Baker–Nathan effect, hyperconjugation and polarizability effects in isolated molecules

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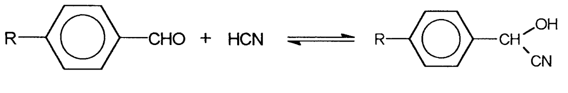
The Baker–Nathan effect in alkyl-substituted benzene derivatives has been reinvestigated on the basis of the AM1 calculated enthalpies of formation, correlations of the known gas-phase basicities and *ab initio* calculated geometries. In neutral molecules any stabilization is absent; protonated species are strongly stabilized, depending on the alkyl polarizability. This dependence was revealed very clearly when the substituent CH_2Bu^t was added to the traditional series, Me, Et, Pr^i, Bu^t. Any hyperconjugative order of alkyl reactivities was not observed in the gas-phase equilibria. Geometrical structures of benzyl, 4-methylbenzyl and 4-*tert*-butylbenzyl cations, calculated at the HF/6-31Gδ and MP2/6-31G** levels, revealed small angle distortions within the CH_3 group attributable to hyperconjugation of the α-hydrogen atoms. However, this effect is much smaller than the total interaction of either Me or Bu^t with the benzene nucleus seen particularly on the shortened C_{ar}–C_{alk} bond and classified formally as a mesomeric effect. One must conclude that the term hyperconjugation has a very restricted meaning in the case of substituted benzyl cations. The well-known limiting formula reflects to a small degree the real structure but hyperconjugation has a negligible effect on energy quantities of these compounds. The Baker–Nathan effect reported in solution kinetics is thus evidently caused by steric hindrance to solvation; in isolated molecules it is not observable.**

Introduction

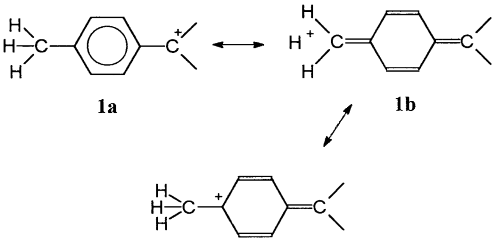
Many classical concepts of organic chemistry concerning effects of substituents have been proposed and/or demonstrated on the basis of reactivities in water or in aqueous solvents, and very often on the dissociation constants.[1] In contrast, the pertinent theoretical models relate to the isolated molecules. We outlined recently a programme by which these concepts could be redefined using the gas-phase reactivities.[2] The first goal was to eliminate the effect of the solvent water, and the second to separate effects operating in the ions and in neutral molecules or in the ground state and transition state, respectively. The necessary experimental quantities were mainly the gas-phase acidities (ΔH°_{acid}) or basicities (proton affinities, E_{pa}), and gas-phase enthalpies of formation ($\Delta_f H^\circ$). The concepts of steric hindrance to resonance,[3] buttressing effect,[4] inductive and mesomeric effects in aromatic derivatives,[5] steric hindrance to solvation[6] and simple cases of the inductive effect in aliphatic derivatives[2] were reinvestigated in this way. In this paper, we deal with the so-called Baker–Nathan effect[7] (BNE) and the related concept of hyperconjugation.[8]

The basic experimental fact was observed on the rates of solvolysis of *para*-substituted benzhydryl chlorides:[7] alkyl substituents enhanced reactivity in the order methyl > ethyl > isopropyl > *tert*-butyl > H, *i.e.* in the reversed order compared to their inductive effects. This fact was explained by hyperconjugation in the cation visualized in the simplest possible structure **1** by the resonance formula **1b**. This explanation assumes inherently that analogous structure **2b** for the *tert*-butyl derivative is less important. Additional examples were found in kinetics.[9] In the field of equilibrium constants, probably the only well documented example is formation of cyanohydrins,[10] eqn. (1), but the effect is very small.

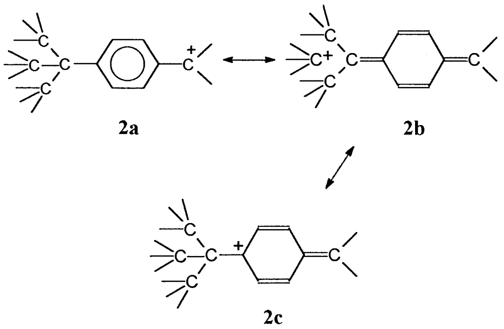


(1)

$R = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$



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



2a **2b** **2c**

At present, one usually distinguishes BNE as an experimental fact, and hyperconjugation as a theoretical concept. The latter has been extended to other compounds and properties; in particular it is being used in the interpretation of enthalpies of formation of simple hydrocarbons.[1,11] The term BNE has been restricted mainly to the reactivities of certain aromatic derivatives substituted with the named alkyls, and is not broadly used at present. The above order of reactivities (methyl is most effective) is called hyperconjugative and the reversed order (*tert*-butyl > isopropyl > ethyl > methyl > H) inductive.[9,12] Alternative explanations were also advanced on the basis of steric hindrance to solvation in bulky *tert*-butyl derivatives,[12] or with mass effects on the entropy term.[13] Sometimes hyperconjugation was completely rejected and explanation in terms of polarizability was found sufficient.[14] In our opinion, some of the inherent problems could be resolved by the same approach as in our previous work,[2–6] referring to gas-phase thermodynamic properties, $\Delta_f H^\circ$ and E_{pa}. However, the present knowledge of experimental quantities is incomplete: while many relevant values of E_{pa} have been reported,[15] the necessary values of $\Delta_f H^\circ$ are not available in the literature.[16] We will try here to substitute for them energies calculated at the semiempirical level (methods AM1 and PM3[17,18]) which were proved recently to be satisfactory for similar problems.[3,5,19] We shall not deal with the whole concept of hyperconjugation but restrict our considerations to the equilibrium processes of aromatic compounds, *i.e.* to substituted benzyl cations. The following questions can be addressed. (*i*) Is the BNE caused only by solvent effects, or is it also observable in the gas-phase equilibria (with respect to the attainable accuracy)? (*ii*) Is the BNE present also in neutral molecules or only in ions (then also in polar transition states)? (*iii*) Is hyperconjugation a possible explanation?

Calculations

Semiempirical calculations were performed by means of the MOPAC6 standard program for the AM1[17] and PM3[18] methods, respectively. The corresponding MO models were first optimized with respect to all geometrical degrees of freedom.

Ab initio calculations were performed by means of the GAUSSIAN94 program.[20] Vibrational analyses were carried out in all cases: all structures are energy minima.

Results and discussion

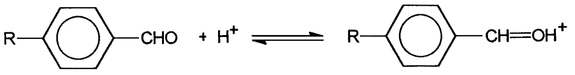
Correlation analysis of gas-phase basicities

Let us start with the statement that in the acid–base equilibria in the gas phase BNE is not observed. Significant examples are the protonation reactions[15] of substituted benzaldehydes, eqn. (2), or α-methylstyrenes, eqn. (3). In the former case, the positive charge is delocalized over the first and second atoms from the benzene nucleus; in the latter it is largely localized on the first atom. Taft and Topsom[15] interpreted the substituent effects of all substituents by the resonance ($\sigma_R{}^+$), field/inductive effect (σ_F) and polarizability (σ_α), using correlation eqns. (4) and (5),

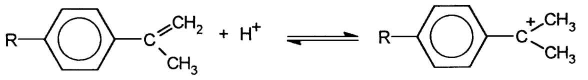
$$-\Delta G_{\mathbf{benzal}} = 0.0 + 132.2\sigma_{\mathbf{R}}{}^+ + 69.5\sigma_{\mathbf{F}} + 20.9\sigma_\alpha; \quad \text{s.d. } 2.1 \; R \; 0.9988 \qquad (4)$$

$$-\Delta G_{\mathbf{MeSt}} = 0.8 + 146.4\sigma_{\mathbf{R}}{}^+ + 79.4\sigma_{\mathbf{F}} + 19.2\sigma_\alpha; \quad \text{s.d. } 2.1 \; R \; 0.9992 \qquad (5)$$

respectively (recalculated here in kJ mol^{-1}). For alkyl substituents, the polarizability term is decisive. However, for all substituents it is the smallest and its significance was in some cases already questioned by the original authors.[15] We recalculated the multiple regressions and obtained only slightly different regression coefficients (not given). The polarization term was significant at the confidence level $\alpha \ll 0.005$ (by comparing the regression with and without this term, *F*-test).



(2)

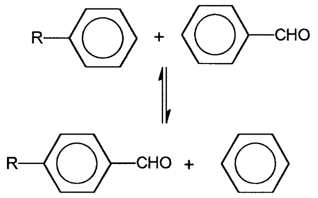


(3)

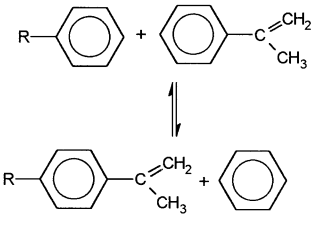
As in other cases, alkyl substituents are of little importance for the success of the correlation equation, and their effects can be masked by other substituents.[21] In the case of substituted benzaldehydes, a direct test is possible based only on the four alkyls. In Fig. 1 the relative experimental basicities have been plotted against σ_α: linearity is good but the slope $\rho_\alpha = 12.6$ differs very much from that in the multiple regression. For substituted methylstyrenes a similar plot would be based only on two points: the slope $\rho_\alpha = 18$ would be only a little different. The most important fact is that the lines in Fig. 1 do not pass through the origin. One must conclude that there are two components of the substituent effect, both increasing the basicity. One is the polarizability increasing with the size of the alkyl group; the other is constant for all alkyl groups. Comparison with the acidity of substituted phenols reveals a similar polarizability effect increasing the acidity but a reversal constant effect decreasing the acidity (Fig. 1). Within the framework of correlation analysis, these constant effects were expressed by the constant $\sigma_R{}^+ = 0.10$, equal for the four alkyl groups.[15] In terms of resonance structures it could be expressed by the formulae **1b** for the methyl group and **2b** for the *tert*-butyl group. It is then difficult to understand why the effects should be equal. In the case of phenols similar formulae with reversed polarity would be necessary: negative hyperconjugation. Although the latter concept is in use,[22] the respective formula could hardly possess any physical meaning. Nevertheless, a particular effect in aromatic derivatives is real since similar plots for aliphatic derivatives do not show any intercept:[23] two examples are reproduced in Fig. 1. In our opinion, better graphical representations of this effect are formulae **1c** and **2c**: the two different alkyl groups may stabilize the positive charge to approximately the same degree. Summarizing, this effect together with polarizability may sufficiently account for all effects observed in the gas phase. No hyperconjugation was proved.

Substituent effects in neutral molecules and in ions

As in our previous papers[2–6] we attempted to deconstruct the substituent effects into the components operating in neutral molecules and those operating in the ions. In the case of substituted benzaldehydes and α-methylstyrenes, this means we needed to construct isodesmic reactions, eqns. (6) and (7). Their reaction enthalpies, ΔH°_6 or ΔH°_7, should express the interaction energy of the two groups on the benzene nucleus or, in other terms, the substituent effect of the alkyl group on the functional group (or *vice versa*). The necessary values of enthalpies of formation, $\Delta_f H^\circ$, were calculated by semiempirical methods for all compounds involved in eqns. (6) and (7). They are listed in Table 1. Comparison with experiments was possible for the unsubstituted compounds and for the simplest series of alkyl-substituted benzenes. We used the latter for a test since we expected better agreement for relative than for absolute values. A plot of $\Delta_f H^\circ$, calculated *vs.* experimental (not shown),



(6)



(7)

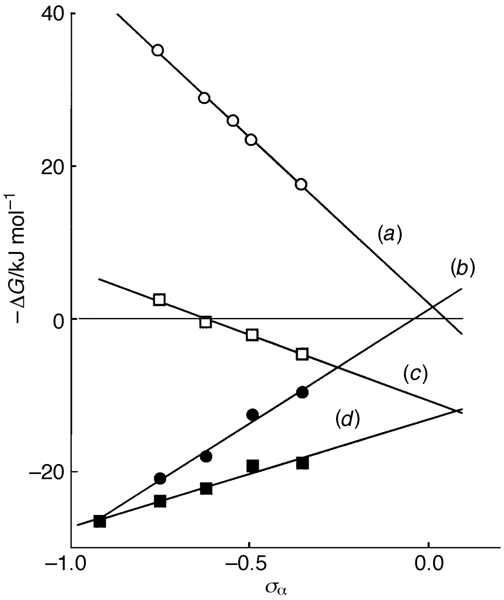
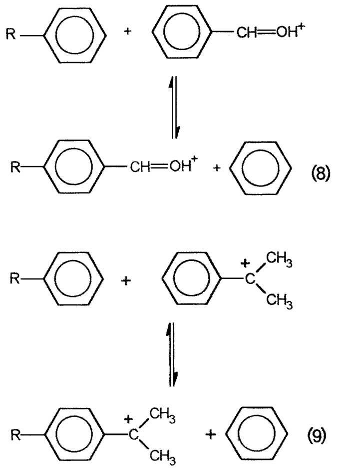
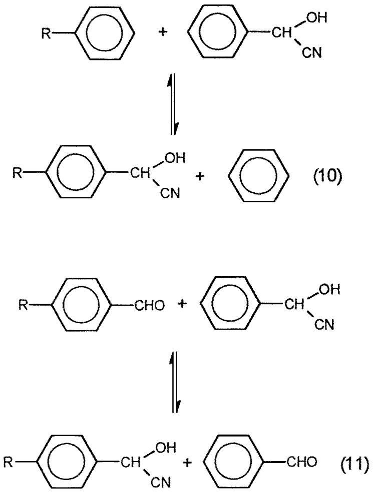


Fig. 1 Dependence of the relative gas-phase acidities ($-\Delta G°$acid) on the polarizability constants σ_α: (*a*) RCH_2OH; (*b*) $RCH_2NH^+(CH_3)_2$; (*c*) 4-RC_6H_4OH; (*d*) 4-$RC_6H_4CHOH^+$. Experimental data ref. 15, one point for the neopentyl derivative calculated in this paper, see Discussion.

revealed a better fit for PM3 while AM1 overestimated evidently the steric crowding in *tert*-butylbenzene. (This means that the calculated difference between *tert*-butylbenzene and isopropylbenzene is too small.) Even PM3 overestimates systematically the steric hindrance and also the stabilizing interaction. Nevertheless, we obtained a good linear dependence for the four alkylbenzenes (standard deviation 3 kJ mol^{-1}) when we excluded the somewhat deviating point for benzene itself. Since $\Delta_f H°$ values in the other series exhibit a similar trend, we have good grounds to believe that the deviations will compensate in the reaction enthalpies $\Delta H°_6$ and $\Delta H°_7$ given in Table 2. From eqns. (2) or (3) on the one hand, and from eqns. (6) or (7) on the other, we constructed eqns. (8) and (9) through a thermodynamic cycle. Their reaction enthalpies $\Delta H°_8$ and $\Delta H°_9$ represent the substituent effects of the alkyl groups on the cationic centre and are also given in Table 2.



Irrespective of the uncertainty inherent in the semiempirical calculations, there is no doubt that the substituent effect on the neutral functional group is negligible while that on the cationic centre is decisive. We will not conclude that a hyperconjugation in neutral molecules is not possible; see for instance the effects on ^{13}C NMR shifts expressed on a completely different scale.[24] However, ionic equilibria are certainly controlled by the effects in the ions. Of the non-ionic reactions, we investigated the already mentioned formation of cyanohydrins, eqn. (1). In the reaction product, the substituent effect is defined by eqn. (10). It is as small as in other neutral molecules of Table 2. Relative values of equilibrium constants relate to the isodemic reaction of eqn. (11): the substituent effect is almost constant for all alkyls (Table 2). Comparison with experimental values in solution[10] reveals that the solvent effect was decisive.



The traditional series of α-branched alkyls has been used in almost all studies of the BNE. However, it is not sufficient for distinguishing polarizability from (positive or negative) hyperconjugation. The reason is that polarizability increases in proportion to the number of hydrogen atoms. Exceptionally, the series has been extended[12] to the substituent neopentyl, $CH_2C(CH_3)_3$, in which the two properties differ sharply. In the absence of experimental data we calculated the assumed gas-phase basicities by semiempirical methods. First, we tested our approach on the lower alkyls, methyl to *tert*-butyl. The calculated relative proton affinities of substituted benzaldehydes δE_{pa} (related to benzaldehyde), were compared with the experimental values[15] in Table 3. Generally, δE_{pa} values were badly underestimated, in PM3 more than in AM1. The disagreement justifies our decision to prefer experimental E_{pa} values in the calculated $\Delta_f H°$ of cations, Table 2, eqns. (8) and (9). Nevertheless, a reasonable estimate is possible using an empirical calibration line. Calibration was carried out with the four alkyl derivatives, separately for AM1 and PM3, the results were averaged. Corrected calibrated δE_{pa} values are also given in Table 3. The calibration lines do not go through the origin. Final agreement with experimental values is quite reasonable (the last two lines of Table 3). The E_{pa} of the neopentyl group was estimated to 25 ± 2 kJ mol^{-1}, not significantly greater than for *tert*-butyl. This value has been also plotted into Fig. 1 and lies with good accuracy on the respective line. (The necessary value of σ_α was calculated by a revised procedure[25] of the original method.[23]) We conclude from this approximate calculation that the effct of neopentyl is of the same order and probably slightly greater than that of *tert*-butyl: in no case is it of the same order as that of the ethyl group. This confirms that the variable effects of alkyl groups are better understood in terms of polarizability than of hyperconjugation.

Hyperconjugative effects on geometry

A proof of possible hyperconjugation was sought in high-level calculations of the benzylic cations **1** and **2** with comparison to the unsubstituted benzyl cation and to the corresponding neutral molecules, 1,4-dimethylbenzene and 1-methyl-4-*tert*-butylbenzene. A meaningful question may be only whether certain predictions from the formula **1b** can actually be observed in the real structure. Particularly some double-bond character of the $C-C(H_3)$ bond and some geometry changes

Table 1 Calculated and experimental enthalpies of formation of *para*-alkyl substituted benzaldehydes, styrenes, α-methylstyrenes and benzaldehyde-cyanohydrins (kJ mol^{-1}, 298 K)[a]

R =	H	CH_3	C_2H_5	Pr^i	Bu^t	CH_2Bu^t
RC_6H_5	92.14	60.29	36.12	19.72	15.24	−18.24
	98.13	*58.96*	*39.60*	*23.61*	*1.36*	*−19.41*
	[82.80]	[50.17]	[29.92]	[3.93]	[−24.2]	[−54.20]
RC_6H_4CHO	−37.33	−70.14	−94.28	−110.72	−115.37	−148.69
	−44.55	*−84.55*	*−103.72*	*−120.15*	*−142.24*	*−168.32*
	[−36.80]					
$RC_6H_4CH{=}CH_2$	161.80	129.66	105.52	89.08	84.48	
	163.93	*124.56*	*105.19*	*89.16*	*66.94*	
	[147.36]	[114.64]				
$RC_6H_4C(CH_3){=}CH_2$	135.60	103.51	79.37	62.93	58.37	
	131.59	*90.33*	*74.60*	*56.74*	*34.52*	
	[112.97]					
$RC_6H_4CH(OH)CN$	34.73	2.43	−21.63	−38.20	−42.80	
	67.40	*27.61*	*8.45*	*−7.78*	*−29.96*	
$RC_6H_4CH{=}OH^+$	668.19	628.70	604.34	587.63	579.80	546.58
	687.49	*645.82*	*627.71*	606.99	*585.66*	*559.18*

[a] Calculated by AM1, in italics by PM3, some experimental values are given in brackets, ref. 16.

Table 2 Calculated enthalpies of the isodesmic reactions, eqns. (6)–(11) (kJ mol^{-1}, 298 K)[a]

R =	CH_3	C_2H_5	Pr^i	Bu^t	CH_2Bu^t
Benzaldehydes, eqn. (6)	−1.0	−0.9	−0.9	−1.1	−1.0
	−0.8	*−0.7*	*−1.1*	*−0.9*	*−6.23*
Styrenes	−0.3	−0.3	−0.3	−0.4	
	−0.2	*−0.2*	*−0.3*	*−0.2*	
	[−0.7]				
Me-styrenes, eqn. (7)	−0.2	−0.2	−0.3	−0.3	
	−2.1	*1.5*	*−0.3*	*−0.3*	
Protonated benzaldehydes, eqn. (8)[b]	−18.7	−19.2	−22.1	−23.6	
	−18.9	*−19.4*	*−21.9*	*−23.8*	
Protonated Me-styrenes, eqn. (9)[b]	−17.0			−30.0	
	−15.1			*−30.0*	
Cyanohydrins, eqn. (10)	−0.5	−0.3	−0.5	−0.6	
	−0.6	*−0.4*	*−0.7*	*−0.6*	
Hydrocyanation, eqn. (11)	0.5	0.6	0.4	0.5	
	0.2	*0.3*	*0.4*	*0.3*	
	[1.7][c]	[1.5][c]	[1.4][c]	[1.3][c]	

[a] See Table 1. [b] Combined values from calculated ΔH°_6 or ΔH°_7 and experimental ΔH°_2 or ΔH°_3. [c] Experimental values in solution, ref. 10.

within the methyl group are predicted. The most important results of the calculations are presented in Table 4. There is no essential difference between the HF and MP2 results as far as the relative values of geometrical parameters are concerned. The improvement of energy values in MP2 is significant but the geometrical parameters are merely shifted and their relative values are little affected. Thus, we believe that the calculation level was sufficient for our purpose. The substituent effects can be observed on three levels.

First, there is an evident and strong conjugation between the positive charge with the benzene π-electrons in all three compounds. Simple counting of the resonance structures predicts the bond length order 1–2 < 2–3 < 6–1: the actual differences are *ca.* 0.03 Å. Very significant is also the double-bond character of the 6–12 bond. Also the angle 2–3–4 is widened as expected from a conjugation in the opposite position.[26,27] In terms of resonance structures, these features are consistent both with **1c**, **2c** and **1b**, **2b**.

Secondly, the substituent effect of the alkyl group is manifested by further shortening of the 1–2 and 6–12 bonds in **1** and **2** with respect to unsubstituted benzyl. The effect is of the order of 0.005 Å and practically equal for methyl and *tert*-butyl. It could be explained by contributions of **1b** and **2b** with similar weights in either case but this would not be consistent with the common concept of hyperconjugation appropriate only for C−H bonds. More likely, it is described as stabilization of **1c** and **2c** by the inductive effect of the alkyl groups. The angle 5–6–1 is reduced by introducing the alkyl groups in agreement with the additive scheme[28] (predicted difference −0.85°, ref. 28): no particular effect is observed.

Thirdly, the difference between methyl and *tert*-butyl derivatives is the most subtle effect, but most important for a possible proof of hyperconjugation. Shortening of the 3–9 bond by 0.02–0.03 Å in **1** could be attributed to hyperconjugation in the sense of the limiting formula **1b** if it were not the same effect when comparing the corresponding neutral molecules, 1,4-dimethylbenzene and 1-methyl-4-*tert*-butylbenzene, see Table 4, lower part. More significant proof was searched for in the geometry of the CH_3 group. The C−H bond lengths in **1** are not equal: the bond situated in a plane perpendicular to the benzene ring is somewhat weakened (0.006 Å longer). Even this effect can be traced to the neutral molecule but it is very weak there (0.002 Å). Also the C−C(H_3) bonds in **2** exhibit similar trends in HF calculations; in MP2 the Bu^t group is rotated so that one methyl group comes into the ring plane. Finally, the most significant changes were found in the H−C−H angles. The angle 16–9–17 between the two C−H bonds, which are nearer to the ring plane, is widened by 1.8°. This is definitely not observed either for **2** or for neutral 1,4-dimethylbenzene. All these changes, although rather small, are in good agreement with formula **1b**: one C−H bond is loosened and the remaining H atoms are approaching the position required by a sp^2 hybridization on C. We can conclude that formula **1b** is quite reasonable and may reflect certain detailed features of the actual structure. However, some of these features are also present in **2**. Furthermore, only some interaction of the methyl group with the benzene ring in **1** was documented, not the pertinent changes within this ring itself. One could expect shorter 1–2 and 4–5 bonds in **1** than in **2**, or smaller angles 2–3–4 and 5–6–1 angles, expected[27] for a donor–acceptor conjugation. This was not found.

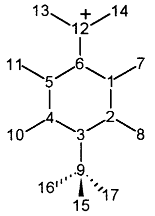
Conclusions

In our opinion, the three questions asked in the Introduction can be answered with some reliability. BNE is certainly due to solvation phenomena and is not observable in the gas phase. In solution, the best description would be in terms of steric hindrance to solvation. In this respect, it is merely the behaviour of *tert*-butyl derivatives which is more irregular than that of methyl derivatives. In the gas phase, the effect of *tert*-butyl is always the strongest within the classical series Me < Et < Pr^i < Bu^t but can be exceeded by neopentyl and by still larger groups. It is best described in terms of polarizability. In addition, there is another aspect of substituent effects that is con-

Table 3 Calculated and experimental relative proton affinities, δE_{pa}, of *para*-alkyl substituted benzaldehydes (kJ mol^{-1}, 298 K)

	CH_3	C_2H_5	Pr^i	Bu^t	CH_2Bu^t	Uncertainty
Calculated AM1	−6.7	−6.9	−7.2	−10.3	−10.3	0
Calibrated AM1	−19.5	−19.8	−20.2	−25.4	−25.4	1
Calculated PM3	−1.7	−0.5	−2.9	−4.1	−4.5	0
Calibrated PM3	−20.0	−18.2	−22.2	−23.9	−24.6	1
Calibrated average	−19.7	−19.0	−21.2	−24.6	−25.0	2
Experimental ref. 15	−18.8	−19.2	−22.2	−23.8		0.8

Table 4 Calculated geometries and energies of the benzylic cations[a]



	H (benzyl cation)		CH_3 (**1**)		Bu^t (**2**)		ΔBu^t–CH_3	
	HF[b]	MP[b]	HF[b]	MP[b]	HF[b]	MP[b]	HF[b]	MP[b]
Bond length/Å								
1–2	1.362	1.379	1.356	1.373	1.355	1.373	−0.001	0.000
2–3	1.403	1.408	1.415	1.416	1.420	1.423		
3–4	1.403	1.408	1.415	1.416	1.420	1.419		
4–5	1.362	1.379	1.356	1.373	1.355	1.376	−0.001	+0.003
5–6	1.436	1.437	1.439	1.436	1.438	1.436		
6–1	1.436	1.437	1.439	1.436	1.438	1.437		
3–9	1.076	1.084	1.496	1.489	1.527	1.509	+**0.031**	+**0.020**
6–12	1.357	1.373	1.352	1.369	1.351	1.370	−0.001	+0.001
9–15	—	—	**1.089**	**1.093**	1.550	1.543		
9–16	—	—	1.082	1.087	1.541	1.529		
9–17	—	—	1.082	1.087	1.541	1.543		
Angle (°)								
2–3–4	122.82	122.26	120.44	120.06	118.86	118.97	−1.58	−1.09
5–6–1	119.12	120.35	118.24	119.61	117.64	119.21	−0.60	−0.40
15–9–16	—	—	107.8	107.7	109.43	108.86		
15–9–17	—	—	107.9	107.7	109.43	109.57		
16–9–17	—	—	**109.6**	**109.5**	108.26	108.87		
Dihedral angle (°)								
2–3–9–15	—	—	−89.6	−89.2	−88.34	−59.36		
E total	−268.899 20	−269.795 62	−307.950 13	−309.032 98	−425.058 96	−426.547 66		
Corresponding neutral molecules:								
3–9			1.511	1.506	1.538	1.525	+**0.027**	+**0.019**
6–12			1.511	1.506	1.510	1.505	−0.001	−0.001
9–15			**1.086**	**1.091**	1.541	1.535		
15–9–16			107.8	107.6				
15–9–17			107.4	107.6				
16–9–17			**107.8**	**108.0**				
2–3–9–156			−60.3	−88.7				
E total			−308.793 80	−309.879 22	−425.900 89	−427.431 39		

[a] Bond lengths in Å, bond angles in degrees, energies in a.u. Calculated values of the remaining geometrical parameters can be obtained on request from the author for correspondence. [b] HF/6-31G** or MP2/6-31G**, respectively.

stant for all alkyl groups. Within the framework of correlation analysis it must be classified formally as a resonance effect since it is absent in aliphatic compounds (Fig. 1). In terms of resonance structures, it is best pictured by **1c** or **2c** with the inductive effect of alkyl groups contributing to the stability.

As expected from the beginning, all the effects of alkyl groups in the series are due to a lowered energy of the cations. Effects in neutral molecules are minute, not exceeding the possible uncertainty.

Finally, concerning the principle of hyperconjugation, it seems that the original intuitive proposal[7] was not completely unreasonable. Formula **1b** is a picture representing a few observable properties of the real structure. However, some of these properties are also present in **2b** or also in the corresponding neutral molecules. Most importantly, all these features are only seen in molecular geometry and have no measurable effects on the energies and reactivities. Note that our whole discussion of hyperconjugation has been restricted to its importance in benzyl cations and should not be extended to further compounds, such as enthalpies of formation of olefins.[11]

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