The Mills–Nixon effect and chemical reactivity—methyl cation affinity of some cycloalkabenzenes

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The problem of the methyl cation attack on carbon atoms belonging to the benzene moiety fused to small rings is explored by the *ab initio* models at the MP2 level of sophistication. It is shown that the β-position is more reactive than the α-site in kinetically controlled reactions, which is in accordance with the original Mills–Nixon postulate. On the other hand, it appears that in thermodynamically controlled electrophilic substitution reactions the α-site should be slightly preferred for three-, four- and five-membered annelated rings. The differences between the methyl cation affinities MCA_β and MCA_α are analyzed and resolved into angular strain and the cationic resonance contribution. The latter involves the hyperconjugation/conjugation and relaxation effects. It turns out that the angular strain contribution is inversely proportional to the size of the annelated ring, whereas the opposite is the case for the cationic resonance interaction. Their interplay determines the selectivity and its extent in the electrophilic substitution reactions. The same analysis is applicable to other electrophilic groups.

Introduction

The Mills–Nixon effect[1] has been and still is a subject of long-standing research interest, debates and misunderstandings. This is hardly surprising because fused benzenoid systems involving small ring(s) embody two of the most exciting facets of chemistry, namely, aromaticity and angular strain. While the role of π-electrons in determining the aromaticity in planar systems is not quite clear and has been questioned by some researchers,[2–4] the angular strain can be undoubtedly ascribed to the changes within the σ-framework. In any case, juxtaposition of the σ-strain and π-electron network leads to some unusual properties of fused systems,[5] which deserve wider attention. It is well established by now that the annelation of small ring(s) to an aromatic moiety leads to some new and interesting physicochemical features,[6–11] not to mention structural changes,[12] of the aromatic fragment. One of the most important aspects of molecular behavior is reactivity and, remarkably enough, small fused ring(s) introduce a significant regioselectivity within the aromatic fragment for electrophilic substitution reactions.[13–15] The proton has been used in these previous investigations as the electrophilic probe *par excellence*. In the present work we would like to examine the $^+CH_3$ cation as a representative of larger electrophilic groups and explore its attack on the benzene moiety annelated to several small carbocycles of increasing size. In this way we address not only the question of the importance of the Mills–Nixon effect in determining the most favourable position of the $^+CH_3$ substitution on the aromatic perimeter, but we intend also to shed some light on the dependence of the degree of regioselectivity on the size and shape of carbocycles. This is of some relevance because the directional ability of small rings in the electrophilic substitution reactions represents one of the most striking manifestations of the Mills–Nixon effect. Furthermore, the role of the resonance will be carefully scrutinized and an attempt to delineate the angular strain contribution from the resonance interaction will be made in determining the methyl cation affinity (MCA). Finally, it is noteworthy that the methyl cation is an interesting reactant on its own, since it plays an important role in Friedel–Crafts alkylation reactions[16] and in interstellar synthesis.[17] Hence, detailed understanding of its chemical behaviour should be rewarding.

Methodology

In our previous investigations of the methyl cation affinity of substituted benzenes,[18] we found that the MP2(fc)/6-31G**//HF/6-31G* + ZPVE(HF/6-31G*) model was a very good compromise between accuracy and practicality. It involves optimization of all independent structural parameters at the HF/6-31G* level and subsequent verification of true minima on the potential energy hypersurface by vibrational analyses. The resulting vibrational frequencies are used for estimating the zero point energies (ZPVE(HF/6-31G*)). The latter were multiplied by a common empirical weighting factor 0.9135.[19] Subsequently, the effect of electron correlation is obtained by the single point MP2(fc)/6-31G**//HF/6-31G* calculation. This model will be denoted heretofore as M(I). However, since the small(er) ring fusion produces sometimes subtle deformations of the aromatic fragment, we performed more accurate optimization of molecular geometries at the MP2(fc)/6-31G* level of theory. The rest remains the same as before, yielding the MP2(fc)/6-31G**//MP2(fc)/6-31G* + ZPVE(HF/6-31G*) model, which will be abbreviated as M(II). All calculations were carried out using the GAUSSIAN 94 program.[20]

Results and discussion

Fused molecules considered here are depicted in Fig. 1 together with benzene, its mono- and dialkyl derivatives and corresponding methyl cation derivatives. The latter will be useful in interpreting the Mills–Nixon effect in terms of the angular strain

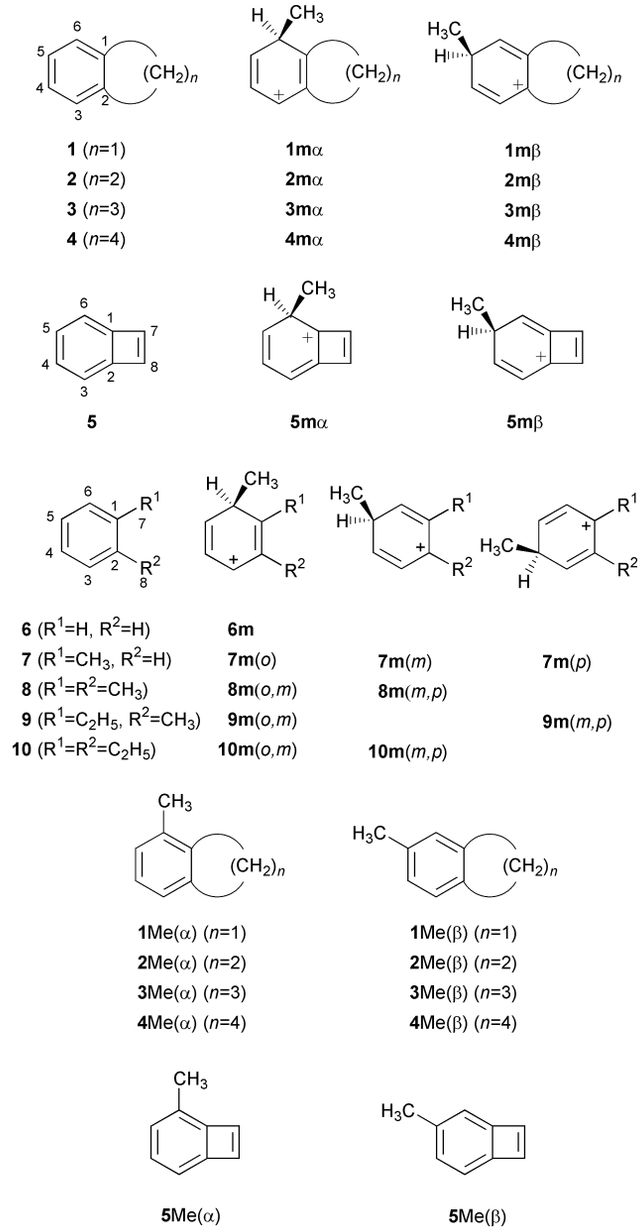


Fig. 1 Schematic representation of the fused systems.

and hyperconjugation/conjugation contributions. It should be pointed out that in Fig. 1 molecules are represented by their dominating resonance structures, which imply specific partial π-electron localization patterns and partial positive charge localization. It will become apparent later on that σ-bond localization and rehybridization are central in this respect. These features, deduced by chemical intuition and embodied in resonance structures, are corroborated by actual calculations of molecular geometries, total and π-bond orders as well as the total atomic densities and formal charges (*vide infra*). However, it should be strongly pointed out that these resonance structures should not be taken *ad literam*, because there is neither a perfect localization of π-bonds nor a fixed positive charge. Rather, the positive charge is completely spread over the conjugate acids as a consequence of the electron density relaxation effect.

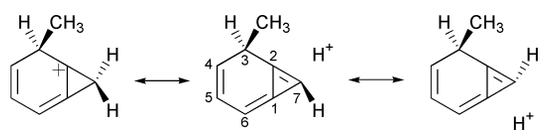
Energetic properties

Let us focus on the energetic properties first, because they are crucial for the understanding of the phenomenon in question. Consider the methyl cation affinity (MCA) defined by the general equation (1):[18]

$$\mathrm{MCA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha + (\Delta \mathrm{ZPVE})_\alpha + E(^+\mathrm{CH_3})_{\mathrm{tot}} \quad (1)$$

where $(\Delta E_{\mathrm{el}})_{\mathrm{ga}} = [E(\mathrm{B}) - E(\mathrm{B_aCH_3^+})]$ and $(\Delta \mathrm{ZPVE})_\alpha = [\mathrm{ZPVE(B)} - \mathrm{ZPVE(B_\alpha CH_3^+}]$ are the electronic and zero-point vibrational energy contributions to the $^+CH_3$ affinity. Here, B and BCH_3^+ denote a base in question and its conjugate acid produced by the $^+CH_3$ attack, respectively, and α stands for the site of the $^+CH_3$ attack. The total energy of the $^+CH_3$ cation $E(^+\mathrm{CH_3})_{\mathrm{el}} + \mathrm{ZPVE}(^+\mathrm{CH_3})$ is denoted by $E(^+\mathrm{CH_3})_{\mathrm{tot}}$.

Total molecular and ZPV energies are given in Table 1. Perusal of the presented data shows that models M(I) and M(II) give very similar results. This is gratifying because the M(I) model is simpler and consequently can be applied to quite large systems without a significant loss in accuracy. Analysis of the methyl cation affinities (MCAs) reveals that they depend on the size of the annelated ring, but also on the number of its CH_2 groups. The latter is compatible with ample evidence that the relaxation effect arising from the electron density reorganization in the resulting conjugate acids, obtained by protonation, is of paramount importance.[21–23] It is common knowledge that the redistribution of the electron density upon protonation in planar systems takes place through the conjugation effect, hyperconjugation and *via* the σ-electron framework transmission. It is obvious that the hyperconjugation is of some importance in benzene annelated to CH_2-carbocycles as discussed already by Faust *et al.*[24] The same could be expected for $^+CH_3$ attack on the aromatic carbon atoms in cycloalkabenzenes, with a notable difference—the hyperconjugation should be considerably amplified in cations, because it is coupled to the relaxation effect. We shall include both effects in a common resonance term for convenience, since it is impossible to disentangle them at present. For instance, the cationic resonance interaction in the methyl cation derivative of **1** substituted at the α-position is well described by the no-bond–double-bond VB structures depicted in Scheme 1.



Scheme 1

It is important to notice that position C(2) of the aromatic moiety is heavily involved in the hyperconjugation (*i.e.* the cationic resonance), whereas position C(1) remains largely inactive, leading to asymmetry in the pseudo-π interaction over the three-membered ring. The opposite occurs upon $^+CH_3$ attack at the β-position, implying that the hyperconjugation is switched from the C(2)–C(7) to the C(1)–C(7) bond as easily checked by examining Pauling's resonance structures. It should be also kept in mind that inactive atoms in the resonance mechanism still may participate in charge relaxation process through the σ-electron density channel, thus contributing to the overall reorganization effect. In order to delineate the cationic resonance effect transmitted *via* the hyperconjugation–relaxation mechanism on one hand and the angular strain influence imposed by an annelated ring on the other, we shall consider first the increment in the methyl cation affinity (MCA) of toluene for the *ortho*-position attack [eqn. (2)]:

$$[E_{\mathrm{tot}}(\mathbf{7}) - E_{\mathrm{tot}}(\mathbf{7m}(o))] - [E_{\mathrm{tot}}(\mathbf{6}) - E_{\mathrm{tot}}(\mathbf{6m})] = I^+(\mathrm{CH_3})_o \quad (2)$$

Here I^+ stands for the $^+CH_3$ attack and $(CH_3)_o$ denotes the effect of an *ortho*-positioned methyl group. Hence, the increment $I^+(CH_3)_o$ describes the effect of an *ortho*-CH_3 group on the MCA of **7** relative to free benzene. It is useful to recall that the theoretical estimate of the MCA of benzene is 81.4 kcal mol^{-1} being only 0.4 kcal mol^{-1} higher than the experimental

Table 1 Total molecular energies (arbitrary units), $ZPVE_{sc}$ energies/kcal mol^{-1} and MCAs/kcal mol^{-1} as obtained by the M(I)[a] and M(II)[a] models

				MCA[i]	
Molecule	M(I)	M(II)	$ZPVE_{sc}$.[b]	M(I)	M(II)
1	−269.39974	−269.40090	64.5	—	—
1mα	−308.88334	−308.88599	88.1	81.7	82.6
1mβ	−308.88945	−308.89155	88.4	85.3	86.0
2	−308.64307	−308.64399	82.8	—	—
2mα	−348.13625	−348.13835	106.6	87.6	88.2
2mβ	−348.14030	−348.14216	106.7	90.0	90.4
3	−347.87334	−347.87434	101.1	—	—
3mα	−387.37010	−387.37228	125.1	89.6	90.3
3mβ	−387.37321	−387.37523	125.1	91.6	92.2
4	−387.06159	−387.06259	119.1	—	—
4mα	−426.56143	−426.56346	143.2	91.4	92.0
4mβ	−426.56238	−426.56446	143.1	92.2	92.9
5	−307.38602	−307.38878	68.2	—	—
5mα	−346.87990	−346.88450	91.9	88.1	89.2
5mβ	−346.90255	−346.90477	92.5	101.7	101.3
6	−231.50460	−231.50530	61.7	—	—
6m	−270.98786	−270.98953	85.6	81.2	81.8
7	−270.69143	−270.69217	78.5	—	—
7m(*o*)	−310.18451	−310.18620	102.7	87.1	87.6
7m(*m*)	−310.17960	−310.18153	102.5	84.2	84.9
7m(*p*)	−310.18632	−310.18796	102.5	88.5	89.0
8	−309.87860	−309.87942	95.7	—	—
8m(*o*,*m*)	−349.37521	−349.37734	119.7	89.5	90.3
8m(*m*,*p*)	−349.37720	−349.37911	119.6	90.8	91.5
9	−349.06058	−349.06158	113.4	—	—
9m(*o*,*m*)	−388.55819	−388.56056	137.6	89.9	90.7
9m(*m*,*p*)	−388.56086	−388.56294	137.6	91.6	92.3
10	−388.24111	−388.24222	131.1	—	—
10m(*o*,*m*)	−427.73910	−427.74135	155.4	90.1	90.8
10m(*m*,*p*)	−427.74202	−427.74431	155.0	92.3	93.1

[a] M(I) and M(II) refer to MP2(fc)/6-31G**//HF/6-31G* and MP2(fc)/6-31G**//MP2(fc)/6-31G*, respectively. [b] The zero point vibrational correction is calculated at HF/6-31G* level and scaled by 0.9135.[19] [c] Methyl cation affinities (in kcal mol^{-1}).

value.[18] However, a methylene (CH_2) group of an annelated carbocycle in **1** has only two C–H bonds in contrast to a methyl group in toluene, which makes a difference in the extent of the relaxation effect. Consequently, after normalization of $I^+(CH_3)_o$ to a single C–H bond, one has to take into account the numbers of relevant C–H bonds in **1m**α and **7m**(*o*). This leads to the conclusion that a fraction (5/7) of the increment $I^+(CH_3)_o$ gives the resonance contribution to the MCA in **1m**α. Finally, it has to be mentioned that a subscript tot in eqn. (2) implies a sum of the electronic and ZPV energies. The change in the MCA of cyclopropabenzene relative to benzene is given then by formula (3):

$$[E_{tot}(\mathbf{1}) - E_{tot}(\mathbf{1m}\alpha)] - [E_{tot}(\mathbf{6}) - E_{tot}(\mathbf{6m})] = \mathrm{MCA}(\mathbf{1})_\alpha - \mathrm{MCA}(\mathbf{6}) = E^{(1)}(\mathrm{MN_{ang}})_\alpha + E^{(1)}(\mathrm{MN_{res}})_\alpha \quad (3)$$

or, in other words, $\mathrm{MCA}(\mathbf{1})_a = \mathrm{MCA(b)} + E^{(1)}(\mathrm{MN_{ang}})_\alpha + E^{(1)}(\mathrm{MN_{res}})_a$, where MCA(b) denotes the methyl cation affinity of benzene, whereas $E^{(1)}(\mathrm{MN_{ang}})_\alpha$ and $E^{(1)}(\mathrm{MN_{res}})_\alpha = (5/7)I^+(CH_3)_o$ reflect the angular and the resonance contribution to the Mills–Nixon effect, respectively. An analogous expression holds for β-$^+CH_3$ attack yielding $\mathrm{MCA}(\mathbf{1})_\beta = \mathrm{MCA(b)} + E^{(1)}(\mathrm{MN_{ang}})_\beta + E^{(1)}(\mathrm{MN_{res}})_\beta$, where $E^{(1)}(\mathrm{MN_{res}})_\beta = (5/7)\ I^+(CH_3)_p$, since in this case the *para*-carbon atom is activated by resonance. It follows that a difference in the methyl cation affinity between α- and β-attacks is given by eqn. (4):

$$\mathrm{MCA}(\mathbf{1})_\alpha - \mathrm{MCA}(\mathbf{1})_\beta = [E^{(1)}(\mathrm{MN_{ang}})_\alpha - E^{(1)}(MN_{ang})_\beta] + [E^{(1)}(MN_{res})_\alpha - E^{(1)}(\mathrm{MN_{res}})_\beta] \quad (4)$$

where

$$E^{(1)}(\mathrm{MN_{res}})_\alpha - E^{(1)}(\mathrm{MN_{res}})_\beta = (5/7)[I^+(CH_3)_o - I^+(CH_3)_p] \quad (5)$$

Treatment of cyclopropabenzene (**1**) was paradigmatic for the remainder of the series **1**–**4**. Hence, we can straightforwardly write a general formula yielding a difference in methyl cation affinities for β- and α-attacks:

$$\Delta^{(n)}(\mathrm{MCA})_{\beta\alpha} = \Delta^{(n)}(\mathrm{MN_{ang}})_{\beta\alpha} + \Delta^{(n)}(\mathrm{MN_{res}})_{\beta\alpha} \quad (6)$$

for n = **1**, **2**, **3** and **4**, where

$$\Delta^{(n)}(\mathrm{MCA})_{\beta\alpha} = \mathrm{MCA}_\beta - \mathrm{MCA}_\alpha \quad (6a)$$

$$\Delta^{(n)}(\mathrm{MN_{ang}})_{\beta\alpha} = \Delta^{(n)}(\mathrm{MN_{ang}})_\beta - \Delta^{(n)}(\mathrm{MN_{ang}})_\alpha \quad (6b)$$

and

$$\Delta^{(n)}(\mathrm{MN_{res}})_{\beta\alpha} = \Delta^{(n)}(\mathrm{MN_{res}})_\beta - \Delta^{(n)}(\mathrm{MN_{res}})_\alpha \quad (6c)$$

The resonance contributions for particular systems are:

$$\Delta^{(2)}(\mathrm{MN_{res}})_\alpha = (7/9)I^+(CH_3,CH_3)_{o,m} = \mathbf{8} - \mathbf{8m}\alpha - \mathrm{MCA}(\mathbf{6}) \quad (7a)$$

$$\Delta^{(2)}(\mathrm{MN_{res}})_\beta = (7/9)I^+(CH_3,CH_3)_{m,p} = \mathbf{8} - \mathbf{8m}\beta - \mathrm{MCA}(\mathbf{6}) \quad (7b)$$

$$\Delta^{(3)}(\mathrm{MN_{res}})_\alpha = (9/11)I^+(CH_2CH_3,CH_3)_{o,m} = \mathbf{9} - \mathbf{9m}\alpha - \mathrm{MCA}(\mathbf{6}) \quad (7c)$$

$$\Delta^{(3)}(\mathrm{MN_{res}})_\beta = (9/11)I^+(CH_3,CH_2CH_3)_{m,p} = \mathbf{9} - \mathbf{9m}\beta - \mathrm{MCA}(\mathbf{6}) \quad (7d)$$

$$\Delta^{(4)}(\mathrm{MN_{res}})_\alpha = (11/13)I^+(CH_2CH_3,\ CH_2CH_3)_{o,m} = \mathbf{10} - \mathbf{10m}\alpha - \mathrm{MCA}(\mathbf{6}) \quad (7e)$$

Table 2 MCA values/kcal mol^{-1} for molecules **1**–**5** as obtained by the M(I) and M(II) models, the latter being given within brackets. They are partitioned into angular strain and resonance contributions $E^{(n)}(MN_{ang})$ and $E^{(n)}(MN_{res})$, respectively

Entity[a]	**1**	**2**	**3**	**4**	**5**[b]
$MCA^{(n)}(\alpha)$	81.6	87.5	89.6	91.4	88.1
	[82.5]	[88.2]	[90.3]		[89.2]
$MCA^{(n)}(\beta)$	85.2	90.0	91.5	92.1	101.7
	[85.8]	[90.5]	[92.1]		[101.3]
$\Delta(MCA)_{\beta\alpha}$	3.6	2.5	1.9	0.7	13.6
	[3.3]	[2.3]	[1.8]		[12.1]
$E^{(n)}(MN_{ang})\alpha$	−3.7	−0.1	1.3	2.8	−0.9
	[−3.4]	[−0.1]	[1.2]		
$E^{(n)}(MN_{ang})\beta$	−1.1	1.4	1.8	1.5	1.1
	[−1.0]	[1.2]	[1.8]		
$\Delta E^{(n)}(MN_{ang})_{\beta\alpha}$	2.6	1.5	0.5	−1.3	2.0
	[2.4]	[1.3]	[0.6]		
$E^{(n)}(MN_{res})_{\alpha}$	4.3	6.5	7.2	7.5	7.8
	[4.2]	[6.6]	[7.4]		
$E^{(n)}(MN_{res})_{\beta}$	5.2	7.5	8.6	9.5	18.8
	[5.1]	[7.6]	[8.6]		
$\Delta E^{(n)}(MN_{res})_{\beta\alpha}$	0.9	1.0	1.4	2.0	11.6
	[0.9]	[1.0]	[1.2]		
$\delta^{(n)}(MCA)_{\alpha}$	0	5.9	8.0	9.8	6.5
$\delta^{(n)}(MN_{ang})_{\alpha}$	0	3.6	5.0	6.5	2.8
$\delta^{(n)}(MN_{res})_{\alpha}$	0	2.2	2.9	3.2	3.5
$\delta^{(n)}(MCA)_{\beta}$	0	4.8	6.3	6.9	16.5
$\delta^{(n)}(MN_{ang})_{\beta}$	0	2.5	2.9	2.6	2.2
$\delta^{(n)}(MN_{res})_{\beta}$	0	2.3	3.4	4.3	13.6

[a] Differences Δ in various energies related to β- and α-$^{+}CH_3$ attack are defined as follows: $\Delta^{(n)}(MCA) = MCA^{(n)}(\beta) - MCA^{(n)}(\alpha)$; $\Delta E^{(n)}(MN_{ang})_{\beta\alpha} = E^{(n)}(MN_{ang})\beta - E^{(n)}(MN_{ang})_{\alpha}$ and $\Delta E^{(n)}(MN_{res})_{\beta\alpha} = E^{(n)}(MN_{res})_{\beta} - E^{(n)}(MN_{res})_{\alpha}$. For the definition of δ-entities, see text. [b] $E^{(n)}(MN_{ang})_{\alpha}$ and $E^{(n)}(MN_{ang})\beta$ are determined *via* eqns (8) and (9).

$$\Delta^{(4)}(MN_{res})_{\beta} = (11/13)I^{+}(CH_2CH_3, CH_2CH_3)_{m,p} = \mathbf{10} - \mathbf{10m}\beta - MCA(\mathbf{6}) \quad (7f)$$

The resulting MCA values, the corresponding angular strain and resonance contributions are summarized in Table 2, where some interesting trends can be seen. Let us first dwell on the selectivity in the electrophilic aromatic reactivity toward the $^{+}CH_3$ cation. It appears that MCA(β) is larger than MCA(α) in all molecules. The difference $\Delta^{(n)}(MCA)_{\beta\alpha}$ is decreasing, however, from 3.6 to only 0.7 kcal mol^{-1}. Consequently, it follows that smaller fused rings induce larger selectivity in the electrophilic attack of the $^{+}CH_3$ cation. This finding conclusively shows that the Mills–Nixon effect is operative in fused systems. Partitioning of the difference in the methyl cation affinity of fused systems **1**–**4** relative to a free benzene MCA value into the angular strain and resonance interaction components is instructive. Perusal of the data reveals that both $E^{(1)}(MN_{ang})_{\alpha}$ and $E^{(1)}(MN_{ang})_{\beta}$ are negative in **1** implying a disconcerted and destructive interference of two partial localization patterns of the electron density: one caused by the annelation of the highly strained three-membered ring representing the ground state (**GS**) memory effect, and the other occurring in the conjugate acids spurred by the $^{+}CH_3$ attack. The degree of mismatching is higher for α-substitution thus making this position less susceptible to the cationic methylation. Hence, the picture put forward by us for the protonation of the annelated benzenes [13] holds for the methyl cation affinity too. It is noteworthy that $E^{(n)}(MN_{ang})_{\alpha}$ and $E^{(n)}(MN_{ang})_{\beta}$ increase as n increases and that inequality $E^{(n)}(MN_{ang})_{\beta} > E^{(n)}(MN_{ang})_{\alpha}$ holds for all molecules except tetralin **4**, where the opposite takes place. There are simple relationships describing the functional dependence of the angular strain interference energies on the angle φ of the annelated carbocycle. The latter is defined relative to the straight line passing through the carbon junction atoms. The least square fit gives:

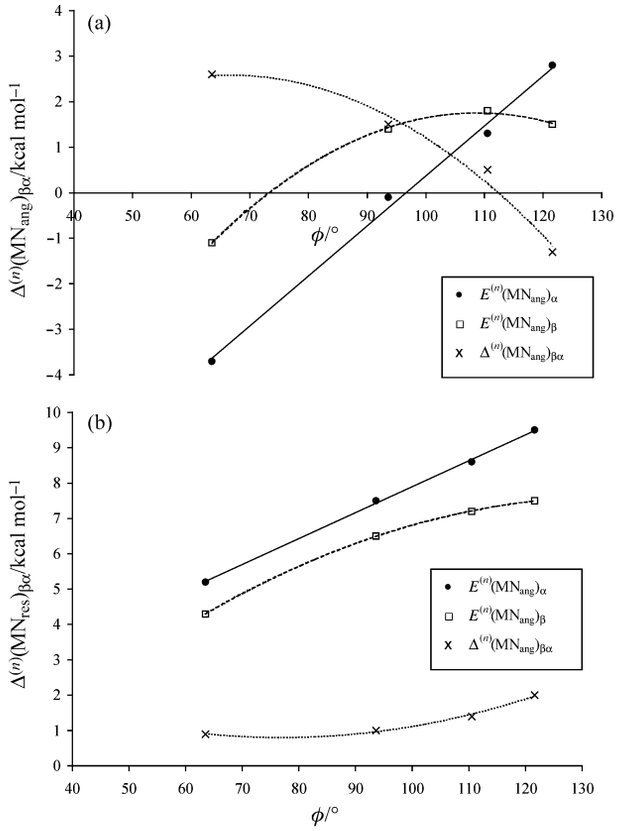


Fig. 2 (a) Dependence of the angular strain contribution to the MN effect on the angle φ (b) Dependence of the cationic resonance contribution to the MN effect on the angle φ.

$$E^{(n)}(MN_{ang})_{\alpha} = 0.1097\varphi - 10.6 \text{ kcal mol}^{-1} \quad (8)$$

and

$$E^{(n)}(MN_{ang})_{\beta} = -0.0014\varphi^2 + 0.3032\varphi - 14.7 \text{ kcal mol}^{-1} \quad (9)$$

where φ is expressed in degrees and the constants have correct physical units yielding results in kcal mol^{-1}. It appears that $E^{(n)}(MN_{ang})_{\alpha}$ and $E^{(n)}(MN_{ang})_{\beta}$ are linear and quadratic functions of φ, respectively (Fig. 2a), possessing correlation coefficients R^2 as high as 0.995 and 0.999 (in the same sequence). The corresponding average absolute errors are 0.2 and 0.1 kcal mol^{-1}, respectively. Hence, interpolations in the range of 60–120° and cautious extrapolations outside this range should provide quite reliable estimates of the angular strain influence on the orientational ability of small rings to control electrophilic substitutions. Specifically, the difference $\Delta E^{(n)}(MN_{ang})_{\beta\alpha}$ consistently decreases as the size of the fused ring increases, as intuitively expected. Concomitantly, the angular strain favours the β-position as a rule, tetralin being a notable exception. The resonance terms (Table 2) assume larger values than their angular strain counterparts. Their functional dependence on angle φ (Fig. 2b) is explicitly given by relations (10) and (11):

$$E^{(n)}(MN_{res})_{\alpha} = -0.0006\varphi^2 + 0.1726\varphi - 4.1 \text{ kcal mol}^{-1} \quad (10)$$

and

$$E^{(n)}(MN_{res})_{\beta} = 0.0733\varphi + 0.6 \text{ kcal mol}^{-1} \quad (11)$$

exhibiting a correlativity as high as 0.999. Importantly, variations of their differences $\Delta E^{(n)}(MN_{res})_{\beta\alpha}$ are less pronounced

Table 3 Total molecular energies (in au) of systems **1**–**5** as obtained by theoretical models M(I) and M(II). Relative energies of isomers are given in kcal mol^{-1}

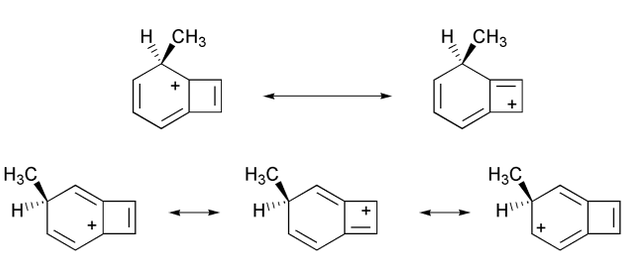
	Total molecular energies			$E_{tot}^{(n)}$Me(α) − $E_{tot}^{(n)}$Me(β)	
Molecule	M(I)	M(II)	$ZPVE_{sc}$	M(I)	M(II)
1Me(α)	−308.58798	−308.58917	81.3	−1.2	−1.1
1Me(β)	−308.58607	−308.58745	81.3	—	—
2Me(α)	−347.83113	−347.83206	99.6	−1.0	−0.9
2Me(β)	−347.82942	−347.83052	99.5	—	—
3Me(α)	−387.06121	−387.06224	118.0	−0.5	−0.5
3Me(β)	−387.06017	−387.06117	117.8	—	—
4Me(α)	−426.24837	−426.24943	136.2	0.4	0.4
4Me(β)	−426.24851	−426.24962	135.9	—	—
5Me(α)	−346.57382	−346.57669	85.1	−0.5	−0.5
5Me(β)	−346.57295	−346.57587	85.1	—	—

than the angular $\Delta E^{(n)}(MN_{ang})_{\beta\alpha}$. However, in contrast to the $\Delta E^{(n)}(MN_{ang})_{\beta\alpha}$ term, it increases along the series albeit rather slowly. On the basis of these results one can draw the following conclusion: both angular strain and resonance terms act synergistically preferring the β-methyl cation attack in molecules **1**–**3**. In tetralin, the $\Delta E^{(4)}(MN_{ang})_{\alpha}$ component is more advantageous for the α-site, but the resonance interaction prevails making β-substitution still energetically somewhat more profitable. This is in harmony with recent experimental results of Fornarini *et al.*,[25] which show that Me_3C^+ attack occurs almost exclusively at the β-position in systems **2**–**4**. Other experimental evidence is also in accord with the general idea that the electrophilic substitution predominantly takes place at β-carbon atoms.[26–29] Apparently, this holds for kinetically controlled reactions, since Wheland's σ-complex mimics the transition state (structure) (**TS**). It is interesting to point out within this context that the final products of the electrophilic $^+CH_3$ reactions—the methylated derivatives of cycloalkabenzenes **1**–**3**—are more stable if the CH_3 group is attached at the α-position. The differences are small but significant, exhibiting a mild decrease as the size of the fused ring increases, obviously depending on the MN-effect (Table 3). Consequently, in thermodynamically controlled reactions α-substituted derivatives can be expected. Tetralin (**4**) behaves differently once again, since **4**Me(β) is slightly more stable than **4**Me(α). It is interesting to mention that greater stability of α-isomers is consistent with enhanced acidity of this position in cycloalkabenzenes involving small rings.[30] Streitwieser *et al.*[31] put forward an argument based on the rehybridization of the carbon junction atoms in order to explain this finding.

Cyclobutabenzene **5** deserves particular attention, because the hyperconjugation mechanism is replaced with considerably stronger conjugation interaction in the neutral molecule. The latter shifts the π-density from the annelated (*ipso*) bond to two *ortho* C–C bonds thus relieving the antiaromaticity. It is conceivable that the $^+CH_3$ attack will further diminish the antiaromatic interactions, particularly at the β-position substitution. This conjecture directly follows from examination of the relevant Pauling's resonance structures, where the spin-pairing patterns involving a cyclobutadiene-like distribution of π-bonds are omitted as unimportant (Scheme 2).

Indeed, the β-electrophilic attack is more compatible with the π-localization in the initial neutral molecule and is also associated with an additional resonance structure. This feature leads to a strong discrimination in the electrophilic reactivity, yielding values as high as 13.6 [12.1] kcal mol^{-1} for $\Delta^{(5)}(MCA)_{\beta\alpha}$, as obtained by the M(I) [M(II)] models. We shall try to estimate the dominance of the cationic resonance effect in the β-$^+CH_3$ conjugate acid **5m**β over **5m**α by using eqns. (8) and (9) to determine $\Delta^{(5)}(MN_{ang})_{\beta\alpha}$. Employing the angle $\varphi = 88.3°$ one obtains that $\Delta^{(5)}(MN_{ang})_{\beta\alpha} = 2.0$ kcal mol^{-1}. Since $\Delta^{(5)}(MCA)_{\beta\alpha} = 13.6$ kcal mol^{-1}, it follows that the resonance contribution to the preference of the β-position is $\Delta^{(5)}(MN_{res})_{\beta\alpha} = 11.6$ kcal mol^{-1}. It is noteworthy that the resonance contribution $\Delta^{(5)}(MN_{res})_{\beta}$ is as high as 18.8 kcal mol^{-1} (Table 2). In other words, the resonance effect is overwhelming, but both resonance and the angular strain act in the same direction thus making the β-site dramatically more reactive and susceptible to the electrophilic attack.

Finally, a word on the variation of $MCA^{(n)}(\alpha)$ and $MCA^{(n)}(\beta)$ is in order. For this purpose we shall take the most strained system **1** as the origin of scale and define the differences $\delta^{(n)}(MCA)_{\alpha} = MCA^{(n)}(\alpha) - MCA^{(1)}(\alpha)$, $\delta^{(n)}(MN_{ang})_{\alpha} = E^{(n)}(MN_{ang})_{\alpha} - E^{(1)}(MN_{ang})_{\alpha}$ and $\delta^{(n)}(MN_{res})_{\alpha} = E^{(n)}(MN_{res})_{\alpha} - E^{(1)}(MN_{res})_{\alpha}$. The corresponding entities for the β-position are defined analogously. Perusal of the data shows that $\delta^{(n)}(MCA)_{\alpha}$, $\delta^{(n)}(MN_{ang})_{\alpha}$ and $\delta^{(n)}(MN_{res})_{\alpha}$ increase along the series **1**–**4** and that the angular strain contribution to MCA_{α} dominates. Comparing $\delta^{(n)}(MN_{res})_{\alpha}$ and $\delta^{(n)}(MN_{res})_{\beta}$ one concludes that their trends are very similar, implying that the cationic resonance increases with larger number of CH_2 groups in the annelated carbocyclic ring. This is in agreement with the idea of an increase in the electron density relaxation effect. Unlike the α-methylation event, the cationic resonance is more pronounced for the β-attack, in particular for cyclobutabenzene (**5**) as discussed above. We conclude that the partitioning of the MCAs into the angular strain and cationic (hyperconjugation/conjugation) resonance components put forward here, offers a simple and intuitively appealing insight in the variation of the susceptibility toward electrophilic $^+CH_3$ attack. The same approach can be straightforwardly applied to other electrophilic groups.



Scheme 2

Structural parameters and charge distributions

The bond lengths of molecules **1**, **5**, benzene (**6**) and their methyl cation derivatives are given in Table 4. Their variations are discussed in great detail elsewhere[13,32,33] and need not be repeated here. We shall recapitulate only the salient features. The C–C bond distances of the aromatic perimeter of the neutral molecules should be compared to the free benzene value, except for the annelated (*ipso*) bond in **1**, which is highly strained and thus differs greatly from C–C bonds in aromatics. Consequently, it should be gauged against the double bond in (deformed) cyclopropene.[32,33] In that case it appears that the fused bond in **1** is considerably stretched. In contrast, adjacent (*ortho*) bonds are somewhat compressed due to rehybridization

Table 4 Bond distances (Å) and angles (degrees) of cyclopropabenzene (**1**), cyclobutabenzene (**5**), benzene (**6**) and their methyl cation derivatives. π-Electron density is described by Löwdin π-bond orders, atomic densities and formal charges as calculated from MP2(fc)/6-31G* wavefunctions[a]

Bond/angle	HF (MP2)	π-bo	Mayer[b] bo	HF (MP2)	π-bo	Mayer[b] bo	HF (MP2)	π-bo	Mayer[b] bo		π-Densities and (total charges)[c]		
1	Neutral molecule			α-Methylated cation			β-Methylated cation			Atom	Neutral	α-Me^+	β-Me^+
C(1)–C(2)	1.332 (1.352)	0.60	1.23	1.316 (1.342)	0.61	1.32	1.365 (1.365)	0.52	1.15	C(1)	0.94 (−0.05)	0.89 (−0.01)	0.73 (0.10)
C(1)–C(6)	1.370 (1.382)	0.61	1.36	1.377 (1.390)	0.48	1.30	1.390 (1.393)	0.53	1.26	C(2)	0.94 (−0.05)	0.74 (0.08)	0.90 (−0.02)
C(2)–C(3)	1.370 (1.382)	0.61	1.36	1.468 (1.452)	0.31	0.99	1.330 (1.361)	0.65	1.49	C(3)	0.99 (−0.16)	1.07 (−0.14)	0.82 (−0.03)
C(3)–C(4)	1.400 (1.409)	0.62	1.32	1.505 (1.490)	0.28	0.98	1.503 (1.486)	0.29	0.98	C(4)	0.98 (−0.15)	0.81 (−0.05)	1.06 (−0.15)
C(4)–C(5)	1.395 (1.408)	0.63	1.36	1.355 (1.384)	0.64	1.49	1.502 (1.485)	0.29	1.01	C(5)	0.98 (−0.15)	0.93 (−0.13)	0.78 (−0.02)
C(5)–C(6)	1.400 (1.409)	0.62	1.32	1.434 (1.424)	0.48	1.22	1.365 (1.385)	0.66	1.44	C(6)	0.99 (−0.16)	0.81 (−0.00)	0.93 (−0.11)
C(1)–C(7)	1.494 (1.504)	0.17	0.90	1.491 (1.513)	0.15	0.86	1.490 (1.490)	0.20	0.90	C(7)	1.13 (−0.28)	1.15 (−0.24)	1.15 (−0.24)
C(2)–C(7)	1.494 (1.504)	0.17	0.90	1.499 (1.496)	0.18	0.91	1.486 (1.506)	0.13	0.86	C(Me)	– (−)	– (−0.42)	– (−0.43)
C–C(methyl)	—			1.551 (1.559)		0.87	1.556 (1.567)		0.85				
5	Neutral molecule			α-Methylated cation			β-Methylated cation			Atom	Neutral	α-Me^+	β-Me^+
C(1)–C(2)	1.422 (1.420)	0.47	1.14	1.434 (1.405)	0.44	1.23	1.456 (1.451)	0.35	1.04	C(1)	0.95 (−0.01)	0.96 (−0.01)	0.69 (0.17)
C(1)–C(6)	1.342 (1.368)	0.72	1.56	1.326 (1.365)	0.65	1.50	1.394 (1.394)	0.54	1.27	C(2)	0.95 (−0.01)	0.68 (0.20)	0.99 (−0.03)
C(2)–C(3)	1.342 (1.368)	0.72	1.56	1.471 (1.445)	0.31	1.02	1.314 (1.340)	0.75	1.69	C(3)	1.00 (−0.18)	1.05 (−0.15)	0.95 (−0.14)
C(3)–C(4)	1.440 (1.429)	0.48	1.15	1.518 (1.496)	0.24	0.95	1.512 (1.502)	0.23	0.94	C(4)	0.99 (−0.17)	0.95 (−0.13)	1.06 (−0.14)
C(4)–C(5)	1.358 (1.386)	0.74	1.53	1.330 (1.364)	0.68	1.63	1.506 (1.489)	0.28	1.00	C(5)	0.99 (−0.17)	0.96 (−0.14)	0.71 (−0.02)
C(5)–C(6)	1.440 (1.429)	0.48	1.15	1.477 (1.449)	0.37	1.10	1.363 (1.383)	0.66	1.43	C(6)	1.00 (−0.18)	0.90 (−0.10)	0.96 (−0.16)
C(1)–C(7)	1.517 (1.521)	0.17	0.93	1.504 (1.530)	0.13	0.91	1.445 (1.458)	0.35	1.07	C(7)	0.95 (−0.15)	0.80 (−0.01)	0.93 (−0.12)
C(2)–C(8)	1.517 (1.521)	0.17	0.93	1.440 (1.482)	0.29	1.01	1.495 (1.501)	0.20	0.94	C(8)	0.95 (−0.15)	0.93 (−0.11)	0.77 (0.00)
C(7)–C(8)	1.333 (1.360)	0.87	1.73	1.363 (1.371)	0.68	1.58	1.358 (1.380)	0.72	1.52	C(Me)	— (−)	— (−0.41)	— (−0.44)
C–C(methyl)	—		1.553	(1.591)	0.81	1.549	(1.557)	0.87					

6	Neutral molecule			Methyl cation			Atom	Neutral	Methyl cation
C(1)–C(2)	1.386 (1.397)	0.62	1.36	1.353 (1.377)	0.64	1.47	C(1)	0.98 (−0.17)	0.92 (−0.13)
C(1)–C(6)	1.386 (1.397)	0.62	1.36	1.409 (1.408)	0.53	1.27	C(2)	0.98 (−0.17)	0.79 (−0.03)
C(2)–C(3)	1.386 (1.397)	0.62	1.36	1.481 (1.466)	0.30	1.02	C(3)	0.98 (−0.17)	1.06 (−0.16)
C(3)–C(4)	1.386 (1.397)	0.62	1.36	1.481 (1.466)	0.30	1.02	C(4)	0.98 (−0.17)	0.79 (−0.03)
C(4)–C(5)	1.386 (1.397)	0.62	1.36	1.353 (1.377)	0.64	1.47	C(5)	0.98 (−0.17)	0.92 (−0.13)
C(5)–C(6)	1.386 (1.397)	0.62	1.36	1.409 (1.408)	0.53	1.27	C(6)	0.98 (−0.17)	0.76 (−0.00)
C(3)–C(methyl)	— —	—		1.558 (1.568)	—	0.85	C(Me)	— (—)	— (−0.42)

[a] Hartree–Fock and MP2 bond distances, the latter being given within parentheses. Atomic π-densities, effective total charges and π-bond orders are obtained by Löwdin partitioning technique[37,38] employing MP2/6-31G* wavefunctions [b] Total bond orders are obtained by using Mayer's recipe.[39] [c] π-atomic densities and formal atomic charges (given within parentheses).

of the carbon junction atoms, which shifts s-character from *ipso*- to *ortho*-bond(s). This is followed by a redistribution of π-bond orders, which exhibit very small but consistent alternation in **1**. The variations of total bond orders is more pronounced, since it reflects a combined σ- (rehybridization) and π- (partial localization) effect. The change in benzene structure upon the cationic methylation (Table 4) is relevant for a better understanding of the forthcoming discussion. The C–C bonds of the aromatic ring linked to the newly formed sp^3 cationic center are dramatically lengthened because of rehybridization and abolished conjugation. The latter is replaced, however, by a rather strong hyperconjugation as evidenced by the π-bond order of 0.30 (Table 4). Subsequent vicinal C–C bonds are localized in the sense that they have high π- and total

Table 5 NICS(1) values for six- and four membered rings in some studied systems

Molecule	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
6-Membered ring	−13.0	−12.6	−12.7	−12.8	−5.6	−12.5	−12.7	−13.3	−12.3	−13.3
4-Membered ring	—	−1.7	—	—	13.3	—	—	—	—	—

Cations:	**2m**α	**2m**β	**5m**α	**5m**β	**6m**	**8m**α	**8m**β
6-Membered ring	−4.8	−4.8	−2.5	−2.8	−5.7	−6.5	−5.6
4-Membered ring	−2.2	−2.2	6.0	1.9	—	—	—

bond orders, assuming values 0.64 and 1.47, respectively. Distal C–C bonds are involved in π-bonding too, albeit to a lesser extent as illustrated by the π-bond order of 0.53. Apparently, the variation of π- and total bond orders is much more pronounced in **6m** than in cyclopropabenzene (**1**). Consequently, if these two density distributions are superimposed, then the more stable methyl cation derivative will be the one, which perturbs the bonding pattern of **6m** the least. This is obviously **1m**β because the π-bond orders found in **6m** are hardly changed. Moreover, they become more compatible with σ-bonds in the critical C(6)–C(1)–C(2)–C(3) region. For example, in the fused C(1)–C(2) bond possessing high p-character, the π-bond order is diminished relative to that in **1**. This finding should be advantageous, because small rings favor hybrids with larger p-content. On the contrary, the π-bond order in C(2)–C(3) is increased in **1m**β compared to the corresponding value in **1**, which is more compatible with high s-content of this *ortho* bond. A more detailed analysis shows that the electronic distribution of **6m** fits better with that of **1**, if the sp^3 center coincides with the β-carbon atom, compared to α-substitution. An appreciable variation of π-bond and total bond orders is found in **5**, where σ- and π-electrons act in a concerted and cooperative fashion. It is obvious that the electron density distributions over the C(6)–C(1)–C(2)–C(3) fragment in **5m**β and **5** are more compatible than is the case for **5m**α. It is important to observe that π-bond orders for the C(1)–C(2) and C(7)–C(8) bonds in **5m**β (**5m**α) are 0.35 (0.47) and 0.72 (0.87), respectively. Hence, it is clear that the antiaromatic interaction within the four-membered ring in **5m**β is considerably lower. In addition, it is worth noting that the π-bond orders along C(1)–C(7) and C(2)–C(8) are considerably enhanced in **5m**α and **5m**β, respectively, as expected from inspection of Pauling's resonance structures. In this respect, it is interesting to examine the antiaromatic/aromatic character of particular rings in some of the studied systems. For that purpose a simple criterion provided by the nucleus independent chemical shifts (NICS) put forward by Schleyer *et al.*[34,35] will be employed. They are in good agreement with a number of other criteria of antiaromaticity/aromaticity within a particular family of compounds,[36] but a word of caution is necessary. NICS values give only qualitative information on the energetic destabilization/stabilization termed the antiaromaticity/aromaticity. A proper treatment of the antiaromatic/aromatic features of cyclic compounds requires a high level of theory involving explicit account of the electronic correlation.[4] The NICS(1) parameters are calculated by the gauge invariant HF/6-31G* model by placing the chemical shift operator 1 Å above the center of a given rng. The reference NICS(1) values in benzene and cyclobutadiene (CBD) assume −12.5 and 24.7 ppm, respectively (Table 5). It is interesting to observe that methylated benzene **6m** has NICS(1) = −5.7 meaning that about half of the aromatic stabilization is retained upon the $^+CH_3$ attack. Another point of interest is that the aromaticity of the benzene ring in annelated systems **1**–**4** is not changed by the ring strain effect and the partial σ- and π-localization. This is in accordance with our finding that the nondynamical correlation energy of π-electrons in the localized model compound cyclohexatriene (D_{3h}) is very similar to that in benzene (D_{6h}).[4] Additionally, the NICS(1) indices in systems **6**–**9** are almost constant and close to the benzene value. A sharp decrease in the aromaticity of the six-membered rings takes place in **5m**α and **5m**β assuming values 6.0 and 1.9, respectively, implying that the conjugate acid of the latter (**5m**β) is more delocalized and less antiaromatic. This is in harmony with our previous discussion. Interestingly, four-membered rings in **2**, **2m**α and **2m**β exhibit a slight aromaticity, which is somewhat unexpected. The largest antiaromaticity was identified in the CBD ring of **5**, but even in this case it is roughly by 50% lower than in free cyclobutadiene.

Concluding remarks

Taking into account earlier studies and present results we would like to suggest the following definition of the Mills–Nixon effect: "It is a perturbation of the aromatic moiety exerted by fusion of one (or several) nonaromatic angularly strained molecule(s)".[12] This perturbation is reflected in the characteristic partial bond localization and deformation of the aromatic fragment leading ultimately to modifications of a number of physical and chemical properties. The most important manifestation of the MN effect is its directional ability in the electrophilic substitution reactions. Convincing evidence is presented here, which unequivocally shows that the β-position is energetically preferred for the $^+CH_3$ attack in systems **1**–**4**.

The difference in the methyl cation affinity $\Delta^{(n)}(MCA)_{\beta\alpha}$ has two contributions: $\Delta E^{(n)}(MN_{ang})_{\beta\alpha}$ and $\Delta E^{(n)}(MN_{res})_{\beta\alpha}$ or the angular strain and the cationic resonance contributions, respectively. They are disentangled here for the first time thus shedding light on the interplay between the σ-rehybridization and accompanying deformation of the σ-skeleton of the aromatic moiety, and the strong cationic resonance effect occurring in the conjugate acids. It is this interplay which determines the selectivity in the electrophilic aromatic substitution reactions of fused benzenes. It is noteworthy that oxygen and NH derivatives of **1** substituted at position 7 exhibit even larger selectivity than the parent compound discussed above.[40] Moreover, it is interesting to mention that in systems exhibiting the reversed MN effect, the orientational ability of small ring(s) in controlling the electrophilic reactivity is diametrically opposed to that in MN systems.[41,42] Hence, it follows that the electrophilic reactivity of fused molecules is well understood. A point of utmost importance is the fact that the MN effect on the electrophilic reactivity is a result of a combined action of angular strain and cationic resonance. Consequently, all attempts to reduce either the MN or reversed MN effect to the angular strain influence only are condemned to fail. Such a standpoint can be safely considered as rebutted.

Finally, it should be pointed out that analysis of the electrophilic reactivity of other fused cyclopropparenes should be rewarding, particularly if extended to derivatives possessing substituent(s) on the benzene ring, because some of them exhibit remarkable properties. For example, dihydrocyclobutabenzene (**2**) with attached electron withdrawing group(s) is quite stable towards strong protic acids.[43] This is of some importance since such systems could be used in the synthesis of high-performance polymers requiring strong acids and high temperatures.

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