Simple Ab Initio Model for Calculating the Absolute Proton Affinity of Aromatics

Zvonimir B. Maksić,*,[†,‡] Borislav Kovačević,[†] and Damir Kovaček[†]

*Quantum Chemistry Group, Department of Chemistry, Rudjer Bošković Institute, P.O. Box 1016,
10001 Zagreb, Croatia, and Faculty of Science and Mathematics, The University of Zagreb, Marulićev trg 19,
10000 Zagreb, Croatia*

Received: May 20, 1997; In Final Form: July 9, 1997[⊗]

It is shown that a simple scaled Hartree−Fock (ScHF) model describes very well the ring proton affinity (PA) of a vast variety of polysubstituted benzenes, naphthalenes, and biphenylenes. Its utility in predicting PAs of large alternant aromatics is illustrated on pyrene and monofluoropyrenes. The calculated PAs are in accordance with the available experimental evidence providing at the same time useful complementary information. Finally, it is found that PAs in polyfluoropyrenes follow the same simple additivity rule, based on the independent substituent approximation (ISA), which was observed earlier in smaller alternant aromatic systems. The origin of the additivity property of the proton affinity is briefly discussed.

Introduction

The proton affinity is pivotal in understanding the proton transfer reactions, basicity of molecules, and susceptibility toward the electrophilic substitutions in aromatics.[1] It is consequently of great importance to gather information on the proton affinity of chemically interesting systems as much as possible. Unfortunately, absolute proton affinities (PAs) are difficult to measure experimentally.[2,3] They depend on the choice of the coupled proton transfer reactions and a selection of the gauge (anchor) compound, thus leading to various "ladders" of PAs. Additionally, the experimental PAs are related to the most reactive site in a molecule as a rule. It is gratifying that theoretical methods offer not only supplementary but also a complementary approach instead by treating all possible protonation positions on an equal footing. The most sophisticated method is given by the G2 procedure,[4,5] which provides very accurate absolute PAs in smaller molecules. However, it is not economical or even feasible in large systems. The simpler G2(MP2), CBS-4, and CBS-Q schemes[6,7] are also quite accurate, but they are still too intricate to be very practical. The density functional theory (DFT) is not as reliable as one might wish,[8] although the recent advances are encouraging.[9] We have shown on the other hand that the MP2(fc)/6-31G**//HF/6-31G* + ZPE(HF/6-31G*) model gives results in good agreement with experiment for a large variety of polysubstituted benzenes and naphthalenes.[10−14] Although this approach is relatively simple, it is still too demanding if very large systems are to be studied. It is the aim of this work to show that a much simpler procedure based on the scaled Hartree−Fock (ScHF) model performs equally well. The ScHF model is at the same time more accurate and more reliable than earlier simplified theoretical treatments based on the electrostatic potentials.[15,16] We carried out also AM1[17] calculations of PAs in multiply substituted aromatics for the sake of comparison.

2. Theoretical Model

Proton affinities are calculated employing the general equation

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

where $(\Delta E_{\mathrm{el}})_\alpha = [E(\mathrm{B}) - E(\mathrm{BH}_\alpha^+)]$ and $(\Delta\mathrm{ZPE}_{\mathrm{v}})_\alpha = [\mathrm{ZPE}(\mathrm{B}) - \mathrm{ZPE}(\mathrm{BH}_\alpha^+)]$ are the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. Here, B and BH^+ denote the base in question and its conjugate acid, respectively, and α stands for the site of proton attack. The model M(I) widely exploited earlier with a surprising success was the MP2(fc)/6-31G**//HF/6-31G* + ZPE (HF/6-31G*) procedure, which implies that ZPE was estimated at the HF/6-31G* level multiplied by a common empirical factor 0.89.[18] We note in passing that use of the HF/6-31G* model in estimating ZPEs is justified a posteriori by good accordance of the calculated PAs with available experimental results. Moreover, the difference in ZPE in benzene and its *σ*-protonated form is 7.1 and 6.9 (in kcal/mol) as computed by the MP2(fc)/6-31G* and HF/6-31G* models, respectively. It follows that ZPEs do not depend on finer details of the molecular wave functions. This conclusion is supported by a simple additivity rule which holds for ZPEs.[19,20] Although the M(I) procedure is conceptually and computationally relatively simple, it is still not very practical if large aromatics are to be studied. The question arises, therefore, whether we can avoid a costly vibrational analysis and the final single-point MP2 calculation in reproducing consequences of the proton attack on the aromatic ring in very large systems. More specifically, could we consistently use the HF/6-31G* model in employing eq 1 but omitting vibrational analyses at the same time? The answer is affirmative as described below. The heart of the corresponding approximate model is an observation that a change in $\mathrm{ZPE}_{\mathrm{v}}$ upon protonation on the aromatic rings is fairly constant, being 6.4 kcal/mol with an absolute average deviation of only 0.3 kcal/mol. Hence, $(\Delta\mathrm{ZPE}_{\mathrm{v}})_\alpha$ in eq 1 can be safely replaced by the average value of 6.4 kcal/mol without introducing a significant error. Further, it appears that there is a very good linear correlation between the $(\Delta E_{\mathrm{el}})_\alpha$ calculated at the MP2(fc)/6-31G**//HF/6-31G* and HF/6-31G* levels of theory. It follows accordingly that protonation at the aromatic fragment is given with good accuracy by the approximate relationship

$$\mathrm{PA}(\mathrm{B}_\alpha) = 0.8633\Delta E_{\mathrm{el}}(\mathrm{HF/6\text{-}31G^*})_\alpha + 12.9 \quad (\mathrm{kcal/mol}) \qquad (2)$$

The scaled Hartree−Fock model based on eq 2 will be referred to as M(II). It is also of interest to examine the performance of the AM1 semiempirical scheme in predicting PAs of substituted aromatics. For this purpose one can use eq 1, where $(\Delta E_{\mathrm{el}})_\alpha$ is determined by using the total molecular AM1

---

* Corresponding author. Fax: +385-1-425497. E-mail: zmaksic@spider.irb.hr.

[†] Rudjer Bošković Institute.

[‡] The University of Zagreb.

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

S1089-5639(97)01678-2 CCC: $14.00

TABLE 1: Proton Affinity of Some Substituted Benzenes and Naphthalenes As Obtained by Theoretical Models M(I)−M(IV) Described in the Text (in kcal/mol)

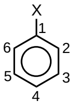
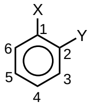
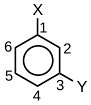
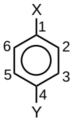
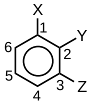
				proton affinity					deviation		
X	Y	Z	H^+	M(I)	Δ ZPE	M(II)	M(III)	M(IV)	δ_2	δ_3	δ_4
											
OH			2	193.0	7.0	193.7	190.8	190.8	0.7	−2.2	−2.2
OH			3	179.9	6.0	178.4	177.8	178.0	−1.5	−2.1	−1.9
OH			4	195.5	7.2	196.6	194.6	194.6	1.1	−0.9	−0.9
F			2	179.4	6.5	180.7	180.8	180.9	1.3	1.4	1.5
F			3	172.5	6.0	172.9	172.3	172.6	0.4	−0.2	0.1
F			4	181.6	6.5	183.1	182.0	182.2	1.5	0.4	0.6
CH_3			2	186.2	5.7	187.9	188.1	188.1	1.7	1.9	1.9
CH_3			3	182.9	6.3	183.7	184.1	184.1	0.8	1.2	1.2
CH_3			4	187.3	6.2	189.3	189.4	189.4	2.0	2.1	2.1
											
CH_3	CH_3		3	189.0	6.0	188.6	189.6	189.5	−0.4	0.6	0.5
CH_3	CH_3		4	189.7	6.2	190.2	190.6	190.6	0.5	0.9	0.9
F	F		3	172.2	6.4	171.9	171.1	171.4	−0.3	−1.1	−0.8
F	F		4	175.0	6.4	175.3	172.4	172.7	0.3	−2.6	−2.3
OH	OH		3	193.5	6.8	191.2	190.7	184.6	−2.3	−2.8	−8.9
OH	OH		4	197.5	7.2	196.6	192.4	192.4	−0.9	−5.1	−5.1
OH	CH_3		3	186.5	5.7	183.2	183.0	183.2	−3.3	−3.5	−3.3
OH	CH_3		4	198.2	7.2	198.6	195.5	195.6	0.4	−2.7	−2.6
OH	CH_3		5	187.4	6.1	186.5	184.9	185.1	−0.9	−2.5	−2.3
OH	CH_3		3	194.4	7.0	193.6	195.4	195.4	−0.8	1.0	1.0
											
CH_3	CH_3		2	192.1	6.4	193.4	193.0	193.0	1.3	0.9	0.9
CH_3	CH_3		4	193.3	6.4	194.9	194.4	194.5	1.6	1.1	1.2
CH_3	CH_3		5	186.0	6.4	185.5	185.7	185.8	−0.5	−0.3	−0.2
OH	OH		2	203.1	7.3	201.2	200.6	200.5	−1.9	−2.5	−2.6
F	F		5	165.6	5.8	167.6	162.2	162.6	2.0	−3.4	−3.0
OH	CH_3		2	198.3	7.2	198.5	197.8	197.8	0.2	−0.5	−0.5
OH	CH_3		4	201.2	7.3	201.8	199.2	199.2	0.6	−2.0	−2.0
OH	CH_3		5	183.3	6.0	180.2	179.5	179.7	−3.1	−3.8	−3.6
OH	CH_3		6	199.7	7.1	200.1	199.6	199.5	0.4	−0.1	−0.2
											
CH_3	CH_3		3	189.1	6.3	189.8	189.7	189.7	0.7	0.6	0.6
OH	OH		2	193.1	7.2	193.0	188.1	188.2	−0.1	−5.0	−4.9
F	F		3	172.4	6.4	172.8	171.3	171.5	0.4	−1.1	−0.9
OH	CH_3		2	196.5	7.1	196.0	195.4	195.3	−0.5	−1.1	−1.2
OH	CH_3		3	185.4	5.5	182.7	184.0	184.1	−2.7	−1.4	−1.3
											
F	F	F	5	168.6	6.4	167.0	170.8	163.1	−1.6	2.2	−5.5
F	F	F	4	174.0	6.7	173.5	170.8	171.1	−0.5	−3.2	−2.9
CH_3	CH_3	CH_3	4	195.1	6.3	195.3	195.4	195.3	0.2	0.3	0.2
CH_3	CH_3	CH_3	5	192.1	6.3	192.1	191.2	191.9	0.0	−0.9	−0.2
CN	CH_3	F	4	170.5	6.2	168.5	171.9	172.2	−2.0	1.4	1.7
CN	CH_3	F	5	165.9	5.7	168.2	169.5	169.8	2.3	3.6	3.9
CN	CH_3	F	6	173.0	6.4	172.6	173.5	173.8	−0.4	0.5	0.8
CN	F	CH_3	4	167.9	5.5	165.0	168.0	168.2	−2.9	0.1	0.3
CN	F	CH_3	5	170.3	6.3	172.1	173.2	173.4	1.8	2.9	3.1
CN	F	CH_3	6	169.1	5.9	168.7	170.0	170.3	−0.4	0.9	1.2
OH	CH_3	CH_3	4	203.0	7.2	202.6	200.3	200.2	−0.4	−2.7	−2.8
OH	CH_3	CH_3	5	190.0	6.3	187.9	186.4	186.5	−2.1	−3.6	−3.5
OH	CH_3	CH_3	6	200.1	7.0	198.9	197.7	197.6	−1.2	−2.4	−2.5

TABLE 1 (Continued)

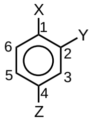
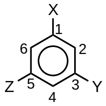
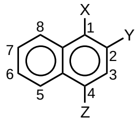
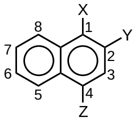
				proton affinity					deviation		
X	Y	Z	H^+	M(I)	Δ ZPE	M(II)	M(III)	M(IV)	δ_2	δ_3	δ_4
											
F	F	F	3	171.1	6.4	170.4	169.2	169.4	−0.7	−1.9	−1.7
F	F	F	5	175.0	6.4	174.7	170.9	171.1	−0.3	−4.1	−3.9
F	F	F	6	165.5	6.4	163.7	161.6	162.0	−1.8	−3.9	−3.5
CH_3	CH_3	CH_3	3	194.5	6.1	194.0	194.3	194.3	−0.5	−0.2	−0.2
CH_3	CH_3	CH_3	5	195.3	6.4	196.1	195.5	195.6	0.8	0.2	0.3
CH_3	CH_3	CH_3	6	191.6	6.2	190.6	191.1	191.1	−1.0	−0.5	−0.5
F	F	CH_3	3	178.3	6.3	177.9	176.7	176.9	−0.4	−1.6	−1.4
F	F	CH_3	5	181.7	6.4	181.8	178.3	178.5	0.1	−3.4	−3.2
F	F	CH_3	6	175.6	6.4	174.2	173.0	173.2	−1.4	−2.6	−2.4
F	CH_3	CH_3	3	185.2	6.0	185.1	184.0	184.0	−0.1	−1.2	−1.2
F	CH_3	CH_3	5	186.9	6.2	187.4	185.4	185.6	0.5	−1.5	−1.3
F	CH_3	CH_3	6	186.1	6.1	184.8	184.3	184.4	−1.3	−1.8	−1.7
CH_3	CH_3	OH	3	200.1	6.6	198.9	196.1	196.2	−1.2	−4.0	−3.9
CH_3	CH_3	OH	5	201.7	7.0	201.4	200.6	200.6	−0.3	−1.1	−1.1
CH_3	CH_3	OH	6	188.9	5.9	186.2	184.2	184.4	−2.7	−4.7	−4.5
F	OH	CH_3	3	191.2	6.8	190.1	188.8	188.8	−1.1	−2.4	−2.4
F	OH	CH_3	5	195.6	7.1	195.3	191.0	190.5	−0.3	−4.6	−5.1
F	OH	CH_3	6	181.3	6.2	178.1	177.1	177.3	−3.2	−4.2	−4.0
CH_3	F	CN	3	170.5	6.4	169.6	172.3	172.4	−0.9	1.8	1.9
CH_3	F	CN	5	172.4	6.4	171.7	173.1	173.3	−0.7	0.7	0.9
CH_3	F	CN	6	164.8	5.6	166.0	168.1	168.4	1.2	3.3	3.6
F	CN	CH_3	3	167.7	6.0	167.5	169.0	169.2	−0.2	1.3	1.5
F	CN	CH_3	5	167.4	5.7	165.4	167.8	168.1	−2.0	0.4	0.7
F	CN	CH_3	6	167.8	6.3	169.8	172.1	172.3	2.0	4.3	4.5
CH_3	CN	F	6	164.8	6.4	166.3	168.4	168.7	1.5	3.6	3.9
CH_3	CN	F	5	170.2	7.0	168.4	171.6	171.8	−1.8	1.4	1.6
CH_3	CN	F	3	170.6	7.1	170.6	172.6	172.8	0.0	2.0	2.2
F	CH_3	CN	3	167.3	5.6	165.5	167.9	168.1	−1.8	0.6	0.8
F	CH_3	CN	5	168.2	5.7	167.1	169.0	169.2	−1.1	0.8	1.0
F	CH_3	CN	6	167.9	6.2	169.1	171.8	172.0	1.2	3.9	4.1
											
F	F	F	4	180.0	6.9	179.0	177.2	177.4	−1.0	−2.8	−2.6
1,2,3,4 tetrafluorobenzene, 5-protonated											
				168.2	6.6	166.2	161.6	162.1	−2.0	−6.6	−6.1
1,2,3,4,5 pentafluorobenzene, 6-protonated											
				166.8	6.8	164.2	159.6	159.9	−2.6	−7.2	−6.9
											
H	H	H	1	194.8	6.6	194.6	196.2	196.2	−0.2	1.4	1.4
CN	H	H	2	178.6	6.3	177.7	181.2	181.4	−0.9	2.6	2.8
CN	H	H	3	179.0	6.4	181.0	182.8	182.9	2.0	3.8	3.9
CN	H	H	4	182.6	6.2	180.1	185.3	185.3	−2.5	2.7	2.7
CN	H	H	5	184.9	6.3	184.5	187.8	187.9	−0.4	2.9	3.0
CN	H	H	6	178.9	6.2	181.1	183.4	183.5	2.2	4.5	4.6
CN	H	H	7	180.2	6.2	180.7	183.5	183.5	0.5	3.3	3.3
CN	H	H	8	184.9	6.3	185.9	188.6	188.6	1.0	3.7	3.7
H	CN	H	1	183.3	6.4	181.9	185.8	185.9	−1.4	2.5	2.6
H	CN	H	3	180.1	6.4	180.7	182.6	182.8	0.6	2.5	2.7
H	CN	H	4	180.8	6.3	182.3	186.2	186.3	1.5	5.4	5.5
H	CN	H	5	183.4	6.3	184.6	187.7	187.7	1.2	4.3	4.3
H	CN	H	6	180.0	6.1	179.2	182.4	182.6	−0.8	2.4	2.6
H	CN	H	7	178.5	6.2	180.6	183.1	183.2	2.1	4.6	4.7
H	CN	H	8	184.7	6.3	183.7	187.2	187.2	−1.0	2.5	2.5
CN	F	H	4	176.6	6.1	172.2	176.1	176.3	−4.4	−0.5	−0.3
CN	F	H	5	180.8	6.2	179.8	182.2	182.3	−1.0	1.4	1.5
CN	F	H	6	178.4	6.3	180.8	181.7	181.8	2.4	3.3	3.4
CN	F	H	7	176.5	6.1	175.5	177.8	178.0	−1.0	1.3	1.5
CN	F	H	8	183.4	6.3	184.4	186.3	186.3	1.0	2.9	2.9

TABLE 1 (Continued)

				proton affinity					deviation		
X	Y	Z	H^+	M(I)	Δ ZPE	M(II)	M(III)	M(IV)	δ_2	δ_3	δ_4
											
CN	H	F	2	173.9	6.2	171.8	174.0	174.3	−2.1	0.1	0.4
CN	H	F	3	181.2	6.6	181.5	183.5	183.6	0.3	2.3	2.4
CN	H	F	5	181.7	6.1	180.2	179.7	182.6	−1.5	−2.0	0.9
CN	H	F	6	175.8	6.2	178.6	180.8	180.9	2.8	5.0	5.1
CN	H	F	7	176.0	5.9	174.3	176.7	176.9	−1.7	0.7	0.9
CN	H	F	8	181.5	6.2	183.2	185.8	185.8	1.7	4.3	4.3

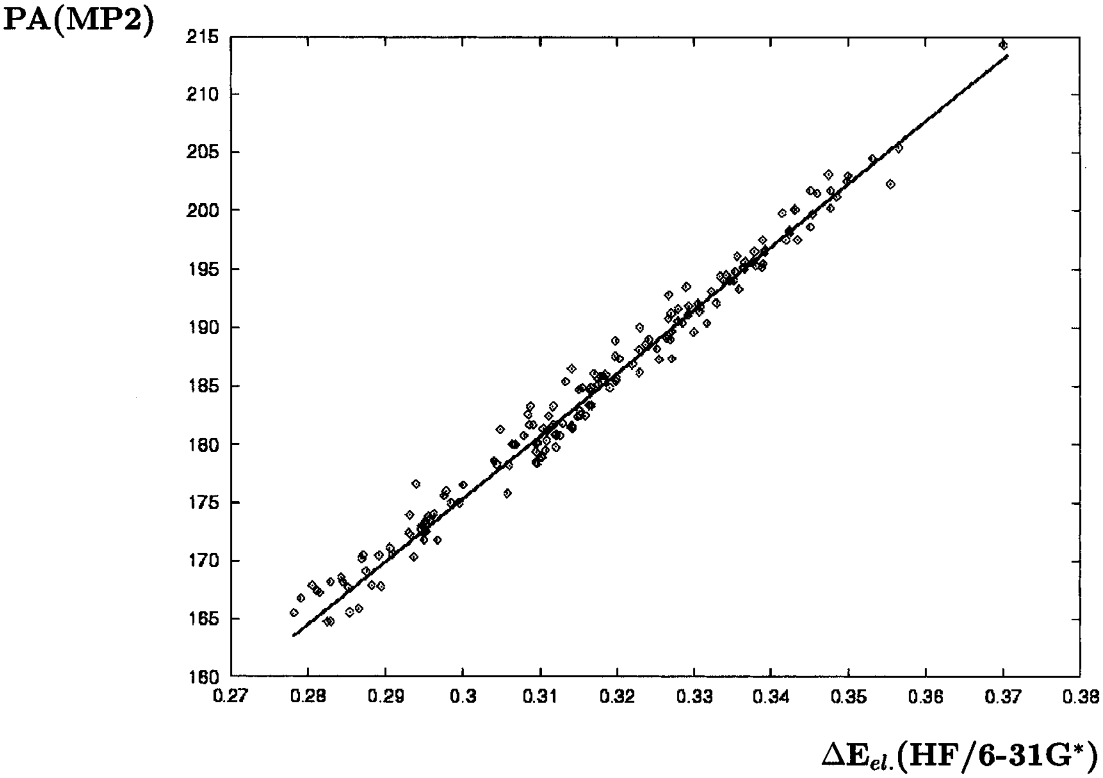


Figure 1. Linear relation between ΔE_{el}(MP2) and ΔE_{el}(HF) for substituted benzenes, naphthalenes, and biphenylenes.

energies (model M(III)) leading to

$$\mathrm{PA}(\mathrm{B}_\alpha) = 1.2167\Delta E_{\mathrm{el}}(\mathrm{AM1})_\alpha + 23.0 \quad (\mathrm{kcal/mol}) \quad (3)$$

Finally, one can utilize eq 4:

$$\mathrm{PA}(\mathrm{B}_\alpha) = \Delta H_{\mathrm{f}}^\circ(\mathrm{B}) + \Delta H_{\mathrm{f}}^\circ(\mathrm{H}^+) - \Delta H_{\mathrm{f}}^\circ(\mathrm{BH}_\alpha{}^+) \quad (\mathrm{kcal/mol}) \quad (4)$$

where $\Delta H_{\mathrm{f}}^\circ$ represents the AM1 heat of formation of the species, stated between parentheses, in the gas phase. This approach is signified as M(IV). The experimental $\Delta H_{\mathrm{f}}^\circ(\mathrm{H}^+)$ value for the proton of 367.2 kcal/mol[21] is employed here. The corresponding correlation with the MP2 PA values reads

$$\mathrm{PA}(\mathrm{B}_\alpha) = 1.2055[\Delta H_{\mathrm{f}}^\circ(\mathrm{B}) - \Delta H_{\mathrm{f}}^\circ(\mathrm{BH}_\alpha{}^+)] + 404.3 \quad (\mathrm{kcal/mol}) \quad (5)$$

3. Quantitative Appraisal of the Model and Prospects

The calculated proton affinities for a large number of substituted benzenes and naphthalenes deduced by models M(I)−M(IV) are presented in Table 1. The PA values offered by the reliable MP2 (or M(I)) model served as gauge values of very good quality. Hence, the deviation δ_1 from the M(I) model is zero by definition. In contrast, deviations $\delta_i = \mathrm{PA}(\mathrm{M}(i)) - \mathrm{PA}(\mathrm{M(I)})$, where $i = 2$, 3, and 4, reflect a performance of the Hartree−Fock and AM1 models in reproducing the proton affinity of the aromatic ring positions. It appears that the scaled HF model (eq 2) performs particularly well, as evidenced by the correlation coefficient $R = 0.99$ and the absolute average $|\delta_2|_{\mathrm{av}}$ value of 1.2 kcal/mol. Pictorially this is illustrated by Figure 1. Since the reference M(I) model is in good accordance with the experimental values within a margin of 1−2 kcal/mol as a rule,[10,11,13,14] it follows that the scaled HF model provides a simple and useful tool for exploring proton affinities in very large alternant aromatics. On the other hand the semiempirical AM1 scheme is somewhat less satisfactory irrespective of the use of the total electronic energy ΔE_{el} or $\Delta(\Delta H_{\mathrm{f}}^\circ)$ heats of formation (Figure 2). This is reflected by lower correlation coefficients $R_3 = R_4 = 0.96$ and average absolute deviations $|\delta_3|_{\mathrm{av}} = 2.6$ kcal/mol (or $|\delta_4|_{\mathrm{av}} = 2.4$ kcal/mol). Consequently, the AM1 semiempirical model is capable of reproducing a general trend of changes in PAs but should be used with a due caution if quantitative information is required. Furthermore, it

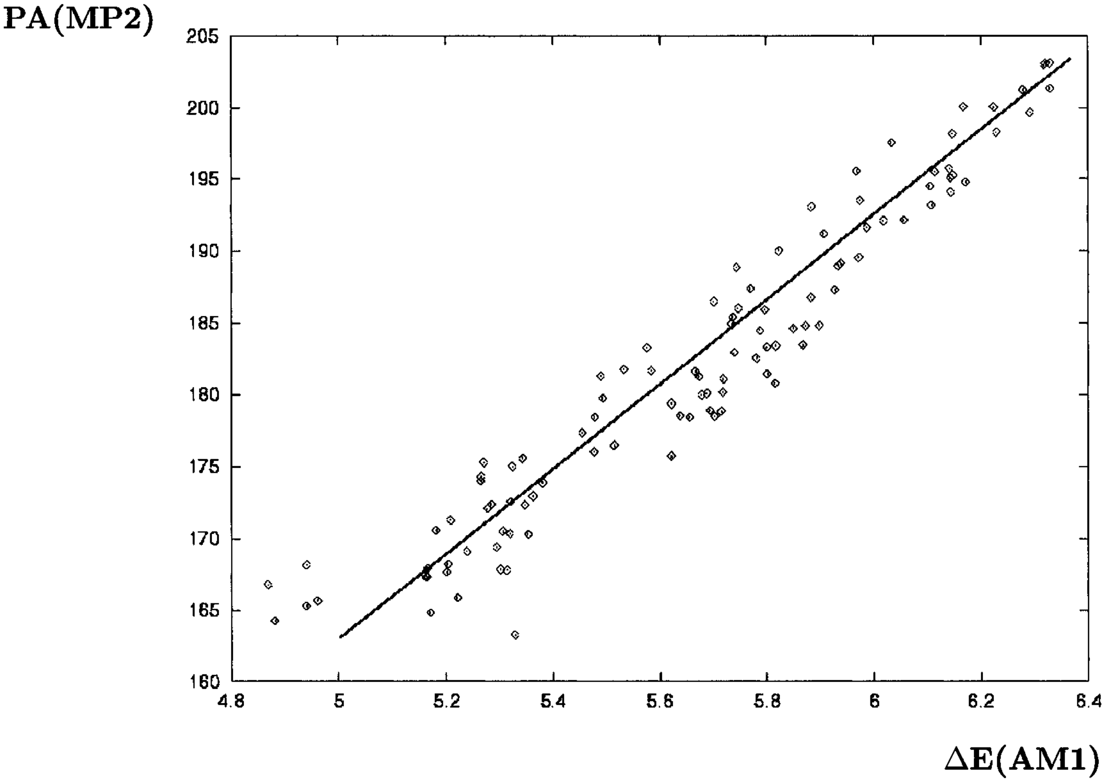


Figure 2. Linear relation between ΔE_{el}(MP2) and ΔE_{el}(AM1) for substituted benzenes and naphthalenes.

seems that the proton affinities provided by the AM1 procedure have to be separately correlated for each family of characteristic compounds (vide infra).

We shall focus now on biphenylenes (Table 2). The scaled HF model M(II) embodied in eq 2 reproduces the MP2 (M(I)) results with the usual accuracy found in substituted benzenes and naphthalenes. In contrast, PAs predicted by the AM1 scheme and eqs 3 and 4 are at variance by as much as 6.1 and 5.7 kcal/mol, respectively. Obviously, if the AM1 procedure is to be useful in the substituted biphenylenes and higher phenylenes, then specific new weighting factors are required. The least squares fit method yields the following correlations for biphenylenes:

$$\mathrm{PA}(\mathrm{B}_\alpha) = 1.5745\Delta E_{el}(\mathrm{AM1})_\alpha - 24.4 \quad (\mathrm{kcal/mol}) \qquad (6)$$

and

$$\mathrm{PA}(\mathrm{B}_\alpha) = 1.5232[\Delta H_f{}^\circ(\mathrm{B}) - \Delta H_f{}^\circ(\mathrm{BH}_\alpha{}^+)] + 462.3 \quad (\mathrm{kcal/mol}) \qquad (7)$$

The separate parametrization in biphenylenes reestablishes a fairly good accordance with the MP2 results. However, it should be stressed that eqs 6 and 7 exhibit a persistent average absolute deviations of ~2 kcal/mol, implying that the AM1 scheme is by a factor of 2 less accurate than the HF/6-31G* model.

The present analysis shows that the scaled HF and AM1 models are capable of mimicking the MP2 calculations of PAs in large aromatic systems. The Hartree−Fock approach is superior in this respect and should be preferentially employed whenever possible.

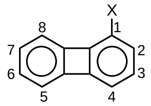
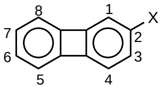
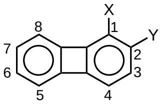
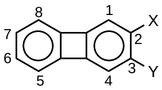
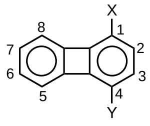
4. Applications of the Scaled Hartree−Fock Model

4.1. Proton Affinities of Pyrene and Its Monofluoroderivatives. After establishing reliability of the scaled HF model M(II) one can utilize it as a tool in studying PAs of large aromatic compounds. Pyrene (**1**) and its fluorinated derivatives (**2**), (**3**), and (**4**) will serve as suitable illustrative examples (Table 3). It should be mentioned that pyrene is very interesting per se in view of the carcinogenic activity of some of its substituted and annelated derivaitves as well as because of its omnipresence in polluted environments.[22] It appears that the M(II) model yields a PA of pyrene in excellent agreement with the most recent experimental evaluated value of 207.8 kcal/mol.[23] Moreover, the model calculations unequivocally show that protonation takes place at position 3. This is in harmony with the experimental NMR studies described by Laali.[24] We mention in passing that higher susceptibility of position 3 toward the proton attack can be qualitatively and pictorially rationalized by the larger number of resonance structures in Pauling's sense.[25] The alternative sites of the proton attack 1 and 4 are considerably less favorable. More specifically, protonation at position 3 is energetically more advantageous than proton attack at the 2 or 4 carbon atoms by 10 and 15.7 kcal/mol, respectively, as obtained by the M(II) model. This is in qualitative accordance with earlier PI-Dewar type of calculations, which gave 8.8 and 20.5 kcal/mol for these positions correspondingly.[26] This type of agreement between simplified semiempirical and ab initio calculations in pure hydrocarbons is expected. It disappears as a rule, however, in molecules possessing heteroatoms with lone pairs.

Since protonation represents a good model for electrophilic substitution, it is not surprising that nitration, bromination, chlorination, and acylation take place in pyrene predominantly at position C(3).[22]

In **2** the favorable positions are 3 and 5, in full harmony with appearance of the corresponding cations in superacid media as revealed by NMR measurements.[27] More precisely, these two pyrenium ions occur in a mixture with a ratio 45:55. It is worth mentioning that fluorination at the C(10) carbon atom deactivates all but one position, C(6) being this exception. Similarly,

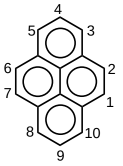
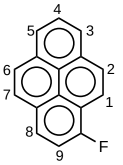
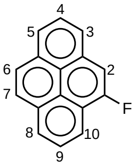
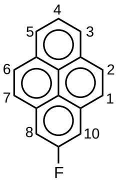
TABLE 2: Proton Affinity of Some Substituted Biphenylenes As Offered by Theoretical Models M(I)−M(IV) (in kcal/mol)

			proton affinity					deviation						proton affinity					deviation		
X	Y	H^+	M(I)	ΔZPE	M(II)	M(III)	M(IV)	δ_2	δ_3	δ_4	X	Y	H^+	M(I)	ΔZPE	M(II)	M(III)	M(IV)	δ_2	δ_3	δ_4
 																					
H		1	191.1	6.0	191.4	193.2	193.2	0.3	2.1	2.1	CN		4	181.4	6.1	181.2	181.7	182.0	−0.2	0.3	0.6
H		2	200.2	6.6	201.4	201.6	201.2	1.2	1.4	1.0	CN		5	180.9	5.9	182.1	183.4	183.6	1.2	2.5	2.7
F		2	197.5	6.7	198.3	197.4	197.1	0.8	−0.1	−0.4	CN		6	191.4	6.4	192.2	191.7	191.6	0.8	0.3	0.2
F		3	194.0	6.5	193.8	189.8	189.8	−0.2	−4.2	−4.2	CN		7	190.4	6.4	192.7	192.5	192.4	2.3	2.1	2.0
F		4	190.8	6.2	190.0	190.5	190.4	−0.8	−0.3	−0.4	CN		8	182.5	5.8	181.6	183.0	183.3	−0.9	0.5	0.8
F		5	185.7	6.0	186.3	186.8	186.8	0.6	1.1	1.1	OH		2	204.5	6.8	204.3	205.9	205.3	−0.2	1.4	0.8
F		6	197.5	6.7	199.0	199.5	199.1	1.5	2.0	1.6	OH		4	199.8	6.6	198.0	199.9	199.4	−1.8	0.1	−0.4
F		7	196.5	6.5	196.8	195.8	195.4	0.3	−0.7	−1.1	OH		5	192.8	5.9	190.0	190.4	190.3	−2.8	−2.4	−2.5
F		8	188.2	6.2	189.1	191.7	191.6	0.9	3.5	3.4	OH		6	202.3	6.9	205.6	207.6	207.0	3.3	5.3	4.7
CN		2	191.8	6.6	192.2	190.6	190.6	0.4	−1.2	−1.2	OH		7	201.5	6.5	200.4	199.4	198.9	−1.1	−2.1	−2.6
CN		3	187.4	6.4	190.2	189.6	189.7	2.8	2.2	2.3	OH		8	195.1	6.5	196.5	201.2	200.8	1.4	6.1	5.7
 																					
F		1	188.1	6.3	187.9	188.3	188.3	−0.2	0.2	0.2	CN		4	179.5	6.1	181.3	182.0	182.3	1.8	2.5	2.8
F		3	202.5	6.9	202.5	201.5	201.1	0.0	−1.0	−1.4	CN		5	181.7	5.8	180.5	182.2	182.5	−1.2	0.5	0.8
F		4	185.5	6.2	186.3	184.5	184.8	0.8	−1.0	−0.7	CN		6	189.6	6.4	191.8	191.8	191.8	2.2	2.2	2.2
F		5	189.0	6.2	190.1	190.1	190.1	1.1	1.1	1.1	CN		7	190.4	6.4	190.9	191.1	191.0	0.5	0.7	0.6
F		6	196.7	6.5	196.8	194.3	194.1	0.1	−2.4	−2.6	CN		8	180.4	5.9	181.4	183.0	183.3	1.0	2.6	2.9
F		7	198.6	6.6	199.9	198.1	197.9	1.3	−0.5	−0.7	OH		3	214.3	7.4	213.5	216.8	215.8	−0.8	2.5	1.5
F		8	187.6	6.0	186.2	185.2	185.4	−1.4	−2.4	−2.2	OH		4	190.6	6.2	190.6	190.1	190.1	0.0	−0.5	−0.5
CN		1	180.9	6.2	182.0	182.3	182.5	1.1	1.4	1.6	OH		7	205.4	6.9	206.2	206.3	205.8	0.8	0.9	0.4
CN		3	188.6	6.5	188.3	188.1	188.1	−0.3	−0.5	−0.5	OH		6	201.7	6.4	199.9	198.9	198.6	−1.8	−2.8	−3.1
 																					
F	F	3	196.1	6.7	194.8	190.4	190.4	−1.3	−5.7	−5.7	CN	CN	3	178.2	6.3	178.8	178.1	178.5	0.6	−0.1	0.3
F	F	4	185.9	6.2	185.2	182.0	182.2	−0.7	−3.9	−3.7	CN	CN	4	171.8	6.1	172.8	172.1	172.6	1.0	0.3	0.8
F	F	5	185.7	6.0	185.0	183.5	183.6	−0.7	−2.2	−2.1	CN	CN	5	173.4	5.7	172.9	173.9	174.4	−0.5	0.5	1.0
F	F	6	194.0	6.5	194.3	192.3	192.2	0.3	−1.7	−1.8	CN	CN	6	182.6	6.3	183.8	183.4	183.6	1.2	0.8	1.0
F	F	7	195.1	6.5	195.2	192.3	192.2	0.1	−2.8	−2.9	CN	CN	7	182.4	6.2	183.6	183.5	183.7	1.2	1.1	1.3
F	F	8	184.9	6.0	183.9	183.9	184.0	−1.0	−1.0	−0.9	CN	CN	8	173.8	5.7	173.1	174.3	174.7	−0.7	0.5	0.9
 																					
F	F	4	181.8	6.4	182.5	179.9	180.2	0.7	−1.9	−1.6	CN	CN	4	171.8	6.2	173.7	173.0	173.5	1.9	1.2	1.7
F	F	5	185.9	6.1	185.4	181.9	182.0	−0.5	−4.0	−3.9	CN	CN	5	172.7	5.8	172.6	173.9	174.3	−0.1	1.2	1.6
F	F	6	195.6	6.6	195.9	190.7	190.6	0.3	−4.9	−5.0	CN	CN	6	181.4	6.3	183.2	183.1	183.3	1.8	1.7	1.9
 																					
F	F	2	191.8	6.6	191.4	186.2	186.1	−0.4	−5.6	−5.7	CN	CN	2	179.8	6.5	182.1	179.6	180.1	2.3	−0.2	0.3
F	F	7	194.0	6.6	194.6	193.9	193.6	0.6	−0.1	−0.4	CN	CN	7	182.5	6.3	184.1	183.5	183.7	1.6	1.0	1.2
F	F	8	184.8	6.1	184.4	185.5	185.5	−0.4	0.7	0.7	CN	CN	8	173.5	5.7	173.2	174.2	175.9	−0.3	0.7	2.4

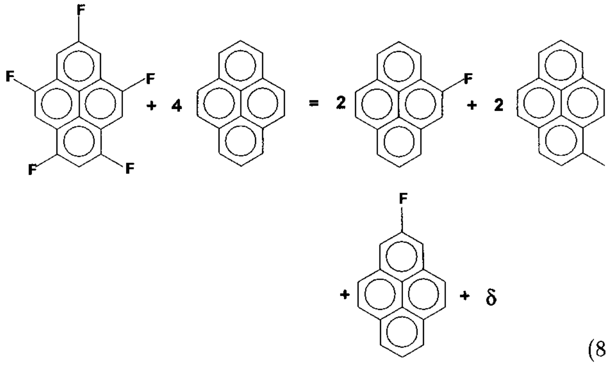
NMR experiments[27] indicate that protonation of **3** yields two cations resulting by the proton attack at positions 3 and 5 in approximate ratio 40:60. This is in nice agreement with the corresponding PAs of 206.8 and 207.2 kcal/mol, respectively (Table 3). Finally, fluorination at the apical position 9 in **4** yields only one protonated form with the sp^3 CH_2 center at positions 8 or 10, in full accordance with the NMR results.[27] It appears that these two carbon atoms are deactivated very little compared to the parent system **1**, whereas all other carbons of the molecular perimeter in **4** exhibit considerable decrease in their PAs. Consequently, their cations do not appear in experimental conditions. It follows that the scaled HF model offers a practical and reliable vehicle for exploring the proton affinity and electrophilic reactivity in large planar systems. We note in closing this paragraph that the AM1 models M(III) and M(IV) overshoot the ab initio results by ~2 kcal/mol.

4.2. Additivity of PAs in Polyfluorinated Pyrenes. Recently, it was shown that the proton affinity of multiply substituted aromatic compounds followed a very simple additivity rule, enabling its quick estimate once the PA of the parent hydrocarbon and increments describing the effect of particular substituents were known.[10−13] To put it in another way, the additivity rule is based on a simple concept of the independent substituent approximation (ISA). It is of interest to examine the additivity rule of thumb in larger aromatics in order to get an idea about propagation of the substituent effects in extended π-systems. Let us, therefore, consider PAs in polyfluorinated pyrenes depicted in Figure 3. Derivation of the additivity

TABLE 3: Theoretical Proton Affinities of Pyrene (1) and Its Monofluoroderivates as Predicted by Models M(II)−M(IV) in kcal/mol

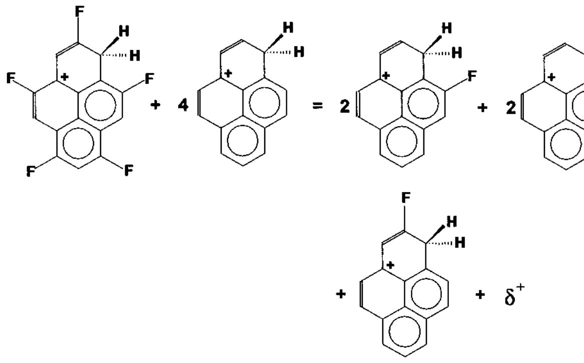
Molecule	Protonation	M(II)	M(III)	M(IV)
 **1**	1	198.1	201.0	200.2
	3	208.0	210.4	210.2
	4	192.3	193.9	193.9
 **2**	1	196.2	197.9	197.9
	2	196.6	199.2	199.3
	3	206.9	208.6	208.5
	4	188.4	189.7	189.8
	5	206.9	208.7	208.6
	6	198.5	200.0	199.9
	7	195.0	196.9	196.9
	8	203.4	203.8	203.7
	9	191.7	192.8	192.8
 **3**	2	199.4	202.4	202.3
	3	206.8	208.8	208.4
	4	188.7	189.7	189.7
	5	207.2	208.9	208.7
	6	195.1	197.5	197.4
	7	194.9	196.8	196.8
	8	202.3	203.9	203.8
	9	189.4	190.3	190.3
	10	203.5	204.6	204.5
 **4**	1	196.1	198.0	198.0
	2	191.8	194.1	194.1
	3	202.8	204.6	204.4
	4	191.2	191.2	191.2
	10	206.7	208.4	208.2

formula is straightforward if the concept of homodesmic reactions[28] is employed. For example, the homodesmic reaction for system **5** and its protonated form $(\mathbf{5})_3$ reads



(8a)

and



(8b)

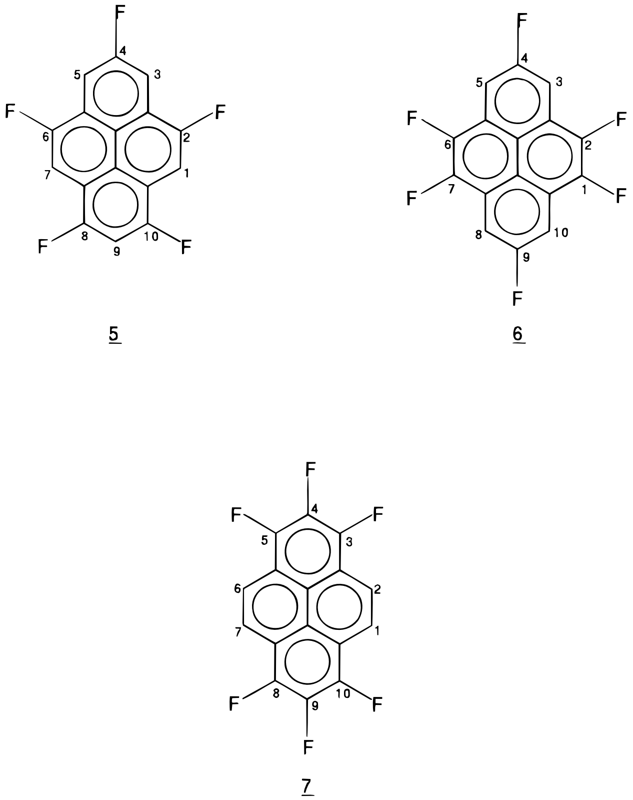
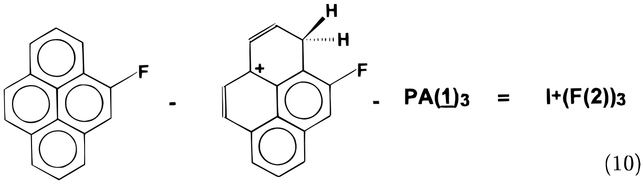


Figure 3. Schematic representation and atomic nubering of some polyfluorinated pyrenes.

After taking a difference between (8a) and (8b) and some elementary rearrangements one obtains

$$PA(\mathbf{5})_3 = PA(\mathbf{1})_3 + 2I^{+}(F(2))_3 + 2I^{+}(F(10))_3 + I^{+}(F(4))_3 + \Delta \quad (9)$$

Here $\Delta = \delta - \delta^{+}$, whereas I^{+} are increments in PA due to fluorination at particular position F(n). For instance, $I^{+}(F(2))_3$ is defined as



(10)

where $PA(\mathbf{1})_3$ is the proton affinity of pyrene corresponding to the proton attack at the C(3) carbon atom.

PA increments in monofluoropyrenes **2**−**4** are given in Table 4. They are small in absolute values and negative in sign with very few exceptions, as discussed earlier. By using the additivity formulas, one can easily obtain proton affinities of polyfluorinated pyrenes **5**−**7**, which compare well with PA values offered by the scaled Hartree−Fock model. Deviations from the M(II) calculations Δ are typically 1−2 kcal/mol, which is quite satisfactory. Examination of the interference

TABLE 4: PA Increments in Monofluoropyrenes 2−4 $I^+(F_n)$ and the Proton Affinities of Polyfluorinated Pyrenes 5−7 Compared to Approximate Estimates Obtained by the Additivity Rule (in kcal/mol)

		proton positions									
molecule	entity	1	2	3	4	5	6	7	8	9	10
2	$I^+(F(2))$	−1.9	−1.5	−1.1	−3.9	−1.1	0.4	−3.1	−4.6	−0.6	
3	$I^+(F(3))$		1.3	−1.2	−3.6	−0.8	−3.0	−3.2	−5.7	−2.9	−4.5
4	$I^+(F(4))$	−2.0	−6.3	−5.2	−1.1	−5.2	−6.3	−2.0	−1.3		−1.3
5	PA	185.9		194.7		194.7		185.9		182.0	
	$PA_{ad.}$	185.1		194.3		194.3		185.1		182.6	
	δ	2.9		2.9		2.9		2.9		2.9	
	$-\delta^+$	−1.9		−2.2		−2.2		−1.9		3.5	
	Δ	1.0		0.7		0.7		1.0		−0.6	
6	PA			190.5		190.5			190.5		190.5
	$PA_{ad.}$			189.3		189.3			189.3		189.3
	δ			13.8		13.8			13.8		13.8
	$-\delta^+$			−12.2		−12.2			−12.2		−12.2
	Δ			1.6		1.6			1.6		1.6
7	PA	184.3	184.3				184.3	184.3			
	$PA_{ad.}$	183.7	183.7				183.7	183.7			
	δ	21.9	21.9				21.9	21.9			
	$-\delta^+$	−20.9	−20.9				−20.9	−20.9			
	Δ	1.0	1.0				1.0	1.0			

energies δ and δ^+ in neutral bases and their cationic conjugate acids reveals remarkable similarity. Hence, it is their cancellation $\delta - \delta^+ = \Delta \cong 0$ which leads to a surprisingly well-preserved additivity property of the proton affinity. It should be stressed that δ and δ^+ sometimes assume substantial values like in systems **6** and **7**, where they are as large as $\simeq$14 and $\simeq$22 kcal/mol, respectively. Thus it follows that protonation does not significantly affect intramolecular interactions of F atoms.

5. Conclusion

We have shown that the scaled Hartree−Fock (ScHF) model describes very well the ring proton affinity of a wide variety of polysubstituted benzenes, naphthalenes, and biphenylenes. The average absolute deviation from the full MP2 calculations, which in turn are very close to the best available experimental results, is on the order of 1 kcal/mol. The scaled AM1 approach can also be useful, but systems involving annelated small (antiaromatic) ring(s) like biphenylenes have to be separately correlated. In spite of this special treatment the average absolute error remains persistently higher than that of the ScHF model, being $\simeq$2 kcal/mol. Further, it is conclusively shown that the ScHF model provides a practical tool in exploring the proton affinity of very large alternant aromatics, as evidenced by results obtained in pyrene and its mono- and polyfluoro derivatives. The calculated PAs are in accordance with available experimental evidence, offering at the same time additional useful information. Finally, it is shown that multiply fluorinated pyrenes follow a simple ISA additivity rule observed earlier in benzenes, naphthalenes, and biphenylenes.[10−13] The origin of this additivity is found in the remarkable similarity of the intramolecular interference energies in initial bases and their conjugate acids.

Acknowledgment. We thank the University of Zagreb Computation Center and the IBM project “Academic Initiative for Croatia” for donation of the computing time. We thank the referees for useful comments and suggestions.

References and Notes

(1) Maksić, Z. B.; Eckert−Maksić, M. In *Theoretical and Computational Chemistry, Vol. 5, Theoretical Organic Chemistry*; Parkany, C., Ed.; Elsevier: Amsterdam, in press.

(2) Mautner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448.

(3) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(4) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(5) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 4885.

(6) Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1994**, *231*, 345.

(7) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *116*, 11299.

(8) Schmiedekamp, A. M.; Topol, I. A.; Michejda, C. J. *Theor. Chim. Acta* **1995**, *92*, 83.

(9) Chandra, A. K.; Goursot, A. *J. Phys. Chem.* **1996**, *100*, 11596.

(10) Eckert-Maksić, M.; Klessinger, M.; Maksić, Z. B. *Chem. Phys. Lett.* **1995**, *232*, 472; *J. Phys. Org. Chem.* **1995**, *8*, 435; *Chem. Eur. J.* **1996**, *2*, 155.

(11) Kovaček, D.; Maksić, Z. B.; Novak, I. *J. Phys. Chem.* **1997**, *101*, 1147.

(12) Maksić, Z. B.; Eckert-Maksić, M.; Klessinger, M. *Chem. Phys. Lett.* **1996**, *26*, 572.

(13) Eckert-Maksić, M.; Klessinger, M.; Antol, I.; Maksić, Z. B. *J. Phys. Org. Chem.* **1997**, *10*, 415.

(14) Eckert-Maksić, M.; Hodošček, M.; Kovaček, D.; Maksić, Z. B.; Primorac, M. *J. Mol. Struct. (THEOCHEM)*, in press.

(15) Davis, D. W.; Shirley, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 7898.

(16) Catalán, J.; Yáñez, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 741.

(17) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(18) Hehre, J. W.; Radom, L.; von Schleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Willey-Interscience: New York, 1986; and references cited therein.

(19) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

(20) Ibrahim, M. R.; Fataftah, Z. A. *Chem. Phys. Lett.* **1986**, *125*, 149.

(21) Stull, D. R.; Prophet, H., Eds. *JANAF Thermochemical Tables*, Nat. Stand. Ref. Data. Ser., Nat. Bur. Stand., NSRDS-NBS 37, U.S. Govt. Printing Office, Washington, DC.

(22) Laali, K. K.; Hansen, P. E. *J. Org. Chem.* **1991**, *56*, 6795, and references cited therein.

(23) According to a new NIST proton affinity scale completed by Dr. E. Hunter and Dr. S. Lias. We thank Dr. Hunter for making these results available prior to publication.

(24) Laali, K. K. *Chem. Rev.* **1996**, *96*, 1873.

(25) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

(26) Dewar, M. J. S.; Denninton, R. D., II *J. Am. Chem. Soc.* **1989**, *111*, 3804.

(27) Laali, K. K.; Hansen, P. E. *J. Org. Chem.* **1993**, *58*, 4096.

(28) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 313; *J. Chem. Soc., Perkin Trans 2* **1976**, 1222.