

# Empirically corrected ab initio calculation of proton NMR chemical shifts of antiaromatic hydrocarbons

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## Abstract

Rablen and co-workers have developed an ab-initio based protocol for calculating proton NMR chemical shifts drawn from a wide range of molecules (80 molecules, 161 shifts) with a standard deviation of 0.15 ppm. When the Rablen model was applied to the protons of a set of five relatively large aromatic hydrocarbons, the fit was excellent ( $\Phi=0.05$  ppm), but when it was applied to the protons of a set of antiaromatic hydrocarbons, it failed badly ( $\Phi=0.73$  ppm). The failure is identified with the well known too-small HOMO–LUMO gap arising from the B3LYP procedure employed in the Rablen model and the intrinsically small HOMO–LUMO gaps of antiaromatic species.

Five empirical fixes for the failure are developed. Each markedly improves the fit of the antiaromatic NMR proton shifts. The best of them, based on graph theory, gives a standard deviation of only 0.10 ppm for the 16 antiaromatic proton shifts, a standard deviation of 0.05 ppm for the 19 aromatic proton shifts, and a standard deviation of 0.14 ppm for the combined set of 196 proton shifts.

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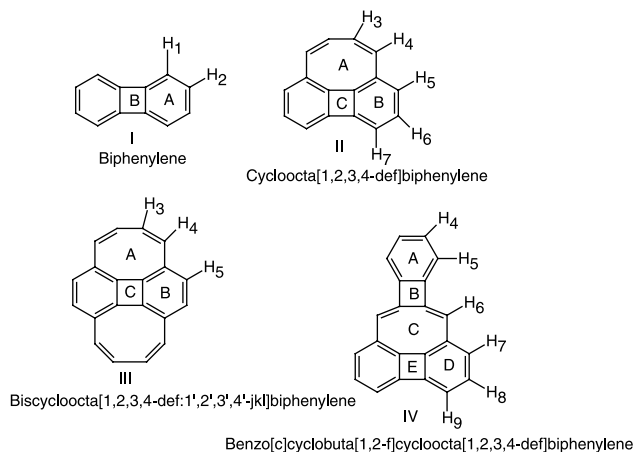
**Keywords:** Antiaromatic; Proton chemical shifts; Ab-initio; Hückel; Graph theory; ASC

## 1. Introduction

The concept of aromaticity has played a seminal role in the development of chemical bonding theory [1–3]. Kekulé started the process with his recognition that aromatic molecules possessed a core ring of six carbon atoms and unlike alkenes were chemically persistent [4–6]. Hückel rationalized Kekulé's representation of benzene as having six equivalent carbons and provided a quantitative basis for distinguishing aromatic and olefinic species [7,8]. This perspective gradually evolved into a three-way classification scheme: aromatic, olefinic, and antiaromatic [9]. The antiaromatic class, consisting in its simplest representation of rings containing  $4n$   $\pi$ -electrons, proved particularly troublesome because molecules designed as examples proved either to be experimentally inaccessible or disappointingly olefinic due to geometric distortions. An important long-standing exception was biphenylene, **I**, with its sandwiching of an antiaromatic four-membered ring between a pair of aromatic benzene rings [10].

Our contribution to this extensively studied area consisted

of designing and synthesizing a series of molecules that simultaneously contained connected structural elements from each of the three categories and the essential feature that these elements were geometrically constrained to lie in a common plane. Of the several molecules synthesized, the three shown here as **II**, **III**, and **IV** are representative [11–17]. The hydrocarbon set **I–IV** will play a special role in this article.



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The design of hydrocarbons **II–IV** was based on a graph-theoretical perspective of the stability of hydrocarbons [18–20]. From this point of view the set of Kekulé structures that can be drawn for any  $\pi$ -electron hydrocarbon do not

Table 1  
Ring currents calculated by simple and iterated Hückel (relative to benzene = 1.00)

Ring	Simple Hückel	Iterated Hückel	Ring	Simple Hückel	Iterated Hückel
Antiaromatic			Aromatic		
I-A	0.270	0.608	V-A	1.093	1.001
I-B	−1.748	−0.804	VI-A	1.084	0.916
II-A	−2.637	−0.705	VI-B	1.279	1.235
II-B	−0.594	0.369	VII-A	1.137	1.064
II-C	−1.263	−0.745	VII-B	0.975	0.804
III-A	−6.717	−1.071	VIII-A	1.152	1.063
III-B	−4.185	−0.091	VIII-B	1.068	0.922
III-C	0.886	−0.093	IX-A	1.068	0.845
IV-A	1.127	0.966	IX-B	1.305	1.247
IV-B	0.679	0.180			
IV-C	−0.701	−0.313			
IV-D	0.013	0.478			
IV-E	−1.632	−0.777			

represent valence-bond wavefunctions. Rather, they are symbolic representations of the non-zero expansion elements of the Hückel (molecular orbital) secular determinant [21]. Since expansion elements of a determinant possess an algebraic sign, so do these Kekulé structure representations. As it works out, with cyclic  $\pi$ -electron hydrocarbons that possess rings containing only  $4n + 2$  carbon atoms the Kekulé structures all have the same sign. However, when rings containing  $4n$  carbon atoms are present, the signs can be either positive or negative. The rules for deciding which sign to assign are straightforward and won't be repeated here [19]. It is useful to define the Algebraic Structure Count, ASC, as the absolute value of the algebraic sum of the signed Kekulé structures. For benzenoid hydrocarbons, since the structures have the same sign their ASC values are simply equal to the number of Kekulé structures, KSC. For any antiaromatic species,  $ASC < KSC$ .

What begins to make the graph-theory approach truly useful is that the absolute value of the product of the Hückel eigenvalues (in beta units), however irrational the individual values, is exactly  $(ASC)^2$ , an integer. Since the eigenvalues are bounded as  $(\pm 3)$ , in a comparison of two hydrocarbons with the same number of carbon atoms, the one with the smaller ASC value is most likely to have a smaller HOMO–LUMO gap and a smaller total  $\pi$ -electron energy.

Even more powerful is the result that to an excellent approximation the total  $\pi$ -electron energy is given by

$$E_{\pi} \text{ (in beta units)} = A \ln(ASC) + B n + C v, \quad (1)$$

where  $n$  is the number of  $\pi$ -atoms and  $v$  is the number of formal bonds between the  $\pi$ -atoms ( $v=6$  for benzene;  $v=11$  for naphthalene) [22,23]. The A, B, and C parameters can be evaluated either by fitting a set  $\pi$ -hydrocarbon energies or, as spelled out in the Appendix A, by fitting the function  $|x|$  to the expression  $a_1 \ln(|x|) + a_0 + a_2 x^2$  over the range  $3 \geq x \geq 0.1$  and  $-0.1 \leq x \leq -3$ .

Since all alkenes have only one Kekulé structure, it follows that the quantity  $A \ln(ASC)$  is the molecular orbital delocalization energy relative to a reference polyalkene having the same number of atoms and bonds. It is useful to define an

'antiaromaticity index' as  $\ln(KSC/ASC)$ , a quantity proportional to the difference in energy between an antiaromatic hydrocarbon and the energy it would have had if all of the Kekulé structures had the same sign.

Hydrocarbon	KSC	ASC	$\ln(KSC/ASC)$ ,
<b>I</b>	5	3	0.51
<b>II</b>	6	2	1.10
<b>III</b>	7	1	1.95
<b>IV</b>	9	5	0.59

These KSC and ASC values make it clear that the sequence **I**, **II**, and **III** is one of sharply increasing antiaromaticity. This expectation is consistent with their respective chemical stabilities, colors (a measure of the HOMO–LUMO gap), and their NMR chemical shifts (see Table 1). Hydrocarbon **I** is an extremely stable yellow solid; **II** is a chemically reactive, but otherwise stable brick red solid; **III** is an extremely reactive, unstable blue-black solid with a half-life in the solid phase of seconds. The values for **IV**, which has a stability comparable to **I**, illustrates that the degree of antiaromaticity depends on more than the number of  $4n$ -membered rings present and their interconnectivity as reflected in their ASC values is an essential factor.

At the time these antiaromatic hydrocarbons were prepared, practical ab-initio methods for calculating proton shifts were not available, although semi-empirical techniques served fairly well. McWeeny had developed an exquisite computational procedure using Hückel molecular orbitals to calculate ring currents [24]. Haigh, Mallion and Armour showed that with these currents and a suitable geometric model for calculating the induced magnetic field at each proton, a set of 66 aromatic proton shifts could be correlated with a  $\Phi=0.06$  ppm [25]. This procedure failed badly, however, ( $\Phi=1.81$  ppm) with the antiaromatic proton shifts, presumably because the Hückel assumption of uniform  $\pi$ -bond lengths was invalid. Indeed, by making the Hückel  $\beta$ -values a function of bond length and the bond lengths a simple linear function of the Hückel bond order, after iteration to self consistency (characterized in Section 2), the proton chemical shifts for the antiaromatic protons could be fit with a  $\Phi=0.17$  ppm [14,16,17]. A number of geometry

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