

Measures to evaluate heteroaromaticity and their limitations: Story of skeletally substituted benzenes

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Abstract. *Ab initio* HF, MP2, CCSD(T) and hybrid density functional B3LYP calculations were performed on a series of skeletally mono- and di-substituted benzenes, (CH)₅Z and (CH)₄Z₂, Z = C⁻, N, O⁺, Si⁻, P, S⁺, Ge⁻, As, Se⁺, BH⁻, NH⁺, AlH⁻, SiH, PH⁺, GaH⁻, GeH and AsH⁺. Various measures of aromaticity such as the bond length equalization, homodesmotic equations, singlet–triplet energy difference (ΔE_{s-t}), chemical hardness (*h*) and out-of-plane distortive tendency are critically analysed. The relative energy ordering in skeletally disubstituted benzenes displays trends that are inexplicable based on conventional wisdom. In general, the ortho-isomer is found to be the least stable when the substituent is from the second row, whereas if the substituent is from the fourth row, the ortho-isomer is the most stable. Various qualitative arguments, including (a) lone pair–lone pair repulsion, (b) the sum of bond strengths in the twin Kekule forms, and (c) the rule of topological charge stabilization (TCS), are used to explain the observed relative energy trends. The rule of TCS in conjunction with the sum of bond strengths is found to predict the relative energy ordering reasonably well. The reactivity of this class of compounds is assessed based on their singlet–triplet energy differences, chemical hardness and the frequencies corresponding to out-of-plane skeletal distortions. These reactivity indices show less kinetic stability for the compounds with substituents from the fourth row and point to the fact that the thermodynamically most stable compounds need not be the least reactive ones. The ΔE_{s-t} values indicate that the *p*-framework of benzene weakens upon skeletal substitutions.

Keywords. Aromaticity; heteroaromaticity; skeletally substituted benzenes; theoretical calculations; DFT.

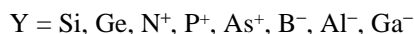
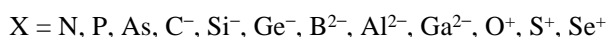
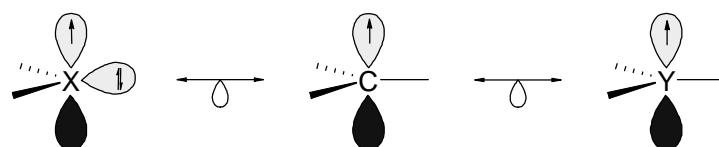
1. Introduction

Aromaticity has been one of the most important paradigms in organic and physical organic chemistry.¹ Five- and six-membered rings with 6*p*-electrons, with benzene being the classic example, remains the most important class of aromatic compounds which provide the basis for the concept of aromaticity.^{1,2} In spite of being a fundamentally important concept, precise definition and characterization of the concept of aromaticity is elusive.

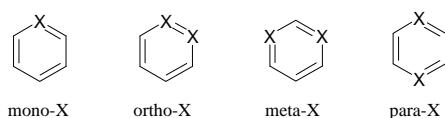
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The three main criteria that are being used to measure aromaticity are the geometric, energetic and magnetic. When a cyclic conjugated molecule exhibits bond delocalization or if the bond alternation is close to zero, it is called an aromatic molecule. One of the prime energetic criteria for quantifying aromaticity is the calculation of resonance energies using the homodesmotic and the superhomodesmotic equations. This depends on the way in which the equations are set up. The magnetic criteria, which includes the diamagnetic susceptibility exaltation (Λ) and nucleus-independent chemical shift (NICS) values are extensively used to define aromaticity quantitatively.³ In a recent study on cyclic isomers of $(\text{CH})_2\text{B}_2\text{N}_2$, Cerunsak *et al*⁴ have exposed the limitations of the utility of ring currents and density maps as measures of describing the aromatic character in heterocycles.⁴ Similarly, Baldrige *et al*⁵ in their elaborate study on silabenzenes pointed out the limitations of NICS approach in this class of compounds. Some other measures that have been used to define aromaticity include chemical hardness, the propensity of the molecule to resist puckering etc. While defining aromaticity of the polycyclic aromatic hydrocarbons is complicated, it is even more complicated for the heteroaromatics. The distortive nature of the *p*-electrons in benzene and the *s*-enforcement of regular D_{6h} geometry in benzene have been unambiguously established recently.⁶ Thus, it is not possible to conceive a straightforward relationship between bond length equalization in benzenoid compounds and their aromaticity.

The heteroanalogs of benzene where one or more methine groups are replaced by isovalent atoms/ions/groups are of much interest to the experimental chemists and the theoreticians. Scheme 1 displays the three possibilities for skeletal substitutions on the benzene ring. The various possible skeletally mono- and di-substituted benzenes



Scheme 1.

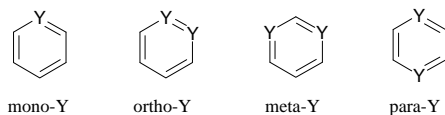
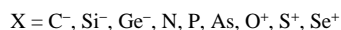


mono-X

ortho-X

meta-X

para-X



mono-Y

ortho-Y

meta-Y

para-Y



Scheme 2.

involving X and Y substituents are considered in the present study (scheme 2). We have addressed the effect of skeletal substitution on the benzenoid framework systematically through computational studies.⁷ A majority of the above compounds have been synthesized and possess rich chemistry and this set of compounds provide a good basis for the applicability of various criteria to define aromaticity. Assessing the perturbations caused by skeletal replacement of one or more carbon atoms in the benzene ring has been a challenging task and interesting in its own right.⁷⁻⁹ Several experimental and theoretical studies were directed to unravel the subtle ways in which the stability, reactivity, and other properties of the planar **6p**-systems are affected upon skeletal replacements of one or more C or methine groups in benzene by heteroatoms. The group V heterobenzenes and their valence isomers have been subjected to extensive theoretical and experimental studies.¹⁰ Similarly, silaromaticity has been a vividly debated topic and much experimental and theoretical work is concentrated on studying this class of compounds. Recently, the strategy of employing bulky protecting groups on Si centres paved the way to many silaromatic compounds.¹¹ We performed exploratory computational studies on the valence isomers of silabenzene and disilabenzenes.^{12,13} As the aim of the study is to assess the effect of skeletal substitutions, the present study is restricted to skeletally mono- and di-substituted compounds. In all mono- and di-skeletally substituted benzenes the planar structures were assumed to correspond to the global minima.⁷⁻¹³ However, previous studies indicate that replacement of more than two carbon units in the benzenoid framework would lead to a situation, especially in third and fourth row substitutions, where the planar structure does not correspond to a global minima on the potential energy surface as the nonplanar structure become energetically competitive.¹⁴

It was observed that properties like thermodynamic stability, chemical hardness, bond delocalization, reactivity, out-of-plane distortive tendency etc. of this class of compounds are the results of interplay among various competing and intricate factors. Therefore, we report a systematic *ab initio* study at correlated levels, as well as those based on density functional theory. The present study evaluates the skeletal perturbations on the mono- and di-substituted benzenes and attempts to answer the following questions, which in turn will further our understanding of heteroaromaticity. (a) How are the thermodynamic stabilities, gauged by the homodesmotic equations, affected upon skeletal substitution? (b) How do we account for the computed relative stabilities of the positional isomers? (c) What is the interrelationship among the structure, stability and reactivity? (d) Will a weaker **p**-framework enhance or restrict bond delocalization? (e) What is the effect of substitution on the in-plane and out-of-plane skeletal distortions?

2. Computational details

All the structures considered in this study were optimized within the symmetry constraints using the default gradient procedures implemented in the Gaussian program at the HF/6-31G* level of theory.¹⁵ The stationary points thus obtained were characterized by frequency calculations. Again the full geometry optimizations and frequency calculations were carried out at B3LYP/6-31G* level of theory¹⁶ to refine the geometries further and to reconfirm the nature of the stationary points. Optimizations at the MP2 level were done using 6-31G* and 6-31G** basis sets for X and Y substituents respectively. These were found to be quite similar in this class of compounds. The effect of adding a set of diffuse functions on the geometries of anionic systems is studied using the 6-31+G* basis set at the MP2 level. Earlier calculations indicate that MP2 energies

are closer to those obtained by the coupled cluster method compared to the B3LYP energies. Hence, MP2 optimized geometries were chosen for further single point calculations. Coupled cluster method has been found to be reliable for this class of compounds where the wavefunctions are not multideterminantal in nature. CCSD(T)/6-31G* single point calculations were done on the MP2 optimized geometries. As the inclusion of diffuse functions is essential in modelling the energetics of anionic and dianionic compounds, single point energy calculations were performed using the 6-31++G* and 6-311++G** basis sets at the MP2 level. The best estimates of the energies, which include a correction factor at the MP2 level for the rather inadequate basis set used at CCSD(T) level, were thus obtained using the following equations.

For cationic and neutral systems for the X substituent:

$$\Delta E = \Delta E_{\text{CCSD(T)}} + \Delta E_{(\text{MP2/6-31G**}-\text{MP2/6-31G*})} + \Delta ZPE. \quad (1)$$

For anionic systems for the X substituent:

$$\Delta E = \Delta E_{\text{CCSD(T)}} + \Delta E_{(\text{MP2/6-31++G*}-\text{MP2/6-31G*})} + \Delta E_{(\text{MP2/6-31G**}-\text{MP2/6-31G*})} + \Delta ZPE. \quad (2)$$

For cationic and neutral systems for the Y substituent:

$$\Delta E = \Delta E_{\text{CCSD(T)}} + \Delta E_{(\text{MP2/6-311+G**}-\text{MP2/6-31G**})} + \Delta H. \quad (3)$$

For anionic systems for the Y substituent:

$$\Delta E = \Delta E_{\text{CCSD(T)}} + \Delta E_{(\text{MP2/6-311++G**}-\text{MP2/6-31G**})} + \Delta H. \quad (4)$$

Zero point energy correction (ΔZPE) and enthalpy correction (ΔH) were done using the thermochemical data obtained from the frequency calculations at the B3LYP/6-31G* level. A scaling factor of 0.98 was used for both zero point energy (ZPE) and enthalpy (H) corrections. The above best estimates are designed to mimic the results obtained at the CCSD(T) level with a high quality basis set, although the basis set effects were considered only at the MP2 level. Such formalisms used in G1 and G2 levels of theory were found to yield satisfactory results for a wide range of compounds.

The natural charges were obtained at the HF/6-31G* level on the MP2 optimized geometries using the NBO subroutine implemented in the Gaussian-98 program package.¹⁷ All the calculations were done using the Gaussian-98 suite of programs.¹⁸ The optimized geometries, the molecular orbitals and the nature of the normal modes of the harmonic frequencies were examined using the MOPLLOT program.¹⁹

3. Results and discussion

In this section, the equilibrium geometries and their salient features regarding the planarity and bond delocalization are given first. This is followed by a discussion on the thermodynamic stabilities based on the homodesmotic equations (5)–(8). Next, the computed relative stabilities of the various positional isomers are given followed by a critical analysis of various factors, which control the relative stability orderings. Finally, the singlet–triplet energy differences, the chemical hardness, the out-of-plane distortive

tendencies as well as the origin for the delocalization in benzenoids are given. Previous studies indicate dramatic differences in the bonding and structural patterns between the compounds containing the second and the third or fourth row substituents.²⁰

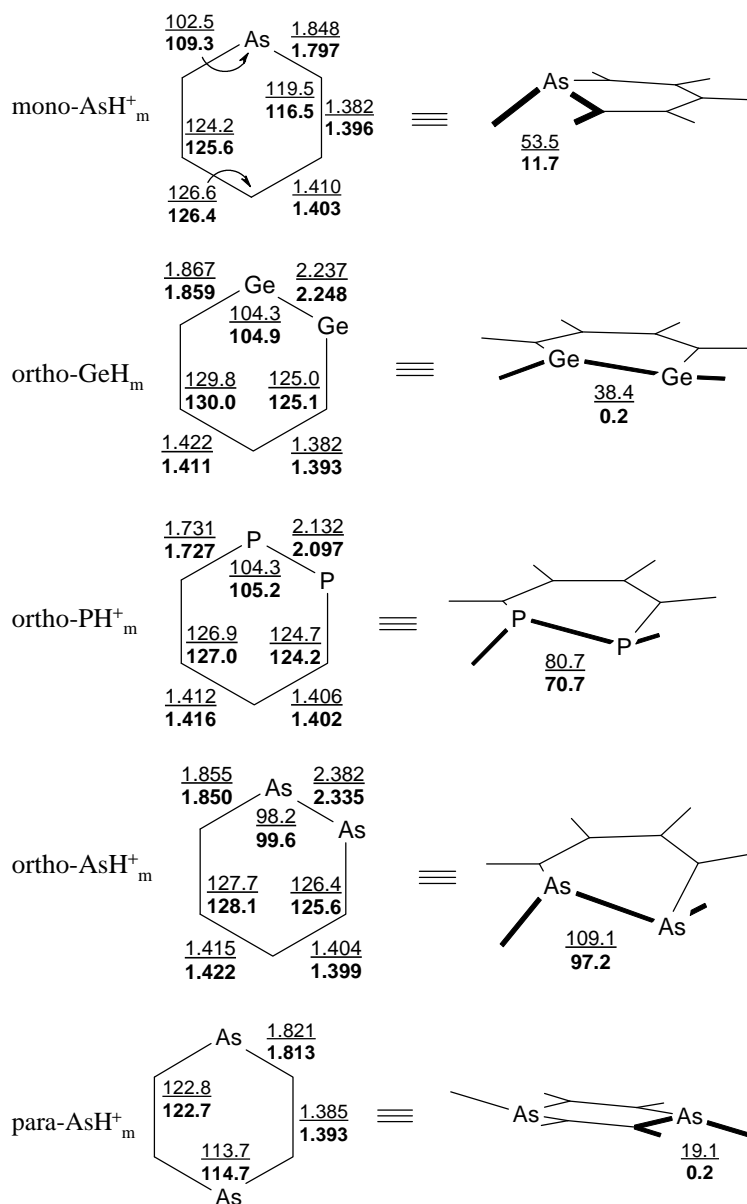


Figure 1. Principal geometric parameters of the puckered minimum energy structures obtained at the B3LYP/6-31G* (underlined) and MP2/6-31G** (bold) levels. Only the non-planar structures are shown here. Bond lengths are given in Å and dihedral angles are given in degrees.

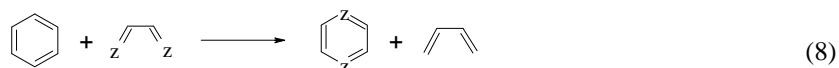
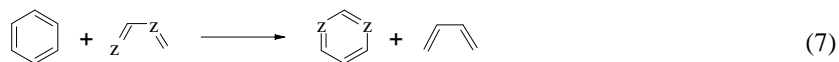
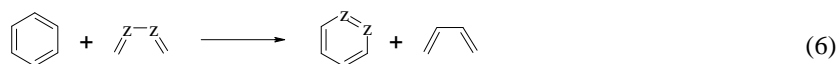
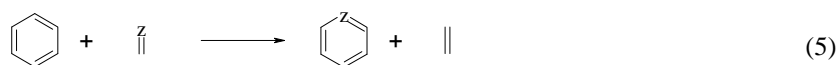
3.1 Equilibrium geometries

The geometries obtained at the B3LYP and the MP2 levels are very similar in most of the cases. Inclusion of diffuse functions seems to be essential for the geometries of the anionic and dianionic systems. Examination of the geometric parameters of the skeletally substituted benzenes indicates that the strain imparted due to the interspersion of heteroatoms of diversified size and electronegativity is reflected only on the bond angles and the bond lengths are hardly affected. The C–C bond lengths are similar to the aromatic bond lengths, while those of C–X and X–X are in-between the corresponding standard single- and double-bond lengths. Hence, according to the criterion of bond length equalization, skeletally substituted benzenes are expected to be aromatic.

Frequency calculations were done to ascertain whether the planar structures are minima or not on the potential energy surface. B3LYP/6-31G* level designates all except mono-AsH⁺, ortho-PH⁺, ortho-GeH, ortho-AsH⁺ and para-AsH⁺ as minima on their respective potential energy hypersurfaces. The normal mode of the imaginary frequency corresponds to the out-of-plane distortion of the hydrogen atom connected to the heteroatoms, which is then followed to obtain the minima (figure 1). However, the HF/6-31G* method designates mono-AsH⁺, ortho-GeH and para-AsH⁺ as minima. Reoptimizing the puckered structure of mono-AsH⁺ at the MP2/6-31G** level reduces the pyramidalization at the As centre, which is reflected on the energy difference between the planar and the puckered structures. The energy difference of 7.4 kJ/mol obtained at the B3LYP level reduces to 0.02 kJ/mol at the MP2 level. Optimizing the non-planar structures, ortho-GeH_m and para-As_m⁺ collapsed to virtually planar structures indicating that these two planar forms are very likely to be minima at the MP2 level. The energy difference between the planar transition states and the corresponding puckered minima obtained at the B3LYP level are 18.0 (ortho-PH⁺), 0.3 (ortho-GeH), 57.8 (ortho-AsH⁺) and 0.6 kJ/mol (para-AsH⁺). The energy difference between the planar and the non-planar structures obtained for ortho-PH⁺ and ortho-AsH⁺ at the MP2 level are 16.3 and 37.0 kJ/mol respectively. The optimized geometries of all the mono- and di-skeletally substituted benzenes indicate fully delocalized nature.

3.2 Thermodynamic stabilities

Homodesmotic equations are constructed to assess the thermodynamic stabilities of the skeletally substituted benzenes considered in this study (scheme 3). The reaction energies



Z = X or Y

Scheme 3.

corresponding to (5), (6), (7) and (8) obtained using the best estimates of the energetics in (1)–(4) are given in table 1. When charged compounds are involved in the homodesmotic equation, the stability of the skeletally substituted benzene is overestimated. In general, mono-Z are more stable than the corresponding disubstituted benzenes, except when $Z = \text{As}, \text{NH}^+, \text{SiH}$ and GeH . All para-Z isomers are unstable except for para- C^- . However, most of the compounds considered are more stable than those which are experimentally known such as, mono-N, ortho-/para-/meta-N, ortho-/meta-/para- C^- , mono-P, meta-/para-P, mono-SiH, etc. Thus, from the thermodynamic point of view, these skeletal substitutions do not seem to bring in high instability and so may very well be synthetically viable.

3.3 Relative energies

The best estimates of the relative energies of the skeletally disubstituted benzenes calculated using (1)–(4) are given in table 2. The relative energy orderings obtained at the MP2, B3LYP and CCSD(T) levels are quite similar in most of the cases. The best estimates calculated using the above scheme were shown to be in excellent agreement with the relative energies obtained using the G2 level calculations for the valence isomers of benzene.^{7,10,21} Also, in a recent study on the silabenzene, reported by Martin, Baldrige and others⁵ the computed relative energies of the disilabenzene at the CCSD(T)/cc-pVTZ level is in good agreement with our results. The correlation of the best estimates of the relative energies involving the various substituents is provided in figure 2. In all the cases, the ortho-isomers are the least stable ones when the substituent

Table 1. The reaction energies, of the homodesmotic (5) for the monosubstituted benzenes, $(\text{CH})_5\text{ZH}$ and (6), (7) and (8) for the disubstituted benzenes, $(\text{CH})_4(\text{ZH})_2$ (scheme 3) obtained using the best estimates of total energies. All values in kJ mol^{-1} .

Z	ΔE			
	mono- Z^a	ortho- Z^b	meta- Z^c	para- Z^d
C^-	-38.7	69.1	-6.9	-3.8
N	17.4	47.3	26.5	49.0
O^+	-63.3	31.2	-0.7	70.1
Si^-	-25.1	9.7	8.9	44.5
P	1.5	2.7	10.7	27.1
S^+	-83.4	-28.9	-27.6	10.7
Ge^-	-57.4	-47.0	-8.9	55.5
As	1.8	-12.3	16.8	43.5
Se^+	-74.7	-33.2	-14.2	29.5
BH^-	-46.7	9.2	0.3	17.3
NH^+	-38.4	-40.7	-19.7	40.9
AlH^-	-46.3	40.6	59.0	114.4
SiH	16.2	17.4	13.2	27.4
PH^+	-46.7	-20.7	-16.9	20.6
GaH^-	14.4	21.9	63.3	103.0
GeH	24.1	8.2	18.6	45.5
AsH^+	-33.0	-22.0	-2.7	43.8

Obtained using ^a(5), ^b(6), ^c(7) and ^d(8)

Table 2. The best estimates of the relative energies of the skeletally disubstituted benzenes. All values in kJ/mol.

Structure	Best estimate ^a	Structure	Best estimate ^b
ortho-C ⁻	0.0	ortho-BH ⁻	0.0
meta-C ⁻	-65.2	meta-BH ⁻	-67.6
para-C ⁻	-82.7	para-BH ⁻	-56.1
ortho-N	0.0	ortho-NH ⁺	0.0
meta-N	-91.3	meta-NH ⁺	-128.6
para-N	-73.5	para-NH ⁺	-114.6
ortho-O ⁺	0.0	ortho-AIH ⁻	0.0
meta-O ⁺	-260.3	meta-AIH ⁻	-2.4
para-O ⁺	-189.3	para-AIH ⁻	61.6
ortho-Si ⁻	0.0	ortho-SiH	0.0
meta-Si ⁻	-11.4	meta-SiH	-19.3
para-Si ⁻	8.4	para-SiH	28.5
ortho-P	0.0	ortho-PH ⁺	0.0
meta-P	20.7	ortho-PH ⁺ _m	-15.8
para-P	27.6	meta-PH ⁺	-44.2
ortho-S ⁺	0.0	para-PH ⁺	-46.7
meta-S ⁺	-23.5	ortho-GaH ⁻	0.0
para-S ⁺	-23.1	meta-GaH ⁻	63.6
ortho-Ge ⁻	0.0	para-GaH ⁻	107.3
meta-Ge ⁻	44.6	ortho-GeH	0.0
para-Ge ⁻	61.7	meta-GeH	54.4
ortho-As	0.0	para-GeH	92.4
meta-As	85.8	ortho-AsH ⁺	0.0
para-As	93.0	ortho-AsH ⁺ _m	-37.4
ortho-Se ⁺	0.0	meta-AsH ⁺	23.4
meta-Se ⁺	58.1	para-AsH ⁺	16.0
para-Se ⁺	55.7		

^aCalculated using (1) for cationic and neutral systems, and (2) for anionic systems;^bCalculated using (3) for cationic and neutral systems, and (4) for anionic systems

is from the second row. However, if the substituent belongs to the fourth row, the ortho-isomer is the most stable one. Straightforward correlations cannot be made to explain the observed trends; some qualitative arguments however are used in the following sections to explain the relative stability orderings.

3.4 Factors controlling the relative stabilities

3.4a Repulsion between lone pairs: Repulsion between the two lone pairs on the heteroatomic centres in the X type substituted benzenes is of significant importance in estimating the stability of the ortho-isomers with respect to the other two isomers. In meta- and para-isomers, *lp-lp* repulsion is not significant since the two heteroatomic centres are separated by one- and two-methine groups respectively. Figure 3 depicts the correlation of the molecular orbital energies of the two lone pair combinations and the three *p*-orbitals of ortho-X obtained at the HF/6-31G* level. A value of 12 eV has been deducted from the anionic systems and the same magnitude is added to the cationic systems, to fit a similar scale. This is done after systematically monitoring the shift in orbitals upon adding and removing two electrons from their corresponding neutral

counterparts. The bonding and the anti-bonding combinations of the lone pairs are designated by lp and lp^* respectively. When the substituent is from the second row ($X = C^-, N$ or O^+), lp lies much below lp^* . For the third and fourth row substituents ($X = Si^-, P, S^+, Ge^-, As$ or Se^+), not only the $lp-lp^*$ gap reduces but also the lp^* lies lower compared to lp in all the cases. This indicates that the lone pair-lone pair repulsion does not play a vital role in deciding the stability of the skeletally di-substituted benzenes when the substituent is from the third or fourth row. However, the significant lone pair-lone pair repulsion accounts for the instability of the ortho-isomer compared to the meta-/para-isomers with second row substituents.

3.4b Cumulative bond strengths: The sum of the bond strengths in the twin Kekule forms proves to be a useful measure to explain the relative stability of the ortho-isomers with respect to the corresponding meta- and the para-isomers.⁷ The number and types of bonds present in the twin Kekule forms of the ortho-isomers are different from that in the meta- and para-isomers. However, meta- and para-isomers having the same types and number of single and double bonds in both the Kekule forms have the same values for the sum of bond strengths and hence could not be compared. Reaction energies corresponding to (9b) and (10b) essentially compare the cumulative bond strengths in the twin Kekule forms of the ortho-isomer with respect to the meta-/para-isomers (scheme 4). In other words, the reaction energies give the relative of the bond strengths in the twin Kekule forms of the meta-/para-isomers with respect to those of the ortho-isomers.

Table 3 depicts the reaction energies corresponding to (9b) and (10b) calculated at the CCSD(T)/6-31G*//MP2/6-31G** level. A positive value of the reaction energy indicates the preference for the ortho-isomers and a negative value denotes the preference for meta-/para-isomers. In all the cases, where dianionic or dicationic species are involved, the meta-/para-isomers are favoured due to electrostatic repulsion between the heteroatomic centres in the ortho-isomers. However, the increase in ΔE values while going from the second to the fourth row substituents indicates that ortho-isomer is more preferred when $Z = Ge^-, As, Se, GaH^-, GeH$ and AsH^+ . The higher negative value for the second row substituents explains the stability of meta-/para-isomers over the ortho-

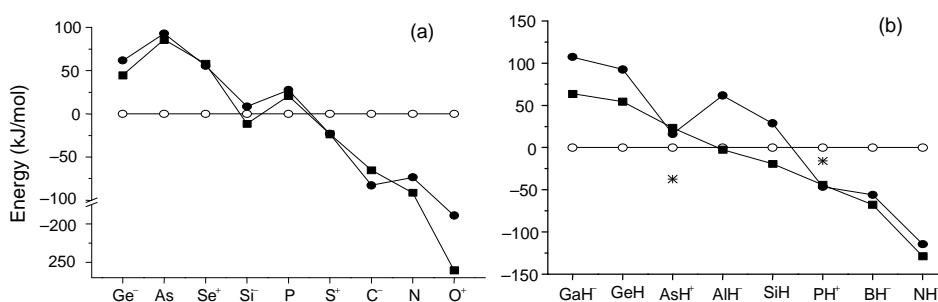


Figure 2. The correlation of the best estimates of relative energies of the skeletally disubstituted benzenes, (a) $(CH_4)_X_2$ and (b) $(CH_4)_Y_2$, obtained using (1)–(4). The energies of the ortho-, meta- and para-isomers are represented by ○, ■ and ● respectively. The energies of the non-planar ortho-isomers are represented by the ‘*’ symbol.

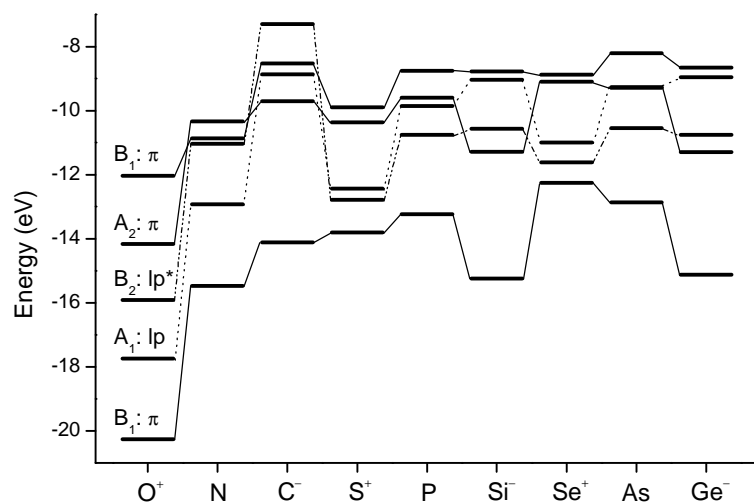
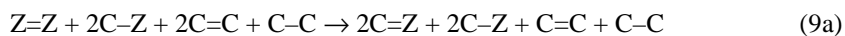
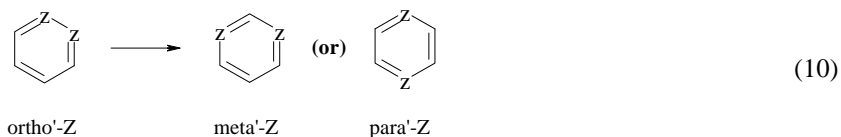
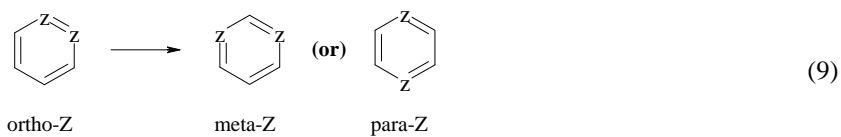


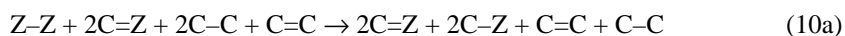
Figure 3. The correlation of the orbital energies of ortho-X. An amount of 12 eV is added to the dicationic orbital energy values and similar magnitude is deduced for the dianionic systems to fit to the scale. All *p* orbitals (A_2 and B_1) are connected with solid lines, *lp-lp* bonding combinations (A_1) are connected with dotted lines, and dot-dot-dashed lines connect *lp-lp* antibonding combination (B_2).



Equation (9a) on simplification reduces to the following,



Similarly, equation (9a) reduces to



Scheme 4.

isomers. The instability of ortho-N and the stability of ortho-P and ortho-As over their corresponding meta- and para-counterparts are reflected in the negative values of ΔE when $X = N$ and in the positive values when $X = P$ and As. Similarly, the stability of ortho-Ge can be explained based on the ΔE values. The sum of the bond strengths in the twin Kekule forms indicate that there is gradual preference for the ortho-isomer to be more stable when we move from the second to the fourth row substituents. Thus, the sum of the bond strengths seems to play a crucial role in deciding the relative stability orderings of the skeletally di-substituted benzenes.

3.4c Topological charge stabilization: Gimarc's rule of topological charge stabilization (TCS) states that, 'Nature prefers to place atoms of greater electronegativity in those positions where the topology of the structure tends to pile up extra charge'.²² Similarly, the less electronegative elements would prefer to replace those centres with less electron density. The rule of TCS has been demonstrated as a valuable tool in explaining the stability of the positional isomers.²³ An attempt is made to explain the relative stabilities of the skeletally disubstituted isomers based on the charges obtained in the monosubstituted benzenes.

Figures 4a and b depict the natural group charges obtained using the HF/6-31G* calculations on the MP2 geometries. Table 4 compares the computed relative energy ordering with the TCS predicted ones. The rule of topological charge stabilization excellently reproduces the computed stability ordering for the second row substituents, though it fails to explain the stability of the ortho-isomer for the fourth row substituents. The stability ordering between the meta- and para-isomers is however predicted correctly in most of the cases.

3.5 Origin of delocalization

It is known that the benzene skeleton, when present in a molecule without a C_6 axis, such as naphthalene, triphenylene, buckminsterfullerene, buckyballs, triannulated benzenes etc. exhibits significant localization.²⁴ The skeletally substituted benzenes considered in the study with a wide ranging substituents of different electronegativities and sizes involving cationic and anionic systems are expected to show considerable localization. In

Table 3. Reaction energies corresponding to (9b) and (10b) to compare the cumulative bond strengths between the ortho- and meta-/para-isomers, obtained at CCSD(T)/6-31G**//MP2/6-31G** level. All values in kJ mol^{-1} .

X	ΔE^a	ΔE^b	Y	ΔE^a	ΔE^b
C^-	-694.1	-620.4	BH^-	-658.5	-568.1
Si^-	-347.7	-364.4	AlH^-	-262.2	-359.2
Ge^-	-250.8	-296.2	GaH^-	-196.2	-298.9
N	-98.0	-54.9	SiH	67.3	-20.8
P	42.0	19.0	GeH	148.0	33.3
As	137.5	77.2	NH^+	-1015.4	-787.9
O^+	-1680.9	-1112.2	PH^+	-598.1	-606.8
S^+	-828.9	-692.7	AsH^+	-468.3	-519.5
Se^+	-606.8	-564.4	-	-	-

Obtained using ^a(9b), ^b(10b)

contrast, they are found to be delocalized in terms of bond length equalization, despite the strain imparted by the varying substituents. Shaik and co-workers^{6,25} have proved that the **p**-electrons in benzene have a distortive propensity avoiding delocalization using the Kekule crossing model (scheme 5). This is due to the large vertical gap between the twin Kekule forms. The **s**-framework is symmetrizing and is responsible for the complete delocalization in benzene. The singlet–triplet gaps of all the skeletally substituted benzenes are found to be lower than that of benzene (*vide infra*) indicating that their **p**-frameworks are weakened upon skeletal substitution. Hence, all the skeletally substituted benzenes have lower vertical gaps between the twin Kekule forms. *The smaller vertical gaps indicate lower distortive propensity of the p-electron component compared to benzene, which effectively conveys that the weaker p-frameworks have less distortive propensity and have higher tendency towards delocalization.* Hence, delocalization as an indicative for stability and aromaticity of benzenoid systems should be viewed critically.

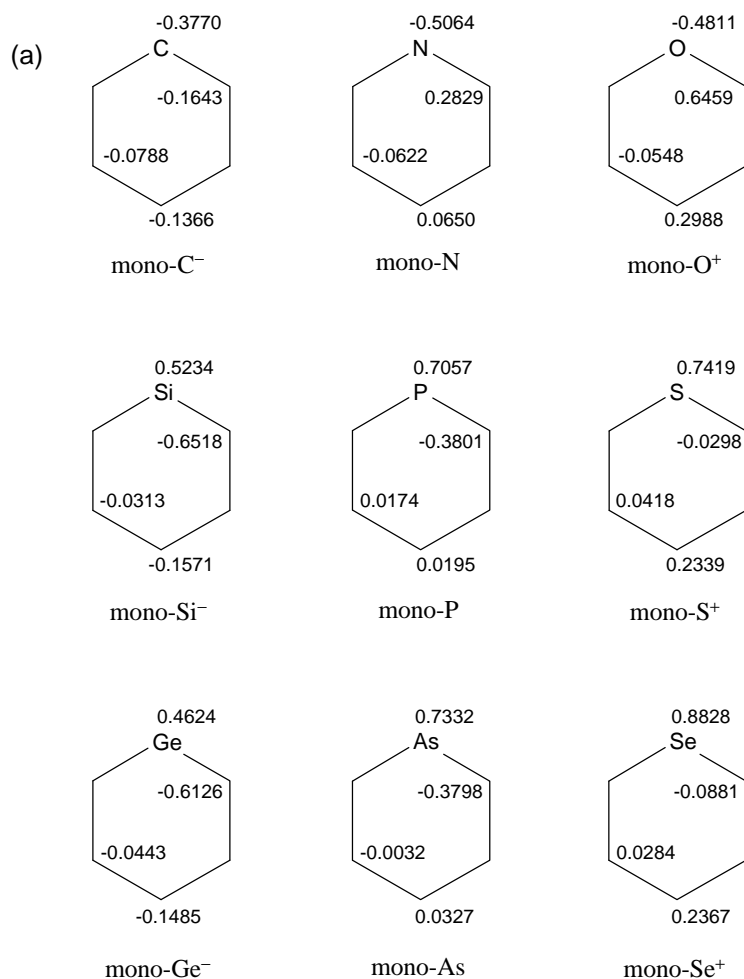


Figure 4. (a) (Caption on facing page.)

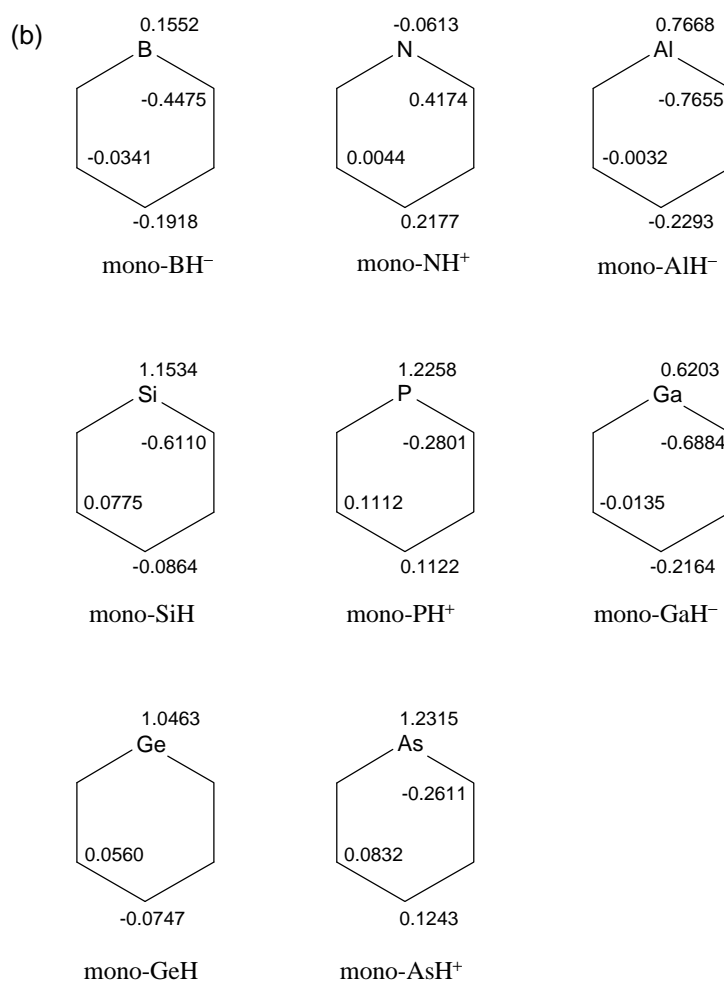


Figure 4. Natural group charges in the monosubstituted benzenes, (CH)₅X (a) and (CH)₅Y (b) obtained at the HF/6-31G**//MP2/6-31G** level.

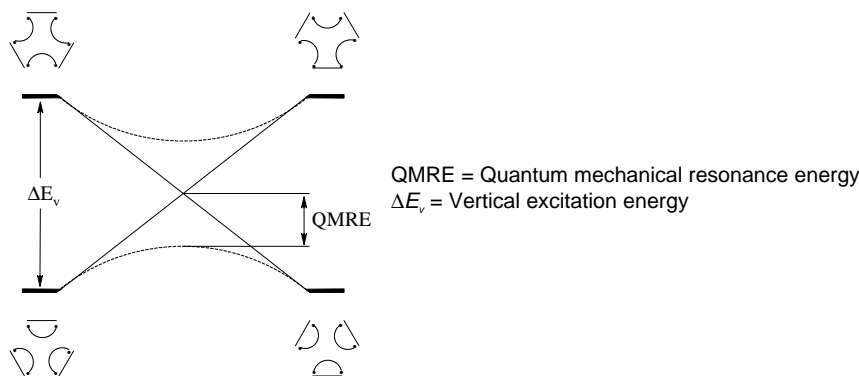
3.6 Singlet–triplet energy differences (ΔE_{s-t}) and chemical hardness (h)

The absolute chemical hardness, the HOMO-LUMO energy gap and the relative chemical hardness values have been proven to be indicators of aromaticity in cyclic conjugated systems. Chemical hardness (h) is defined as half the HOMO-LUMO energy gap within Koopman's approximation.²⁶ Hiberty *et al* have used the singlet–triplet energy difference to explain the reactivity of para-P with respect to the other two positional isomers.²⁷ Figures 5 and 6 depict the correlation of ΔE_{s-t} and h values for the various substituents. The stability ordering predicted by ΔE_{s-t} and h values are very similar in most of the cases. There seems to be linear relationship between ΔE_{s-t} and h values (figure 7). Comparison of the singlet–triplet gaps and the hardness values of the skeletally substituted benzenes with those of benzene, indicates that skeletal substitution in benzene

Table 4. The computed stability ordering of the skeletally disubstituted benzenes and the predicted stability ordering based on the natural group charges obtained at HF/6-31G**//MP2/6-31G** level using the rule of TCS.^a

Substituent	Expected stability ordering ^b	Observed stability ordering ^b
N	$m > p > o$	$m > p > o$
O ⁺	$m > p > o$	$m > p > o$
Si ⁻	$m > p > o$	$m > o > p$
P	$p \approx m > o$	$o > m \approx p$
S ⁺	$p > m > o$	$p \approx m > o$
Ge ⁻	$m > p > o$	$o > m > p$
As	$p > m > o$	$o > m \approx p$
BH ⁻	$m > p > o$	$m > p > o$
NH ⁺	$m > p > o$	$m > p > o$
AlH ⁻	$m > p > o$	$m \approx o > p$
SiH	$m > p > o$	$m > o > p$
PH ⁺	$p \approx m > o$	$p \approx m > o$
GaH ⁻	$m > p > o$	$o > m > p$
GeH	$m > p > o$	$o > m > p$
AsH ⁺	$p > m > o$	$o > p > m$

^aSubstituents, C⁻ and Se⁺ are not included as they have the same electronegativities;
^b*o*, *m* and *p* correspond to ortho-, meta- and para-skeletally disubstituted isomers respectively



Scheme 5.

leads to destabilization or decrease in aromaticity. In general, the mono-Z are less stable than benzene and the skeletally disubstituted benzenes are less stable than mono-Z. Among the di-substituted isomers, the stability ordering is found to be meta-Z > ortho-Z > para-Z, a trend that is observed in most of the cases. This points to the fact that the thermodynamically most stable compounds need not be the least reactive.

3.7 Out-of-plane distortivity

One of the geometric criteria of aromaticity, which has been used as an aromaticity index, is the harmonic force constants corresponding to the out-of-plane distortive modes.²⁸ This provides an idea of how rigid these molecules are towards puckering and thus the

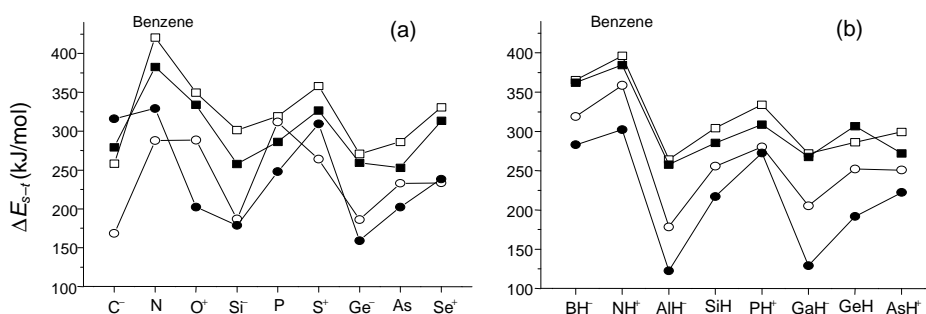


Figure 5. The correlation of singlet-triplet energy differences of the skeletally substituted benzenes, (a) $(CH)_4X_2$ and (b) $(CH)_4Y_2$, obtained at the B3LYP/6-31G* level. Skeletally monosubstituted benzenes are represented by \square . The singlet-triplet energy differences of ortho-, meta- and para-isomers are given by \circ , \blacksquare and \bullet respectively. The singlet-triplet energy difference in benzene obtained at the same level is given for comparison.

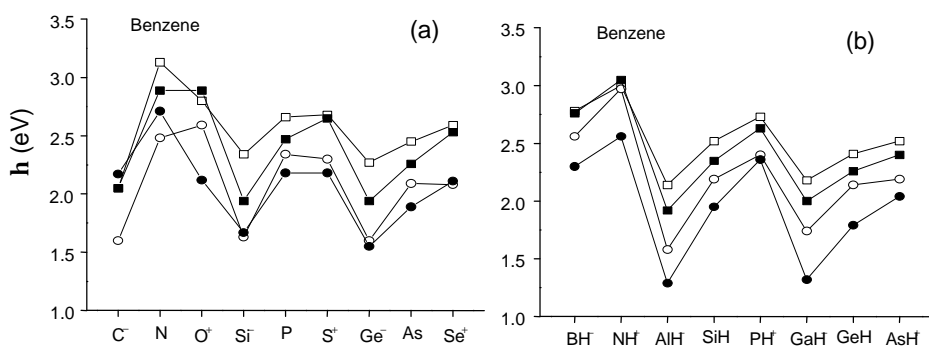


Figure 6. The correlation of chemical hardness of the skeletally substituted benzenes, (a) $(CH)_4X_2$ and (b) $(CH)_4Y_2$, obtained at the B3LYP/6-31G* level. Skeletally monosubstituted benzenes are represented by \square . The chemical hardness values of ortho-, meta- and para-isomers are given by \circ , \blacksquare and \bullet respectively. The hardness value of benzene obtained at the same level is given for comparison.

frequencies corresponding to the out-of-plane distortive modes can be used to assess the reactivity and aromaticity of **6p**-systems. Comparison of the first few B3LYP/6-31G* harmonic frequencies corresponding to the out-of-plane distortive modes indicates that distortive tendency increases on skeletal substitution, especially when the substituent is from the third/fourth row. Distortive tendency measured as the magnitude of the harmonic frequencies corresponding to out-of-plane distortivity predicts similar trends as done by chemical hardness values and singlet-triplet energy differences.

4. Conclusions

This study provides a detailed theoretical report on the skeletally mono- and di-substituted benzenes. Various measures of aromaticity, such as bond length equalization,

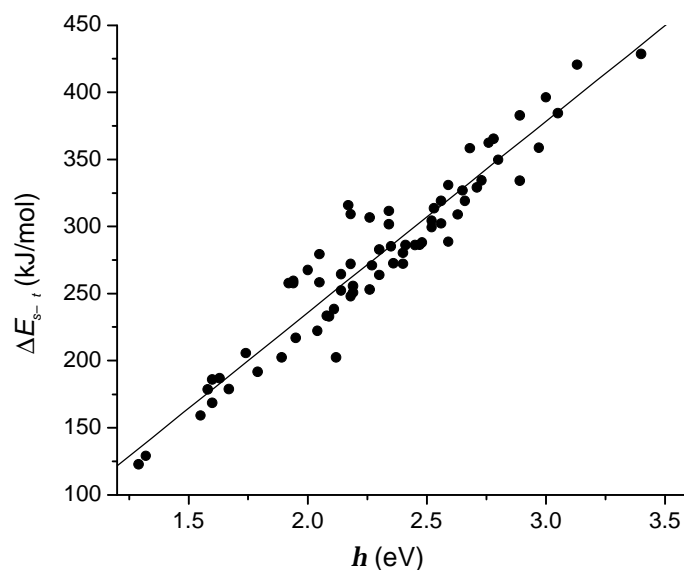


Figure 7. The plot of the singlet–triplet energy difference against the chemical hardness values of benzene, and all the skeletally mono- and di-substituted isomers considered in the present study. The solid line represents the linear relationship between them.

the homodesmic equations, chemical hardness, singlet–triplet energy differences, out-of-plane distortivity are analysed. Bond length equalization suggests that all the molecules are aromatic. According to the energy criteria (homodesmic equations), most compounds are as aromatic as benzene is. Singlet–triplet energy differences, chemical hardness and out-of-plane distortivities predict similar trends in aromaticity. The reactivity measures such as singlet–triplet gap, hardness and out-of-plane distortivity indicate that the thermodynamically least stable molecule need not be the most reactive. All the skeletally substituted benzenes show bond delocalization in terms of bond length equalization. The thermodynamic stability of this class of compounds as assessed by the homodesmic equations, indicate that many of these molecules are more stable than those that are experimentally observed. The relative stability of the skeletally disubstituted benzenes are controlled by various factors; the sum of bond strengths in conjunction with the rule of topological charge stabilization seems to account for the observed relative energy trends. Weaker *p*-frameworks have a higher propensity towards bond delocalization, which is in line with Shaik’s Kekule crossing model. Straightforward correlations among delocalization, thermodynamic stability and reactivities are not possible. On skeletal substitution, the propensity for ring puckering becomes more particularly for the third and fourth row substituents.

Our studies expose the limitations and strengths of: (a) Homodesmic equations, (b) geometric criterion, (c) magnetic criterion, (d) ring currents, (e) singlet–triplet gaps, (f) chemical hardness, as descriptors to evaluate ‘aromaticity’. Qualitative concepts, such as (a) the sum of bond strengths, (b) Gimarc’s rule of TCS, (c) orbital and charge effects, were thoroughly scrutinized to ascertain the relative stability orderings in skeletally

substituted benzenes. These studies warrant reorientation in our understanding of 'aromaticity', in general and 'heteroaromaticity' in particular.

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