Additivity of the Proton Affinity in Aromatics: Fluorinated Naphthalenes[⊥]

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Received: July 1, 1996; In Final Form: November 13, 1996[⊗]

Absolute proton affinities (PAs) of fluorinated naphthalenes and their additivity are considered theoretically by utilizing the MP2(fc)/6-31G**//HF/6-31G*+ZPE(HF/6-31G*) model. The hierarchy of the PAs in the parent naphthalene compound $(PA)_1 > (PA)_2 > (PA)_{8a}$, where subscripts denote sites of the protonation, is interpreted in terms of the aromaticity defect. Since the fluorine substitution influences PA values in remote parts of the molecular systems, it is concluded that the long range interactions in fluorine derivatives are transmitted via the mobile π-electrons thus giving rise to significant resonance effects. It is also shown that the additivity formula based on the independent substituent approach works very well in polysubstituted naphthalenes as evidenced by a very small average absolute deviation, with one notable exception—protonation at the ipso-position. In this case the out-of-plane bending of the C−F bond leads to considerable puckering of the aromatic ring which is not present in the parent naphthalene. Consequently, the influence of a substituent on the PA at the same carbon center cannot be considered a small perturbation which results in deviations from the strict additivity. Finally, it should be pointed out that low PA values for ipso-protonation are compatible with the (per)fluoro effect. The origin of the additivity is briefly considered. It appears that it is a consequence of cancellation of the many-body effects in the initial (base) and final (conjugated acid) states. The same formula of additivity (*mutatis mutandis*) should be applicable in other polysubstituted aromatics.

1. Introduction

Proton transfer reactions play a very important role in chemistry and biochemistry, e.g., to mention only acid−base catalyzed reactions.[1−3] On the other hand, the proton affinity (PA) is interesting *per se* since it represents a fundamental thermodynamic property. Gas-phase experimental or single molecule theoretical proton affinities reflect intrinsic electronic features. Combination of these PA values with thermodynamic data measured in solution provides a valuable source of information on solvent effects thus enabling a clear-cut distinction to be made between intrinsic and external (intermolecular) interactions. Additionally, the proton is the simplest example of the electrophilic substituent group, which has proved very useful in developing a general picture of the electrophilic reactivity of aromatics,[4] particularly in elucidating the effect of annealation of small strained rings.[5,6] We note in passing that the angular strain considerably affects basicity through rehybridization[7] as confirmed by a meticulous theoretical analysis by Yáñez et al.[8] recently. Experimental determination of PAs encounters some difficulties since they are estimated usually by measuring gas-phase equilibrium constants for reactions

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ \qquad (1)$$

implying that, strictly speaking, only the relative values for bases B_1 and B_2 could be obtained.[9,10] Choice of different anchor (gauge) base(s) leads to different PA ladders. Concomitantly, a problem of the absolute scale is still an open question. Another shortcoming of the experimental approach is that only the most stable protonated species can be observed as a rule. Theoretical calculations are free from these constraints since they give absolute proton affinities and treat all protonation sites on equal footing. However, a very high level of theory (G2) is required for obtaining completely reliable results.[11] Since this theoretical framework is not practical for large(r) molecular systems, much effort has been devoted to select a more feasible scheme capable of reproducing PAs in substituted aromatics.[12−14] It turns out that simpler schemes like G2(MP2) perform very well, but they are still too intricate for large systems. On the other hand, the density functional methods are efficient, but their results at the present stage are not as accurate as one might wish.[12,14] We have shown that the MP2(fc)/6-31G**//HF/6-31G*+ZPE(HF/6-31G*) model reproduces proton affinities in substituted benzenes with good accuracy for a large variety of substituents.[15,16] More importantly, it appears that the proton affinities in polysubstituted benzenes are given by the simple additivity rule once the increments for monosubstituents are known.[16] The additivity rule gives interesting insight into the intramolecular interactions in aromatic systems shedding more light on the substituents effects.[16] The latter have been subject matter of intensive investigations for several decades, most notably by Hammett, Taft, Topsom and some others.[17−24] However, a vast majority of the studies was confined to substituted benzenes. It is desirable to extend investigations of substituent effects to larger aromatics. In the present work we consider PAs in polyfluorinated naphthalenes aiming to show that they follow the same additivity rule. Fluorine is chosen as a substituent *par excellence* for two reasons. Firstly, it leads to unique and fascinating chemistry[25] resulting in a number of unusual molecular properties. Thanks to an extremely high

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[⊥] Dedicated to Professor Rolf Gleiter on the occasion of his 60th birthday.

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[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

S1089-5639(96)01925-1 CCC: $14.00

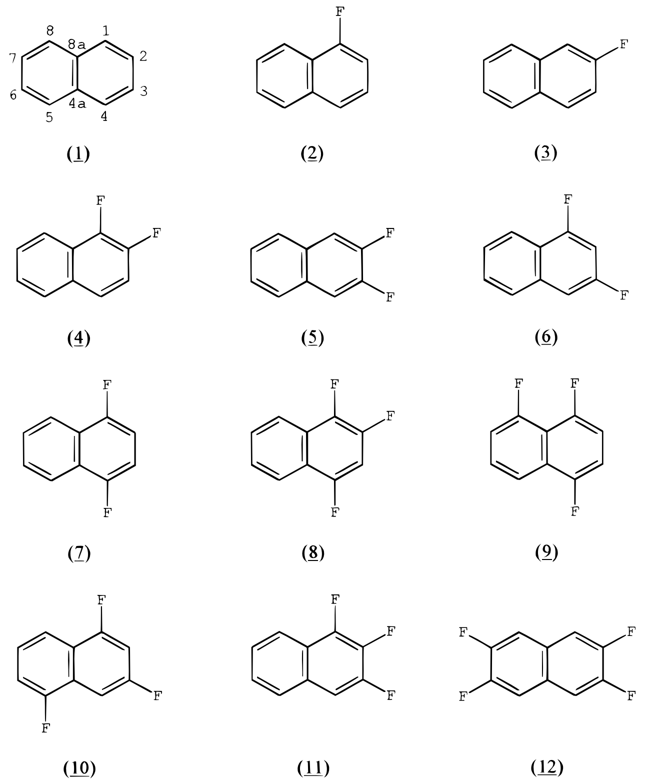


Figure 1. Schematic representation and numbering of atoms of naphthalene and its fluorine-substituted derivatives.

electronegativity fluorine exhibits completely new features like the perfluoroeffect[26,27] or the negative hyperconjugation.[28,29] It is also noteworthy that multiple fluorination transforms fused Mills−Nixon (MN) molecules into anti-MN systems.[30] Secondly, fluorine derivatives of naphthalene are free of any conformational complications, thus providing a clear-cut test for the PA additivity. The studied systems are depicted in Figure 1.

2. Method

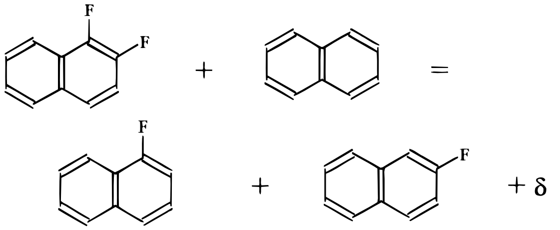
Proton affinities are calculated using the general equation

$$\mathrm{PA(B)} = E(\mathrm{B}) + \mathrm{ZPE(B)} - [E(\mathrm{BH}^+) + \mathrm{ZPE}(\mathrm{BH}^+)] \quad (2)$$

where B and BH^+ denote the base and its conjugate acid, respectively. The GAUSSIAN 94 program[31] was employed throughout this work. All independent structural parameters were optimized at the HF/6-31G* level, and the minima were verified by vibrational analyses. The corresponding vibrational frequencies are used for calculating the zero-point vibrational energy (ZPE). The latter were multiplied by the standard empirical weighting factor of 0.89.[32] Explicit inclusion of the ZPEs is crucial for quantitative description of the absolute values of PAs since the protonated forms have one more atom and an additional chemical bond. Equally important is an estimate of the correlation energy in aromatic moieties like naphthalene. This is achieved by the single-point MP2(fc)/6-31G**//HF/6-31G* model, where (fc) denotes frozen $(1s)^2$ core electrons in the course of the Møller−Plesset second-order perturbation calculations. It should be mentioned that the use of larger 6-31G** basis set is plausible in the final calculation, since a good description of H atoms in the protonation process is mandatory for reasonable performance of the model. The model has been calibrated against the PA value in phenol.[15] Inclusion of the polarization function on H atoms improved agreement with experiment by 2 kcal/mol. A similar improvement was found in naphthalene (*vide infra*). Earlier results[15,16] and data presented in this paper provide additional evidence that the MP2(fc)/6-31G**//HF/6-31G*+ZPE(HF/6-31G*) model is a good compromise between efficiency and accuracy. This does not mean that the model employed is universal. In fact, protonation at atoms possessing diffuse lone pair(s) may require use of more refined (diffuse) basis sets[33] or even higher levels of theory.[8,34]

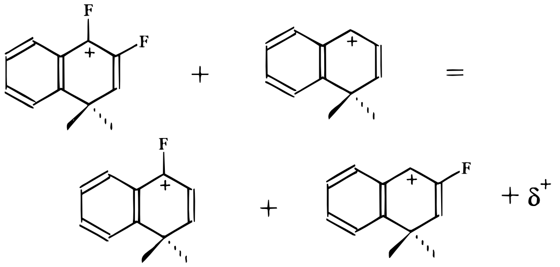
3. Results and Discussion

The Additivity Concept. A brief analysis of the additivity idea is in place here as a prelude to a general discussion. Assuming that the interaction between substituents is reasonably small or approximately the same in the initial and protonated compound, the additivity rule governing PAs in polysubstituted naphthalenes is easily derived by using the fruitful idea of homodesmic chemical reactions.[35] Let us consider, for instance, the PA of 1,2-disubstituted naphthalene. The corresponding coupled homodesmic reactions 3a and 3b are of the form



(3a)

and

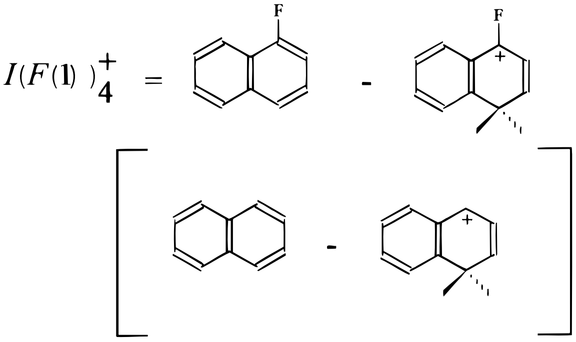


(3b)

where δ and δ^+ should be relatively small in view of the similarity of chemical bonding in the molecular systems involved. Subtracting eqs 3a and 3b, one obtains

$$\mathrm{PA}(\mathrm{C_{10}H_6F_{(1)}F_{(2)}H^+_{(4)}}) = \mathrm{PA(naphthalene)} + I(F(1))^+_4 + I(F(2))^+_4 + \Delta \quad (4)$$

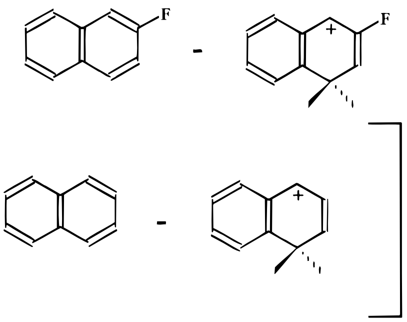
Here numbers within the inner parentheses denote positions of substitutions and the site of protonation, respectively.



(5a)

and

$I(F(2))_4^+ =$



(5b)

Finally, Δ is given by a difference $\Delta = \delta - \delta^+$. Apparently, the increments describe a change in the PA of naphthalene due to the presence of a substituent at a particular position within the aromatic moiety. It is also clear that a combined contribution from two substituents was obtained as if each of them was independent. Therefore, this model could be called "the independent substituent approach" (ISA). Entities δ and δ^+ are related to interference energies of substituents themselves and their superposition with the protonated center, respectively. If δ and δ^+ are of the same magnitude, then the additivity should work rather well. This point will be discussed in some more quantitative detail later. The generalization of the additivity formula (eq 4) is straightforward

$$\mathrm{PA(subst.\ naphthalene)} = \mathrm{PA(naphthalene)} + \sum_{\mathrm{X}} I(\mathrm{X})^+_{\mathrm{H}(n)} \tag{6}$$

where the summation is extended over all substituents X and n denotes the position of proton attack.

Structural Properties. We shall commence discussion with a brief survey of the structural features of naphthalene and its three protonated forms. It is generally accepted that the latter correspond to the transition structures in the course of the electrophilic substitution reactions thus being of considerable interest. Their geometric parameters are displayed in Table 1 together with results for benzene and benzenonium ion, which are given for the sake of comparison. Simple descriptors of the chemical bonding like s-characters of the local hybrid AOs, π-bond orders, and atomic charges extracted from the HF/6-31G* wave functions are presented for interpretative purposes. The hybridization parameters describe local atomic polarization of the electron density, whereas the latter two indices are related to the electron density shift toward centers of double bonds and to the intramolecular charge transfer, respectively. Hybridization s-characters are deduced by making use of the NBO analysis,[36] while π-bond orders and atomic charges correspond to the Löwdin symmetrical partitioning of the electron density distribution.[37]

It was found earlier that the HF/6-31G* CC bond distances of the naphthalene skeleton are in good agreement with the X-ray structural data.[38] Further improvement is achieved here by the density functional calculations employing the hybrid B3-LYP/6-31G* method[39] and MP2(fc)/6-31G* procedure, which in turn involve the effect of the electron correlation. Results presented in Table 1 show that the average absolute error dropped from 0.010 Å (HF/6-31G*) to 0.005 Å (B3-LYP/6-31G*). We note in passing that the B3-LYP/6-31G* procedure yields 1.397 Å for the CC bond distance in benzene in perfect harmony with experiment. It is also worth mentioning that the computationally efficient B3-LYP/6-31G* model yields structural parameters similar to results of the more intricate MP2(fc)/6-31G* procedure (Table 1). This holds true in particular for neutral molecules. In the protonated forms differences are more pronounced, but both sets of data are mutually consistent. A point of considerable importance is that CC distances and the corresponding π-bond orders in naphthalene exhibit significant alternation, in spite of the fact that **1** is formally an aromatic system. Since the aromaticity defect plays an important role in determining PAs of the planar systems, its discussion in some more detail is pertinent. Extent of double-bond fixation can be estimated by the localization indices $L_m(d)$ and $L_m(\pi)$ defined as[40]

$$L_m(d) = \sum_n |d^{(n)}_{\mathrm{CC}} - \bar{d}_{\mathrm{CC}}|/\text{Å} \tag{7a}$$

and

$$L_m(\pi) = \sum_n |\pi^{(n)}_{\mathrm{CC}} - \bar{\pi}_{\mathrm{CC}}| \tag{7b}$$

where $\bar{d}_{\mathrm{CC}}$ and $\bar{\pi}_{\mathrm{CC}}$ denote the average CC bond distance and the average π-bond order, respectively. Further, m stands for the molecule in question whereas n signifies a particular CC bond. Clearly, $L_m(d)$ and $L_m(\pi)$ are both zero for perfectly delocalized aromatic molecules. Their increase, on the other hand, reflects the presence of the partial π-electron localization and concomitant bond length alternation. It is of some interest to establish the upper limit for the $L(d)$ index which would correspond to the perfectly localized double bonds in benzene and naphthalene. The problem is, however, definition of the interatomic distance corresponding to the idealized single C−C sp^2−sp^2 bond. We prefer to model it by the C−C bond in cyclooctatetraene, which possesses sp$^{2.2}$−sp$^{2.2}$ hybridization as estimated by the IMO (iterative maximum overlap) approximation.[41] The calculated C−C bond distance by the IMO procedure is 1.46 Å, in excellent agreement with the electron diffraction measurements.[41] It is interesting to mention that virtually the same value (1.459 Å) was obtained for the $d(\mathrm{C_{sp2}}-\mathrm{C_{sp2}})$ bond distance in the twisted D_{2d} triplet state of ethylene by using the MP3/6-31G** method.[42] Employing the C=C bond length in ethylene of 1.34 Å, one can easily construct the cyclohexatriene model system which describes perfectly frozen Kekule structure of benzene. The corresponding localization index $L(d)$ is 0.36, implying that partial double-bond fixation in deformed benzene systems provides $L(d)$ values within the range 0.00−0.36. Analogous upper limit for naphthalene is $L(d) = 0.655$, i.e. slightly less than twice the value characterizing the model cyclohexatriene system. Indices $L(d)$ calculated by using the HF/6-31G*, B3-LYP/6-31G* and MP2(fc)/6-31G* bond distances for benzenonium ion, **1**, **1**$_1$, **1**$_2$, and **1**$_{8a}$ systems assume values (0.25, 0.21, 0.19), (0.30, 0.23, 0.21), (0.35, 0.33, 0.30), (0.48, 0.40, 0.35), and (0.55, 0.45, 0.38) given within parentheses, respectively. It is interesting to observe that $L(d)$ values decrease for the same molecule as the role of the electron correlation increases in the sequence of the HF, B3-LYP, and MP2 models, as intuitively expected. However, in spite of the electron correlation smoothing out effect, a considerable amount of localization is still present in naphthalene and its protonated forms. It should be mentioned that the experimental localization indices $L(d)$ in benzenonium ion[43] and naphthalene[38b] are 0.28 and 0.25, respectively, thus being in good accordance with theoretical estimates. It is also interesting to notice that the protonated naphthalenes are more localized than benzenonium ion or the parent naphthalene itself. Since the sigma (Wheland) complexes represent rather well the transition structures for the electrophilic substitution reactions, one concludes that a loss in the delocalization energy substantially influences the height of the energy barriers.

TABLE 1: Selected Structural Parameters of Naphthalene and Its Protonated Forms As Obtained by the HF/6-31G*, B3-LYP/6-31G*, and MP2(fc)/6-31G* Models. Hybridization Parameters, Bond Orders, and Atomic Charges As Estimated by the HF/6-31G* Model (Distances and Angles in Å and deg, Respectively)

		distance/angle							
molecule	bond/angle	HF//6-31G*	B3-LYP//6-31G*	MP2(fc)//6-31G*	s-character (%)	$\pi_{\text{b.o.}}$	atom	charge	π_{density}
benzene	C−C	1.386	1.397	1.397	35.1−35.1	0.66	C	−0.16	0.98
	C−H	1.076	1.087	1.087	29.6−100.0		H	0.16	
benzenonium ion	C(1)−C(2)	1.478	1.473	1.466	27.6−32.3	0.28	$C_{(1)}$	−0.29	1.14
	C(2)−C(3)	1.353	1.372	1.376	36.8−35.4	0.78	$C_{(2)}$	0.02	0.70
	C(3)−C(4)	1.410	1.413	1.409	32.4−35.1	0.55	$C_{(3)}$	−0.20	1.03
	C(1)−H	1.094	1.109	1.109	22.5−100.0		$C_{(4)}$	0.09	0.60
	C(2)−H	1.075	1.087	1.088	30.7−100.0		$H_{C(1)}$	0.24	
							$H_{C(2)}$	0.22	
1	C(1)−C(2)	1.358	1.377	1.380	36.6−36.3	0.76	$C_{(1)}$	−0.16	0.99
	C(2)−C(3)	1.416	1.417	1.410	33.9−33.9	0.52	$C_{(2)}$	−0.17	0.98
	C(1)−C(8a)	1.420	1.421	1.422	33.8−33.5	0.51	$C_{(8a)}$	−0.01	0.96
	C(4a)−C(8a)	1.409	1.434	1.430	32.9−32.9	0.57	$H_{C(1)}$	0.16	
	C(8a)−C(1)−C(2)	120.8	120.9	119.3			$H_{C(2)}$	0.17	
	C(1)−C(2)−C(3)	120.3	120.3	119.9					
	C(4a)−C(8a)−C(1)	119.0	118.8	120.7					
1$_{1}$	C(1)−C(2)	1.483	1.479	1.474	26.9−32.6	0.26	$C_{(1)}$	−0.28	1.14
	C(2)−C(3)	1.349	1.368	1.371	37.0−35.7	0.79	$C_{(2)}$	0.02	0.70
	C(3)−C(4)	1.413	1.414	1.411	32.3−35.2	0.52	$C_{(3)}$	−0.22	1.06
	C(4)−C(4a)	1.401	1.406	1.404	35.6−32.5	0.58	$C_{(4)}$	0.09	0.62
	C(4a)−C(8a)	1.415	1.434	1.430	33.0−32.6	0.52	$C_{(4a)}$	−0.07	1.04
	C(1)−C(8a)	1.499	1.498	1.490	27.9−31.3	0.22	$C_{(8a)}$	0.07	0.83
	C(4a)−C(5)	1.416	1.424	1.422	34.3−33.2	0.51	$C_{(5)}$	−0.08	0.87
	C(5)−C(6)	1.366	1.379	1.380	36.4−35.0	0.72	$C_{(6)}$	−0.16	0.98
	C(6)−C(7)	1.401	1.409	1.410	33.6−34.8	0.59	$C_{(7)}$	−0.04	0.81
	C(7)−C(8)	1.386	1.397	1.394	35.2−34.9	0.65	$C_{(8)}$	−0.18	1.02
	C(8)−C(8a)	1.382	1.391	1.395	34.4−36.0	0.66	$H_{C(1)}$	0.22	
	C(8a)−C(1)−C(2)	115.7	116.7	116.7			$H_{C(2)}$	0.21	
	C(1)−C(2)−C(3)	123.0	122.2	122.1			$H_{C(3)}$	0.21	
	C(2)−C(3)−C(4)	118.7	119.3	119.2			$H_{C(4)}$	0.21	
	C(3)−C(4)−C(4a)	123.9	123.6	123.6			$H_{C(5)}$	0.19	
	C(4)−C(4a)−C(8a)	119.0	119.1	118.9			$H_{C(6)}$	0.20	
							$H_{C(7)}$	0.20	
							$H_{C(8)}$	0.19	
1$_{2}$	C(1)−C(2)	1.477	1.472	1.465	33.3−26.6	0.28	$C_{(1)}$	0.06	0.65
	C(2)−C(3)	1.488	1.484	1.478	28.3−31.4	0.24	$C_{(2)}$	−0.28	1.13
	C(3)−C(4)	1.331	1.355	1.360	37.7−37.4	0.87	$C_{(3)}$	−0.08	0.86
	C(4)−C(4a)	1.449	1.438	1.434	31.5−33.3	0.39	$C_{(4)}$	−0.18	1.02
	C(4a)−C(8a)	1.441	1.456	1.449	31.6−31.9	0.43	$C_{(4a)}$	0.13	0.76
	C(1)−C(8a)	1.362	1.377	1.381	36.8−34.6	0.73	$C_{(8a)}$	−0.06	1.04
	C(4a)−C(5)	1.391	1.402	1.405	35.0−34.0	0.62	$C_{(5)}$	−0.19	1.04
	C(5)−C(6)	1.378	1.389	1.388	34.8−35.8	0.68	$C_{(6)}$	0.00	0.74
	C(6)−C(7)	1.417	1.420	1.418	34.4−32.8	0.52	$C_{(7)}$	−0.18	1.00
	C(7)−C(8)	1.353	1.371	1.375	35.6−37.0	0.78	$C_{(8)}$	−0.06	0.85
	C(8)−C(8a)	1.437	1.437	1.432	32.4−33.4	0.42	$H_{C(1)}$	0.21	
	C(8a)−C(1)−C(2)	123.1	122.4	122.4			$H_{C(2)}$	0.22	
	C(1)−C(2)−C(3)	115.0	116.2	116.4			$H_{C(3)}$	0.20	
	C(2)−C(3)−C(4)	122.0	121.3	121.1			$H_{C(4)}$	0.20	
	C(3)−C(4)−C(4a)	121.0	121.2	120.9			$H_{C(5)}$	0.20	
	C(4)−C(4a)−C(8a)	120.0	120.0	120.4			$H_{C(6)}$	0.21	
							$H_{C(7)}$	0.20	
							$H_{C(8)}$	0.20	
1$_{8a}$	C(1)−C(2)	1.334	1.359	1.368	38.1−36.6	0.81	$C_{(1)}$	−0.08	0.87
	C(2)−C(3)	1.441	1.430	1.423	31.9−33.6	0.38	$C_{(2)}$	−0.17	1.00
	C(3)−C(4)	1.361	1.383	1.383	36.5−35.7	0.70	$C_{(3)}$	−0.01	0.76
	C(4)−C(4a)	1.410	1.411	1.410	32.9−34.8	0.53	$C_{(4)}$	−0.20	1.05
	C(4a)−C(8a)	1.485	1.494	1.481	30.3−27.4	0.29	$C_{(4a)}$	0.16	0.71
	C(1)−C(8a)	1.491	1.489	1.478	30.9−28.5	0.18	$C_{(8a)}$	−0.13	1.06
	C(8a)−C(1)−C(2)	120.7	120.4	120.0			$H_{C(1)}$	0.20	
	C(1)−C(2)−C(3)	119.7	120.3	120.5			$H_{C(2)}$	0.20	
	C(2)−C(3)−C(4)	123.0	122.2	121.9			$H_{C(3)}$	0.21	
	C(3)−C(4)−C(4a)	119.8	120.6	120.5			$H_{C(4)}$	0.20	
	C(4)−C(4a)−C(8a)	118.6	118.5	118.6			$H_{C(8a)}$	0.27	

It is noteworthy that the molecular plane in **1**$_1$ and **1**$_2$ protonated forms is preserved thus ensuring an effective π-electron delocalization. In contrast, protonation at position 8a leads to unsymmetrical pyramidalization of the carbon atom in question as evidenced by the dihedral angle H−C(8a)−C(4a)−C(2) of 110.7°. The naphthalene skeleton becomes puckered, which additionally decreases the π-electron delocalization energy. Consequently, it is plausible to assume that **1**$_{8a}$ should be the least stable protonated form. This is, however, only a part of the story (*vide infra*). As a final remark we notice that the same qualitative conclusions can be drawn by analyzing $L_m(\pi)$ localization indices.

Another point of significant interest is redistribution of charge upon protonation. Proton attracts on average 0.6$|e|$ of the

TABLE 2: Total Molecular Energies *E* (in au), Zero-Point Energies ZPE (in kcal/mol), and the Proton Affinity (in kcal/mol) of Naphthalene (1) As Estimated by the MP2 and DFT Models[a,b]

molecule	*E*(HF)	ZPE	DFT	*E*(MP2)	DFT	MP2
1	−383.355 05	88.3	−385.90544	−384.67581		
$\mathbf{1}_1$	−383.690 34	94.9	−386.23774	−384.99676	201.3	194.8 (194.7)[c]
$\mathbf{1}_2$	−383.684 33	94.8	−386.23266	−384.98975	198.8	190.5
$\mathbf{1}_{8a}$	−383.652 06	94.4	−386.96332	−384.96332	182.1	174.3

[a] *E*(HF) and *E*(MP2) are related to energies obtained by the HF/6-31G* and MP2(fc)/6-31G**//HF/6-31G* models, respectively. Results obtained by B3-LYP/6-31G**//B3-LYP/6-31G* method is denoted by DFT. Protonation sites are denoted by subscripts. PA values are estimated by the MP2(fc)/6-31G**//HF/6-31G*+ZPE(HF/6-31G*) model. [b] ZPE values are HF/6-31G* results multiplied by a common weighting factor 0.89. [c] Reference 8.

Figure 2. Predominant valence bond structures of 1- and 2-protonated naphthalene.

electron density, which is pumped out of the naphthalene moiety. Surprisingly, the protonated carbon atom has more negative charge than in the parent molecule. This finding strongly indicates that the electron density reorganization energy plays an important role in the protonation process.

Energetic Properties. Total molecular energies, ZPEs, and PAs for the protonated naphthalene forms are given in Table 2. It appears that position 1 is most susceptible to proton attack. The corresponding MP2 proton affinity is in excellent agreement with experiment.[10] The DFT single-point B3-LYP/6-31G**//B3-LYP/6-31G* method gives proton affinities which are systematically too large by 7−8 kcal/mol (Table 2). This is not unresonable, but it is obvious that the optimal combination of the exchange and correlation functionals remains to be found. In fact, PAs could provide very useful clue in this respect. A hierarchy of PAs, $(PA)_1 > (PA)_2 > (PA)_{8a}$, is compatible with the localization criteria $L(d)$ and $L(\pi)$ discussed earlier, which shows that the aromaticity defect is the smallest in $\mathbf{1}_1$ and the largest in $\mathbf{1}_{8a}$. An interesting qualitative argument can be put forward to illuminate the fact that $(PA)_{8a}$ is the lowest proton affinity of **1**. Protonation at the 8a position produces formally the acyclic nonatetrenyl ion in contrast to the proton attack at positions 1 and 2 resulting in benzenoid 1-phenylallyl and 2-vinylbenzyl cations.[44] The loss of aromaticity in the former case is obviously the largest. A reason behind the more pronounced susceptibility toward the proton attack of position 1 relative to position 2 is very instructive. It is well-known that a substantial bond fixation takes place in benzenonium ion exhibiting a quite characteristic pattern,[5] which is reflected *inter alia* in the corresponding $L(d)$ index (*vide supra*). Careful examination of the B3-LYP/6-31G* and MP2(fc)/6-31G* geometries shows that a dominant mode of π-bond localization of the benzenonium ion is preserved to some extent in the protonated forms $\mathbf{1}_1$ and $\mathbf{1}_2$ leading to slightly predominant pairing schemes shown in Figure 2. One observes that the $\mathbf{1}_1$ protonated system preserves the benzene-like delocalization in the left wing of the naphthalene moiety to a large extent. This finding is supported by the localization indices $L(d)_{lr}$, where subscript denotes the left(ring) benzene fragment. B3-LYP/6-31G* $L(d)_{lr}$ values for $\mathbf{1}_1$ and $\mathbf{1}_2$ are 0.10 and 0.15, respectively, thus indicating higher localizability in $\mathbf{1}_2$ and subsequently larger aromaticity defect. The average bond distances of the benzene moieties in $\mathbf{1}_1$ and $\mathbf{1}_2$ are 1.406 and 1.413 Å, respectively, reflecting a more pronounced blowup effect in the benzene fragment of the latter protonated system. These structural and energetic features lead to a more favorable α-protonation by 4.3 kcal/mol, which in turn is the final state effect. Two brief additional comments are in place here: Pauling's prediction of the increased electrophilic reactivity of the α-position in naphthalene relative to the β-position was based on the VB structures polarized by the incoming electrophile,[45] because naphthalene is an alternant system possessing concomitantly a uniform π-density distribution along the perimeter. Hence the ground state density distribution ρ does not offer any distinction between the protonation at positions 1 and 2, discrimination being introduced completely by the difference in the delocalization caused by protonation as discussed above. Secondly, the PA value obtained by the MP2(fc)/6-31G*//HF/6-31G*+ZPE-(HF/6-31G*) model is only 191.6 kcal/mol, thus being too low by 3 kcal/mol. This gives an additional piece of evidence that the polarization functions placed on H atoms are important for quantitative estimates of the proton affinity.

Total molecular energies and ZPEs of mono- and polysubstituted fluoronaphthalenes are given in Table 3. Proton affinities of molecules **2**−**12** are presented in Table 4 together with the increments for monosubstituted fluoronaphthalenes **2** and **3**. A brief analysis of the increments is worthwhile. It reveals that fluorination deactivates almost all positions with few exceptions. A change in PA at remote positions like 6 and 7 in **2** and position 7 in **3** is indicative of the π-electron interaction between F lone pair and the aromatic π-system leading to significant delocalization or resonance effect. The largest deactivation is found, however, for the ipso-protonation. It is a consequence of the out-of-plane shift of fluorine which leads to significant puckering of naphthalene ring. It should be mentioned, however, that the low values of $(PA)_{ipso}$ are compatible at the same time with the perfluoro effect[26,27] and the complementary π-electron fluoro effect put forward by Liebman et al.[46] It can be easily shown that the following relationship holds for an initial molecule M which is going to be protonated

$$PA(M) = D_e(M-H) + IP(H) - IP(M)_1 \qquad (8)$$

where $D_e(M-H)$ is the bond dissociation energy of the molecule M−H, IP(H) is the ionization potential of the hydrogen atom (IP(H) = 13.6 eV), and $IP(M)_1$ is the first ionization potential of the parent molecule M.[47] It is well established that fluorinated and particularly multiply fluorinated compounds possess considerably stabilized σ-MOs if the systems are planar, the π-manifold being almost unaffected. However, in nonplanar systems all MOs of the carbon skeleton are significantly stabilized,[26,27,46] which is exactly the case for the ipso-protonation. Since $IP(M)_1$ increases the corresponding ipso-PA value decreases, as evidenced by the present results (Table 4). Enhanced susceptibility of positions 2 and 4 in **2** and position 1 in **3** on the other hand can be rationalized in the following simple and intuitively appealing way. Let us consider conjugative interaction of the fluorine atom with the naphthalene moiety, which introduces some double-bond character in the CF bond. There are only three resonance structures which preserve aromaticity of the left wing benzene fragment (Figure

TABLE 3: Total Molecular Energies *E* (in au) and Zero-Point Energies ZPE (in kcal/mol) for Mono- and Polysubstituted Fluoronaphthalenes[a]

molecule	*E*(HF)	ZPE	*E*(MP2)
2	−482.206 46	83.7	−483.686 45
2$_1$	−482.521 09	90.6	−483.985 51
2$_2$	−482.536 99	90.3	−484.003 83
2$_3$	−482.525 58	90.0	−483.992 64
2$_4$	−482.544 46	90.3	−484.011 29
2$_5$	−482.536 89	90.2	−484.001 76
2$_6$	−482.523 98	89.8	−483.993 04
2$_7$	−482.531 20	90.1	−483.995 23
2$_8$	−482.533 66	90.0	−484.002 04
3	−482.206 30	83.5	−483.685 69
3$_1$	−482.541 69	90.3	−484.008 77
3$_2$	−482.512 27	90.5	−483.973 76
3$_3$	−482.530 44	90.1	−483.995 68
3$_4$	−482.526 59	90.0	−483.995 51
3$_5$	−482.531 67	89.9	−483.999 80
3$_6$	−482.534 82	90.1	−483.998 40
3$_7$	−482.524 28	89.9	−483.992 33
3$_8$	−482.539 16	90.1	−484.004 11
4	−581.049 36	78.8	−582.688 47
4$_1$	−581.368 28	86.1	−582.993 96
4$_2$	−581.361 76	86.1	−582.985 46
4$_3$	−581.363 03	83.4	−582.990 20
4$_4$	−581.374 69	85.5	−583.004 12
4$_5$	−581.370 43	85.2	−582.997 47
4$_6$	−581.366 99	85.2	−582.994 28
4$_7$	−581.363 03	85.1	−582.990 07
4$_8$	−581.374 76	85.3	−583.002 28
5	−581.050 08	78.7	−582.688 74
5$_1$	−581.369 75	85.4	−582.999 94
5$_2$	−581.354 12	85.8	−582.975 84
5$_3$	−581.354 12	85.8	−582.975 84
5$_4$	−581.369 75	85.4	−582.999 94
5$_5$	−581.373 10	85.2	−583.000 48
5$_6$	−581.367 84	85.1	−582.994 35
5$_7$	−581.367 84	85.1	−582.994 35
5$_5$	−581.373 10	85.2	−583.000 48
6	−581.056 91	78.8	−582.695 22
6$_1$	−581.356 58	85.7	−582.983 19
6$_2$	−581.381 00	85.6	−583.007 82
6$_3$	−581.352 88	85.7	−582.975 58
6$_4$	−581.394 06	85.7	−583.021 59
6$_5$	−581.384 85	85.4	−583.008 19
6$_6$	−581.363 19	84.8	−582.994 79
6$_7$	−581.380 76	85.3	−583.003 06
6$_8$	−581.374 47	85.0	−583.003 94
7	−581.055 98	78.9	−582.695 46
7$_1$	−581.374 93	86.1	−583.000 11
7$_2$	−581.377 71	85.6	−583.005 84
7$_3$	−581.377 71	85.6	−583.005 84
7$_4$	−581.374 93	86.1	−583.000 11
7$_5$	−581.378 35	85.3	−583.005 50
7$_6$	−581.369 21	85.1	−582.996 80
7$_7$	−581.369 21	85.1	−582.996 80
7$_8$	−581.378 35	85.3	−583.005 50
8	−679.898 13	74.0	−681.696 46
8$_1$	−680.220 53	81.4	−682.006 99
8$_2$	−680.202 24	81.3	−681.987 07
8$_3$	−680.213 07	80.9	−682.001 37
8$_4$	−680.204 62	81.3	−681.992 45
8$_5$	−680.211 48	80.3	−682.000 29
8$_6$	−680.211 53	80.4	−681.997 48
8$_7$	−680.200 33	80.0	−681.991 07
8$_8$	−680.218 89	80.5	−682.004 97
9	−679.900 62	74.0	−681.700 03
9$_1$	−680.214 09	81.2	−682.000 47
9$_2$	−680.219 81	80.8	−682.006 93
9$_3$	−680.211 22	80.5	−682.002 91
9$_4$	−680.216 69	81.3	−682.001 03
9$_5$	−680.227 27	80.6	−682.015 35
9$_6$	−680.204 16	80.2	−681.993 48
9$_7$	−680.217 44	80.6	−682.006 68
9$_8$	−680.205 02	81.0	−681.989 49
10	−679.906 83	74.0	−681.705 36
10$_1$	−680.202 59	81.0	−681.987 94
10$_2$	−680.220 12	80.6	−682.010 72
10$_3$	−680.199 28	81.0	−681.980 72
10$_4$	−680.237 30	80.9	−682.026 71
10$_5$	−680.215 48	81.1	−681.997 48
10$_6$	−680.215 77	80.4	−682.003 78
10$_7$	−680.221 25	80.5	−682.005 42
10$_8$	−680.228 14	80.5	−682.018 34
11	−679.892 49	74.0	−681.690 56
11$_1$	−680.195 47	81.1	−681.984 16
11$_2$	−680.201 81	81.3	−681.986 00
11$_3$	−680.186 19	81.1	−681.969 36
11$_4$	−680.216 02	80.9	−682.006 47
11$_5$	−680.211 01	80.5	−681.997 00
11$_6$	−680.199 10	80.2	−681.989 60
11$_7$	−680.205 70	80.4	−681.991 13
11$_8$	−680.208 03	80.3	−681.997 54
12	−778.743 56	69.0	−780.700 36
12$_1$	−779.051 02	75.6	−781.002 51
12$_2$	−779.036 60	76.1	−780.980 03

[a] Abbreviations denote the same entities as in Table 2.

3), which are consequently the most important ones. This elementary argument explains in qualitative terms slight amplification of the proton affinities at positions mentioned above, in view of their increased negative charge (the ground state effect). The lower limit of the ground state atomic charge effect is given by the increments $I^{+}_{\mathbf{22}}$ and $I^{+}_{\mathbf{24}}$ being 2.0 and 2.4 (in kcal/mol), respectively. Analogously, a contribution $I^{+}_{\mathbf{31}} = 1.1$ kcal/mol can be identified as the effect of the ground state electron density distribution in **3**. This is of importance since the fact that most of the increments are negative and a finding that PAs generally assume lower values as the fluorination progresses strongly indicates that the significant π-electron fluoro effect[47] is operative here.

Perusal of the data presented in Table 4 shows that the additivity formula (eq 9) works very well as evidenced by a low average absolute error of 0.8 kcal/mol. The largest deviations (errors) from the full ab initio calculations are found at some ipso-positions as expected. Influence of a substituent (F atom) at this protonation site is too strong to be considered a small perturbation, in contrast to cases where substituent is placed at more remote positions. If the ipso-protonations are excluded, the average absolute deviation for additivity drops to only 0.4 kcal/mol, which is remarkable indeed.

A breakdown of the deviation Δ into components δ and $-\delta^{+}$ is interesting. It shows that the interference energies δ and δ^{+} are sometimes quite appreciable. However, they cancel out to a very large extent. This is in accordance with our earlier extensive calculations in polysubstituted benzenes.[16] For example, the interference energies δ in **4**, **6**, and **7** are 4.8, 0.6, and 0.8 (in kcal/mol), respectively, which is compatible with the fact that the former compound is ~4 kcal/mol less stable than **6** and **7**. More importantly, δ^{+} interference energies δ^{+}_{4i} ($i = 3-8$) in compound **4**, where i denotes the protonation position, are 4−5 kcal/mol, thus leading to small deviation Δ from the additivity rule. Other illustrative and convincing cases can be easily found in Table 4. It appears that appreciable δ and δ^{+} values occur whenever two or more F atoms assume vicinal positions (viz. **4**, **5**, **8**, **11**, and **12**). Conversely, they are rather small in systems **6**, **7**, and **10**, where proximity of F atoms is absent. It follows that the protonated center does not

TABLE 4: Increments I_n^+ of the Proton Affinity Induced by Single Fluorine Substitution, PAs of Polysubstituted Fluoronaphthalenes, and the Corresponding Additivity Values As Offered by the MP2(fc)/6-31G//HF/6-31G*+ZPE(HF/6-31G*) Model (in kcal/mol)[a]**

		proton positions							
molecule	entity	1	2	3	4	5	6	7	8
2	PA	180.7	192.5	185.8	197.2	191.4	186.2	187.4	191.7
	I_{2n}^+	−14.1	2.0	−4.7	2.4	−3.4	−4.3	−3.1	−3.1
3	PA	195.9	173.7	187.9	187.9	190.7	189.6	186.1	193.2
	I_{3n}^+	1.1	−16.8	−2.6	−6.9	−4.1	−0.9	−4.4	−1.6
4	PA	184.4	179.1	182.7	191.3	187.5	185.5	182.9	190.4
	$\mathrm{PA_{ad}}$	181.8	175.7	183.2	190.3	187.3	185.3	183.0	190.1
	Δ	2.6	3.4	−0.5	1.0	0.2	0.2	−0.1	0.3
	δ	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8
	$-\delta^+$	−2.2	−1.4	−5.3	−3.8	−4.6	−4.6	−4.9	−4.5
5	PA	188.6	173.0	173.0	188.6	189.1	185.4	185.4	189.1
	$\mathrm{PA_{ad}}$	189.0	171.1	171.1	189.0	189.1	185.2	185.2	189.1
	Δ	−0.4	1.9	1.9	−0.4	0.0	0.2	0.2	0.0
	δ	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
	$-\delta^+$	−4.7	−2.4	−2.4	−4.7	−4.3	−4.1	−4.1	−4.3
6	PA	173.8	189.3	169.0	197.9	189.8	181.9	186.7	187.5
	$\mathrm{PA_{ad}}$	173.8	189.9	169.0	198.3	189.8	181.8	186.5	187.6
	Δ	0.0	−0.6	0.0	−0.4	0.0	0.1	0.2	−0.1
	δ	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	$-\delta^+$	−0.6	−1.2	−0.6	−1.0	−0.6	−0.5	−0.4	−0.7
7	PA	184.0	188.0	188.0	184.0	188.1	182.9	182.9	188.1
	$\mathrm{PA_{ad}}$	183.1	187.8	187.8	183.1	188.3	183.1	183.1	188.3
	Δ	0.8	0.2	0.2	0.8	−0.2	−0.2	−0.2	−0.2
	δ	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
	$-\delta^+$	0.0	−0.6	−0.6	0.0	−1.0	−1.0	−1.0	−1.0
8	PA	187.5	175.1	184.5	178.5	184.4	182.6	178.9	187.2
	$\mathrm{PA_{ad}}$	184.2	171.0	185.2	176.2	184.2	182.2	178.7	186.7
	Δ	3.3	4.1	−0.7	2.3	0.2	0.4	0.2	0.5
	δ	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3
	$-\delta^+$	−3.0	−2.2	−7.0	−4.1	−6.1	−6.1	−6.1	−5.8
9	PA	181.4	185.8	183.6	181.7	191.3	178.0	185.8	174.7
	$\mathrm{PA_{ad}}$	180.0	184.7	183.5	179.7	190.7	178.4	185.1	174.2
	Δ	1.3	1.1	−0.1	2.0	0.6	−0.4	0.7	0.5
	δ	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
	$-\delta^+$	−3.0	−3.3	−4.4	−1.3	−3.8	−4.9	−3.7	−4.2
10	PA	170.4	185.0	165.8	194.8	176.3	184.0	181.8	189.9
	$\mathrm{PA_{ad}}$	170.4	185.6	165.9	195.2	175.7	183.8	181.8	190.0
	Δ	0.0	−0.6	−0.1	−0.4	0.6	0.2	0.0	−0.1
	δ	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
	$-\delta^+$	−0.8	−1.5	−0.8	−1.1	−0.1	−0.5	−0.7	−0.8
11	PA	177.1	178.1	167.8	191.3	185.8	181.4	182.2	186.4
	$\mathrm{PA_{ad}}$	174.9	173.1	166.4	191.4	185.7	180.9	182.1	186.0
	Δ	2.2	5.0	1.4	−0.1	0.1	0.5	0.1	0.4
	δ	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7
	$-\delta^+$	−7.5	−4.7	−8.3	−9.8	−9.6	−9.2	−9.6	−9.3
12	PA	183.1	168.5	168.5	183.1	183.1	168.5	168.5	183.1
	$\mathrm{PA_{ad}}$	183.3	165.8	165.8	183.3	183.3	165.8	165.8	183.3
	Δ	−0.2	2.7	2.7	−0.2	−0.2	2.7	2.7	−0.2
	δ	9.3	9.3	9.3	9.3	9.3	9.3	9.3	9.3
	$-\delta^+$	−9.5	−6.6	−6.6	−9.5	−9.5	−6.6	−6.6	−9.5

[a] Difference between the full calculations and the additivity estimates $\mathrm{PA_{ad}}$ is Denoted by Δ. Interference energies δ and δ^+ defined by the homodesmic reactions 3a and 3b yield $\Delta = \delta - \delta^+$.

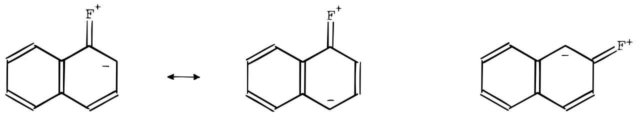


Figure 3. Predominant valence bond structures of 1- and 2-fluoronaphthalene.

change to any significant extent the interference energy, which already exists between substituents. We believe that this is a general feature although one cannot exclude a possibility of some exceptions (like, e.g., the ipso-protonation). However, they could and should be identified and separately treated.

4. Conclusion

The applied theoretical model of medium complexity gives a PA of naphthalene in good accordance with experiment. The hierarchy of PAs—$(PA)_1 > (PA)_2 > (PA)_{8a}$—is rationalized by the aromaticity defect concept. We have also shown that the additivity rule of thumb, based on the independent substituent approach (ISA), performs very well in describing PAs of a large number of polyfluorinated naphthalenes. This is evidenced by a very low average absolute deviation from the full ab initio results. Influence of the substituted F atoms on the planar π-systems can be treated as perturbation with one notable exception—ipso protonation. In the latter case F atom is shifted out of the molecular plane leading to appreciable distortion of naphthalene moiety which exhibits significant ring puckering. Thus, the effect of ipso-substitution cannot be treated as a small perturbation. Consequently, significant deviations from additivity sometimes occur there. Finally, it should be mentioned that lower PA values for the ipso-protonation are compatible with the (per)fluoro effect. The present results and earlier calculations[16] provide abundant evidence that the origin of the additivity in PAs lies in cancellation of the many-body interaction energies δ in the original (initial) base and δ^+ in the (final) conjugated acid. Finally, since the π-system is an efficient relay of the intramolecular interactions, it is concluded that the same type of the additivity formulas—*mutatis mutandis*—should work in other planar aromatic compounds as well.

Acknowledgment. We acknowledge the financial support for this work in the form of Grant RP940601 and the computer time made available to us by the National University of Singapore and NSRC. We thank also the University of Zagreb Computation Center and the IBM project "Academic Initiative for Croatia" for donation of the computing time.

Supporting Information Available: Table of total molecular energies and zero-point energies for mono- and polysubstituted molecules **2**−**12** (4 pages). Ordering information is given on any current masthead page.

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