	$\text{GB}(\text{B})^b$
3E	3,4-Me ₂	Pr ⁿ ₂ S	+1.4 ± 0.2	834.3
		CH ₃ COCH ₂ COCH ₃	+2.4 ± 0.2	
		Pr ⁱ ₂ O	+9.0 ± 0.1	
4E	3,5-Me ₂	Pr ⁿ ₂ S	-2.2 ± 0.2	830.7
		CH ₃ COCH ₂ COCH ₃	-1.2 ± 0.1	
		Pr ⁱ ₂ O	+5.4 ± 0.1	
C ₆ H ₅ NH ₂ 5E	3,4,5-Me ₃	Pr ⁿ ₂ S	+13.8 ± 0.5	847.0
		C ₆ H ₅ NH ₂	-5.0 ± 0.2	
		2,4-Me ₂ C ₆ H ₄ CO ₂ Me	+7.3 ± 0.3	
6E	3-Me	Pr ⁿ ₂ S	+8.6 ± 0.1	842.0
		CH ₃ COCH ₂ COCH ₃	-7.7	
		Pr ⁱ ₂ O	-1.7 ± 0.2	
7E	4-Me	Pr ⁱ ₂ CO	+5.8 ± 0.1	823.9 (822.2) ^c
		CH ₃ COCH ₂ COCH ₃	-4.1 ± 0.2	
		Pr ⁱ ₂ O	+2.2 ± 0.1	
		Pr ⁱ ₂ CO	+9.7 ± 0.1	827.7 (826.0) ^c

^a Gibbs energies for the reaction $\text{BH}^+ + \text{Ref.} = \text{Ref. H}^+ + \text{B}$; quoted uncertainties correspond to the standard deviation for 3–4 measurements. ^b Absolute Gibbs energies of basicity ($\text{BH}^+ \rightarrow \text{B} + \text{H}^+$) anchored to $\text{GB}(\text{C}_6\text{H}_5\text{COCH}_3) = 825.9\text{ kJ mol}^{-1}$, values previously published in ref. 4 were referenced to $\text{GB}(\text{C}_6\text{H}_5\text{COCH}_3) = 846.2\text{ kJ mol}^{-1}$ as proposed by M. Meot-Ner (Mautner) and L. W. Sieck, *J. Am. Chem. Soc.*, 1991, **113**, 4448. This large upward shift was later questioned. ^c In parentheses, values calculated from the reported methyl substituent effects (ref. 12).



controlled by the uncertainty of $\Delta_f H^\circ$, given⁵ as $\pm 1.7\text{--}1.9\text{ kJ mol}^{-1}$. When BE is calculated according to eqn. (1) or eqn. (1a), the combined error could reach up to 5–6 kJ mol⁻¹. However, in our opinion it is evident that the relative accuracy within our series is better. It follows clearly from the trend in the whole set, also from the linear dependence⁴ of $\Delta_f H^\circ$, experimental and calculated by AM1: the standard deviation of 1.1 kJ mol⁻¹ suggests a somewhat smaller uncertainty of experimental values than originally estimated, irrespective of the approximate character of the calculations. The acidity or basicity measurements in the gas phase are more precise and do not increase the overall error. The pK measurements in water are the most accurate of all. In Table 3 (last column), we give our estimates of the limiting uncertainty: in the following discussion we make particular comments only about values which are at least twice as large.

Let us compare first BE and the deviation from additivity. Both are very similar quantities (lines 1 and 2) since they differ

only by the interaction energy in the pertinent dimethylbenzene, eqn. (1). The only difference exceeding the experimental error appears in the case of 5 and arises from the interaction energy in 1,2,3-trimethylbenzene, in accordance with eqn. (1a).

The following lines of Table 3 are given only in terms of BE or ΔBE , and present these quantities under different conditions. As far as the effects on acidity or basicity are concerned, ΔBE and deviation from additivity are equal.

The most important result now is that BE in compounds 3–5, in which no *ortho* substituents are present, is of similar magnitude, or sometimes even greater than in the classical model (*i.e.* the difference between 1 and 2), in which the *ortho* substitution has been considered as essential. The smallest value, for 4, may not exceed the experimental error, but more convincing than the individual values is the regular increase of BE in the sequence $4 < 3 < 5$, and also the fact that all values are positive. Positive values were also found⁴ for 2,4- and 2,5-dimethylbenzoic acids in which a classical BE is not possible. Of the compounds investigated here, the strong BE in 5 is of decisive importance. Let us stress that it has nothing in common with the steric crowding of the three methyls but expresses, according to eqn. (1a), only the non-classical BE between the COOH group and the block of methyl groups.

We conclude that an interaction between non-adjointing groups is an experimental fact. In the original experimental work,⁵ the enthalpies of formation were expressed by an additive scheme, BE being accounted for by an additional constant term. The values of $\Delta_f H^\circ$ calculated in this way may well serve as a first approximation, but when applied to differential values, this scheme fails (Table 3, line 3). In the

Table 3 Buttrressing effect in methyl-substituted benzoic acids in different states (kJ mol^{-1} , 298 K)^a

Position of the methyl groups	Compound						δ^e
	1 ^b 2,3	2 ^b 2,5	$\Delta(1-2)$	3 3,4	4 3,5	5 3,4,5	
$\Delta_f H^\circ$ (neutral acid, g)	12.1	7.8	4.3	7.5	4.5	15.0	3
[deviation from additivity] ^d	13.6	8.3	5.3	9.0	4.3	20.6	3
	(4.0) ^e	(0) ^e	(4.0) ^e	(0) ^e	(0) ^e	(4.0) ^e	
$\Delta_f H^\circ$ (deprotonated acid, g)	9.2	6.6	2.6	8.2	4.8	13.8	3
$\delta\Delta_{\text{acid}} H^\circ$ (g)	2.9	1.2	1.7	-0.7	-0.3	1.2	0.5
$\delta\Delta_{\text{acid}} H^\circ$ (aq) ^f	8.8	11.5	-2.7		10.4		?
$\delta\Delta_{\text{acid}} G^\circ$ (aq) ^g	1.18	-0.19	1.37	-0.07	-0.19	0.22	0.1
$\Delta_f H^\circ$ (protonated acid, g) ^h	14.5	8.4	6.1	8.4	5.2	15.7	3
$\delta\Delta_{\text{bas}} H^\circ$ (g) ^h	2.4	0.6	1.8	0.9	0.7	0.7	0.6
$\delta\Delta_{\text{bas}} G^\circ$ (aq) ^h		-0.3 ⁱ					0.2

^a BE is positive if the species under scrutiny possesses a higher energy than anticipated from reference compounds, see *e.g.* eqn. (1). For ionization processes, a positive ΔBE corresponds to a stronger acidity or a weaker basicity. ^b Data in these columns are slightly different from those previously published,⁴ due to new values for the acidities and basicities of the reference compounds **6**, **7** and **6E**, **7E** (this paper), and to slight changes (ref. 16) in $\Delta_f H^\circ$. ^c Estimated average experimental error in the whole line, obtained as a combination of the uncertainties of all quantities involved in the calculation. ^d Deviations from additivity, calculated according to eqn. (3). ^e Deviations from additivity as anticipated according to the group additivity scheme with correction terms (ref. 5). ^f Calculated from the literature data [ref. 8(c)]. ^g From the data of ref. 8(b). ^h Relative experimental basicities of the acids were assumed to be equal to the basicities of the methyl esters. ⁱ From the data of ref. 17.

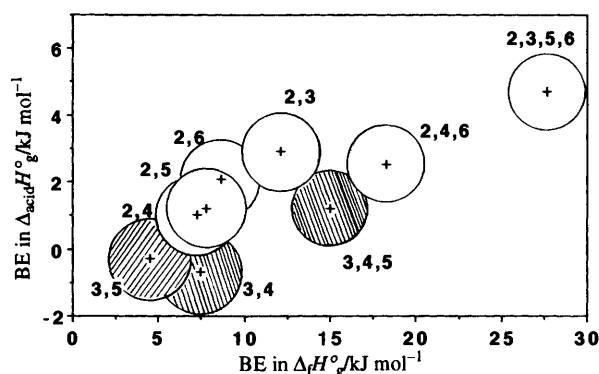


Fig. 1 Plot of the buttrressing effect (BE) in methyl-substituted benzoic acids: in the enthalpies of formation in the gas phase (x-axis) and in the acidities in the gas phase (y-axis). Data from Table 3 and from ref. 4, the latter corrected according to some new values of $\Delta_{\text{acid}} H^\circ$ (this paper) and $\Delta_f H^\circ$ (ref. 16).

standard additivity scheme,¹⁸ no BE is incorporated (zeroth approximation).

In the deprotonated forms of 3-5, BE is practically of the same magnitude (Table 3, line 4) as in neutral molecules. It follows that ΔBE is not observable in the gas-phase acidity within experimental error (line 5), except possibly for the trimethyl-derivative **5**. In this respect the classical model is more sensitive: BE of **1** is smaller in the anion than in the acid by just one quarter, so that a ΔBE can be observed even on the acidity. We may say that the difference in the apparent steric size of the COOH and COO⁻ groups (responsible for the steric effects on acidity) is observable only in the presence of an *ortho* substituent. With compounds **3** and **4**, the calculated ΔBE for acidity is negative but does not exceed the experimental error. Let us stress that in the whole of Table 3 the values are positive; a few apparently negative values are statistically insignificant: BE appears as a general phenomenon which destabilizes the crowded molecule. This suggests that the definition proposed here may be meaningful.

The most objective confirmation of the reality of BE can be obtained from a graphical representation (Fig. 1) where the values of BE, arising from two independent sources, *viz.* enthalpies of formation and gas-phase acidities, are plotted. Taking into account the relatively large experimental uncertainty, it is evident that the two series of data are related and probably controlled by the same factor. BE increases gradually with the number of methyl groups and with their adjoining positions: it may become quite strong even in the non-

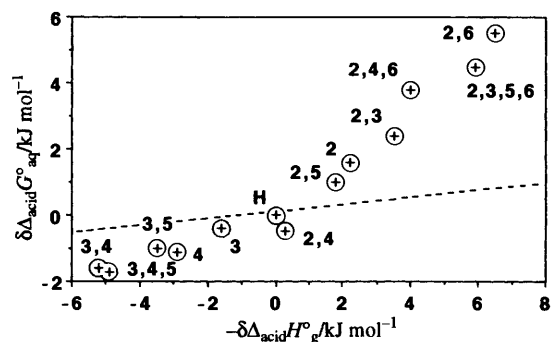


Fig. 2 Plot of the acidities of methyl-substituted benzoic acids, $\delta\Delta_{\text{acid}} G^\circ$ in water (y-axis) *vs.* the acidities, $\delta\Delta_{\text{acid}} H^\circ$ (practically equal to $\delta\Delta_{\text{acid}} G^\circ$, see the Experimental section) in the gas phase (x-axis). Previous data⁴ were complemented by three new points; two points were corrected according to the measurements reported in this paper. The broken line is valid for polar substituents (ref. 11).

classical cases of 3,4,5- and 2,4,6-trimethylbenzoic acids. On the side of low values it can be traced down to 3,5-dimethylbenzoic acid **4**, but only in the enthalpies of formation. In the acidity values, it is observable only in *ortho* derivatives (even quite clearly in **2**) and possibly in **5**. Summarizing, BE exists without any doubt, even outside the classical definition, *i.e.* when all substituents are not in the immediate neighbourhood.

The acidity in water can be discussed in terms of either enthalpies or Gibbs energies but the Gibbs energies are more precise. BE values based on enthalpies in water (Table 3, line 6) are surprisingly large and quite irregular, for instance BE for **2** is greater than for **1**. These results raise doubts about the reliability of ΔH° obtained^{8c} from the temperature dependence of dissociation constants. In terms of ΔG° (Table 3, line 7), BE reflects reasonably the gas phase values. In 3-5 the gas-phase effects are attenuated more, and in the *ortho* derivatives **1** and **2**, less. Particularly, the difference between **1** and **2** is virtually unchanged when going from the gas phase to water: note, however, the disagreement in the literature.^{3,8c} For the sake of consistency, we have chosen the data of Luning^{8b} available for the whole set of compounds under study. In Fig. 2, acidities of methyl-substituted benzoic acids are plotted, aqueous solution *vs.* gas phase. The plot reveals an obvious difference between the behaviour of *ortho*-substituted and the remaining derivatives. Among the latter compounds, there is an approximate linear dependence, the substituent effects being reduced in water by a factor of 0.3. The substituent effects for *ortho* derivatives are less attenuated (by a factor of about 0.9), *i.e.* the anions are less

solvated. ΔBE in the acidity in water is also attenuated compared to ΔBE in the gas-phase acidity. For compounds without *ortho* substituents, ΔBE is attenuated so much in water that the detection limit is reached and the dissociation constants in aqueous solution are effectively additive. Therefore, gas-phase data were essential for revealing the existence of BE in these compounds.

The basicities are less telling for the evaluation of ΔBE . In the case of esters without *ortho* substituents, the interaction is practically equal in the protonated form and in the neutral molecule: hence, no ΔBE can be observed for the basicity values. In the case of *ortho* derivatives, ΔBE is observable but rather small. Concerning the basicities in solution, scarce data have been reported for benzoic acids in sulfuric acid,¹⁷ and no ΔBE was revealed.

Conclusions

Our results confirm that a tris-derivative generally has an excess of energy over the sum which could be predicted according to the energy of the pertinent bis-derivatives. What may be surprising is that this excess energy (denoted here BE) can be observed even when all substituents are not in the immediate neighbourhood. In the gas-phase enthalpies of formation, a possible small effect can be traced even in benzene derivatives without substituents in the adjoining position (4). However, in the acid–base equilibria, the effect is not very different in the ion compared to the neutral molecule: in addition, it is strongly attenuated in solution. This is why it was not discovered sooner, *viz.* in the studies dealing with the ionization in water, and why the substituent effects have been believed to be generally additive.

For the time being, we prefer to accept this excess energy as an experimental fact and refrain from suggesting any interpretation. It is evidently not understandable when the molecule is represented by the very rough approximation of Stuart–Briegleb models. In molecular mechanics, the van der Waals interaction is not restricted to any short distance but is calculated also from pair-wise interactions and cannot explain any excess energy, although it is known that this approximation is unsatisfactory.¹⁹ An electrostatic interaction (dipole–dipole) might be also considered since BE is absent or very weak in trimethylbenzenes²⁰ and the presence of a polar group seems necessary. However, even this effect should be additive and would not account for the excess energy. It should be emphasized that all our examples to date are from benzene derivatives and any participation of the benzene nucleus is not excluded. However, compounds with strong interaction between substituents and the benzene ring (resonance) were excluded from our considerations. In organic chemistry terms we may thus say that our BE is essentially of steric origin although the term 'steric' is not well defined.

We are of the firm opinion that our definition of BE is meaningful: in the original examples it is identical with the earlier definition but can be applied much more broadly and allows even small, previously unobservable effects to be revealed. It may thus represent a step in extending the theory of substituent effects from bis-derivatives to tris-derivatives.

There remains a question of whether 'buttressing effect' is the best term for our generalized concept. For the time being we are unable to suggest a better alternative, also for the reason that the term is in common use and our definition is valid without change for the known early examples.

Acknowledgements

Thanks are due to Dr C. Turrión (CSIC, Madrid) for a sample of 3,4,5-trimethylbenzoic acid. The stay of O. E. at the University of Nice-Sophia Antipolis was supported by a grant from the Conseil Général des Alpes Maritimes, France and by the Czech Grant No 203/96/1658.

References

- (a) M. Rieger and F. H. Westheimer, *J. Am. Chem. Soc.*, 1950, **72**, 19; (b) F. H. Westheimer, in *Steric Effects in Organic Chemistry*, ed. N. S. Newman, John Wiley & Sons, New York, 1956, p. 523.
- I. Eventova, E. B. Nadler, E. Rochlin, J. Frey and Z. Rappoport, *J. Am. Chem. Soc.*, 1993, **115**, 1290.
- J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton, *J. Chem. Soc.*, 1954, 1470.
- M. Decouzon, P. Ertl, O. Exner, J.-F. Gal and P.-C. Maria, *J. Am. Chem. Soc.*, 1993, **115**, 12071.
- M. Colomina, P. Jiménez, M. V. Roux and C. Turrión, *J. Chem. Thermodyn.*, 1984, **16**, 1121; 1987, **19**, 1139.
- K. Kalfus, J. Kroupa, M. Večeřa and O. Exner, *Collect. Czech. Chem. Commun.*, 1975, **40**, 3009.
- J. Shorter and F. J. Stubbs, *J. Chem. Soc.*, 1949, 1180.
- (a) J. F. J. Dippy and S. C. R. Hughes, *Tetrahedron*, 1963, **19**, 1527; (b) B. Lüning, *Acta. Chem. Scand.*, 1960, **14**, 321; (c) J. M. Wilson, N. E. Gore, J. E. Sawbridge and F. Cardenas-Cruz, *J. Chem. Soc., B*, 1967, 852.
- (a) R. M. Stone and D. E. Pearson, *J. Org. Chem.*, 1961, **26**, 257; (b) W. Polaczkowa, W. Porowska and B. Dybowska, *Rocz. Chem.*, 1961, **35**, 1263.
- R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1987, **16**, 1.
- T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, 1977, **99**, 2222.
- F. Mishima, M. Fujio and T. Tsuno, *Tetrahedron Lett.*, 1986, **27**, 951.
- G. Bouchoux, P. Jaudon, M. Decouzon, J.-F. Gal and P.-C. Maria, *J. Phys. Org. Chem.*, 1991, **4**, 285.
- M. Berthelot, M. Decouzon, J.-F. Gal, C. Laurence, J.-Y. Le Questel, P.-C. Maria and J. Tortajada, *J. Org. Chem.*, 1991, **56**, 4490.
- S. G. Lias, J. E. Bartmess, J. F. Liebman, T. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, Suppl. 1.
- M. Bureš, R. Holub, J. Leitner and P. Voňka, *Termochemické veličiny organických sloučenin (Thermochemical Quantities of Organic Compounds)*, Publishing Centre of the Institute of Chemical Technology, Prague, 1992 (in Czech).
- R. I. Zalewski, in *Chemistry of Functional Groups. Supplement B: The Chemistry of Acid Derivatives*, ed. S. Patai, John Wiley & Sons, New York, 1992, vol. 2, p. 305.
- E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data*, 1993, **22**, 805.
- S. Fitzwater and L. S. Bartell, *J. Am. Chem. Soc.*, 1976, **98**, 5107.
- O. Exner, Paper presented at the 7th Meeting on Stereochemistry, Trest (Czech Republic), April 23–26, 1995.

Paper 5/06842H

Received 16th October 1995

Accepted 5th December 1995