

Stability of bicalicene isomers - a topological study

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Abstract. Bicalicene is the conjugated hydrocarbon obtained by joining two calicene fragments. This can be done 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 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 to synthesize a 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 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.

Fig. 1 comes about here

On the other hand, condensing two calicene fragments can be done in two different ways, resulting in the isomeric compounds **3** and **4**, see Fig. 1. Experimentally,^{3,4} only the isomer **3** has been obtained. Until today, the 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 the isomer

4. Aihara⁹ examined cyclic π -electron conjugation and topological resonance energy of **3** and **4** and found that the aromatic properties of both isomers should be similar.

In what follows we shall refer to compound **3** as to the *trans*-bicalicene, whereas **4** will be called *cis*-bicalicene. In this paper, we undertake a topological (graph-theory-based) analysis of the mutual stability of *cis*- and *trans*-bicalicene. In particular, we try to discover the (topological) reasons why the *cis*-isomer is less stable than its *trans*-congener. As the considerations in the subsequent section show, standard theory does not suffice for this, and special mathematical techniques need to be employed.

STANDARD TOPOLOGICAL APPROACH FOR PREDICTING STABILITY ORDER OF POLYCYCLIC CONJUGATED HYDROCARBONS

The relations between the structure of polycyclic conjugated π -electron systems and their chemical and thermodynamic stability can be successfully assessed by means of topological considerations, and were subject to numerous studies; for details see the monographs,¹²⁻¹⁴ reviews,¹⁵⁻¹⁷ and the references 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 greater total π -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

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

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 even (eight) double bonds are cyclically rearranged. Therefore, from the standard point of view, resonance should in fact destabilize both isomers **3** and **4**.^{12,14,15,18,20}

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

Fig. 2 comes about here

2. The HMO total π -electron energy of *cis*- and *trans*-bicalicene are, respectively, equal to 22.60 and 22.78 β -units. The respective topological resonance energies²⁸⁻³⁰ are 0.47 and 0.55 β -units. These values are obtained under the (tacit) assumption that steric strain can be disregarded. In the case of 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, the comparison of total π -electron energies and resonance energies of **3** and **4** would be meaningful. If so, then^{9,13,31} the *trans*-bicalicene would be by ca. $0.18 \beta \approx 25$ kJ/mol more stable 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 the 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-

109 membered ring (c). Only their mutual arrangement differs. When other stability-
110 determining structural features are equal, such a difference in the mutual arrangement
111 of the rings should not cause a significant effect.

112
113 Fig. 3 comes about here
114

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

120 It should be also noted that the ef -method is insensitive to the actual
121 distribution of the π -electron charges, which means that it properly reproduces also the
122 cyclic-conjugation patterns pertaining to the ionic and doubly-ionic resonance
123 structure **3c**, **3d**, **4c**, **4d** (cf. Fig. 2).

124
125 Table I comes about here
126

127 For individual rings of both bicalicene isomers, the ef -values were earlier
128 calculated by Aihara.⁹ From the data given in Table I, we see that the respective
129 energy effects have very similar values. From this, Aihara concluded that there is no
130 significant difference between the aromaticity of **3** and **4**. When energy effects of pairs
131 of rings are added to the cyclic-conjugation pattern, (calculated by the method
132 elaborated in Ref. 33), the picture becomes significantly different. Whereas in the case
133 of pairs of rings of equal size (a, a' and b, b') the ef -values are nearly the same in **3** and
134 **4**, the four pairs of rings a, b significantly more stabilize the *cis*-isomer **4** than the
135 *trans*-isomer **3**.

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

- 140
141 5. Finally, although the presence of 3-membered rings indicates a strong steric strain in
142 the bicalicene molecules, it is difficult to envisage why this strain would be much
143 different in the two isomers **3** and **4**.

Summarizing the above points, we see 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 predict by certainty whether the *cis*- or the *trans*-form is the most stable isomer. The fact that *trans*-bicalicene is an existing, well defined, and long-time known compound, whereas *cis*-bicalicene has never been obtained, remains obscure. In the subsequent section we show how this difficulty could be overcome.

A CONCEALED GRAPH-THEORETICAL DIFFERENCE BETWEEN 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 the isomers **3** and **4**. For this, we focus our attention to 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 is known for a long time^{12,17,37} that $\det A(G)$ is a sensitive measure of stability of polycyclic conjugated π -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. Anyway, among pairs of conjugated isomers, the one having greater $\det A(G)$ is expected to have greater total π -electron and resonance energies, and a smaller HOMO-LUMO gap,¹² therefore being 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 what follows, we are interested in the Sachs graphs embracing all vertices of G . Let $\Gamma(G)$ be the set of all such Sachs graphs. As usual in the case of molecular graphs, we assume that the number n of vertices is even. (Recall that for the molecular graphs of bicalicene, $n = 16$.) Then

$$\det A(G) = \sum_{S \in \Gamma(G)} (-1)^{p(S)} 2^{c(S)} \quad (1)$$

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

We now apply formula (1) 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. We discuss this case 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.

Fig. 4 comes about here

Sachs graphs of Types 1, 2, and 4 contribute equally to the values of $\det A(G_3)$ and $\det A(G_4)$. Therefore, we focus our attention to those of Type 3.

The Sachs graphs of Type 3 are $S_4, S_5, S_6, S_7, S_{12}, S_{13}, S_{14}, S_{15}$. By inspecting Fig. 4, we see 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, $S_4, S_5, S_6, S_7, S_{12}, S_{13}$ have an even number of components, whereas S_{14}, S_{15} have an odd number of components. This has the consequence that all S_4, S_5, S_6, S_7 have an increasing contribution to $\det A(G_3)$, whereas the contributions of $S_{12}, S_{13}, S_{14}, S_{15}$ to $\det A(G_4)$ cancel each other. This subtle difference may be the cause of different stability of **3** and **4**. Indeed, by applying Eq. (1) we now have:

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

$$\det A(G_4) = 2 \times (-1)^8 2^0 + 1 \times (-1)^1 2^1 + 2 \times (-1)^6 2^2 + 1 \times (-1)^7 2^2 + 1 \times (-1)^5 2^2 + 1 \times (-1)^4 2^4 = 16$$

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 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 $\sqrt{\det A(G_4)} = 4$, what may be understood so that *cis*-bicalicene behaves like a conjugated π -electron systems having four Kekulé structures. Then $\sqrt{\det A(G_3)} = 5.66$ would imply that *trans*-bicalicene behaves like a π -electron systems having about six Kekulé structures. As a curiosity we notice that the number of Kekulé and ionic resonance structures of *cis*-bicalicene is 4, and those of *trans*-bicalicene is 6, cf. Fig. 2.

CONCLUDING REMARKS

The conclusion of our 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 of stability is not sufficient to prevent *cis*-bicalicene of being a well-defined, reasonably stable and experimentally obtainable compound. Therefore, *cis*-bicalicene should be an attractive and challenging target for synthesis.

I Z V O D

STABILNOST IZOMERA BIKALICENA – TOPOLOŠKA STUDIJA

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Bikalicen je konjugovani ugljovodonik dobiven spajanjem dva kalicenska fragmenta. To se može učiniti na dva načina, što dovodi do dva izomera bikalicena (tentativno označena kao *cis* i *trans*). *Trans* izomer je stabilno jedinjenje dok je *cis*-bikalicen manje stabilan i do sada nije dobiven. U okviru standardne topološke teorije konjugovanih π -elektronskih sistema, ovakve razlike u stabilnosti izomernih dikalicena se ne mogu objasniti. Za to je potrebno da se upotrebe posebne graf-teorijske metode.

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Table and Figure Captions

TABLE I. Energy effects of cyclic conjugation in the rings and pairs of rings of *trans*-bicalicene (**3**) and *cis*-bicalicene (**4**). The labeling of the rings is indicated in Fig. 3. Note that individual rings in **3** and **4** have almost equal energy effects. The same is true for the pairs of rings *a,a'* and *b,b'*. In contrast to this, the four pairs of rings *a,b* significantly more stabilize the *cis*-isomer than the *trans*-isomer.

Fig. 1. Calicene (**1**) and the two isomeric bicalicenes (*trans*-bicalicene, **3**, and *cis*-bicalicene, **4**). The *cis*-isomer **3** was synthesized from di(*t*-butyl)thiocalicene (**2**), in which reaction the *trans*-isomer (**4**) is not obtained.^{3,4}

Fig. 2. The Kekulé structures of *trans*-bicalicene (**3a**, **3b**) and *cis*-bicalicene (**4a**, **4b**) and well as their ionic (**3c**, **4c**) and doubly-ionic (**3d**, **4d**) resonance forms. Structure **3c** is one of the 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**, **3b** 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^{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.

Fig. 3. Labeling of the rings of the bicalicene isomers.

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, S_{10} , and in an evident manner correspond to the Kekulé structures **3a**, **3b**, **4a**, **4b** depicted in Fig. 2. The Sachs graphs of Type 2 are S_3, S_{11} . The Sachs graphs of Type 3 are S_4, S_5, S_6, S_7 and $S_{12}, S_{13}, S_{14}, S_{15}$ corresponding to *trans*- and *cis*-bicalicene, respectively. The Sachs graphs of Type 4 are S_8, S_{16} . Note that all S_4, S_5, S_6, S_7 and two among $S_{12}, S_{13}, S_{14}, S_{15}$ contain a three- and a five-membered cycle and for these holds $p(S) = 6, c(S) = 2$. On the other hand, one among $S_{12}, S_{13}, S_{14}, S_{15}$ 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 different stability of **3** and **4**.

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<i>cycle</i>	3	4
<i>a</i> , <i>a'</i>	0.3059	0.3207
<i>b</i> , <i>b'</i>	0.2422	0.2430
<i>c</i>	-0.0026	-0.0028
<i>a</i> + <i>a'</i>	0.0338	0.0325
<i>a</i> + <i>b</i>	0.2494	0.4101
<i>a</i> + <i>b'</i>	0.2494	0.4543
<i>a'+b</i>	0.2494	0.4543
<i>a'+b'</i>	0.2494	0.4101
<i>b</i> + <i>b'</i>	0.0611	0.0583

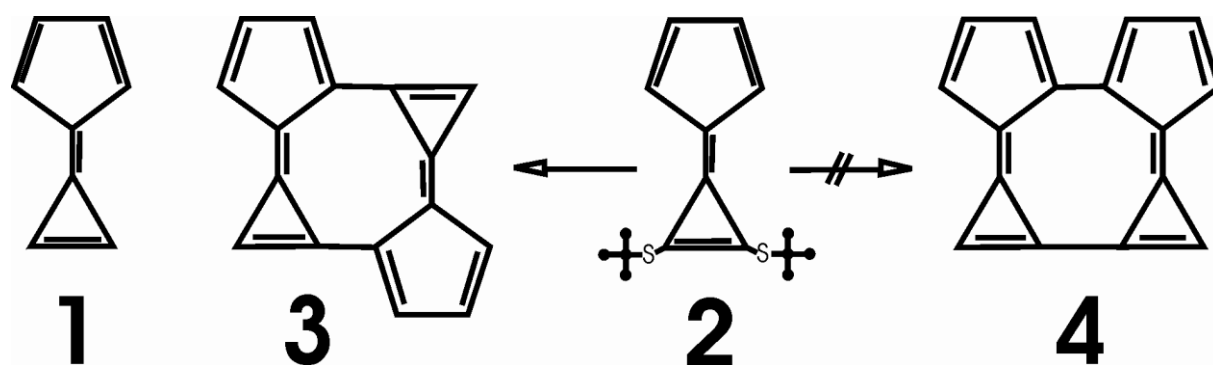


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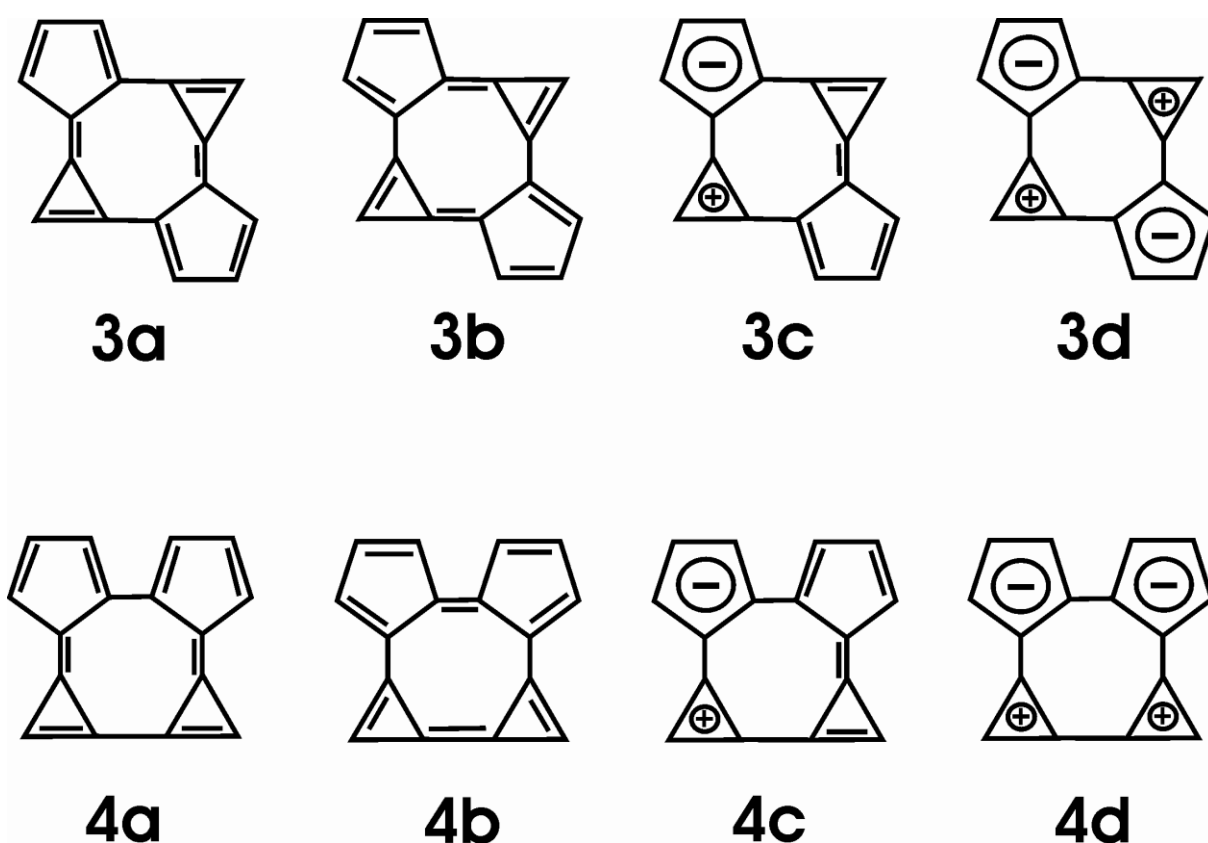
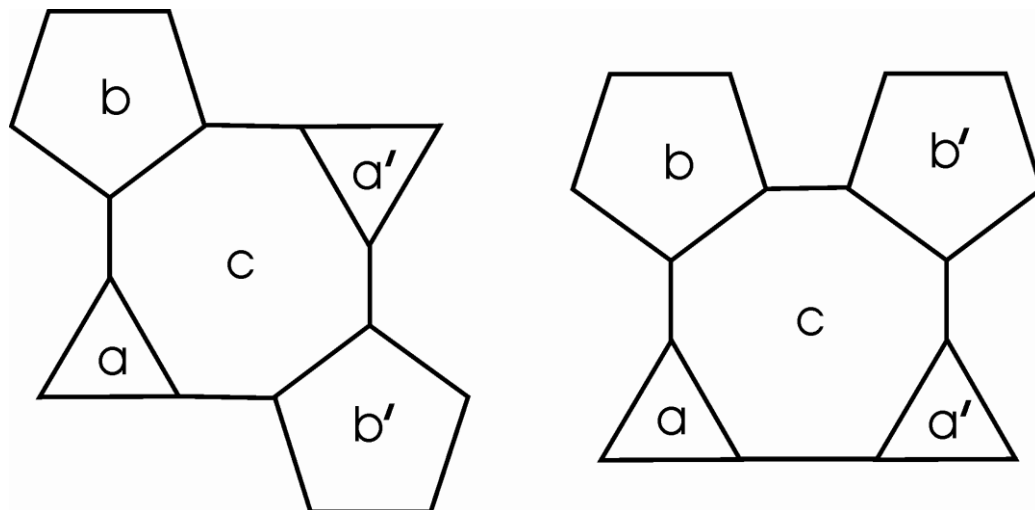


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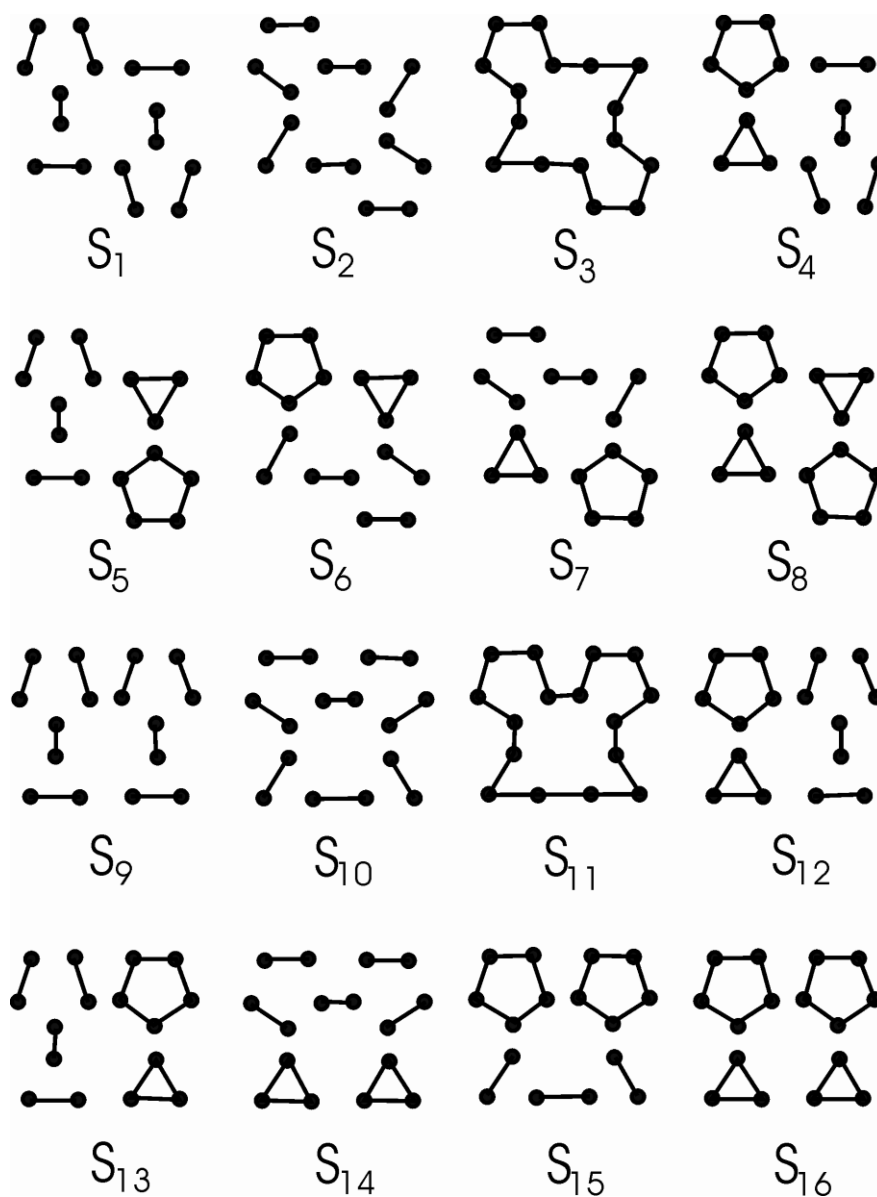


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411 Fig. 4. The 16-vertex Sachs graphs of the molecular graphs of *trans*- and *cis*-bicalicene. Sachs
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