COMMENTS

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

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Aromaticity is an important concept in chemistry, which cannot be exactly defined.[1,2] This simple fact has two consequences, (1) there are many "measures" of aromaticity and (2) some of them are ill-founded. The method recommended by Bao and Yu[3] belongs to the second category. We shall stick to their terminology and notation. In order to estimate the extra stabilization energy (ESE) of an aromatic system, a choice of the reference structure should be made first. The authors consider the all-trans hexatriene as an illustrative case for their approach. This planar polyene is a delocalized π-system, albeit to a modest extent. The bonds $C_1{=}C_2$, $C_2{=}C_3$, and $C_3{=}C_4$ are denoted as A, B, and C, respectively. In the GL structure with restricted optimization (Figure 1a), the submatrices of the Fockian matrix related to interactions between the π manifolds of the bonds A, B, and C are set equal to zero. The same holds for the overlap **S** matrix. In the GE-1 restricted structure (Figure 1b), the submatrix between A and B is explicitly taken into account, but the submatrices between A and C as well as those between B and C are forced to vanish. Finally, the structure G (Figure 1c) has all independent geometric parameters optimized without any restrictions, thus corresponding to the ground state. Structures GL and GE-1 should help in estimating the effect of π-electron delocalization. The results obtained by the B3LYP/6-31G* method were given in angstroms for the bond distances and in hartrees for the total energy.[3] The first estonishing outcome of 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 $C_2{-}C_3$ both in GE-1 (1.456 Å) and G (1.450 Å). If conjugation was 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 differences in energies are $E(\mathrm{GL}) - E(\mathrm{G}) = -6.8$ and $E(\mathrm{G}\text{-}1) - E(\mathrm{G}) = -3.9$ (in kcal mol^{-1}). This cannot be true, and the subsequent discussion is therefore fatally flawed. It is, therefore, not surprising that conjecture following these computations, namely, that π-electron conjugation destabilizes π-system, is incorrect.

Bao and Yu[3] extend their analysis to aromatic stabilization. In the artificial "fully localized" π-electron picture GL$_b$ of benzene (Figure 2a), the Fock operator matrix elements F^{π}(A,B), F^{π}(A,C), and F^{π}(B,C), where A, B, and C denote π-AOs of different "localized" π-double bonds, are neglected as well as the corresponding overlap integrals. In the hypothetical structure GE$_b$-1, the matrix elements between the $C_1{-}C_2$ and $C_3{-}C_4$ π-bonds are switched on. Results are again illogical. The conjugated bond $C_2{-}C_3$ in GE$_b$-1 (Figure 2b) is significantly longer (1.474 Å) than that in GL$_b$ (1.449 Å). Similarly, the GE$_b$-1 structure is less stable than GL$_b$ by 9.4 kcal mol^{-1}, implying again that the π-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 kcal mol^{-1}.

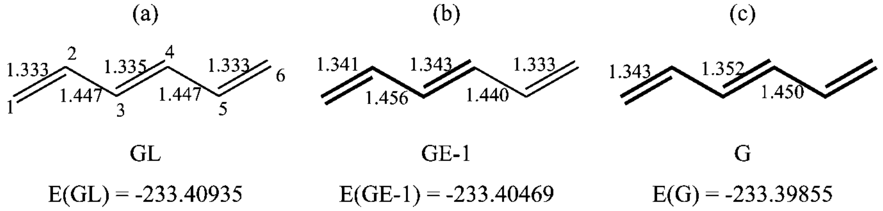

Figure 1. (a) GL is the structure with "fully localized" π-bonds (see text), (b) GE-1 corresponds to the structure with permitted π-interaction between the left and central π-double bonds, whereas the right π-double bond is kept "fully localized", and (c) G is the ground-state fully optimized structure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

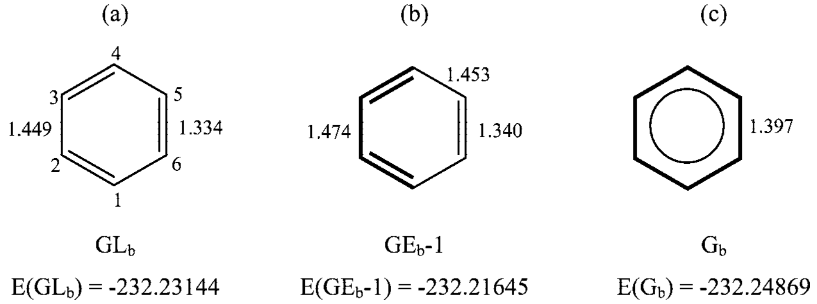

Figure 2. (a) the GL$_b$ structure is obtained by neglecting Fock and overlap matrix elements between π-AOs belonging to different π-double bonds; (b) the Fock and overlap matrix elements are switched on between two π-double bonds denoted by thick lines in GE$_b$-1; (c) full optimization yields the ground state of benzene G$_b$. The double bond with switched on interactions are depicted by thick lines.

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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.[3] 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 thought was as follows. Since the π-electron delocalization obviously "destabilizes" the π-system, the fictitious structure FG possessing three *cis*-1,3-butadiene substructures should be three times less stable than GL_b, that is, by 28.2 kcal mol^{-1}. If this value is added to the difference of $E(GL_b) - E(G_b) = 10.8$ kcal mol^{-1}, then the extra stabilization energy ESE of benzene is as large as 39 kcal mol^{-1}. Bao and Yu[3] 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 and tetrazine, furan-like species, monosubstituted benzenes, benzenes fused to small rings including heteroatoms, and biphenylenes. Unfortunatly, because the conclusions in all of these additional systems have the same faulty analyses at their foundation, these results are completely meaningless. In conclusion, it is perhaps fitting to repeat an appeal voiced previously by Hoffmann, Schleyer and Schaefer:[4] "More Realism, Please!"

References and Notes

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(5) Figure 3 of ref 3.

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