

Response to “Comment on the paper "Restricted Geometry Optimization: A Different Way to Estimate Stabilization Energies for Aromatic Molecules of Various Types"”

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Supporting information.

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1. σ - π Energy Partition

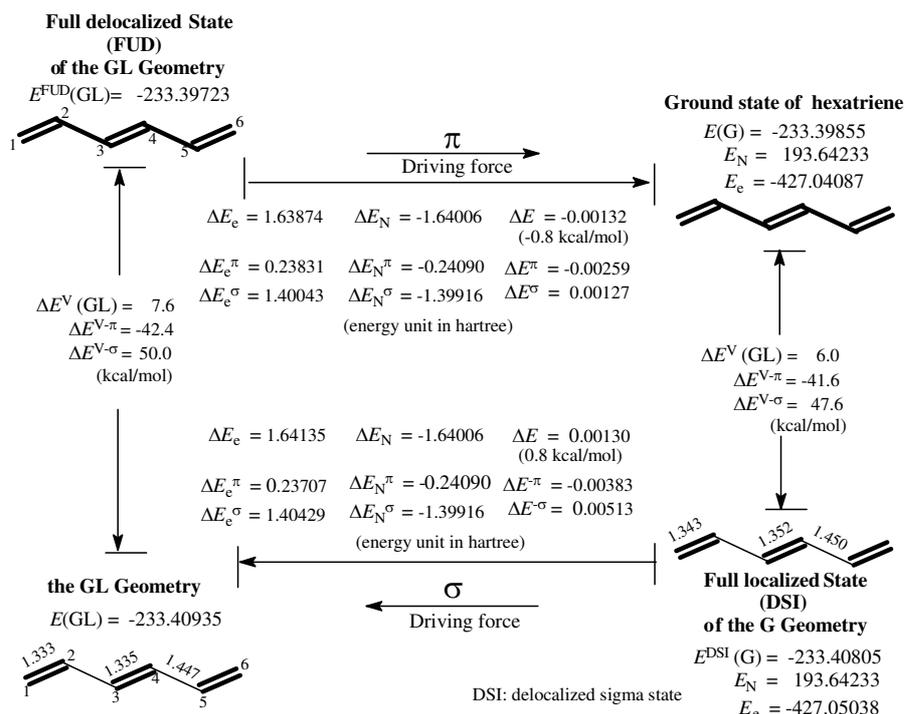


Figure 1. The ground state of 1,3,5-hexatriene, and the restrictedly optimized GL geometries. Molecular energies E , the nuclear repulsion E_{N} , the total electronic energies E_{e} , and the π and σ components of the molecular energy differences (Vertical resonance energy) E^{V} at the B3LYP/6-31G*. Where, the energies of the FUD state were obtained from the single point energy calculation for the GL geometry, the energies of the DSI state were obtained from the restricted single point energy calculation for molecule hexatriene.

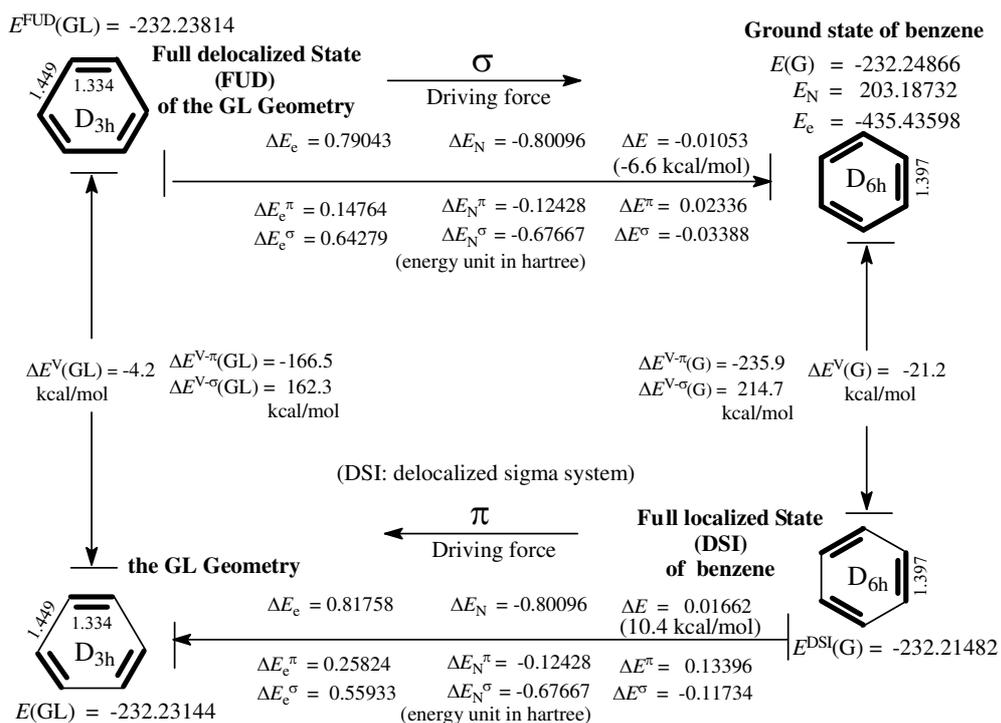


Figure 2. The ground state of benzene, and the restrictedly optimized GL geometries. Molecular energies E , the nuclear repulsion E_N , the total electronic energies E_e , and the π and σ components of the molecular energy differences (Vertical resonance energy) E^V at the B3LYP/6-31G* level. Where, the energies of the FUD state were obtained from the single point energy calculation for the GL geometry, the energies of the DSI state were obtained from the restricted single point energy calculation for molecule hexatriene.

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The following resonance energies are from literature

Table 1.

Resonance energies for benzene (D_{6h} -2) and benzene at the 1,3,5-cyclohexatriene geometry (D_{3h} -1) calculated with different methods, orbitals and wavefunctions (in kcal/mol)

Symmetry	Method	Orbitals	Energy
D_{6h}	Pauling	Local	-25.37
D_{6h}	Pauling	Delocal	-19.82
D_{6h}	Pauling	Breathing	-44.13
D_{6h}	VRE	Local	-25.13
D_{6h}	VRE	Delocal	-9.65
D_{6h}	VRE	Breathing	-14.26
D_{6h}	Bond-distorted VRE ^a		-62.80
D_{6h}	TRE	Local	-11.32
D_{6h}	TRE	Delocal	-7.44
D_{6h}	TRE	Breathing	-12.05
D_{3h}	Pauling	Local	-7.74
D_{3h}	Pauling	Delocal	-8.38
D_{3h}	Pauling	Breathing	-29.53
D_{3h}	Bond-distorted VRE ^a		-49.78

The Table 1 was quoted from the reference (van Lenthe, J. H.; Havenith, R. W. A.; Dijkstra, F.; Jennekens, L.W. *Chem. Phys. Lett.* **2002**, *361*, 203).

In Table 1, three vertical resonance energies (VRE) for benzene, as well as three theoretical resonance energies (TRE), arose from the three different ways to optimize D_{6h} and D_{3h} geometries using VB program. One of three values of VRE is -25.1 kcal/mol, and the corresponding TRE is -11.3 kcal/mol. These values for both the VRE and TRE are considerably lower than most previously reported values (range 5 to 95 kcal/mol) ((a) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048.; (b) Janoschek, R. *J. Mol. Struct. (Theochem.)*. **1991**, *229*, 197.; (c) Bernardi, F.; Celani, P.; Olivucci, M.; Robb, M. A.;Suzzi-Valli, G. *J. Am. Chem. Soc.* **1995**, *117*, 10531.; H. Kollmar, J. *Am. Chem. Soc.* *101* (1979) 4832.; (d) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem. Rev.* **2001**, *101*, 1501.)

In our method, as shown by the data in Figure 2, VRE for benzene is -21.2 kcal/mol, and TRE, the energy difference [$E(G) - E(GL)$], is -10.8 kcal/mol.

Table 2 Optimal structural parameters (bond lengths [Å] and bond angles [°]) of benzene, cyclobutadiene, all-*trans*-1,3,5-hexatriene, and *trans*- and *cis*-1,3-butadiene with the 6-311+G(d,p) basis set. Vertical (E_{VR}) and adiabatic (E_{AR}) resonance energies (see text) are in kcal mol⁻¹.

Molecule	Structural parameters			E_{VR}	E_{AR}	$E_{VR}-E_{AR}$
	R(C ₁ C ₂)	R(C ₂ C ₃)	∠H ₁ C ₁ C ₂			
benzene	1.386	1.386	120.0	91.6	57.5	34.8
1,3,5-cyclohexatriene	1.314	1.522	121.6			
cyclobutadiene	1.320	1.565	135.1	10.9	10.3	0.6
localized form of C ₄ H ₄	1.317	1.595	135.4			
<i>trans</i> -1,3,5-hexatriene	R(C ₁ C ₂)	R(C ₂ C ₃)	R(C ₃ C ₄)			
	1.324	1.463	1.329	23.5	20.8	2.7
localized form of C ₆ H ₈	1.316	1.517	1.312			
<i>trans</i> -1,3,5,7-octatetraene	R(C ₁ C ₂)	R(C ₂ C ₃)	R(C ₃ C ₄)	R(C ₄ C ₅)		
	1.325	1.463	1.330	1.459	36.2	31.8
localized form of C ₈ H ₁₀	1.315	1.517	1.312	1.518		4.4
<i>trans</i> -butadiene	R(C ₁ C ₂)	R(C ₂ C ₃)				
	1.323	1.468		11.0	9.9	1.1
localized form of <i>trans</i> -C ₄ H ₆	1.316	1.517				
<i>cis</i> -butadiene	1.323	1.480		10.0	9.1	0.9
localized form of <i>cis</i> -C ₄ H ₆	1.315	1.529				

The Table 2 was quoted from ref. (Yirong Mo, Y.; Schleyer, P. von R.; *Chem. Eur. J.* **2006**, *12*, 2009). In addition, -74.3 kcal/mol value of VRE was reported by Mo's paper in 1994 (Mo, Y.; WU, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048).

Table 3. Vertical Resonance Energies (B_0) for Delocalized Species

entry	species	B_0 values, kcal/mol			
		VB value	ref	MO(CI) value	ref
1	Li ₃	7 ^a	117		
2	H ₃	43 ^a	117		
3	FHF	43 ^a	112		
4	CH ₃ -H-CH ₃	41 ^a	111		
5	C ₃ H ₅ (allyl radical)	10-14 ^b	148		
5a	C ₃ H ₅ (allyl radical)	23 ^c (20) ^c	111 ^d (149)		
6	H ₃ ⁻	28 ^e	150		
7	(X-CH ₃ -X) ⁻	20 ± 3 ^e	110(a) 151		
8	C ₃ H ₅ ⁻ (allyl anion)	50 ^c	149		
9	H ₆			119 ^g	5
10	C ₆ H ₆ (benzene)	65 ^c (62 ^f) [74 ^a]	111 ^d (127)[153]	85 ^g (112 ^h)	2(154)
11	C ₆ H ₆ (benzene); <i>exptl</i>	55 ⁱ (65) ^j	155(156)		
12	N ₆ (hexazine)			103 ^g	5
13	C ₄ H ₄ (cyclobutadiene)	21 ^k (22 ^l)[15 ^l]	158(111) ^d [127]	30 ^g	5
14	C ₈ H ₈ (cyclooctatetraene)	49 ^{c,k}	111 ^d		

^a Using classical VB with localized AOs and a mixture of covalent and ionic structures. ^b Using RGVB (semidelocalized AOs). ^c Using bond-distorted orbitals where semidelocalization is permitted only to the centers that are formally bonded in the Kekulé structure. This method leads to more realistic B_0 values than those produced by removing the constraints over the sites of semidelocalization. ^d B_0 values from ref 111 are variational VBSCF/6-31G quantities (i.e., the energies of the delocalized state as well as of the single structure are variationally determined). ^e Using extended Hückel, calibrated to reproduce VB results as in *a*. ^f Using CASSCF projection into the space of Kekulé structures. ^g Using an input of a localized guess (following ref 157) and getting B_0 as $B_0 = E(\text{guess}) - E(\text{SCF})$. ^h Using the same method as in *g*, but with SINDO1 and with guess optimization. ⁱ Experimental value, estimated from the transition energy to the excited state; $B_0 = \Delta E(S_0 - S_1)/2$. ^j Experimental value, estimated by use of thermochemistry and empirical force constants. ^k Planar structure with $r_{C=C} = 1.4016$ Å from ref 164a.

2. The Physical Meaning of Destabilizing Energy Differences ΔE^{An} .

The energy difference ΔE^{An} between the GE-m and GL geometries can be considered as the energy effect associated with the local resonance interaction between two double bonds in the GL geometry. According to the classical viewpoint, resonance interaction should be stabilization, and the single bond $r_{v,s}$ between two interacting double bonds -C(u)=C(v)- and -C(s)=C(t)- should be shortened. However, as shown by Figure 3, such energy effect is always destabilizing, and the corresponding single bond $r_{v,s}$ is lengthened due to the local π orbital interactions.

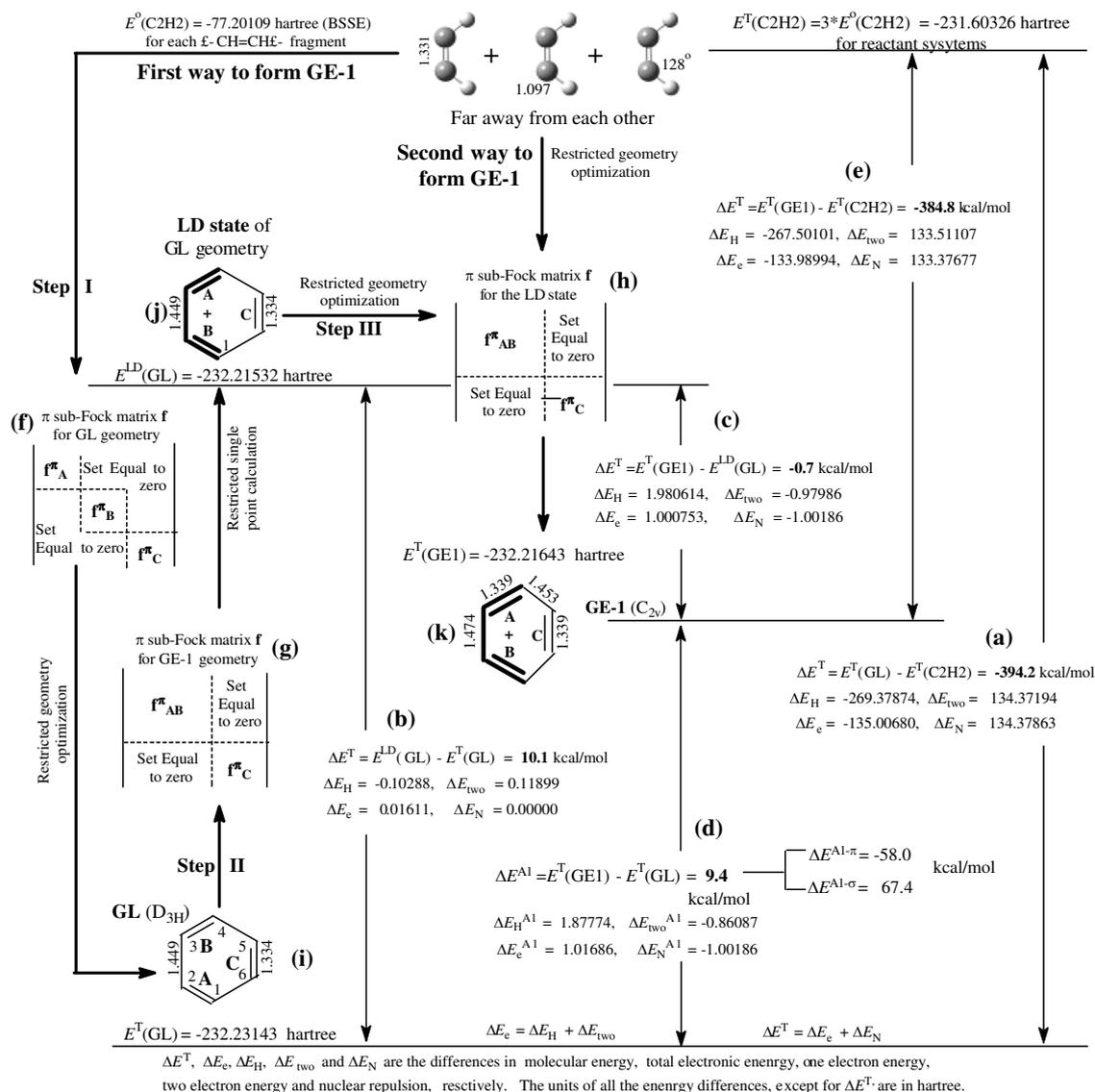


Figure 3. A Fictitious thermodynamic cycle for the formation of the GE-1 geometry of benzene; (a, b, c, d and e) Various energies differences at B3LYP/6-31G*; (f and h) the settings for the restricted optimization of the GL and GE-1 geometries; (g) the setting for the single point energy calculation for the GL geometry; (i, j and k) the optimized geometries GL and GE-1, where the thin lines mean that the π systems were artificially localized on their respective double bonds and thick lines in the GE-1 geometry and in the LD state of the GL geometry mean that one of the π systems was artificially delocalized on the group C1=C2-C3=C4 .

In order to understand the physical meaning of the destabilizing energy differences ΔE^{An} , molecular energies, denoted as $E^T(\text{GE1})$, $E^T(\text{GL})$, for the GE-1 and GL geometry of benzene, as well as the sum $E^T(\text{C2H2})$ of molecular energies for three fragments -CH=CH- , were partitioned into total electron energy E_c and nuclear repulsion E_N , where E_c is the sum of one electron energy E_H and two electron energy E_{two} . The molecular energy for each fragment -CH=CH- was obtained from geometry optimization using unrestricted B3LYP/6-31G* calculation. Afterward, this molecular

energy was corrected for the basis set superposition error (BSSE). As shown by the practical calculations for the $-\text{CH}=\text{CH}-$ fragment, the unrestricted B3LYP calculation can ensure that each molecular orbital has a correct electron occupancy, and it can also guarantee that the π and σ molecular orbitals are, thoroughly, separated out.

In Figure 3, there are two ways to form the GE-1 geometry, which forms a thermodynamic cycle for the formation of the GE-1 geometry. The first way is a multi-step procedure, and it includes the steps I, II and III which are denoted by the thick lines with arrowhead at the left side of the Figure 3. In this way, the GL geometry was dealt as an “intermediate” (a factitious intermediate) between the reactant systems (the three $-\text{CH}=\text{CH}-$ fragments) and the GE-1 geometry. As shown by Figure 3a, the molecular energy difference between the reactant systems and GL geometry is -394.2 kcal/mol, and it resulted from the interactions between the three fragments (Figure 3f). Of all the components of this energy difference, the absolute value of the one electron energy difference ΔE_{H} (-269.378740 hartree) is the greatest, and $|\Delta E_{\text{H}} + \Delta E_{\text{two}}| > \Delta E_{\text{N}}$, indicating that in the GL geometry, the bond energy (-394.2 kcal/mol) between three $-\text{CH}=\text{CH}-$ fragments mainly resulted from state electronic interactions between the different fragments.

In order to search for the driving force for distorting the GL geometry to the GE-1 geometry, it is necessary to construct a LD (locally delocalized) electronic state of the GL geometry. In the LD electronic state, as shown by the thick lines in Figure 3j, the π -electrons, originally localized on two different fragments $\text{C}(1)=\text{C}(2)$ and $\text{C}(3)=\text{C}(4)$ (Figure 3i), become delocalizing on the $\text{C}(1)=\text{C}(2)-\text{C}(3)=\text{C}(4)$ group, and meanwhile the molecular geometry (GL) was kept unchanged. In the second step of the first way, as shown by the π sub-Fock matrices in Figure 3g and 3h, the single point energy calculation for the GL geometry (restricted single point energy calculation) was performed under the conditions same as those used to obtain the GE-1 geometry, and it provided the GL geometry with a LD electronic state.

If the delocalization of π -electrons was so fast that the structure of the GL geometry was kept unchanged at the moment when delocalization of the π -electrons was finished. In this case, as shown by the energy differences between the DL electronic state and GL geometry (Figure 3b), two electron energy difference $[E_{\text{two}}^{\text{DL}}(\text{GL}) - E_{\text{two}}(\text{GL})]$ (0.11899 hartree) is destabilizing, and it is greater in the absolute value than the one electron energy difference ΔE_{H} (-0.10288 hartree), leading to $\Delta E^{\text{T}} = [E^{\text{LD}}(\text{GL}) - E^{\text{T}}(\text{GL})]$ (10.1 kcal) > 0 . Therefore, the electron repulsion ($\Delta E_{\text{two}} > 0$) is a driving force for distorting the GL geometry toward the GE-1 geometry. As a result, the bond length $r_{2,3}$ was lengthened from 1.334 Å in the GL geometry to 1.474 Å in the GE-1 geometry, and meanwhile the nuclear repulsion decreased from 203.99144 hartree for the GL geometry to 202.9896 hartree for the GE-1 geometry. At last, the GE-1 geometry was formed, and the molecular energy difference, $[E^{\text{T}}(\text{GE-1}) - E^{\text{T}}(\text{GL})] = 9.4$ kcal/mol (Figure 2d).

Emphatically, the molecular energy difference $[E^{\text{T}}(\text{GE-1}) - E^{\text{T}}(\text{GL})]$ is only 2.4% of the molecular energy difference (-394.2 kcal/mol) between the reactant systems and GL geometry, and it is so small that in the GL and GE-1 geometry, the lengths of the single bond $\text{C}2-\text{C}3$ between the double bonds $\text{C}1=\text{C}2$ and $\text{C}3=\text{C}4$ are both shorter than

the length (1.54 Å) of a standard Carbon-carbon single bond although the length (1.474 Å) in the GE-1 geometry is longer than that (1.449 Å) in the GL geometry.

3. The Difference, in the Way to Change Nuclear Repulsion, between Benzene and Hexatriene.

In order to search for potential correlation between energetic and geometrical criteria, the difference in the way to change in the repulsion energy between benzene and hexatriene is compared

The nuclear repulsion energy, E_{nu} , between the bonded carbon atoms can be written as equation (1):

$$E_{nu} = E_{nu1} + E_{nu2} = \sum_i^n [(q^2 / R_i) + \sum_i^m (q^2 / r_i)] \quad (1)$$

where q is the nuclear charges of carbon atom, and R_i and r_i are the lengths of the formal single and double bonds. In the case of the benzene molecule, as shown by comparison of the bond lengths in the G and GL geometries (Figure 2), $d(r_i) = [r_i(G) - r_i(GL)] > 0$ and $d(R_i) = [R_i(G) - R_i(GL)] < 0$. Accordingly, we have the following first and second order derivatives of the nuclear repulsion energy when $dR = dr_i = -dR_i$:

$$\begin{aligned} dE_{nu} / dR &= (-\partial E_{nu1} / \partial R_i) + \partial E_{nu2} / \partial r_i = q^2 \sum_{i=1}^{n=3} [(1 / R_i^2) - (1 / r_i^2)] \\ &= q^2 \sum_{i=1}^{n=3} (r_i^2 - R_i^2) / (r_i^2 R_i^2) < 0 \end{aligned} \quad (2)$$

$$\begin{aligned} dE_{nu}^2 / dR^2 &= \partial^2 E_{nu1} / \partial R_i^2 + \partial^2 E_{nu2} / \partial r_i^2 = 2q^2 \sum_{i=1}^{n=3} [(1 / R_i^3) + (1 / r_i^3)] \\ &= 2q^2 (\sum_i^n (R_i^3 + r_i^3) / (R_i^3 r_i^3)) > 0 \end{aligned} \quad (3)$$

when $r_i = R_i$

$$dE_{nu} / dR = 0$$

Therefore, the nuclear repulsion energy is minimum when $r_i = R_i$

On the other hand, as shown by Figure 1, $dR_i > 0$, $dr_i > 0$, and $dr_i > dR_i > 0$ for hexatriene. We have:

$$dE_{nu} / dR = \partial E_{nu1} / \partial R_i + \partial E_{nu2} / \partial r_i = -[q^2 \sum_{i=1}^{n=2} [(1 / R_i^2) + \sum_{i=1}^{n=3} (1 / r_i^2)]] < 0 \quad (4)$$

In the case of hexatriene, the nuclear repulsion monotonically decreases as the bond length alternation decreases, and the first order derivative for hexatriene is greater, in the absolute value, than that for benzene. At B3LYP/6-31G*, for example, the decrease $\Delta E_N = [E_N(G) - E_N^{FUD}(GL)]$ (-0.80096 hartree) in the nuclear repulsion of the benzene is 0.5 time as great as the decrease (-1.64006 hartree) in that of hexatriene, and meanwhile the gain $\Delta E = [E(G) - E^{FUD}(GL)]$ (-0.0105 hartree = -6.6 kcal/mol) in the molecular energy of benzene is about eight times of the gain (-0.00132 hartree = -0.8 kcal/mol) in that of hexatriene. Correspondingly, the energy differences ΔE^A are -10.8

(benzene) and 6.8 (hexatriene) kcal/mol, where ΔE^A can also be written as $\Delta E^A = \Delta E^V(\text{GL}) + [E(\text{G}) - E^{\text{FUD}}(\text{GL})]$ (Figure 2) from the thermodynamic viewpoint. It seems reasonable to say that aromaticity of benzene can be partly ascribed to the ability of the six-membered to gain the extra stabilization energy (-39.0 kcal/mol) via the way to minimize the nuclear repulsion energy.