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Absolute proton affinities of some substituted toluenes: the additivity rule of thumb for *ipso* attack

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ABSTRACT: The problem of the *ipso* protonation of toluene and its predominantly disubstituted derivatives was considered by the MP2(fc)/6–31G**//HF/6–31G*+ZPE(HF/6–31G*) theoretical model. The substituents involved covered a wide range of different donor–acceptor capabilities. It is shown that the calculated MP2 *ipso* proton affinities of substituted toluenes follow *mutatis mutandis* the same additivity rule which was found earlier to be operative in polysubstituted benzenes, naphthalenes and biphenylenes. The additivity equation is both intuitively appealing and useful, being able to offer quantitative estimates of the proton affinity by very simple calculation. It is based on the concept of the increment, which in turn describes the influence of a single substituent on the proton affinity. Any substituent behaves as a rule as if the other were non-existent, thus giving rise to the independent substituent approximation (ISA). The performance of the additivity rule of thumb is very good, as evidenced by the average absolute deviation of 1 kcal mol^{-1}. Larger deviations are possible, but they rarely occur, being indicative of a difference in interactions between substituents in the initial neutral base and in the final cationic conjugate acid. Finally, it follows as a corollary of the present analysis that protonation *ipso* to the CH_3 group is never thermodynamically the most favourable site of proton attack in the benzene ring, provided that there is a single unsubstituted carbon atom within the aromatic moiety. The relevance of *ipso* protonation in persubstituted benzenes is briefly discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: *ipso* proton affinities; additivity; disubstituted toluenes

INTRODUCTION

Notwithstanding its small size, the proton occupies a very prominent position in organic chemistry and biochemistry, playing an important role in ubiquitous proton transfer reactions, catalysis, charge and mass transport processes in membranes, in determining the acid–base properties of compounds, etc.[1–3] The intrinsic absolute or 'dilute gas-phase' experimental proton affinities (*PA*s) serve as useful probes of the electronic structure and charge density distribution in molecules. In particular, *PA*s are closely related to the notion of the electrophilic substitution reactivity of aromatic compounds. Recently, we have shown that the *PA* is an indicator of the effect exerted on the aromatic nucleus by the annelated small rings in the so-called Mills–Nixon and in reversed Mills–Nixon systems.[4–8] Finally, comparison of the intrinsic *PA*s with those measured in solutions provides some information on the extent of the solvent–solute effects. It is therefore not surprising that the proton affinity is the subject of continuous research interest and that a lot of effort is devoted to its determination both in gas and liquid phases by experimental[9–14] and theoretical methods. The latter also proved useful in describing features of the very strong bases called the proton sponges.[15–17] Recently, we have conclusively shown that the MP2(fc)/6–31G**//HF/6–31G*+ZPE(HF/6–31G*) model reproduced the experimental *PA*s of a number of aromatic compounds such as benzene, naphthalene, biphenylene and their monosubstituted derivatives.[18] Moreover, it appears that the *PA* of polysubstituted aromatics follows a simple additivity rule based on the independent substitutent approximation (ISA) model.[18–22] This implies that the PA of a multiply substituted aromatic compound is easily retrieved if the effect of monosubstitutions is known in advance, which in turn are embodied in the corresponding increment. A high quantitative performance of this rule is remarkable for all positions within the ring except the *ipso* position. The latter requires a separate treatment involving a definition of a new origin of the scale measuring the substituent

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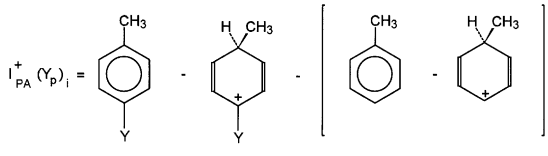
effects. To be more specific, the origin of the scale of *PA* values of polysubstituted benzenes is the proton affinity of a free parent benzene. In the case of *ipso* protonation, e.g. at the C—F bond in multiply substituted benzenes, however, the reference level is given by the *ipso PA* value of fluorobenzene.[23] In other words, increments of various other substituents are measured relative to the PA_{ipso} of monofluorobenzene. In this way the additivity rule is restored and actually works very well in polysubstituted fluorobenzenes.[23] In the present work we examined the *ipso* proton affinity of toluene and its polysubstituted derivatives involving F, CN, OH and CHO groups as substituents, which exhibit widely different electronic demands. It should be strongly pointed out that we consider here only the *ipso* proton attack in the ring. This should be kept in mind because the most favorable protonated species sometimes involve protonations at heteroatoms as in the case of CN and CHO groups.

THEORETICAL MODEL AND BASIC RELATIONSHIPS

All calculations were carried out by utilizing MP2(fc)/6–31G**//HF/6–31G*+ZPE(HF/6–31G*) approach (MP2 model), which happened to be a very good compromise between feasibility, economic costs and reliability.[17–23] Initial bases and their conjugate acids were optimized at the HF/6–31G* level and the minima on the potential energy surface were verified by vibrational analysis. The corresponding frequencies were used in estimating the zero-point vibrational energies, ZPE_v. The Hartree–Fock values are scaled by the customary common factor of 0.89. It should be pointed out that, once the theoretical model has been chosen, the results are independent of any experimental ladder of *PA* values existing in the literature. The *ipso* proton affinity of substituted toluenes were computed by employing a general equation:

$$PA(T_i) = (\Delta E_{el})_i - (\Delta ZPE_v)_i \qquad (1)$$

The concept of the PA increment is pivotal. It describes a change in the *ipso* PA of toluene due to a particular substituent placed at the specific position on the aromatic ring. For example:

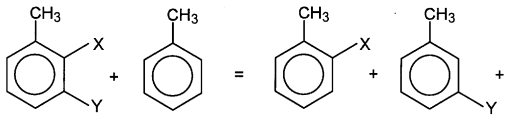


(2)

Here the subscript *p* denotes the *para* position of the substituent Y_p relative to the CH_3 group attachment, which coincides with the site of protonation at the same time. Analogous expressions hold for *ortho* and *meta* locations of substituents. Following the standard analysis available elsewhere,[18–23] one obtains

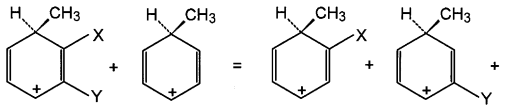
$$PA(\text{subst.toluene})_i = PA(\text{toluene})_i + n_o I^+_{PA}(X_o)_i + n_m I^+_{PA}(Y_m)_i + n_p I^+_{PA}(Z_p)_i + \Delta(X, Y, Z) \qquad (3)$$

where n_o, n_m and n_p denote numbers of *ortho*, *meta* and *para* substituents, respectively. Deviation from the strict additivity is given by Δ(X, Y, Z). Analysis of this entity is interesting. Let us suppose that toluene has only two substituents X_o and Y_m. Then $\Delta(X_o, Y_m)$ is given by the difference $\Delta(X_o,Y_m) = \delta(X_o, Y_m) - \delta^+(X_o, Y_m)$, where δ and δ^+ are defined by the homodesmic reactions[25]



(4)

and



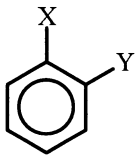
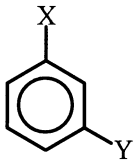
(5)

It appears that δ and δ^+ are usually small and positive entites as a rule, implying that their difference is an even smaller number, thus contributing to the very good performance of the simple additivity Eqn (3). All computations were performed using the GAUSSIAN 94 program.[24]

RESULTS AND DISCUSSION

The increments for the *ipso* protonation of singly substituted toluenes are compared with the corresponding increments of monosubstituted benzenes in Table 1. Similarity of these two sets of data is apparent, but it is important to note that $I^+_{PA}(Y)_i$ are usually slightly higher than their $I^+_{PA}(Y)$ counterparts. In this context, one should point out that the *PA* of toluene protonated at the *ipso* position is 0.9 kcal mol^{-1} (1 kcal = 4.184 kJ) lower [*PA*(toluene)$_i$ = 179.0 kcal mol^{-1}] than the *PA* of benzene, which is 179.9 kcal mol^{-1}.[19] We note in passing that the latter value is in excellent accord with the most recent experimental result which yields *PA* (benzene) = 180.0 kcal mol^{-1}.[10] The close similarity between these two *PA*s is a consequence of the fact that the out-of-plane shift of the CH_3 group on *ipso* protonation does not destroy the planarity of the benzene ring. A survey of the increments shows that there are two types of substituents. The first group, consisting of OH and CH_3 substituents, activates the *ipso* protonation of toluene, this being particularly pronounced if they are placed at the *ortho* and *para* positions. This feature is easily rationalized by the electron density releasing property alias π-back-donation of the OH group and by the well known hyperconjugative ability of the CH_3 group. The second class of substituents involves CN and

Table 1. Comparison of increments of the *PA* of monosubstituted benzenes with the corresponding entites related to the *ipso* protonated singly substituted toluenes as offered by the MP2 model (in kcal mol^{-1})

X	Y	$PA(X = CH_3)_i$	I^+_{PA} (Y)$_i$	PA(X = H)	I^+_{PA} (Y)
					
CH_3 or H	F	178.9	−0.1	179.4	−0.5
	CN	166.5	−12.5	166.8	−13.1
	OH	192.0	13.0	193.0	13.1
	CHO	173.3	−5.8	172.7	−7.2
	CH_3	185.1	6.1	186.2	6.3
					
CH_3 or H	F	172.0	−7.0	172.5	−7.4
	CN	163.4	−15.6	164.0	−15.9
	OH	179.1	0.1	179.9	0.0
	CHO	170.4	−8.6	171.8	−8.1
	CH_3	182.1	3.1	182.9	3.0
					
CH_3 or H	F	181.2	2.2	181.6	1.7
	CN	166.0	−13.0	166.7	−13.2
	OH	195.1	16.1	195.5	15.6
	CHO	170.6	−8.4	171.6	−8.3
	CH_3	186.4	7.4	187.3	7.4

CHO groups, which are strongly electron-demanding fragments, thus deactivating the *ipso* position towards the proton or, better expressed, to electrophilic substitution in general. This feature is particularly pronounced for the CN group, which is a very strong acceptor of both σ-and π-electrons. A borderline case is provided by fluorine, which weakly activates the *para* position and strongly deactivates the *meta* positioned CH_3 group. These characteristics determine the selectivity of the substituted toluenes towards protonation (see later). Before proceeding further, it is worth mentioning that the absolute *PA*s of monosubstituted benzenes are in excellent agreement with the most recent experimental data. This is described and discussed in Ref. 18 and will not be repeated here.

The absolute *PA*s of some disubstituted toluenes undergoing *ipso* attack calculated by the MP2 model are compared with the additivity values obtained by using Eqn (3) in Table 2. The degree of compatibility of these data is surprisingly high, as evidenced by the average absolute deviation from the additivity $|\Delta\ (Y, Z)|_{av} = |PA(MP2)_i - PA(add)_i|_{av} = 1.0$ kcal mol^{-1}. It follows that the *ipso PA* of disubstituted toluenes can be obtained by a very simple calculation. Although the average error $|\Delta\ (Y, Z)|_{av}$ is as low as 1 kcal mol^{-1}, it is in some cases large, *ca* 3 kcal mol^{-1}. These systems are particularly interesting and will be discussed later. The performance of the additivity equation can be somewhat improved by the least-squares fitting procedure:

$$PA(\mathrm{MP2}) = 8.8 + 0.952PA(\mathrm{add}) \qquad \text{in kcal/mol} \quad (6)$$

The straight line (Fig. 1) has a standard deviation $\sigma = 0.9$ and a correlation coefficient $r = 0.998$. The high corre-

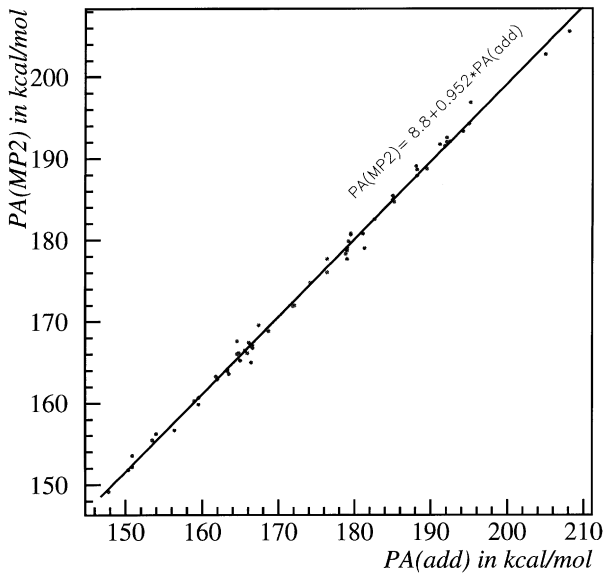
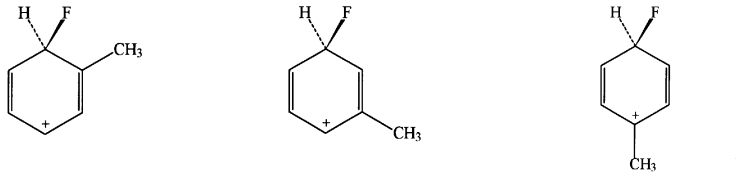


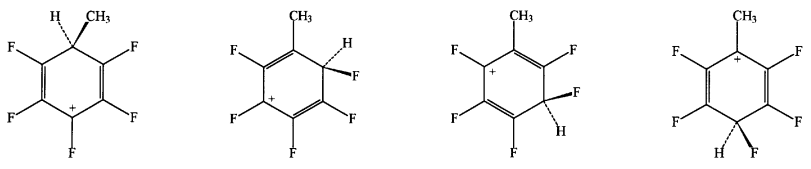
Figure 1. Linear correlation between the *ipso* proton affinity of polysubstituted benzenes as obtained by the MP2 model and the additivity rule

lativity shows that additivity of the *PA* is a genuine property. The increments given in Table 1 and the additivity Eqn (3) provide direct hints as to how one can increase the susceptibility of the *ipso* position of toluene towards electrophilic substitution. For instance, the largest *PA* in disubstituted toluenes is predicted in 2,4-dihydroxytoluene. By the same token one can considerably diminish the *ipso* reactivity by a deliberate choice and distribution of substituents around the aromatic fragment, e.g. in 2,5- and 3,4-dicyanotoluenes. Moreover, employing the increments for benzene and toluene (Table 1), it is possible to determine the most reactive sites in disubstituted toluenes towards electrophilic substitution. A couple of typical examples are given for illustrative purposes. Consider 2,3-dihydroxytoluene, which has one of the highest *ipso PA* values [$PA(\text{add})_i$ = 192.1]. It appears that all other unsubstituted carbon atoms of the aromatic ring have appreciably higher *PA*s: *PA* (C-4) = 200.4, *PA* (C-5) = 198.5 and *PA* (C-6) = 201.8 kcal mol^{-1}. Their variation is less pronounced, implying that interplay of substituents can sometimes substantionally decrease regioselectivity. Similarly, in 2,3-bis(formyl)toluene the *PA*s for C-1, C-4, C-5 and C-6 are 164.6, 172.0, 166.5 and 169.8 kcal mol^{-1}, respectively, as predicted by the additivity rule. Again, the *ipso* position is less favorable than other carbon atoms if those substituted by the strong electron-withdrawing groups are excluded (viz. the *ipso* protonation of fluorobenzenes[23]), presumably because of the benzene ring puckering caused by the out-of-plane shifts of the electronegative group. The reason why the *ipso* position of toluene is less energetically profitable is easy to understand. The methyl group considerably activates all positions (Table 1) except the *ipso* position, where the change in the *PA* induced by *ipso* attack is very small, being 0.9 kcal mol^{-1} [$PA(\text{toluene})_i$ = 179.0 kcal mol^{-1}]. In contrast, the CH_3 group stabilizes *ortho*, *meta* and *para* carbons by 6.3, 3.0 and 7.4 kcal mol^{-1}, respectively. It is therefore not surprising that *ipso* protonation in monosubstituted benzenes occurs only on rare occasions, one of them being in benzosilane.[26] However, the *ipso* protonation is important in, e.g., acid-catalyzed isomerization reactions of arylalkanes.[27] Obviously, the *ipso* protonation occurs in persubstituted benzenes where heteroatoms are not the most favorable



$I^{+}_{PA}[(CH_3)_o]_{F1} = 12.2$ $I^{+}_{PA}[(CH_3)_m]_{F1} = 7.2$ $I^{+}_{PA}[(CH_3)_p]_{F1} = 12.1$

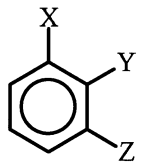
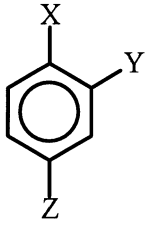
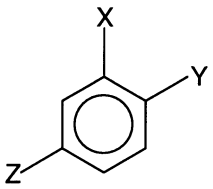
Scheme 1. Increments for the *ipso* protonation of fluorobenzene due to the *ortho*-, *meta*- and *para*-positioned methyl group (in kcal mol^{-1})



PA=176.3 PA=158.7 PA=163.3 PA=157.6

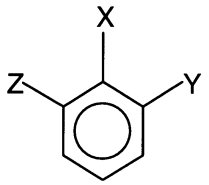
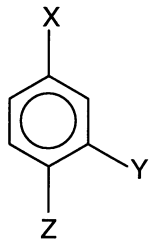
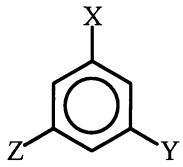
Scheme 2. Proton affinities of pentafluorinated toluene as estimated by the additivity equation (in kcal mol^{-1})

Table 2. Comparison of proton affinities of some disubstituted toluenes as obtained by the MP2 *ab initio* model and the additivity rule of thumb: deviations from the strict additivity $\Delta(Y, Z)$ are decomposed into $\delta(Y, Z)$ and $\delta^{+}(Y, Z)$ energies of interference (all entities in kcal mol^{-1})

X	Y	Z	$PA(X)_i$	PA(add)	$\Delta(Y, Z)$	$\delta(Y, Z)$	$\delta^{+}(Y, Z)$
							
CH_3	F	F	171.9	171.9	0.0	4.7	4.7
	CN	CN	153.5	150.9	2.6	3.7	1.0
	OH	OH	192.6	192.1	0.5	−1.1	−1.7
	CHO	CHO	167.6	164.6	3.0	5.4	2.3
	CH_3	CH_3	188.7	188.2	0.5	1.5	0.9
	F	CN	164.1	163.3	0.8	2.1	1.2
	F	OH	177.7	179.0	−1.3	0.6	1.9
	CN	F	160.7	159.5	1.2	1.9	0.7
	CN	OH	167.2	166.6	0.6	−1.3	−1.9
	OH	F	184.9	185.0	−0.1	0.4	0.4
	OH	CN	177.7	176.4	1.3	−1.3	−2.8
							
CH_3	F	F	180.8	181.1	−0.3	0.7	1.0
	CN	CN	155.5	153.5	2.0	2.8	0.7
	OH	OH	205.6	208.1	−2.5	0.6	3.0
	CHO	CHO	166.1	164.8	1.3	1.1	−0.3
	CH_3	CH_3	192.1	192.5	−0.4	0.0	0.4
	F	CN	166.2	165.9	0.3	1.1	0.8
	F	OH	194.3	195.0	−0.7	0.2	0.9
	CN	F	168.8	168.7	0.1	1.1	0.9
	CN	OH	182.6	182.6	0.0	0.0	0.0
	OH	F	193.4	194.2	−0.8	0.3	1.0
	OH	CN	178.7	179.0	−0.3	−0.1	0.0
							
CH_3	F	F	172.1	171.9	0.2	1.2	1.0
	CN	CN	152.2	150.9	1.3	2.1	0.7
	OH	OH	192.0	192.1	−0.1	1.2	1.2
	CHO	CHO	166.0	164.6	1.4	1.1	−0.4
	CH_3	CH_3	187.9	188.2	−0.3	0.1	0.4
	F	CN	163.9	163.3	0.6	0.7	0.0
	F	OH	179.1	179.0	0.1	1.1	1.0
	CN	F	159.8	159.5	0.3	0.7	0.3
	CN	OH	166.8	166.6	0.2	−0.4	−0.7
	OH	F	185.4	185.0	0.4	1.0	0.5
	OH	CN	176.0	176.4	0.4	−0.4	−0.2

Continued

Table 2. cont'd.

X	Y	Z	$PA(X)_i$	PA(add)	Δ(Y, Z)	δ(Y, Z)	δ^+(Y, Z)
							
CH_3	F	F	178.3	178.8	−0.5	1.1	1.5
	CN	CN	156.3	154.0	2.3	2.9	0.5
	OH	OH	202.8	205.0	−2.2	1.0	3.1
	CHO	CHO	169.6	167.4	2.2	3.8	1.7
	CH_3	CH_3	191.8	191.2	0.6	1.4	0.8
	F	CN	165.0	166.4	−1.4	−1.0	0.3
	F	OH	191.5	191.9	−0.4	1.3	1.5
	CN	OH	180.7	179.5	1.2	0.7	−0.7
							
CH_3	F	F	174.7	174.2	0.5	4.7	4.1
	CN	CN	151.8	150.4	1.4	2.9	1.3
	OH	OH	196.9	195.2	1.7	−1.1	−2.8
	CHO	CHO	162.9	162.0	0.9	3.9	2.9
	CH_3	CH_3	188.7	189.5	−0.8	0.1	0.8
	F	CN	160.3	159.0	1.3	2.1	0.8
	F	OH	189.1	188.1	1.0	0.5	−0.6
	CN	F	166.5	165.6	0.9	2.1	1.1
	CN	OH	180.8	179.5	1.3	−1.3	−2.7
	OH	F	179.0	181.3	−2.3	0.5	2.8
	OH	CN	167.4	166.1	1.3	1.0	−0.4
							
CH_3	F	F	165.3	165.0	0.3	0.7	0.4
	CN	CN	149.1	147.8	1.3	2.8	1.4
	OH	OH	179.9	179.2	0.7	0.3	−0.4
	CHO	CHO	163.3	161.8	1.5	1.0	−0.7
	CH_3	CH_3	184.7	185.2	−0.5	−0.3	0.2
	F	CN	156.6	156.4	0.2	1.1	0.7
	F	OH	172.0	172.1	−0.1	−0.4	−0.4
	CN	OH	163.6	163.5	0.1	0.1	−0.1

sites of attack, as for example in pentafluorinated toluene. Let us consider this case in more detail. For this purpose, we need the influence of the CH_3 group on *ipso* protonation in the C—F fragment. The corresponding increments I^{+}_{PA} $(CH_3)_{F_i}$ are given in Scheme 1.

It is noteworthy that CH_3 group significantly stabilizes the *ipso* protonation of the C—F carbon atom, particularly if it is attached at the *ortho* and *para* positions. Employing increments given in Table 1 and those published earlier,[23] one can easily deduce the proton affinities of pentafluorotoluene by using the additivity rule of thumb. The resulting *PA*s are given in Scheme 2.

It appears that the energetically most profitable *ipso* protonation occurs at the methyl group, as intuitively expected. Interestingly, one can easily deduce that protonation in pentamethylfluorobenzene will take place at the C—F carbon atom, which is a counter-intuitive result, the corresponding PA_i being 207.4 kcal mol^{-1}, whereas the *ipso* proton attack at *ortho*-, *meta*- and *para*-situated CH_3 groups yields *PA* values of 198.6, 194.7 and 199.6 kcal mol^{-1}, respectively. It is worth mentioning that protonation of some alkyl-substituted phenols in magic acid solutions may take place both at the alkoxy group and at the alkyl-substituted center.[28]

Finally, a general comment on the additivity is in place here. Perusal of the data in Table 2 shows that the deviations from additivity Δ (Y, Z) are small because δ(Y, Z) and δ^{+}(Y, Z) are of the same sign as a rule, thus cancelling out to considerable extent. If they are of opposite signs, then larger deviations might occur as in the case of 2-hydroxy-3-cyanotoluene.

CONCLUSION

It has been shown that the MP2(fc)/6–31G**//HF/6–31G*+ZPE(HF/6–31G*) model satisfactorily describes the *ipso* proton affinity of toluene and some of its di- and polysubstituted derivatives. The calculated *PA* (MP2) values can be successfully reproduced by the additivity rule based on the independent substituent approximation (ISA), which performs surprisingly well as evidenced by a large number of earlier applications[18–23] and by the present results. The average absolute deviation from additivity is 1 kcal mol^{-1}. Larger deviations are possible, but they rarely occur, being indicative of a difference in interactions between substituents in the initial neutral base and in the final cationic conjugate acid. An important outcome of the present analysis is the conclusion that protonation *ipso* to the methyl group is never thermodynamically the most favorable site of attack within the aromatic moiety, if a single unsubstituted carbon atom is available within the benzene ring. However, *ipso* protonation is very important in persubstituted benzenes and in acid-catalyzed isomerization reactions of arylalkanes.[27]

REFERENCES

1. R. P. Bell. *The Proton in Chemistry*. Cornell University Press, Ithaca, NY (1973).
2. R. Stewart. *The Proton: Applications to Organic Chemistry*. Academic Press, Orlando, FL (1985).
3. E. Caldin and V. Gold (Eds). *Proton-Transfer Reactions.* Chapman and Hall, London (1975).
4. M. Eckert-Maksić, Z. B. Maksić and M. Klessinger. *Int. J. Quant. Chem.* **49,** 383 (1994); *J. Chem. Soc., Perkin Trans. 2* 285 (1994).
5. M. Eckert-Maksić, W. M. F. Fabian, R. Janoschek and Z. B. Maksić. *J. Mol. Struct. (Theochem)* **338,** 1 (1995).
6. M. Eckert-Maksić, M. Klessinger, D. Kovaček and Z. B. Maksić. *J. Phys. Org. Chem.* **9,** 269 (1996).
7. Z. B. Maksić, D. Kovaček and B. Kovačević. *El. J. Theor. Chem.* **1,** 65 (1996).
8. M. Eckert-Maksić, Z. Glasovac, Z. B. Maksić and I. Zrinski. *J. Mol. Struct. (Theochem)* **366,** 173 (1996).
9. S. G. Lias, J. F. Liebman and R. D. Levin. *J. Phys. Chem. Ref. Data* **13,** 695 (1984).
10. (a) J. E. Szulejko and T. B. McMahon. *J. Am. Chem. Soc.* **115,** 7839 (1993); (b) E. Hunter. NIST, personal communication.
11. B. J. Smith and L. Radom. *J. Am. Chem. Soc.* **115,** 4885 (1993); *Chem. Phys. Lett.* **231,** 345 (1994).
12. A. K. Chandra and A. Goursot. *J. Phys. Chem.* **100,** 11596 (1996).
13. B. Amekraz, J. Tortajada, J. P. Morizur, A. I. González, O. Mó, M. Yañez, I. Leito, P. C. Maria and J. F. Gal. *New J. Chem.* **20,** 1011 (1996).
14. A. I. González, O. Mó, M. Yañez, E. Léon, J. Tortajada, J. P. Morizur, I. Leito, P. C. Maria and J. F. Gal. *J. Phys. Chem.* **100,** 10490 (1996).
15. J. A. Platts, S. T. Howard and K. Woźniak. *J. Org. Chem.* **59,** 4647 (1994).
16. J. A. Platts and S. T. Howard. *J. Org. Chem.* **61,** 4480 (1996).
17. B. Kovačević and Z. B. Maksić. *Chem. Phys. Lett.* **288,** 289 (1998).
18. Z. B. Maksić and M. Eckert-Maksić. in *Theoretical and Computational Chemistry*, edited by P. Politzer and Z. B. Maksić, Vol. 5, *Theoretical Organic Chemistry*, edited by C. Parkanyi, Elsevier, Amsterdam, (1998), p. 203.
19. M. Eckert-Maksić, M. Klessinger and Z. B. Maksić. *J. Phys. Org. Chem.* **8,** 435 (1995); *Chem. Eur. J.* **2,** 1251 (1996).
20. D. Kovaček, Z. B. Maksić and I. Novak. *J. Phys. Chem.* **101,** 1147 (1997).
21. M. Eckert-Maksić, M. Klessinger, I. Antol and Z. B. Maksić. *J. Phys. Org. Chem.* **10,** 415 (1997).
22. Z. B. Maksić, B. Kovačević and D. Kovaček. *J. Phys. Chem.* **101,** 7446 (1997).
23. Z. B. Maksić, M. Eckert-Maksić and M. Klessinger. *Chem. Phys. Lett.* **260,** 572 (1996).
24. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople. *Gaussian 94, Revision C.1.* Gaussian, I. Pittsburgh, PA (1995).
25. P. George, M. Trachtmann, C. W. Bock and A. M. Brett. *Tetrahedron* **32,** 313 (1976); *J. Chem. Soc., Perkin Trans.* 2 1222 (1976).
26. Z. B. Maksić, D. Kovaček and M. Primorac. in preparation.
27. G. A. Olah and A. Molnar. *Hydrocarbon Chemistry*. Wiley, New York (1995).
28. J. W. Larsen and M. Eckert-Maksić. *Croat. Chem. Acta* **45,** 503 (1973).

