A Theoretical Study of the Structures, Energetics, Stabilities, Reactivities, and Out-of-Plane Distortive Tendencies of Skeletally Substituted Benzenes $(CH)_5XH$ and $(CH)_4(XH)_2$ ($X = B^-$, N^+, Al^-, Si, P^+, Ga^-, Ge, and As^+)

U. Deva Priyakumar and G. Narahari Sastry*

Department of Chemistry, Pondicherry University, Pondicherry - 605 014, India

gnsastry@yahoo.com

Received October 4, 2001

Ab initio molecular orbital theory at Hartree−Fock (HF), post-Hartree−Fock (MP2 and CCSD(T)), and the hybrid density functional theory (B3LYP) calculations were done on the mono-$(CH)_5XH$ and diskeletally substituted $(CH)_4(XH)_2$ benzenes ($X = B^-$, N^+, Al^-, Si, P^+, Ga^-, Ge, and As^+). The computed relative energies of the disubstituted isomers show interesting trends. While the *ortho*-isomer is the most stable for $X = Ga^-$, Ge, and As^+, *meta* was found to be the most stable for $X = B^-$, N^+, Al^- and Si, and *para* was found to be the most stable for $X = P^+$. Various intricate factors that govern the relative stabilities, such as the sum of bond strengths in the twin Kekule forms, rule of topological charge stabilization (TCS), and electrostatic repulsion were critically examined. The sum of bond strengths in the twin Kekule forms was proved to be quite a successful measure in predicting the relative stability orders between *ortho*- and *meta*-/*para*-isomers. The rule of TCS breaks down especially in the presence of overwhelming factors such as the differences in the cumulative bond strengths of the two positional isomers; however, the stability ordering between the *para*- and *meta*-isomers is successfully predicted in most cases. The tendency for ring puckering increases a great deal especially when the substituents are from 3rd or 4th row. Extension of the popular inverse relationship between the thermodynamic stability and reactivity was found to be inapplicable for this class of compounds. The computed singlet−triplet energy differences and the chemical hardness (η) values indicate that the skeletal substitution weakens the π-strength of the benzenoid system and increases their reactivity.

1. Introduction

The properties exhibited by some of the 6π electronic six- and five-membered ring compounds containing one or more heteroatoms and their resemblance to benzene are central to the development of the concept of aromaticity.[1−3] Molecules with double bonds between carbon and higher row heavy atoms, once thought to be impossible, have flourished in the last 20 years and witnessed meaningful interplay between ingenious experimental techniques and quantitative theoretical calculations.[4−6] It is to be noted that the definition of 'aromaticity' always had its ambiguities and more so in the case of molecules containing one or more third or fourth row atoms. Although, a variety of magnetic criteria such as magnetic susceptibility exaltation and NICS have been very useful tools to measure aromaticity,[7] the limitations of these were exposed when applied to silabenzenes in a recent study.[8] Therefore, assessing the effect of perturbations induced by replacement of one or more ring carbon atoms by main group elements is a challenging task.[9−11] There exist primarily two classes of isolobal fragments (X and Y, Scheme 1), which can replace the methine unit in the benzene skeleton without disrupting the number of π-electrons. The obvious replacement (type X) is that 'C' is replaced by a heteroatom bearing equal number of

(1) (a) Minkin, V.; Simkin, B.; Glukhotsev, M. *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994. (b) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986. (c) Bergmann, E. D.; Pullman, B., Eds. *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity;* Jerusalem Symposium on Quantitative Chemistry and Biochemistry; Israel Academy of Science and Humanities: Jerusalem, 1971; Vol. III. (d) Badger, G. M.; *Aromatic Character and Aromaticity*; University Press: Cambridge, 1969. (e) Katritzky, A. R.; Karelson, M.; Malhotra, N. *Heterocycles* **1991**, *32*, 127. (f) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Hafelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783.

(2) (a) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem. Rev.* **2001**, *101*, 1501. (b) Jug, K.; Hiberty, P. C.; Shaik, S. *Chem. Rev.* **2001**, *101*, 1477. (c) Shurki, A.; Shaik, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2205. (d) Hiberty, P. C.; Danovich, D.; Shurki, A.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 7760. (e) Shaik. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (f) Baird, N. C. *J. Org. Chem.* **1986**, *51*, 3907. (g) Hiberty, P. C.; Shaik, S.; Ohanessian, G.; Lefour, J.-M. *J. Org. Chem.* **1986**, *51*, 3908. (h) Glendening, E. D.; Faust, R.; Streitwieser, A.; Volhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, *115*, 10952.

(3) (a) Yu, Z.-H.; Xuan, Z.-Q.; Wang, T.-X.; Yu, H.-M. *J. Phys. Chem. A* **2000**, *104*, 1736. (b) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048.

(4) Markl, G. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds., Thieme: Stuttgart, Germany, 1990; p 220.

(5) (a) Escudie, J.; Ranaivonjatovo, H.; Rigon, L. *Chem. Rev.* **2000**, *100*, 3639. (b) Tokitoh, N. *Pure Appl. Chem.* **1999**, *71*, 495.

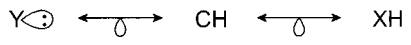
(6) (a) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (b) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217. (c) Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105. (d) Nyulaszi, L.; Veszpremi, T.; Reffy, J. *J. Phys. Chem.* **1993**, *97*, 4011. (e) Nyulaszi, L.; Veszpremi, T. *J. Phys. Chem.* **1996**, *100*, 6456.

(7) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2638.

(8) Baldridge, K. K.; Uzan, O.; Martin, J. M. L. *Organometallics* **2000**, *19*, 1477.

10.1021/jo0161781 CCC: $22.00
Published on Web 12/12/2001

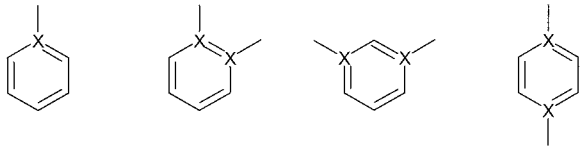
Scheme 1



Y = N, P, As, C^-, Si^-, Ge^-, B^{2-}, Al^{2-}, Ga^{2-}, O^+, S^+, Se^+

X = Si, Ge, N^+, P^+, As^+, B^-, Al^-, Ga^-

Scheme 2



mono-X ***ortho*-X** ***meta*-X** ***para*-X**

X = B^-, N^+, Al^-, Si, P^+, Ga^-, Ge, As^+

valence electrons such as, Si, Ge, N^+, P^+, B^-, Al^-, etc. (Scheme 2).

Shaik, Hiberty, and co-workers have convincingly demonstrated that π-electrons in polycyclic aromatic hydrocarbons exhibit the propensity to distort from the delocalized form in general and benzene in particular.[2,3] The recent experimental demonstration of exaltation of b_{2u} frequency in the first excited state of benzene by Haas and Zilberg provided with the missing experimental proof of π-distortive tendency and effectively lead to a consensus.[12] This twist to our traditional understanding of aromaticity warrants a revised and systematic studies of $(4n+2)\pi$ systems and systematic computational studies are of significant importance in probing the structures, bonding, and reactivity aspects.

The chemistry of group V heterobenzenes, as well as C^-, O^+, and S^+ substituted benzenes is well developed.[4,9,13−15] Heteroaromatics, whose presence is ubiquitous in biologically active molecules, also have potential application in material science.[16] Boratabenzene (**mono-B^-**), pyridinium (**mono-N^+**), and phosphinium (**mono-P^+**) ions are well-known.[4,17,18] In case of B^- substitution, the di-, tri-, and tetra-substituted isomers are also known as Li^+ salts and mainly as ligands in quite a few transition metal sandwich compounds.[18] In contrast, despite the considerable interest in sila- and germabenzenes, the generation of these species encountered enormous difficulty and the synthesis of a derivative of silabenzene is achieved only recently.[19] The recent observation of the alkali salts of the dianionic $(CH)_4C_2^{2-}$ should be inspiring for the generation of the polyanionic benzenoid frameworks.[20] The clusters involving C, Si, Al, and P make the study of these compounds interesting building bridges between heteroaromatics and main group inorganic chemistry.[21,22] The heavy atom analogues of the allyl systems, $CH_2-CH-XH_2^+$ (X = Si, Ge, Sn and Pb) are stabilized by significant π-conjugative interaction and have planar equilibrium geometries.[23] However, experimental knowledge concerning this is limited due to the elusive nature of such compounds. Traditionally, the stability associated with the benzenoid framework is assumed to lie in the extent of delocalization prevalent in the system and its resistance to ring puckering.[1] Previous calculations indicate that the planar structures should distinctly be more stable than other isomers, for mono-, di-, and trisubstituted benzenes.[9] Thus for the given structural formulas, we assume the planar isomers to be the most important.

We have undertaken a thorough study on how the skeletal substitutions perturb the benzenoid framework $(CH)_n(XH)_{6-n}$, when X is isoelectronic to 'C'. The present study is restricted to skeletally mono- and disubstituted benzenes. The previous results indicate that further substitution leads to a situation where the benzenoid framework need not represent the global minima on the potential energy surface and the nonplanar structures become energetically competitive.[24]

The following questions are addressed in this study: (a) How does mono- and disubstitution affect delocalization? (b) How the thermodynamic and kinetic stabilities are affected upon skeletal substitution? (c) What factors

(9) (a) Priyakumar, U. D.; Sastry, G. N. *J. Am. Chem. Soc.* **2000**, *122*, 11173. (b) Colombet, L.; Volatron, F.; Maitre. P.; Hiberty, P. C. *J. Am. Chem. Soc.* **1999**, *121*, 4215. (c) Priyakumar, U. D.; Dinadayalane, T. C.; Sastry, G. N. *Chem. Phys. Lett.* **2001**, *336*, 343. (d) Priyakumar, U. D.; Dinadayalane, T. C.; Sastry, G. N. *Chem. Phys. Lett.* **2001**, *337*, 361. (e) Priyakumar, U. D.; Dinadayalane, T. C.; Sastry, G. N. *New J. Chem.* **2002**, in press. (f) Hoffmann, M.; Schleyer, P. v. R.; Regitz, M. *Eur. J. Org. Chem.* **1999**, 3291.

(10) (a) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204. (b) Baldridge, K. K.; Gordon, M. S. *J. Organomet. Chem.* **1984**, *271*, 369. (c) Chandrasekhar, J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *289*, 51. (d) Chandrasekhar, J.; Schleyer, P. v. R.; Baumgartner, R. O. W.; Reetz, M. T. *J. Org. Chem.* **1983**, *48*, 3453. (e) Blustin, P. H. *J. Organomet. Chem.* **1979**, *166*, 21. (f) Schlegel, H. B.; Coleman, B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6499. (g) Dewar, M. J. S.; Holder, A. J. *Heterocycles* **1989**, *28*, 1135.

(11) (a) Fink, W. H.; Richards, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 3393. (b) Matsunaga, N.; Cundari, T. R.; Schmidt, M. W.; Gordon, M. S. *Theor. Chim. Acta* **1992**, *83*, 57. (c) Chiavarino, B.; Crestoni, M. E.; Marzio, A. D.; Fornarini, S.; Rosi, M. *J. Am. Chem. Soc.* **1999**, *121*, 11204. (d) Jemmis, E. D.; Kiran, B. *Inorg. Chem.* **1998**, *37*, 2110. (e) Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 144.

(12) (a) Hass, Y.; Zilberg, S. *J. Am. Chem. Soc.* **1995**, *117*, 5387. (b) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *J. Am. Chem. Soc.* **1996**, *118*, 666.

(13) (a) Nyualaszi, L.; Szieberth, D.; Veszpremi, T. *J. Org. Chem.* **1995**, *60*, 1647. (b) Palmer, M. H.; Findlay, R. H.; Moyes, W.; Gaskell, A. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 841.

(14) (a) Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. (b) Burrow, P. D.; Ashe, A. J., III; Bellville, D. J.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 425. (c) Herndon, W. C. *Tetrahedron Lett.* **1979**, 3283. (d) Clark, D. T.; Scanlan, I. W. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1222. (e) Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 3293. (f) Ashe, A. J., III; Sharp, R. R.; Tolan, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5451. (g) Ashe, A. J., III; Bahl, M. K.; Bomben, K. D.; Chan, W.-T.; Gimzewski, J. K.; Sitton, P. G.; Thomas, T. D. *J. Am. Chem. Soc.* **1979**, *101*, 1764.

(15) *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R.; Rees, C. W.; Seriven, E. F. V., Eds.; Elsevier Science Ltd.: Oxford, 1996.

(16) (a) Pozharskii, A. F.; Soldatenkov, A. T.; Katritzky, A. R. *Heterocycles in Life and Society*; John Wiley and Sons Ltd.: England, 1997. (b) Joule, J. A.; Smith, G. F., *Heterocyclic Chemistry*; Chapman & Hall: London, 1995.

(17) (a) Piancatelli, G.; Scettri, A.; D'Auria, M. *Synthesis* **1982**, 245. (b) Ajito, K.; Takahashi, M.; Ito, M. *Chem. Phys. Lett.* **1989**, *158*, 193.

(18) (a) Rogers, J. S.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 730. (b) Scheschkewitz, D.; Menzel, M.; Hoffmann, M.; Schleyer, P. v. R.; Geiseler, G.; Massa, W.; Harms, K.; Berndt, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2936. (c) Balzereit, C.; Winkler, H. J.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2306. (d) Herberich, G. E.; Hebner, B. *Chem. Ber.* **1982**, *115*, 3115.

(19) (a) Wakita, K.; Tokitoh, N.; Okazaki, R.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648. (b) Wakita, K.; Tokitoh, N.; Okazaki, Nagase, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 634. (c) Markl, G.; Schlosser, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 963.

(20) Bachrach, S. M.; Hare, M.; Kass, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 12646.

(21) (a) Wang, L.-S.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, *122*, 7681. (b) Li, X.; Wang, L.-S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033. (c) Boldyrev, A. I.; Simons, J.; Li, X.; Wang, L. − S. *J. Am. Chem. Soc.* **1999**, *121*, 10193.

(22) (a) Purath, A.; Dohmeier, C.; Ecker, A.; Koppe, R.; Krautscheid, H.; Schnockel, H.; Ahlrichs, R.; Stoermer, C.; Friedrich, J.; Jutzi, P. *J. Am. Chem. Soc.* **2000**, *122*, 6955. (b) Blanksby, S. J.; Schroder, D.; Dua, S.; Bowie, J. H.; Schwarz, H. *J. Am. Chem. Soc.* **2000**, *122*, 7105.

(23) (a) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275. (b) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9287. (c) Kato, T.; Gornitzka, H.; Baceiredo, A.; Schoeller, W. W.; Bertrand, G. *Science* **2000**, *289*, 754.

control the relative stabilities of the positional isomers? (d) What is the interrelationship among the structures, stability, and reactivity? (e) Will a weaker π-framework enhance or curtail bond delocalization? (f) What is the effect of substitution on the skeletal distortions? Ab initio (SCF and post-SCF) and gradient corrected hybrid DFT methodologies were employed to obtain the reliable quantitative results on the structure, energetics, and other physicochemical properties of the systems. The applicability of qualitative rules such as the sum of bond strengths in the twin Kekule forms, the rule of Topological Charge Stabilization (TCS), electrostatic repulsion, and isodesmic equations is tested on this class of molecules. Singlet−triplet gaps and chemical hardness (η) are used to gauge their reactivity. The above qualitative analysis along with the measurements of propensity of the in-plane and out-of-plane distortive tendency may provide broader insights and may reorient our understanding of heteroaromaticity.

2. Computational and Technical Details

All the calculations were done using Gaussian 94 suite of programs.[25] Initially all the geometries considered in the study are optimized at the HF/6-31G* level, and the nature of the stationary points were characterized by frequency calculations. Later, B3LYP/6-31G* computations[26] are employed to recalculate all the optimized geometries and frequencies. The geometries are further refined by reoptimizing at the MP2/6-31G** level. The geometric parameters are found to be essentially identical at B3LYP and MP2 levels in most of the cases, while the bond lengths are consistently underestimated at HF level. The effect of adding a set of diffuse functions on the geometries of the anions is studied at the MP2/6-31+G* level. Addition of one set of diffuse functions has very small effect on the geometry. However, the energies are expected to show higher dependence on the basis set. The geometries obtained at the MP2/6-31G** level, which is proven to be a better method for this class of compounds, are taken for single point energy calculations at higher levels and with basis sets of triple-ζ quality.[9b,e,20] CCSD(T) single point calculations are done with 6-31G* basis set. Additionally, 6-311+G** (for neutral and cationic species) and 6-311++G** (for anions) are used at MP2 level. Recent studies on anionic and dianionic systems show that these basis sets could well reproduce the experimental results.[20,21,27] Previous studies indicate that coupled cluster method is fairly reliable in general and particularly in dealing with systems of this class.[9] The best estimates for the relative energies are obtained using eq 1 for cationic and neutral systems and eq 2 for anionic systems.

$$\Delta E = \Delta E_{\mathrm{CCSD(T)}} + \Delta E_{(\mathrm{MP2/6-311+G^{**}\ -\ MP2/6-31G^{**}})} + \Delta H \quad (1)$$

$$\Delta E = \Delta E_{\mathrm{CCSD(T)}} + \Delta E_{(\mathrm{MP2/6-311++G^{**}\ -\ MP2/6-31G^{**}})} + \Delta H \quad (2)$$

Enthalpy correction, ΔH is obtained at the B3LYP/6-31G* level.

The natural charges are calculated at the MP2/6-31G** level using the NBO algorithm[28] implemented in Gaussian 94. The geometric parameters and the nature of the normal modes were examined using the graphical interface program, MOPLOT.[29] In the paper we discuss only the MP2/6-31G** optimized geometries and the best estimates for the energetics using eqs 1 and 2 unless otherwise specified.

3. Results and Discussion

3.1. Equilibrium Geometries. The geometries of the monosubstituted benzenes are discussed first. This is followed by the presentation of the geometries of the anionic species of the disubstituted benzenes with X = B^-, Al^-, and Ga^-. The neutral and cationic disubstituted benzenes are discussed next. As the HF method is known for grossly underestimating the bond lengths, only the B3LYP and MP2 geometries are given. For anions and dianionic systems, geometries refined by using 6-31+G* basis set, which is of split-valence quality augmented with a set of diffuse functions in addition to the polarization functions, at the MP2 level. B3LYP/6-31G*, MP2/6-31G**, and MP2/6-31+G* geometries were found to be very similar both for mono- and disubstituted benzene isomers in a majority of the cases. Usually, the differences are less than 0.010 Å in bond lengths and 0.5° in angles, but the fourth row substituted systems show greater sensitivity as a function of method.

3.1.1. Monosubstituted Benzenes. Figure 1 depicts the skeletal bond lengths and bond angles for the monosubstituted benzenes obtained at the B3LYP/6-31G* and MP2/6-31G** levels. The geometries of all the planar isomers at both the levels are very similar except in **mono-Ga**$^-$, where the difference in the C−Ga bond length predicted by these two levels is 0.019 Å. The geometric parameters obtained at the MP2/6-31+G* are given only for the anionic systems. Augmenting the basis set with a set of diffuse functions imparts negligible changes in the geometry with a maximum of 0.006 Å in bond lengths and less than half a degree in angles. None of the substitutions trigger any noteworthy bond alternations, despite substantial variations in the bond angles. It is also important to note that the bond lengths of the monosubstituted isomers are very close to the estimated aromatic bond lengths (see Supporting Information, Table S7). All the planar structures are characterized as minima except **mono-As**$^+$. The geometries of the corresponding minimum energy structure, **mono-As**$^+_{\mathbf{m}}$ predicted by B3LYP and MP2 levels are significantly different, especially the puckering of the skeleton is grossly overestimated by the B3LYP level as evident from Figure 1. This is also reflected in the energy difference between **mono-As**$^+$ and **mono-As**$^+_{\mathbf{m}}$. The difference of 7.4 kJ/mol at B3LYP level drops to 0.02 kJ/mol at the MP2 level. Hence, at MP2 level, the planar form of **mono-As**$^+$ is

(24) (a) Schroder, D.; Schwarz, H.; Wulf, M.; Sievers, H.; Jutzi, P.; Reiher, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3513. (b) Gimarc, B. M.; Zhao, M. *Inorg. Chem.* **1996**, *35*, 3289. (c) Nagase, S.; Ito, K. *Chem. Phys. Lett.* **1986**, *126*, 43. (d) Zhao, M.; Gimarc, B. M. *Inorg. Chem.* **1996**, 35, 5378. (e) Clabo, D. A., Jr.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 1664. (f) Sax, A.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651. (g) Shaik, S. S.; Hiberty, P. C.; Ohnessian, G.; Lefour, J.-M. *J. Phys. Che*m, **1988**, *92*, 5086. (h) Ohanessian, G.; Hiberty, P. C.; Lefour, J.-M.; Flament, J.-P.; Shaik, S. S. *Inorg. Chem.* **1988**, *27*, 2219. (i) Warren, D. S.; Gimarc, B. M.; Zhao, M. *Inorg. Chem.* **1994**, *33*, 710. (j) Warren, D. S.; Gimarc, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 5378.

(25) Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Ragavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J., Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc.: Pittsburgh, PA, 1995.

(26) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(27) Simons, J.; Jordan, K. D. *Chem. Rev.* **1987**, *87*, 535.

(28) Glendening, E. D.; Reed. A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

(29) Bally, T.; Albrecht, B.; Matzinger, S.; Sastry, G. M. Moplot 3.2, University of Fribourg, 1997.

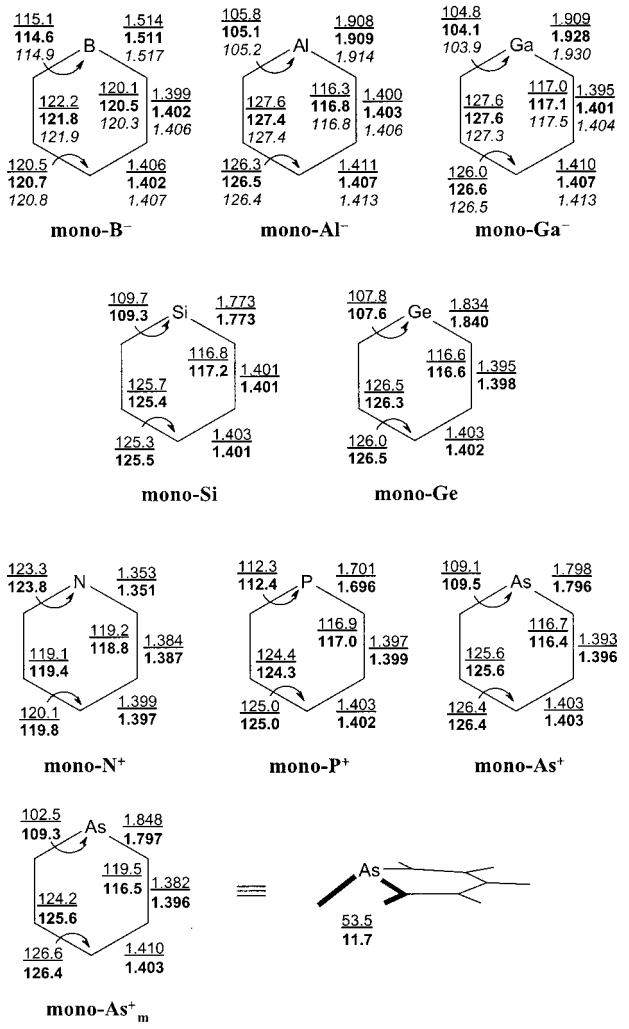


Figure 1. Selected geometric parameters of monosubstituted benzenes, $(CH)_5XH$, obtained at B3LYP/6-31G* (underlined), MP2/6-31G** (bold) and MP2/6-31+G* (italics) levels. Bond lengths are in angstroms, and angles are in degrees.

virtually a minimum with a very soft potential for the out-of-plane bending of the hydrogen attached to As.[30]

3.1.2. **Disubstituted Benzenes.** The important skeletal parameters of the three positional isomers of anionic, neutral, and cationic disubstituted benzenes are given in Figure 2, Figure 3, and Figure 4, respectively. The frequency analysis characterized that all the planar structures, except ***ortho*-P**$^+$ and ***ortho*-As**$^+$, are minima at the HF level. In contrast, the B3LYP frequencies indicate that in addition to the above, ***ortho*-Ge** and ***para*-As**$^+$ are also transition states. The normal modes corresponding to the imaginary frequency are followed, and nonplanar structures were characterized as minima. However, upon reoptimizing the nonplanar structures at the MP2 level, both ***ortho*-Ge** and ***para*-As**$^+$ collapse to virtually flat structures.

3.1.2.1. Anionic Species, $(CH)_4(XH)_2$, X = B$^-$, Al$^-$, Ga$^-$. A perusal at Figure 2 reveals that all the computed bond lengths are similar to the aromatic bond length, particularly at MP2 level (for comparison see Table S7 in Supporting Information). Expectedly, anionic systems particularly the heavier analogues show some changes in the geometry as a function of method and basis set. While the differences are not so significant for X = B$^-$ and Al$^-$, all the three Ga$^-$ substituted isomers show differences ranging from 0.003 to 0.081 Å and up to 3.5° in angles. We refrain from augmenting the basis set further for getting better geometries due to two reasons: (a) the known drawback or the erroneous behavior of Pople type basis set when augmented with more sets of diffuse functions,[31] (b) the initial attempts to augment with more sets of diffuse functions resulted in severe SCF convergence problems. However, the trends obtained at all levels, in general, point that the strain due to the incorporation of heteroatoms with varied sizes is reflected only on the bond angles and not in bond lengths. However, interestingly these variations as we go to higher levels of theory do not alter the broad qualitative features. All the optimized bond lengths are close to the aromatic bond lengths at all levels of theory, except in ***para*-Ga**$^-$, which exhibits a fair amount of localization at the MP2/6-31+G* level.

3.1.2.2. Neutral Species, $(CH)_4(XH)_2$, X = Si, Ge. Among the neutral isomers, B3LYP and MP2 geometries are similar except for ***ortho*-Ge**. ***ortho*-Ge** is computed to be a saddle point at the B3LYP level, the energy difference between the planar and the nonplanar (with C_2 point group) counterparts being only 0.3 kJ/mol. However, at MP2/6-31G** level the puckering is too low, and thus the optimized geometry corresponds virtually to a minimum. Here also, all the structures show bond lengths very similar to aromatic bond lengths, despite substantial perturbations witnessed in the internal bond angles.

3.1.2.3. Cationic Species, $(CH)_4(XH)_2$, X = N$^+$, P$^+$, As$^+$. Among the cationic species, the geometries obtained for the planar isomers at the B3LYP and MP2 levels are similar. The frequency calculations on the planar forms of ***ortho*-P**$^+$, ***ortho*-As**$^+$, and ***para*-As**$^+$ characterize them as transition states. The minimum energy structures with lower symmetry (C_2 point group for ***ortho*-P**$^+$ and ***ortho*-As**$^+$ and C_{2h} point group for ***para*-As**$^+$) are characterized; the hydrogens attached to the heteroatoms are substantially tilted out-of-plane. Also in case of ***ortho*-P**$^+$ and ***ortho*-As**$^+$, the X_2 moiety is considerably puckered with respect to the C_4 framework. However, the optimization of the C_{2h} minimum energy structure of ***para*-As**$^+$ gave back the planar structure at the MP2 level. Hence, B3LYP level in general, tends to overestimate the ring puckering of this class of compounds.

A quick look at Figures 2−4 indicates that all the skeletally disubstituted isomers possess delocalized geometries irrespective of the type of substitution and the charge present on the system. The strain that was introduced by skeletal substitution completely transforms into angular strain and leaves the bond lengths entirely untouched. It seems rather surprising to note that almost all molecules which have lower symmetry other than D_{6h} in benzenoid frameworks, e.g., naphthalene, anthracene, triphenylene, C_{60}, etc., show significant bond alternations.[32] However, as we go to 4th row substituents, the propensity for ring puckering increases significantly. Similar observations were made in our earlier study on

(30) Experimentally, it has been reported that arsabenzene has no proton affinity, and hence the proton attacks the 'C' site rather than As. See: Ashe, A. J., III; Chan, W − T.; Smith, T. W.; Taba, K. M. *J. Org. Chem*. **1981**, *46*, 881.

(31) Skurshi, P.; Gutowski, M.; Simons, J. *Int. J. Quantum Chem*. **2000**, *80*, 1024.

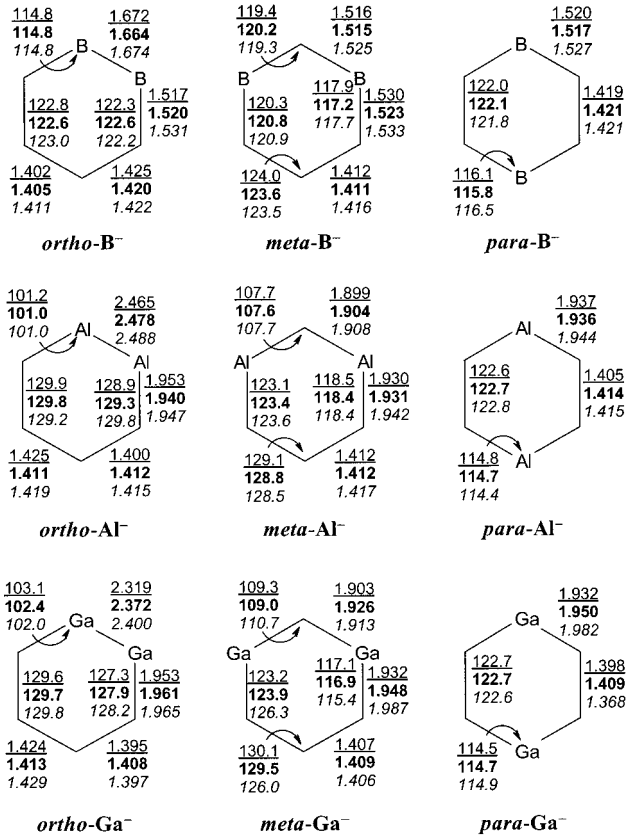


Figure 2. Selected geometric parameters of disubstituted benzenes, $(CH)_4(XH)_2$, X = B^-, Al^-, and Ga^-, obtained at B3LYP/6-31G* (underlined), MP2/6-31G** (bold) and MP2/6-31+G* (italics) levels. Bond lengths are in angstroms, and angles are in degrees.

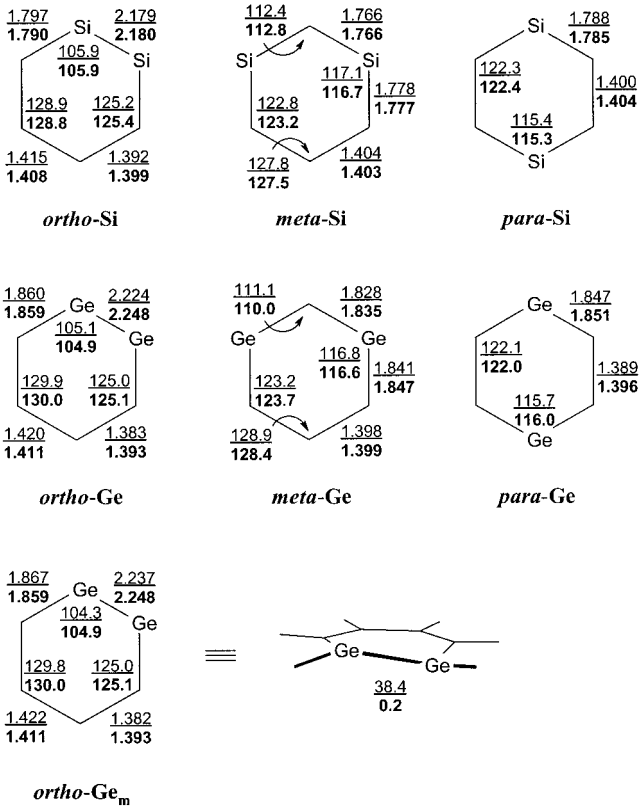


Figure 3. Selected geometric parameters of disubstituted benzenes, $(CH)_4(XH)_2$, X = Si and Ge, obtained at B3LYP/6-31G* (underlined) and MP2/6-31G** (bold) levels. Bond lengths are in angstroms, and angles are in degrees.

the positional isomers of $(CH)_4X_2$ (X = N, P, C^-, Si^-, O^+, and S^+).[9a] Our study assumes that one of these planar form of isomers corresponds to global minimum on their respective energy surfaces; while this is probably true

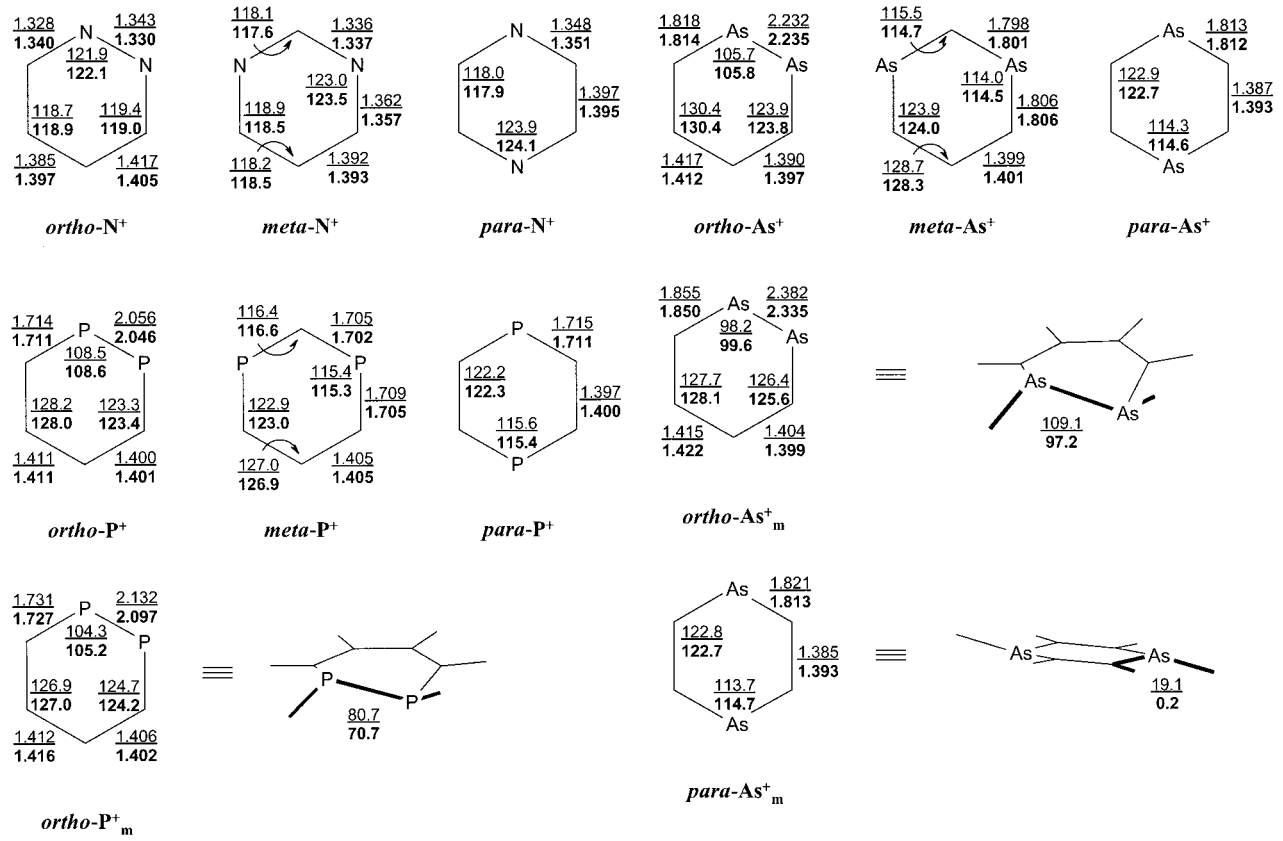
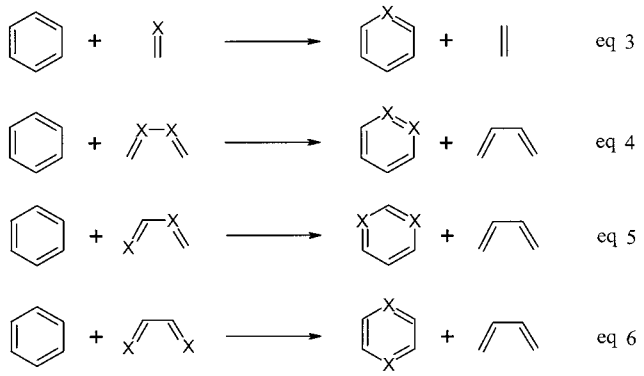


Figure 4. Selected geometric parameters of disubstituted benzenes, $(CH)_4(XH)_2$, X = N^+, P^+, and As^+, obtained at B3LYP/6-31G* (underlined) and MP2/6-31G** (bold) levels. Bond lengths are in angstroms, and angles are in degrees.

Scheme 3



in a majority of cases studied here, violation to this proposition may be seen going to the 4th row substituted isomers.

3.2. Energetics. First, the effect of the skeletal replacement of C by an isovalent ion/atom on its thermodynamic stability is assessed using the following homodesmic eqs 3, 4, 5, and 6 (Scheme 3). Table 1 gives the results of the homodesmic equations using the best estimates of the total energies. The stabilities of the charged monosubstituted benzenes are overestimated as the right-hand side of the equation bears the charge on bulkier species.

Table 1. The Reaction Energies, of the Homodesmic Eqs 3 for the Monosubstituted Benzenes $(CH)_5XH$ and Eqs 4, 5, and 6 for the Disubstituted Benzenes $(CH)_4(XH)_2$ (Scheme 3) Obtained Using the Best Estimates of Total Energies. All Values Are Given in kJ Mol^{-1}

X	mono-Δ*E* (3)	*ortho*-Δ*E* (4)	*meta*-Δ*E* (5)	*para*-Δ*E* (6)
B^-	−46.7	9.2	0.3	17.3
N^+	−38.4	−40.7	−19.7	40.9
Al^-	−46.3	40.6	59.0	114.4
Si	16.2	17.4	13.2	27.4
P^+	−46.7	−20.7	−16.9	20.6
Ga^-	14.4	21.9	63.3	103.0
Ge	24.1	8.2	18.6	45.5
As^+	−33.0	−22.0	−2.7	43.8

Table 1 reveals that monosubstitutions do not bring in any instability in most of the cases. **mono-Si**, is found to be the least stable compound next to **mono-Ge**, and recent synthetic achievement of this should encourage experimental attempts toward hitherto unknown heteroaromatics considered in this study. Therefore, the synthesis of other monosubstituted isomers, with the appropriate steric protection by bulky substituents should be well within the realm.

The results of the isodesmic equations indicate that all the *para*-isomers show significant destabilization and are computed to be less stable when compared to their mono-, *ortho*- and *meta*-counterparts. All the dianionic systems show some instability. However, the lower magnitudes of most of the compounds suggest that they are not very unstable in the thermodynamic sense. The diboratabenzenes (***ortho*-B**$^-$, ***meta*-B**$^-$, and ***para*-B**$^-$) observed experimentally[18] are found to be unstable. Similarly, the stabilities of disilabenzenes (***ortho*-Si**, ***meta*-Si**, and ***para*-Si**) are comparable to the experi-

(32) (a) Hirsch, A. *The Chemistry of the Fullerenes*; Georg Thieme Verlag: Stuggart: New York, 1994; pp 25−26. (b) Schullman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1996**, *118*, 8470. (c) Sastry, G. N.; Jemmis, E. D.; Mehta, G.; Shah, S. R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1867. (d) Priyakumar, U. D.; Sastry, G. N. *J. Org. Chem.* **2001**, *66*, 6523. (e) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

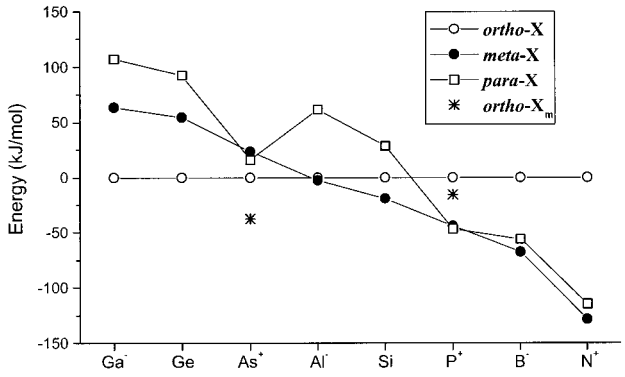


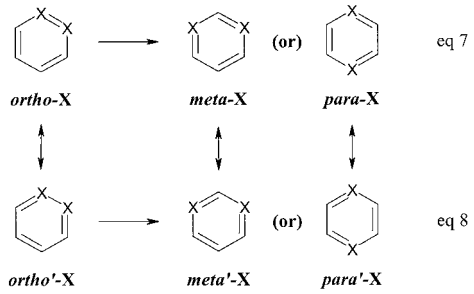
Figure 5. Best estimates (obtained from eqs 1 and 2) of the relative energies of the positional isomers (*ortho*, *meta*, and *para*) of the skeletally disubstituted benzenes $(CH)_4(XH)_2$; (X = B^-, N^+, Al^-, Si, P^+, Ga^-, Ge, and As^+).

mentally known silabenzene (**mono-Si**).[19] Thus, from a thermodynamic point of view, *ortho*- and *meta*-isomers show consistently higher stability over *para*-isomers.

3.3.1. Relative Stabilities of the Positional Isomers. The trends of the relative energies as well as the absolute values themselves were found to be very similar at DFT, MP2, and CCSD(T) levels in a majority of cases (See Table S2 in the Supporting Information). However, significant changes in the magnitudes of stability and even orderings in the disubstituted isomers is observed for X = Al^- and Si. Previous calculations on silabenzenes also indicated that the relative energies of disubstituted isomers are different using cc-pVDZ and cc-pVTZ basis sets at B3LYP level.[8] The basis set corrected values using a triple-ζ function, the best estimates are in excellent agreement with the previous CCSD(T)/cc-pVTZ calculations.[8] Therefore, our best estimates which include a basis set correction is likely to take care of the inadequacy of basis set used at CCSD(T) level. Figure 5 correlates the relative energies of the three isomers for the various substituents, which were studied here. In a few cases, where the planar forms do not correspond to minimum, the relative energies of the corresponding nonplanar minima are also indicated. The variations in the relative stability magnitudes as a function of substituent are far from obvious. Thus, a combination of several factors decides the relative stability ordering of the disubstituted isomers, and some of them are discussed in the following sections.

3.3.2. The Sum of Bond Strengths in the Twin Kekule Forms. One factor that distinguishes the *ortho*-isomer from the *meta* and *para* is the different types (and number) of single and double bonds in the skeleton. This criterion, used by Hiberty et al. to explain the relative stability ordering of *ortho*-, *meta*-, and *para*-phosphinine, was found to be a very useful tool to estimate the relative stabilities in skeletally disubstituted benzenes.[9b] *meta*- and *para*-isomers have the same number and types of double and single bonds in both the Kekule forms (Scheme 4), and in contrast the *ortho*-isomer will have different number and types of bonds in its two Kekule forms compared to the *meta*- and *para*-isomers. So the stability/instability of the *ortho*-isomers compared to the *meta*- and *para*-isomers can be compared based on the cumulative bond strengths of the constituent Kekule forms. Scheme 4 shows that the eqs 7b and 8b essentially predict the differences between the relative cumulative bond strengths of *ortho*-isomer and *meta*-/*para*-isomers.

Scheme 4



$$X{=}X + 2C - X + 2C{=}C + C - C \rightarrow 2C{=} X + 2\,C - X + C{=}C + C - C \quad (7a)$$

On simplification, eq 7a reduces to eq 7b

$$H_2X{=}XH_2 + H_2C{=}CH_2 \rightarrow 2\,H_2C{=}XH_2 \quad (7b)$$

Similarly, eq 8a reduces to eq 8b

$$X - X + 2C{=}X + 2C - C + C{=}C \rightarrow 2C{=} X + 2\,C - X + C{=}C + C - C \quad (8a)$$

$$H_2X - XH_2 + H_2C - CH_2 \rightarrow 2\,H_2C - XH_2 \quad (8b)$$

The reaction energies of the eqs 7b and 8b obtained at the CCSD(T) level are given in Table 2. Obviously, the results indicate a high preference toward right-hand side, for X bearing either a positive or negative charge due to electrostatic reasons. However, higher magnitudes of ΔE for X = B^- and N^+ and gradual increase in ΔE while going from B^- to Ga^- and N^+ to As^+ indicate that there is a gradual preference for the *ortho*-isomer, i.e., toward the left side of the equation, to be more stable for the 4th row substituted isomers and *meta*-/*para*-isomers to be more stable for 2nd row substituents. The results indicate that there is a preference for the *ortho*-isomer to be more stable for X = Ga^-, Ge and As^+; *meta*-/*para*-isomer to be more stable for X = B^- and N^+. Table 2 indicates that two C−X bonds are not preferred when compared to one C−C bond and one X−X bond for 4th row atoms. The high stability of *ortho*-isomer for X = Ge over *meta*/*para*, a result which is in contrast to X = Si can readily be accounted for, following the above argument.

3.3.3. The Rule of Topological Charge Stabilization (TCS). The Gimarc's rule of Topological Charge Stabilization (TCS) which 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" was found to be a very powerful guiding principle in predicting the relative energy orderings for the positional isomers.[33] We have found out that this rule works reasonably well in predicting the relative stabilities of the heteroaromatic positional isomers.[9a,34] Figure 6 depicts the natural charges for all the monosubstituted benzenes obtained at the MP2/6-31G** level. Table 3 gives the relative energy ordering of the positional

(33) Gimarc, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 1979.
(34) (a) Frison, G.; Sevin, A.; Avarvari, N.; Mathey, F.; Floch, P. L. *J. Org. Chem.* **1999**, *64*, 5524. (b) Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem. A* **1999**, *103*, 2141.

Table 2. The Reaction Energies Corresponding to Eqs 7b and 8b 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 Are Given in kJ Mol^{-1}**

X	ΔE (kJ mol^{-1}) from eq 7b	ΔE (kJ mol^{-1}) from eq 8b
B^-	−658.5	−568.1
Al^-	−262.2	−359.2
Ga^-	−196.2	−298.9
Si	67.3	−20.8
Ge	148.0	33.3
N^+	−1015.4	−787.9
P^+	−598.1	−606.8
As^+	−468.3	−519.5

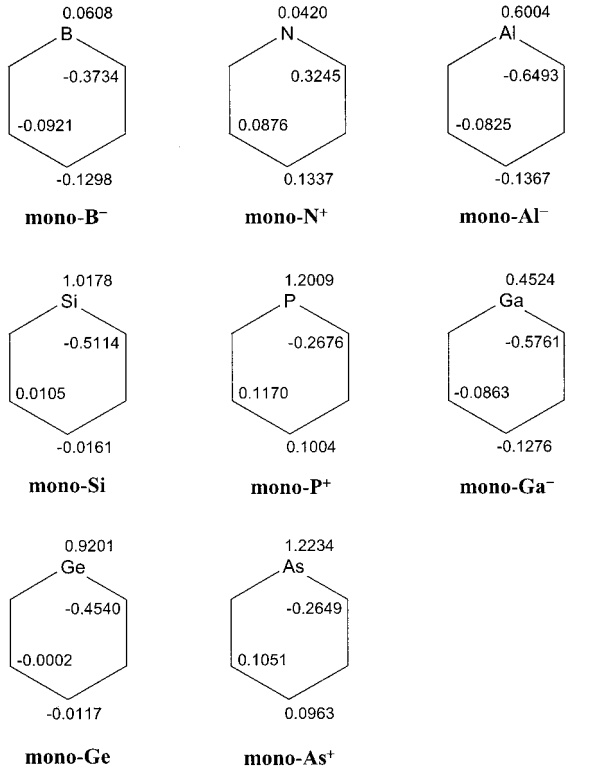


Figure 6. Natural group charges for the monosubstituted benzenes, $(CH)_5XH$ obtained at the MP2/6-31G** level.

Table 3. The Computed Stability Ordering and the Predicted Stability Ordering Based on the Natural Group Charges Obtained at the MP2/6-31G Level Using the rule of TCS[a]**

substituent	expected stability ordering	observed stability ordering
B^-	m > p > o	m > p > o
N^+	m > p > o	m > p > o
Al^-	m > p > o	m ≈ o > p
Si	m > p > o	m > o > p
P^+	m > p > o	p ≈ m > o
Ga^-	m > p > o	o > m > p
Ge	m > p > o	o > m > p
As^+	m > p > o	o > p > m

[a] o, m, and p correspond to *ortho*-, *meta*-, and *para*-skeletally disubstituted isomers, respectively.

isomers obtained and those predicted by the TCS rule.

The rule of TCS predicts the stability ordering to be *meta* > *para* > *ortho* irrespective of the substituent. This rule breaks down, in predicting the relative stabilities, especially in cases where the substituents are more electropositive in nature. However, the stability of the *meta*- over *para*-isomers in majority of the cases may be traced to the TCS. Hence, the rule of TCS fails in the presence of overwhelming factors, which operate against it. The high stability of *ortho*-isomers for more electropositive substituents may be due to the preference for the X═X bond.

Table 4. The Singlet−Triplet Gap (kJ mol^{-1}) Obtained for the Disubstituted Benzenes at the B3LYP/6-31G* Level. (428.4 kJ mol^{-1} for Benzene at the Same Level)

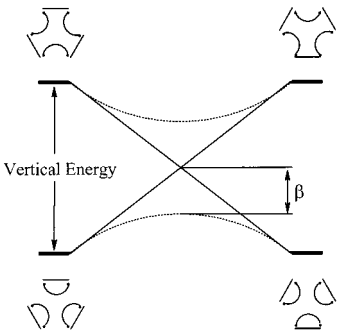
X	mono-	*ortho*-	*meta*-	*para*-
B^-	365.4	319.0	362.3	282.8
N^+	396.2	358.7	384.5	302.2
Al^-	264.4	178.6	257.7	122.7
Si	304.2	255.6	285.2	217.0
P^+	334.2	280.3	308.9	272.6
Ga^-	271.9	205.5	267.5	129.0
Ge	286.2	252.2	306.6	191.6
As^+	299.3	250.7	272.2	222.2

3.3.4. Electrostatic Repulsion. Another factor that decides the relative stabilities of the positional isomers is how best each of these isomers optimizes the charge repulsion. The group charges are evaluated and used to gauge the Coulombic repulsion in a planar hexagonal system. A look at the calculated natural charges indicates (given in the Supporting Information Figure S1) that *meta*-isomer should benefit most from the charge distribution in most cases. However, for X = P^+ and As^+, where the group charge on the two heteroatomic centers is equal to, or more than unity, in all positional isomers, the electrostatic repulsion for the *para*-isomers will be the least. Therefore, the *meta*-isomer do not enjoy any special stabilization effect over *para* for X = P^+ or As^+ which is in contrast to other substituents. Hence, for X = P^+ and As^+, *meta*- and *para*-isomers are almost of same energy, as in these two cases the TCS and the electrostatic repulsion operate against each other and the near equality of the relative energies points out that they may be of same magnitude. Obviously, the *ortho*-isomer is expected to get the maximum destabilization due to this electrostatic repulsion, in all the cases. The high stability of *ortho*-isomer for electropositive substituents may be due to the preference for the X═X bond.

3.4. Singlet−Triplet Energy Differences. The singlet−triplet energy differences, ΔE_{s-t} which gauge the strength of π-framework and estimate the reactivity of the benzenoid framework, obtained at the B3LYP/6-31G* level are given in Table 4. Thus, a higher singlet−triplet gap is assumed to correspond to a stronger π-bonding and lower reactivity. ΔE_{s-t} of all the substituted benzenes are low when compared to benzene (see Table 4). The disubstituted isomers have lower ΔE_{s-t} compared to the monosubstituted benzenes. Among the disubstituted ones, the *meta*-isomer has the highest and the *para* has the lowest ΔE_{s-t}, consistently irrespective of the nature of the substituent.

The ΔE_{s-t} may be taken as a quantity proportional to the vertical gap between the twin Kekule forms of the benzenoid framework (Scheme 5). Obviously, a higher vertical gap increases the distortive propensity of the π-electrons, while a decrease in the vertical gap enhances the π-delocalization.[2] Importantly, all skeletal substitution considered in the study results in lower vertical gaps (Table 4). The singlet−triplet gaps and reaction energies of the isodesmic equations consistently account for the lower kinetic and thermodynamic stability of skeletally substituted benzenes, particularly those involving fourth row atoms/ions.

Scheme 5



β = Quantum mechanical resonance energy

3.5. The Origin of Delocalization. It is well-known that in polycyclic aromatic hydrocarbons, the absence of 6-fold symmetry results in significantly localized structures in cyclic conjugated systems, irrespective of the aromaticity. For example, the ground state structures of naphthalene, anthracene, fullerenes, buckybowls, etc., and virtually every other aromatic hydrocarbon, can easily be depicted with a single dominant Kekule form, exhibiting substantial bond localization.[32,35] Larger differences in the electronegativity between the substituted X and C results in greater disparities in the π-electron density, with more electronegative atom bearing more charge, which appears to inhibit the electronic delocalization within the ring. Thus, the skeletally substituted benzenes are expected to show lower π-electron delocalizations. In sharp contrast, all the mono- and disubstituted benzenes exhibit delocalized geometries and effectively preclude the possibility of describing the geometric structure with a single Kekule form. Obviously, unlike in benzene, this delocalization is not a symmetry enforced one. Considering Shaik's curve crossing model, the π-electrons in benzene have a significant distortive propensity and held in delocalized form due to a strong σ-framework[2] (Scheme 5). It occurred to us that the strong delocalization character exhibited by these substituted benzenes arises, as the distortive propensity of the π-electrons decreases substantially in the skeletally substituted analogues of benzene. The lower singlet−triplet energy gap for the substituted systems results in lower vertical excitation energies between the two Kekule forms. Therefore, according to Kekule crossing model, the propensity for the π-distortion decreases in cases where the vertical energy gap is smaller. However, the out-of-plane distortive tendency of the ring is an entirely independent aspect, which will be analyzed in the following section. *Therefore, these results indicate that a weaker benzenoid π-framework will have a reduced π-distortive propensity to localize and thus will exhibit higher delocalization tendency.*

There exist two different possibilities to distort for a planar 6π-system, namely an in-plane distortion, which results in localized double and single bonds, and out-of-plane distortion, which causes ring-puckering. The lower singlet−triplet gaps of the skeletally substituted benzenes, especially in cases where the substituents are from 3rd or 4th row, reveal that the propensity of the π-electrons to localize diminishes.

(35) However, similar to the skeletally substituted benzenes, the other substituted benzenes also show high degree of delocalization.

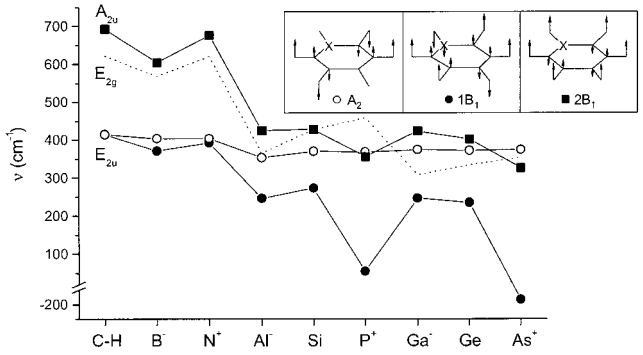


Figure 7. The correlation of the out-of-plane distortive frequencies of the monosubstituted benzenes as a function of substituent. The out-of-plane modes (solid lines) whose frequencies substantially deplete are only shown. The dotted lines correspond to the in-plane distortion.

3.6. Out-of-Plane Distortive Tendencies. One prime criterion for aromaticity in geometric terms for the monocyclic systems is a rigid planar 6π (or 2π) skeleton. The computed harmonic frequencies will be a useful indicator to assess the rigidity of the planar skeleton and thereby the aromaticity of the compound. Harmonic frequencies obtained at the B3LYP/6-31G* level are used in the following discussion. Figure 7 gives the correlation of the frequencies of the few lowest modes, which correspond to the out-of-plane distortions (in solid lines) as well as the in-plane distortion (dotted line) of the monosubstituted benzenes. The doubly degenerate E_{2u} will split into A_2 and B_1 and the A_{2u} mode transforms to B_1 type mode in going from D_{6h} to C_{2v} symmetries. In the C_{2v} symmetric monosubstituted isomers the A_2 and B_1 correspond to the out-of-plane motions and A_1 and B_2 correspond to in-plane motions. In all the monosubstituted derivatives considered here, the lowest energy normal mode (B_1) corresponds to the out-of-plane distortions (Figure 7). Both the B_1 modes vary similarly as a function of the substituent. The propensity for out-of-plane distortion, as indicated by the magnitude of the harmonic frequencies, increases for the 3rd and 4th row atom/ion substituted isomers. According to this analysis, when X = P^+ and As^+, the puckering tendencies are expected to be maximum. A_2 mode is less affected since there is no contribution to the normal mode from the heteroatom (see the inset in Figure 7). However, for X = Ga^-, Ge, and As^+, the frequencies corresponding to the A_1 mode (in-plane distortion) become significantly lower and come between the A_2 and B_1 modes. We did not encounter such problems in our earlier studies of mono- and disubstituted benzenes where X = N, P, C^-, Si^-, O^+, and S^+.[9a] The nature of the vibrational modes is analyzed using MOPLOT program, which enables to graphically depict the normal modes from Gaussian output.[29] A critical examination of the nature of normal modes indicates that they are more or less independent of the substituent. Idealized pictures of the three out-of-plane distortive modes are depicted as an inset in Figure 7. Although the absolute harmonic frequencies might warrant a bigger basis set,[36] the 6-31G* basis set should be good enough to faithfully reproduce the trends in a group

(36) Torii, H.; Ishikawa, A.; Takashima, R.; Tasumi, M. *J. Mol. Struct. (THEOCHEM)* **2000**, *500*, 311.

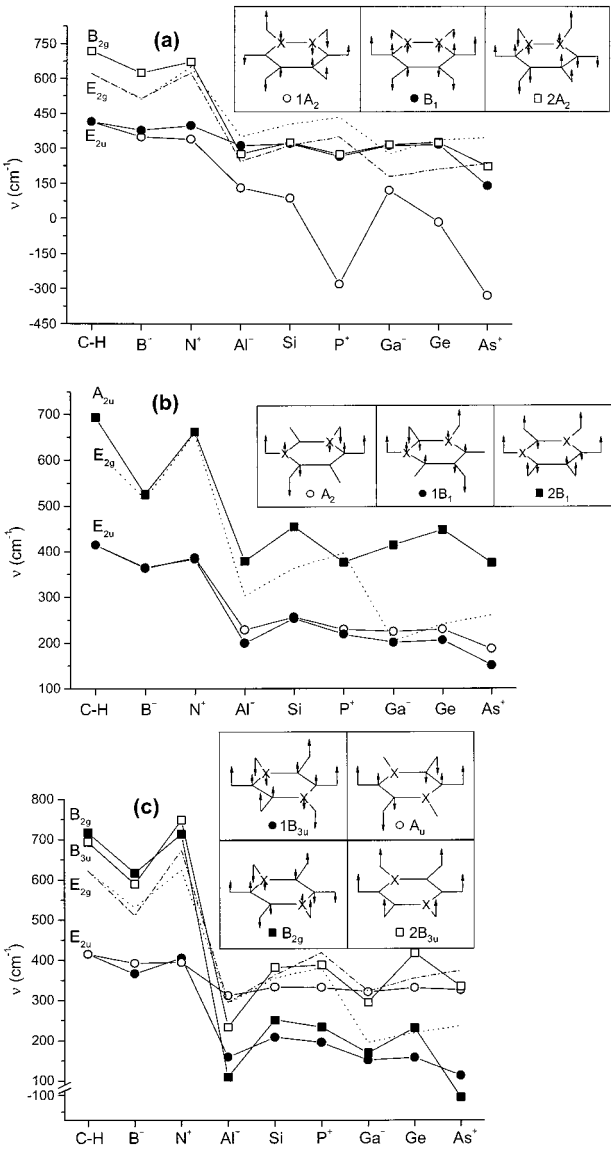


Figure 8. The correlation of the out-of-plane distortive frequencies of the disubstituted benzenes (*ortho* (a), *meta* (b), and *para* (c)) as a function of substituent. The out-of-plane modes (solid lines) whose frequencies substantially deplete are only shown. The dotted lines correspond to the in-plane distortion.

of very similar compounds.[37] While the A_2 mode remains virtually the same for all the substituents, a strong coupling between the two B_1 modes is seen especially in compounds with the third and fourth row substituents.

Figures 8a, 8b, and 8c depict the correlation of the first few harmonic frequencies that correspond to out-of-plane distortions and in-plane distortions of *ortho*-, *meta*-, and *para*- isomers, respectively, as a change of the type of substitution. Figures 7 and 8a−c indicate that the magnitude of the in-plane vibrational frequencies becomes gradually lower going from the second to the fourth row atoms. Thus, the in-plane distortive tendency increases especially for the fourth row substituted benzenes. In the *ortho*-isomer the doubly degenerate E_{2u} mode splits into A_2 and B_1, with the A_2 becoming much softer. Interestingly, the magnitude of the B_1 frequency is essentially independent of the type of substituent. In *para*-isomers, the B_{2g} mode becomes very soft when the substituent is from the 3rd or 4th row. In all the cases, the *meta*-isomer shows restrain to out-of-plane distortion, compared to their *ortho*- and *para*-counterparts.

3.7. The Chemical Hardness (η). According to the maximum hardness principle: There seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible. A high value of chemical hardness (η) indicates high kinetic stability and low reactivity, and thus it was found to be a cardinal index for the molecular structure, bonding, and reactivity.[38] A quantitative definition for hardness has been conceived from the density functional theory. The hardness of an N-electron system with total energy E and external potential $v(r)$ is given by

$$\eta = {}^1/_2(\partial^2 E/\partial N^2)_{v(r)}$$

Using finite difference approximation,[39] the equation has been approximated as

$$\eta = (\text{ionization potential} - \text{electron affinity})/2$$

Alternatively, using Koopman's approximation, it may be written as

$$\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$$

where ϵ_{LUMO} and ϵ_{HOMO} are the energies of the lowest unoccupied molecular orbital and highest occupied molecular orbital, respectively. The most prominent observation is that, compared to benzene, the η values of mono- and disubstituted isomers decrease substantially. The HOMO and LUMO energies along with the symmetry labels and the chemical hardness (η) computed at the B3LYP and HF levels are depicted in Table S6, of the Supporting Information. All the disubstituted isomers have lower η compared to the monosubstituted isomers except for ***meta*-N$^+$**. When we consider that the kinetic stability of the species are directly related to their hardness, then the stability of the disubstituted isomers are much lower compared to the monosubstituted ones. Among the disubstituted isomers, the *meta*-isomer always was found to be the hardest and the *para* the softest without any exceptions. Thus the hardness measure indicates that *para* is the most reactive positional isomer irrespective of the substituent, which is in good agreement with the prediction by ΔE_{s-t} criterion. Importantly, although *ortho*-isomer was found to be the most stable in a large number of cases, they are expected to be much more reactive than *meta*-isomer and thus become kinetically unstable. There is a very good correlation between η and ΔE_{s-t}, and these criteria are quite useful in assessing the reactivity of these compounds.

4. Conclusions

This study presents a comprehensive theoretical analysis of the mono- and diskeletally substituted benzenes where one and two of the skeletal C atoms are substi-

(37) The harmonic frequencies obtained at the HF/6-31G* level show essentially the same trends qualitatively.

(38) (a) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423. (b) Zhou, Z.; Parr, R. G. *Tetrahedron Lett.* **1988**, *29*, 4843. (c) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371. (d) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785. (e) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2092.

(39) Pearson, R. G. *Inorg. Chem.* **1998**, *27*, 734.

tuted by X = B^-, N^+, Al^-, Si, P^+, Ga^-, Ge, and As^+. Skeletal substitution on thermodynamics of benzenoid framework of these heteroaromatics was found to be not so significant. All the mono- and disubstituted isomers possess delocalized geometries. Straightforward correlations among delocalization, thermodynamic stability, out-of-plane and in-plane distortions, and reactivities are not possible. The relative stabilities of the positional isomers are controlled by a combination of various intricate factors and the criterion based on the sum of bond strengths in conjunction with the rule of topological charge stabilization was found to be the best way to predict these relative stability orderings. The rule of topological charge stabilization is a useful guiding principle to estimate the relative stabilities of the positional isomers, but breaks down dramatically in the presence of overriding energetic factors. Electrostatic repulsion seems to be significant in cationic species compared to anionic species. The singlet−triplet gaps, the reaction energies of the isodesmic equations as well as the chemical hardness points to significant instability of *para*-isomers, especially for heavier analogues.

Our present and previous studies[9a] indicate that weaker π-frameworks have a higher tendency toward delocalization in terms of bond length equavalization. Thus, the propensity of the delocalization seems to be higher for weaker π-frameworks, which is inconformity with Shaik's Kekule crossing model.[2] The present study points that the mono- and disubstitutions on the benzene makes it more susceptible for in-plane as well as out-of-plane distortive propensity despite enhancing the tendency to π-delocalization. The computed singlet−triplet energy difference (ΔE_{s-t}), the absolute chemical hardness (η), and the out-of-plane distortive tendency, indicators of reactivity, suggest that the thermodynamically most stable isomer need not be the least reactive.

Acknowledgment. CSIR (No. 01(1681)/00/EMRII) is thanked for the financial assistance. U.D.P. thanks UGC, New Delhi, for a Junior Research Fellowship. We thank Professor E. D. Jemmis for extending computational facilities.

Supporting Information Available: Tables S1 and S2 giving the total energies of the di- and monosubstituted benzenes obtained at various levels and Table S3 giving the relative energies. Tables S4 and S5 giving the optimized Cartesian coordinates of all the molecules, the absolute chemical hardness (Tables S6), the C−X and C═X bond lengths along with the estimated aromatic bond lengths (Table S7), the natural group charges of the skeletally disubstituted benzenes (Figure S1). This information is available free of charge via the Internet at (http://pubs.acs.org).

JO0161781