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Stability of bicalicene isomers – A topological study

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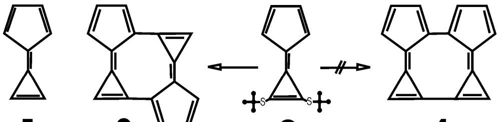
Abstract: Bicalicene is a conjugated hydrocarbon obtained by joining two calicene fragments. This can be realized in two different ways, thus resulting in two bicalicene isomers (tentatively referred to as *cis* and *trans*). The *trans* isomer is a stable compound whereas *cis*-bicalicene appears to 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.



1 **3** **2** **4**

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]

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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. Experimentally,[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**. Aihara[9] examined the 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 the following, compound **3** will be named *trans*-bicalicene, whereas **4** will be called *cis*-bicalicene. In this paper, a topological (graph-theory-based) analysis of the mutual stability of *cis*- and *trans*-bicalicene is undertaken. In particular, an attempt is made to discover the (topological) reasons why the *cis*-isomer is less stable than its *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.

STANDARD TOPOLOGICAL APPROACH FOR PREDICTING THE 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 the subject of 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 the 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]

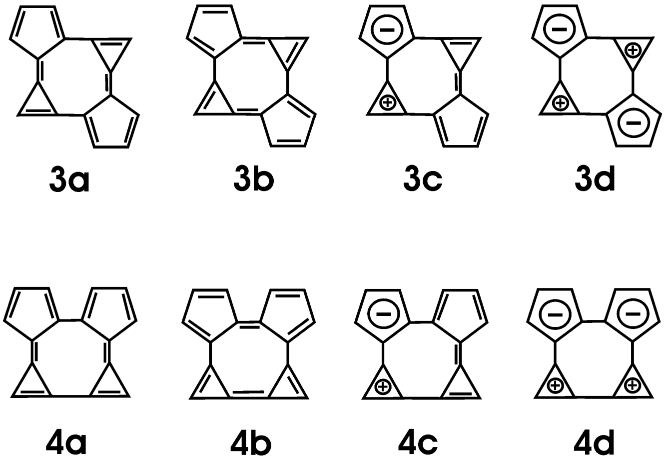
5. With other structural features being equal, the species with greater steric strain is less stable.[25–27]

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 aromatic 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**.[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 ambits 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.



3a **3b** **3c** **3d**

4a **4b** **4c** **4d**

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** ↔ **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[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 π-electron energy of *cis*- and *trans*-bicalicene are, respectively, equal to 22.60 and 22.78 β-units*. The respective topological resonance energies[28–30] 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

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* $1\beta \approx 138.9$ kJ mol^{-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*. $0.18\beta \approx 25$ 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.

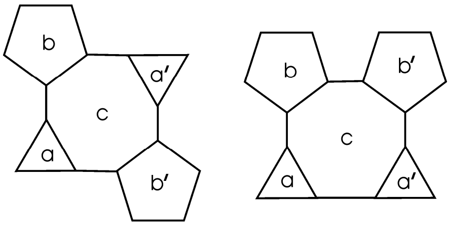

Fig. 3. Labeling of the rings of the bicalicene isomers.

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 I. Energy effects (β-units) 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. 2. 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 stabilize more the *cis*-isomer than the *trans*-isomer

Cycle	**3**	**4**
a, *a'*	0.3059	0.3207
b, *b'*	0.2422	0.2430
c	–0.0026	–0.0028
a+*a'*	0.0338	0.0325
a+*b*	0.2494	0.4101
a+*b'*	0.2494	0.4543
a'+*b*	0.2494	0.4543
a'+*b'*	0.2494	0.4101
b+*b'*	0.0611	0.0583

It should also be noted that the *ef*-method is insensitive to the actual distribution of the π-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 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. In any case, among pairs of conjugated isomers, the one having the greater $\det A(G)$ is expected to have greater total π-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

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

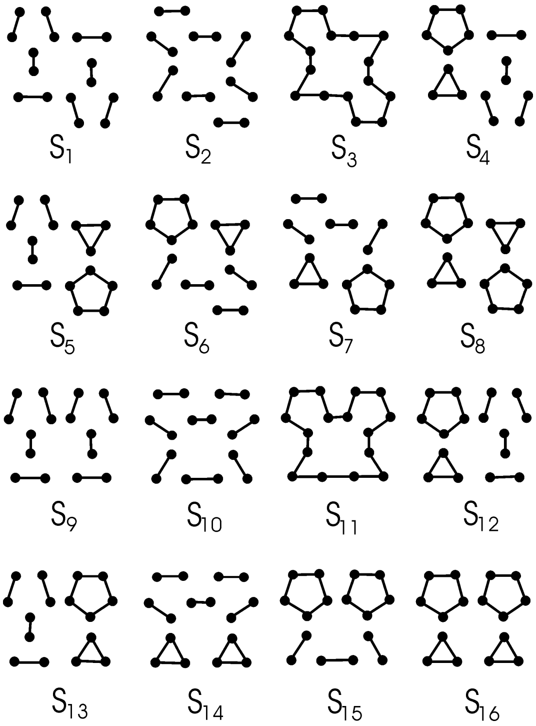

Fig. 4. The 16-vertex Sachs graphs of the molecular graphs of *trans*- and *cis*-bicalicene. Sachs graphs of Type 1 are S_1, S_2, S_9 and S_{10}, and in an evident manner correspond to the Kekulé structures **3a**, **3b**, **4a** and **4b** depicted in Fig. 2. Sachs graphs of Type 2 are S_3 and S_{11}. 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 π-electron system 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, 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 (тентативно 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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