Theoretical Study of Wheland Intermediates in Benzocycloalkenes: Vindication of the Mills–Nixon Hypothesis

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Structural and energetic properties of *o*-xylene and three benzocycloalkenes involving a three, four or five membered fused carbocycle are considered together with their Wheland intermediates by HF/6-31G* and single point MP2(fc)//HF/6-31G* procedures. It is conclusively shown that protonation of the arylic α-position is energetically less favourable than β-protonation, in accordance with the original Mills–Nixon (MN) hypothesis and the experimental evidence gathered by electrophilic substitution reaction studies. More specifically, it is found that the difference $E_\alpha^{(n)} - E_\beta^{(n)}$ is an inverse linear function of the C–C–C angle in the annelated carbocycle, where two carbon atoms of the C–C–C fragment belong to the fused bond. The origin of the different susceptibility of α- and β-sites toward electrophilic attack is analysed by means of a new energy partitioning scheme based on homodesmic reactions, which gives interesting insight into the nature of intramolecular interactions in Wheland complexes. It is shown that the difference in reactivity can be traced down to the compatibility or incompatibility of two π-electron localization modes. The first is related to the ground state and is induced by the angular strain of the annelated carbocycle, thus reflecting a 'memory' effect, whereas the other one occurs in the transition structure (TS) (simulated by the Wheland complex) because of protonation and concurrent formation of the sp^3 centre within the aromatic fragment. The competition between these two antagonistic localization patterns is responsible for enhanced reactivity of β-sites over the α-positions.

Aromatic molecules anneleated to small rings are of particular interest since they involve two characteristic juxtaposed and competing bonding patterns: aromaticity of the π electrons and Baeyer strain caused by angular deformation of the σ-electron density in the molecular plane. It was shown by Mills and Nixon as early as 1930 that a fused small ring was capable of changing the direction of electrophilic substitution of the benzene nucleus.[1] Thus, the higher reactivity of the β- relative to the α-position in electrophilic substitution of β-hydroxyindan in contrast to reversed reactivities in β-hydroxytetralin was rationalized by partial π-bond fixation within the benzene ring. This intriguing effect of small rings on the reactivity of the aromatic fragments has been studied subsequently by a number of researchers[2–9] providing evidence for the Mills–Nixon (MN) effect in fused systems. A survey of the experimental results in electrophilic substitution reactions was produced recently by Taylor.[10] Interestingly, structural X-ray data[11–15] and NMR measurements[16–19] are not unambiguous, giving rise to some controversy. Studies by modern quantum chemistry methods reveal the structural consequences of the MN effect in annelated molecules,[20–24] although there are some notable exceptions, as *e.g.* benzoborirene and benzocyclopropenyl cation where anti-MN distortions are to be expected.[25] Earlier theoretical work has been reviewed elsewhere.[26] It is noteworthy that a clear-cut case for MN systems is given by fullerene C_{60}, as pointed out by Fowler *et al.*[27] Finally, it should be mentioned that some most recent EPR measurements support the notion of the MN effect.[28]

In spite of the importance of the MN effect in aromatic electrophilic substitution reactions, theoretical studies in this area are practically nonexistent to the best of our knowledge. In order to fill the gap we report here *ab initio* calculations on Wheland σ complexes[29] obtained by protonation of some benzocycloalkenes; according to Hammond's postulate,[30] these intermediates closely represent the corresponding transition structures in electrophilic substitutions. The present results show that it is not only the ground state electron distribution which is responsible for the distinct reactivities of the aromatic α- and β-positions, but also the electron redistribution in the transition structure. In particular, the difference in reactivity is a result of the degree of matching or mismatching of different π-electron localization modes taking place in the ground state and transition structures represented by the Wheland intermediates.

Methodology.—The adopted theoretical procedure has to be a good compromise between accuracy and feasibility. It should be practical enough to allow full geometry optimization of the studied molecules and yet it should be rigorous enough to provide reliable results. Recent calculations show that the SCF level of theory employing a basis set of 6-31G* quality is satisfactory if structural parameters are desired. Since we are interested in energetic properties, however, electron correlation should be taken into account. This was achieved by single point MP2(fc)//HF/6-31G* calculation, where (fc) stands for frozen inner-core electrons in the course of computation of the correlation energy. Although the second order Møller–Plesset perturbation theory (MP2) gives only a portion of the correlation energy, we believe that this method is adequate for the problem under consideration. This is substantiated by the calculation of the benzene proton affinity (183.0 kcal mol^{-1}) which is in excellent agreement with the experimental value of 183.1 kcal mol^{-1} obtained by ion cyclotron resonance measurements.[31] Therefore, it is expected that the relative stability of Wheland intermediates for α- and β-substitution is well reproduced. All calculations are performed by using the GAUSSIAN-90 program package.[32] Finally, it should be pointed out that the electrophilic substituent is modelled by a proton.

Table 1 Total molecular energies E, E_α and E_β (in a.u.) of parent *o*-xylene and benzocycloalkenes and their Wheland σ complexes for protonation at the aromatic α- and β-positions, together with energy differences $E_\alpha - E_\beta$ (in kcal mol^{-1})

Molecule	Method[a]	E	E_α	E_β	$E_\alpha - E_\beta$
Benzene	SCF	−230.703 14	−231.014 69	−231.014 68	—
	MP2	−231.456 48	−231.748 14	−231.748 14	—
o-Xylene (**1**)	SCF	−308.773 97	−309.099 61	−309.102 39	1.75
	MP2	−309.795 74	−310.102 66	−310.103 73	0.7
Benzocyclopentene (**2**)	SCF	−346.645 43	−346.971 33	−346.976 53	3.3
	MP2	−347.790 01	−348.096 59	−348.100 79	2.6
Benzocyclobutene (**3**)	SCF	−307.565 43	−307.885 89	−307.893 25	4.6
	MP2	−308.579 22	−308.880 18	−308.885 37	3.25
Benzocyclopropene (**4**)	SCF	−268.463 11	−268.775 04	−268.785 70	6.7
	MP2	−269.351 88	−269.642 35	−269.650 13	4.9

[a] HF/6-31G* and MP2(fc)//HF/6-31G*(MP2) energies obtained for HF/6-31G* optimized geometries.

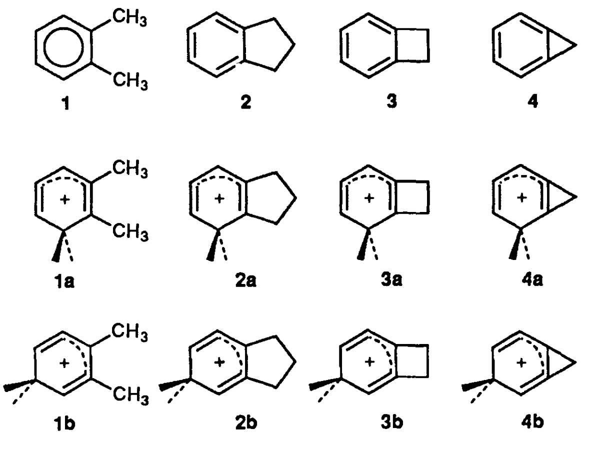


Fig. 1 Schematic representation of the examined molecules and their protonated forms

Results and Discussion

Structural features of the MN-systems are rather well understood.[20–26] Hence we shall not dwell on their detailed description. Instead, some of their more striking properties, relevant for the forthcoming discussion of molecular energetics, will be briefly mentioned. It appears that the annelated small ring(s) exert a perturbation on the aromatic fragment leading to its deformation in size and shape. Variation in bond angles in benzene is strongly pronounced as a rule. Thus the C–C–C angle at the carbon junction atoms are enlarged whereas angles between bonds emanating from the central carbon atoms (α-position to the small carbocycle) assume rather acute values. This is a consequence of the angular-strain spillover from the small ring into the benzene fragment and a tendency to diminish bending of the bent bonds. Changes in bond distances within the benzene moiety are usually small but still significant. For instance, distances of bonds adjacent (*ortho*) to the fused (*ipso*) bond are somewhat diminished and more localized, leading to preference of the corresponding Kekulé structure over its counterpart. In other words, a specific resonance structure is partially 'frozen' yielding a characteristic mode of π-electron localization indicated schematically in Fig. 1. Another point of considerable interest is the geometric and electronic structure of protonated benzene which serves as the simplest model of the Wheland σ complex. The length of the C–C bonds vicinal to the sp^3 site is substantially reduced exhibiting a high degree of π-electron localization. This pattern of localization is crucial for understanding aromatic electrophilic substitution reactions (*vide infra*).

We shall focus now on the energetic properties of the systems under investigation. The relevant results are collected in Table 1. The proton affinity (PA) of oxylene is of some interest since a comparison with experiment provides an additional piece of evidence for the reliability of the adopted theoretical procedure. More specifically, the difference in PA values of the β-position of *o*-xylene and of benzene assumes values of 10.6 and 10.25 kcal mol^{-1} for HF/6-31G* and MP2(fc)//HF/6-31G* calculations respectively, which is in good agreement with the observed value of 9.8 kcal mol^{-1} observed in the ion cyclotron resonance measurements.[33] For the α-position, the difference in PA values of *o*-xylene relative to benzene is somewhat smaller, assuming values of 8.9 (9.6) kcal mol^{-1}, where the MP2(fc)//HF/6-31G* result is given within parentheses.

Examination of data presented in Table 1 shows that the difference in total energies of the α- and β-Wheland σ complexes is always positive implying that the β-intermediates are more stable in accordance with the experimental electrophilic substitution reaction studies.[2–10] Hence the present results provide strong theoretical evidence that the original Mills–Nixon hypothesis is correct. Further, $E_\alpha - E_\beta$ increases with decreasing size of the annelated ring from a value of 1.75 kcal mol^{-1} in **1** to a value of 6.7 kcal mol^{-1} in **4** at the HF/6-31G* level of computation. The corresponding values for MP2(fc)//HF/6-31G* procedure read 0.7 and 4.0 kcal mol^{-1} respectively. This is compatible with a stronger influence of the angular strain in smaller fused rings.

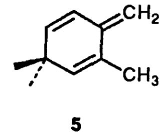
The linear relationsips eqns. (1a, b) pertaining to the results for fused benzocycloalkenes are obtained by the least square fit method, possessing correlation coefficients $R = 0.9996$ and

$$\text{HF/6-31G*: } E_\alpha - E_\beta = 11.15 - 6.980\varphi \quad \text{(1a)}$$

and

$$\text{MP2(fc)//HF/6-31G*: } E_\alpha - E_\beta = 7.68 - 4.611\varphi \quad \text{(1b)}$$

0.994, respectively. Here, $E_\alpha - E_\beta$ is given in kcal mol^{-1}, whereas the small ring angle φ, formed by a fused (ipso) bond and a side of the strained carbocycle merging at the carbon junction atom, is in degrees. It is gratifying that the points corresponding to protonated *o*-xylenes (**1**) are completely off the straight lines (Fig. 2) indicating that different effects are operative in this compound and in fused hydrocarbons (**2**–**4**). Indeed, the origin of $E_\alpha - E_\beta$ in **1** has nothing to do with the angular strain but can be traced down to inductive and hyperconjugative interactions instead, as may be verified by considering the possible valence bond (VB) structures. Their examination shows that many resonance structures of the α- and β-intermediates are alike with one notable exception provided by the no-bond structures depicted as **5** and **6**.



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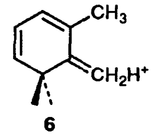

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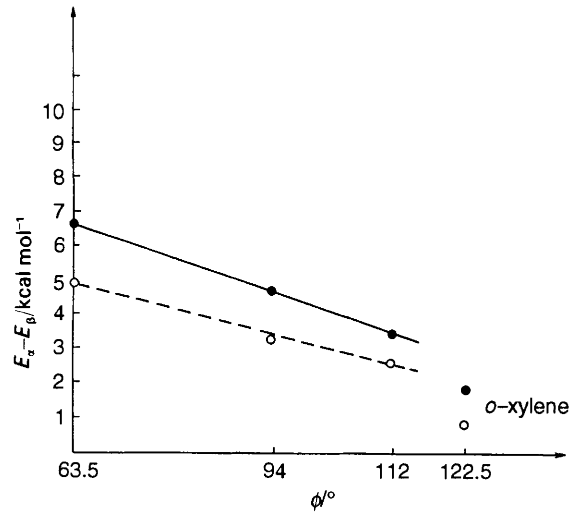
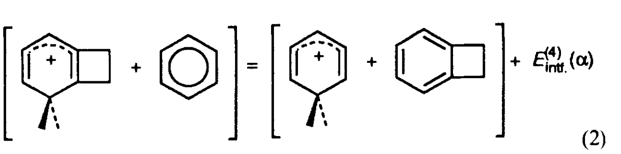


Fig. 2 Linear dependence of the difference in total energies between α- and β-Wheland's intermediates and the angle φ of the annelated small ring related to the carbon junction atom. Full and open circles correspond to HF/6-31G* and MP2//HF/6-31G* calculations, respectively.

The former (**5**) describes an unfavourable cross-(hyper)conjugated resonance structure appearing in the β-complex as compared to the hexatriene pattern (**6**) in the corresponding α-complex. Their difference indicates that a slight energetic preference of the β-intermediate can be understood by the prevailing influence of the inductive effect. Rationalization of the results for benzocycloalkenes is given in the following section.

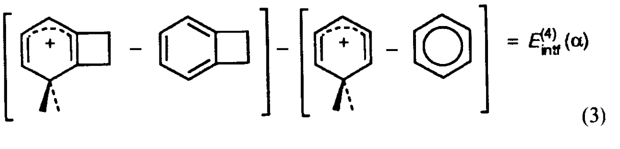
Interpretation of the MN Effect.—Homodesmic chemical reactions[34,35] are a useful vehicle in exploring the nature of intramolecular interactions. In this type of hypothetical reaction the number of atoms of the same element, specific types of covalent bonds and approximate hybridizations are preserved in the products. This is significant since it diminishes the role of electron correlation to a minimum in contrast to its paramount importance in chemical reactions in general.

As an illuminative example we shall consider the following homodesmic reaction related to benzocyclobutene and its α-protonated form.



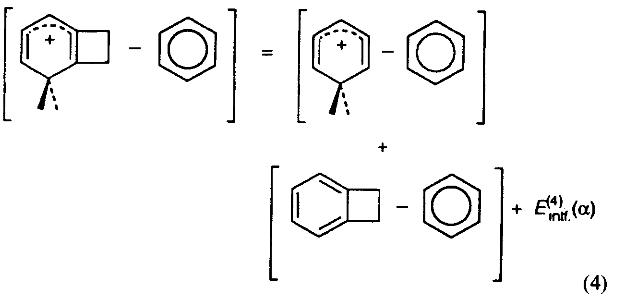
(2)

Here structural formulae represent total energies of the corresponding molecular system whereas $E^{(4)}_{\mathrm{intf.}}(\alpha)$ stands for the interference energy of two events which simultaneously perturb the benzene ring: (a) fusion of the small ring and (b) protonation at α-position. The upper index (4) is related to the number of carbon atoms in the annelated small ring. It is useful to observe that $E^{(n)}_{\mathrm{intf.}}(p)$, where $p = \alpha$ or β, can be expressed by the difference in the negative proton affinities (PAs) of the corresponding benzocycloalkene and that of benzene as given by eqn. (3):



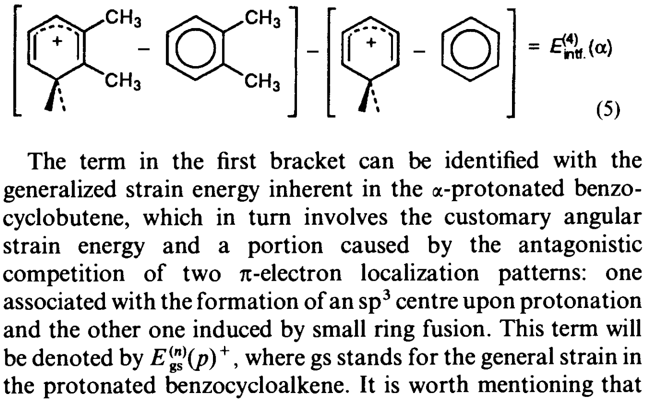
(3)

One easily finds out that $E^{(4)}_{\mathrm{intf.}}(\alpha)$ is a positive entity. As already mentioned, fusion with smaller rings leads to increased s-character and higher π-bond order in the aromatic C–C bonds adjacent to the annelated bond. This partial double-bond fixation is opposite to that required by protonation at the α-position. In contrast, the localization associated with β-protonation is compatible with the localization mode in the parent benzocyclobutene for two of three benzene bonds around the carbon junction atoms. It is exactly this matching or mismatching that causes a decrease in stability of the α-protonated σ complex relative to the β-protonated one. It is important to note that the homodesmic reaction expressed as eqn. (2) can be rewritten as eqn. (4), by subtracting the energies



(4)

of two benzene molecules. Eqn. (4) shows that the effect of protonation in benzocycloalkenes can be decomposed into two components: (a) protonation of the benzene ring and (b) fusion of the small ring and their mutual interference, tacitly assuming that benzene is taken as a reference level. An enlightening way of analysing $E^{(n)}_{\mathrm{intf.}}(p)$ itself is provided by rewriting eqn. (3) as eqn. (5).



(5)

The term in the first bracket can be identified with the generalized strain energy inherent in the α-protonated benzocyclobutene, which in turn involves the customary angular strain energy and a portion caused by the antagonistic competition of two π-electron localization patterns: one associated with the formation of an sp^3 centre upon protonation and the other one induced by small ring fusion. This term will be denoted by $E^{(n)}_{\mathrm{gs}}(p)^+$, where gs stands for the general strain in the protonated benzocycloalkene. It is worth mentioning that the degree of incompatibility of the two localization modes is greater in the α-protonated benzocycloalkene than in the reference 'strain free' α-protonated *o*-xylene. The second bracket is the strain energy of the parent benzocycloalkene $E^{(n)}_{\mathrm{s}}$, defined in the usual way[34,35] by the corresponding homodesmic reaction. Finally, the last two terms in eqn. (5) give the negative PA values of the α-position of *o*-xylene and of benzene, respectively. Their difference is equal to $E^{(o\text{-xyl})}_{\mathrm{intf.}}(\alpha)$ as directly follows, *mutatis mutandis*, from eqn. (4). Hence, one can express the interference energy in general as eqn. (6). It appears that the

$$E^{(n)}_{\mathrm{intf.}}(p) = E^{(n)}_{\mathrm{gs}}(p)^{+} - E^{(n)}_{\mathrm{s}}(p) + E^{(o\text{-xyl})}_{\mathrm{intf.}}(p) \qquad (6)$$

interference energy can be interpreted as activation of the position p (α or β) *via* hyperconjugative interaction with CH_2 groups of the small fused carbocycle mimicked by the two methyl groups in *o*-xylene and given by $E^{(o\text{-xyl})}_{\mathrm{intf.}}(p)$, and the difference in the destabilizing strain energies of the protonated Wheland σ-complex and the parent benzocycloalkene. Total energies of alkanes necessary for calculating the energy components appearing in eqn. (6) are given in Table 2. The energy partitioning of the interference energies $E^{(n)}_{\mathrm{intf.}}(p)$ according to the analysis presented above is summarized in Table 3. A survey of the data offers some interesting conclusions. The generalized strain energy $E^{(n)}_{\mathrm{gs}}(\alpha)^{+}$ is always greater than $E^{(n)}_{\mathrm{gs}}(\beta)^{+}$. The corresponding values of HF/6-31G* [MP2(fc)//HF/6-31G*] calculations are 1.5(1.9), 2.8(2.6) and 4.9(4.2) for n = 5, 4 and 3, respectively. This is compatible with the interpretation based on the mismatching of π-electron bond fixation patterns and the underlying unfavourable interaction of σ and π electrons in the Wheland intermediates. Both the ground state strain $E^{(n)}_{\mathrm{s}}$ and $E^{(n)}_{\mathrm{gs}}(p)^{+}$ ($p = \alpha, \beta$) sharply increase with a decrease in size (n) of the fused carbocycle. Furthermore, the activation of the α- and β-positions of *o*-xylene relative to benzene can be estimated by the $E^{(o\text{-xyl})}_{\mathrm{intf.}}(p)$ values. The rather large energies $\{-8.5\ (-9.6)$ and $-10.6\ (-10.2)$ obtained by HF/6-31G* [MP2(fc)//6-31G*]$\}$ can be traced down to an interplay between the hyperconjugative and inductive interactions with CH_2 groups as indicated earlier. At present, we are not able to separate these two effects. It should be emphasized, however, that the difference between $E^{(o\text{-xyl})}_{\mathrm{intf.}}(\alpha)$ and $E^{(o\text{-xyl})}_{\mathrm{intf.}}(\beta)$ is rather small ($\sim$0.6 kcal mol^{-1} by the MP2 method). Since $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ is given by the difference $E^{(n)}_{\mathrm{intf.}}(\alpha) - E^{(n)}_{\mathrm{intf.}}(\beta)$ of the corresponding interference energies [*cf.* eqn. (4) for α- and β-protonation], one obtains eqn. (7), where n stands for the number of atoms in the fused carbocycle as before. The

$$E^{(n)}_{\alpha} - E^{(n)}_{\beta} = E^{(n)}_{\mathrm{intf.}}(\alpha) - E^{(n)}_{\mathrm{intf.}}(\beta) = [E^{(n)}_{\mathrm{gs}}(\alpha)^{+} - E^{(n)}_{\mathrm{gs}}(\beta)^{+}] + [E^{(o\text{-xyl})}_{\mathrm{intf.}}(\alpha) - E^{(o\text{-xyl})}_{\mathrm{intf.}}(\beta)] \qquad (7)$$

last term is a constant corresponding to the difference in activation of α- and β-positions of *o*-xylene relative to benzene. Hence, the variation in $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ is governed by the difference $E^{(n)}_{\mathrm{gs}}(\alpha)^{+} - E^{(n)}_{\mathrm{gs}}(\beta)^{+}$ in the generalized strain energies of the Wheland complexes of α- and β-substitution. As this difference rises along the series n = 5, 4, 3 the difference $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ in reactivity of α- and β-sites increases, the latter being always more reactive. It is noteworthy that the strain energy of the ground state parent hydrocarbon does not explicitly appear in eqn. (7). Nevertheless, the influence of the ground state is present in the $E^{(n)}_{\mathrm{gs}}(\alpha)^{+} - E^{(n)}_{\mathrm{gs}}(\beta)^{+}$ term, which determines the degree of compatibility and incompatibility of π-bonding patterns taking place in the ground state and in the protonated σ complexes of α- and β-substitution as discussed above. In other words, a molecule in its transition structure (TS), modelled by the corresponding intermediate, remembers its ground state geometry which is better adapted for β-protonation ('memory' effect).

Table 2 Total molecular energies E_{SCF} and E_{MP2} of simple alkanes (in a.u.) as calculated by the HF/6-31G* (SCF) and MP2(fc)//HF/6-31G*(MP2) procedures at HF/6-31G* optimized geometries

Molecule	E_{SCF}	E_{MP2}
Ethane	−79.228 76	−79.494 51
Propane	−118.263 65	−118.659 97
Butane	−157.298 40	−157.825 54
Pentane	−196.332 96	−196.990 93

Conclusion

The present calculations conclusively show that the original MN hypothesis is justified. The Wheland intermediates for α-substitution possess higher energy than the β-counterparts in accordance with the experimental evidence. Furthermore, it is found that the difference in reactivity $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ is an inverse linear function of the size of the fused small carbocycle as intuitively expected. It appears also that $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ is equal to the difference in interference energies $E_{\mathrm{intf.}}(\alpha) - E_{\mathrm{intf.}}(\beta)$, which in turn describes two juxtaposed effects simultaneously present in protonated benzocycloalkenes: formation of an sp^3 centre with the accompanying π-bond localization pattern and perturbation of benzene induced by angular strain. The latter leads to the characteristic partial π-bond localization in the ground state of the parent hydrocarbons which is partly retained in the transition structure. The degree of mismatching and antagonistic behaviour of these two localization patterns determines essentially the difference in reactivity of α- and β-aryl sites toward electrophilic substitutions. Since the partial π localization in the benzene ring is caused predominantly by rehybridization, it appears that diminished electrophilic reactivity of α-positions is a consequence of disconcerted action of σ and π electrons. A special energy partitioning technique is developed based on homodesmic reactions, which relates $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ to the generalized strain energy appearing in Wheland intermediates and reflecting the degree of σ- and π-electron antagonism.

Finally, electrophilic aromatic substitution reactivity in benzocycloalkanes is considered here by taking the proton as prototype of an electron-deficient species attacking the benzene ring. Much of the recent experimental research interest in this field has been focused on π-excessive heteroaromatic systems by employing more complex electrophilic groups.[10,36] Our objective is to extend the present calculations to model systems involving strong electron-donating heteroatomic substituents, which enhance the basicity of the benzene ring, and to estimate the role of solvent effects.[37]

Acknowledgements

A portion of this work has been performed during stay of two of us (M. E. M. and Z. B. M.) at the *Organisch-Chemisches Institut*

Table 3 Decomposition of the interference energy and the difference in protonation energy $E^{(n)}_{\alpha} - E^{(n)}_{\beta}$ into contributions describing various modes of intramolecular interactions as obtained by HF/6-31G* and MP2(fc)//HF/6-31G* calculations. The latter are given within parentheses[a]

Molecule	$E^{(n)}_{\mathrm{gs}}(p)^{+}$	$E^{(n)}_{\mathrm{s}}$	$E^{(n)}_{\mathrm{gs}}(\alpha)^{+} - E^{(n)}_{\mathrm{gs}}(\beta)^{+}$	$E^{(n)}_{\mathrm{intf.}}(p)$	$E^{(n)}_{\mathrm{intf.}}(p)$	$E^{(n)}_{\alpha} - E^{(n)}_{\beta}$
2a	2.6 (5.1)	2.8 (4.9)	—	−8.85 (−9.6)	−9.0 (−9.4)	0
2b	1.1 (3.2)	2.8 (4.9)	1.5 (1.9)	−10.6 (−10.2)	−12.3 (−12.0)	3.2_5 (2.6)
3a	34.3 (37.0)	31.1 (33.3)	—	-8.8_5 (−9.6)	-5.6_5 (5.9)	0
3b	31.5 (34.4)	31.1 (33.3)	2.8 (2.6)	−10.6 (−10.2)	−10.2 (−9.1)	4.5_5 (3.7)
4a	82.0 (82.4)	73.4 (72.0)	—	-8.8_5 (−9.6)	-0.2_5 (0.7_5)	0
4b	77.1 (78.2)	73.4 (72.0)	4.9 (4.2)	−10.6 (−10.2)	−6.9 (−4.1)	6.6_5 (4.9)

[a] In kcal mol^{-1}. (p) Denotes position of protonation α or β.

der Westfälischen Wilhelms-Universität in Münster. One of us (M. E. M.) would like to thank Alexander von Humboldt Foundation for financial support. The other (Z. B. M.) would like to use this opportunity to thank University of Münster for granting visiting professorship.

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Paper 3/04204I
Received 19*th July* 1993
Accepted 19*th October* 1993