

**Response to i°Comment on the paper "Restricted Geometry Optimization: A Different Way to Estimate Stabilization Energies for Aromatic Molecules of Various Types"i±**

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4 **Response to “Comment on the paper "Restricted Geometry Optimization:**  
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6 **A Different Way to Estimate Stabilization Energies for Aromatic**  
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8 **Molecules of Various Types"”**  
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12  
13 Zhong-Heng Yu\* and Peng Bao  
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4 **Abstract:** it is unprofessional to make comments out of personal feeling. The most of the comments  
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7 are incorrect, and the some of those are rude. Our detail responses are presented.  
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### 10 **Annotations of the words, phrases and acronyms often used in the response**

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15 1. “Commenter”: Zvonimir B. Maksić.

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18 2. “Our title paper”: “Restricted Geometry Optimization: A Different Way to Estimate  
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20 Stabilization Energies for Aromatic Molecules of Various Types”.

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23 3. “Figure (s)”: referring to as Figure (s) of the supporting information.

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26 4. “FG”: Fictitious geometry (cyclohexatriene) of benzene.

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29 5. “Charge transfer interactions”: the inter-double bond (fragment) interactions between the  
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31 corresponding pair of vacant and occupied (fragment) molecular  
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33 orbitals.

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36 6. “Exchange interactions”: the inter-double bond (fragment) interactions between the  
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38 corresponding pairs of occupied (fragment) molecular orbitals, and  
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40 those between the corresponding pairs of vacant (fragment)  
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42 molecular orbitals.  
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### 50 **1. About the Possibility of Exactly Defining Aromaticity**

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52 The commenter wrote: “*Aromaticity is important concept in chemistry, which cannot be*  
53  
54 *exactly defined.*<sup>1,2</sup>” ( in line 16 of page 1)

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57 It is really difficult to exactly define aromaticity, but we don’t think it cannot be done  
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59 forever, which is why so many efforts have been made to develop experimental and  
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4 theoretical methods in literature<sup>1a</sup>. The commenter denoted that his conclusion was from  
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7 Schleyer's paper (ref. 1b in the response). It is misleading according to the following  
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10 Schleyer's words (Particularly, the words with underline)<sup>1b</sup>: "*The failure to find correlations*  
11  
12 *between aromaticity criteria may only reflect deficiencies in the procedures currently used to*  
13  
14 *devise and to evaluate such indexes. I am not convinced that the search for a global*  
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16 *aromaticity index "has to be abandoned". This challenge may be met by the development of*  
17  
18 *more highly refined methods to dissect aromaticity effects from other influences. I hope that*  
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20 *some clever scientist will find a direct or indirect way to employ an easily determinable*  
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22 *quantity, like HOMA or NICS in modified form, to deduce accurate stabilization energies due*  
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24 *to cyclic electron delocalization in all kinds of complex systems."*  
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## 31 **2. About the Comment on Our Calculation Method.**

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33 The commenter wrote: "*Aromaticity is important concept in chemistry, which cannot be*  
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35 *exactly defined. This simple fact has two consequences: (1) there are many "measures" of*  
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37 *aromaticity and (2) some of them are completely meaningless. The method recommended by*  
38  
39 *Bao and Yu belongs to the second category"* ( in the lines from 16 to 19 of page 1).  
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44 Firstly, we would not like to make comment whether the uses of the words "simple fact"  
45  
46 and "measures" in the comment are professional or not. The commenter should know our  
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48 method is based on the principle of the Morokuma's energy decomposition.<sup>2</sup> The modified  
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50 Fock (density) matrix, obtained from partly deleting the elements of the matrix, has been  
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52 widely used in the various fields of organic chemistry,<sup>3</sup> which have made the great  
53  
54 contributions to developing theoretical chemistry. The Kollmar,<sup>3a</sup> Jug<sup>3b</sup> and Morokuma<sup>2</sup>  
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56 procedures are all based on the modified Fock matrix and have played an important role in  
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4 developing the methods of calculating (aromatic) resonance energy (including  $\pi$ - $\sigma$  energy  
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6 partition). Emphatically, our  $\pi$ - $\sigma$  energy partition can be used in any conjugated molecule no  
7  
8 matter whether it is planar or nonplanar.<sup>4</sup> Therefore, our title and related papers<sup>4</sup> have been  
9  
10 positively cited and commented.<sup>5</sup> We wonder whether the commenter has concluded that  
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12 all such related research and computations, reported in literature, are completely meaningless.  
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14 However, as shown by an inspection of the list of the commenter's papers, he seems not  
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16 professional enough to be able to comment on the energy decomposition method.  
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### 22 **3. About the Number of Decimal Places**

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25 The commenter said: *"The first eye-catching detail is that the bond distances and total*  
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27 *molecular energies are given in four and seven decimal places, respectively. This is*  
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29 *unrealistic! Too many decimal places are unphysical and are generally considered silly."*  
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33 ( in lines from 48 to 53 of page 1)  
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36 An appeal of Hoffmann, Schleyer and Schaefer,<sup>6</sup> published one year after the publication  
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38 of our title paper, meant itself that there were no unionized regulations for the use of decimal  
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40 places in the physical quantities such as bond length and energy. In the papers published in  
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42 the journals Science, J. Am. Chem. Soc. and Chem. Rev. and the Table of conversion factors  
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44 et. al., it is not difficult to find that the thermal energies (energy unit in kcal/mol) of chemical  
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46 bonds were given in two decimal places<sup>7a</sup> and energies (energy unit in eV) were given in from  
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48 four to six decimal places.<sup>3i</sup> Similarly, X-ray crystallographic measurement data for bond  
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50 length, except for the data for C-H bond, were given in four decimal places in the some  
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52 professional papers,<sup>7b-d,5n</sup> and the bond length is expressed as five decimal places in the  
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54 software Gauss View. In the field of theoretical calculations, it is easy to find that the  
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4 distance<sup>7e</sup> and bond length<sup>7f</sup> (the unit in Å) were given in four decimal places and the  
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6 energies (unit in hartree<sup>7g</sup> and kcal/mol<sup>7h</sup>) were, respectively, given in 7 and 2 decimal places.  
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9 In the Table of conversion factors and physical constant,<sup>7i,j</sup> particularly, the numbers of  
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11 decimal places in various units are mostly greater than those suggested by Hoffmann,  
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13 Schleyer and Schaefer. Typically, for example, Bohr radius  $a_0 = 0.52918 \text{ \AA}$ , and gas  
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15 constant<sup>7j</sup>  $R = 8.314472 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , which are well known. In a word, there are too many  
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17 such examples if the commenter can carefully read the literatures.  
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23 Interestingly, the energies (unit in kcal/mol) were presented as integer in the commenter's  
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25 paper.<sup>7k</sup> In the same paper of the commenter,<sup>7l</sup> especially, the some of the energies (unit in  
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27 kcal/mol) were presented as integer but others were given in one decimal place. We don't  
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29 think that such expressions are standard.  
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34 Besides, the use of the words "silly" and "scientific illiteracy" in the paper<sup>6</sup> is different  
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36 from in the comments. In the latter case, it is the comment on the specific researchers.  
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38 Therefore, it is very rude and unprofessional that these two words appeared in the comment,  
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40 which violates the ACS (American Chemical Society) ethical obligations of reviewers.<sup>8</sup>  
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45 In our title paper, molecular energies, as the intermediate data, were directly obtained  
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47 from the output file of PC-Gamess program (Granovsky, A. A. www  
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49 <http://classic.chem.msu.su/gran/gamess/index.html>), and these were given in ten decimal  
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51 places in the output data file. Emphatically, the ESEs (energy unit in kcal/mol), as the  
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53 eventual energy data, were given in one decimal place, indicating the number of decimal  
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55 places in the value of ESE was correctly quoted.  
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60 Anyway, we have accepted the commenter's suggestions in the supporting information of

our response.

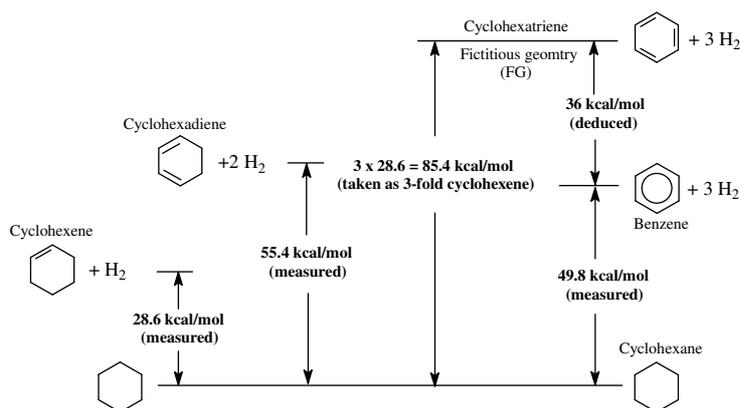
**4. About Definition of Aromatic Resonance Energy and about Use of the FG (cyclohexatriene) Geometry in the Measurement and Calculation of Aromatic Resonance Energy for Benzene.**

Commenter said: “*The fully optimized benzene structure Gb is now more stable than the artificial system GLb, but only by 10.8 kcal mol<sup>-1</sup>. This would correspond to the aromatic stabilization, although the number is much lower than any of the estimates in the literature. Bao and Yu found it unsatisfactory too<sup>3</sup>. Consequently, they constructed the third fictitious structure FG<sup>5</sup>. It is composed of three double bond lengths C1=C2 of the structure GEb-1 separated by three conjugated bonds C2-C3 from the same artificial structure. The line of thoughts was as follows. Since the  $\pi$ -electron delocalization obviously “destabilizes” the  $\pi$ -system, the fictitious structure FG possessing three cis-1,3-butadiene substructures should be three times less stable than GLb, i.e. by 28.2 kcal mol<sup>-1</sup>. If this values is added to the difference between  $E(GLb) - E(Gb) = 10.8$  kcal mol<sup>-1</sup>, then the extra stabilization energy ESE of benzene is as large as 39 kcal mol<sup>-1</sup>. Bao and Yu found this number beautiful enough to be recommended as the aromatic stabilization of benzene. Needless to say, this is completely arbitrary.*” (in the lines from 4 to 54 of page 3)

We really wonder whether the commenter knows the Kistiakowsky’s procedure and whether he understands the prerequisites to the determination of aromatic resonance energy.

Aromaticity is referred to as the phenomenon that the thermodynamic stability of the system is enhanced with respect to a structurally analogous model system (reference structure) as far as the energetic criterion is concerned.<sup>1a</sup> Therefore, **aromatic resonance**

energy of an aromatic molecule (such as benzene) is referred to as an extra stabilization energy with respect to its reference structure (such as cyclohexatriene) having a delocalized  $\pi$  system, and the two prerequisites for determining aromatic resonance energy are as follows: the choosing of reference structure and the finding out of a physical quantity satisfying the additivity condition.



Scheme 1. Kistiakowsky's procedure for experimentally determining aromatic stabilization energy of benzene.

In as early as 1936, thus, Kistiakowsky developed an experimental procedure for measuring aromatic resonance energy of benzene,<sup>9</sup> which is well known in the field of organic chemistry. In any standard textbook of organic chemistry<sup>10</sup> and related literature such as refs. 1a and 7a, Kistiakowsky's procedure was schemed and described (Scheme 1).

Kistiakowsky's procedure is based on the fact that heat (55.4 kcal/mole) of hydrogenation of cyclohexadiene is almost exactly twice the heat (28.6 kcal/mole) of hydrogenation of cyclohexene. Thus, as expected by Scheme 1, the heat of hydrogenation of the cyclohexatriene (it was named FG geometry in our title paper) should be  $3 \times 28.6 = 85.8$  kcal/mol if heats of hydrogenation of three carbon-carbon double bonds were still additive in the case of cyclohexatriene. In fact, cyclohexatriene is not a real molecule, and heat of

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4 hydrogenation for benzene is 49.8 kcal/mol. Therefore, 36 kcal/mol ( $85.8 - 49.8 = 36$ )  
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6 deviation from the additivity was found in the benzene molecule, and it was suggested as  
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8 aromatic resonance energy of benzene. Certainly, this amount can be considered as the  
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10 molecular energy (or enthalpy) difference between the FG and ground states of benzene, and  
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12 it can also be named the extra stabilization energy (ESE) of benzene with respect to its  
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14 reference structure (cyclohexatriene).  
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20 In our title paper, it was confirmed first that the energy differences  $[E(\text{GE-n}) - E(\text{GL})]$   
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22 between the corresponding GE-n and GL geometries are additive in each acyclic polyene, i. e.  
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24  $[E(\text{G}) - E(\text{GL})] \approx \Sigma[E(\text{GE-n}) - E(\text{GL})]$  and  $[E(\text{G}) - E(\text{GL})] - \Sigma[E(\text{GE-n}) - E(\text{GL})] \approx 0$ . In  
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26 the case of benzene, the molecular energy difference  $\Delta E^{\text{A1}} = [E(\text{GE-1}) - E(\text{GL})]$  between the  
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28 GE-1 and GL geometries is 9.4 kcal/mol. If these three energy differences  $\Delta E^{\text{An}}$  ( $n = 1, 2, 3,$   
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30 and  $\Delta E^{\text{A1}} = \Delta E^{\text{A2}} = \Delta E^{\text{A3}}$ ) were additive, the expected geometry of the ground state of  
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32 benzene would be similar to the FG (cyclohexatriene) geometry in which the lengths of the  
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34 single and double bonds would be equal to those of the C2–C3 and C1=C2 bonds in the GE-1  
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36 geometry. Correspondingly, the molecular energy difference  $[E(\text{FG}) - E(\text{GL})]$  between the  
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38 expected ground state (FG geometry) and GL geometry would be about  $3\Delta E^{\text{A1}}$  (28.2  
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40 kcal/mol), i.e.  $[E(\text{FG}) - E(\text{GL})] \approx 3x[E(\text{GE-1}) - E(\text{GL})]$ . In fact, cyclohexatriene is not a real  
41  
42 molecule, the energy difference  $[E(\text{G}) - E(\text{GL})]$  between the G and GL geometries of  
43  
44 benzene is -10.8 kcal/mol. In this case,  $([E(\text{G}) - E(\text{GL})] - 3 x [E(\text{GE-1}) - E(\text{GL})]) = [E(\text{G}) -$   
45  
46  $E(\text{GL})] - [E(\text{FG}) - E(\text{GL})] = E(\text{G}) - E(\text{FG}) = -10.8 - 28.2 = -39.0 \neq 0$ , indicating -39  
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48 kcal/mole deviation from the additivity was found in the benzene molecule (this detail  
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50 derivation is meant to help the commenter to understand the principle of our procedure). In  
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4 our title work, the quantity -39.0 kcal/mol is defined as ESE of benzene with respect to its  
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6 reference structure FG, and it is the molecular energy difference  $[E(G) - E(FG)]$  between the  
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8 G and FG states of benzene. Emphatically, therefore, it is a misunderstanding of definition of  
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10 aromatic resonance energy for the commenter to say: "*The fully optimized benzene structure*  
11  
12 *Gb is now more stable than the artificial system GLb, but only by 10.8 kcal mol<sup>-1</sup>. This*  
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14 *would correspond to the aromatic stabilization, although the number is much lower than any*  
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16 *of the estimates in the literature*".

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23 Accordingly, there are no differences, in the use of additive principle and in the  
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25 supposing of the fictitious geometry (FG), between the Kistiakowsky's procedures and ours.  
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27 The fundamental difference between the two procedures is in the choosing and constructing  
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29 of the reference structure (s) as well as in the type of physical quantity satisfying additivity.  
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### 32 33 34 **5. About the Signs of the Energy Differences $[E(GL) - E(G)]$ and $[E(GE-1) - E(G)]$**

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36 The commenter wrote: "*these calculations is that the bond length between two*  
37  
38 *"localized" bonds in GL (1.447 Å) is shorter than that in the corresponding conjugated bond*  
39  
40 *C2-C3 both in GE-1 (1.456 Å) and G (1.450 Å). If conjugation were operative, then the*  
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42 *opposite should be the case. The most striking result, however, is that the ground state G is*  
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44 *unstable relative to artificial structures GL and GE-1. The difference in energies  $E(GL) -$*   
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46  *$E(G) = -6.8$  and  $E(GE-1) - E(G) = -3.9$  (in kcal mol<sup>-1</sup>). This is obviously wrong and the*  
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48 *subsequent discussion is unscientific. It is, therefore, not surprising that conjecture following*  
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50 *these computations, namely, that  $\pi$ -electron conjugation destabilizes  $\pi$ -system, is*  
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52 *unacceptable*". ( in the lines from 31 to 43 of page 2)

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Firstly, we would refute the commenter's argument using the following Kollmar's words

(1979).<sup>3a</sup> “The  $\pi$  energy of the reference state is obtained from a Hückel calculation using a model Hückel operator with all those matrix elements set to zero which correspond to interactions between atomic orbitals separated by a single bond.” and “Energies obtained by this procedure can in principle be lower or higher than the energy of the actual system. In addition, the calculated energy is not a real physical quantity since it does not correspond to any state of any real physical system”. Therefore, it is unprofessional to question the signs of the following energy differences:  $[E(\text{GL}) - E(\text{G})]$  and  $[E(\text{GE-1}) - E(\text{G})]$  ( In the comment, the symbol  $E(\text{GE-1})$  was wrong written as  $E(\text{G-1})$ ).

Then, we would like to interpret why it is reasonable that the energy difference, such as  $[E(\text{GE-1}) - E(\text{GL})] > 0$ , is destabilizing. According to the data presented in Figures 1, 2 and 3 of the supporting information as well as according to those in our related papers,<sup>4</sup> the energy difference, such as  $\Delta E^{\text{A1}} = [E(\text{GE-1}) - E(\text{GL})]$  between the GE-1 and GL geometries of benzene, can be partitioned into various components using the following general expressions (1) to (7):

$$\Delta E = \Delta E_e + \Delta E_N \quad (1)$$

where  $\Delta E_e$  and  $\Delta E_N$  are total electron and nuclear repulsion energy differences, respectively.

$$\Delta E_e = \Delta E_H + \Delta E_{\text{two}} \quad (2)$$

where  $\Delta E_H$  and  $\Delta E_{\text{two}}$  are one and two electron energy differences, respectively.

$$\Delta E_e = \Delta E_e^\pi + \Delta E_e^\sigma \quad (3)$$

where  $\Delta E_e^\pi$  and  $\Delta E_e^\sigma$  are the  $\pi$  and  $\sigma$  components of total electron energy difference,<sup>3k</sup> respectively

$$\Delta E_N = \Delta E_N^\pi + \Delta E_N^\sigma \quad (4)$$

where  $\Delta E_N^\pi$  and  $\Delta E_N^\sigma$  are the  $\pi$  and  $\sigma$  components of nuclear repulsion difference,<sup>3k</sup> respectively

$$\Delta E = (\Delta E_e^\pi + \Delta E_N^\pi) + (\Delta E_e^\sigma + \Delta E_N^\sigma) = \Delta E^\pi + \Delta E^\sigma \quad (5)$$

where  $\Delta E^\pi$  and  $\Delta E^\sigma$  are the  $\pi$  and  $\sigma$  components of molecular energy difference, respectively the following partitions are available only at ab initio theory level:

$$\Delta E_e = \sum_{n=1}^n \Delta E_{e-n} + \sum_{n=1}^{n-1} \sum_{m=n+1}^n \Delta E_{e-nm} \quad (6)$$

where  $\Delta E_{e-n}$  and  $\Delta E_{e-nm}$  are the energy effects associated with FMO interactions occurring, respectively, in the double bonds such as C1=C2 (subscript “e-1”, n = 1) and C3=C4 (subscript “e-2”, n = 2) and occurring between the double bonds C1=C2 and C3=C4 (subscript “e-12”, n = 1 and m = 2), et. al.

The following partitions are available only at ab initio theory level, and related Fock and overlap integral matrices over AO (atomic orbital) basis set should be transferred into those over FMO (fragment molecular orbitals):<sup>4a-c</sup>

$$\Delta E_{e-nm} = \Delta E_{mn-CT} + \Delta E_{mn-EX} \quad (7)$$

where  $\Delta E_{mn-CT}$  and  $\Delta E_{mn-EX}$  are the charge transfer and exchange energy differences, respectively.

$$\Delta E_e^\pi = \sum_{n=1}^n \Delta E_{e-n}^\pi + \sum_{n=1}^{n-1} \sum_{m=n+1}^n \Delta E_{e-nm}^\pi \quad (8)$$

$$\Delta E_e^\sigma = \sum_{n=1}^n \Delta E_{e-n}^\sigma + \sum_{n=1}^{n-1} \sum_{m=n+1}^n \Delta E_{e-nm}^\sigma \quad (9)$$

At *ab initio* and DFT (density function theory) theory levels, therefore, the components of the energy difference, such as  $\Delta E^{A1} = [E(\text{GE-1}) - E(\text{GL})]$ , are complex. Particularly, as shown by the data in Figures 1 and 2 of the supporting information, the  $\pi$ -interactions between the double bonds has a great effect on the  $\sigma$  framework, and the size and sign of the

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4 energy difference (vertical resonance energy)  $\Delta E^V$  depend upon which components,  
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7  $|\Delta E_e^{V-\sigma}|$  or  $|\Delta E_e^{V-\pi}|$ , is greater.  
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10 On the contrary, the one of earliest resonance energy calculations was based on the  
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12 Hückel theory (1931), and the resonance energy for benzene is  $-2\beta$ ,<sup>11a-c</sup> indicating the  
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14 resonance energy (about  $-120 \sim -140$  kcal/mol,  $\beta = 60 \sim 70$  kcal/mol<sup>11d</sup> or  $64.5$  kcal/mol<sup>11e</sup>)  
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16 for benzene is stabilizing. As indicated by Jug, Hiberty and Shaik (2001)<sup>3e</sup>, “*The*  
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18 *contemporary theories of electronic structure of that time were unable to describe benzene in*  
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20 *a satisfactory manner. The Hückel method gave a beautifully simple solution of the*  
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22 *dilemma*”..... “*In this way, a stabilizing delocalization energy of  $-2\beta$  was obtained. This*  
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24 *led to the conclusion that delocalization of  $\pi$  electrons was a stabilizing factor which in turn*  
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26 *is responsible for the  $D_{6h}$  structure of benzene. Since it was believed that in benzene there is a*  
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28 *resonance interaction between two Kekule’ structures, the delocalization energy was also*  
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30 *called resonance energy*”. Accordingly, the earliest conclusion that  $\pi$ -electron  
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32 delocalization is stabilization came from the Hückel method. In the Hückel method, however,  
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34 only  $\pi$  electrons are involved and the coulomb and resonance integrals,  $\alpha_i$  and  $\beta_{ij}$  are constant  
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36 in benzene and its reference molecule ethylene. As a result, the effect of the  $\pi$ -interactions  
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38 between the double bonds on the  $\sigma$  system, denoted as  $(\Delta E_e^\sigma)$ , has been artificially excluded.  
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40 Hence, it is certain that the value ( $-21.2$  kcal/mol in Figure 2 of supporting information) of  
41  
42 the energy difference  $\Delta E^V(G)$  is greatly different from that of HRE (Hückel resonance energy,  
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44  $-120 \sim -140$  kcal/mol) although the two energy effects both arise from the  $\pi$ -electron  
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46 delocalization.  
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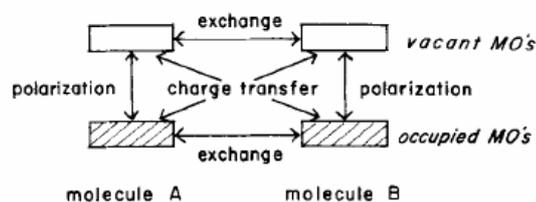
Particularly, as shown by our practical calculations (including our previous works<sup>4c</sup>) and

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4 by literature,<sup>12</sup> the exchange energy effect  $\Delta E_{mm-EX}$  is more destabilizing than the charge  
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6 transfer energy effect  $\Delta E_{mm-CT}$  is stabilizing. In the case of the GE-1 geometry of benzene, as  
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8 a result, the energy differences of  $\Delta E_e^{A1}$  and  $\Delta E^{A1}$  are always destabilizing (Figures 3c~3d),  
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10 leading to the following results: the length of the bond C2-C3 in the GE-1 geometry being  
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12 longer than that in the GL geometry, and molecular energy for the GE-1 geometry being  
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14 higher than that for the GL geometry. Emphatically, GE-n and GL are the fictitious  
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16 geometries, and the GL geometry resulted from GE-1 geometry via the way to artificially  
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18 exclude the destabilizing components from the GE-1 geometry. At ab initio and DFT theory  
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20 levels, therefore, the size and sign of resonance energy depend upon whether the exchange  
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22 interaction between double bonds is artificially excluded from the localized system (a  
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24 fictitious geometry) or not.  
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34 In some calculation methods such as BLW (block-localized wavefunction) method,<sup>13</sup> as  
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36 emphasized by Mo, Lin, Wu and Zhang,<sup>13d</sup> the exchange interactions are not artificially  
37  
38 excluded from the localized (reference) geometry. As a result, resonance energy, obtained  
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40 from BLW method, is always stabilizing. It may be one of the reasons why 91.6 kcal/mol  
41  
42 value (6-311+G\*\*) of vertical resonance (VRE) for benzene, obtained from BLW method by  
43  
44 Mo in 2006<sup>13e</sup>, is greater than that (74.3 kcal/mol<sup>13f</sup>, STO-6G) reported by Mo in 1994.  
45  
46 Particularly, as emphasized by Mo, 74.3 value of VRE for benzene is quite near to the value  
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48 (77 kcal/mol<sup>3a</sup>) by Kollmar (in addition, value of VRE for benzene, reported by Shak,<sup>13g</sup> is 65  
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50 kcal/mol at VBSCF/6-31G level).  
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58 In our program as well as in Kollmar and Jug procedures, on the contrary, all the charge  
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60 transfer and exchange interactions between the double bonds are artificially excluded from

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4 the localized geometry. The  $\pi$ -electron delocalization results from the charge transfer and  
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7 exchange interactions between double bonds rather than only from the charge transfer  
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10 interaction according to the following Morokuma's words (1976):<sup>2b</sup> "We now define the  
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12 *components of the interaction on the following principles which are based on traditional*  
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14 *viewpoints and physical meanings (Fig.1): (i) Electrostatic: the classical electrostatic*  
15  
16 *interaction between occupied MO'S which does not cause any mixing of MO'S. (ii)*  
17  
18 *Polarization: the interaction which causes the mixing between the occupied and vacant*  
19  
20 *MO'S within each molecule. (iii) Exchange: the interaction between occupied MO'S which*  
21  
22 *causes electron exchange and delocalization between molecules. (iv) Charge Transfer: the*  
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24 *interaction which causes intermolecular delocalization by mixing the occupied MO'S of one*  
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26 *molecule with the vacant MO'S of the other and vice versa."*  
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Figure 1. Interaction and mixing of MO's via various components of molecular interaction.

(here, Figure 1 is referred to as the original Figure 1 of Morokuma's paper (ref. 2b))

We would like to publish a paper to show the effects of the exchange interactions on the size and sign of resonance energy through comparison of our calculation results with those from BLW method if necessary.

Facing the incessant developments of calculation theory and method, we can't really understand why the commenter, as a quantum chemist, stiffly keeps his feeling (so called classic viewpoint) unchanged. The commenter should read a great number of literatures

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4 before making the comments.  
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## 7 **6. About Controversy on Resonance Stabilization.** 8

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10 The commenter wrote: “*Bao and Yu continue to discuss ESE of benzene heteroanalogues*  
11 *like pyridine, pyrazine, pyrimidine, 1,2,5-triazine, pyridazine and tetrazine, furan-like species,*  
12 *monosubstituted benzenes, benzenes fused to small rings including heteroatoms and*  
13 *biphenylenes. All conclusions obtained by Bao and Yu<sup>3</sup> analyses are unscientific and*  
14 *meaningless*” ( from line 56 of page 3 to line 7 of page 4).  
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23 We wonder once more whether the commenter knows the great controversy<sup>13g,14,3e</sup>, taken  
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25 place from 1980’s to 1990’s, on  $\pi$ -distortive propensity. The controversy was arisen by Shaik  
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27 and Hiberty in 1980’s. Shaik and his collaborators said:<sup>14d</sup> “*the  $\pi$ -electrons of allyl radical*  
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29 *(1) and benzene (2) prefer to distort to their localized  $\pi$ -components, much like the*  
30  
31  *$\pi$ -electrons of singlet cyclobutadiene (3). These distortive propensities in 1 and 2 are,*  
32  
33 *however, quenched by the  $\sigma$ -frames that strongly prefer regular geometries with uniform*  
34  
35 *C-C bond lengths. Consequently,  $\pi$ -electronic delocalization in 1 and 2 turns out to be a*  
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37 *byproduct of a geometric constraint and occurs despite the opposite inherent tendency of the*  
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39  *$\pi$ -electrons. This result touches a key question of chemical epistemology: is electronic*  
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41 *delocalization a driving force of stability and geometric shape?” Epiotis criticized the*  
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concept of resonance stabilization vividly to support Shaik’s viewpoint.<sup>15a</sup> Recently, as  
shown by a quantum chemical analysis of  $\alpha$ -substituent effects on alkyl and vinyl cations,  
delocalization does not always stabilize.<sup>15b</sup>

In our title paper, the shaik’s conclusion was supported. In strained aromatic compounds  
 $C_6X_3$  (tris-benzocyclobutenobenzene,  $X = -C_6H_4-$ ),  $C_6X_3$  (triscyclobutenobenzene-like

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4 species, X = -CH=CH-, -BH=BH-, -NH=NH-) and C<sub>6</sub>X<sub>3</sub> (tris-cyclopropenobenzene-like  
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6 species, X = -BH- and -NH-), as shown by the geometrical data obtained from the  
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8 restricted geometry optimizations (Figure 8 in our title paper), it is the  $\pi$  interactions between  
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10 the central phenyl ring and annelating groups X, rather than SIBL (strained-induced bond  
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12 localization), which distort the central phenyl ring away from equal bond lengths. Besides, as  
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14 shown by the geometrical data presented in the GE-7 and G geometries of substituted  
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16 benzenes (Figure 7 in our title paper), it is resonance interaction between substituent and  
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18 phenyl ring to distort phenyl ring.  
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26 Therefore, our calculation results, the length of single bond C2-C3 between two double  
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28 bonds C1=C2 and C3=C4 in the GE-1 geometry being longer than that of the corresponding  
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30 bond in the GL geometry no matter whether molecule is aromatic (benzene) or not  
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32 (hexatriene), also support Shaik's viewpoint.  
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37 In a way similar to the commenter's way, at last, we conclude our response also with the  
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39 Schleyer's comments (2001)<sup>1b</sup> on Shaik's works: "*The related review by S. Shaik, A. Shurki,*  
40  
41 *D. Danovich, and P. C. Hiberty emphasizes the duality of the  $\pi$ -component of*  
42  
43 *benzene.....The basis for the conclusion that the D<sub>6h</sub> structure of benzene is due to the  $\sigma$*   
44  
45 *framework, now widely accepted, is applied instructively to interpret a number of related*  
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47 *aromatic, antiaromatic, and strained systems."*  
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53 **Acknowledgment.** This work was supported by the National Natural Science Foundation of  
54  
55 China (Grants 20472088 and 20672119).  
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58 **Supporting Information Available:** The following information were detailed: (i)  $\sigma$ - $\pi$   
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60 Energy Partition; (ii) The Physical Meaning of Destabilizing Energy Differences; (iii)The

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4 Difference, in the Way to Change Nuclear Repulsion, between Benzene and Hexatriene is  
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6 compared in order to search for the potential correlation between energetic and geometrical  
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8 criteria.  
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