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Structures, Energetics, Relative Stabilities, and Out-of-Plane Distortivities of Skeletally Disubstituted Benzenes, $(CH)_4X_2$ (X = N, P, C^-, Si^-, O^+, and S^+): An ab Initio and DFT Study

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Abstract: The positional isomers of disubstituted benzenes, $(CH)_4X_2$ (X = N, P, C^-, Si^-, O^+, and S^+), are studied using ab initio molecular orbital theory at Hartree−Fock (HF), MP2, and CCSD(T) levels and also using density functional theory (B3LYP). All of the planar structures are characterized as minima, and they show fully delocalized geometric parameters, with no significant sign of bond fixation. The ortho isomer is computed to be the least stable in all cases except when X = P and Si^-. While meta isomer is more stable than para in general, exceptions are seen for C^- and S^+ substitutions. Various factors that affect the relative stabilities of positional isomers, viz., (a) lone pair−lone pair (lp−lp) repulsion, (b) electrostatic interaction, (c) bond strengths in the corresponding valence isomers, and (d) topological charge stabilization (TCS), are invoked to explain the computed pattern of relative stabilities. The strengths and limitations of each of these aspects in controlling the geometries and energetics of the three isomeric forms are assessed. The lp−lp interaction is found to be insignificant in the isomers bearing third row atom substituents. The rule of TCS excellently accounts for the distinction between meta and para isomers. The sum of the bond strengths of the constituent Kekule forms derived from bond increment schemes successfully explain the differences in the stability between ortho and meta/para isomers. The effect of skeletal disubstitution on the out-of-plane distortivity in the three isomeric forms is discussed by examining the changes in the frequencies of normal modes. The tendency for ring-puckering increases as more heteroatom substituents from the third row replace the CH groups in the ring. Comparisons were made with the monosubstituted analogues, and the effect of adding one more heteroatom substituent on the out-of-plane distortive modes is analyzed.

1. Introduction

Planar 6π-systems, with benzene as a prototype, represent the most extensively studied species in organic chemistry and form the basis and testing ground for many of the existing theoretical principles, as well as for formulating new theoretical principles and refining the existing ones for more than a century.[1−5] Replacement of one CH unit by a heteroatom or an isoelectronic group, which can be broadly classified into three types as shown in Scheme 1 and the consequent structural and electronic perturbations are subjected to extensive experimental and theoretical studies.[6−10] All of the skeletal monosubstituted species have fully delocalized equilibrium geometries, and by using a variety of procedures they are shown to be highly aromatic in nature, albeit with small quantitative differences. Inorganic benzenes with borazine as the prototype are textbook examples.[11] The replacement of all CH units by isoelectronic heteroatoms such as N, P, SiH, and As, which results in N_6, P_6, Si_6H_6, and As_6, received attention due to their inherent symmetry. In sharp contrast to benzene, none of them have the planar-π system as a global minima on their respective potential

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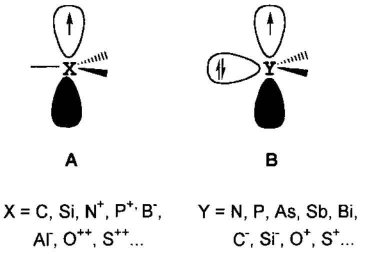
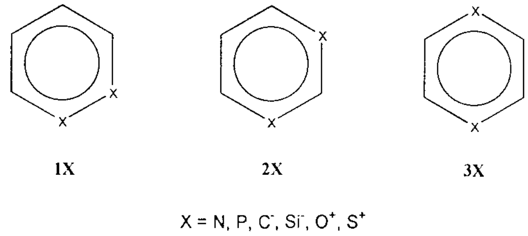
Scheme 1. Different Categories of Isolobal Fragments to CH: (A) Involving X Atom Isoelectronic to C; (B) the Substituent Bearing a Lone Pair, and the Atom Y Is Isoelectronic to N; (C) Ylidic Substituent



Scheme 2. Ortho (**1**), Meta (**2**), and Para (**3**) Skeletally Disubstituted Benzene Isomers with Substituent Atoms or Ions Bearing a Lone Pair



energy surfaces.[12] Obviously, the replacement of all of the CH units by isoelectronic species are not going to follow the same relative energy ordering as the $(CH)_6$ isomers.[12] The distortivity of π-electrons in benzene and the adaptation of D_{6h} geometry by stronger σ-symmetrization compared to weak π-distortivity proposed by Shaik and Hiberty have gained general acceptance in recent years after more than a decade-old controversy.[3,4] In this context, it is interesting to explore the structural and electronic perturbations caused by replacing more CH groups in the benzene skeleton, by groups bearing a lone pair (Scheme 1).[13−16]

The present study is focused on molecules derived from benzene by replacing two CH groups by isoelectronic atoms/ions bearing a lone pair (Scheme 2) and critically examines the factors controlling the relative stabilities of these isomers as well as the alterations of structural and electronic factors due to the skeletal disubstitution. In this family, the nitrogen analogues pyrimidine (**1N**), pyridazine (**2N**), and pyrazine (**3N**) constitute the most important species possessing fully delocalized structures and are subjects of extensive theoretical and experimental studies.[13] The relative stabilities of these isomers are thought to be mostly controlled by the lone pair−lone pair repulsion, with the ortho isomer being the least stable. The analogous phosphorus compounds, diphosphinines (**1P**, **2P**, and **3P**) are relatively less understood, but the synthesis of **2P** and **3P** was successfully accomplished.[16] A recent theoretical study on diphosphinines indicates that in P-substituted isomers, the ortho isomer is the most stable.[14] This rather surprising reversal of the relative stability orderings between the N and P substitutions highlights the involvement of intricate factors. The gas-phase preparation of $(CH)_4C_2^{2-}$ compounds as alkali metal salts prove that the observation of the analogous silicon compounds should be coming up.[17] The other possibility to observe these compounds is as ligands in transition metal complexes.[18] The dianionic 6π-systems are common in boron chemistry, and numerous examples are available with these as ligands in sandwich compounds.[19]

The monosubstituted cationic analogues are well documented: The synthesis of pyrylium salts, first prepared 130 years ago, can be easily accomplished by different procedures. The sulfur analogue, thiopyrylium cation, is well-known for a long time, and the apparent permanent stability of pyrylium and thiopyrylium ions are recognized as quite unusual quite a while ago.[20] Therefore, the chemistry of skeletally disubstituted isomers is interesting in its own right. The ubiquitous presence of heteroaromatics in biologically active molecules makes them extremely important.[21] A recent study on fused heterobicycles indicates that the most stable positional isomer need not be the most aromatic.[22] It is also to be noted that thermodynamic stability and reactivity need not always have inverse relationship.[23]

The present study, which is the first systematic, comparative, computational study of skeletally disubstituted benzenes where the substituents bear a lone pair, addresses the following aspects. (a) How does the skeletal disubstitution affect the delocalization? (b) What are the factors controlling the relative stabilities of the three positional isomers? (c) How is the distortive tendency of π-electrons affected by skeletal disubstitution? (d) How are the out-of-plane distortive modes of planar 6π-systems altered on sequential substitution? Standard ab initio and DFT calculations were performed to answer the above questions.

2. Methods

All calculations have been done using the Gaussian 94 program package.[24] Initially, all of the structures are fully optimized within the given symmetry constraints using gradient procedures at Hartree−Fock,

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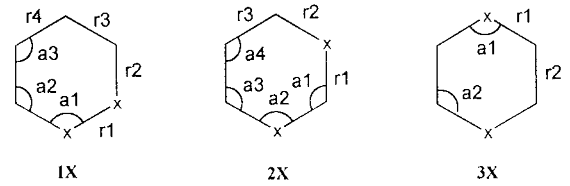
MP2, and the hybrid density functional B3LYP level, which used Becke's three-parameter gradient corrected exchange and LYP correlation functional[25] as implemented in the Gaussian 94 program package. The 6-31G* basis set which is of double-ζ quality and includes a set of d-polarization functions is used initially in conjunction with all methods for performing geometry optimizations. The geometries are optimized using standard gradient techniques, which are default parameters set in the Gaussian 94 program. The nature of all of the optimized stationary points were characterized by frequency calculations at HF and B3LYP level. Both methods characterized all of the structures considered in the present study as minima on the potential energy surface. Due to the known deficiency of the MP2 and B3LYP methods to accurately predict the energetics, single-point calculations are done at the CCSD(T) level.[26] The CCSD(T) method is well-established for chemical problems that are not severely multireference in nature.[27] Therefore, it can be taken as a reference, as results obtained at this level have good quantitative accuracy. Zero-point energy corrections are done by using a scaling factor of 0.98 at the B3LYP level.[28] CCSD(T) and MP2 calculations are performed with frozen-core approximation. The better agreement of the MP2 method with that of the CCSD(T) level when compared to the B3LYP method prompted us to undertake the optimized geometries for further single point calculations at the MP2 level. Further, the effects of basis sets on energetics are also estimated at the MP2 level. The effect of adding a set of polarization functions on the peripheral hydrogens seems to be negligible as the energetics of 6-31G* and 6-31G** levels are virtually identical, and the deviation is less than 1 kJ mol^{-1} in all cases except in the phosphorus systems (even there the maximum deviation is 3.2 kJ mol^{-1}). Although there are substantial deviations in the internal bond angles from idealized 120°, especially for **1P**$-$**3P**, the bond fixation character in any of the isomers is absent.

The effect of adding one set of diffuse functions on the energetics of the anionic systems is estimated. Previous studies on this class of compounds conclude that the methods based on single determinant wave function adequately represent structure and energetics; therefore, dynamic correlation is not considered very important. The atomic and group (the charges on hydrogens are summed up to heavy atoms to which they are connected) charges are calculated on the basis of Mulliken and natural population analyses.[29] The NBO analysis is performed using the subroutine implemented in Gaussian 94.

3. Results and Discussion

3.1. Equilibrium Geometries. The neutral isomers **1N**$-$**3N** and **1P**$-$**3P** are discussed first. Comparison with the previous theoretical studies and experimental data is given for these systems. Next given are the structures and energetics of anionic systems, **1C**$^-$$-$**3C**$^-$. This is followed by the presentation of the results on cationic systems **1O**$^+$$-$**3O**$^+$ and **1S**$^+$$-$**3S**$^+$. The numbering of the skeletal structural parameters used in Tables 1$-$6 are to be deciphered from Scheme 3.

Scheme 3. Designation of Skeletal Geometric Parameters, Which Are Used in Tables 1$-$6



3.1.1. The N- and P-Substituted Analogues. The optimized geometries of the structures at various levels are given in Tables 1 and 2 for N- and P-substituted isomers, respectively. While the HF method displays its characteristic underestimation of aromatic bond lengths,[30] B3LYP and MP2 give excellent results, which are in conformity with the X-ray structural studies for N-substituted isomers and previous computational studies for both. Comparison with earlier theoretical studies indicate that refining energetics and geometries using larger basis sets at MP2 level provides little improvements in the results.[13,14] Therefore, the results obtained by 6-31G* basis set only are used. The optimized geometrical parameters correspond to fully delocalized π-systems for all of the isomers (Tables 1 and 2).

3.1.2. The C$^-$- and Si$^-$-Substituted Analogues. Tables 3 and 4 depict the optimized geometrical parameters for C$^-$ and Si$^-$ disubstitutions. **1C**$^-$ experiences the most distorted structure and virtually leads to a single bond between the carbons bearing lone pairs using the 6-31G* basis set. While bond localization decreases going to **2C**$^-$ and **3C**$^-$, these structures are still very delocalized. In **1C**$^-$ a small amount of bond alternation which is seen at the HF level, minimizes drastically at correlated levels, and delocalization gets reinforced. The *r*1 bond length is overestimated by the 6-31G* basis set, and inclusion of a set of a diffuse function (6-31+G*) brings it back to normal range. Also, a significant lowering of the total energy is seen for all C$^-$ isomers. The differences in geometries upon adding diffuse functions on Si$^-$ isomers are less significant (Table 4). Comparison of geometries of C$^-$ isomers obtained at the MP2/6-31G* level with MP2/6-311+G* optimized geometries shows excellent agreement.[17] The slightly longer C$-$C (*r*1) bond in **1C**$^-$ is traced mainly to the electrostatic repulsion rather than the indication for bond fixation, which would localize to one of the Kekule forms. Thus correlation and augmenting diffuse functions to the basis set are important for obtaining good equilibrium geometries.

3.1.3. The O$^+$- and S$^+$-Substituted Analogues. The HF, B3LYP, and MP2 optimized geometries of O$^+$- and S$^+$-substituted isomers are given in Tables 5 and 6. The bond localization is maximum for the **1O**$^+$ isomer in the series. In contrast **3O**$^+$ is fully delocalized. Again, electrostatic repulsion may primarily be attributed for elongated *r*1. Expectedly this effect is much less for S$^+$ isomers. The effect of electron correlation on geometry is very significant in case of **1O**$^+$.

In general, the MP2 and B3LYP methods are in excellent agreement with each other (Tables 1$-$6), for all of the structures considered here. Comparison with the previous calculations on N-, P-, and C$^-$-substituted analogues indicate that improving the quality of basis set has only minor impact on the geometries. All of the bond lengths are between single and double bonds and are close to those in monosubstituted benzenes. Thus, disubstitution effectively maintains the delocalized pattern of the planar 6π-system, and none of the perturbations enforces significant bond localization. Thus, the strain is shown only in the internal bond angles and not on bond lengths. The effect of the method (HF, B3LYP, or MP2) does not have any noticeable

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Table 1: Important Optimized Geometrical Parameters (Bond Lengths, *r*1−*r*4, in Å and Angles, *a*1−*a*4, in Degrees) of **1N**, **2N**, and **3N** at HF, B3LYP, and MP2 Levels Using 6-31G* Basis Set

	1N			**2N**			**3N**		
parameter	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
*r*1	1.310	1.336	1.348	1.319	1.338	1.343	1.319	1.338	1.345
*r*2	1.310	1.336	1.344	1.321	1.339	1.344	1.386	1.397	1.396
*r*3	1.394	1.399	1.398	1.382	1.394	1.393			
*r*4	1.367	1.384	1.386						
*a*1	120.0	119.3	119.0	126.9	127.4	127.4	116.6	115.8	115.3
*a*2	123.3	123.8	124.1	116.2	115.7	115.6	121.7	122.1	122.4
*a*3	116.7	116.8	116.9	122.3	122.4	122.3			
*a*4				116.0	116.4	116.9			

Table 2: Important Optimized Geometrical Parameters (Bond Lengths, *r*1−*r*4, in Å and Angles, *a*1−*a*4, in Degrees) of **1P**, **2P**, and **3P** at HF, B3LYP, and MP2 Levels Using 6-31G* Basis Set

	1P			**2P**			**3P**		
parameter	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
*r*1	2.076	2.124	2.110	1.720	1.741	1.738	1.731	1.750	1.745
*r*2	1.742	1.752	1.747	1.725	1.745	1.741	1.379	1.388	1.392
*r*3	1.373	1.388	1.392	1.386	1.395	1.396			
*r*4	1.401	1.404	1.401						
*a*1	105.5	104.9	105.1	130.6	131.5	131.6	103.2	102.5	102.3
*a*2	128.8	129.3	129.4	103.7	102.9	102.9	128.4	128.7	128.8
*a*3	125.7	125.8	125.5	128.0	128.4	128.5			
*a*4				125.9	126.0	125.7			

Table 3: Important Optimized Geometrical Parameters (Bond Lengths, *r*1−*r*4, in Å and Angles, *a*1−*a*4, in Degrees) of **1C**$^-$, **2C**$^-$, and **3C**$^-$ at HF, B3LYP, and MP2 Levels Using 6-31G* Basis Set (Geometrical Parameters Given in Parenthesis Are Obtained Using 6-31+G* Basis Set)

	1C$^-$			**2C**$^-$			**3C**$^-$		
parameter	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
*r*1	1.509	1.511 (1.436)	1.498 (1.435)	1.428	1.441 (1.433)	1.444 (1.435)	1.417	1.426 (1.420)	1.427 (1.421)
*r*2	1.406	1.422 (1.415)	1.432 (1.428)	1.421	1.428 (1.421)	1.425 (1.418)	1.405	1.418 (1.420)	1.419 (1.422)
*r*3	1.418	1.422 (1.418)	1.415 (1.413)	1.395	1.409 (1.410)	1.410 (1.412)			
*r*4	1.374	1.396 (1.399)	1.401 (1.404)						
*a*1	115.3	115.3 (117.8)	115.1 (117.4)	131.8	133.0 (128.6)	133.6 (128.9)	107.8	107.7 (110.8)	107.1 (110.6)
*a*2	126.5	126.8 (123.7)	127.3 (124.3)	110.3	109.3 (112.8)	108.7 (112.5)	126.1	126.2 (124.6)	126.5 (124.7)
*a*3	118.2	117.9 (118.5)	117.6 (118.4)	123.6	124.4 (122.8)	125.1 (123.3)			
*a*4				120.4	119.6 (120.0)	118.9 (119.5)			

impact on the bond angles. Comparisons with previous studies indicate that the quality of the 6-31G* basis set is adequate for studying this class of compounds. Thus, the 6-31G* basis set at the MP2 level is adequate to calculate equilibrium geometries for all cases except for dianionic systems where the 6-31+G* basis set, augmented with a set of diffuse functions, has to be employed. Although, **1C**$^-$ and **1O**$^+$ show some tendency to give localized geometries with small bond length alternation in the ring, in general bond delocalization is very high in all isomers. In both the cases, **1C**$^-$ and **1O**$^+$**,** HF grossly overestimates bond alternations compared to both the MP2 and B3LYP levels.

3.2. Relative Energies of the Positional Isomers. The relative energies of all of the isomers considered in this study at HF, B3LYP, and MP2 levels using the 6-31G* basis set are given in Table 7. The quantitative differences between HF and the other two levels are significant, indicating the need for the inclusion of electron correlation. Although the geometries are very similar at the MP2 and B3LYP levels, the energetics are not; except for N-substituted ones, and even the trends are not matching in some cases, viz., Si$^-$ and S$^+$ substituents (Table 7). Single-point energies at MP3, MP4SDQ, CCSD and CCSD(T) levels show trends (Table 8) that are very similar to that of the MP2 level. The nonoscillations in predicting the relative stability ordering of the positional isomers in the perturbation series imparts confidence in believing the MP2 numbers. The best estimate of relative energies are obtained using the following procedure (eq 1) for the neutral and dicationic species. ZPE corrections are done with scaled B3LYP frequencies, and the improvement with basis set is gauged at MP2 level as shown in eq 1.

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

For the anionic systems (the C$^-$ and Si$^-$ substitutions), the best estimate is obtained using eq 2.

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

Comparison of Tables 7 and 8 clearly shows the superiority of the MP2 method over B3LYP in all cases, except for O$^+$-

Table 4: Optimized Geometrical Parameters (Bond Lengths, $r1-r4$, in Å and Angles, $a1-a4$, in Degrees) of **1Si**$^-$, **2Si**$^-$, and **3Si**$^-$ at HF, B3LYP, and MP2 Levels Using 6-31G* Basis Set (Geometrical Parameters Given in Parenthesis Are Obtained Using 6-31+G* Basis Set)

	1Si$^-$			**2Si$^-$**			**3Si$^-$**		
parameter	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
$r1$	2.329	2.379 (2.370)	2.355 (2.346)	1.822	1.844 (1.836)	1.844 (1.837)	1.850	1.865 (1.863)	1.856 (1.854)
$r2$	1.876	1.876 (1.870)	1.862 (1.860)	1.841	1.859 (1.856)	1.852 (1.850)	1.389	1.400 (1.403)	1.406 (1.410)
$r3$	1.378	1.399 (1.403)	1.407 (1.410)	1.396	1.406 (1.410)	1.407 (1.411)			
$r4$	1.415	1.415 (1.418)	1.406 (1.411)						
$a1$	101.8	101.5 (101.8)	101.7 (102.0)	128.3	130.1 (128.1)	130.8 (128.7)	101.1	100.3 (101.6)	100.2 (101.6)
$a2$	130.6	130.8 (130.4)	131.0 (130.6)	103.9	102.3 (104.0)	101.7 (103.5)	129.4	129.8 (129.2)	129.9 (129.1)
$a3$	127.6	127.7 (127.8)	127.3 (127.3)	127.5	128.6 (127.8)	129.1 (128.4)			
$a4$				128.8	128.2 (128.2)	127.6 (127.6)			

Table 5: Important Optimized Geometrical Parameters (Bond Lengths, $r1-r4$, in Å and Angles, $a1-a4$, in Degrees) of **1O**$^+$, **2O**$^+$, and **3O**$^+$ at HF, B3LYP, and MP2 Levels Using 6-31G* Basis Set

	1O$^+$			**2O$^+$**			**3O$^+$**		
parameter	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
$r1$	1.362	1.459	1.459	1.269	1.295	1.298	1.293	1.322	1.334
$r2$	1.265	1.286	1.293	1.342	1.359	1.361	1.394	1.403	1.400
$r3$	1.444	1.440	1.427	1.373	1.388	1.388			
$r4$	1.345	1.371	1.383						
$a1$	120.6	118.8	118.8	120.4	120.8	121.1	126.5	124.7	123.9
$a2$	122.6	123.7	123.6	122.5	122.0	121.7	116.8	117.7	118.0
$a3$	116.8	117.5	117.6	119.3	119.2	119.2			
$a4$	-	-	-	116.0	116.8	117.1			

Table 6: Important Optimized Geometrical Parameters (Bond Lengths, $r1-r4$, in Å and Angles, $a1-a4$, in Degrees) of **1S**$^+$, **2S**$^+$, and **3S**$^+$ at HF, B3LYP, and MP2 Levels Using 6-31G* Basis Set

	1S$^+$			**2S$^+$**			**3S$^+$**		
parameter	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
$r1$	2.030	2.075	2.026	1.670	1.691	1.679	1.671	1.699	1.694
$r2$	1.649	1.679	1.682	1.701	1.714	1.689	1.383	1.390	1.393
$r3$	1.421	1.413	1.400	1.381	1.393	1.399			
$r4$	1.366	1.392	1.409						
$a1$	106.5	106.2	106.8	130.7	130.5	130.1	106.2	105.5	105.2
$a2$	129.2	128.9	128.5	104.6	104.7	105.3	126.9	127.3	127.4
$a3$	124.3	124.9	124.7	128.1	127.6	127.1			
$a4$				124.0	125.0	125.0			

disubstituted positional isomers. Surprisingly, in this case B3LYP gives a better agreement with the CCSD(T) result, and the stability of the para isomer (**3O**$^+$) is grossly overestimated at the MP2 level. Figure 1 gives the plot of relative energies of the positional isomers studied here using the best estimate. Thermodynamic stabilities of meta (**2**) and para (**3**) isomers are comparable in all cases and are different from that of ortho isomers. Between meta and para, the meta form is more stable for P, N, Si$^-$, and O$^+$, while para is preferred for C$^-$ and S$^+$ substituents. Factors that control the relative stabilities of the positional isomers are discussed next.

3.2.1. Repulsion between the Lone Pairs. The repulsion between the lone pairs appears to be the most straightforward factor which accounts for the lower stability of the ortho isomer, when compared with that of the para and meta isomers. Figure 2 gives the correlation of the three occupied π orbitals and the bonding and antibonding combinations of lone pairs, designated as lp and lp* respectively, for the ortho isomer. The second row substituents exhibit normal behavior with the bonding (lp) combination lying lower than antibonding (lp*) combination,

Table 7: Relative Energies (in kJ mol^{-1}) of the Various Positional Isomers (Energies Are on the Geometries Optimized at the Same Level)

structure	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
1N	0.0	0.0	0.0
2N	−114.1	−94.8	−92.3
3N	−86.6	−77.8	−76.9
1P	0.0	0.0	0.0
2P	31.9	37.3	23.5
3P	39.7	44.3	35.5
1C$^-$	0.0	0.0	0.0
2C$^-$	−99.2	−88.6	−94.6
3C$^-$	−118.4	−113.5	−123.6
1Si$^-$	0.0	0.0	0.0
2Si$^-$	−3.2	3.7	−3.7
3Si$^-$	15.7	15.8	12.2
1O$^+$	0.0	0.0	0.0
2O$^+$	−335.2	−261.1	−277.0
3O$^+$	−197.4	−194.5	−239.2
1S$^+$	0.0	0.0	0.0
2S$^+$	−20.2	−1.1	−15.3
3S$^+$	3.6	5.2	−29.1

Table 8: Important Relative Energies (in kJ mol^{-1}) of Various Isomers Considered on MP2/6-31G* Geometries[a]

structure	MP3	MP4SDQ	CCSD	CCSD(T)	best estimate[b]
1N	0.0	0.0	0.0	0.0	0.0
	(−263.48779)	(−263.49677)	(−263.49758)	(−263.53761)	
2N	−96.0	−97.2	−97.5	−94.2	−91.3
3N	−78.9	−77.8	−78.2	−75.5	−73.5
1P	0.0	0.0	0.0	0.0	0.0
	(−835.97033)	(−835.97814)	(−835.97892)	(−836.01861)	
2P	27.4	24.5	25.3	24.3	20.7
3P	34.5	32.1	32.8	32.0	27.6
1C$^-$	0.0	0.0	0.0	0.0	0.0
	(−229.90396)	(−229.91380)	(−229.91350)	(−229.95362)	
2C$^-$	−96.8	−95.9	−96.8	−95.0	−65.2
3C$^-$	−122.1	−120.4	−121.5	−120.5	−82.7
1Si$^-$	0.0	0.0	0.0	0.0	0.0
	(−732.10752)	(−732.11716)	(−732.11708)	(−732.15605)	
2Si$^-$	−0.8	−5.2	−5.7	−6.6	−11.4
3Si$^-$	10.5	7.5	7.2	6.2	8.4
1O$^+$	0.0	0.0	0.0	0.0	0.0
	(−303.44671)	(−303.46634)	(−303.46496)	(−303.50596)	
2O$^+$	−286.1	−276.2	−278.4	−265.8	−260.3
3O$^+$	−219.5	−194.0	−195.9	−193.9	−189.3
1S$^+$	0.0	0.0	0.0	0.0	0.0
	(−948.83476)	(−948.84279)	(−948.84253)	(−948.88415)	
2S$^+$	−15.7	−21.0	−22.8	−22.5	−23.5
3S$^+$	−19.2	−16.3	−19.0	−21.3	−23.1

[a] All calculations are done in 6/31G* basis set. The total energies (in hartrees) of only the reference structures are given. [b] The best estimates are done by employing eq 1 for neutral and cationic systems and eq 2 for anionic systems.

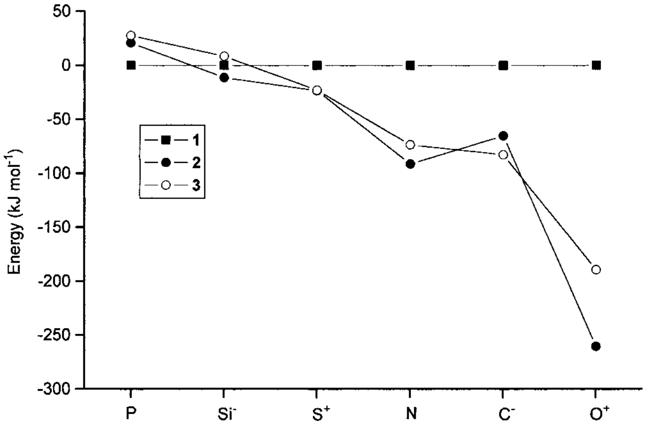

Figure 1. Best estimates of relative energies (kJ mol^{-1}) of the positional isomers. **1**, **2**, and **3** correspond to ortho, meta, and para isomers, respectively.

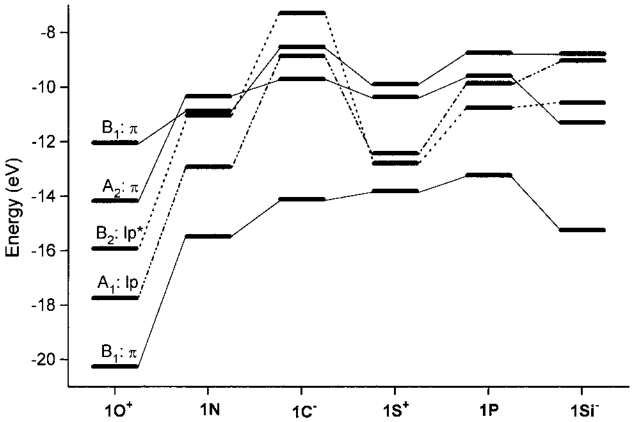

Figure 2. The correlation of the orbital energies of ortho-disubstituted benzenes. To fit to the same scale, an amount of 12 eV is added to the dicationic orbital energy values, and the same is deduced for the dianionic systems. This is done after monitoring the shifts in the orbitals upon adding and removing two electrons from their neutral counterparts. All π orbitals are connected with solid lines, lp−lp bonding combinations are connected with dotted lines, and dot−dot−dash lines connect lp−lp antibonding combination.

with significant separation indicating prominent lp−lp repulsion. Surprisingly, the lp* lies below the lp for all three of the third row substituents. The substantial lp−lp* gap in the ortho isomers of the second row substituents are to be traced to the long X−X distances. The stability of lp* over lp for the third row substituents clearly shows the lack of repulsion between the lone pairs and the presence of through-bond coupling. For C$^-$, the interaction between the lone pairs is very high, and thus the lp* orbital becomes higher than the occupied π-manifold and becomes the HOMO of the system. Splitting between the B$_1$ and A$_2$, which arises from the degenerate E$_u$ set of orbitals in benzene, increases proportionately with the electronegativity difference between the heteroatom and C. Similar correlation diagrams for the meta- and para- isomers are given in the Supporting Information.

3.2.2. Bond Strengths in the Twin VB Structures. One factor that distinguishes the stability of ortho isomer from meta and para isomers is the bond strengths in the twin Kekule structures and their resonance energies, as noticed by Hiberty et al.[14] for P isomers. The single and double bond strengths are taken from the previous studies,[31] and the sums of bond strengths for the twin Kekule forms of each of these isomers are given in Figure 3. Obviously, in this case both the Kekule forms of meta and para isomers will have identical bond strengths, with ortho being different.[32] Thus, this method will be able to distinguish between ortho versus meta/para. Accordingly, the ortho isomer is significantly less stable for N and O$^+$ substituents, with the latter experiencing the maximum unfavorable bond strengths in the ortho position. According to this criterion, Si$^-$ should

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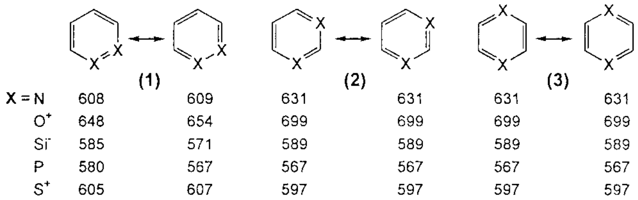
[31] (a) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (b) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

[32] The twin Kekule structures in the ortho isomer have different bonds (two X=C, two C=C, one C−X, and one C−C bonds in one Kekule form and one X−X, two C=X, one C=C, two C−C bonds in the other). However, both the Kekule structures in the meta and para isomers have two C=X, two C−X, one C−C, and one C=C bonds (Figure 3).



X =	(1)	(1)	(2)	(2)	(3)	(3)
N	608	609	631	631	631	631
O^+	648	654	699	699	699	699
Si^-	585	571	589	589	589	589
P	580	567	567	567	567	567
S^+	605	607	597	597	597	597

Figure 3. Bond strengths of the twin Kekule structures obtained by using bond increment scheme for ortho, meta, and para isomers. All values are in kcal mol^{-1} (1 kcal = 4.18 kJ).

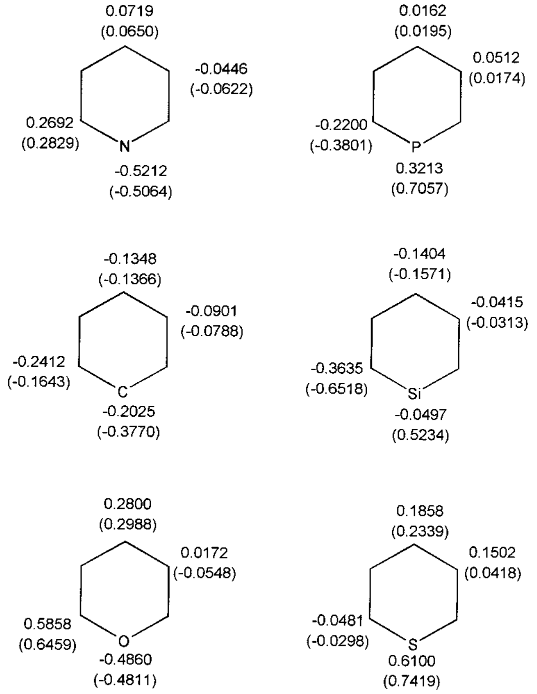


Figure 4. Mulliken and natural atomic charges (values in parentheses) of the mono substituted isomers at HF/6-31G* level on MP2/6-31G* geometries. Calculations are done on appropriately charged molecules.

show a marginal preference for meta/para positions over ortho, while P and S$^+$ should show a clear preference for ortho position. However, as it is not the sole determining factor that decides the relative stabilities (vide infra), a one-to-one correspondence is not observed.

3.2.3. Topological Charge Stabilization. Gimarc's rule of TCS met with tremendous success in predicting the relative stabilities of the positional isomers.[33] According to this model, the more electronegative atoms occupy sites with higher electron density, and less electronegative substituents occupy sites with less electron density. We make an attempt here to apply the same rule in predicting the relative preferences for further substitutions on monosubstituted benzenes. Consequently, the charge analyses on monoskeletally substituted benzene isomers are done using Mulliken and natural population analyses (Figure 4), which provide preferences for the occupation site to the second substituent. Therefore, in the N-substituted case, as N is more electronegative than C and it prefers to occupy a site with higher electron density, the preference for the meta position is highest, followed by the para and ortho positions. This clearly explains the relative stabilities of these isomers. Similarly, O$^+$ and Si$^-$ substituents prefer the meta site, while S$^+$ prefers to occupy the para position. However, the rule could not explain the relative stability orderings in P isomers. This is understandable because topological charge stabilization is only one factor among many intricate factors that control the relative stabilities. In P isomers, the relative bond strengths also play a dominant rule, which places the ortho isomer in an advantageous position. However, the relative stability orderings of the meta and para isomers are correctly described in all of the cases. Thus, the TCS model is very helpful in understanding the relative stabilities of the positional isomers and successfully explains the preferences between the meta and para positions in all of the cases. The application of the rule of TCS successfully explains the relative stabilities of the positional isomers involving different heteroatoms in general. It is interesting to note that the relative positional isomer stabilities in some of the recently studied 6π-planar systems can readily be explained by this rule.[34]

Table 9: Energies of Formation Corresponding to Homodesmic Equations (eq 3)[a]

	ΔE (kJ mol^{-1})					
structure no.	N	P	C^-	Si^-	O^+	S^+
1	86.7	−20.4	581.2	380.0	1016.8	657.7
2	−5.6	3.1	486.6	376.4	739.8	642.4
3	9.7	13.1	457.7	392.3	777.7	628.6

[a] The MP2/6-31G* level is used.

3.3. Homodesmic Equations. The ΔE of the reactions corresponding to the following homodesmic equation (eq 3) are given in Table 9.

$$2(CH)_5X \rightarrow (CH)_4X_2 + (CH)_6 \qquad (3)$$

In general, disubstitution leads to destabilization, except in the case of **1P** and **2N**, for the planar aromatic systems. Understandably, the destabilization is more significant in ionic systems due to the Coulombic repulsion, with the cationic ones being the most destabilized. However, in the neutral cases the stabilities of disubstituted isomers are similar to those of monosubstituted ones. Thus, in general thermodynamic stability decreases drastically going from mono- to disubstitution in ionic systems and does not change significantly for neutral analogues, except for **1N** where the destabilization is attributed to the strong lp−lp repulsion.

3.4. Localization versus Delocalization. It is rather surprising to note that all of the structures exhibit highly delocalized geometries, except in cases where a strong electrostatic repulsion is present. This is in contrast to the scenario in polycyclic aromatic hydrocarbons, as virtually every other planar aromatic system, such as naphthalene, phenylenes, fullerenes, and buckybowls, exhibits a great degree of localization,[35] due to the π-distortivity which is inherent in cyclic conjugated systems. Here a reduction of symmetry and perturbations with varying electronegativities and charges do not seem to bring in localization, which may point to the fact that π-distortivity is much less in this system compared to that in the parent system, benzene. According to Shaik's Kekule crossing model, the responsible factor for the π-distortivity is large vertical excitation gap between the two Kekule forms, which in turn depends on double bond strength, thereby leading to weaker double bonds, resulting in lower vertical gaps.[36] Obviously, the vertical gap

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[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.* **1999**, *103*, 2141.

[35] (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.

[36] Shaik, S.; Zilberg, S.; Haas, Y. *Acc. Chem. Res.* **1996**, *29*, 211.

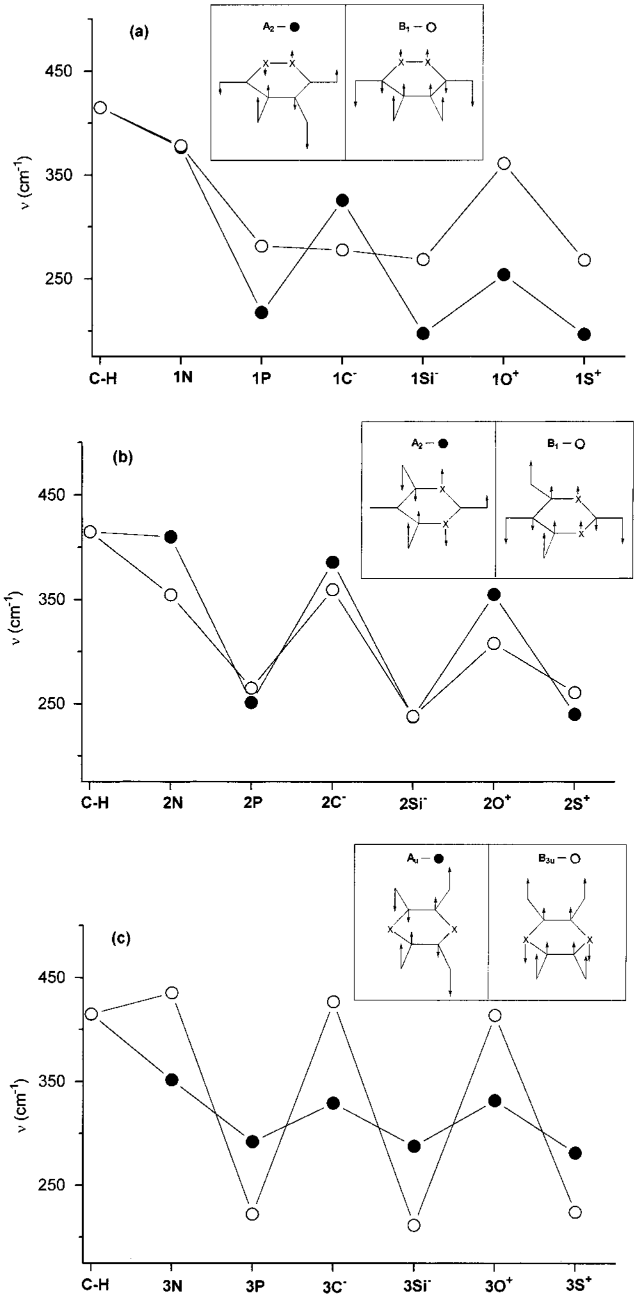

Figure 5. Correlation of normal modes corresponding to out-of-plane vibrations of (a) ortho, (b) meta, and (c) para isomers. The out-of-plane E_u mode in benzene splits into two A_2 and B_1 (in ortho and para) and as A_u and B_{3u} (in para) due to lowering of symmetry. These normal modes which corresponds to out-of-plane distortions are given in insets. All substituents show virtually the same characteristics except in **1C**$^-$ where the mode is exclusively localized to skeleton with little contribution from hydrogens.

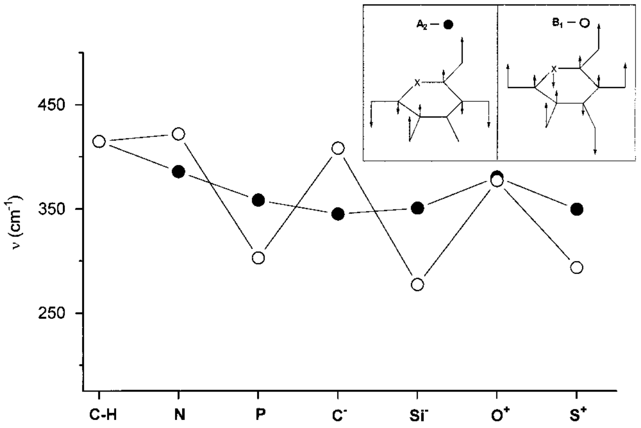

Figure 6. The correlation of normal modes corresponding to out-of-plane vibrations in monosubstituted benzenes. Schematic representation of the A_2 and B_1 out-of-plane modes are shown in the inset. All substituents have virtually the same characteristics.

is reduced substantially as more heteroatom substituents replace the CH groups in the benzene ring, which in turn reduces π-distortivity. Thus, high delocalization present in these heteroaromatics is probably due to less π-distortivity in these compounds compared to that of parent benzene molecule. *Thus, it may be misleading to attribute high delocalization of π-systems to high stability. Ironically, the reverse may actually be true, that weak π-systems might result in strongly delocalized structures.*

3.5. Out-of-Plane Distortions. The normal mode corresponding to out-of-plane distortions in benzene is a degenerate E_u mode, which splits into A_2 and B_1 modes for ortho and meta isomers (C_{2v} point group) and into B_{3u} and A_u modes for the para isomer (D_{2h} point group). The correlations of these out-of-plane distortive frequencies are given in Figure 5a−c. Figure 5a depicts the variation of normal modes, A_2 and B_1, as a function of disubstitution in ortho isomers, which shows that the magnitude of frequencies corresponding to out-of-plane distortions decreases, indicating the susceptibility of the planar structure to pucker. While the N substituent has only a minor effect; **1P**, **1Si**$^-$, **1O**$^+$, and **1S**$^+$ experience sharp decrease in the magnitude of the A_2 mode. Interestingly the second row substituents with higher lp−lp repulsions when compared to third row counterparts have higher frequencies, clearly indicating that lp−lp repulsion has only a minor impact on the out-of-plane distortivity. The lower frequencies in **1C**$^-$ and **1O**$^+$ may be traced partly to Coulombic repulsion. The nature of the vibrational modes is ascertained with the help of the MOPLOT program.[37] The pictorial depiction of the modes corresponding to each of these motions is given as insets in Figure 5a−c. Differences in the modes as a function of substituent are negligible, and thus only an idealized picture is given.

The meta isomers show similar trends to those of ortho (Figure 5b). However, here as well as in para substituions (Figure 5c), a clear demarcation between the vibrational modes of the second and third row is seen. Interestingly, while the gap between the two out-of-plane distortive modes is very little in meta, and it is significant in the ortho and para isomers. In para isomers the B_{3U} mode, which is mostly based on the heteroatoms, exhibits interesting variations as a function of the substituent: While similar or even a little exaltation of its frequency is observed when compared to pristine benzene for second row substituents, the magnitude of this frequency becomes extremely low for the third row substituents (Figure 5c). The A_u mode, which is devoid of contribution from the heteroatoms, remains less affected. Therefore, the propensity to undergo out-of-plane distortion is higher for substituents involving third row atoms. The other reasons for lower vibrational frequencies is due to the fact that third row substituents bring in enormous angular strain in the six membered ring, and out-of-plane deviations definitely help in decreasing the angular strain.

Figure 6 depicts the correlation of A_2 and B_1 modes where A_2 is devoid of contribution from X, and B_1 has substantial contribution from X. The frequencies of out-of-plane distortive

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

mode B_1 are clearly much lower for the third row substituents compared to those of the second row. In contrast, A_2 has much smaller variation, indicating that ring puckering is mainly controlled by the pyramidalization tendency of the heteroatom substituent and weaker C−X π-bond strengths where X is a third row substituent rather than by lp−lp repulsion.

4. Conclusions

Ab initio MO and DFT studies on skeletally disubstituted benzenes, with the substituent bearing a lone pair, confirm that the planar structures are fully delocalized in all three isomeric positions (ortho, meta, and para) and are minima on their respective potential energy surfaces. The relative stability of the positional isomers is dictated by a combination of the factors, such as (a) lp−lp interaction, (b) topological charge stabilization, (c) electrostatic repulsion, (d) the bond strengths of the constituent Kekule structures. The effect of lp−lp repulsion is minimal in arresting the delocaliztion in the third row substituted isomers. Significant lp−lp repulsive interactions are present in the second row substituted ortho isomers as reflected in their energetics. The rule of TCS, although not decisive, is an extremely helpful guiding tool in predicting the relative stabilities. The strain due to the substitution by large heteroatoms is shown exclusively on bond angles and not on bond lengths and thus did not trigger any bond fixation. These systems are expected to face lower π-distortivity, which is given as a factor responsible for showing high bond delocalizaion. Therefore, it is argued that bond delocalization does not necessarily correspond to high stability. The out-of-plane distortivity upon substitution is analyzed in detail by correlating the normal modes of substituted and unsubstituted isomers. Thermodynamic stability, aromaticity, bond delocalization, reactivity, etc. of this class of compounds are often the net results of interplay among various competing factors, and straightforward correlations among the above quantities are not possible.

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Supporting Information Available: Tables of MP2/6-31G* optimized Cartesian coordinates, total energies, and ZPEs, Figures S1a and S1b depicting the correlation of three occupied π orbitals and bonding and antibonding combinations of the lone pairs of meta and para isomers, respectively, Figure S2 giving the Mulliken and the natural charges of the skeletally disubstituted benzenes (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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