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Proton affinity of substituted naphthalenes

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ABSTRACT: The absolute proton affinity (*PA*) of aromatic carbons of monosubstituted naphthalenes with CH_3, OH, CHO, NO_2 and Cl substituents was calculated at the MP2(fc)/6–31G**//HF/6–31G* + ZPVE(HF/6–31G*) level of theory. Increments corresponding to unsubstituted positions within the naphthalene skeleton were estimated. They can be used in estimating *PA*s of polysubstituted naphthalenes by using a simple additivity rule based on the independent substituent approximation (ISA). It is shown that increments are good indicators of the electrophilic substitution reactivity. The proton affinities of a large number of polysubstituted methylnaphthalenes was examined employing the additivity equation. It was found that the protonated forms, which exhibit the largest *PA*s, correspond to arenium ions observed by NMR spectroscopy in superacid media. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: proton affinity; substituted naphthalenes

INTRODUCTION

The absolute proton affinity (*PA*) is one of the most fundamental thermodynamic properties of bases. It is intimately related to the intrinsic (gas-phase) basicity, providing valuable hints about the electrophilic reactivity at the same time. Hence, gathering of information on *PA*s is an important but not always easy task. Both experiment and theory face some limitations in providing accurate *PA*s of large(r) molecules. The measured values are commonly obtained either by the bracketing (equilibrium) procedure[1] or from the metastable proton complexes (kinetic procedure) of two related bases.[2,3] In many cases the *PA*s estimated by these two approaches differ significantly beyond the error margin.[4] Moreover, experimental measurements offer the relative proton affinity (*RPA*), as a rule being related to the most reactive site only. On the other hand, theory is capable of providing very accurate *PA*s by the G2 method, but only for small(er) molecules.[5,6] Unfortunately, G2 and related methods cannot be applied to large molecules of chemical interest. However, there are simpler theoretical models, which represent a good compromise between accuracy and reliability on one side and feasibility on the other, thus extending the range of applications of the theory in leading to reliable *PA*s. One way is given by the use of the DFT formalism with large basis sets.[7,8] An alternative pathway is based on the HF/6–31G* optimization of structures followed by the single-point MP2 calculation, as will be discussed later.[9,10] Our relatively simple theoretical model gave results in excellent accordance with the best available experimental data for the first-row atoms. Furthermore, we have been able to show that *PA*s in heavily substituted benzenes follow a transparent rule rooted in the independent substituent approximation (ISA).[11] Preliminary results obtained for some disubstituted naphthalenes strongly indicate that a similar additivity rule holds in these aromatic systems too.[12,13] The purpose of the present work was twofold: (1) to provide *PA* increments for monosubstituted naphthalenes involving some of the most important functional groups in organic chemistry, which in turn will describe the variation in the proton affinity as a function of the position within the naphthalene perimeter, and (2) to illustrate the use of the ISA model in estimating the *PA*s of polysubstituted naphthalenes. The closely related electrophilic reactivity of these compounds will also be briefly discussed.

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BASIC DEFINITIONS AND COMPUTATIONAL DETAILS

Proton affinities are calculated employing the equation

$$PA(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha - (\Delta ZPVE)_\alpha \qquad (1)$$

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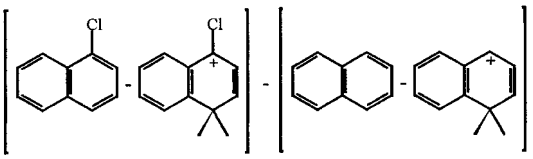
where $(\Delta E_{el})_\alpha = [E(B) - E(BH_\alpha^+)]$ and $(\Delta ZPVE)_\alpha = [ZPVE(B) - ZPVE(BH_\alpha^+)]$ are the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. In our case B represents naphthalene and BH_α^+ is its conjugate acid produced by protonation at position α. We have shown that the *PA* can be obtained from the additivity equation without a significant loss in accuracy:

$$PA(\text{subst. naphth.})_\nu = PA(\text{naphth.})_\nu + \Sigma_x I^+(X_\mu)_\nu \quad (2)$$

where μdenotes the position of the substituent and ν the protonation site. Summation is extended over all substituents X within a molecule, whereas increments $I^+(X_\mu)_\nu$ reflect a change in the *PA* at position ν, relative to the free naphthalene value, due to a substituent attached to the carbon atom C_μ. For example:

$I^+(Cl_\alpha)_4 =$ 

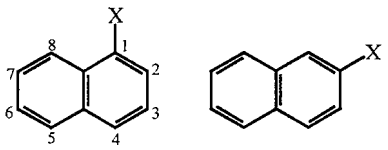
(3)

where chlorine is placed at the α-position 1.

The model of choice in our investigations of the *PA*s in aromatics is denoted by MP2(fc)/6–31G**//HF/6–31G* + ZPVE(HF/6–31G*). It implies optimization of all independent structural parameters at the HF/6–31G* level. Minima on the potential energy surface are verified by the vibrational analyses. The corresponding frequencies are used in estimates of the zero-point vibrational energies applying a common weighting factor of 0.89.[14] Finally, a single-point MP2(fc) calculation is carried out employing the 6–31G** basis set. This model in a shorthand notation will be denoted as MP2. Finally, the Gaussian 94 program[15] was utilized throughout this work.

RESULTS AND DISCUSSION

Total molecular and zero-point vibrational energies of studied bases denoted $n\alpha$ and $n\beta$ (n = 1–5) and depicted in Fig. 1, are summarized in Table 1. The corresponding values pertaining to their protonated forms are also given. A striking feature of the data presented is given by the fact that *ZPVE* contributions to the *PA* values denoted Δ*ZPVE*s are fairly constant. They cluster around 6.5 kcal mol^{-1} with an average absolute deviation of only 0.2 kcal mol^{-1}. (1 kcal = 4.184 kJ). It should be mentioned that singular deviations never exceed 0.8 kcal mol^{-1}. Employing the energies presented in Table 1 and the proton affinities of the parent naphthalene (194.8 and 190.5 kcal mol^{-1} for α and β sites, respectively[13]) one can deduce increments $I^+(X_\mu)_\nu$ for a large



X = CH_3; **1α** X = CH_3; **1β**
OH; **2α** OH; **2β**
CHO; **3α** CHO; **3β**
NO_2; **4α** NO_2; **4β**
Cl; **5α** Cl; **5β**

Figure 1. Schematic representation of α- and β-substituted naphthalenes

selection of widely different substituents encompassing CH_3, OH, CHO, CN, NO_2, F and Cl. They are collected in Table 2. In this connection it should be mentioned that we did not consider *ipso* protonation, because this requires a separate treatment.[16] The reason behind the different behavior of the *ipso*-protonated forms is given by a change in the mode of interaction between the aromatic fragment and the out of the molecular plane shifted substituent (group). A good example is provided by F atom in fluorobenzene, where *ipso* protonation produces puckering of the benzene ring, which in turn cannot be neglected.[16] However, the methyl group represents a notable exception as evidenced by the *ipso*-proton affinity of toluene. It is only by −0.9 kcal mol^{-1} lower than the *PA* value of free benzene.[17] Indeed, calculations have revealed that the out-of-plane shift of the methyl group in toluene leads to a negligible ring puckering dihedral angle (0.8°), which is compatible with the 'inertness' of the CH_3 group. Consequently, the *ipso* protonation of a C atom bonded to a methyl group can be treated as any other position within the aromatic moiety to a good approximation. It appears that increments for the *ipso*-protonated α-methyl- and β-methyl-naphthalene are −0.8 and −1.2 kcal mol^{-1}, respectively, thus being comparable to the $I^+(CH_3)_{ipso}$ in toluene of −0.9 kcal mol^{-1}. These increments will be used later in considering the protonation of highly methylated naphthalenes.

A survey of the increments discloses a picture which is in harmony with chemical experience gained in studies of the electrophilic reactivity of aromatics in general and benzene in particular.[18] This is not unexpected because the proton affinity is a good indicator of the susceptibility towards electrophilic substitution. For instance, we have conclusively shown that the *PA* values reproduce well the selectivity in the electrophilic reactions of benzene fused to small strained rings (Mills–Nixon effect), in good accordance with numerous experimental findings.[19–21] We shall show in the forthcoming discussion that the proton affinity is closely related to the orientational properties of various substituents, attached to the

Table 1. Total molecular energies *E* (a.u.) at the HF and MP2 levels of theory and zero-point vibrational energies [*ZPVE* (kcal mol^{-1})] of molecules *n*α and *n*β (*n* = 1–5) and their ring-protonated species

Molecule	*E*(HF)	*ZPVE*	*E*(MP2)	Molecule	*E*(HF)	*ZPVE*	*E*(MP2)
1α	−422.39084	105.0	−423.86288	**1**β	−422.39284	104.8	−423.86334
1α_1	−422.72527	112.0	−424.18321	**1**β_1	−422.73778	111.3	−424.19354
1α_2	−422.72854	111.3	−424.18481	**1**β_2	−422.72067	111.8	−424.17622
1α_3	−422.72259	111.5	−424.17987	**1**β_3	−422.72810	111.3	−424.18299
1α_4	−422.73542	111.4	−424.19165	**1**β_4	−422.72999	111.3	−424.18765
1α_5	−422.72906	111.6	−424.18599	**1**β_5	−422.73000	111.3	−424.18770
1α_6	−422.72113	111.4	−424.17981	**1**β_6	−422.72987	111.2	−424.18371
1α_7	−422.72450	111.4	−424.18006	**1**β_7	−422.72448	111.2	−424.18120
1α_8	−422.72850	111.4	−424.18783	**1**β_8	−422.73376	111.2	−424.18938
2α	−458.21027	91.0	−459.71262	**2**β	−458.20950	90.8	−459.71107
2α_2	−458.56086	98.2	−460.04972	**2**β_1	−458.56709	98.1	−460.05338
2α_3	−458.53745	97.5	−460.02774	**2**β_3	−458.54935	97.7	−460.03607
2α_4	−458.56944	98.3	−460.05725	**2**β_4	−458.53864	97.3	−460.03092
2α_5	−458.55374	98.2	−460.03435	**2**β_5	−458.54150	97.2	−460.03435
2α_6	−458.53431	97.1	−460.02866	**2**β_6	−458.55510	97.9	−460.03927
2α_7	−458.55005	97.7	−460.03458	**2**β_7	−458.53580	97.8	−460.02779
2α_8	−458.54519	97.4	−460.03794	**2**β_8	−458.55645	97.8	−460.04272
3α	−496.08212	94.4	−497.70068	**3**β	−496.08631	94.2	−497.70274
3α_2	−496.39264	100.4	−497.99910	**3**β_1	−496.40368	100.5	−498.00985
3α_3	−496.39719	100.5	−497.99955	**3**β_3	−496.40582	100.6	−498.00862
3α_4	−496.39672	100.5	−498.00476	**3**β_4	−496.40823	100.5	−498.00991
3α_5	−496.40017	100.5	−498.00704	**3**β_5	−496.41081	100.6	−498.01231
3α_6	−496.39881	100.6	−498.00000	**3**β_6	−496.40061	100.4	−498.00527
3α_7	−496.39381	100.4	−497.99976	**3**β_7	−496.40498	100.5	−498.00507
3α_8	−496.40542	100.7	−498.00843	**3**β_8	−496.40764	100.5	−498.01258
4α	−586.81895	90.6	−588.66587	**4**β	−586.82741	90.5	−588.67090
4α_2	−587.11681	96.7	−588.95740	**4**β_1	−587.13115	96.9	−588.96835
4α_3	−587.12640	96.9	−588.95999	**4**β_3	−587.13257	96.9	−588.96592
4α_4	−587.12124	96.5	−588.96470	**4**β_4	−587.13784	96.8	−588.96762
4α_5	−587.13340	96.8	−588.96921	**4**β_5	−587.14155	96.8	−588.97132
4α_6	−587.12654	96.7	−588.95894	**4**β_6	−587.12686	96.5	−588.90395
4α_7	−587.12573	96.7	−588.96121	**4**β_7	−587.13418	96.7	−588.96298
4α_8	−587.13924	96.9	−588.97154	**4**β_8	−587.13702	96.7	−588.97270
5α	−842.25294	82.8	−843.70034	**5**β	−842.25512	82.7	−843.70064
5α_2	−842.57655	89.3	−844.01389	**5**β_1	−842.58498	89.3	−844.02108
5α_3	−842.57207	89.2	−844.00549	**5**β_3	−842.57711	89.2	−844.00990
5α_4	−842.58271	89.3	−844.02104	**5**β_4	−842.57703	89.1	−844.00985
5α_5	−842.58039	89.2	−844.01479	**5**β_5	−842.58026	89.1	−844.01328
5α_6	−842.57132	89.4	−844.00556	**5**β_6	−842.57828	89.1	−844.01173
5α_7	−842.57455	89.1	−844.00829	**5**β_7	−842.57342	90.0	−844.00580
5α_8	−842.58146	89.2	−844.01604	**5**β_8	−842.58365	89.2	−844.01759

naphthalene moiety, in controlling the electrophilic attack. More specifically, higher *PA* values indicate higher yields of products in kinetically controlled reactions.

We commence discussion with the methyl substituent. It is useful to give *PA* increments of toluene for the sake of comparison; they are 6.3, 3.0 and 7.4 kcal mol^{-1} for *ortho*, *meta* and *para* protonation, respectively,[11] and represent a close similarity with the corresponding values in α-methylnaphthalene and for the C(1) and C(3) positions in β-methylnaphthalene (Table 2). It is well known that basicity of methylbenzenes increases with increasing number of CH_3 groups.[22] This was confirmed by a very good linear relationship[11] between the proton affinity of the family of methylated benzenes, obtained by the additivity rule, and the measured relative basicities of Brown and Brady.[23] Higher basicity implies enhanced electrophilic reactivity. It is found, for instance, that toluene is 10^4 times more reactive in the chlorination reaction than benzene under the same conditions.[24] By the same token one would expect increased basicity and consequently amplified electrophilic reactivity of α- and β-methylnaphthalenes. According to the calculated increments, positions 2 and 4 should be more reactive in α-methylnaphthalene than other carbon atoms of the ring. Similarly, position 1 should be by far the most reactive site in β-methylnaphthalene. This is indeed the case. Alcorn and Wells[25] found that nitration takes place

Table 2. Increments $I^+(X_\mu)_\nu$ (in kcal mol^{-1}) for monosubstituted naphthalenes where μ represents either the α-or β-position[a]

		Substituent						
Protonation site	Position	CH_3	OH	CHO	CN	NO_2	F	Cl
C(2)	α	5.2	13.8	−9.2	−12.0	−14.6	2.0	−0.2
C(3)		1.9	0.8	−9.1	−11.6	−11.7	−4.7	−5.4
C(4)		5.1	14.3	−10.1	−12.2	−14.9	2.4	−0.1
C(5)		1.5	−0.1	−8.7	−10.0	−12.6	−3.4	−3.9
C(6)		2.0	1.7	−8.9	−11.7	−12.7	−4.3	−5.6
C(7)		2.1	4.8	−8.8	−10.3	−13.4	−3.1	−3.6
C(8)		2.7	2.9	−8.0	−10.0	−11.6	−3.1	−3.1
C(1)	β	6.0	12.7	−8.4	−11.5	−13.7	1.1	−0.3
C(3)		3.6	6.5	−5.0	−10.4	−12.3	−2.6	−2.9
C(4)		2.2	−0.6	−8.3	−14.0	−13.2	−6.9	−7.2
C(5)		2.3	1.7	−6.9	−11.3	−10.7	−4.1	−5.0
C(6)		4.1	8.3	−6.9	−10.5	−12.3	−0.9	−1.7
C(7)		2.6	1.2	−7.1	−12.0	−11.3	−4.4	−6.3
C(8)		3.4	6.3	−6.7	−10.1	−9.3	−1.6	−2.4

[a] The absolute proton affinities are obtained by adding each increment to the *PA* of the parent naphthalene. The latter values are 194.8 and 190.5 kcal mol^{-1} for positions 1 and 2, respectively.

predominantly at position 4 in the former compound followed by NO_2 substitutions at positions 2 and 8 depending on the method applied. In β-methylnaphthalene position 1 is by far the most favorable.[25] Further, bromination of α-methylnaphthalene yields 70% of the 4-bromo derivative.[26] Analogously, bromination of β-methylnaphthalene gives the 1-bromo derivative as found by Adams and Binder.[27]

The hydroxy group is another substituent which activates virtually all carbon atoms belonging to the naphthalene perimeter with two notable exceptions: positions 5 and 4 in α-and β-methylnaphthalenes, respectively. Deactivation of these carbons relative to the parent naphthalene is almost negligible. More importantly, the variation in increments related to the OH group is much more pronounced than for the previous CH_3 substituent. This leads to a stronger directional effect. Early work showed that 2-naphthol upon chlorination yields 1-chloro-2-naphthol.[28] More recent quantitative measurements of the distribution of isomers obtained by nitration are related to methoxynaphthalenes.[29] These results are expected to hold for hydroxynaphthalenes also, in view of the same mode of interaction between OH and OCH_3 groups with the aromatic fragment. The underlying mechanism is that of lone pair back-bonding of the oxygen atom, which donates some electron density to the π-aromatic manifold. This effect is stronger for the OCH_3 group owing to the additional reservoir of electron density provided by the methyl group, but essentials of the interaction are qualitatively and persistently the same. Gas chromatographic analyses have shown that the 4-nitro-α-methoxynaphthalene derivative appeared in amounts between 75 and 90%. For β-methoxynaphthalene the 1-NO_2 isomer was produced in 70% yield, whereas the remaining 30% of products was distributed over 6-NO_2 and 8-NO_2 derivatives.[29] These findings are in agreement with calculated increments of the OH group (Table 2). Finally, it should be pointed out that the protonated forms 1-H^+-β-naphthol and 4-H^+-α-naphthol have been observed in superacids by Olah *et al*.[30]

Formyl, cyano and nitro groups belong to a family of strongly electron-withdrawing substituents, which considerably deactivate an aromatic nucleus.[18] This is also evident from inspection of their increments, which assume low negative values. It is generally believed that these substituents retard the first ring much more than the unsubstituted ring.[31] This conjecture is not completely correct, as evidenced by the presented increments, which do not exhibit appreciable variation. In fact, they are almost uniformly distributed over both rings, with very few exceptions. Hence one can safely say that the substitution reactions in general will occur with considerably more difficulty than in a free naphthalene. Nevertheless, some regiospecific selectivity can be observed as determined by the least deactivated sites. As an illustrative example we mention that nitration of α-nitronaphthalene gives 1,8- and 1,5-dinitronaphthalenes.[31] Further, it was found that both α- and β-formylnapththalenes give 8-NO_2 derivatives,[32] in accordance with the corresponding increments. Nitration of position 3 in β-formylnaphthalene is obviously unfavorable owing to the proximity of the CHO and NO_2 groups.

F and Cl atoms exhibit ambivalent behavior. They mildly deactivate carbon atoms of the naphthalene ring, with a few notable exceptions. The latter encompass positions 2 and 4 in α-fluoronaphthalene and position 1 in β-fluoronaphthalene. It is therefore not surprising that the protonated species were captured with the proton almost exclusively at position 4 in α-halonaphthalenes and

position 1 for β-fluoronaphthalenes.[33] Similarly, nitration of β-halonaphthalenes takes place at position 1.[31]

In the last section we consider the reactivity of di- and multi-substituted naphthalenes. In order to obtain the resulting combined increments, one makes use of the additivity rule. For example, examination of the total increments in 1-nitro-β-methylnaphthalene shows that the largest increment of -8.2 kcal mol^{-1} is related to position 8. Additional nitration of this compound gives a derivative with the second NO_2 attached to the C(8) carbon.[31] Analogously, dinitration of β-hydroxynaphthalene yields the dinitro derivative with NO_2 groups placed at positions 1 and 6 in accordance with increment analysis.

Sulfonation of tri- and tetramethylnaphthalenes[34] yields the most abundant derivative in accordance with the sum of the CH_3 group increments given in Table 2 in all but two cases: 1,4,5-trimethyl- and 1,6,7-trimethylnaphthalene. In these systems the —HSO_3 group apparently prefers a benzene fragment possessing more CH_3 substituents owing to a specific interaction. *Ipso* sulfonation does not take place since the positive increment of one methyl group would be lost and replaced by small but negative increment for the proton *ipso* attack (see above).

Finally, we consider here the most stable protonated forms of methylated naphthalenes, which have been studied in superacid media by NMR spectroscopy.[35] Absolute proton affinities obtained by the additivity Eqn. (2) are given in Table 3. Values corresponding to the arenium ions observed in experiments are marked with asterisks. It appears that the ionic form occurring under the experimental conditions upon protonation corresponds to the largest absolute proton affinity, as one would intuitively expect. There are some cases where two (or more) different protonated species of the same compound are identified. They again correspond to the highest *PA* values for that molecule. Only one discrepancy was found for 1,4,6,7-tetramethylnaphthalene. Here the *ipso* protonation at positions 1 and 4 becomes competitive, but this was not corroborated by experiments. Moreover, the largest *PA* value is associated with position 5, which was not identified either. The origin behind this discrepancy is not clear, but each rule has its exceptions. We note in passing that the highest *PA* and related basicity are found in heptamethylnaphthalene. The position most susceptible to the proton attack is the unsubstituted carbon atom C(8) for reasons discussed above. A slightly lower proton affinity is estimated in octamethylnaphthalene. The data presented in Table 3 nicely illustrate that basicity increases with increasing number of methyl groups. It is remarkable that the theoretical results obtained for isolated molecules reflect much of the electrophilic reactivity found in condensed phases exhibiting strong polar medium effects. This finding deserves further theoretical efforts in estimating explicitly the solvent effects in these systems. It is gratifying that the gas-phase results offer useful information on the reactivity in solvents, at least at the qualitative level.

CONCLUSION

The calculated absolute proton affinity of monosubstituted naphthalenes pertaining to the carbon atoms of the ring exhibits variations which strongly depend on the nature of the substituent. They are much more pronounced for electrodative than for electrocaptive substituents. Changes in *PA* values relative to naphthalene taken as the reference compound are conveniently described by increments $I^{+}(X_{\mu})_{\nu}$. They depend on the position of the substituent on the naphthalene skeleton and on the site of the proton attack. According to increments the studied substituents can be divided in three groups: (1) those which activate practically all naphthalene carbon atoms except the *ipso* position, typical representatives being electron-releasing groups such as CH_3 and OH; (2) substituents which deactivate all ring positions because of their considerable σ- and π-electron withdrawing power, as exemplified by CHO, CN and NO_2; and (3) the ambivalent halogen F and Cl atoms, which are strong σ-acceptors and weak π-electron donors. Hence it appears that present results are in harmony with a rich empirical knowledge.[18] However, distributions of the *PA* increments over the naphthalene framework offer more quantitative information. It is shown that increments in mono- and disubstituted naphthalenes generally reflect the regioselectivity of substituents in electrophilic reactions. In particular, they are able to predict the most abundant product in these reactions as a rule, if the latter are kinetically controlled. It should be kept in mind, however, that the distribution of resulting isomers in electrophilic reactions sometimes depends critically on the type of reactants.[36] It is shown that arenium ions produced by protonation of polysubstituted methylnaphthalenes and experimentally observed are those isomers which correspond to the highest *PA* values. Theoretical predictions are in accordance with NMR measurements of these persistent cations identified in superacid media.[33,35] Hence *PA* increments can be employed, if handled with due care, in predicting sites of electrophilic attack in substituted methylnaphthalenes. In particular, there should be a close linear relationship between the *PA*s estimated by the additivity rule and the basicity of these compounds.

As a final comment, a relation to the early concept of a cation localization energy L_{ν}^{+} should be mentioned. The latter was introduced by Wheland[37] as a reactivity index related to the formation of σ-complexes in electrophilic reactions. It can be shown that L_1^{+} and L_2^{+}, e.g. in naphthalene, assume values 2.30(β) and 2.48(β), respectively within the HMO model.[38] Since smaller L_{ν}^{+} energy implies less severe perturbation of the initial

Table 3. Proton affinities (in kcal mol^{-1}) as obtained by the additivity Eqn. (2)[a]

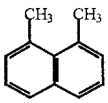
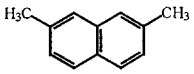
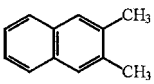
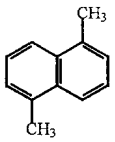
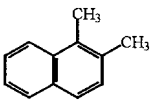
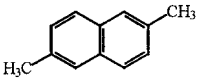
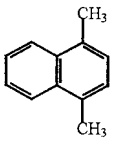
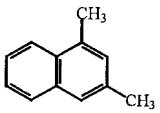
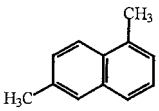
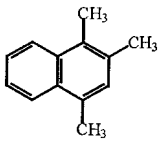
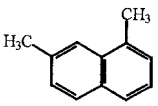
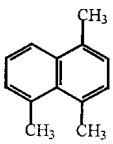
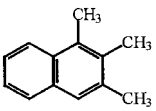
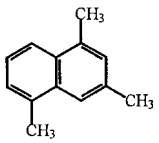
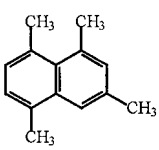
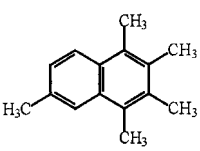
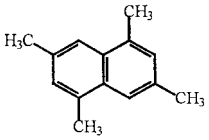
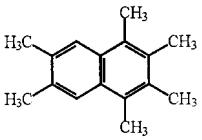
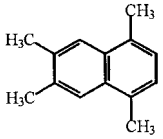
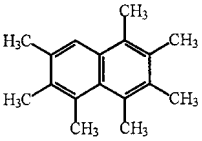
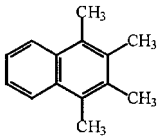
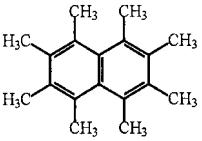
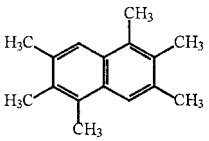
Molecule	Atom-H$^+$	PA_{ad}[b]	Molecule	Atom-H$^+$	PA_{ad}[b]
	C(1)	196.7		C(1)	204.2*
	C(2)	197.8		C(2)	191.9
	C(3)	194.4		C(3)	198.2
	C(4)	201.4*		C(4)	199.3
	C(1)	203.0*		C(1)	195.5
	C(2)	192.9		C(2)	197.7
	C(5)	200.5		C(3)	194.5
	C(6)	197.2		C(4)	202.6*
	C(1)	200.0		C(1)	204.9*
	C(2)	194.5		C(2)	193.4
	C(3)	196.0		C(3)	196.7
	C(4)	202.1*		C(4)	200.4
	C(5)	198.6			
	C(6)	196.6			
	C(7)	195.2			
	C(8)	200.9			
	C(1)	199.1*		C(1)	196.2
	C(2)	197.6		C(2)	199.3
	C(5)	199.0		C(3)	191.2
	C(6)	194.6		C(4)	205.9*
				C(5)	199.7
				C(6)	195.1
				C(7)	196.7
				C(8)	199.8
	C(1)	196.3		C(1)	205.1*
	C(2)	199.8		C(2)	196.4
	C(3)	195.0		C(3)	201.2
	C(4)	203.3*		C(4)	201.3
	C(5)	202.3		C(5)	201.3
	C(6)	191.3		C(6)	198.7
	C(7)	196.2		C(7)	197.2
	C(8)	199.7		C(8)	202.4
	C(1)	197.4		C(1)	200.6
	C(2)	198.4		C(2)	199.6
	C(3)	196.5		C(3)	199.7
	C(4)	202.2*		C(4)	201.8
	C(5)	198.5		C(5)	198.2
	C(6)	196.1		C(6)	199.8
	C(7)	191.4		C(7)	196.5
	C(8)	203.5*		C(8)	204.1*
	C(1)	202.2		C(1)	197.7
	C(2)	198.1		C(2)	201.3
	C(3)	194.8		C(3)	193.3
	C(4)	208.1*		C(4)	208.6*
	C(5)	202.0		C(5)	198.9
	C(6)	199.2		C(6)	200.3
	C(7)	199.3		C(7)	198.6
	C(8)	203.2		C(8)	204.6
	C(1)	200.4		C(1)	209.3
	C(2)	203.4		C(2)	204.1
	C(3)	195.3		C(3)	202.6
	C(4)	210.1*		C(4)	210.7*
	C(5)	204.0		C(5)	210.7*
	C(6)	202.2		C(6)	200.1
	C(7)	203.8		C(7)	204.9
	C(8)	204.1		C(8)	206.9

Table 3. Continued

Molecule	Atom-H^+	PA_{ad}[b]	Molecule	Atom-H^+	PA_{ad}[b]
	C(1)	201.1		C(1)	213.0*
	C(2)	203.9		C(2)	206.7
	C(3)	197.4		C(5)	212.9
	C(4)	210.6*		C(6)	203.7
	C(1)	204.8		C(1)	214.5
	C(2)	204.3*		C(2)	208.7
	C(5)	207.2		C(3)	208.8
	C(6)	197.0		C(4)	215.7
				C(5)	212.1
				C(6)	207.5
				C(7)	205.6
				C(8)	218.0*
	C(1)	207.3*		C(1)	217.2*
	C(2)	200.0		C(2)	210.8
	C(5)	204.7			
	C(6)	201.3			
	C(1)	209.4			
	C(2)	206.9			
	C(3)	203.6			
	C(4)	216.5*			

[a] The proton affinity of naphthalene is 194.8 kcal mol^{-1} and corresponds to the α-proton attack. β-Protonation yields a lower value of 190.5 kcal mol^{-1}.
[b] The protonated sites observed in NMR experiments are marked with asterisks.

π-system, it follows that the electrophilic reactivity of position 1 in naphthalene is more pronounced. This is in accordance with the reactivity studies and the proton affinity values *PA*(1) and *PA*(2). In principle, one could make a comparison between $L^+(X_\mu)_\nu$ values in substituted naphthalenes and the corresponding *PA* increments. The problem is that heteroatoms have to be parametrized in the HMO model, which is always more or less arbitrary. It is possible to select parameters for various substituents such that $L^+(X_\mu)_\nu$ values become compatible with increments $I^+(X_\mu)_\nu$, but such an effort would not pay off since both semiempirical and simplified *ab initio* models are feasible in large systems nowadays.

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