

# Is Superbenzene Superaromatic?

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**Abstract:** The electronic structure calculations on the kekulene (superbenzene) molecule were carried out at the HF/STO-3G and HF/6-31G\*\* levels. The HF/6-31G\*\* energies were also calculated for a number of benzenoid hydrocarbons. The energies were decomposed into average nodal contributions from which a "superconjugation-free" reference energy for the kekulene molecule was estimated. The computed HF energy of kekulene was found to be lower than its reference counterpart by 32.9 kcal/mol at the STO-3G level and by 25.4 kcal/mol at the 6-31G\*\* level. This indicates the extra stabilization (superaromaticity) due to the presence of a circular formation of benzenoid rings. Geometry optimizations of the kekulene molecule at the HF/STO-3G and HF/6-31G\*\* levels yielded planar geometries in agreement with the experimental structure. The inner hydrogen atoms are found to be linked by "weak" bonds according to Bader's theory of atoms in molecules.

## Introduction

Kekulene<sup>1</sup> (Figure 1) was first synthesized in 1983 by Staab and collaborators.<sup>2</sup> It was also Staab who coined the names superbenzene, due to the resemblance of its six-sided ring to the benzene molecule, and kekulene.<sup>3</sup>

Kekulene has been the subject of several theoretical and experimental studies. Its fluorescence and phosphorescence spectra have been studied and compared to the results of semiempirical calculations.<sup>4</sup> Vogler studied the electronic structure and calculated the proton chemical shifts of the kekulene molecule and compared his results to experiment.<sup>5,6</sup> X-ray analysis has determined that the kekulene molecule, which is composed of a circular formation of benzenoid rings (a "super-ring"; Figure 1), is planar within experimental error with a mean deviation from the average plane of only 0.07 Å.<sup>7</sup> The molecular geometry of kekulene has been the subject of two recent theoretical studies involving molecular mechanics.<sup>8,9</sup>

The goal of the research presented in this paper is to employ ab initio quantum-mechanical calculations in an attempt to answer three questions related to the structure of the kekulene molecule. It has become a cliché of organic chemistry that cyclic conjugation can give rise to both energetic stabilization and destabilization. These phenomena are well-known as aromaticity and antiaromaticity, respectively.<sup>10,11</sup> The first problem investigated in this paper is whether "superconjugation" resulting from the presence of the ring of benzenoid rings yields analogous "superaromatic" or "superantiaromatic" energetic effects. Although the pattern of the carbon-carbon bonds in the kekulene molecule is best explained<sup>8</sup> by a system of localized Clar sextets,<sup>12</sup> the fact that the molecule is planar despite the presence of a steric overcrowding of the inner hydrogen atoms hints at the significance of superconjugation. The question of the planarity constitutes the second goal of this paper. In particular we attempt to find

out whether the small deviations from planarity found experimentally<sup>7</sup> are reproduced by ab initio calculations. Finally, we investigate the nature of interactions between the inner hydrogen atoms.

The organization of the paper is as follows: Computational details are explained in the following section. In the third section, we employ the model of additive nodal increments as a method for constructing a hypothetical "superconjugation-free" reference structure for kekulene. This is followed by the presentation of results and discussion.

## Computational Details

The total Hartree-Fock (HF) energies of the anthracene, phenanthrene, tetracene, benzanthracene, and chrysene molecules were calculated on a Cray Y-MP supercomputer at the HF/6-31G\*\* level with the GAUSSIAN 88 suite of programs.<sup>13</sup> Geometry optimizations were performed within the  $C_{2v}$  or  $C_1$  symmetry groups as appropriate. Geometry optimizations of the kekulene molecule in both the  $D_{6h}$  and  $C_{3v}$  symmetries were carried out on a Silicon Graphics IRIS-4D 240GTS digital computer with the TURBOMOLE system of programs<sup>14</sup> using the STO-3G and the 6-31G\*\* basis sets. The latter calculation, which involved 792 basis functions, required ca. 40 h of CPU time per iteration of the geometry optimization.

## Additive Nodal Increments

A proper reference structure is of central importance to the definition of aromaticity and superaromaticity. In order to assess superaromaticity of the kekulene molecule, we construct a suitable hypothetical reference structure which allows for a full retention of the local (benzenoid) conjugation, but ignores any extra conjugation that originates from the presence of a "super-ring". To accomplish this end, the model of additive nodal increments (ANI) is employed.

For a benzenoid hydrocarbon with a molecular graph  $G$ , one can create the corresponding dualist  $G'$  by replacing all of the hexagons with dots (Figure 2, part a; for definition of  $G$  and  $G'$  see refs 15 and 16). The vertices of  $G'$  are called nodes. While dissecting the dualists into their nodes (Figure 2, part b), one finds that (excluding the benzene molecule) there are 12 different types of nodes pertinent to benzenoid graphs.<sup>17</sup> It has been shown both numerically<sup>17</sup> and algebraically<sup>18</sup> that isonodal hydrocarbons

(1) Systematic name: 15,23:16,22-dimethenobenzo[1,2-*a*:4,5-*a'*]dipentaphene. Also known as cyclo[*d.e.d.e.d.e.d.e.d.e.d.e.*]dodecakisbenzene (2) and /28.18.17.9.7/-dodecacene (Cioslowski, J.; Turek, A. M. *Tetrahedron*, **1984**, *40*, 2161).

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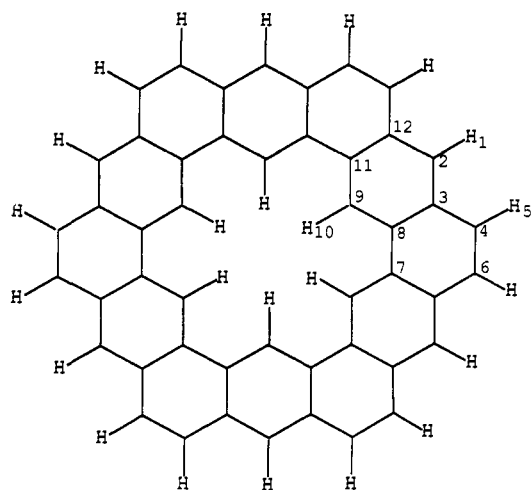


Figure 1. Molecular skeleton of the kekulene molecule.

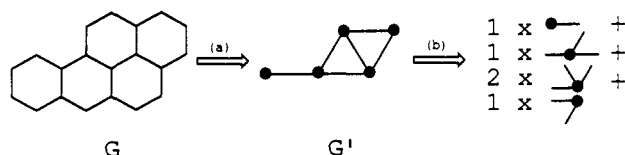


Figure 2. A molecular graph, its dualist, and corresponding nodes.



Figure 3. Three types of nodes pertinent to cata-condensed benzenoid hydrocarbons.

(hydrocarbons with an equal number of nodes of each type) have very similar Hückel total  $\pi$ -electron energies,  $E_\pi$ , and that these energies are approximately given by

$$E_\pi \approx \sum_{i=1}^{12} n_i E_i \quad (1)$$

where  $n_i$  is the number of nodes of type  $i$ , and  $E_i$  is the nodal energy increment for a node of type  $i$ . Thus, the values of  $E_\pi$  are to a large degree additive. The additivity stems from the fact that all the local conjugation effects are correctly included in the model.

In this paper, we invoke the additive nodal increments (ANI) concept to approximate the total HF energies rather than the  $\pi$ -electron energies of benzenoid hydrocarbons. In particular, we demonstrate below that the total HF energy,  $E_{\text{HF}}$ , of any cata-condensed benzenoid hydrocarbon that is free of steric overcrowding is approximately equal to

$$E_{\text{HF}} \approx n_1 E_1 + n_2 E_2 + n_3 E_3 \quad (2)$$

where  $n_i$  and  $E_i$  ( $i = 1, 2, 3$ ) are the numbers and the nodal energy increments for the three types of nodes present in cata-condensed systems (Figure 3). One should remark that, since the values of  $E_{\text{HF}}$  are basis-set dependent, so are the nodal energy increments,  $E_i$ .

In order to determine the nodal energy increments of the nodes 1–3 to the total energy of cata-condensed benzenoid hydrocarbons, a least-squares fitting weighted by the number of rings was carried out. The proper weighting allows for treating hydrocarbons of different size on an equal footing. The total energies,  $E_{\text{HF}(i)}$ , of the anthracene, phenanthrene, tetracene, benzantracene, and chrysene molecules were used in minimization of the error function

$$L = \sum_{i=1}^5 [E_{\text{HF}(i)} - (n_{1i} E_1 + n_{2i} E_2 + n_{3i} E_3)]^2 (n_{1i} + n_{2i} + n_{3i})^{-2} \quad (3)$$

Table I. Nodal HF Energy Increments for the Cata-Condensed Benzenoid Hydrocarbons<sup>a</sup>

	level of theory	
	HF/STO-3G <sup>b</sup>	HF/6-31G** <sup>c</sup>
Total Energies <sup>d</sup>		
anthracene	-529.4725 (-529.4724)	-536.0167 (-536.0167)
phenanthrene	-529.4874 (-529.4875)	-536.0277 (-536.0278)
tetracene	-680.2535 (-680.2564)	-688.6601 (-688.6625)
benzantracene	-680.2770 (-680.2714)	-688.6783 (-688.6736)
chrysene	-680.2838 (-680.2865)	-688.6824 (-688.6847)
Nodal Energy Increments <sup>e</sup>		
node 1	-189.3442	-191.6854
node 2	-150.7840	-152.6459
node 3	-150.7990	-152.6570
rms error/ring	0.0008	0.0006
maximal error/ring	0.0014	0.0012

<sup>a</sup>All energies in atomic units. <sup>b</sup>Reference 19. <sup>c</sup>Present work, energies at the HF/6-31G\*\* optimized geometries. <sup>d</sup>Values of the fitted total energies in parentheses. <sup>e</sup>See Figure 3 for a description of the nodes.

Table II. HF, Reference, and Stabilization Energies of the Kekulene Molecule<sup>a</sup>

	level of theory	
	HF/STO-3G	HF/6-31G**
HF energy	-1809.5502	-1831.8168
ref energy	-1809.4978	-1831.8573
		(-1831.8550) <sup>b</sup>
stabilization energy	-0.0524	-0.0405
rms error	0.0092	0.0077
maximal error	0.0168	0.0141

<sup>a</sup>All values in atomic units. <sup>b</sup>Uncorrected value, see text for explanation.

where  $E_j$  is the nodal energy increment of the  $j$ th node and  $n_{ji}$  is the number of type  $j$  nodes in the  $i$ th molecule. The results of this fitting for both the HF/STO-3G and HF/6-31G\*\* energies are presented in Table I. The former fitting was carried out with the HF/STO-3G energies which were taken from calculations of Schulman et al.<sup>19</sup>

Not surprisingly, inspection of the results reveals that for the five hydrocarbons studied, the ANI approach yields total HF energies that are in excellent agreement with the true ones. The HF/STO-3G energies are reproduced within 0.8 mhartree (0.5 kcal/mol) of the rms error per ring and 1.4 mhartree (0.9 kcal/mol) of the maximal error per ring. The HF/6-31G\*\* errors are even smaller, amounting to 0.6 mhartree (0.4 kcal/mol) of the rms error and 1.2 mhartree (0.8 kcal/mol) of the maximal error.

Taking the above considerations into account, one can construct a "superconjugation-free" reference structure for the kekulene molecule that has six type 2 nodes and six type 3 nodes (Figure 4). The predicted HF energy of this structure is

$$E_{\text{ANI}} = 6E_2 + 6E_3 \quad (4)$$

The values of  $E_{\text{ANI}}$  are listed in Table II as the "reference energy".

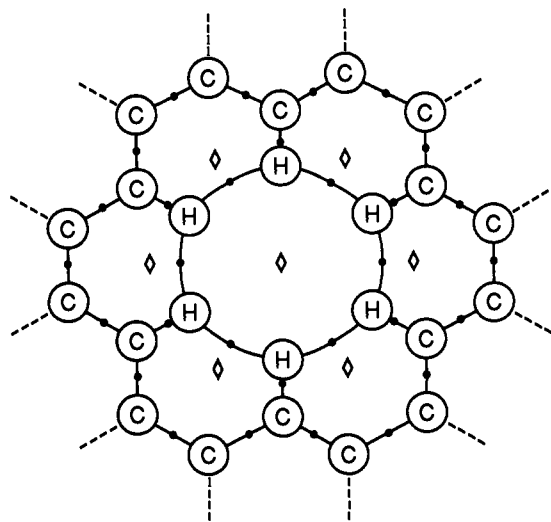
Taking the above error estimates into account, we believe that the reference energy,  $E_{\text{ANI}}$ , is determined with the accuracy of not less than 16.8 mhartree (10.5 kcal/mol) at the HF/STO-3G level and 14.1 mhartree (8.9 kcal/mol) at the HF/6-31G\*\* level.

## Results and Discussion

The HF/6-31G\*\* optimized geometries for the anthracene, phenanthrene, tetracene, benzantracene, and chrysene molecules are displayed in Figure 5, parts a–e. The corresponding total energies are listed in Table I. The HF energy of both the kekulene molecule and the kekulene reference structure are given in Table

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**Figure 6.** The molecular graph of the central portion of the kekulene molecule (the geometry and the electron density computed at the HF/6-31G\*\* level). Nuclei are denoted by circles, bond points by heavy dots, and ring points by diamonds.

geometry corresponds to a minimum on the potential energy hypersurface. This is in variance with the molecular mechanics calculations<sup>8,9</sup> which predict a slightly nonplanar  $D_{3d}$  structure as the minimum.

We note (Table III) that the geometries of the kekulene molecule optimized at the HF/STO-3G and HF/6-31G\*\* levels agree very well with the X-ray data of Staab et al.<sup>7</sup> In particular, the characteristic pattern of benzene rings ( $C_2-C_3$ ,  $C_3-C_8$ , and  $C_8-C_9$ ) linked through a series of single ( $C_3-C_4$  and  $C_7-C_8$ ) and double ( $C_4-C_6$ ) bonds is well-reproduced. The distortions of the bond angles from the value of  $120^\circ$  are also well-reflected in the calculated geometries. The inner C-H bonds ( $C_9-H_{10}$ ) are calculated to be shorter than the outer ones ( $C_2-H_1$  and  $C_4-H_5$ ) by ca. 0.01 Å, as expected.

The distances between the inner hydrogen atoms (1.853 Å at the HF/STO-3G level and 1.851 Å at the HF/6-31G\*\* level) are shorter than the sum of their van der Waals radii. This gives rise to the question concerning the nature of interactions between these atoms. We analyzed both the HF/STO-3G and the HF/6-31G\*\* electron densities with the aid of Bader's topological theory of atoms in molecules.<sup>20</sup> For both densities, there exist

highly curved bond paths between the hydrogen atoms (Figure 6) giving rise to "weak" bonds that have been recently found in several organic molecules.<sup>21</sup> At the present moment we are unable to attach any physical significance to these bonds.

### Conclusions

The absence of large variations in the carbon-carbon bond lengths is not a prerequisite for stabilization due to either aromaticity or superaromaticity. The comparison between the anthracene and phenanthrene molecules can serve as an example. Despite much larger variations in the carbon-carbon bond lengths (compare parts a and b in Figure 5) and the presence of two sterically crowded hydrogen atoms, phenanthrene has lower energy (see Table II) and therefore can be regarded as more aromatic. Ab initio electronic structure calculations demonstrate that the kekulene molecule is stabilized not only by the conjugation within benzene rings (aromaticity) but also by the conjugation within the super-ring of benzene rings (superaromaticity). We arrived at this conclusion by carefully analyzing the energetics of the kekulene molecule itself and the reference structure that does not allow for superconjugation. From the magnitude of the energy difference, compared to the possible random errors in the energy of the reference structure, we conclude that the extra stabilization is a real physical effect. The stabilization is strong enough to overcome steric repulsion of the inner hydrogen atoms and retain planarity of the molecule. We believe that, since reactions that conserve the number of nodes (isonodal reactions) also conserve the number of individual bonds, inclusion of electron correlation would change the computed stabilization energy by an insignificant amount.

In the kekulene molecule we find yet another example of bonds, as defined within Bader's topological theory of atoms in molecules, that are in variance with the expectations based on "chemical intuition".

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