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Aromaticity is an important concept in chemistry, which cannot be exactly defined.\textsuperscript{1,2} This simple fact has two consequences: (1) there are many "measures" of aromaticity and (2) some of them are completely meaningless. The method recommended by Bao and Yu\textsuperscript{3} belongs to the second category. Let us neglect a collection of arbitrary or wrong statements in the Introduction and focus on the main point of the paper. 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 polynene is delocalized $\pi$-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 (Fig. 1a) the submatrices of the Fockian matrix related to interactions between the $\pi$ 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 (Fig. 1b) the submatrix between A and B is explicitly taken into account, but the submatrices between A and C as well as B and C are forced to vanish. Finally, the structure G (Fig. 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 $\pi$-electron delocalization. The results obtained by the B3LYP/6-31G* method were given in Å for the bond distances and in hartrees for the total energy\textsuperscript{3}. The first eyecatching detail is that the bond distances and total molecular energies are given in four and seven decimal places, respectively. This is unrealistic! Too many decimal places are unphysical and are generally considered silly\textsuperscript{4}. It is in place to cite P. B. Medawer in this context:\textsuperscript{4} "There is no surer indicator of scientific illiteracy than the quotation of
numerical data to a degree of precision greater than the experimental observations warrant. The same applies to computations. Further, the first astonishing outcome of

![Diagram](image)

**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 C2-C3 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 $E(GL) - E(G) = -6.8$ and $E(GE-1) - E(G) = -3.9$ (in kcal mol$^{-1}$). 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$^3$ extend their analysis to aromatic stabilization. In the artificial "fully localized" $\pi$-electron picture GL$^b$ of benzene (Fig. 2a) the Fock operator matrix elements $F^z(A,B)$, $F^z(A,C)$ and $F^z(B,C)$, 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$^b$-1 the matrix elements between the C1-C2 and C3-C4 $\pi$-bonds are switched on. Results are again illogical. The conjugated bond C2-C3 in GE$^b$-1 (Fig. 2b) is significantly longer (1.474 Å) than that in GL$^b$ (1.449 Å). Similarly, GE$^b$-1 structure is less stable than GL$^b$ by 9.4 kcal mol$^{-1}$ 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 kcal mol\(^{-1}\).

\[
\begin{align*}
\text{(a)} & \quad \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
1.449 \\
2 \\
3 \\
4 \\
5 \\
6
\end{array}
\end{array}
\end{array} \\
\text{GL}_b \\
E(\text{GL}_b) = -232.23144
\end{align*}
\begin{align*}
\text{(b)} & \quad \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
1.474 \\
1.340
\end{array}
\end{array}
\end{array} \\
\text{GE}_{b-1} \\
E(\text{GE}_{b-1}) = -232.21645
\end{align*}
\begin{align*}
\text{(c)} & \quad \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
1.397
\end{array}
\end{array}
\end{array} \\
\text{G}_b \\
E(\text{G}_b) = -232.24869
\end{align*}
\]

**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\(^3\). 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 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 kcal mol\(^{-1}\). If this value is added to the difference between \( E(\text{GL}_b) - E(\text{G}_b) = 10.8 \) 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-triazone, pyridazine...
and tetrazine, furan-like species, monosubstituted benzenes, benzenes fused to small rings including heteroatoms and biphenylenes. All conclusions obtained by Bao and Yu\textsuperscript{3} analyses are unscientific and meaningless. It is fitting to conclude the present comment by an appeal of Hoffmann, Schleyer and Schaefer: More Realism, Please!\textsuperscript{4}.

References and Notes


(5) Figure 3 of ref. 3.