# Restricted Geometry Optimization: A Different Way To Estimate Stabilization Energies for Aromatic Molecules of Various Types

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*Received: November 10, 2006; In Final Form: February 9, 2007*

At RHF, MPn, and DFT levels, a procedure of geometry optimization under the restrictions of $\pi$-orbital interactions (GOR) was developed, thus providing a conjugated molecule with the following two types of localized reference geometries: a "GL" geometry where all double bonds are localized, and *n* different "GE-n" geometries, in each of which only two double bonds were permitted to conjugate. Interestingly, the molecular energy differences between the corresponding pairs of GE-*n* and GL geometries were found to be additive in each of the acyclic polyenes, and these were not additive for benzene. As a result, an extra stabilization energy (ESE) value of −39.0 kcal/mol was found in benzene. Afterward, GOR was applied to benzene- and furan-like species, strained aromatic molecules, and substituted benzenes, and the calculated ESEs for these molecules were found to be in reasonable ranges. The GOR can isolate a specific group from other groups, and it has several special functions. First, with regard to the substituent effect, the ESE difference between substituted benzene and benzene can be partitioned into conjugative and inductive parts. Second, the behavior of strained aromatic molecules can be ascertained from the roles of their resonance interactions, strained-induced bond localization (SIBL), and inductive effects, indicating that it is resonance interactions, rather than SIBL, which are responsible for localizing double bonds. Emphatically, it is the GL and GE-*n* geometries of aromatic molecules, rather than nonaromatic compounds, which can be used as the reference structures for calculating ESE. Particularly, these localized geometries are no longer arbitrary.

## 1. Introduction

Aromaticity is one of the most important general concepts in organic chemistry.[1] Now, as indicated by Balaban,[2] aromaticity extends equally well to both inorganic and organometallic chemistry. Many efforts have been made in order to evaluate the aromaticities of aromatic molecules of various types. Quantities such as the Hückel resonance energy,[3a] Dewar resonance energy,[3b] Hess−Schaad resonance energy,[3c] and Schleyer's isomerization stabilization energy (ISE)[3d] have all been suggested as being the important energetic criterion. As with the energetic criterion, the harmonic oscillator model of aromaticity[4] may be considered to be the most reliable among the aromatic indices based on geometry, while the nucleus-independent chemical shift[5] is often considered to be a better criterion.[6] In addition, many empirical values of resonance energy, calculated by using heats of reaction (combustion, hydrogenation, dehydrogenation, tautomeric equilibria, etc.),[7] have been reported, and the application of isodesmic and homodesmotic reactions has furthered the rapid progress in the field of aromaticity.[6] Recently, the following indicators of aromaticity, referred to as the para-delocalization index[8a,8b] and the six-center delocalization index,[8c,8d] were both defined as electron-delocalization criteria.

So far, the main problem in estimating various resonance energies is still deciding the choice of an appropriate reference structure. Particularly, the choice is always arbitrary, and strain, hyperconjugation, and differences in the types of bonds and hybridization are not taken into account.[3d] In consequence, the estimated stabilization energies, even for benzene, may range by over 50 kcal/mol.[6,9] Accordingly, a reasonable reference structure must satisfy the following requirements: (i) the reference structure is a particular geometry (or geometries) of the aromatic molecule, that is in order to ensure that there are no obvious differences in the types of bonds and the hybridization as well as in the strain and hyperconjugation between the aromatic molecule and its reference structure; (ii) the geometry of the reference structure should be obtained from the geometry optimization to guarantee that the reference structure is not arbitrary, and that its $\pi$ systems should be localized on their respective bonds; (iii) the energy effects related to the reference structure are additive for acyclic polyenes but are not additive for aromatic molecules.

In order to obtain such reference structures, a program for optimizing the geometry based on restrictions of the $\pi$ orbital interactions between the double bonds has been developed, hereafter abbreviated to the "restricted geometry optimization". As detailed in this work, the restricted geometry optimization is a new way to evaluate the stabilization energies for six- and five-membered rings, substituted benzenes, and strained aromatic compounds. Moreover, this method makes it feasible to investigate quantitatively the following: substituent effects and their influence on the aromaticity of the phenyl ring; resonance interactions, strained-induced bond localization (SIBL) and inductive effects, and their roles in determining the geometry of strained aromatic molecules.

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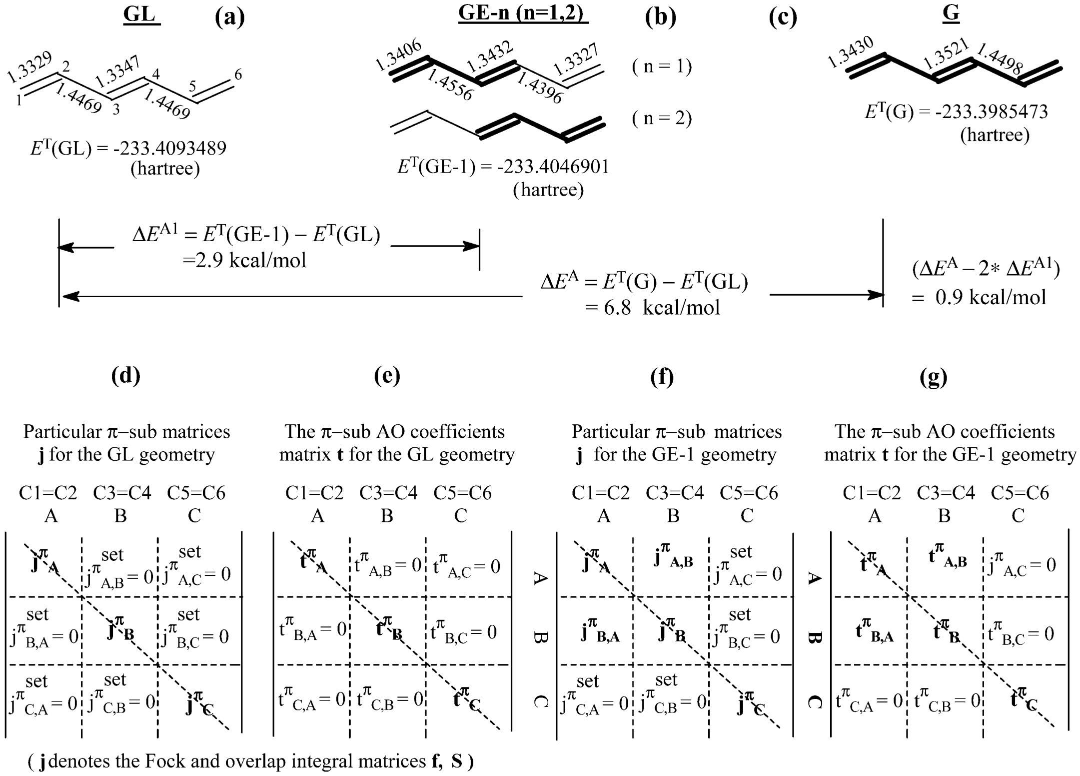


**Figure 1.** G (ground state geometry), GL (geometry having localized double bonds), and GE-*n* (the *n*th particular geometry) geometries of hexatriene were obtained from the full and restricted geometry optimizations at the B3LYP/6-31G* level; (d and f) the settings for optimizing the GL and GE-1 geometries; (e and g) the $\pi$ blocks of the coefficient matrices for the GL and GE-1 geometries. In a specific geometry, the thick and thin lines indicate that all the $\pi$ orbital interactions between the double bonds have been set equal to zero except for those between the double bonds denoted by the thick lines.

## 2. Computational Methods

In this work, all calculations were performed by using the PC GAMESS version (Granovsky, A. A., http://classic-.chem.msu.su/gran/gamess/index.html) of the GAMESS (US) QC package.[10] The restricted optimizations of various geometries were performed at B3LYP/6-31G* if there is no special indication. Afterward, a frequency calculation on the restrictedly optimized geometry was performed.

The restricted geometry optimization is based on the fundamental principle of the method in which the specific elements of the AO (atomic orbital) Fock matrix **f** are deleted.[11,12] In order to ensure that the $\pi$ systems are absolutely localized on their respective double bonds while the $\pi$ bonds are localized on specific bonds, the restricted geometry optimization for hexatriene (*trans*-1,3,5-hexatriene, Figure 1), for example, should be performed under the following conditions: in each SCF iteration, the elements of the AO Fock and the overlap integral matrices **f** and **s**, denoted as $f^{\pi}_{ij}$ and $s^{\pi}_{ij}$, are set equal to zero (at the DFT and ab initio levels, it is impossible for the SCF iteration to converge if the related elements $s_{ij}$ are not set equal to zero) when AO $\phi_i \in$ the $\pi$ system of the double bond P, and AO $\phi_j \in$ the $\pi$ system of the double bond Q, where P, Q = A, B, C, and P $\neq$ Q (Figure 1d). The restricted geometry optimization provides hexatriene with a GL (geometry having localized double bonds) geometry in which three $\pi$ systems have been artificially localized on the HC1H═C2H− (A), −HC3═C4H− (B), and −HC5═ HC6H (C) double bonds (groups), and the $\sigma$ system is delocalized over the whole molecular framework (Figure 1e).

A GE-*n* (the *n*th particular geometry) geometry of hexatriene can also be obtained from the restricted geometry optimization when all of the elements $f^{\pi}_{ij}$ and $s^{\pi}_{ij}$ between the double bonds are set equal to zero (Figure 1b,f) except for those between a specific pair of double bonds. When $n = 1$, for example, the $\pi$ systems of the GE-1 geometry have been artificially localized on the HC1H═C2H−HC3═C4H− and −HC5═HC6H groups (Figure 1g).

In this work, molecular energies of the G (ground state), GL, and GE-*n* geometries are denoted as $E^T$(G), $E^T$(GL) and $E^T$(GE-*n*), respectively.

## 3. Results and Discussion

**3.1. Molecular Energy Differences between Corresponding Pairs of G and GL Geometries Are Additive for Each Acyclic Polyene.** According to Figure 1f,g, the GE-1 geometry of hexatriene can be considered as a particular geometry that resulted from the $\pi$ orbital interactions between two localized double bonds, denoted as HC1H═C2H− and −HC3═C4H−, in the GL geometry. Interestingly, the C2−C3 single bond (1.4556 Å) in the GE-1 geometry of hexatriene, denoted by a thick line between the C1═C2 and C3═C4 double bonds (Figure 1b), is longer than the corresponding bond (1.4469 Å) in the GL geometry (Figure 1a). Meanwhile, the molecular energy difference $\Delta E^{A1} = [E^T(\text{GE-1}) - E^T(\text{GL})]$ between the GE-1 and GL geometries is 2.9 kcal/mol. In hexatriene, there are two particular geometries GE-*n* ($n = 1, 2$) that have the same molecular energy (Figure 1b), and $[\Delta E^{A} - (\Delta E^{A1} + \Delta E^{A2})] = [\Delta E^{A} - 2\Delta E^{A1}] = (6.7782 - 5.8470) = 0.9$ kcal/mol (Figure 1), where $\Delta E^{A} = [E^T(\text{G}) - E^T(\text{GL})]$ is the molecular energy difference between the G and GL geometries.

In a series of *trans*-polyenes H−(CH═CH)$_n$−H ($n$ = 3, 4, 5, 6, 7), as shown by the curved lines in Figure 2, the sum $\sum\Delta E^{An}$ of the energy differences $\Delta E^{An}$ is a linear function of the total number $n$ of double bonds in the polyene chain.

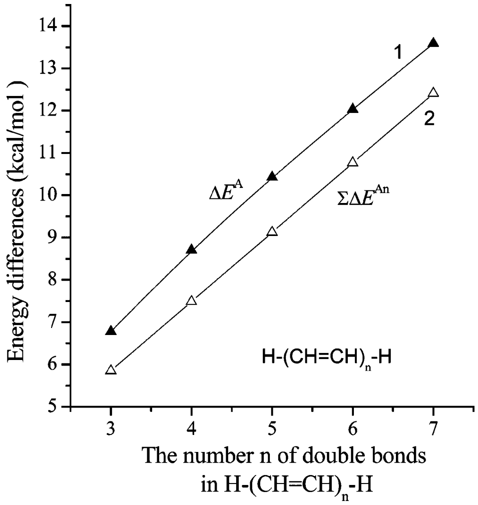


**Figure 2.** Molecular energy differences, $\Delta E^{A} = E^{T}(G) - E^{T}(GL)$, and the sum $\sum\Delta E^{An}$ are approximately the linear function of the total number $n$ of double bonds in *trans*-polyenes ($n = 3, 4, 5, 6, 7$). $\Delta E^{A} = 0.42716 + 2.3059n - 0.06112n^2$, and $\sum\Delta E^{An} = 0.93444 + 1.63653n$.

Particularly, the quantity ($\Delta E^{A} - \sum\Delta E^{An}$), i.e. the vertical distance between the two curved lines in Figure 2, slightly changes as $n$ increases. For example, $[\Delta E^{A} - 2\Delta E^{A1}] = 6.7782 - 5.8470 = 0.9$ kcal/mol ($n = 3$; hexatriene), $[\Delta E^{A} - (2\Delta E^{A1} + \Delta E^{A2})] = 8.7 - 7.5 = 1.2$ kcal/mol ($n = 4$; 1,3,5,7-octatetraene), and $[\Delta E^{A} - 2(\Delta E^{A1} + \Delta E^{A2} + \Delta E^{A3})] = 13.6 - 12.4 = 1.2$ kcal/mol ($n = 7$; 1,3,5,7,9,11,13-tetradecaheptaene), indicating that the energy differences $\Delta E^{An}$ for each of the acyclic polyenes are additive. According to the fact that the aromatic stabilization energy is usually calculated from additive schemes,[6,13] it is important that the energy differences $\Delta E^{An}$ for each of the polyenes were found to be additive.

**3.2. Extra Stabilization Energies of Benzene-like Species.** The total number $N$ of GE-$n$ geometries of a molecule depends upon the number of localized double bonds in the GL geometry, while the number $K$ of GE-$n$ geometries that have different molecular energies depends upon the symmetry of the GL geometry. In practical calculations therefore, $K$ corresponds to the number of GE-$n$ geometries that need to be optimized.

In the cases of benzene, $N = 3$ and $K = 1$, and the molecular energy difference $\Delta E^{A1} = E^{T}(\text{GE-1}) - E^{T}(\text{GL})$ between the GE-1 and GL geometries is 9.4 kcal/mol (Figure 3). If these three energy differences $\Delta E^{An}$ ($n = 1, 2, 3$, and $\Delta E^{A1} = \Delta E^{A2} = \Delta E^{A3}$) were additive, the expected geometry of the ground state of benzene would be similar to the FG (fictitious geometry) geometry in which the lengths of the single and double bonds would be equal to those of the C2$-$C3 and C1$=$C2 bonds in the GE-1 geometry. Correspondingly, the molecular energy difference $\Delta E^{A} = [E^{T}(\text{FG}) - E^{T}(\text{GL})]$ between the expected ground state (FG geometry) and GL geometry would be about $3\Delta E^{A1}$ (28.2 kcal/mol). In fact, the energy difference $\Delta E^{A}$ between the G and GL geometries is $-10.8$ kcal/mol (Figure 3), indicating that a $-39.0$ kcal/mol deviation from the additivity was found in the benzene molecule. In this work, the quantity $(\Delta E^{A} - 3\Delta E^{A1}) = -39.0$ kcal/mol is defined as the extra stabilization energy (ESE) of benzene. Of all the theoretical values of the resonance energy for benzene, the value $-39.0$ kcal/mol obtained from the restricted geometry optimization at B3LYP/6-31G* as well as the values of $-33.2$,[3d] $-33.9$,[14a] $-33.1$,[14b] and $-36.7$[14c] kcal/mol (all the positive stabilization energies that were reported in the original literature are changed to negative in this work) are closest to the well-known experimental value ($-36$ kcal/mol).[15] In the procedure for determining the ESE of benzene, emphatically, it is the restrictedly optimized geometries GL and GE-$n$ of benzene itself, rather than a nonaromatic molecule (or molecules), that are to be used as the reference structures. Moreover, the choices of the localized reference structures GL and GE-$n$ are no longer arbitrary, because these localized reference structures were obtained from the restricted geometry optimizations. Factors such as strain, hybridization effects, and conjugation and repulsive interactions are all taken into account. The restricted geometry optimization seems to be a reasonable procedure for calculating the resonance energies of various types of aromatic compounds.

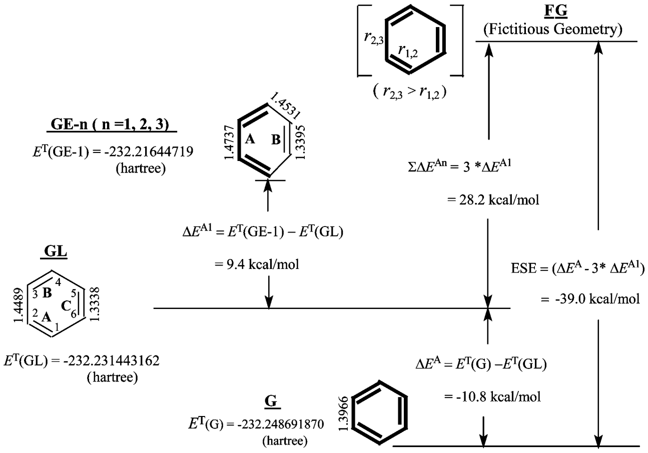


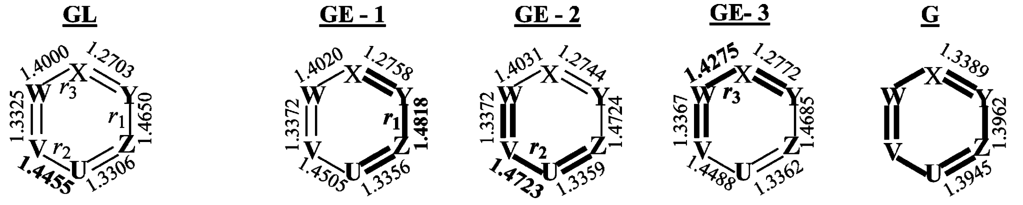
**Figure 3.** Procedure for calculating the extra stabilization energy (ESE) of benzene, and the G, GL, and GE-1 geometries, as indicated by the thin and thick lines, were obtained from the full and restricted geometry optimizations at the B3LYP/6-31G* level. The thin and thick lines have the same meanings as in Figure 1.

**TABLE 1: Extra Stabilizing Energies (ESEs) of Benzene, Energy Effects $\Delta E^{A1}$ Associated with the Local $\pi$ Interactions between the $-$C1$=$C2$-$ and $-$C3$=$C4$-$ Double Bonds, and the Corresponding Change, $dr_{2,3} = r_{2,3}(\text{GE-1}) - r_{2,3}(\text{GL})$, in the Length $r_{2,3}$ of the Single Bond $-$C2$-$C3$-$[a]**

| optimization methods | $\Delta E^{A1}$ | $dr_{2,3}$ (Å) | $\sum\Delta E^{An} = 3\Delta E^{A1}$ | $\Delta E^{A}$ | ESE = $E^{A} - \sum E^{An}$ |
|---|---|---|---|---|---|
| B3LYP/6-31G* | 9.4 | 0.0248 | 28.2 | −10.8 | −39.0 |
| B3LYP/6-311G** | 11.2 | 0.0273 | 33.6 | −6.5 | −40.1 |
| B3LYP/6-311G(2df,p) | 14.6 | 0.0536 | 43.9 | 2.7 | −41.2 |
| MP2(Full)/6-31G* | 46.9 | 0.0749 | 140.7 | 89.5 | −51.2 |
| MP2(Full)/6-311G** | 64.5 | 0.0860 | 193.5 | 136.1 | −57.3 |
| RHF/6-31G* | 27.8 | 0.0867 | 83.5 | 37.1 | −46.5 |
| RHF/6-311G** | 31.8 | 0.0987 | 95.3 | 46.7 | −48.6 |

[a] Energy unit in kcal/mol.

In order to determine which calculation method is more reasonable, the ground state geometries of benzene, as well as its GL and GE-$n$ ($n = 1, 2, 3$) geometries, were optimized by using the B3LYP, RHF, and MP2(Full) methods. As shown by the data presented in Table 1, the MP2 method provides benzene with the greatest stabilizing ESE, and the corresponding ESEs are greater in the absolute value than 50 kcal/mol. On the contrary, the absolute values of the ESE obtained from the B3LYP optimizations (about 40 kcal/mol) are the smallest. At the 6-31G* level, for example, the values of the ESE for benzene are $-39.0$ (B3LYP), $-46.5$ (RHF), and $-51.2$ (MP2) kcal/mol, and the corresponding values of $\Delta E^{A}$ are $-10.8$, 37.1, and 89.5 kcal/mol. Particularly, the size of the Gaussian basis set has a slight effect on the B3LYP value of the ESE. At the B3LYP level, for example, the values of the ESE for benzene are $-39.0$ (6-31G*), $-40.1$ (6-311G**), and $-41.2$ (6-311G(2df,p)). Therefore, B3LYP/6-31G* will be used to calculate the ESEs



The bond length difference $dr_n = r_n(\text{GE-n}) - r_n(\text{GL})$ ( n =1, 2, 3 ) ( X = N, Y = Z = U = V = W = C, Pyridine )

| $E^T$(GL) hartree | Nitrogen atoms | $\Delta E^{A1}$ kcal/mol | $dr_1$ Å | $\Delta E^{A2}$ kcal/mol | $dr_2$ Å | $\Delta E^{A3}$ kcal/mol | $dr_3$ Å | $\Delta E^A$ kcal/mol | **ESE** kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
| -248.2650680 | ( X=**N** ) | 5.6 | 0.0168 | 10.3 | 0.0268 | 10.1 | 0.0275 | -12.5 | -38.5 |
| -264.3004125 | ( Y=W=**N** ) | 10.9 | 0.0294 | 6.4 | 0.0185 | 5.6 | 0.0203 | -14.6 | -37.5 |
| -264.2982518 | ( X=U =**N** ) | 3.8 | 0.0110 | 11.0 | 0.0299 | 11.0 | 0.0299 | -11.9 | -37.8 |
| -264.2705978 | ( X=W =**N** ) | 6.1 | 0.0167 | 6.1 | 0.0167 | 9.9 | 0.0413 | -10.7 | -32.6 |
| -280.3375261 | ( X=Z =V=**N** ) | 6.3 | 0.0225 | 6.3 | 0.0225 | 6.3 | 0.0225 | -17.1 | -36.1 |
| -296.2997324 | ( X=Y =U=V=**N** ) | 3.8 | 0.0131 | 11.2 | 0.0502 | 3.8 | 0.0131 | -13.4 | -32.2 |

$$\text{EXE} = \Delta E^A - (\Delta E^{A1} + \Delta E^{A2} + \Delta E^{A3}) \text{ where } \Delta E^A = E^T(\text{G}) - E^T(\text{GL}) \text{ and } \Delta E^{An} = E^T(\text{GE-n}) - E^T(\text{GL}) \text{ ( n= 1, 2, 3)}$$

**Figure 4.** ESEs for benzene-like species. The GL, GE-*n*, and G geometries were obtained from the full and restricted geometry optimizations at the B3LYP/6-31G* level. The thin and thick lines have the same meanings as in Figure 1.

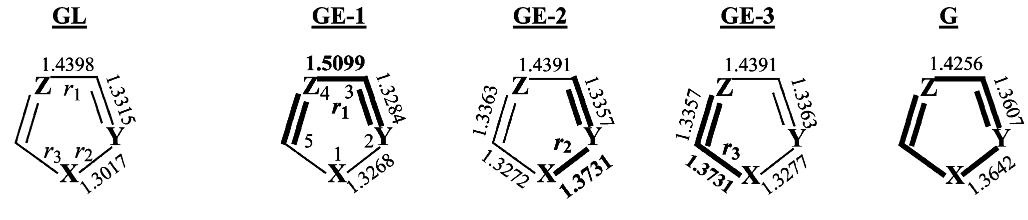
for aromatic molecules of various types, because the B3LYP/6-31G* ESE value of −39.0 kcal/mol for benzene is closest to the experimental value (−36 kcal/mol).

At the B3LYP/6-31G* level, as shown by the data presented in Figure 4, the ordering of the ESEs for benzene-like species is as follows: |−39.0| (benzene) > |−38.5| (pyridine) > |−37.8| (pyrazine) > |−37.5| (pyrimidine) > |−36.1| (1,3,5-triazine) > |−32.6| (pyridazine) > |−32.2| (tetrazine) kcal/mol. The theoretical and experimental stabilization energies of benzene-like species reported in the literature depend strongly on the reference structures and calculation models used. The stabilization energies (denoted as the Bird's REs in this section) of benzene-like species, obtained from Bird's modification of the harmonic oscillator stabilization energy (HOSE) model,[16] are −44.9 (1,3,5-triazine), −44.1 (pyridine), −43.9 (pyridazine), −40.1 (pyrimidine), −39.2 (tetrazine), −38.8 (pyrazine), and −38.4 (benzene). The ordering of the Bird's REs is inconsistent with that of the ESEs. Abnormally, however, all the Bird's REs of benzene-like species are greater in the absolute value than that (−38.4 kcal/mol) for benzene. The resonance energies, as determined from energies of hydrogenation, were found to be as follows: −36 (benzene), −34 (pyridine), −33 (pyrimidine), −32 (pyrazine), −25 (1,3,5-triazine), −26 (pyridazine), −16 (tetrazine),[17] and their ordering is in good agreement with that of the ESEs. When the range of a set of stabilization energies is defined as the difference between the maximum and minimum values of this set, the ranges were found to be the following: 6.5 kcal/mol for a set of Bird's REs, 20 kcal/mol for a set of resonance energies obtained from the energies of hydrogenation, and 6.8 kcal/mol for a set of ESEs obtained from the restricted geometry optimizations. As far as the ordering and range are concerned, it seems to be more reasonable that the ESE is used to evaluate the aromaticity of benzene-like species.

Frequency calculations indicated that the G, GL, and GE-*n* geometries of each benzene-like species correspond to minima with no imaginary frequency.

**3.3. Extra Stabilization Energy for Furan-like Species.** The GL, GE-*n* ($n$ = 1, 2, 3), and G geometries of furan-like species were optimized at B3LYP/6-31G*, and no imaginary frequency was found for each of these geometries. The difference between benzene- and furan-like species is in the number of $\pi$-electrons on each peripheral atom. In furan molecules, for example, two $\pi$-orbital interactions, resulting in the GE-2 and GE-3 geometries (Figure 5), involve the same $\pi$ system that consists of only a lone electron pair on the oxygen atom. In the GE-2 geometry resulting from the local $\pi$ interaction between the O1 atom and the C2═C3 double bond, the two bonded atoms O1 and C2 formally have three $\pi$ electrons, but the two bonded atoms in each GE-*n* geometry of benzene always have two $\pi$ electrons. In a furan-like species, therefore, three schemes for calculating the ESE are suggested, and these are as follows: ESE-I = $\Delta E^A - [\Delta E^{A1} + {}^2/_3(\Delta E^{A2} + \Delta E^{A3})]$, ESE-II = $\Delta E^A - [\Delta E^{A1} + {}^1/_2(\Delta E^{A2} + \Delta E^{A3})]$, and ESE-III = $\Delta E^A - [\Delta E^{A1} + \Delta E^{A2} + \Delta E^{A3}]$. The coefficient $^1/_2$ in the scheme for determining ESE-II means that the contributions $\Delta E^{A2}$ and $\Delta E^{A3}$, made by two local $\pi$ interactions involving the same lone pair, to $\sum\Delta E^{An}$ should be halved. The coefficient $^2/_3$ in the scheme for determining ESE-I means that the contributions made by the interactions involving three $\pi$ electrons, should be transferred into those made by the normal interaction involving two $\pi$ electrons. The orderings of these three sets of ESEs (B3LYP/6-31G*) are as follows: (i) ESE-I, |−32.5| (2-aza-pyrrole) > |−30.7| (pyrrole) ≈ |−30.7| (imidazole) > |−24.5| (furan) > |−24.3| (2-aza-furan) > |−24.2| (oxazole) kcal/mol; ESE-II, |−22.8| (imidazole) > |−22.2| (2-aza-pyrrole) > |−21.4| (pyrrole) > |−18.1| (oxazole) > |−17.1| (furan) > |−17.0| (2-aza-furan) kcal/mol; ESE-III, |−53.1| (2-aza-pyrrole) > |−49.4| (pyrrole) > |−46.5| (imidazole) > |−39.3| (furan) > |−39.0| (2-aza-furan) > |−36.3| (oxazole) kcal/mol. Obviously, the ESE-III is overestimated because most of the ESEs-III are greater in the absolute value than the ESE of benzene.

The Bird's modification of the HOSE mode provided imidazole and pyrrole with −34.9 and −31.8 kcal/mol of the resonance energy, respectively. Recently, the aromatic stabilization energies for furan-like species, based on heterocyclic reference systems and denoted as Cyrański's ASEs (aromatic stabilization energies), were reported, and these had values of −23.7 (2-aza-pyrrole), −20.6 (pyrrole), −18.8 (imidazole), −17.3 (2-aza-furan), −14.8 (furan), and −12.4 (oxazole) kcal/



The single bond length difference $dr_n = r_{n(GE\text{-}1)} - r_{n(GL)}$ ( X = O, Y = X = C Furan )

| $E^T$(GL) hartree | O and N Atoms | $\Delta E^{A1}$ kcal/mol | $dr_1$ Å | $\Delta E^{A2}$ 1 kcal/mol | $dr_2$ Å | $\Delta E^{A3}$ kcal/mol | $dr_3$ Å | $\Delta E^{A}$ kcal/mol | **ESE-I** kcal/mol | **ESE-II** kcal/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| -230.0740259 | (X=**O**) | 28.5 | 0.0701 | 22.2 | 0.0714 | 22.2 | 0.0714 | 33.5 | -24.5 | -17.1 |
| -210.2189096 | (X=**N**) | 26.6 | 0.0675 | 28.0 | 0.0638 | 28.0 | 0.0638 | 33.3 | -30.7 | -21.4 |
| -226.2577961 | (X=**N**, Z=**N**) | 26.2 | 0.0766 | 30.2 | 0.0660 | 17.2 | 0.0462 | 27.1 | -30.7 | -22.8 |
| -246.1144854 | (X=**O**, Z=**N**) | 28.0 | 0.0797 | 23.7 | 0.0727 | 12.6 | 0.0544 | 28.0 | -24.2 | -18.1 |
| -246.0758361 | (X=**O**, Y=**N**) | 20.7 | 0.0523 | 23.2 | 0.1041 | 20.9 | 0.0675 | 25.8 | -24.3 | -17.0 |
| -226.2443336 | (X=**N**, Y=**N**) | 20.1 | 0.0537 | 33.0 | 0.0811 | 28.6 | 0.0632 | 28.7 | -32.5 | -22.2 |

$$\text{ESE-I} = \Delta E^{A} - (\Delta E^{A1} + 2/3 * (\Delta E^{A2} + \Delta E^{A3}), \qquad \text{ESE-II} = \Delta E^{A} - (\Delta E^{A1} + 1/2 * (\Delta E^{A2} + \Delta E^{A3})$$

where $\Delta E^{A} = E^T(G) - E^T(GL)$ and $\Delta E^{An} = E^T(\text{GE-n}) - E^T(GL)$ ( n = 1, 2, 3)

**Figure 5.** Two types of ESEs for furan-like species were obtained from the restricted geometry optimizations at B3LYP/6-31G*. The thin and thick lines have the same meanings as in Figure 1.

mol.[18] The ordering of Cyrański's ASEs is totally consistent with the "rule"[3e] that aromaticity increases with decrease in the electronegativity difference between a heteroatom and its neighboring atoms, where the ordering of the ESE-I values is consistent with this "rule". Dewar's aromatic energy (−25.6 kcal/mol) of pyridine[13b] is smaller in the absolute value than the corresponding Schleyer's ISE (about −33 kcal/mol). However, Cyrański's ASE (−20.6 kcal/mol) for pyrrole is less in the absolute value than the corresponding Dewar's aromatic energy (−22.5 kcal/ mol[13b]). It seems that Cyrański's method underestimates the stabilization energy of furan-like species. Recently, the block-localized wave function (BLW) method provides furan and pyrrole with the following two sets of extracyclic resonance energies: −25.8 (furan) and −34.2 (pyrrole) kcal/mol; −12.8 (furan) and −17.9 (pyrrole) kcal/mol.[14c] The first set of extracyclic resonance energies are close to the −24.5 and −30.7 kcal/mol ESE-I values for furan and pyrrole, respectively.

As shown by the points 1−6 in Figure 6, six energy effects $\Delta E^{An}$, associated with the local $\pi$ interactions between the corresponding K1 (K = N, O) atom and the X2=Y3 (X, Y = N, C) double bond, are 33.0 (2-aza-pyrrole), 28.0 (pyrrole), 17.2 (imidazole), 23.2 (2-aza-furan), 22.2 (furan), and 12.6 (oxazole) kcal/mol, and their ordering is totally consistent with the "rule". However, the energy effect $\Delta E^{An}$ at point 5 is about 1 kcal/mol less than that at point 4, and the difference is so small that it cannot be ensured that the ESE-I for 2-aza-furan is in the absolute value greater than that for furan. On the basis of the fact that the ordering of the ESE-IIs is very different from that of the ESE-Is, as well as according to Nyulászi's conclusion[19] that the electron lone pair should mainly determine the aromatic stabilization of furan-like species, the scheme for calculating ESE-II seems to underestimate the role of the electron lone pair in determining ESE. Therefore, the first set of ESEs (ESE-I) for furan-like species seem to be more reasonable as far as the three sets of ESEs are concerned.

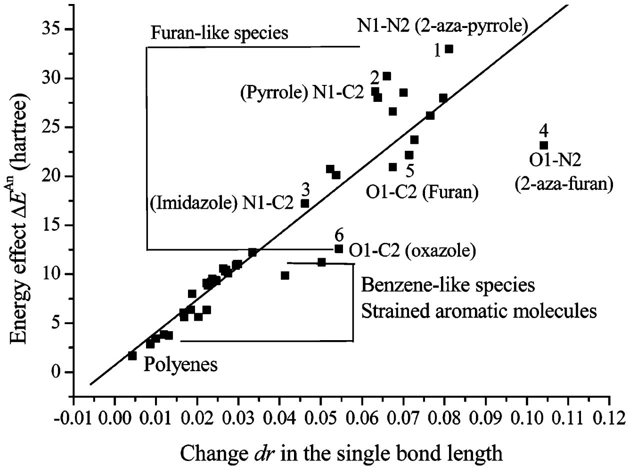
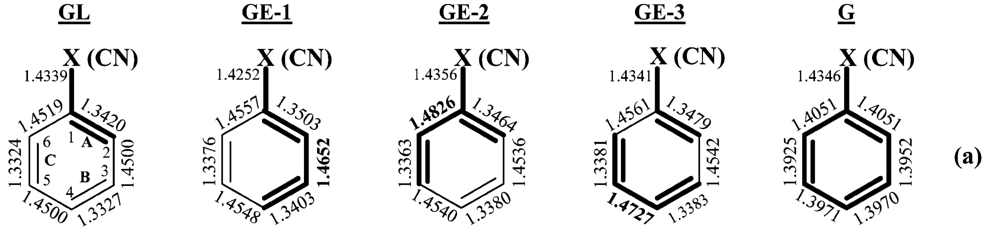


**Figure 6.** Relationship between the energy effect $\Delta E^{An}$ and the d*r*, where d$r$ = [$r_n$(GE-*n*) − $r_n$(GL)] is the change in the length of the single bond due to the local $\pi$ interaction between a specific pair of the double bonds. In the GE-*n* geometries of aromatic molecules of various types, the single bonds $r_n$ between two double bonds denoted by the thick lines include X−Y (X, Y = C, N, and O) ones. $\Delta E^{An}$ = 0.7024 + 335.17638*dr*, and the correction coefficient is 0.93431.

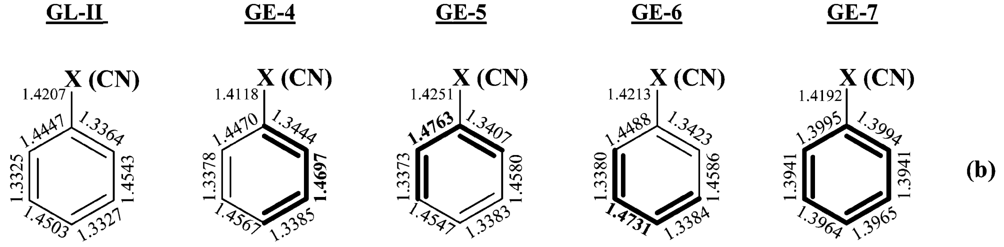
**3.4. Substituent Effects.** In order to quantify the effects of substituent groups X on aromaticity, the GL geometry of a monosubstituted benzene (SB) is still considered as a restrictedly optimized geometry, in which three $\pi$ systems are localized on the A (X−C1=C2H−), B (−HC3=C4H−) and C (−HC5=C6H−) groups, respectively, and its GE-*n* geometries result from the local $\pi$ interactions between the corresponding pairs of localized $\pi$ systems in the GL geometry. In the GL geometry of cyanobenzene, for example, three $\pi$ systems are localized on the three groups −C1(CN)=C2H− (A), −HC3=C4H− (B), and −HC5=C6H− (C) (Figure 7a). In the case of multisubstituted benzene such as 1,2,3-tri-hydrox-benzene, three $\pi$ systems are localized on the three groups −C1(OH) =C2-



| -X | $E^T$(GL) (hartree) | $\Delta E^{A1}$ (kcal/mol) | $\Delta E^{A2}$ (kcal/mol) | $\Delta E^{A3}$ (kcal/mol) | $\Delta E^{A}$ (kcal/mol) | ESE(SB) |
|---|---|---|---|---|---|---|
| -CN | -324.4735052 | 6.9 | 9.9 | 8.8 | -11.7 | -37.3 |
| -$NO_2$ | -436.7310054 | 6.7 | 10.0 | 8.7 | -12.3 | -37.6 |
| -F | -331.4676775 | 11.1 | 9.0 | 9.1 | -9.2 | -38.3 |
| -OH | -307.4507779 | 10.6 | 9.6 | 9.1 | -8.8 | -38.1 |
| -$NH_2$ | -287.5904363 | 10.5 | 9.6 | 9.4 | -5.9 | -35.5 |
| 1,2,4-tri OH | -457.8909984 | 14.2 | 10.8 | 8.8 | -3.0 | -36.8 |
| 1,3,5-tri $NO_2$ | -845.7157453 | 7.4 | 7.4 | 7.4 | -13.1 | -35.2 |
| 1- $NH_2$-4-$NO_2$ | -492.0922042 | 3.2 | 9.0 | 10.1 | -10.0 | -32.2 |

ESE(SB) of whole substituted benzene = $\Delta E^{A}$ - ( $\Delta E^{A1} + \Delta E^{A2} + \Delta E^{A3}$)

where $\Delta E^{A} = E^{T}(G) - E^{T}(GL)$ and $\Delta E^{An} = E^{T}(GE\text{-}n) - E^{T}(GL)$ ( n= 1, 2, 3)



| -X | $E^T$(GL-II) (hartree) | $\Delta E^{A4}$ (kcal/mol) | $\Delta E^{A5}$ (kcal/mol) | $\Delta E^{A6}$ (kcal/mol) | $\Delta E^{A7}$ (kcal/mol) | ESE(Ph) |
|---|---|---|---|---|---|---|
| -CN | -324.4792125 | 7.0 | 11.1 | 8.8 | -11.7 | -38.5 |
| -$NO_2$ | -436.7431540 | 6.6 | 11.7 | 8.8 | -11.7 | -38.7 |
| -F | -331.4903859 | 7.5 | 10.6 | 8.9 | -11.7 | -38.8 |
| -OH | -307.4763578 | 7.3 | 11.1 | 9.1 | -11.4 | -38.8 |
| -$NH_2$ | -287.6140349 | 7.9 | 10.6 | 9.3 | -11.1 | -38.9 |
| 1,2,4-tri OH | -457.9653216 | 7.1 | 9.2 | 9.6 | -12.8 | -38.8 |
| 1,3,5-tri $NO_2$ | -845.7542232 | 8.5 | 8.5 | 8.5 | -11.9 | -37.4 |
| 1- $NH_2$-4-$NO_2$ | -492.1244674 | 5.9 | 9.9 | 11.5 | -11.7 | -38.9 |

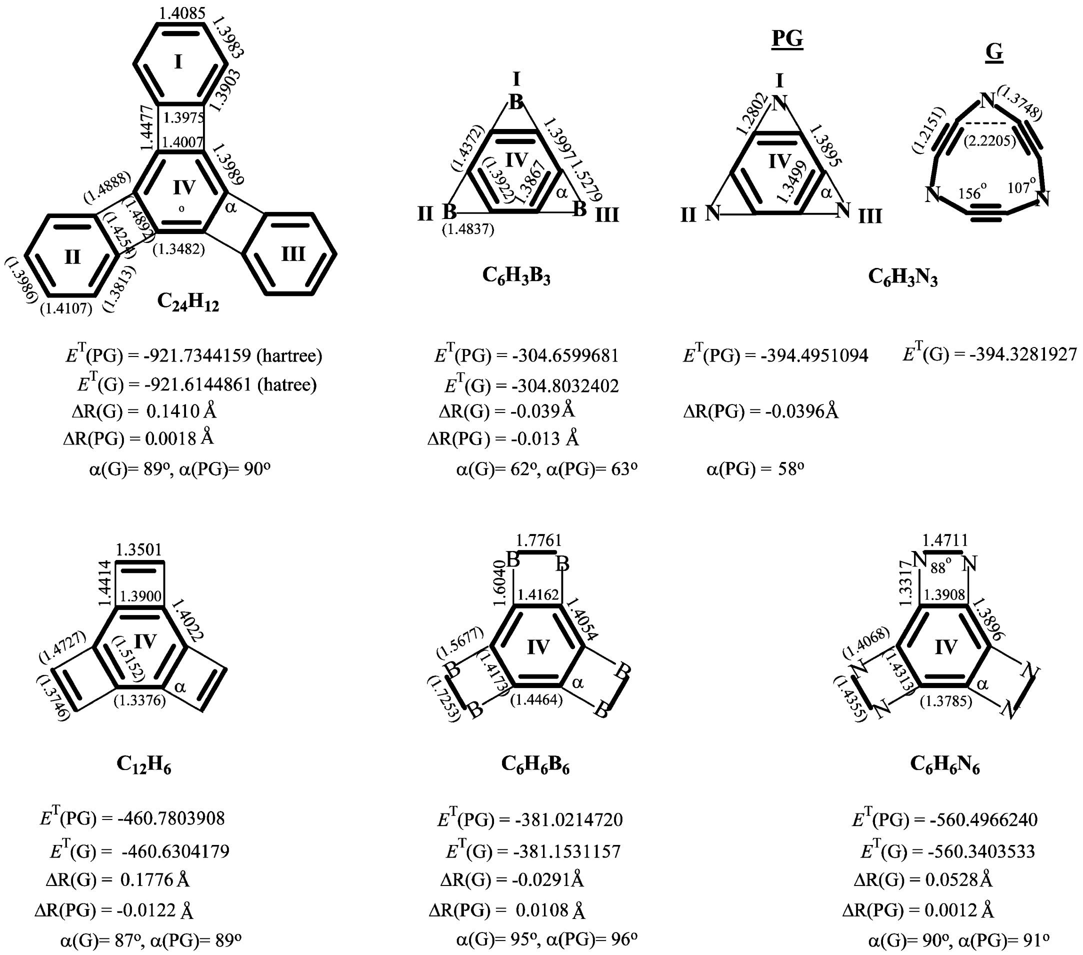
ESE(Ph) of the isolated pheneyl ring = $\Delta E^{A7}$ - ( $\Delta E^{A4} + \Delta E^{A5} + \Delta E^{A6}$ ) where $\Delta E^{An} = E^{T}(GE\text{-}n) - E^{T}(GL\text{-}II)$ ( n = 4, 5, 6,7)

**Figure 7.** Geometry data for the G, GL, and GE-*n* geometries of cyanobenzen, the ESEs(SB) for substituted benzenes, and the ESEs(Ph) for the isolated rings. (a) The single thick line between the group X and the phenyl ring indicates that the $\pi$ orbital interactions between these groups were not set equal to zero. (b) The single thin line between the group X and the phenyl ring indicates that the $\pi$ orbital interactions between these groups have been set equal to zero. In each of the geometries, the $\pi$ orbital interactions between the double bonds connected by the single thin lines have been set equal to zero no matter whether these double bonds are denoted by the thin or thick lines.

(OH)−, −C3(OH)=C4H−, and −HC5=C6H−. Due to all the dihedral angles being set equal to 0° or 180°, as indicated by the frequency calculations, one imaginary frequency was found for the planar GL geometry of each of the two monosubstituted benzenes Ph−X (X = −$NO_2$ and −$NH_2$), and its normal coordinates show that each of these two GL geometries is a maximum with respect to the motions of the substituent atoms in the directions perpendicular to the molecular plane but is a minimum with respect to the remaining coordinates.

The ordering of the ESEs for monosubstituted benzenes (Ph−X) is as follows: |−39.0| (X = −H) > |−38.3| (X = −F) > |−38.1| (X = −OH) > |−37.6| (X = −$NO_2$) > |−37.3| (X = −CN) > |−35.5| (X = −$NH_2$) kcal/mol, indicating that the substituents always weaken the aromaticity of the phenyl ring no matter whether they are an electron-withdrawing or electron-releasing group. Besides, as shown by the ESE for 1-amino-4-nitrobenzene (−32.2 kcal/mol), the "pushing" and "pulling" effects exerted by the electron-releasing and electron-withdrawing groups −$NH_2$ and $NO_2$, respectively, enhance the resonance interaction between the phenyl ring and its substituents. The ESEs for 1,2,4-tri-hydoxybenzene and 1,3,5-tri-nitrobenzene are −36.8 and −35.2 kcal/mol, respectively, indicating that aromaticity decreases as the number of substituent groups increases.

The ordering of the resonance stabilization energies for substituted benzenes reported in the literature depends upon the calculation method as well as on the structures of the reference



$E^T$(PG) = -921.7344159 (hartree)
$E^T$(G) = -921.6144861 (hatree)
ΔR(G) = 0.1410 Å
ΔR(PG) = 0.0018 Å
α(G)= 89°, α(PG)= 90°

$E^T$(PG) = -304.6599681
$E^T$(G) = -304.8032402
ΔR(G) = -0.039 Å
ΔR(PG) = -0.013 Å
α(G)= 62°, α(PG)= 63°

$E^T$(PG) = -394.4951094 $E^T$(G) = -394.3281927
ΔR(PG) = -0.0396 Å
α(PG) = 58°

$E^T$(PG) = -460.7803908
$E^T$(G) = -460.6304179
ΔR(G) = 0.1776 Å
ΔR(PG) = -0.0122 Å
α(G)= 87°, α(PG)= 89°

$E^T$(PG) = -381.0214720
$E^T$(G) = -381.1531157
ΔR(G) = -0.0291 Å
ΔR(PG) = 0.0108 Å
α(G)= 95°, α(PG)= 96°

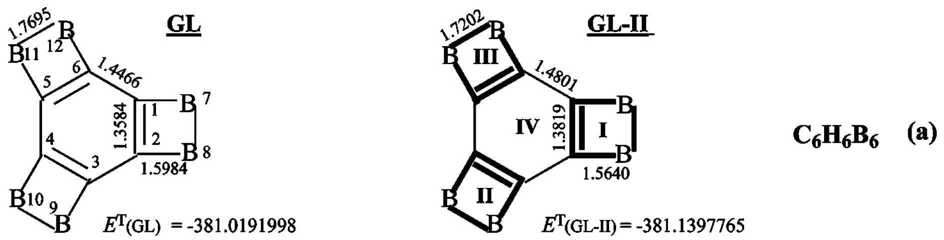
$E^T$(PG) = -560.4966240
$E^T$(G) = -560.3403533
ΔR(G) = 0.0528 Å
ΔR(PG) = 0.0012 Å
α(G)= 90°, α(PG)= 91°

**PG (the Particular Geometries)**
( in each of which four π systems have been isolated each other)

**Figure 8.** Molecular energies $E^T$(G) and $E^T$(PG) of the ground states (G) and their PG geometries, bond lengths $R$, bond length differences $\Delta R = R_{endo} - R_{exo}$ between the endo-and exo-bonds, and the bond angles, denoted as α(G) and α(PG), for the G and PG geometries. The PG geometries of the molecules were obtained from the restricted geometry optimization at B3LYP/6-31G*, and these are all set to be planar. In each PG geometry, the single bonds between four groups I, II, III, and IV are denoted by the thin lines, indicating that the π systems of these four groups have been artificially isolated each other. The data in the parentheses are the bond lengths in the ground state geometries.

systems. The ASEs for substituted benzenes (Ph−X) are as follows: −33.5 (X = −CN), −33.4 (X = $-NO_2$), −34.1 (X = −OH), −33.2 (X = −H), −33.2 (X = $-NH_2$), and −33.1 (X = −F) kcal/mol.[20] The ASEs of substituted benzenes are mostly greater in the absolute value than that of benzene, and their ordering indicates that the electron-withdrawing substituents stabilize the benzene ring, while the electron-releasing substituents destabilize it. The aromatic stabilization energies for substituted benzenes, originally denoted as ASE(3), obtained from a relatively well strain-balanced homodesmotic approach, are −33.3 (X = $-NH_2$), −32.7 (X = −H), −32.7 (X = −F), −32.1 (X = −OH), −31.6 (X = −CN), −31.3 (X = $-NO_2$),[20] where the ASE(3) of only aminobenzene is greater in the absolute value than that of benzene. The ordering of the ASE(3) is different from that of the ASEs, but it is roughly consistent with that of the ESEs. Besides, it is a fundamental difference between the three sets of stabilization energies that all the ESEs of substituted benzenes are less in the absolute value than that of benzene.

To understand the ways a substituent group can weaken the aromaticity of a phenyl ring, five geometries of each substituted benzene, denoted as GL-II, GE-4, GE-5, GE-6, and GE-7 (Figure 7b), were obtained from the restricted geometry optimization. In each of these geometries, as indicated by the thick and thin lines in Figure 7b, the π orbital interactions between substituent X and the phenyl ring have been set equal to zero. Therefore, the π system (or systems) of the substituent groups has been artificially isolated from the π system (systems) of the phenyl ring. In this case, the phenyl group is referred to as the isolated phenyl ring, and its ESE(Ph) = $[\Delta E^{A7} - (\Delta E^{A4} + \Delta E^{A5} + \Delta E^{A6})]$, where $\Delta E^{An} = E^T(\text{GE-}n) - E^T(\text{GL-II})$ ($n$ = 4, 5, 6, 7) (Figure 7b). The difference [ESE(SB) − ESE(Ph)] in the extra stabilization energy between the substituted benzene (SB) and its isolated phenyl ring can be used to evaluate the conjugative effect of a substituent. Similarly, the difference [ESE(Ph) − ESE(benzene)] between benzene and the isolated phenyl ring in a substituted benzene can be used to quantify the inductive effect of a substituent. The differences [ESE(SB) − ESE(Ph)] are as follows: 6.7 (1-amino-4-nitro) > 3.4 ($-NH_2$) > 2.1 (trinitro-) > 2.0 (tri-hydroxy) > 1.2 (−CN) > 1.1 ($-NO_2$) > 0.7 (−OH) > 0.4 (−F) kcal/mol. The differences [ESE(Ph) − ESE(benzene)] are as follows: 1.72 (trinitro) > 0.49 (−CN) > 0.31 ($-NO_2$) > 0.26 (tri-hydroxy) > 0.25 (−F) > 0.22 (−OH) > 0.16 ($-NH_2$) kcal/mol. The conjugative effect always plays a predominant role in determining the ESE of substituted benzene. An exception is found in 1,3,5-trinitrobenzene where

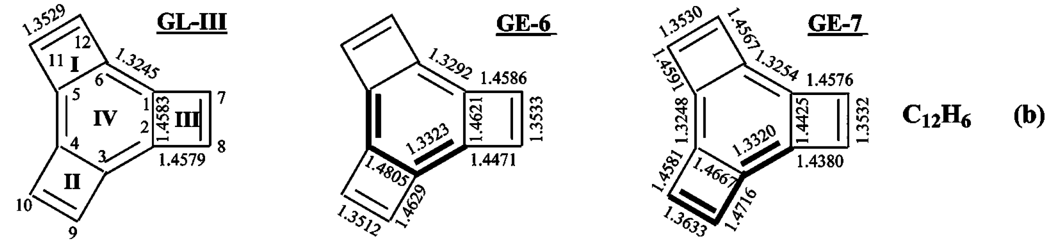


| GE-n Geometry | Interactiing grouops | length $R_{i,j}$ of single bond (Å) | Moleular energy (hartree) | Energy effect $\Delta E^{An}$ (kcal/mol) |
|---|---|---|---|---|
| GE-1 | C1=C2 C3=C4 in GL | C2--C3 $R_{2,3}$ = 1.4736 | -381.0025545 | 10.4 |
| GE-2 | C1=C2 B7=B8 in GL | C1--B7 $R_{1,7}$ =1.5612 | -381.0610348 | -26.3 |
| GE-3 | C1=C2 B9=B10 in GL | non-bonded interaction | -381.0218467 | -1.7 |
| GE-4 | B7=B8 B9=B10 in GL | non-bonded interaction | -381.0191998 | 0.0 |
| GE-5 | Rings I and II in GL-II | C2--C3 $R_{2,3}$ =1.4815 | -381.1369143 | 1.8 |

ESE of whole molecule = $\Delta E^A - [3*\Delta E^{A1} + 3*\Delta E^{A2} + 6*\Delta E^{A3} + 3*\Delta E^{A4}] = -84.0 - (-57.4) = -26.6$ kcal/mol

. where $\Delta E^A = [E^T(G) - E^T(GL)]$ and $\Delta E^{An} = E^T(GE\text{-}n) - E^T(GL)$

ESE(CR) of the central ring = $[E^T(G) - E^T(GL\text{-}II)] - 3* [E^T(GE\text{-}5) - E^T(GL\text{-}II)] = -8.4 -5.4 = -13.8$ kcal/mol.



$E^T$(GL-III) = -460.7341167 hartree

$\Delta E^{A6} = E^T(GE\text{-}6) - E^T(GL\text{-}III)$ =7.1 kcal/mol

$\Delta E^{A7} = E^T(GE\text{-}7) - E^T(GL\text{-}III)$ = 2.4 kcal/mol

| GE-n Geometry | Interactiing grouops | | Moleular energy (hatree) | Energy effect $\Delta E^{An}$ (kcal/mol) |
|---|---|---|---|---|
| GE-8 | C2=C3 C11=C12 | non-bonded interaction | -460.7342754 | -0.1 |
| GE-9 | C9=C10 C11=C12 | non-bonded interaction | -460.7342325 | -0.1 |

ESE of whole molecule = $\Delta E^A - [3.0*\Delta E^{A6} + 6.0*\Delta E^{A7} + 3.0*\Delta E^{A8} + 3*\Delta E^{A9}] = 30.2$ kcal/mol.

where $\Delta E^A = E^T(G) - E^T(GL\text{-}III)$ and $\Delta E^{An} = E^T(GE\text{-}n) - E^T(GL\text{-}III)$ ( n = 6, 7, 8, 9)

**Figure 9.** (a) Procedure for calculating ESEs of $C_6B_6H_6$ and $C_6B_3H_3$ whose $\Delta R(G) < 0$. In the GL-II geometry, the $\pi$ orbital interactions between the groups connected by the single thin lines have been set equal to zero although these groups are denoted by the thick lines. (b) That for calculating ESEs of $C_6X_6$ (X = CH, NH) whose $\Delta R(G) > 0$.

[ESE(SB) − ESE(Ph)] (2.1 kcal/mol) ≈ [ESE(Ph) − ESE(benzene)] (1.7 kcal/mol), indicating that conjugative and inductive effects both weaken the aromaticity of the phenyl ring. In a word, the $\pi$ electron system in the phenyl ring always resists the perturbation caused by a substituent so as to maintain, as far as possible, an unchanged electron structure.[20] Correspondingly, the length $r_{c1,X}$ of the formal single bond between the phenyl ring and its substituent increases due to the local $\pi$ interaction between them. In monosubstituted benzenes, for example, the differences in the bond length $r_{c1,X}$ between the G and GE-7 geometries are 0.0801 (X = −F), 0.0733 (X = −OH), 0.0394 (X = $-NO_2$), 0.0154 (X = −CN), 0.0599 (X = $-NH_2$) Å.

**3.5. Strained Aromatic Compounds. 3.5.1. Bond Localization in Strained Aromatic Compounds.** In the ground states of the strained aromatic molecules $C_{24}H_{12}$ (tris-benzocyclobutenobenzene),[21] $C_6X_6$ (X = CH, BH, and NH, tris-cyclobutenobenzene-like species),[22] and $C_6X_3$ (X = BH and NH, tris-cyclopropenobenzene-like species),[22,23] as shown by the bond lengths presented in the parentheses in Figure 8, bond length alternation is found in the central aromatic ring IV. In the literature,[22a] bond localization in strained aromatic compounds was explained on the basis of the following three approaches: aromaticity ($4n + 2$) and antiaromaticity ($4n$) ($\pi$ effects); SIBL dependent on strain and bond curvature; combined $\pi$ and $\sigma$ effects. According to the corresponding relationship between $n$ and the sign of $\Delta R$ in the ground states of the molecules $C_6X_3$ (X = BH, $CH_2$, NH) ($n$ is the number of $\pi$ electrons in each of the three-membered rings, and $\Delta R = R_{endo} - R_{exo}$ is the bond length difference between the endo- and exo-bonds), the $\pi$ effects were considered to be much more important than SIBL in determining the geometry of the central ring.[23] However, as questioned by Stanger,[22a] $C_6X_3$ molecules are not appropriate probes to distinguish between the $\pi$ effects and

SIBL, because the aromaticity−antiaromaticity and SIBL results are of the same sign of $\Delta R$. Suitable systems, therefore, would seem to be $C_6X_6$ (X = BH, CH, NH), where the two factors would suggest opposite signs of $\Delta R$. In line with the analyses of the structures, Stanger concluded that SIBL is responsible for the bond localization in $C_6X_6$ molecules. To understand the role of the $\pi$ effects in determining the geometry of the central ring, $C_{12}H_6$ (tris-cyclobutadienobenzene) was complexed by three tricarbonyliron groups; groups that can withdraw $\pi$ charges from the four-membered rings. As a result, and as shown by X-ray diffraction,[22b] the bond lengths of the central ring are equalized. However, it is impossible for the three groups to specifically withdraw the $\pi$ charges from the three double bonds which are attached to the central ring, so the exo- and endo-bond lengths (1.443 and 1.468 Å) are rather longer than the CC (1.3966 Å, Figure 3) bonds in benzene. A method that can separate the $\pi$ system of the central ring from those of the small rings is therefore needed to comprehend the driving forces for distorting the central ring. Certainly, the restricted geometry optimization makes it feasible.

In Figure 8, as indicated by the thick and thin lines, the particular geometries (PG) were obtained from the restricted optimization. In the particular geometry of the $C_{24}H_{12}$ molecule, for example, the local $\pi$ interaction between each pair of aromatic rings P and Q (P, Q = I, II, III, IV, and P ≠ Q) has been set equal to zero. In this case, the central ring is called the isolated central ring. According to the absolute values of $\Delta R$, the molecules presented in Figure 8 can be divided into two groups. $C_{24}H_{12}$, $C_6H_3B_3$, and $C_6X_6$ (X = CH, BH, NH) belong to the first group, while $C_6H_3N_3$ belongs to the second. A comparison of the geometry data presented in Figure 8 shows the following features: (i) In the PG geometries of the first group molecules, the bonds in the central ring are approximately equalized, and the bond length differences, denoted as $\Delta R$(PG), in the central rings are 0.0012 ($C_6H_6N_6$), 0.0018 ($C_{24}H_{12}$), 0.0108 ($C_6H_6B_6$), −0.0122 ($C_{12}H_6$), and −0.013 ($C_6H_3B_3$) Å. (ii) When the X atoms are electropositive, $\Delta R < 0$ is suggested.[22a] This role should not be changed by the localization of the $\pi$ systems. In fact, $\Delta R$(PG) and $\Delta R$(G) for each of $C_6X_6$ (X = CH, BH) have opposite signs. (iii) Strain arises from the abnormal decrease in the bond angle α, resulting in $\Delta R > 0$.[22a] The fact that the endo-bonds are slightly longer than the exo-bonds in the PG geometries of $C_6X_6$ (X = BH and NH) and that there is a slight difference in the bond angle α between the ground state and its PG geometry (Figure 8) seem to indicate that strain has a slight effect on the geometry of the central ring. On the basis of the above features, it is the $\pi$ orbital interactions between the central ring and the X groups, rather than SIBL, which distort the central ring away from equal bond lengths. Whether $\Delta R(G) > 0$ or $\Delta R(G) < 0$ is only a secondary effect, it seems to be the combination of various effects such as SIBL, inductive effects, and the ways in which the $\pi$ electrons can be delocalized.

The exception to the fact concerns the equalized bonds in the PG geometry, which was found in the PG geometry of $C_6H_3N_3$. $\Delta R(PG) = -0.0396$ Å for $C_6H_3N_3$ is due to the geometrical restriction.

**3.5.2. Extra Stabilization Energies of Strained Aromatic Compounds.** According to the signs of $\Delta R$(G) (Figure 8), there are two schemes for calculating the ESEs for strained aromatic molecules. In the ground states of the $C_6H_6B_6$ and $C_6H_3B_3$ molecules, for example, its $\Delta R(G) < 0$, so the endo-bonds in the GL geometry should be considered as double bonds. In this case, the whole molecule ESE = $[E^T(G) - E^T(GL)] - 3[E^T(GE\text{-}1) - E^T(GL)] - 3[E^T(GE\text{-}2) - E^T(GL)]$ (Figure 9a). However, it is possible that the $\pi$ interaction occurs between a pair of nonbonded double bonds. Therefore, the ESE of a strained aromatic molecule should be corrected. In $C_6H_6B_6$, for example, the GE-$n$ ($n$ = 3, 4) geometries are two restrictedly optimized geometries resulting from the nonbonded $\pi$ interactions (Figure 9a). Accordingly, the corrected ESE = $[E^T(G) - E^T(GL)] - 3[E^T(GE\text{-}1) - E^T(GL)] - 3[E^T(GE\text{-}2) - E^T(GL)] - 6[E^T(GE\text{-}3) - E^T(GL)] - 3{*}[E^T(GE\text{-}4) - E^T(GL)]$ (Figure 9a), and its values are −26.6 ($C_6H_6B_6$) and −22.3 ($C_6H_3B_3$). In addition, as shown by the GL-II and GE-5 geometries in Figure 9a, the ESE(CR)s for the central rings of $C_6H_6B_6$ and $C_6H_3B_3$ are calculable, and their values are −12.0 ($C_6H_3B_3$) and −13.8 ($C_6B_6H_6$) kcal/mol, respectively.

In the ground states of $C_6X_6$ (X = CH, NH), $\Delta R(G) > 0$. The exo-bonds have to be considered as double bonds in the GL geometry (in Figure 9b, the GL geometry of $C_{12}H_6$ is denoted as GL-III). Obviously, it is impossible to calculate the ESE for the central rings. According to the scheme described by Figure 9b, the ESEs for the whole molecule $C_6X_6$ are 30.2 (X = CH) and 60 (X = NH) kcal/mol. In line with the signs of the ESEs for whole molecules, $C_6H_6B_6$ and $C_6H_3B_3$ are aromatic, and $C_6X_6$ (X = CH, NH) is anti-aromatic.

There are two schemes to calculate the ESE(ICR) of the isolated central ring (ICR) IV (Figure 8) according to the sign of $\Delta R$. When $\Delta R < 0$, ESE(ICR) = $[E^T(PG) - E^T(GL)] - 3[E^T(GE\text{-}1) - E^T(GL)]$ (the PG geometries are presented in Figure 8, and GL and GE-1 geometries are done in Figure 9a). Its values are −27.9 ($C_6H_3B_3$) and −32.8 ($C_6H_6B_6$) kcal/mol. When $\Delta R > 0$, ESE(ICR) = $[E^T(PG) - E^T(GL\text{-}III)] - 3[E^T(GE\text{-}6) - E^T(GL\text{-}III)]$ (the GL-III and GE-6 geometries are presented in Figure 9b), and its values are −45.7 ($C_6H_6N_6$) and −50.4 ($C_{12}H_6$). It is impossible to calculate the ESE(ICR) when $\Delta R > 0$, because the values of the ESE(ICR) are much greater in the absolute value than the ESE (39 kcal/mol) for benzene.

The ESE difference [ESE(CR) − ESE(ICR)] between the central and isolated central rings are 16.0 ($C_6H_3B_3$) and 19.0 ($C_6H_6B_6$) kcal/mol, respectively, which can be ascribed to the $\pi$ orbital interactions between the central ring and the X groups. The differences [ESE(ICR) − ESE(benzene)] between the isolated central ring (ICR) in a strained aromatic molecule and benzene are 11.1 ($C_6H_3B_3$) and 6.2 ($C_6H_6B_6$) kcal/mol, respectively. On the basis of a comparison of the differences [ESE(Ph) − ESE(benzene)] and [ESE(ICR) − ESE(benzene)], it is reasonable to say that SIBL plays a greater role in determining ESE of the central ring than the inductive effect.

## 4. Conclusions

Importantly, the energy differences $\Delta E^{An} = [E^T(GE\text{-}n) - E^T(GL)]$ associated with the local $\pi$ interactions between the corresponding pairs of double bonds in the GL geometry were found to be additive in each of the acyclic polyenes, and a −39.0336 kcal/mol deviation from the additivity, defined as the extra stabilization energy, was found in benzene. Emphatically, as a fundamental feature of our method, it is the localized geometries GL and GE-$n$ of the aromatic molecule, rather than a nonaromatic molecule (or molecules), to be used as the localized reference structures for the calculation of the extra stabilization energy. Particularly, the localized reference geometries GL and GE-$n$ are no longer arbitrary, because these were obtained from the restricted geometry optimizations.

The restricted geometry optimization was successfully applied to aromatic molecules such as benzene- and furan-like species, strained aromatic molecules, and substituted benzenes. Strikingly, the calculated extra stabilizing energies for these molecules are in reasonable ranges. Particularly, the restricted geometry optimization can isolate the $\pi$ system of a specific group from those of other groups. Therefore, the restricted geometry optimization has several special functions. First, a substitute effect can be partitioned into the conjugative and inductive parts, which indicated that the conjugative effect plays the predominant role in determining substituent effects. Second, in determining the behaviors of the central ring, it is feasible to distinguish the roles of the resonance interactions, SIBL, and inductive effects. Here, it is the resonance interactions rather than SIBL, which results in bond length alternation in the central ring of strained aromatic molecules. However, it is the combination of resonance interactions, SIBL, and inductive effects, which results in the large decrease in the ESE of the central ring.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of China (Grants 20472088 and 20672119).

**Supporting Information Available:** Data of the optimization and the interpretation of physical meaning of the destabilizing energy differences $\Delta E^{A}$ and $\Delta E^{An}$ are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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