Stability of bicalicene isomers – A topological study

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Abstract: Bicalicene is a conjugated hydrocarbon obtained by joining two calicene fragments. This can be realized in two different ways, thus resulting in two bicalicene isomers (tentatively referred to as cis and trans). The trans isomer is a stable compound whereas cis-bicalicene appears to be less stable and has never been prepared. The stability order of the bicalicene isomers cannot be rationalized by means of the standard topological theory of conjugated π-electron systems, and requires a special graph-theory-based analysis.

Keywords: calicene; bicalicene; molecular graph; cyclic conjugation; total π-electron energy.

INTRODUCTION

Calicene (compound 1 in Fig. 1) is a well known non-alternant conjugated hydrocarbon.1,2 In the 1980s, Yoshida et al., starting from di(t-butyl)thiocalicene (2) succeeded in synthesizing compound 3 consisting of two condensed calicene fragments. This non-alternant polycyclic conjugated hydrocarbon, named bicalicene, was found to be a reasonably stable aromatic species. It immediately attracted the attention of theoreticians, and its π-electron properties were the subject of a number of quantum chemical investigations.3,5–11 Thus, from a theoretical point of view, the properties of bicalicene (3) are reasonably well understood.

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On the other hand, condensing two calicene fragments can be realized in two
different ways, resulting in the isomeric compounds 3 and 4, see Fig. 1. Expe-
rimentally,3,4 only isomer 3 has been obtained. Until today, isomer 4 has not
been synthesized and the general opinion is that it is less stable than 3. Curiously,
however, none of the theoretical studies of bicalicene,3,5–8,10,11 with a single
exception,9 considers or even mentions isomer 4. Aihara9 examined the cyclic
\( \pi \)-electron conjugation and topological resonance energy of 3 and 4 and found
that the aromatic properties of both isomers should be similar.

In the following, compound 3 will be named \textit{trans}-bicalicene, whereas 4 will
be called \textit{cis}-bicalicene. In this paper, a topological (graph-theory-based) analysis
of the mutual stability of \textit{cis}- and \textit{trans}-bicalicene is undertaken. In particular, an
attempt is made to discover the (topological) reasons why the \textit{cis}-isomer is less
stable than its \textit{trans}-congener. As the considerations in the subsequent section
show, the standard theory does not suffice for this, and special mathematical
techniques need to be employed.

\textbf{STANDARD TOPOLOGICAL APPROACH FOR PREDICTING THE STABILITY
ORDER OF POLYCYCLIC CONJUGATED HYDROCARBONS}

The relations between the structure of polycyclic conjugated \( \pi \)-electron
systems and their chemical and thermodynamic stability can be successfully
assessed by means of topological considerations, and were the subject of num-
erous studies; for details see the monographs,12–14 reviews15–17 and the refer-
cences quoted therein. The following structural features are known to be the main
factors determining the stability order of two isomeric polycyclic conjugated
hydrocarbons:

1. The isomer with greater number of Kekulé structures is expected to be
more stable.18,19 If not all Kekulé structures have the same parity, then their
algebraic count needs to be taken into account.20 Ionic resonance structures are
not taken into account.
2. The isomer with the greater total \( \pi \)-electron energy and (consequently)
greater resonance energy is expected to be more stable.17,21
3. The isomer with more rings of size \( 4k + 2 \) and fewer rings of size \( 4k \) is
expected to be more stable.22–24
4. The isomer with greater (stabilizing) cyclic conjugation in the \( (4k + 2) \)-
sized rings and smaller (destabilizing) cyclic conjugation in the \( 4k \)-sized rings
is expected to be more stable.15,18
5. With other structural features being equal, the species with greater steric
strain is less stable.25–27

\textbf{STANDARD TOPOLOGICAL APPROACH APPLIED TO BICALICENE ISOMERS}

When the above listed criteria are applied to the two bicalicene isomers, then
– surprisingly – the conclusion follows that both should be equally stable aro-
matic species. In other words, the fact that cis-bicalicene has never been obtained and that it appears to be less stable than the trans-isomer cannot be accounted for. In particular, the following facts exist:

1. Both isomers of bicalicene have two Kekulé structures, cf. Fig. 2. Thus, if there is some resonance in the case of the trans-isomer, an analogous resonance should exist also in the case of the cis-isomer. It should be noted, however, that the two Kekulé structures of both 3 and 4 are of opposite parity, since an even number (eight) of double bonds are cyclically rearranged. Therefore, from the standard point of view, resonance should in fact destabilize both isomers 3 and 4.\textsuperscript{12,14,15,18,20}

Some authors would also include the ionic and doubly-ionic resonance structures 3c, 3d, 4c and 4d in the consideration but this would lead beyond the ambit of standard topological approaches. In addition, as is explained in point 4 below, such an extension of the resonance model is not necessary at all.

![Diagram](image)

Fig. 2. The Kekulé structures of trans-bicalicene (3a and b) and cis-bicalicene (4a and b), as well as of their ionic (3c and 4c) and doubly-ionic (3d and 4d) resonance forms. Structure 3c is one of four ionic structures, whereas 4c is one of the two possible such structures. Since, in the transformation 3a $\leftrightarrow$ 3b, eight double bonds are cyclically moved, the Kekulé structures 3a and b are of opposite parity, the algebraic structure count of 3 is zero, and no resonance stabilization is to be expected. In accordance with this, conjugated circuit theory\textsuperscript{15,18} would predict a negative resonance energy for the trans-bicalicene 3. Exactly the same applies to cis-bicalicene 4 and its Kekulé structures.

2. The HMO total $\pi$-electron energy of cis- and trans-bicalicene are, respectively, equal to 22.60 and 22.78 $\beta$-units*. The respective topological resonance energies\textsuperscript{28–30} are 0.47 and 0.55 $\beta$-units. These values are obtained under the (tacit) assumption that steric strain can be disregarded. In the case of

* $1\beta \approx 138.9$ kJ mol\textsuperscript{-1}
bicalicenes, the steric strain, especially in the three-membered rings, is far from negligible. Therefore, only under the (doubtful) assumption that the strain energy in both 3 and 4 is equal, would the comparison of the total π-electron energies and resonance energies of 3 and 4 be meaningful. If so, then\(^9,13,31\) the trans-bicalicene would be more stable by \(ca. 0.18\beta \approx 25 \text{ kJ mol}^{-1}\) than its cis-isomer. If so, then according to the total-π-electron-energy/resonance-energy criterion,\(^9,21\) both bicalicene isomers would be predicted to be stable aromatic species, with isomer 4 being somewhat less aromatic than 3.

3. As seen from Figs. 1 and 3, both bicalicene isomers possess equal number of rings of equal size: two three-membered \((a, a')\), two five-membered \((b, b')\) and an eight-membered ring \((c)\). Only their mutual arrangement differs. When other stability-determining structural features are equal, such a difference in the mutual arrangement of the rings should not cause a significant effect.

![Fig. 3. Labeling of the rings of the bicalicene isomers.](image)

4. The energy effects (\(ef\)) of cyclic conjugation in the rings and pairs of rings of the bicalicene isomers are given in Table I.\(^32–34\) Recall that \(ef > 0\) indicates thermodynamic stabilization, whereas rings with negative \(ef\)-values destabilize the respective π-electron system. In the case of bicalicenes, only the central 8-membered ring has such a destabilizing effect, but it is negligibly small.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a, a')</td>
<td>0.3059</td>
<td>0.3207</td>
</tr>
<tr>
<td>(b, b')</td>
<td>0.2422</td>
<td>0.2430</td>
</tr>
<tr>
<td>(c)</td>
<td>−0.0026</td>
<td>−0.0028</td>
</tr>
<tr>
<td>(a+a')</td>
<td>0.0338</td>
<td>0.0325</td>
</tr>
<tr>
<td>(a+b)</td>
<td>0.2494</td>
<td>0.4101</td>
</tr>
<tr>
<td>(a+b')</td>
<td>0.2494</td>
<td>0.4543</td>
</tr>
<tr>
<td>(a'+b)</td>
<td>0.2494</td>
<td>0.4543</td>
</tr>
<tr>
<td>(a'+b')</td>
<td>0.2494</td>
<td>0.4101</td>
</tr>
<tr>
<td>(b+b')</td>
<td>0.0611</td>
<td>0.0583</td>
</tr>
</tbody>
</table>
It should also be noted that the \( ef \)-method is insensitive to the actual distribution of the \( \pi \)-electron charges, which means that it properly reproduces also the cyclic-conjugation patterns pertaining to the ionic and doubly-ionic resonance structure \( 3c, 3d, 4c \) and \( 4d \) (cf. Fig. 2).

For individual rings of both bicalicene isomers, the \( ef \)-values were earlier calculated by Aihara.\(^9\) From the data given in Table I, it could be seen that the respective energy effects have very similar values. From this, Aihara concluded that there is no significant difference between the aromaticity of \( 3 \) and \( 4 \). When energy effects of pairs of rings are added to the cyclic-conjugation pattern, (calculated by the method elaborated in the literature\(^{33}\)), the picture becomes significantly different. Whereas in the case of pairs of rings of equal size \( (a,a' \) and \( b,b') \), the \( ef \)-values are nearly the same in \( 3 \) and \( 4 \), the four pairs of rings \( a,b \) significantly stabilize more the \( cis \)-isomer \( 4 \) than the \( trans \)-isomer \( 3 \).

Thus, if any conclusion would be drawn based on energy effects of cyclic conjugation, then both bicalicene isomers would be predicted to be stable aromatic species, the isomer \( 3 \) somewhat less aromatic than \( 4 \). This conclusion contradicts that which would be inferred based on resonance energy (see point 2 above).

5. Finally, although the presence of 3-membered rings indicates strong steric strain in the bicalicene molecules, it is difficult to envisage why this strain would be much different in the two isomers \( 3 \) and \( 4 \).

Summarizing the above points, it could be seen that, based on standard (usual) topological arguments, the two isomeric bicalicenes would be predicted to be nearly equally stable, and to possess nearly equal aromatic character. By such approaches, one cannot predicted with certainty whether the \( cis \)- or the \( trans \)-form is the more stable isomer. The fact that \( trans \)-bicalicene is an extant, well defined, and long-known compound, whereas \( cis \)-bicalicene has never been obtained, remains obscure. In the subsequent section, it is shown how this difficulty could be overcome.

A CONCEALED GRAPH-THEORETICAL DIFFERENCE BETWEEN THE BICALICENE ISOMERS

In view of the considerations in the previous sections, it remains to examine the effect of the different arrangements of the three- and five-membered rings in isomers \( 3 \) and \( 4 \). For this, attention is focused on the determinant of the adjacency matrix \( A(G) \) of a molecular graph \( G \), and its expression in terms of Sachs graphs\(^{12,13,35,36}\).

It has been known for a long time\(^{12,17,37}\) that the \( \det A(G) \) is a sensitive measure of the stability of polycyclic conjugated \( \pi \)-electron systems. In the case of benzenoid hydrocarbons, \( \det A(G) \) is equal to the square of the number of Kekulé structures. In the case of alternant non-benzenoid compounds, \( \det A(G) \) is
equal to the square of the algebraic structure count. In any case, among pairs of conjugated isomers, the one having the greater \( \det A(G) \) is expected to have greater total \( \pi \)-electron and resonance energies, and a smaller HOMO–LUMO gap,\(^{12} \) therefore more stable.

A Sachs graph of the molecular graph \( G \) is a subgraph of \( G \) consisting of isolated cycles and isolated edges.\(^{12–14} \) In the following, we are interested in the Sachs graphs embracing all vertices of \( G \) are the focus of interest. Let \( \Gamma(G) \) be the set of all such Sachs graphs. As usual in the case of molecular graphs, it is assumed that the number \( n \) of vertices is even. (Recall that for the molecular graphs of bicalicene, \( n = 16 \).) Then:

\[
\det A(G) = \sum_{S \in \Gamma(G)} (-1)^{p(S)} 2^{c(S)} \tag{1}
\]

where \( S \) is a Sachs graph, consisting of \( p(S) \) components of which \( c(S) \) are cyclic.

Formula (1) is now applied to the molecular graphs \( G_3 \) and \( G_4 \) of trans- and cis-bicalicene, respectively. The sets \( \Gamma(G_3) \) and \( \Gamma(G_4) \) have 8 elements each, depicted in Fig. 4.

These can be classified as follows:

**Type 1.** Sachs graphs without cycles, \( c(S) = 0 \), \( p(S) = n / 2 \). Both \( G_3 \) and \( G_4 \) have two such Sachs graphs, pertaining to the two Kekulé structures of \( 3 \) and \( 4 \), cf. Figs. 2 and 4.

**Type 2.** Sachs graphs formed by the perimeter, for which \( c(S) = 1 \), \( p(S) = 1 \).

**Type 3.** Sachs graphs with two cycles. These are depicted in Fig. 4. This case is discussed in more detail below.

**Type 4.** Sachs graphs with four cycles, \( c(S) = 4 \), \( p(S) = 4 \). Both \( G_3 \) and \( G_4 \) have just one such Sachs graph, see Fig. 4.

Sachs graphs of Types 1, 2, and 4 contribute equally to the values of \( \det A(G_3) \) and \( \det A(G_4) \). Therefore, attention was focused on those of Type 3.

The Sachs graphs of Type 3 are \( S_4 - S_7 \) and \( S_{12} - S_{15} \). By inspecting Fig. 4, it could be seen that with the exception of \( S_{14} \) and \( S_{15} \), these all have the property \( p(S) = 6, c(S) = 2 \). On the other hand, \( p(S_{14}) = 7, c(S_{14}) = 2 \) and \( p(S_{15}) = 5, c(S_{15}) = 2 \). Thus, \( S_4 - S_7, S_{12} \) and \( S_{13} \) have an even number of components, whereas \( S_{14} \) and \( S_{15} \) have an odd number of components. This has the consequence that all \( S_4 - S_7 \) have an increasing contribution to \( \det A(G_3) \), whereas the contributions of \( S_{12} - S_{15} \) to \( \det A(G_4) \) cancel each other. This subtle difference may be the cause of the different stabilities of \( 3 \) and \( 4 \). Indeed, by applying Eq. (1), one obtains:

\[
\det A(G_3) = 2 \times (-1)^8 2^0 + 1 \times (-1)^1 2^1 + 4 \times (-1)^6 2^2 + 1 \times (-1)^4 2^4 = 32
\]

and
\[ \det A(G_4) = 2 \times (-1)^8 2^0 + 1 \times (-1)^1 2^1 + 2 \times (-1)^6 2^2 + \\
+ 1 \times (-1)^2 2^2 + 1 \times (-1)^5 2^2 + 1 \times (-1)^4 2^4 = 16 \]

Fig. 4. The 16-vertex Sachs graphs of the molecular graphs of trans- and cis-bicalicene. Sachs graphs of Type 1 are \( S_1, S_2, S_9 \) and \( S_{10} \), and in an evident manner correspond to the Kekulé structures \( 3a, 3b, 4a \) and \( 4b \) depicted in Fig. 2. Sachs graphs of Type 2 are \( S_3 \) and \( S_{11} \). The Sachs graphs of Type 3 are \( S_4 - S_7 \) and \( S_{12} - S_{15} \) corresponding to trans- and cis-bicalicene, respectively. The Sachs graphs of Type 4 are \( S_8 \) and \( S_{16} \). Note that all \( S_4 - S_7 \) and two among \( S_{12} - S_{15} \) contain a three- and a five-membered cycle and for these the condition \( p(S) = 6, c(S) = 2 \) holds. On the other hand, one among \( S_{12} - S_{15} \) possesses a pair of three-membered cycles, satisfying \( p(S) = 7, c(S) = 2 \) and one possesses a pair of five-membered cycles, satisfying \( p(S) = 5, c(S) = 2 \). This subtle difference may be the cause of the different stabilities of 3 and 4.

At this point, one should recall that each Sachs graph represents a particular structural detail of the underlying molecule. In view of this, the above analysis points towards those structural features that are the topological cause of the difference between the two isomeric bicalicenes. The difference may be the result of the fact that in the cis-isomer, some Sachs graphs have opposite parities (equal number of cycles, but a number of components of different parity), whereas in the trans-isomer this does not happen. Equivalently, in trans-bicalicene, there are no Sachs graphs with two cycles of equal size, whereas in the cis-isomer such Sachs graphs do exist.

Although in the case of non-bipartite conjugated hydrocarbons, the square root of \( \det A(G) \) is not directly related to the number of Kekulé structures, it is interesting to observe that \( \sqrt{\det A(G_4)} = 4 \), which may be understood as if cis-bicalicene behaves like a conjugated \( \pi \)-electron system having four Kekulé structures. Then \( \sqrt{\det A(G_3)} = 5.66 \) would imply that trans-bicalicene behaves like a \( \pi \)-electron systems having about six Kekulé structures. As a curiosity, it is
noticed that the number of Kekulé and ionic resonance structures of cis-bicalicene is 4, and the corresponding number for those of trans-bicalicene is 6, cf. Fig. 2.

CONCLUDING REMARKS

The conclusion of the presented analysis of the two isomers of bicalicene is that both satisfy all topological requirements for being stable, moderately aromatic compounds. The cis-isomer is predicted to be somewhat less stable than the trans-isomer, but this decrease in stability is not sufficient to prevent cis-bicalicene from being a possibly well-defined, reasonably stable and experimentally obtainable compound. Therefore, it is concluded that cis-bicalicene should be an attractive and challenging target for synthesis.

ИЗВОД

СТАБИЛНОСТ ИЗОМЕРА БИКАЛИЦЕНА – ТОПОЛОШКА СТУДИЈА

ИВАН ГУТМАН

Природно–математички факултет Универзитета у Крагујевцу и Државни Универзитет у Новом Пазару

Бикалицен је конјуговани угљоводоник добијен спајањем два калиценска фрагмента. То се може учинити на два начина, што доводи до два изомера бикалицена (тенативно означена као cis и trans). Trans изомер је стабилно једињење док је cis-бикалицен мање стабилан и до сада није добијен. У оквиру стандардне тополошке теорије конјугованих π-електронских система, овакве разлике у стабилности изомерних дикалицена се не могу објаснити. За то је потребно да се употребе посебне граф-теоријске методе.

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REFERENCES