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A test of Clar aromatic sextet theory

IVAN GUTMAN*[#], SLAVKO RADENKOVIĆ[#], MARIJA ANTIĆ
and JELENA ĐURĐEVIĆ

Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia

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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

Benzenoid 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 papers^{8–14} and the references cited therein. The “aromatic sextet theory” of Erich Clar^{1,3} 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 rules^{3,15} (*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 works^{18–26} and the references cited therein). In earlier

* Corresponding author. E-mail: gutman@kg.ac.rs

[#] Serbian Chemical Society member.

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studies,^{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 (*i.e.*, molecules without fixed single and double carbon–carbons 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,^{16,17} see Fig. 1.

CLAR FORMULAS OF CHEVRONS

For $n \geq 2$, the formula of the chevron molecule 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 $(1/6)n(n-1)(2n-1)$ Clar formulas.

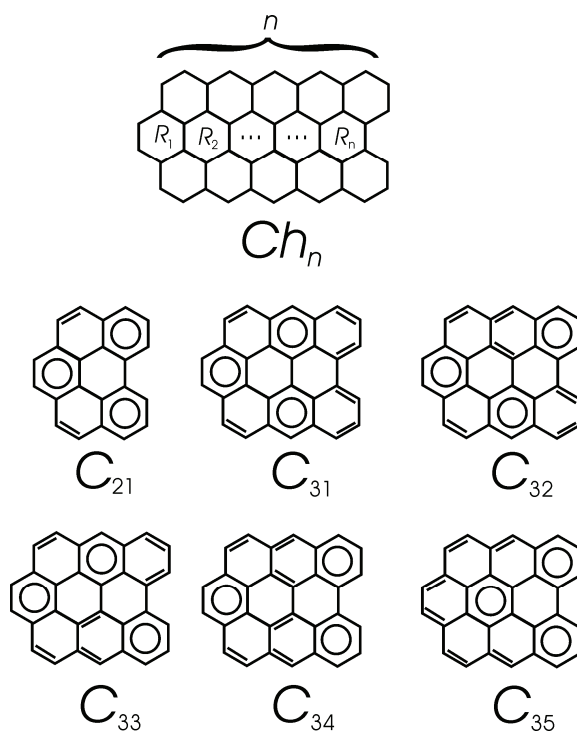


Fig. 1. The general formula of the chevron-type^{16,17} benzenoid hydrocarbon (Ch_n) and the labeling of its central rings. The first member (Ch_2) of this homologous series has a unique Clar formula (C_{21}), but the second member (Ch_3) has already five Clar formulas (C_{31} – C_{35}).

Suppose that the central hexagons of Ch_n are labeled as indicated in Fig. 1. Then, if an aromatic sextet is placed in hexagon R_1 , an additional aromatic sextet can be placed in the upper chain of Ch_n in $n-1$ different ways. The same is the

case with an aromatic sextet in the lower chain of Ch_n . Consequently, there are $(n-1) \times (n-1) = (n-1)^2$ Clar formulas when an aromatic sextet is placed in ring R_1 , see diagram D_1 in Fig. 2. If an aromatic sextet is placed in the central ring R_2 , 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 D_2 in Fig. 2.

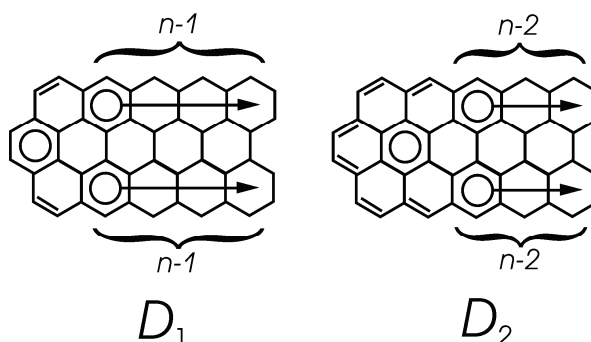


Fig. 2. Diagram D_1 is the usual abbreviated representation^{1,2} of the $(n-1)^2$ Clar formulas of the chevron Ch_n with an aromatic sextet in position R_1 . Diagram D_2 represents the $(n-1)^2$ Clar formulas with an aromatic sextet in position R_2 .

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 , $i = 1, 2, \dots, n$. 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 $i = 1, 2, \dots, n$, 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 π -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 π -electron property or an artifact of the Clar theory.

A PRELIMINARY TEST

A quantitative, graph-theory based measure of cyclic conjugation in π -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.⁸ Thus, $ef = ef(Z)$ is the energy-effect caused by cyclic conjugation of π -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 β , where $\beta \approx -137 \text{ kJ mol}^{-1}$. Note that since β 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 Ch_2 and Ch_3 , but is already violated at 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 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,⁸ 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 I. Energy effects (in β -units, $\beta \approx -137 \text{ kJ mol}^{-1}$) of the central rings R_1, R_2, \dots, R_n of the chevrons Ch_n for $n = 2, 3, 4, 5, 6, 7$ and 8 . The labeling of the rings is indicated in Fig. 1

n	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
2	0.0794	0.0256						
3	0.0792	0.0361	0.0270					
4	0.0757	0.0369	0.0375	0.0280				
5	0.0740	0.0361	0.0376	0.0392	0.0280			
6	0.0737	0.0356	0.0366	0.0393	0.0392	0.0278		
7	0.0738	0.0355	0.0363	0.0381	0.0393	0.0388	0.0277	
8	0.0739	0.0355	0.0363	0.0376	0.0381	0.0390	0.0386	0.0277

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*

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

NUMERICAL WORK

The DFT calculations on the chevrons 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.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^{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 π -electron system; $d_{\text{opt}} = 138.8$ pm, and d_i is an actual bond length.

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

The SCI indices^{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, \dots, R_n of Ch_n for $n = 2, 3, 4, 5, 6, 7$ and 8 , are given in Tables II–IV.

TABLE II. HOMA values of the rings R_1, R_2, \dots, R_n . Other details are the same as in Table I

n	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
2	0.7867	0.3769						
3	0.8197	0.6659	0.3372					
4	0.8012	0.7163	0.6375	0.3314				
5	0.7850	0.7081	0.6893	0.6381	0.3322			
6	0.7792	0.6937	0.6819	0.6917	0.6394	0.3314		
7	0.7797	0.6863	0.6674	0.6846	0.6932	0.6343	0.3277	
8	0.7815	0.6850	0.6597	0.6703	0.6873	0.6883	0.6272	0.3242

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, \dots, 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

n	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
2	-13.39	-2.62						
3	-14.13	-7.96	+0.54					
4	-13.30	-10.70	-4.78	+2.07				
5	-12.30	-10.88	-8.54	-3.58	+2.96			
6	-11.70	-9.83	-9.44	-8.33	-3.13	+3.74		
7	-11.55	-8.67	-8.47	-9.98	-8.67	-2.52	+4.64	
8	-11.64	-7.85	-6.93	-9.25	-10.96	-8.53	-1.46	+5.73

TABLE IV. SCI values of the rings R_1, R_2, \dots, R_n , multiplied by 10^3 . Other details are the same as in Table I. Note that the greater SCI is, the more intense is the respective cyclic conjugation

n	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
2	17.02	6.02						
3	17.51	8.86	5.12					
4	16.48	9.95	7.83	5.27				
5	15.72	9.70	8.96	8.05	5.39			
6	15.46	9.28	8.81	9.23	8.23	5.40		
7	15.47	9.07	8.46	9.11	9.42	8.20	5.35	
8	15.55	9.03	8.27	8.77	9.31	9.38	8.09	5.30

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 π -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 БУРЂЕВИЋ

Природно–математички факултет Универзитета у Крагујевцу

Кларова теорија ароматичног секстета предвиђа да интензитет цикличне конјугације у бензеноидним угљоводоникима шеvronског типа монотонно опада дуж централног ланца. Ова правилност је проверена помоћу неколико независних теоријских метода (са енергетским ефектима одговарајућих шесточланих прстенова, као и помоћу њихових НОМА, 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 шеvronа, док се код виших чланова јављају одступања. То указује на то да Кларова теорија није универзално применљива, чак ни код потпуно конјугованих бензеноидних молекула.

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