A test of Clar aromatic sextet theory

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Abstract. The Clar aromatic sextet theory predicts that the intensity of cyclic conjugation in chevron-type benzenoid hydrocarbons monotonically decreases along the central chain. This regularity has been tested by means of several independent theoretical methods (by the energy effects of the respective six-membered rings, as well as by their HOMA, NICS, and SCI values, calculated at the B3LYP/6-311G(d,p) level of DFT theory). Our results show that the predictions of Clar theory are correct only for the first few members of the chevron homologous series, and are violated at the higher members. This indicates that Clar theory is not universally applicable, even in the case of fully conjugated benzenoid molecules.

Keywords: Clar theory, aromatic sextet, cyclic conjugation, benzenoid hydrocarbons, chevron homologous series.

INTRODUCTION

Benzeneoid hydrocarbons form a class of conjugated π-electron systems the theory of which has been elaborated in due detail.1–7 Cyclic conjugation in benzenoid hydrocarbons was especially much studied, see the papers8–14 and the references cited therein. The “aromatic sextet theory” of Erich Clar1,3 provides the simplest and most direct way by which an insight into the dominant modes of cyclic conjugation of a benzenoid molecule can be gained. In the Clar theory, so-called “Clar formulas” are constructed by placing “aromatic sextets” into some rings of a benzenoid molecule, obeying certain formal rules3,15 (cf. Fig. 1). Rings in which “aromatic sextets” are located are predicted to have a high intensity of cyclic conjugation. The original version of the Clar method is qualitative and has no direct foundation in quantum theory. Eventually, much effort was devoted to providing a quantitative and theoretically founded re-formulation of the Clar model (see the recent works18–26 and the references cited therein). In earlier

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studies,\textsuperscript{13,14,27,28} examples of benzenoid hydrocarbons were found in which the predictions of Clar theory were violated. However, the benzenoid systems in these examples contained fixed single and double carbon–carbon bonds, and thus, it could be argued that the Clar theory was not strictly applicable to them. Herein, a class of fully conjugated benzenoid molecules (\textit{i.e.}, molecules without fixed single and double carbon–carbon bonds) has been detected in which the modes of cyclic conjugation are not in full agreement with the Clar model. These are the members of the chevron homologous series,\textsuperscript{16,17} see Fig. 1.

**CLAR FORMULAS OF CHEVRONS**

For \( n \geq 2 \), the formula of the chevron molecule \( \text{Ch}_n \) (see Fig. 1) is \( C_{8n+6}H_{2n+8} \) and the number of its hexagons is \( 3n \). It will now be shown that this benzenoid system has a total of \( \left( \frac{1}{6} \right) n(n-1)(2n-1) \) Clar formulas.

Suppose that the central hexagons of \( \text{Ch}_n \) are labeled as indicated in Fig. 1. Then, if an aromatic sextet is placed in hexagon R1, an additional aromatic sextet can be placed in the upper chain of \( \text{Ch}_n \) in \( n-1 \) different ways. The same is the
case with an aromatic sextet in the lower chain of $Ch_R$. Consequently, there are $(n-1)\times(n-1) = (n-1)^2$ Clar formulas when an aromatic sextet is placed in ring R1, see diagram D1 in Fig. 2. If an aromatic sextet is placed in the central ring R2, then the aromatic sextets in the upper and lower chains can each be arranged in $n-2$ different ways, resulting in a total of $(n-2)^2$ Clar formulas, see diagram D2 in Fig. 2.

![Diagram D1 and D2](image)

Fig. 2. Diagram $D_1$ is the usual abbreviated representation$^{1,2}$ of the $(n-1)^2$ Clar formulas of the chevron $Ch_n$ with an aromatic sextet in position $R_1$. Diagram $D_2$ represents the $(n-1)^2$ Clar formulas with an aromatic sextet in position $R_2$.

Continuing this argument, it can be seen that there are $(n-i)^2$ Clar formula in which an aromatic sextet is positioned in the central ring $R_i$, $i=1,2,\ldots,n$. Thus the total number of Clar formulas is $\sum_{i=1}^{n} (n-i)^2$, which by direct calculation yields the expression $(1/6)n(n-1)(2n-1)$.

Notice that for $i=1,2,\ldots,n$, the term $(n-i)^2$ monotonically decreases. Thus, the number of Clar formulas in which the ring $R_i$ has an aromatic sextet (rapidly) decreases along the central chain of the chevron $Ch_n$.

The Clar theory yields a pictorial and qualitative description of the conjugation models of the $\pi$-electrons in benzenoid molecules. From an analysis of Clar formulas, it is not possible (or, at least, it is very risky) to obtain any quantitative result concerning cyclic conjugation. However, it is doubtless that the rings of a benzenoid system in which an aromatic sextet is placed in the majority (or all) Clar formulas must be viewed as possessing a high degree of cyclic conjugation. On the other hand, the rings in which an aromatic sextet is placed only in a few (or no) Clar formulas must be predicted as those in which the intensity of cyclic conjugation is low. In other words, the fundamental assumption of Clar theory is that the greater is the number of Clar formulas in which a ring $R$ has an aromatic sextet, the stronger is the cyclic conjugation in this ring.

In the case of the central rings of the chevron-type benzenoids, the Clar theory implies a simple regularity: going along the central chain of $Ch_n$, starting
at the ring $R_1$ and ending at the ring $R_n$, the intensity of cyclic conjugation should monotonically decrease.

The aim of the present work is to check if this regularity is a true $\pi$-electron property or an artifact of the Clar theory.

A PRELIMINARY TEST

A quantitative, graph-theory based measure of cyclic conjugation in $\pi$-electron systems, especially in benzenoid hydrocarbons, is achieved by the energy-effect of the respective cycles. Details of this method have been earlier described several times, e.g., in the review. Thus, $ef = e(Z)$ is the energy-effect caused by cyclic conjugation of $\pi$-electrons along the cycle $Z$ in the underlying conjugated molecule. As usual, in what follows, $ef$ will be expressed in the units of the carbon–carbon resonance integral $\beta$, where $\beta \approx -137$ kJ mol$^{-1}$. Note that since $\beta$ is negative-valued, large (positive) $ef$-values mean a large stabilizing energy-effect caused by conjugation in the cycle $Z$, providing an energetic measure of the intensity of cyclic conjugation in $Z$.

The energy-effects of the central rings of the first few members of the chevron series are presented in Table I. The calculated $ef$-values indicate that the monotonicity rule is obeyed only for $\text{Ch}_2$ and $\text{Ch}_3$, but is already violated at $\text{Ch}_4$ and for all higher chevron homologues. Thus, according to the $ef$-values, if $n$ is large enough, the cyclic conjugation along the central chain of $\text{Ch}_n$, starting at the ring $R_1$ and ending at the ring $R_n$, first decreases, then increases reaching a maximum around the center of the chain, and then decreases again. This is in stark contrast with the predictions of Clar theory.

In view of the fact that the energy-effects are computed based on a relatively crude graph-theory-based model, the results based on $ef$-values (shown in Table I) cannot be considered as sufficient proof of the inadequacy of the Clar theory. Therefore, in order to strengthen the arguments, several other criteria, based on much more sophisticated quantum-chemical approaches, were employed.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>$R_5$</th>
<th>$R_6$</th>
<th>$R_7$</th>
<th>$R_8$</th>
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<td>0.0366</td>
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<td>0.0355</td>
<td>0.0363</td>
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There are several methods for assessing the intensity of cyclic conjugation in individual rings (often referred to as “local aromaticity”) based on high-level $ab$
**Test of Clar Aromatic Sextet Theory**

Initio molecular orbital (MO) and density-functional theoretic (DFT) approaches. Of these, the harmonic oscillator model (HOMA),\textsuperscript{29–31} nucleus-independent chemical shifts (NICS),\textsuperscript{19,32–34} and multicenter (six-center) bond indices (SCI) were used in this work.\textsuperscript{35–38}

**Numerical Work**

The DFT calculations on the chevrons $\text{Ch}_n$ were performed for $n = 2, 3, 4, 5, 6, 7$ and $8$, using the Gaussian 09W package, version 0.1, at the B3LYP/6-311G(d,p) level of theory.\textsuperscript{39} Geometry optimization confirmed that the molecules were perfectly planar. By frequency calculations, it was confirmed that the geometry determined corresponds to a true energy minimum. Bond lengths were taken from the optimized geometry.

The HOMA index\textsuperscript{29–31} was calculated by means of the formula:

$$\text{HOMA} = 1 - \frac{1}{N} \sum_{i=1}^{N} \alpha (d_{\text{opt}} - d_i)^2$$

where $N$ is the number of bonds of the ring considered, $\alpha = 25.77 \times 10^{-3}$ is a normalization constant fixed to give HOMA = 0 for a model anti-aromatic system and HOMA = 1 for a fully delocalized $\pi$-electron system; $d_{\text{opt}} = 138.8$ pm, and $d_i$ is an actual bond length.

NICS values\textsuperscript{32–34} were calculated at the B3LYP/6-311G(d,p) level through the gauge-including atomic orbital method (GIAO).\textsuperscript{40} The NICS-values reported below were calculated 1 Å above the ring center.

The SCI indices\textsuperscript{35–38} were calculated from the B3LYP/6-31G(d) density matrices obtained, starting from the B3LYP/6-311G(d,p) optimized geometries. Calculations of SCI were performed using in-house software.

The numerical values of these three indicators of cyclic conjugation in individual rings of the central rings $R_1, R_2, \ldots, R_n$ of $\text{Ch}_n$ for $n = 2, 3, 4, 5, 6, 7$ and $8$, are given in Tables II–IV.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
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<td>7</td>
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<td>8</td>
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<td>0.6850</td>
<td>0.6597</td>
<td>0.6703</td>
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<td>0.6883</td>
<td>0.6272</td>
<td>0.3242</td>
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**Discussion and Concluding Remarks**

First, by inspection of the data in Tables II–IV, it can be seen that the results of the preliminary test (based on energy-effects) were only partially confirmed. Namely, the DFT-based indices indicate that the predictions of the Clar theory are correct up to $n = 5$ (or, in the case of NICS, up to $n = 6$), but, again, are violated for the higher members of the chevron series.

Nevertheless, the main conclusion of the preliminary test remains. According to the HOMA, NICS, and/or SCI indices, if $n$ is large enough, the cyclic
conjugation along the central chain of $Ch_n$ first decreases, then increases reaching a maximum around the center of the chain, and then decreases again. This breakdown of the Clar theory occurs at $n = 6$ or $n = 7$.

TABLE III. NICS(1) values of the rings $R_1, R_2, \ldots, R_n$. Other details are the same as in Table I. Note that the more negative NICS(1) is, the more intense is the respective cyclic conjugation.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>$R_5$</th>
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<td>+5.73</td>
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</table>

In the earlier chemical literature, countless examples have been offered, demonstrating the correctness of the Clar aromatic sextet theory. The most convincing of these examples (see, for instance, in the books $1, 3, 6$) are based on the comparison of the predictions of Clar theory and experimental findings. It happens, however, that all these example-based confirmations of the validity of Clar theory pertain to relatively small benzenoid molecules. In the present work also, it was found that the Clar theory performs well for the smaller members of the chevron series. Violations of Clar theory seem to occur at larger benzenoids. In the present case, these are the chevron-type species $C_{54}H_{20}, C_{62}H_{22}$.

The main conclusion is thus the following. There is a size-limit above which the $\pi$-electrons of benzenoid molecules behave in a way that violates the predictions of the Clar aromatic sextet theory. Consequently, this theory may be used only for smaller and moderate-sized benzenoids, and then only with a due degree of caution.

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ИЗВОД
ПРОВЕРА КЛАРОВЕ ТЕОРИЈЕ АРОМАТИЧНОГ СЕКСТЕТА
ИВАН ГУТМАН, СЛАВКО РАДЕНКОВИЋ, МАРИЈА АНТИЋ и ЈЕЛЕНА ЂУРЂЕВИЋ
Природно–математички факултет Универзитета у Крагујевцу

Кларова теорија ароматичног секстета предвиђа да интензитет цикличне конјугације у бензеноидним угљоводоницима шевронског типа монотоно опада дуж централног ланца. Ова правилност је проверена помоћу неколико независних теоријских метода (са енергетским ефектима одговарајућих шесточланих прстенова, као и помоћу њихових HOMA, NICS и SCI вредности, рачунатих на B3LYP/6-311G(d,p) нивоу теорије функционала густине). Резултати показују да предвиђања Кларове теорије важе само код првих чланова хомологног низа шеврона, док се код виших чланова јављају одступања. То укazuje на то да Кларова теорија није универзално применљива, чак и код потпуно конјугованих бензеноидних молекула.

(Примљено 20. маја, ревизирано 28. маја 2013)

REFERENCES
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