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Methyl Cation Affinity vs Proton Affinity in Substituted Benzenes: An ab Initio Study

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The proton (PA) and methyl cation (MCA) affinities of benzene and its di- and polysubstituted derivatives are examined at the MP2(fc)/6-31G**//HF/6-31G*+ZPE(HF/6-31G*) theoretical level. The calculated MCA of benzene is in good accordance with the experimental estimate. It is shown that MCAs of polysubstituted benzenes follow the additivity rule, which is analogous to the additivity property of PAs in multiply substituted aromatics. The additivity rule of thumb is based on the independent substituent approach (ISA). It exhibits a high performance being at the same time simple and intuitively appealing. Finally, conclusive evidence is provided which shows that the MCA of polysubstituted benzenes is linearly related to the corresponding proton affinities.

1. Introduction

A broad similarity between carbon and proton basicity has been a subject matter of permanent interest, and it was generally believed that the thermodynamic affinity for carbon parallels that for hydrogen atom.[1] However, there are many examples where the correlation between carbon and hydrogen basicity breaks down thus preventing reliable predictions to be made, if only one of them is known.[2] This is sometimes particularly dramatic in solutions, where H^+ and alkyl cations exhibit pronounced differences in their behavior. It is therefore of interest to examine the gas phase proton (PA) and the methyl cation (MCA) affinities in a series of closely related bases in order to shed more light on their genuine relationship. In addition, methyl cation is very interesting per se, since it plays important role in Friedel−Crafts alkylation reactions,[3] takes part in the interstellar chemical synthesis,[4] and seems to participate in carcinogenic processes by interacting with DNA.[5] Continuing our interest in absolute proton affinities of substituted aromatics,[6−10] we felt it worthwhile to extend our studies to MCAs of some aromatic systems in order to enable a direct comparison of these two closely related entities in a large and important family of organic compounds. In particular, we would like to explore intrinsic MCAs of polysubstituted aromatic compounds to test a simple and transparent additivity rule of thumb based on the independent substituent approximation (ISA), which proved extremely useful in reproducing and rationalizing PAs of multiply substituted benzenes and naphtalenes.[7−10] In the present paper we consider MCAs of mono and disubstituted benzenes in detail by using ab initio methods of intermediate level of sophistication. Additionally, pentafluoro and perfluoro substituted benzene are considered too as typical examples of polysubstituted aromatics. Finally, it should be mentioned that the estimated MCAs correspond to intrinsic absolute values related to dilute gas phase data.

2. Basic Definitions and Computational Details

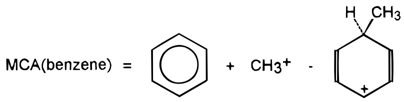
Proton and methyl cation affinities are calculated by using the general equation:

$$\mathrm{PA}(\mathrm{B}_\alpha) \qquad \text{or} \qquad \mathrm{MCA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha + (\Delta \mathrm{ZPE}_v)_\alpha \tag{1}$$

where for protonation $(\Delta E_{\mathrm{el}})_\alpha = [E(\mathrm{B}) - \mathrm{E}(\mathrm{B}_\alpha\mathrm{H}^+)]$ and $(\Delta \mathrm{ZPE}_v)_\alpha = [\mathrm{ZPE}(\mathrm{B}) - \mathrm{ZPE}(\mathrm{B}_\alpha\mathrm{H}^+)]$ are the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. Here, B and BH^+ denote the base in question and its conjugated acid, respectively, and α stands for the site of proton attack. Analogous expressions hold for MCA, where $\mathrm{B}_\alpha\mathrm{H}^+$ should be simply replaced by $\mathrm{B}_\alpha\mathrm{CH_3}^+$. The model widely employed earlier in calculating PAs was MP2(fc)/6-31G**//HF/6-31G*+ZPE(HF/6-31G*) procedure, which gave surprisingly good results as evidenced by comparison with reliable experimental data.[6−10] It involves optimization of all independent structural parameters at the HF/6-31G* level. True minima on the potential energy surfaces were verified by vibrational analyses, which were subsquently used for the zero point vibrational energy estimates ZPE_v. The latter were multiplyed by a common empirical weighting factor 0.89.[11] The electron correlation effect is estimated by the single point MP2(fc)/6-31G**//HF/6-31G* calculation. Hence, the applied method will be denoted heretofore as MP2. All computations are performed by using the Gaussian 94 program package.[12]

3. Results and Discussion

MCA of Benzene. The methyl cation affinity of benzene is of crucial importance since it serves as a reference level of MCA values of di- and polysubstituted benzenes. At the same time it will illustrate the basic difference between MCA and PA entities, the latter being defined for benzene as follows:



(2)

and

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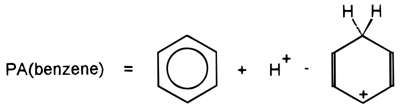
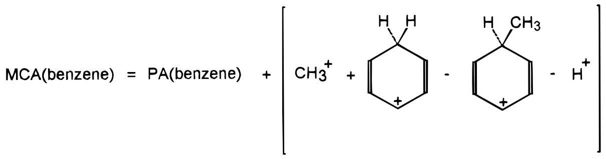


(3)

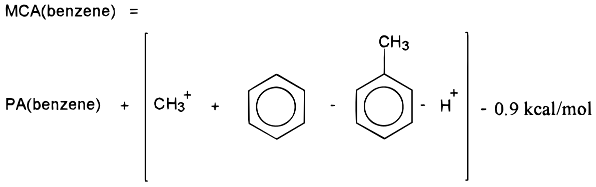
Combining these two equations one obtains:



(4)

It goes without saying that the structural formulas in eqs 2−4 stand for the total molecular energies of these systems. From the use of the MP2 model, the term within parentheses assumes a value −98.5 kcal/mol implying that MCA(benzene) is 81.4 kcal/mol, since the MP2 proton affinity of benzene exactly matches the experimental value of 179.9 kcal/mol.[7] It appears in general (vide infra) that MCAs parallel the corresponding PAs in substituted benzenes being lower on average by ∼97.5 kcal/mol.

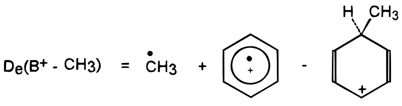
It is of interest to compare theoretical MCA(benzene) value with some experimental estimates of this entity. For this purpose it is useful to observe that PA(toluene)$_{ipso}$ is smaller than the PA(benzene) by −0.9 kcal/mol as obtained both by experiment[14] and theory.[7] By taking into account this finding, one can rewrite eq 4 in a more suitable form:



(5)

Since the experimental heats of formation of systems appearing within parenthesis are available,[15,16] one obtains that their sum assumes a value of −98.0 kcal/mol, implying that the experimental MCA(benzene) = 81.0 kcal/mol. It follows that experiment and theory are in good accordance, the difference being only 0.4 kcal/mol.

There is another interesting relations which interconnects MCAs and PAs and sheds additional light on the chemical similarity between the $\dot{C}H_3$ group and H atom. Since this is of wider chemical interest, it is briefly discussed here. Let us consider the following set of coupled eqs 6 and 8 by denoting benzene and toluene as B and T, respectively. The bond energy between the $\dot{C}H_3$ radical and the benzene cation B^+ is given by

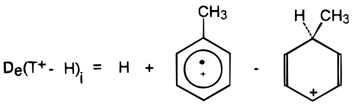


(6)

By combining eqs 2 and 6, one obtains:

$$\mathrm{MCA(B)} = [\mathrm{IP}(\dot{C}H_3) - \mathrm{IP(B)}] + D_e(B^+ - CH_3) \quad (7)$$

where IP stands for the first ionization potential. Furthermore, the bond energy between H atom and the toluene cation T^+, being attacked at the ipso position, is defined by



(8)

Here, the subscript i is related to the ipso protonation of toluene. It is easy to show that a close relation between PA(T)$_i$ and D_e(T^+ − H)$_i$ exists, which is analogous to that between MCA(B) and $D_e(B^+ - CH_3)$ given by eq 6:

$$\mathrm{PA(T)_i} = [\mathrm{IP(H)} - \mathrm{IP(T)}] + D_e(T^+ - H)_i \quad (9)$$

By introducing PA(B)−PA(B) into the right side of eq 7, taking into account that PA(T)$_i$ = PA(B) − 0.9 kcal/mol and employing eq 9, one obtains relation

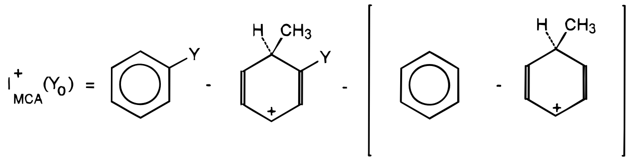
$$\mathrm{MCA(B)} = \mathrm{PA(B)} + [\mathrm{IP(T)} - \mathrm{IP(B)}] + [\mathrm{IP}(CH_3) - \mathrm{IP(H)}] + [D_e(B^+ - CH_3) - D_e(T^+ - H)_i] - 0.9\ \mathrm{kcal/mol} \quad (10)$$

Comparison of eqs 5 and 10 yields

$$[\mathrm{IP(T)} - \mathrm{IP(B)}] + [\mathrm{IP}(\dot{C}H_3) - \mathrm{IP(H)}] + [D_e(B^+ - CH_3) - D_e(T^+ - H)_i] = -98.0\ \mathrm{kcal/mol} \quad (11)$$

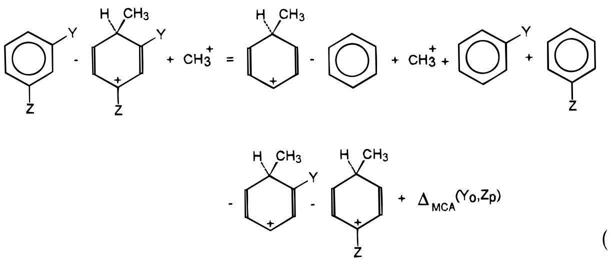
The experimental values of the ionization potentials in questions are known.[15] They assume the following values: IP(CH_3) = 9.84 eV, IP(H) = 13.6 eV, IP(B) = 9.26 eV, and IP(T) = 8.82 eV, which provides an estimate for the difference in the dissociation energies $D_e(B^+ - CH_3) - D_e(T^+ - H)_i = -1.5$ kcal/mol. In other words, dissociation of the CH_3 radical from benzene cation is by 1.5 kcal/mol less costly than cleavage of the ipso H atom leaving behind the toluene π-cation. Moreover, by taking into account experimental errors, this difference becomes practically insignificant . This finding is in accordance with a rich chemical experience that H atom and CH_3 group exhibit a high degree of chemical semblance. The same holds for their cations leading to an intimate relation between the gas phase PAs and MCAs of substituted benzenes as shown by the forthcomming analysis.

Methyl Cation Affinity Increments. MCA increment describes by definition a change in the methyl cation affinity of benzene caused by a particular substituent placed at the specific position within the aromatic ring:



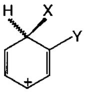
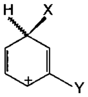
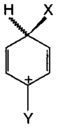
(12)

Here, the subscript o denotes the ortho position of the substituent Y. Analogous expressions hold for meta and para sites. Consider doubly substituted benzene ring. Employing the concept of homodesmic reactions,[17] one can write



(13)

TABLE 1: Increments for the Proton and Methyl Cation Attack in Monosubstituted Benzenes (in kcal/mol)

Cation		PA/I	Y=F	Y=CN	Y=OH	Y=CHO	$Y=CH_3$
	X=H	PA	179.4	166.8	193.1	172.8	186.3
		$I^+_{PA}(Y_o)$	-0.5	-13.1	13.1	-7.1	6.4
	$X=CH_3$	MCA	82.1	69.7	95.0	74.8	87.4
		$I^+_{MCA}(Y_o)$	0.7	-11.7	13.6	-6.6	6.0
	X=H	PA	172.6	164.1	179.9	171.2	183.0
		$I^+_{PA}(Y_m)$	-7.4	-15.9	-0.1	-8.7	3.1
	$X=CH_3$	MCA	74.4	66.1	81.4	73.0	84.5
		$I^+_{MCA}(Y_m)$	-7.0	-15.3	0.0	-8.4	3.1
	X=H	PA	181.6	166.8	195.5	171.6	187.4
		$I^+_{PA}(Y_p)$	1.7	-13.1	15.6	-8.4	7.5
	$X=CH_3$	MCA	83.3	68.8	97.1	73.3	88.7
		$I^+_{MCA}(Y_p)$	2.0	-12.6	15.7	-8.1	7.3

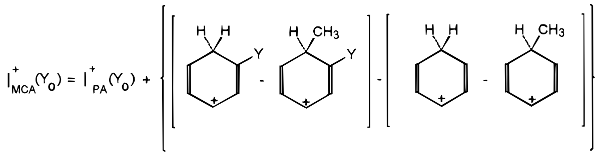
where $\Delta_{MCA}(Y_o, Z_p)$ stands for a difference in the interference energies between substituents Y_o and Z_p. It is easy to see that if $\Delta_{MCA}(Y_o, Z_p)$ would be zero, then the exact additivity of the substituent effects would hold, because eq 13 can be rewriten in the form

$$\mathrm{MCA(B-(Y_o, Z_p))} = \mathrm{MCA(benzene)} + I^+_{\mathrm{MCA}}(\mathrm{Y_o}) + I^+_{\mathrm{MCA}}(\mathrm{Z_p}) + \Delta_{\mathrm{MCA}}(\mathrm{Y_o, Z_p}) \quad (14)$$

where $(B - (Y_o, Z_p))$ signifies benzene substituted at the ortho and para positions relative to the CH_3^+ cation attack. In other words, $\Delta_{MCA}(Y_o, Z_p)$ represents deviation from the strict additivity, which in turn assumes a complete independence of the individual substituent effects. Generalization of formula 14 is straightforward:

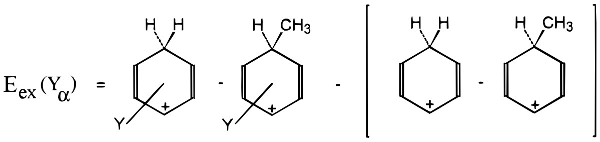
$$\mathrm{MCA(subst.benzene)} = \mathrm{MCA(benzene)} + \sum_X I^+_{\mathrm{MCA}}(X_\mu) + \Delta_{\mathrm{tot}} \quad (15)$$

where the summation is extended over all substituents and μ denotes their position relative to the methyl cation attack. It is also obvious that similar relation mutatis mutandis holds for aromatic systems other than benzene. One should also point out that the deviation from full addittivity in eq 14, $\Delta_{MCA}(Y_o, Z_p) = \delta^n_{MCA}(Y_o, Z_p) - \delta^+_{MCA}(Y_o, Z_p)$, is given by a difference of the interference energies appearing in the homodesmic reactions involving only neutral molecules ($\delta^n_{MCA}(Y_o, Z_p)$) and cationic systems ($\delta^+_{MCA}(Y_o, Z_p)$) of eq 13, respectively. It turns out that these two terms cancel out to a large extent as a rule (vide infra) thus leading to the success of the independent substituent aproximation (ISA) model embodied in eq 14. Increments of the MCA calculated by the MP2 model for substituents Y = F, CN, OH, CHO, and CH_3 are given in Table 1. They compare rather well with the corresponding increments in the proton affinity $I^+_{PA}(Y_\mu)$ (μ = o, m, p), although there are some differences of the second order. This similarity between $I^+_{MCA}(Y_\mu)$ and $I^+_{PA}(Y_\mu)$ calls for their more detailed analysis. If there is a simple relationship between these two types of increments, then it would be possible to express MCA of substituted benzenes in terms of the corresponding proton affinities via eqs 4, 14, and 15. Meticulous analysis of eq 12 reveals that it can be written in the following equivalent form:



(16)

In other words, the increment of the MCA is given by the corresponding proton affinity increment I^+_{PA} plus a change induced by replacing H atom by the CH_3 group. The latter is determined by a term given within the curly parentheses in eq 16. Quite generally one can denote conceived gedanken change of H atom by the CH_3 group as the exchange term



(17)

where α stands for ortho, meta, or para position of the substituent group Y. It is intuitively expected that this term is relatively small in view of the homodesmic character of the molecular systems in question. As an example we note in passing that the term $E_{ex}(Y_o)$ is 0.5 kcal/mol for substituent group Y = OH. It follows that by utilizing eqs 4, 16, and 17 one can transform relationship 14 into

$$\mathrm{MCA(B-(Y_o, Z_p))} = \mathrm{PA(benzene)} + I^+_{\mathrm{PA}}(\mathrm{Y_o}) + I^+_{\mathrm{PA}}(\mathrm{Z_p}) - 98.5 + E_{\mathrm{ex}}(\mathrm{Y_o, Z_p}) + \Delta_{\mathrm{MCA}}(\mathrm{Y_o, Z_p}) \quad \text{in kcal/mol} \quad (18)$$

where the exchange term arising due to a replacement of H atom by the CH_3 group. $E_{ex}(Y_o, Z_p)$ is given by a sum $E_{ex}(Y_o, Z_p) = E_{ex}(Y_o) + E_{ex}(Z_p)$. Generalization of the polysubstituted benzenes in analogy with eq 15 is straightforward and will be not discussed here. Again, the exchange term is not expected to be large. As an illustrative case we give a value of $E_{ex}(Y_o = CH_3, Z_p = CHO)$ which is as small as −0.1 kcal/mol. It appears also that $\Delta_{MCA}(Y_o, Z_p)$ terms are small in most cases. Concominantly, it turns out as a corollary that MCA is closely related to PA being smaller by roughly −98 kcal/mol on average (vide infra), the latter being related to the last three terms in eq 18. The present analysis resulting in eq 18 strongly indicates that the MCA should exhibit the same additivity feature as the proton affinity implying at the same time that the carbon basicity could be easily obtained from the hydrogen basicity as noted earlier by Brauman and Han[2] for a wide range of anions. This is indeed the case as discussed in the next section.

4. Additivity of MCA in Some Disubstituted and Polysubstituted Benzenes

The proton and methyl cation affinities of a number of disubstituted benzenes are displayed in Table 2. Substituents have been deliberately selected to cover a wide range of π-electron donor and acceptor groups. Survey of the present

TABLE 2: Proton Affinities (PAs) and Methyl Cation Affinities (MCAs) in Some Disubstituted Benzenes Obtained by the MP2 Model and the Additivity Rule of Thumb (in kcal/mol)

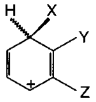
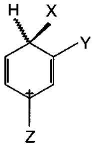
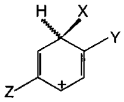
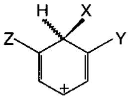
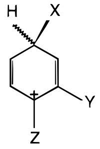
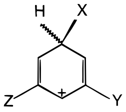
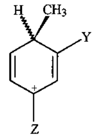
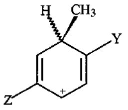
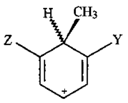
			Proton Affinity (X=H)			Methyl Cation Affinity (X=CH_3)		
Cation	Substituents		MP2	Add.	$\Delta_{PA}(Y,Z)$	MP2	Add.	$\Delta_{MCA}(Y,Z)$
	Y	**Z**						
	F	F	172.1	172.0	0.1	75.2	75.2	0.0
	CN	CN	153.9	151.0	2.9	57.4	54.5	2.9
	OH	OH	193.6	193.0	0.6	95.8	95.0	0.8
	CHO	CHO	166.0	164.1	1.9	68.0	66.4	1.6
	CH_3	CH_3	189.0	189.3	-0.3	89.6	90.5	-0.9
	F	CN	164.5	163.5	1.0	67.8	66.9	0.9
	F	OH	178.1	179.3	-1.2	80.8	82.2	-1.4
	CN	F	161.0	159.5	1.5	64.2	62.8	1.4
	CN	OH	167.6	166.8	0.8	70.5	69.8	0.6
	OH	F	185.9	185.7	0.2	88.2	88.0	0.2
	OH	CN	178.7	177.2	1.5	81.3	79.8	1.5
	F	F	181.1	181.1	0.0	83.9	84.1	-0.2
	CN	CN	155.8	153.7	2.1	59.3	57.1	2.2
	OH	OH	206.2	208.7	-2.5	107.8	110.7	-2.9
	CHO	CHO	164.3	164.4	-0.1	68.0	66.7	1.3
	CH_3	CH_3	193.2	193.7	-0.5	94.2	94.7	-0.5
	F	CN	166.7	166.3	0.4	69.9	69.5	0.4
	F	OH	194.5	195.0	-0.5	97.2	97.8	-0.6
	CN	F	168.9	168.6	0.3	72.0	71.7	0.3
	CN	OH	182.5	182.4	0.1	85.3	85.4	-0.1
	OH	F	194.0	194.8	-0.8	96.2	97.0	-0.8
	OH	CN	179.8	179.9	0.1	82.3	82.4	-0.1
	Y	**Z**						
	F	F	172.4	172.0	0.4	75.5	75.2	0.3
	CN	CN	152.4	151.0	1.4	56.0	54.5	1.5
	OH	OH	193.1	193.0	0.1	95.1	95.0	0.1
	CHO	CHO	163.5	164.1	-0.6	67.8	66.4	1.4
	CH_3	CH_3	189.2	189.3	-0.1	90.1	90.5	-0.4
	F	CN	164.4	163.5	0.9	67.7	66.9	0.8
	F	OH	179.6	179.3	0.3	82.3	82.2	0.1
	CN	F	160.0	159.5	0.5	63.3	62.8	0.5
	CN	OH	167.2	166.8	0.4	70.1	69.8	0.3
	OH	F	186.4	185.7	0.7	88.7	88.0	0.7
	OH	CN	177.2	177.2	0.0	79.6	79.8	-0.2
	F	F	178.3	178.9	-0.6	82.1	82.9	-0.8
	CN	CN	155.9	153.7	2.2	60.4	58.1	2.3
	OH	OH	203.1	206.2	-3.1	105.7	108.6	-2.9
	CHO	CHO	165.4	165.7	-0.3	67.5	68.1	-0.6
	CH_3	CH_3	192.2	192.6	-0.4	92.6	93.4	-0.8
	F	CN	167.1	166.3	0.8	71.3	70.5	0.8
	F	OH	191.3	192.5	-1.2	94.5	95.7	-1.3
	CN	OH	179.3	180.0	-0.7	83.9	83.3	0.6

TABLE 2: (Continued)

	Y	Z						
	F	F	175.0	174.3	0.7	77.0	76.4	0.6
	CN	CN	153.6	150.9	2.7	56.2	53.5	2.7
	OH	OH	197.6	195.5	2.1	99.0	97.1	1.9
	CHO	CHO	164.7	162.9	1.8	66.0	65.0	1.0
	CH_3	CH_3	189.5	190.4	-0.9	91.0	91.8	-0.8
	F	CN	160.8	159.4	1.4	63.2	61.8	1.4
	F	OH	189.5	188.1	1.4	91.2	90.1	1.1
	CN	F	166.8	165.8	1.0	69.1	68.1	1.0
	CN	OH	181.4	179.7	1.7	83.3	81.8	1.5
	OH	F	180.4	181.6	-1.2	81.1	83.4	-2.3
	OH	CN	167.1	166.7	0.4	68.0	68.8	-0.8
	F	F	165.6	165.2	0.4	67.8	67.5	0.3
	CN	CN	149.6	148.2	1.4	52.4	50.9	1.5
	OH	OH	180.4	179.8	0.6	82.1	81.5	0.6
	CHO	CHO	164.2	162.6	1.6	66.3	64.7	1.6
	CH_3	CH_3	186.0	186.1	-0.1	87.3	87.6	-0.3
	F	CN	157.1	156.7	0.4	59.6	59.2	0.4
	F	OH	173.1	172.5	0.6	75.1	74.5	0.6
	CN	OH	164.1	164.0	0.1	66.2	66.2	0.0

data shows that both PAs and MCAs exhibit remarkable additivity, as evidenced by low average absolute deviations $|\Delta_{av}|$ from full MP2 results. Specifically, they read as follows: $|\Delta(PA)_{av}| = 0.9$ and $|(MCA)_{av}| = 1.0$ in kcal/mol, implying that estimates of MCAs in disubstituted benzenes obtained by the additivity formula are somewhat less accurate than their coresponding PA values. Nevertheless, they are still good enough to be useful in predicting MCAs by the back-of-the-envelope calculation. Low average absolute errors do not mean that there are no larger additivity deviations in some cases. For instance, both PAs and MCAs predicted by the ISA additivity rule undershoots the ab initio results by roughly 3 kcal/mol if (CN_o, CN_m) distributions of CN groups take place. In order to get some insight into the origin of such deviation in MCA, let us consider substituents' interference energies $\delta^n_{MCA}(Y_\alpha, Z_\beta)$ and $\delta^+_{MCA}(Y_\alpha, Z_\beta)$ in the initial base and its CH_3^+ substituted species, respectively, as obtained by the corresponding homodesmic reactions. Some characteristic values are collected in Table 3. Perusal of the presented data reveals that the interference energies are reasonably small and positive in most cases. Since deviations from additivity are given by their difference $\Delta_{MCA}(Y_\alpha, Z_\beta) = \delta^n_{MCA}(Y\alpha, Z_\beta) - (\delta^+_{MCA}Y_\alpha, Z_\beta)$, it follows that good performance of the ISA additivity rule is at least partly due to partial cancellation of the interference energies. It appears also that $\delta^+_{MCA}(Y, Z)$ values in the CH_3^+ derivatives are higher than $\delta^n_{MCA}(Y, Z)$ values in the neutral parent compound as a rule, thus leading to negative $\Delta_{MCA}(Y, Z)$ values. This is plausible because CH_3^+ group interacts itself with substituents Y and Z increasing in this way the intramolecular interactions. Larger deviations from additivity in the MCA values are found in systems where disparity between δ^n_{MCA} and δ^+_{MCA} takes place. This is the case, for example, of dicyanobenzene (CN_o, CN_m) where $\delta^n_{MCA} = 3.9$ kcal/mol, whereas δ^+_{MCA} interference energiy assumes a value of only 1.0 kcal/mol. It is interesting to note that there is nothing unusual about double ortho substitutions in general. The additivity rule works in this case well, despite a fact that errors Δ_{MCA} are somewhat higher. However, appreciable interaction energies between ortho substituents and the carbon center attacked by the methyl cation were not found. This situation could be different if sizeable bulky groups were involved.

TABLE 3: Interference Energies Describing Interactions between Substituents in Initial Base and their Methyl Cation Substituted Species (in kcal/mol)

Compound	Substituents		$\delta^n_{MCA}(Y,Z)$	$\delta^+_{MCA}(Y,Z)$	$\Delta_{MCA}(Y,Z)$
	Y	Z			
	F	F	0.8	1.0	-0.2
	CN	CN	2.8	0.7	2.1
	OH	OH	0.2	3.0	-2.8
	CHO	CHO	1.0	-0.3	1.3
	F	CN	1.2	0.8	0.4
	F	F	1.3	1.0	0.3
	CN	CN	2.3	0.7	1.6
	OH	OH	1.3	1.2	0.1
	CHO	CHO	1.0	-0.4	1.4
	F	CN	0.8	0.0	0.8
	F	F	0.8	1.5	-0.7
	CN	CN	2.8	0.5	2.3
	OH	OH	0.2	3.1	-2.9
	CHO	CHO	1.0	1.7	-0.7
	F	CN	1.2	0.3	0.9

Although the performance of the ISA additivity rule for MCAs is quite satisfactory, there is a room for further quantitative improvement of this simple and intuitively appealing model. This is achieved by the least square fitting of MCA(add) estimates to the MCA results provided by the MP2 ab initio method. An excellent straight line is obtained (Figure

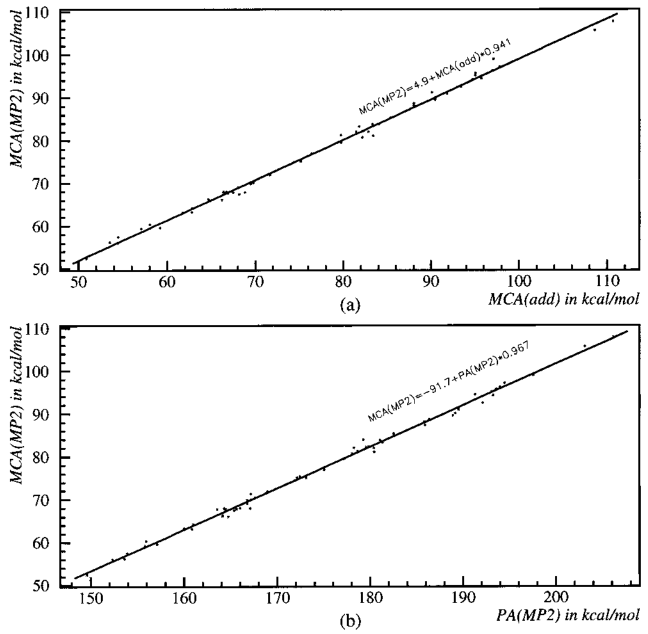


Figure 1. (a) Linear correlation between MCAs of substituted benzenes calculated by the MP2 theoretical model and estimated by the additivity formula. (b) Linear relation between the methyl cation affinities and proton affinities of substituted benzenes.

1a) as evidenced by the standard deviation $\sigma = 0.9$ kcal/mol and the correlation coefficient $R = 0.998$. It reads as

$$\mathrm{MCA(MP2)} = 4.9 + 0.941\ \mathrm{MCA(add)} \qquad \mathrm{kcal/mol} \quad (19)$$

Finally, it is of interest to have at hand a quantitative relationship between the MCA and the corresponding PA values. This linear dependence reads as

$$\mathrm{MCA(MP2)} = -91.7 + 0.967\mathrm{PA(MP2)} \qquad \mathrm{kcal/mol} \quad (20)$$

It is depicted in Figure 1b. Inspection of the graph in question and the corresponding statistical parameters (the average absolute error $|\Delta| = 0.7$ kcal/mol, the standard deviation $\sigma = 0.8$ kcal/mol, and the coefficient $R = 0.998$) reveal a very high correlativity between these two sets of important molecular properties. Consequently, it follows that, if the PAs of substituted benzenes are known, then the MCAs could be easily retrieved by using eq 20 and vice versa. It is plausible to assume that analogous linear relations hold in other aromatic systems.

It is in place to put the present results in the context of the existing knowledge. The most pertinent analysis is that of Brauman and Han.[2] They considered PA and MCA values of a large number of anions A^-, which enabled a use of the experimental enthalpies of formation $\Delta H_f^0(CH_3A)$ and $\Delta H_f^0(HA)$ of methylated and protonated species CH_3A and HA, respectively. By employing an experimental linear correlation between $\Delta H_f^0(CH_3A)$ and $\Delta H_f^0(HA)$, Brauman and Han[2] have been able to deduce a formula:

$$\mathrm{MCA}(A^-) = \mathrm{PA}(A^-) + 0.143\Delta H_f^0(\mathrm{HA}) - 101.7 \qquad \mathrm{kcal/mol} \quad (21)$$

which reproduced the experimental $\mathrm{MCA}(A^-)$ data with the standard deviation of 3 kcal/mol for a range of values over 100 kcal/mol. A salient feature of the formula (21) is that it has a unit slope dependence against $\mathrm{PA}(A^-)$, but it involves enthalpies $\Delta H_f^0(\mathrm{HA})$ of the protonated anions which are not necessarily constant. Our treatment of substituted benzenes represents a complementary study in a sense that neutral systems are protonated and methylated by H^+ and the CH_3^+ cation, respectively. In this case MCAs can be expressed as linear function of PAs alone via eqs 18 and 20 in contrast to the empirical eq 21 related to anions. We do not feel that inclusion of enthalpy of formation into eq 20 would lead to any improvement, particularly since ΔH_f^0 values are not easily deduced from the ab initio results alone.

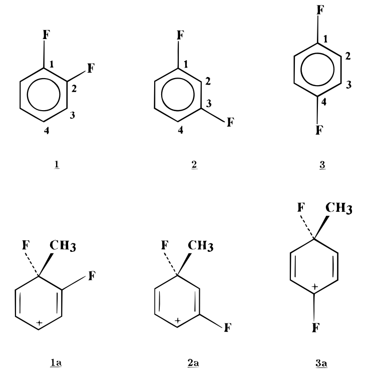
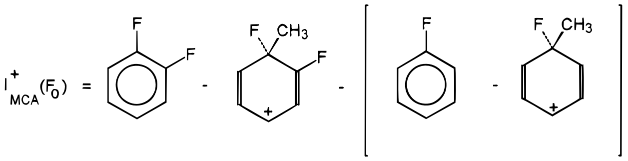


Figure 2. Characteristic molecules selected to describe ortho, meta, and para effect of the correspondingly substituted fluorine atoms on the ipso methyl cation affinity of fluorobenzene.

Methylation of pentafluoro- and perfluorobenzene by the CH_3^+ cation will shed some more light on the possible collective effect in heavily substituted aromatics. It should be stressed, however, that the ipso CH_3^+ attack on carbon atom linked to fluorine cannot be treated in a standard way as described earlier. It appears, namely, that an out-of-molecular-plane shift of fluorine atom leads to significant puckering of the benzene ring introducing in this way additional strain energy and an increased aromaticity defect.[18] Concominantly, the reference level should be changed accordingly. Instead of benzene, one should use the MCA of monofluorobenzene, where the CH_3^+ group is attached to the ipso carbon atom. Then the increment describing influence of the orto substituted fluorine is given by



(22)

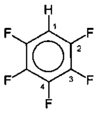
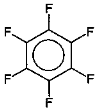
Analogous expressions offer increments for meta and para substituted fluorine atoms. The corresponding molecular systems are shematically shown in Figure 2. It is easy to show that the additivity formula for MCA of polyfluorinated benzenes takes the following form:

$$\mathrm{MCA[pfb]}_i = \mathrm{MCA[fluorobenzene]}_i + n_o I^+_{\mathrm{MCA}}(F_o)_i + n_m I^+_{\mathrm{MCA}}(F_m)_i + n_p I^+_{\mathrm{MCA}}(F_p)_i \quad (23)$$

where subscript i denotes the ipso methylation of the C−F bond. Here n_o, n_m, and n_p stand for numbers of fluorine atoms substituted at ortho, meta and para positions, respectively. The $I^+_{\mathrm{MCA}}(F_\alpha)_i$ increments (α = o, m, p) and the corresponding MCA values of pentafluoro and perfluorobenzenes obtained by the additivity formula 23 are given in Table 4.

It appears that the additivity rule of thumb works very well in highly fluorinated benzenes. Hence, it seems that the ISA model describes MCAs of heavily substituted benzenes in

TABLE 4: Increments for the Ipso Methyl Cation Attack in Polyfluorinated Benzenes and the Corresponding MCA Values Obtained by the Additivity Rule of Thumb and MP2 ab Initio Model (in kcal/mol)

Increments		**1a**	**2a**	**3a**
		$I^{+}_{MCA}(F_o)_i = 4.3$	$I^{+}_{MCA}(F_m)_i = -7.5$	$I^{+}_{MCA}(F_p)_i = 4.7$
MCA	Position	MP2	Add.	Δ
	C(2)	62.1	60.1	2.0
	C(3)	71.4	71.9	-0.5
	C(4)	60.6	60.3	0.3
	C(1)	65.2	64.4	0.8

satisfactory way implying that its extension to encompass other substituents and larger aromatic systems is highly desirable.

Finally, it is worth of mentioning that there is a fairly good correlation between MCAs calculated by the MP2 model with those estimated by the simple Hartree–Fock model:

$$\mathrm{MCA(MP2)} = 22.0 + 0.8902\mathrm{MCA(HF)} \quad \text{in kcal/mol} \quad (24)$$

The standard deviation of this correlation is $\sigma = 2.3$ kcal/mol with the corresponding coefficient $R = 0.985$. Hence, if only a rough estimate of the MCA is sufficient, then one can skip the single-point MP2 calculation, which in large systems might be very demanding. It should be stressed, however, that the simple additivity MCAs have higher correlativity with the MP2 results (viz. eq 19) and significantly lower standard deviation $\sigma = 0.9$ kcal/mol. Thus, it appears that the additivity rule of thumb works considerably better than the Hartree–Fock model. As a final comment we would like to point out that the contribution of the ZPE_v to MCAs is resonably constant being 4.5 kcal/mol on average. The average absolute deviation from this value is 0.5 kcal/mol.

5. Conclusion

The proton affinity and the methyl cation affinity of a number of substituted benzenes are considerd at the MP2 level of theory. It is shown that (a) The theoretical MCA value of benzene is in a good accordance with the experimental estimate. (b) The bond energy between the toluene cation and the H atom attached at the ipso position is comparable to that of the CH_3 group linked to the benzene cation. (c) The MCA values of benzene and its derivatives are lower by some 98 kcal/mol than the corresponding proton affinities. (d) The MCA of di- and polysubstituted benzenes follows mutatis mutandis the same additivity rule as that for the proton affinity which was found to be operative in large number of aromatic compounds.[6–10,19] (e) There is an excellent linear correlation between MCAs and PAs of substituted benzenes, which enables a quick estimate of one of these entities, if the other is known.

In view of the intimate relation between the MCAs and PAs it is plausible to assume that statements a–e hold quite generally for other alternant aromatic compounds and for a much wider selection of the substituent groups. It is also conceivable that affinities toward more bulky alkyl groups (e.g., tertiarybutyl cation, etc.) follow the same pattern. This work is in progress.

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