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ADDITIVITY OF PROTON AFFINITIES: THEORETICAL STUDIES OF FLUORINE- AND METHYL-SUBSTITUTED BENZENES

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Ring proton affinities (*PA*s) in fluorobenzene and toluene were examined by the MP2(fc)/6–31G//HF/6–31G* + *ZPE*(HF/6–31G*) model. The calculated *PA*s are in good accordance with the available experimental evidence, their order being $PA(p) > PA(o) > PA(m) > PA(i)$, where *p, o, m* and *i* stand for *para, ortho, meta* and *ipso* positions, respectively. The relative values of the proton affinities can be interpreted in terms of the ground-state charge distribution (initial state effect) and the characteristic π-bond fixation produced by protonation (final state effect). The influence of the latter is either concerted with the initial charge distribution leading to higher *PA*s (*ortho* and *para* positions) or disconcerted as in *meta* protonation, which has a lower *PA* value. Finally, it is shown that *PA*s in difluorobenzenes and fluorotoluenes are additive and can be reduced to the characteristic *PA*s of fluorobenzene and toluene with good accuracy.**

INTRODUCTION

Notwithstanding its size, the proton occupies one of the dominant positions in chemistry,[1–3] playing an important role in proton transfer reactions, catalysis, solvation and nucleation phenomena in solutions, in charge and mass transport processes in membranes, in determining acidity and basicity, etc. Additionally, the intrinsic or 'dilute gas-phase' proton affinities (*PA*s) serve as very useful probes of the electronic structure of the parent (aromatic) bases and their substituted derivatives inasmuch as they are intimately related to the corresponding substituent constants and the linear free energy relationships.[4] *PA*s might also be useful in studying electrophilic substitution reactivity in aromatics[5] and in discussing effects caused by the fusion of small strained rings to aromatic nuclei.[6] Consequently, it is of great importance to gather as much knowledge about *PA*s as possible. Several experimental techniques have been developed for this purpose.[7] Unfortunately, measured *PA*s usually refer to the most stable protonated species and therefore yield little or no information about alternative sites of protonation.

Modern computational methods of quantum chemistry[8] provide a very useful complementary approach, particularly since they treat all protonated forms at the same footing. A serious bottleneck is given by the size of the molecules under study, since a high level of theory is usually required for quantitative *a priori* estimates of proton affinities. Concomitantly, they are confined to small molecules. It is gratifying that a relatively simple model denoted by MP2(fc)/6–31G**//HF/6–31G* + *ZPE*(HF/6–31G*) seems to give satisfactory *PA*s in substituted benzenes.[9] Hence it is of some interest to apply it in calculations of *PA*s in fluorobenzenes and fluorotoluenes. The motivation for this work was the scarcity of experimental and theoretical data on protonation in this important family of molecules.

Recently, Hrušak *et al.*[10] reported results of a combined *ab initio* and experimental study of protonated fluorobenzene, but their attention was focused on the proton 'ring-walk' mechanism and the problem of the unimolecular loss of the HF molecule. Further, a *PA* value of 181·8 kcal mol^{-1} (1 kcal = 4·184 kJ) has been ascribed to the *ortho* ring position by collisionally induced decomposition mass spectrometric measurements.[11,12] Consequently, the question arises of whether this site is thermodynamically also the most favourable one.

Finally, we address the question of additivity of *PA*s in difluorobenzenes and fluorotoluenes. Such a 'rule of thumb' would be of great help in estimating *PA*s of

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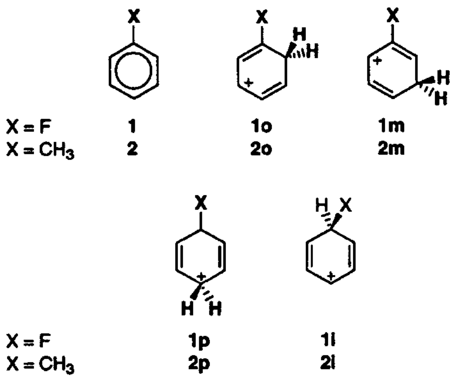
polysubstituted benzenes, which are not easily treated theoretically because of the large number of electrons. An additivity rule can serve also as a useful guide in experimental investigations.

METHOD OF COMPUTATION

The theoretical model should be feasible, economical and reliable. In order to keep the computational efforts at a minimum, all geometries are optimized by the HF/6–31G* model. The latter is employed for the vibrational analysis calculations of the zero point energies (*ZPE*s). The resulting *ZPE*s are multiplied by the empirical scaling factor of 0·89 as usual.[8] Inclusion of the *ZPE* is crucial for a quantitative description of the absolute values of *PA*s since the protonated forms have one more atom and an additional chemical bond. Since benzene is an aromatic moiety, electron correlation should be explicitly taken into account. This is achieved at least partially by single-point MP2(fc)/6–31G**//HF/6–31G* calculations. Again, the lowest order MP calculations are carried out for economical reasons. Frozen $(1s)^2$ electron cores (fc) are assumed in order to increase efficiency. However, a larger 6–31G** basis set is employed in the MP2(fc) single-point procedure since a detailed description of the densities at the hydrogen atoms is a prerequisite for a good performance of the model. Some alternative basis sets and the MP2(fu) procedure, which implies that all electrons are included in the correlation energy calculation, are used too for the sake of comparison. All computations are performed by using the Gaussian 92 program package.[13]



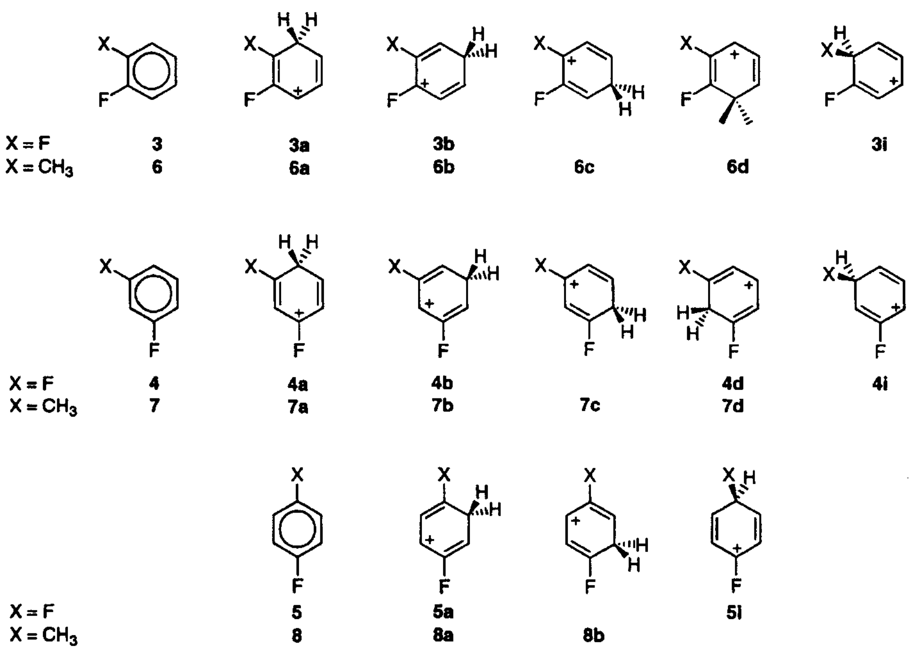
Scheme 1

RESULTS AND DISCUSSION

Proton affinity in fluorobenzene and toluene

The examined systems are presented in Schemes 1 and 2. Proton affinities are calculated using the equation

$$PA(n_i) = E(n) + ZPE(n) - [E(n_i) + ZPE(n_i)] \quad (1)$$



Scheme 2

where n_i refers to the protonated species under study and n without a subscript stands for the unprotonated form. E is the total molecular energy. It should be noted that the PA is defined as a positive entity. We commence the discussion with the protonated fluorobenzenes **1o–1i**. Several theoretical models are examined: HF/6–31G*, MP2(fu)/6–31G*//HF/6–31G*, MP2(fu)/6–311G*//HF/6–31G* and MP2(fc)/6–31G**//HF/6–31G* (Table 1), all of which indicate that the *para* position is most susceptible to the electrophilic attack as evidenced by the largest PA value. This is in accord with some experimental results yielding $PA(\mathbf{1p}) = 182{\cdot}9$ kcal mol^{-1}.[14] In comparing our results with experiment one should keep in mind that the theoretical PA values refer to 0 K. No attempt is made to estimate the influence of the temperature at 300 or 600 K, the latter being used in the actual measurements by Lau and Kebarle.[14] The point is that the experimental PAs are accurate only to within a couple of kcal mol^{-1}.[7] Second, all comparisons will be made within the adopted theoretical model only.

Nevertheless, the experimental data may serve as a useful benchmark in selecting the most appropriate theoretical model. First we note that explicit inclusion of the core electrons in the MP2(fu) procedure has only a minor effect on the calculated PAs, and a negligible effect on the relative values ΔPA, the largest difference between MP2(fc) and MP2(fu) values calculated with

Table 1. Total molecular energies E (in au), ring proton affinities PA (in kcal mol^{-1})[a] and zero point energies ZPE (in kcal mol^{-1})[b] of fluorobenzene (**1**) and toluene (**2**) as calculated by different models

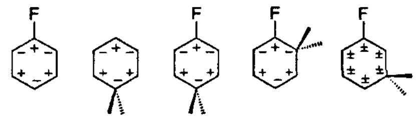
Molecule	Parameter	HF/6–31G*	MP2(fu)/6–31G*//HF/6–31G*	MP2(fu)/6–311G*//HF/6–31G*	MP2(fc)6–31G**//HF/6–31G*
1	*E*	−329·55467	−330·50758	−330·74423	−330·51478
	ZPE	55·4	55·4	55·4	55·4
1o	*E*	−329·86419	−330·79808	−331·02868	−330·81101
	ZPE	61·9	61·9	61·9	61·9
	PA	187·7	175·8	172·0	179·4
	Δ*PA*	−2·9	−2·2	−2·4	−2·2
1m	*E*	−329·84986	−330·78667	−331·01711	−330·79931
	ZPE	61·4	61·4	61·4	61·4
	PA	179·2	169·1	165·2	172·5
	Δ*PA*	−11·4	−8·9	−9·2	−9·1
1p	*E*	−329·86872	−330·80167	−331·03248	−330·81460
	ZPE	61·9	61·9	61·9	61·9
	PA	190·6	178·0	174·4	181·6
	Δ*PA*	0	0	0	0
1i	*E*	−329·83395	−330·76143	−330·99157	−330·77497
	ZPE	62·0	62·0	62·0	62·0
	PA	168·6	152·7	148·6	156·7
	Δ*PA*	−22·0	−25·3	−25·8	−24·9
2	*E*	−269·74016	—	—	−270·69134
	ZPE	76·5	—	—	76·5
2o	*E*	−270·06300	—	—	−270·99815
	ZPE	82·8	—	—	82·2
	PA	196·2	—	—	186·2
	Δ*PA*	−1·8	—	—	−1·1
2m	*E*	−270·05532	—	—	−270·99292
	ZPE	82·8	—	—	82·8
	PA	191·4	—	—	182·9
	Δ*PA*	−6·6	—	—	−4·4
2p	*E*	−260·06559	—	—	−270·99975
	ZPE	82·7	—	—	82·7
	PA	198·0	—	—	187·3
	Δ*PA*	0	—	—	0
2i	*E*	−270·04935	—	—	−270·98593
	ZPE	83·4	—	—	83·4
	PA	187·0	—	—	179·9
	Δ*PA*	−11·0	—	—	−7·4

[a] Relative changes in the proton affinities, Δ*PA*, are calculated by taking the most stable *para*-protonated form as a standard.
[b] *ZPE* values are estimated at the HF/6–31G* level utilizing a common scaling factor of 0·89

the same basis set being 0·2 kcal mol^{-1}. Perusal of the data in Table 1 reveals that PA(**1p**) estimated by the Hartree–Fock model is overestimated by 7 kcal mol^{-1}, whereas MP2 single-point calculations without polarization functions at the hydrogens (MP2/6–31G**//HF/6–31G* and MP2/6–311G*//HF/6–31G*) significantly underestimate the proton affinity. The best accordance with experiment is achieved by the MP2(fc)/6–31G**//HF/6–31G* model, which shows that both the correlation effect and polarization of the hydrogen atoms should be explicitly taken into account. Although the *ZPE* is important in determining the absolute value of *PA*s, its variation ΔZPE is negligible, implying that it can be safely neglected in discussing the relative values of the proton affinities ΔPA. Surprisingly, it appears that relative values ΔPA are fairly well reproduced by all models employed, in spite of the errors in absolute values of *PA*s (see above). It should be noted, however, that HF relative proton affinities are sometimes off by several kcal mol^{-1} from all MP2 values, which in turn are in very good mutual agreement.

It appears that *ortho* protonation is energetically less favourable than *para* protonation. Experiment[11,12,14] shows that PA(**1p**) − PA(**1o**) is 1·1 kcal mol^{-1}, which should be compared with theoretical estimates of *ca* 2 kcal mol^{-1}. This is satisfactory in view of the errors involved both in experimental techniques and theoretical procedures. Further, the *meta* position is less favourable for protonation by *ca* 10 kcal mol^{-1}, whilst the *ipso* site is least favourable, as revealed by ΔPA = −25 kcal mol^{-1}. Similar conclusions may be drawn from the results for the protonated toluenes **2o**–**2i**. Again, the *PA* value is largest for the *para* position. The MP2 value PA(**2p**) = 187·3 kcal mol^{-1} is smaller than the experimental value of 190·0 kcal mol^{-1} from Lau and Kebarle,[14] but is in good agreement with a more recent experimental value of 189·1 kcal mol^{-1}.[15] The *PA*s of the *ortho*, *meta* and *ipso* positions are smaller than that of the *para* position by 1, 4 and 7 kcal mol^{-1}, respectively. In summary, it seems that the MP2(fc)/6–31G**//HF//6–31G* + *ZPE*(HF/6–31G*) model is indeed a useful tool for studying *PA*s in fluorinated benzenes. Since the same conclusion holds for protonated phenols,[9] it is likely that this model will perform very well for all other aromatic systems involving first row substituent atoms.

Our next task is the interpretation of the theoretical results. This can be easily done at the qualitative level by considering π-electron resonance structures describing π-back-donation of the fluorine lone pair to the aromatic ring.[16] It is also of some importance to include polarization resonance structures reflecting induced charge alternation resulting from π-back donation. The charge distribution in fluorobenzene is illustrated by **I** in Scheme 3.



Scheme 3

Analogously, one can easily deduce the charge distribution in the benzenium ion (**II** in Scheme 3). Superposition of these two charge patterns for *para* and *ortho* protonation yields concerted overall density distributions as shown in Scheme 3 (**III** and **IV**). Hence we conclude that protonation at *para* and *ortho* sites are favourable for two reasons: (i) since the atoms in these sites possess negative charge, implying that the interaction with the proton is electrostatically profitable, and (ii) charge redistributions caused by fluorination and protonation are compatible and synactive. The importance of the latter effect was stressed in an earlier study of protonation in benzocycloalkenes.[6] In contrast, bonding patterns **I** and **II** (Scheme 3) are antagonistic for *meta* protonation indicating that this position is not energetically favourable (**V** in Scheme 3). Additionally, formally positively charged *meta* carbon atoms are not suitable for accommodation of the positive proton. It should be pointed out that the charge distributions discussed so far at the qualitative level are substantiated by the HF/6–31G* atomic charges deduced by using Mulliken population analysis. We note in passing that the very low PA(**1i**) value is easily rationalized by the σ-inductive effect of the fluorine atom, which is most pronounced at the site of substitution. It follows that the ordering of proton affinities PA(**1p**) ≈ PA(**1o**) > PA(**1m**) > PA(**1i**) is compatible with the simple intuitive picture just described, in agreement with the results discussed above and given in Table 1. The same analysis applies to the protonation of toluene, although the differences ΔPA are considerably smaller owing to the different σ-inductive effect of the methyl group and the fact that the formal charge of the *meta* position is not positive but rather less negative than that of the *ortho* and *para* positions.

Additivity of proton affinities in polysubstituted benzenes

Since the MP2(fc)/6–31G**//HF/6–31G* + *ZPE*(HF/6–31G*) model is capable of providing quantitative information about *PA*s in fluorobenzene we used it also to calculate *PA*s of difluorobenzenes and fluorotoluenes. The results are given in Table 2. Experimental data on these compounds are scarce. For *m*-difluorobenzene Yamdagni and Kebarle[17] give *PA* = 181·6 kcal mol^{-1}, which compares very

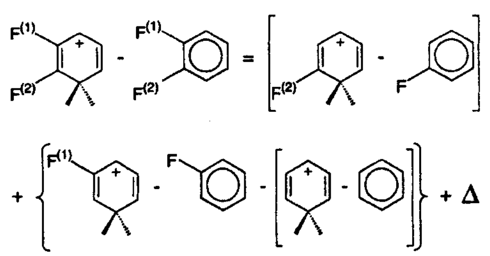
Table 2. Total molecular energies E (in au) and zero point energies ZPE (in kcal mol^{-1}) of difluorobenzenes **3–5** and fluorotoluenes **6–8**

Molecule	*E* (HF)[a]	*ZPE*[b]	*E* (MP2)[c]
Benzene	−230·70314	60·2	−231·50460
Prot. benzene	−231·01468	66·3	−231·80103
3	−428·39819	50·6	−429·51749
3a	−428·69143	57·0	−429·80190
3b	−428·69773	57·0	−429·80658
3i	−428·68117	57·6	−429·78362
4	−428·39819	50·6	−429·52376
4a	−428·71640	57·3	−429·82300
4b	−428·68355	56·4	−429·79697
4d	−428·71093	57·3	−429·81854
4i	−428·66747	57·1	−429·77145
5	−428·40370	50·6	−429·52292
5a	−428·69866	57·0	−429·80786
5i	−428·68910	57·7	−429·79043
6	−368·59274	71·9	−369·70327
6a	−368·89946	77·7	−369·99892
6b	−368·91105	78·4	−370·00853
6c	−368·90330	77·9	−370·00071
6d	−368·90574	78·3	−370·00460
7	−368·59227	71·7	−369·70174
7a	−368·91727	78·3	−370·01186
7b	−368·89119	77·8	−369·99207
7c	−368·91546	78·2	−370·01005
7d	−368·91215	78·3	−370·00787
8	−368·59128	71·7	−369·70131
8a	−368·89900	77·8	−369·99659
8b	−368·90511	78·3	−370·00260

[a] Calculated with the HF/6–31G* model.
[b] Estimated at the HF/6–31G* level using a common scaling factor of 0·89.
[c] Calculated with the MP2(fc)/6–31G**//HF/6–31G* model.

favourably with our computed value $PA(\mathbf{4a}) = 181{\cdot}1$ kcal mol^{-1}.

Utilizing the concept of homodesmic chemical reactions[18,19] in a modified form, the PA values of polysubstituted benzenes may be decomposed into elementary components which are related to the monosubstituted species. This will be demonstrated for the *ortho* protonation in 1,2-difluorobenzene. The negative value of $PA(\mathbf{2a})$ can be written as



(2)

Equation (2) describes protonation as if it occurred in two steps. In the first step, the perturbation by F(1) is neglected and the protonation energy is given by the first brackets on the right-hand side. In the second stage, the perturbation exerted by atom F(1) is included and its influence on the protonation site is determined by the terms in braces. If the processes of difluorination and protonation were perfectly isolated and independent, then the interference Δ would be exactly zero. In that case $PA(\mathbf{3a})$ would be given as a sum of three contributions which can be identified as PAs of the *ortho* and *meta* positions in fluorobenzene, $PA(\mathbf{1o}) = 179{\cdot}4$ kcal mol^{-1} and $PA(\mathbf{1m}) = 172{\cdot}5$ kcal mol^{-1}, whereas the third term is $PA(\text{benzene}) = 179{\cdot}9$ kcal mol^{-1}. It is obvious that equation (2) is invariant with respect to the choice of the perturbing F atom. In reality $\Delta \neq 0$, but it is intuitively expected that its absolute value is small.

Ab initio results for the difluorobenzenes **3–5** and fluorotoluenes **6–8** presented in Table 3 show that additivity works very well for both the HF/6–31G* and the single-point MP2(fc)/6–31G**//HF/6–31G* models. The deviations Δ are lower in the latter case. In general, the additivity rule offers PA values with errors which are close to the experimental uncertainties. There are two exceptions, however, which are noteworthy. Both correspond to *ipso* protonated forms (**3i** and **5i**), which should be kept in mind in future applications. We mention in passing that the protonated difluorobenzenes **3a** and **3b** have been observed in superacid solution at −50 °C with the **3b** form being preferred,[20] in accordance with PAs obtained by additivity and full *ab initio* calculations.

The performance of the additivity rule is encouraging and thus offers a new way of studying PAs in multiply substituted aromatic molecules since the generalization to more complex systems is obvious. It requires the application of equation (2) in several consecutive steps. Thus, in analogy with equation (2), the PA *of* 1,3,5-trifluorobenzene (**9**) may be written either as

$$PA(\mathbf{9}) = [2PA(\mathbf{1o}) - PA(\text{benzene})] - [PA(\mathbf{1p}) - PA(\text{benzene})] \quad (3)$$

or, if PA values for disubstituted benzenes are available, as

$$PA(\mathbf{9}) = PA(\mathbf{4a}) - [PA(\mathbf{1o}) - PA(\text{benzene})] \quad (4)$$

or

$$PA(\mathbf{9}) = PA(\mathbf{4d}) - [PA(\mathbf{1p}) - PA(\text{benzene})]. \quad (5)$$

Using calculated PA values from Table 3, both equations (3) and (4) yield $PA(\mathbf{9}) = 180{\cdot}6$ kcal mol^{-1}, while equation (5) gives $PA(\mathbf{9}) = 180{\cdot}0$ kcal mol^{-1}, in very good agreement with the experimental value of $PA = 181{\cdot}0$ kcal mol^{-1} for 1,3,5-trifluorobenzene.[17]

Table 3. Additivity of the proton affinity in difluorobenzenes and fluorotoluenes (in kcal mol^{-1})

	HF/6–31G*			MP2(fc)/6–31G**//HF/6–31G*		
Molecule	*PA*(calc.)	*PA*(add.)	Δ[a]	*PA*(calc.)	*PA*(add.)	Δ[a]
3a	177·7	177·4	0·3	172·2	172·0	0·2
3b	181·6	180·3	1·3	175·0	174·1	0·9
3i	170·7	166·8	3·9	160·0	156·1	3·9
4a	188·5	188·9	−0·4	181·1	181·1	0·0
4b	168·8	168·9	−0·1	165·6	165·0	0·6
4d	185·0	186·0	−1·0	178·3	178·9	−0·6
4i	158·0	158·2	−0·2	148·9	149·1	−0·2
5a	178·7	177·0	1·7	172·4	171·5	0·9
5i	172·0	169·7	2·3	160·8	158·3	2·5
6a	186·7	186·0	0·7	179·7	178·8	0·9
6b	193·2	192·6	0·6	185·1	184·6	0·5
6c	188·9	187·8	1·1	189·6	179·9	0·7
6d	190·1	189·7	0·4	182·7	182·4	0·3
7a	197·3	197·4	−0·1	188·0	187·5	0·5
7b	181·5	181·2	0·3	176·1	175·5	0·6
7c	196·3	196·3	0·0	187·0	186·8	0·2
7d	194·1	194·5	−0·4	185·5	185·7	−0·2
8a	187·0	186·0	1·0	179·2	178·8	0·4
8b	190·3	189·7	0·6	182·5	182·4	0·1

[a] Δ is defined as Δ = *PA*(calc.) − *PA*(add.).

CONCLUSION

The present results show convincingly that the MP2(fc)/6–31G**//HF/6–31G** + *ZPE*(HF/(6–31G*) model provides a suitable approach for studying protonation in substituted benzenes. The ordering of ring proton affinities is *PA*(**1p**) > *PA*(**1o**) > *PA*(**1m**) > *PA*(**1i**). Agreement with measured *PA*s for *para* and *ortho* positions is good in a quantitative sense. Indirect evidence that the *para* position is the most active site comes from the experimental data obtained by electrophilic substitution reactions. More specifically, sulphonation and bromination of fluorobenzenes give almost exclusively *para* derivatives.[21] Nitration yields a ratio 91·3 : 8·7 for *para* vs *ortho* isomers,[22] whereas the corresponding ratio for benzylation[23] is 85·1 : 14·7. Hence it appears that experiment and theory are in full harmony.

Ring proton affinities in fluorobenzene and toluene are affected by two essentially different features. The first is the initial ground-state effect determined by simple electrostatics and the lowest energy electron density distribution. The second is more subtle and involves matching of the π-electron localization patterns of both the ground state and the protonated benzene (final state effect). If this matching is better, then the *PA*s are higher as exemplified by *ortho* and *para* protonations. Both mechanisms reflect a 'memory effect'. A molecule 'remembers' very well the initial ground-state electron density distribution.

Finally, it is found that *PA*s in polysubstituted benzenes follow a simple additivity rule of thumb, which makes possible their estimation from the corresponding proton affinities of less highly substituted benzenes. The performance of the additivity model is satisfactory with one notable exception: *ipso* positions sometimes exhibit larger deviations from the full *ab initio* calculation, the error being 3–4 kcal mol^{-1}.

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