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ADDITIVITY OF PROTON AFFINITIES IN DISUBSTITUTED NAPHTHALENES

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It is shown, by the MP2(fc)/6–31G//HF/6–31G*+*ZPE*(HF/6–31G*) theoretical model and subsequent use of homodesmic reactions, that the absolute proton affinities in disubstituted naphthalenes involving F and CN substituents satisfy the simple additivity rule, which was previously found to hold in polysubstituted benzenes, the average absolute error being close to 1 kcal mol^{-1}. The origin of the remarkable additivity of substituent effects in determining proton affinities in substituted aromatics and the variations in the values are briefly discussed. © 1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

In previous investigations on polysubstituted benzenes, it was shown that the independent substituent approximation (ISA) leads to an extremely simple and useful rule of thumb permitting rapid estimates of proton affinity (*PA*) values in heavily substituted benzenes with good accuracy.[1,2] We considered it worthwhile to examine *PA*s in other aromatics to check the generality of the additivity rule. In fact, it is plausible to assume that the additivity works even better in larger aromatics, because perturbations exerted by the substituents should be the smaller the larger the aromatic system. Some preliminary calculations on polyfluorinated naphthalenes strongly indicate that this is indeed the case.[3] Proton affinities estimated by the additivity rule may be useful as a guide in experimental work and perhaps even in distinguishng different experimental ladders of *PA* values.[4]

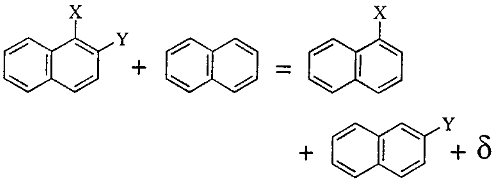
In the present paper, we consider the joint effect of a fluorine and a cyano group on the *PA*s in a number of disubstituted naphthalenes (Figure 1). Unlike fluorine, which is a strong σ-electron acceptor and weak π-electron donor, the CN group is both a σ- and π-electron-withdrawing substituent.

THEORETICAL MODEL

All calculations are based on the MP2(fc)/6–31G**//HF/6–31G*+*ZPE*(HF/6–31G*) model, which in previous investigations has been shown to be a very good compromise between feasibility and reliability.[1] *PA*(add) values are obtained from the additivity equation

$$PA(\text{subst.naphth.}) = PA(\text{naphth.}) + \sum_{X} I(\mathrm{X}_{\mu})_{\nu} \qquad (1)$$

where μ denotes the position of the substituent and ν the protonation site. The increments $I(\mathrm{X}_{\mu})_{\nu}$ measure the change in the *PA* value due to the presence of the substituent X and are defined as the difference between the *PA*s of the monosubstituted and the unsubstituted aromatic hydrocarbon. It can be shown[1] that the deviation from additivity is given by $\Delta = \delta - \delta^{+}$, where δ and δ^{+} are interference energies induced by the substituent in the neutral and protonated species, respectively. δ and δ^{+} are obtained from the following homodesmic reactions, which are characterized by the fact that the number and type of the chemical bonds classified according their state of hybridization is closely matched in reactants and products:[5]



(2a)

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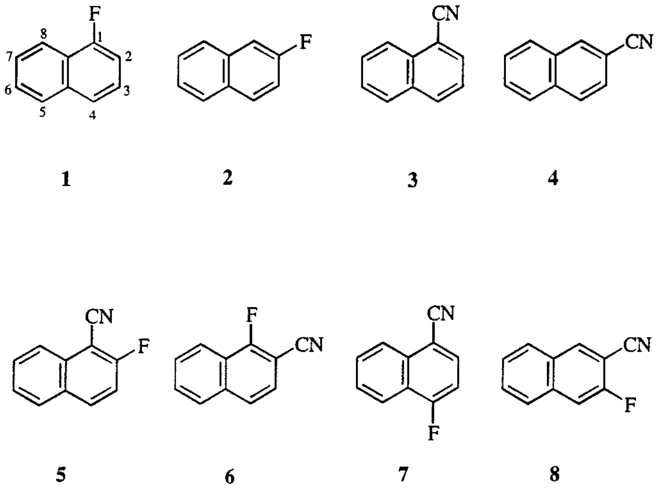
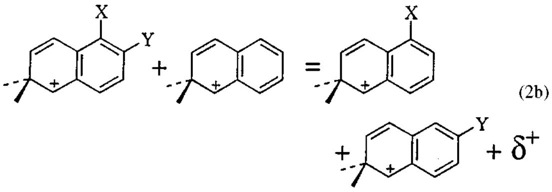


Figure 1. Structural formulae and numbering of atoms of the molecules studied



(2b)

δ and δ^+ are of the same sign and of comparable magnitude, yielding small additivity errors Δ. Computations were carried out by using the Gaussian 94 program.[6]

RESULTS AND DISCUSSION

Total molecular energies E and zero-point energies ZPE for the molecules **1**–**8** and the corresponding protonated species are given in Table 1. From these data the PA values and the increments $I(X_\mu)_\nu$ for the F and CN (compounds **1**–**4**) substituents can be calculated; they are given in Table 2. In Table 3, PA values for the disubstituted compounds **5**–**8** calculated at the MP2 level and by the additivity rule are shown together with Δ values for the deviation from additivity and interference energies δ and δ^+. The *ab initio* MP2 calculated proton affinities are obtained using the equation

$$PA(B_\nu)=[E(\mathrm{B})-E(\mathrm{B}_\nu^+)]+[ZPE(\mathrm{B})-ZPE(\mathrm{B}_\nu^+)] \qquad (3)$$

where B and B_0^+ represent the base in question and its conjugated acid, respectively, and ν denotes the site of the proton attack as usual. It appears that the additivity works very well, as evidenced by the small Δ values, which with one exception [$\Delta(\mathbf{8}_1)=1{\cdot}5$ kcal mol^{-1}; 1 kcal $=4{\cdot}184$ kJ] are near a 0·5 kcal mol^{-1} margin or even smaller. As the MP2 model utilized here gives PA values for ring protonation in very good accord with carefully determined experimental data,[1–3, 7] this means that the simple additivity estimates reach in most cases the chemical accuracy of 1–2 kcal mol^{-1}, which is in general achieved only by highly advanced *ab initio* methods[8] or by meticulously established experimental scales.[4] However, some caution should be exercised in applying the additivity rule of thumb. Since it is a simple model, PA values offered by this equation should be considered as orientational information rather than as exact results.

The surprisingly good performance of the ISA model can be traced to relatively small δ and δ^+ values, which in turn have the same sign and therefore partially cancel in the additivity expression.

It would be useful to put forward at least a qualitative argument rationalizing the variation in PAs depending on substitution and on the position of protonation. This is provided by the localization index:[9]

$$L(d)=\sum_i |d_i(\mathrm{CC})-\overline{d(\mathrm{CC})}| \qquad (4)$$

where $\bar{d}$ is the average CC bond distance and the summation runs over all CC bonds of lengths d_i in the aromatic moiety. A large $L(d)$ value implies more pronounced double-bond localization and a corresponding aromaticity defect. Estimates of the aromaticity defect of the individual rings in naphthalene can be obtained by confining the summation to the corresponding fragment. It should be pointed out that 'aromaticity' is a somewhat vaguely defined term and that different scales for determining the aromatic character are available in the literature. One of the most recent criteria vigorously pursued by Schleyer[10] is the magnetic criterion based on the molecular diamagnetic susceptibility. Here, a simple structural gauge is employed which yields information on aromaticity by using geometric data. For example, protonation of naphthalene in the α-position generally increases the $L(d)$ value of the protonated ring and decreases that of the adjacent ring. Thus, protonation in the 1-position of **4** leads to $L(d)$ values of 0·27 and 0·11 for the protonated and the adjacent ring of **4**, respectively, compared with 0·15 for each ring in unprotonated napththalene. Whereas α-protonation always leads to aromatization of the adjacent ring, β-protonation offers a more complex picture:

Table 1. Total molecular energies E (au) and zero-point energies (ZPE, kcal mol^{-1}) of molecules **1**–**8** and their protonated species[a]

Molecule[b]	E(HF)	ZPE	E(MP2)	Molecule[b]	E(HF)	ZPE	E(MP2)
1	−482.20646	83·7	−483·68645	**2**	−482·20630	83·5	−483·68569
$\mathbf{1}_2$	−482·53699	90·3	−484·00383	$\mathbf{2}_1$	−482·54169	90·3	−484·00877
$\mathbf{1}_3$	−482·52558	90·0	−483·99264	$\mathbf{2}_3$	−482·53044	90·1	−483·99568
$\mathbf{1}_4$	−482·54446	90·3	−484·01129	$\mathbf{2}_4$	−482·52659	90·0	−483·99551
$\mathbf{1}_5$	−482·53689	90·2	−484·00176	$\mathbf{2}_5$	−482·53167	89·9	−483·99980
$\mathbf{1}_6$	−482·52398	89·8	−483·99304	$\mathbf{2}_6$	−482·53482	90·1	−483·99840
$\mathbf{1}_7$	−482·53120	90·1	−483·99523	$\mathbf{2}_7$	−482·52428	89·9	−483·99233
$\mathbf{1}_8$	−482·53366	90·0	−484·00204	$\mathbf{2}_8$	−482·53916	90·1	−484·00411
3	−475·09018	87·7	−476·67827	**4**	−475·09078	87·7	−476·67737
$\mathbf{3}_2$	−475·39415	94·0	−476·97283	$\mathbf{4}_1$	−475·40248	94·1	−476·97971
$\mathbf{3}_3$	−475·40032	94·1	−476·97358	$\mathbf{4}_3$	−475·40029	94·1	−476·97460
$\mathbf{3}_4$	−475·39859	93·9	−476·97912	$\mathbf{4}_4$	−475·40334	94·0	−476·97555
$\mathbf{3}_5$	−475·40679	94·0	−476·98287	$\mathbf{4}_5$	−475·40743	94·0	−476·97979
$\mathbf{3}_6$	−475·40042	93·9	−476·97313	$\mathbf{4}_6$	−475·39754	93·8	−476·97392
$\mathbf{3}_7$	−475·39978	93·9	−476·97526	$\mathbf{4}_7$	−475·40020	93·9	−476·97169
3_8	−475·40923	94·0	−476·98289	$\mathbf{4}_8$	−475·40579	94·0	−476·98168
5	−573·93840	82·9	−575·68560	**6**	−573·93885	83·0	−575·68519
$\mathbf{5}_3$	−574·24415	89·4	−575·97796	$\mathbf{6}_3$	−574·24004	89·4	−575·97619
$\mathbf{5}_4$	−574·23233	89·0	−575·97678	$\mathbf{6}_4$	−574·25389	89·5	−575·98794
$\mathbf{5}_5$	−574·24633	89·1	−575·98439	$\mathbf{6}_5$	−574·25091	89·1	−575·98262
$\mathbf{5}_6$	−574·24804	89·2	−575·97999	$\mathbf{6}_6$	−574·23466	88·9	−575·97553
$\mathbf{5}_7$	−547·23839	89·0	−575·97654	$\mathbf{6}_7$	−574·24425	89·2	−575·97508
$\mathbf{5}_8$	−574·25477	89·2	−575·98797	$\mathbf{6}_8$	−574·24649	89·1	−575·98478
7	−573·94111	83·0	−575·68825	**8**	−573·93774	82·8	−575·68377
$\mathbf{7}_2$	−574·23424	89·2	−575·97514	$\mathbf{8}_1$	−574·23751	89·2	−575·97744
$\mathbf{7}_3$	−574·25206	89·6	−575·98737	$\mathbf{8}_4$	−574·25189	89·5	−575·98564
$\mathbf{7}_5$	−574·24970	89·1	−575·98754	$\mathbf{8}_5$	−574·25268	89·3	−575·98457
$\mathbf{7}_6$	−574·24684	89·2	−575·97815	$\mathbf{8}_6$	−574·23455	88·8	−575·97452
$\mathbf{7}_7$	−574·23892	88·9	−575·97813	$\mathbf{8}_7$	−574·24705	89·2	−575·97788
$\mathbf{7}_8$	−574·25519	89·2	−575·98733	$\mathbf{8}_8$	−574·24441	89·0	−575·98252

[a] ZPEs are HF/6–31G* values multiplied by 0·89. The conversion factor is 1 au = 627·5095 kcal mol^{-1}.

[b] The protonation site is denoted by a subscript.

Table 2. Proton affinities of molecules **1**–**4** and the corresponding increments as obtained by the MP2 model (in kcal mol^{-1})[a]

Molecule	Parameter	Protonation site							
		1	2	3	4	5	6	7	8
1	PA	–	192·5	185·8	197·2	191·4	186·2	187·4	191·7
	$I(\mathrm{F}_1)_n$	–	2·0	−4·7	2·4	−3·4	−4·3	−3·1	−3·1
2	PA	195·9	–	187·9	187·9	190·7	189·6	186·1	193·2
	$I(\mathrm{F}_2)_n$	1·1	–	−2·6	−6·9	−4·1	−0·9	−4·4	−1·6
3	PA	–	178·5	178·9	182·6	184·8	178·8	180·2	184·8
	$I(\mathrm{CN}_1)_n$	–	12·0	−11·6	−12·2	−10·0	−11·7	−10·3	−10·0
4	PA	183·3	–	180·1	180·8	183·5	180·0	178·5	184·7
	$I(\mathrm{CN}_2)_n$	−11·5	–	−10·4	−14·0	−11·3	−10·5	−12·0	−10·1

[a] Conversion factor: 1 au = 627·5095 kcal mol^{-1}.

Table 3. Proton affinities of compounds **5**–**8** as estimated by the MP2 model and the ISA additivity rule of thumb, differences Δ between these two sets of *PA*s and the interference energies (δ and δ^{+}) obtained by homodesmic reactions (2a) and (2b) (in kcal mol^{-1})[a]

		Protonation site							
Molecule	Parameter	1	2	3	4	5	6	7	8
5	*PA*	–	–	177·0	176·6	181·3	178·4	176·5	183·4
	PA_{ad}	–	–	176·3	175·7	180·7	177·9	175·8	183·2
	Δ	–	–	0·7	0·9	0·6	0·5	0·7	0·2
	δ	–	–	1·0	1·0	1·0	1·0	1·0	1·0
	$-\delta^{+}$	–	–	−0·3	−0·1	−0·4	−0·5	−0·3	−0·8
6	*PA*	–	–	176·2	183·5	180·3	176·3	175·7	181·9
	PA_{ad}	–	–	175·4	183·2	180·1	175·4	175·4	181·6
	Δ	–	–	0·8	0·3	0·2	0·6	0·3	0·3
	δ	–	–	1·0	1·0	1·0	1·0	1·0	1·0
	$-\delta^{+}$	–	–	−0·2	−0·7	−0·8	−0·4	−0·7	−0·7
7	*PA*	–	173·8	181·1	–	181·7	175·7	176·0	181·5
	PA_{ad}	–	173·8	180·9	–	181·7	175·7	175·9	181·4
	Δ	–	0·0	0·2	–	0·0	0·0	0·11	0·1
	δ	–	−0·3	−0·3	–	−0·3	−0·3	−0·3	−0·3
	$-\delta^{+}$	–	0·3	0·5	–	0·3	0·4	0·4	0·4
8	*PA*	177·9	–	–	182·7	182·3	176·5	178·2	181·3
	PA_{ad}	176·4	–	–	181·9	181·9	175·6	177·6	180·6
	Δ	1·5	–	–	0·8	0·4	0·9	0·5	0·7
	δ	1·5	–	–	1·5	1·5	1·5	1·5	1·5
	$-\delta^{+}$	0·0	–	–	−0·7	−1·1	−0·6	−1·0	−0·8

[a] Proton affinities predicted by additivity are denoted by PA_{ad}.

whereas in most cases the aromatic character of both rings decreases, the adjacent ring may also be stabilized depending on the relative positions of substituents and protonation site.

In Table 4, total $L(d)$ indices, which are approximately equal to the sum of the indices for the individual rings, are given for molecules **5**–**8**. They are correlated with the MP2 *PA* values by the equation

$$PA_{\mathrm{corr}} = 194{\cdot}4 - 37{\cdot}1\,L(d) \qquad (5)$$

with an absolute average error $\varepsilon_{\mathrm{av}} = 1{\cdot}3$ kcal mol^{-1}, although the individual $\varepsilon = PA - PA_{\mathrm{corr}}$ values show that the relationship is more qualitative than quantitative. It does reveal, however, that lower *PA* values are related to larger aromaticity defects, as is evidenced by the negative coefficient of $L(d)$ in the equation (5). It is worth mentioning that the $L(d)$ criterion employed here is similar to the localization energy (LE) concept used within the Hückel theory a long time ago.[11] There are, however, some important differences too. In the LE model, the protonated center is excluded and π-electrons only are considered. In contrast, the $L(d)$ index involves all CC bond distances, thus simultaneously taking into account changes in both σ- and π-electrons.[12] Finally, it should be kept in mind that the

Table 4. Total localization indices $L(d)$ and the corresponding *PA*s in compounds **5**–**8**

System	$L(d)$	*PA*	PA_{corr}	ε	System	$L(d)$	*PA*	PA_{corr}	ε
$\mathbf{5}_3$	0·49	177·0	176·2	0·8	$\mathbf{6}_3$	0·48	176·2	176·7	−0·5
$\mathbf{5}_4$	0·39	176·6	179·9	−3·3	$\mathbf{6}_4$	0·37	183·5	180·6	2·9
$\mathbf{5}_5$	0·35	181·3	181·4	−0·1	$\mathbf{6}_5$	0·34	180·3	181·9	−1·6
$\mathbf{5}_6$	0·47	178·4	177·0	1·4	$\mathbf{6}_6$	0·46	176·3	177·5	−1·2
$\mathbf{5}_7$	0·47	176·5	177·0	−0·5	$\mathbf{6}_7$	0·47	175·7	176·9	−1·2
$\mathbf{5}_8$	0·34	183·4	181·8	1·6	$\mathbf{6}_8$	0·33	181·9	182·2	−0·3
$\mathbf{7}_2$	0·50	173·8	175·9	−2·1	$\mathbf{8}_1$	0·43	177·9	178·4	−0·5
$\mathbf{7}_3$	0·47	181·1	177·0	4·1	$\mathbf{8}_4$	0·34	182·7	181·8	0·9
$\mathbf{7}_5$	0·36	181·7	181·0	0·7	$\mathbf{8}_5$	0·35	182·3	181·4	0·9
$\mathbf{7}_6$	0·46	175·7	177·3	−1·6	$\mathbf{8}_6$	0·46	176·5	177·3	−0·8
$\mathbf{7}_7$	0·46	176·0	177·3	−1·3	$\mathbf{8}_7$	0·50	178·2	175·9	2·3
$\mathbf{7}_8$	0·33	181·5	182·2	−0·7	$\mathbf{8}_8$	0·33	181·3	182·2	−0·9

aromaticity defect is only part of the protonation effect and that the other factors might also be important in determining the variation in *PA*s. However, we defer a detailed discussion to a later stage when a large variety of widely different substituents will be examined.

CONCLUSION

It is shown that the independent substituent approximation (ISA) performs very well, yielding proton affinities in the disubstituted naphthalenes examined with almost chemical accuracy (1 kcal mol^{-1}). The origin of the surprisingly good results offered by the additivity equation (1) is identified. It is a consequence of the relatively small values of the interference energies between substituents in the initial neutral molecule (δ) and in the resulting conjugated acid (δ^+). They have the same sign as a rule. A crude linear relationship between *PA*s and the aromaticity defect is found in a family of disubstituted naphthalenes involving F and CN substituents. Other factors influencing the variation in *PA*s of substituted naphthalenes will be discussed in forthcoming papers.

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