

**A Comment on the paper "Restricted Geometry Optimization: A Different Way to Estimate Stabilization Energies for Aromatic Molecules of Various Types", Peng Bao and Zhang-Heng Yu J. Phys. Chem. A 2007, 111, 5304-5313.**

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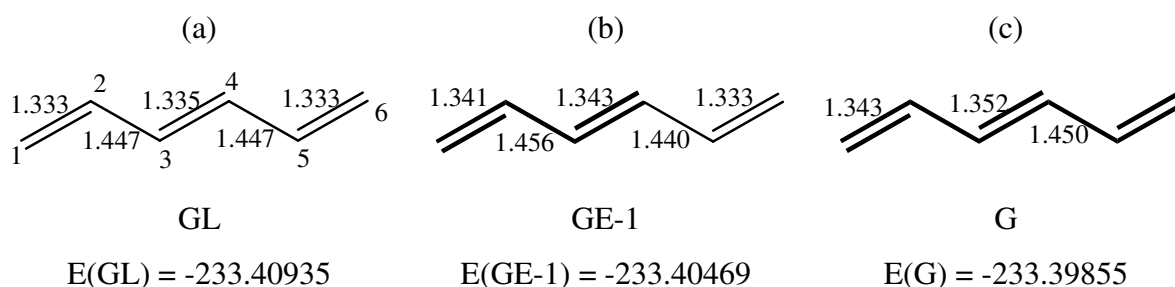
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4 **Estimate Stabilization Energies for Aromatic Molecules of Various Types**", Peng  
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16 Aromaticity is important concept in chemistry, which cannot be exactly defined.<sup>1,2</sup> This  
17 simple fact has two consequences: (1) there are many "measures" of aromaticity and (2)  
18 some of them are completely meaningless. The method recommended by Bao and Yu<sup>3</sup>  
19 belongs to the second category. Let us neglect a collection of arbitrary or wrong  
20 statements in the Introduction and focus on the main point of the paper. We shall stick to  
21 their terminology and notation. In order to estimate the extra stabilization energy (ESE)  
22 of an aromatic system, a choice of the reference structure should be made first. The  
23 authors consider the all-trans hexatriene as an illustrative case for their approach. This  
24 planar polyene is delocalized  $\pi$ -system, albeit to a modest extent. The bonds  $C_1=C_2$ ,  
25  $C_2=C_3$  and  $C_3=C_4$  are denoted as A, B and C, respectively. In the GL structure with  
26 restricted optimization (Fig. 1a) the submatrices of the Fockian matrix related to  
27 interactions between the  $\pi$  manifolds of the bonds A, B and C are set equal to zero. The  
28 same holds for the overlap S matrix. In the GE-1 restricted structure (Fig. 1b) the  
29 submatrix between A and B is explicitly taken into account, but the submatrices between  
30 A and C as well as B and C are forced to vanish. Finally, the structure G (Fig. 1c) has all  
31 independent geometric parameters optimized without any restrictions, thus corresponding  
32 to the ground state. Structures GL and GE-1 should help in estimating the effect of  $\pi$ -  
33 electron delocalization. The results obtained by the B3LYP/6-31G\* method were given in  
34 Å for the bond distances and in hartrees for the total energy<sup>3</sup>. The first eye-catching detail  
35 is that the bond distances and total molecular energies are given in four and seven  
36 decimal places, respectively. This is unrealistic! Too many decimal places are unphysical  
37 and are generally considered silly<sup>4</sup>. It is in place to cite P. B. Medawer in this  
38 context<sup>4</sup>: "There is no surer indicator of scientific illiteracy than the quotation of  
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numerical data to a degree of precision greater than the experimental observations warrant". The same applies to computations. Further, the first astonishing outcome of

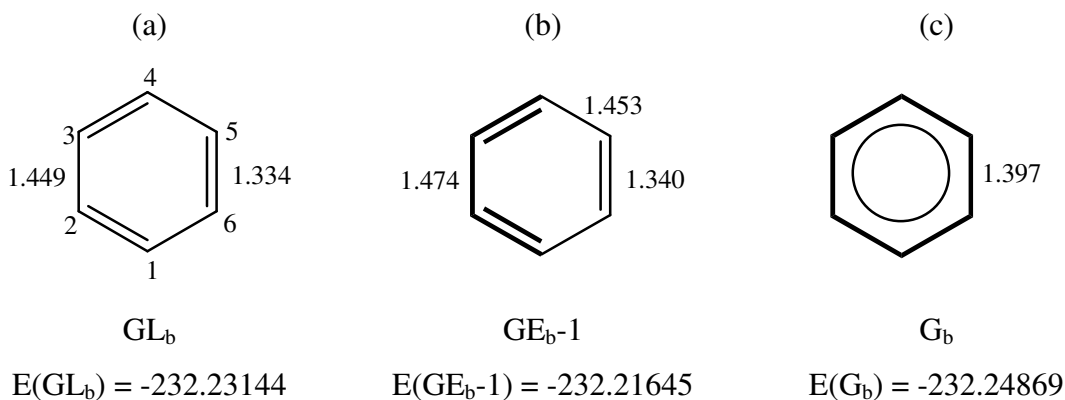


**Fig.1** (a) G2 is the structure with "fully localized"  $\pi$ -bonds (see text), (b) GE-1 corresponds to the structure with permitted  $\pi$ -interaction between the left and central  $\pi$ -double bonds, whereas the right  $\pi$ -double bond is kept "fully localized", (c) G is the ground state fully optimized structure of the zig-zag hexatriene. The double bonds with switched on interactions are depicted by thick lines.

these calculations is that the bond length between two "localized" bonds in GL (1.447 Å) is shorter than that in the corresponding conjugated bond C<sub>2</sub>-C<sub>3</sub> both in GE-1 (1.456 Å) and G (1.450 Å). If conjugation were operative, then the opposite should be the case. The most striking result, however, is that the ground state G is unstable relative to artificial structures GL and GE-1. The difference in energies  $E(\text{GL}) - E(\text{G}) = -6.8$  and  $E(\text{G-1}) - E(\text{G}) = -3.9$  (in kcal mol<sup>-1</sup>). This is obviously wrong and the subsequent discussion is unscientific. It is, therefore, not surprising that conjecture following these computations, namely, that  $\pi$ -electron conjugation destabilizes  $\pi$ -system, is unacceptable.

Bao and Yu<sup>3</sup> extend their analysis to aromatic stabilization. In the artificial "fully localized"  $\pi$ -electron picture GL<sub>b</sub> of benzene (Fig. 2a) the Fock operator matrix elements  $F^\pi(\text{A,B})$ ,  $F^\pi(\text{A,C})$  and  $F^\pi(\text{B,C})$ , where A, B and C denote  $\pi$ -AOs of different "localized"  $\pi$ -double bonds, are neglected as well as the corresponding overlap integrals. In the hypothetical structure GE<sub>b</sub>-1 the matrix elements between the C<sub>1</sub>-C<sub>2</sub> and C<sub>3</sub>-C<sub>4</sub>  $\pi$ -bonds are switched on. Results are again illogical. The conjugated bond C<sub>2</sub>-C<sub>3</sub> in GE<sub>b</sub>-1 (Fig. 2b) is significantly longer (1.474 Å) than that in GL<sub>b</sub> (1.449 Å). Similarly, GE<sub>b</sub>-1 structure is less stable than GL<sub>b</sub> by 9.4 kcal mol<sup>-1</sup> implying again that the  $\pi$ -electron

conjugation included over the cis-1,3-butadiene fragment destabilizes the system. The fully optimized benzene structure  $G_b$  is now more stable than the artificial system  $GL_b$ , but only by  $10.8 \text{ kcal mol}^{-1}$ .



**Fig. 2** (a) the  $GL_b$  structure is obtained by neglecting Fock and overlap matrix elements between  $\pi$ -AOs belonging to different  $\pi$ -double bonds, (b) the Fock and overlap matrix elements are switched on between two  $\pi$ -double bonds donated by thick lines in  $GE_b-1$ , (c) full optimization yields the ground state of benzene  $G_b$ . The double bond with switched on interactions are depicted by thick lines.

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  $FG^5$ . It is composed of three double bond lengths  $C_1=C_2$  of the structure  $GE_b-1$  separated by three conjugated bonds  $C_2-C_3$  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  $GL_b$ , i.e. by  $28.2 \text{ kcal mol}^{-1}$ . If this value is added to the difference between  $E(GL_b) - E(G_b) = 10.8 \text{ kcal mol}^{-1}$ , then the extra stabilization energy ESE of benzene is as large as  $39 \text{ kcal mol}^{-1}$ . Bao and Yu<sup>3</sup> found this number beautiful enough to be recommended as the aromatic stabilization of benzene. Needless to say, this is completely arbitrary.

However, this is not the end of the story. Bao and Yu continue to discuss ESE of benzene heteroanalogues like pyridine, pyrazine, pyrimidine, 1,2,5-triazine, pyridazine

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3 and tetrazine, furan-like species, monosubstituted benzenes, benzenes fused to small  
4 rings including heteroatoms and biphenylenes. All conclusions obtained by Bao and Yu<sup>3</sup>  
5 analyses are unscientific and meaningless. It is fitting to conclude the present comment  
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7 by an appeal of Hoffmann, Schleyer and Schaefer: More Realism, Please!<sup>4</sup>.  
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## 10 11 12 **References and Notes**

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