The Silacyclobutene Ring: An Indicator of Triplet State Baird-Aromaticity

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Abstract: Baird’s rule tells that the electron counts for aromaticity and antiaromaticity in the first \( \pi^* \) triplet and singlet excited states (\( T_1 \) and \( S_1 \)) are opposite to those in the ground state (\( S_0 \)). Our hypothesis is that a silacyclobutene (SCB) ring fused with a \([4n]annulene\) will remain closed in the \( T_1 \) state so as to retain \( T_1 \) aromaticity of the annulene while it will ring-open when fused to a \([4n + 2]annulene\) in order to alleviate \( T_1 \) antiaromaticity. This feature should allow the SCB ring to function as an indicator for triplet state aromaticity. Quantum chemical calculations of energy and (anti)aromaticity changes along the reaction paths in the \( T_1 \) state support our hypothesis. The SCB ring should indicate \( T_1 \) aromaticity of \([4n]annulenes\) by being photoinert except when fused to cyclobutadiene, where it ring-opens due to ring-strain relief.

Keywords: Baird’s rule; computational chemistry; excited state aromaticity; Photostability

1. Introduction

Baird showed in 1972 that the rules for aromaticity and antiaromaticity of annulenes are reversed in the lowest \( \pi^* \) triplet state (\( T_1 \)) when compared to Hückel’s rule for the electronic ground state (\( S_0 \)) [1–3]. The rule has subsequently been confirmed by a series of quantum chemical calculations [3,4], and it has also been shown that \( 4n \) \( \pi \)-electron species can have triplet multiplicity ground states (\( T_0 \)). Interestingly, the \( T_0 \) state cyclopentadienyl cation and the isomeric vinylcyclopropenium cation (a closed-shell singlet) are nearly isoenergetic [5,6], revealing that Baird-aromatic stabilization of triplet state species can be significant [3,7]. It has also been shown through computations that Baird’s rule can be extended to the lowest \( \pi^* \) excited singlet states (\( S_1 \)) of cyclobutadiene (CBD), benzene, and cyclooctatetraene (COT) [8–13]. Thus, \([4n]annulenes\) display aromatic character in both their \( T_1 \) (or \( T_0 \)) and \( S_1 \) states whereas \([4n + 2]annulenes\) display anti-aromaticity. With Hückel’s and Baird’s rules it becomes clear that benzene has a dual character and can be labelled as a molecular “Dr. Jekyll and Mr. Hyde” [3,14,15]. This is in line with the early conclusions by Baird as well as by Aihara [1,16], and the excited state antiaromaticity explains the photoreactivity of many benzene derivatives [14]. On the other hand, CBD and COT are both aromatic in the \( T_1 \) state [17–19].

In the last few years, the excited state aromaticity and antiaromaticity concepts (abr. ES(A)A) have gained gradually more attention [20–22], even though the pioneering experimental studies were presented by Wan and co-workers already in the 80s and 90s [23–28]. We earlier stressed that Baird’s rule can be used as a qualitative back-of-an-envelope tool for the design of photochemically active materials, as well as for the development of new photoreactions [29,30]. Indeed, a recent combined experimental and computational study of a chiral thiopheno-fused COT compound by Itoh and co-workers reveals that the aromatic stabilization energies in both the \( T_1 \) and \( S_1 \) states are extensive (~21 kcal/mol) [31], in agreement with previous computational estimates of \( T_1 \) state (anti)aromatic
(de)stabilization [32,33]. For experimental identification of excited state aromatic cycles vs. anti- and nonaromatic ones, there is a need for suitable indicator moieties. Based on both computations and experiments we recently reported that the cyclopropyl (cPr) group can differentiate T₁ and S₁ state aromatic rings from those that are antiaromatic or nonaromatic in these states [34]. Yet, the cPr group also has a drawback in that the products formed upon ring-opening are not easily identified as they are complicated mixtures or polymeric material.

Herein, we discuss a computational study on the effects of T₁ state (anti)aromaticity of [4n]- and [4n + 2]annulenes on the photochemical ring-opening of a silacyclobutene (SCB) ring fused with an annulene. The SCB ring is interesting because of its ring-strain and high chemical reactivity [35]. One could potentially use the SCB ring as a substituent on an annulene ring, and here it is already known that 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene ring-opens photochemically [36], likely a route for excited state antiaromaticity relief. However, when used as a substituent the opening of the SCB ring will also be affected by conformational factors (Figure 1a). Instead, if fused it sits in the same arrangement regardless of annulene, and thus, should be a more unbiased indicator (Figure 1b).

We argue that the T₁ aromaticity of [4n]annulenoSCBs will hinder the SCB ring from opening as this will lead to loss of T₁ aromaticity, while the T₁ antiaromaticity of [4n + 2]annulenoSCBs instead will enhance the rate for ring-opening. We base this argument on the Bell–Evans–Polanyi principle that says that the activation energy will be proportional to the reaction energy for reactions of the same type [37]. This will lead to a photoreactivity difference which can allow the SCB ring to function as a T₁ aromaticity indicator. Noteworthily, the T₁ state potential energy surfaces (PESs) for electrocyclization reactions of compounds with 4n π-electrons were earlier explored by Mauksch and Tsogoeva [38], and Möbius aromatic transition states were identified in compounds with 8, 10 and 12π-electrons. Yet, the focus of our paper is not on the T₁ state electrocyclic ring-opening of SCB but instead on the explicit effect of the T₁ state (anti)aromaticity of annulenes on the SCB ring-opening when these annulenes are fused to the SCB ring. Earlier, we reported that the shapes of T₁ state PESs for twists about the C=C double bonds (cf. T₁ state Z/E-isomerizations) of [4n]- and [4n + 2]annulenyln substituted olefins are connected to changes in T₁ state (anti)aromaticity of (hetero)annulenyln substituents [39–42]. From this, one can infer that the T₁ state PES of also other photoreactions will vary in dependence of a neighboring [4n + 2]- or [4n]annulene ring. BenzoSCB (2a, Figure 2) should photorearrange to o-silaxylylene (2b), containing a highly reactive Si=C double bond [43], while cyclobuteno-(1a) and cyclooctatetraenoSCB (3a), based on our hypothesis, should be resistant to photochemical ring-openings. Indeed, photochemical ring-opening of 2a in the S₁ state to the transient 2b, trapped by alcohol solvents to yield isolable silylethers in 40–80% yield (Scheme 1), was earlier reported by Kang and co-workers [44]. Additions of alcohols to silenes, particularly naturally polarized ones (Siδ+ = Cδ−), proceed over very low activation barriers (a few kcal/mol) [45] due to the high oxy- and electrophilicity of the sp² hybridized Si atom, making these reactions highly suitable for rapid trapping of transient SCB ring-opened isomers. A potential benefit of the SCB ring over the cyclopropyl group is the persistence of the products formed upon photochemical SCB ring-opening followed by trapping [44,46].

Figure 1. The silacyclobutene (SCB) ring as a substituent (a) and fused to an annulene ring (b).
Scheme 1. The photochemical SCB ring-opening and subsequent trapping of ortho-silaxylylene reported by Kang, K.T. et al. [44].

Our investigation is focused on the $T_1$ state ring-openings rather than the $S_1$ state processes as the triplet states are more easily amenable to computations. We used different aromaticity indices to examine the (anti)aromatic character of ring-closed and ring-opened isomeric structures. If $T_1$ aromaticity of a $[4n]$annulene hinders the SCB ring from opening, then the absence of this reaction upon irradiation should indicate $T_1$ aromaticity. The SCB ring-opening could tentatively be connected to the bond dissociation enthalpies (BDEs) because the C–C BDE in a strain-free compound (90.4 kcal/mol) is slightly higher than the Si–C BDE (88.2 kcal/mol), which in turn is higher than the Si–Si (80.5 kcal/mol) BDE [47, 48]. Although the BDE difference between the strain-free C–C and Si–C bonds is small, strain could be more important in the SCB ring than in the all-carbon cyclobutene ring (vide infra). Here it can be noted that the cyclobutene and disilacyclobut-3-ene rings are less suitable than the SCB ring because the former opens only rarely upon photolysis (e.g., benzocyclobutene does not undergo photochemical ring-opening unless further derivatized) [14, 49], while the latter is unstable and readily oxidized in air to 1,3-disila-2-oxacyclopentenes [50]. It should also be noted that strained four-membered rings with heteroatoms from Groups 15 and 16 are problematic in the context of excited state aromaticity indicators as these heteroatoms provide lone-pair electrons that will interact electronically with the π-conjugated annulene. Additionally, the lowest excited states of compounds with such rings could be of $n\pi^*$ rather than of $\pi\pi^*$ character, leading to excited states for which Baird’s rule is not applicable.

The SCB ring when used as a substituent can also influence the annulene through π-conjugation, yet, when fused onto an annulene its C=C bond is joint with the annulene. Thus, the SCB ring could hold a unique position as a tentative excited state aromaticity indicator unit.

Figure 2. The annulenoSCB ring-openings and the postulated (anti)aromatic characters in the $S_0$ and the $T_1$ states of 1a, 2a, 3a, 1b, 2b, and 3b, respectively, with A = aromatic, AA = antiaromatic, and NA = non-aromatic.
2. Results and Discussion

We first discuss the changes in energies, geometries and (anti)aromaticities in the \( T_1 \) states during ring-opening reactions of the three molecules (Figure 2) in which a SCB ring is fused with either a \([4n]\)annuleno-(cyclobuteno- and cyclooctatetraeno-) ring or a \([4n + 2]\)annuleno-(benzo-) ring. We discuss reaction and activation energies, and subsequently analyze (anti)aromaticity changes through the harmonic oscillator model of aromaticity (HOMA), nucleus independent chemical shift (NICS) and isomerization stabilization energy (ISE) indices as well as anisotropy of the induced current density (ACID) plots. Finally, openings of SCB rings fused with 5- and 7-membered annulene cations and anions are discussed. We also explored the \( T_1 \) PES for SCB ring-opening when fused with polycyclic systems (see Scheme S1), and for comparison the all-carbon analogues of \( 2 \) and \( 3 \) were analyzed.

2.1. Energy Changes

For the first three compounds (1–3), three different methods, two density functional theory methods (B3LYP and OLYP), and one Coupled Cluster method (CCSD(T)) were tested to ensure that the results do not vary extensively with method. Similar results were mostly obtained at the two DFT (B3LYP and OLYP) and CCSD(T) levels, and therefore, only B3LYP energies are given for the remaining compounds unless otherwise noted. Compound \( 2a(T_1) \) had a higher relative energy than that of its ring-opened isomer, \( 2b(T_1) \), by 33.7–38.3 kcal/mol depending on the computational method (Figure 3). Moreover, the activation energy for Si–C bond scission in the \( T_1 \) state was merely 9.0 kcal/mol, 38.3 kcal/mol lower than in the \( S_0 \) state at the B3LYP level. This suggests that an antiaromatic destabilization of the benzene ring in the \( T_1 \) state affected \( 2a(T_1) \) making it highly unstable and prone to cleave the Si–C bond.

![Figure 3. \( T_1 \) state potential free energy surface diagrams for ring-openings of 2,3-cyclobutadieno-1-SCB (1), 2,3-benzo-1-SCB (2) and 2,3-cyclooctatetraeno-1-SCB (3) at (U)B3LYP/6-311G(d,p) (normal print), (U)OLYP/6-311G(d,p) (italics), and (U)CCSD(T)/6-311G(d,p)//(U)B3LYP/6-311G(d,p) (underlined) levels. Values in parenthesis are activation energies. Values for the \( S_0 \) state in black and values for the \( T_1 \) state in red.](image-url)
Interestingly, the T₁ PES of 1 displayed a similar shape as that of 2, since 1b(T₁) is of lower energy than 1a(T₁) despite the fact that CBD is weakly T₁-aromatic [8,13,17,51–53]. At the two DFT levels, 1b(T₁) was even lower than 1a(S₀), likely due to ring-strain relief in 1b(T₁). Furthermore, the activation energy in the T₁ state was lower than that in the S₀ state by 7.7 kcal/mol at B3LYP level. An opposite behavior was observed for 3 in its T₁ state because 3b(T₁) is higher in energy than 3a(T₁) by 11.8–26.1 kcal/mol. Moreover, the activation energies in the T₁ state are very high, 31.0–39.2 kcal/mol, revealing that the SCB ring will remain closed. Thus, for compounds 2 and 3, the energy changes upon ring-opening in the T₁ states fell in line with our hypothesis; ring-opening releases energy in 2 in the T₁ state, while it requires energy in 3. The question was, to what extent these energy changes were linked to changes in (anti)aromaticity (vide infra).

The Si–C bond lengths in 1a, 2a, and 3a are 1.95 Å, 1.92 Å, and 1.90 Å, respectively, which is slightly longer than the normal Si–C bond length (1.87–1.89 Å) [54]. Thus, as one goes to gradually larger annulene rings, the SCB ring gets successively less strained when evaluated based on Si–C bond lengths.

Noteworthily, in the S₀ state, the reaction energy for ring-opening of 2a(S₀) was of opposite sign to the reaction energy in the T₁ state. This reversal in endergonicity and exergonicity when going from the S₀ to the T₁ state of 2 should be a consequence of Baird’s rule being the exact opposite to Hückel’s rule. With regard to compounds 1 and 3 in the S₀ states, the ring-opening of 1a(S₀) was exergonic, in line with relief of both S₀ antiaromaticity and ring-strain, while ring-opening in the non-aromatic isomer 3a(S₀) was endergonic. These energies were a combination of factors; (i) changes in (anti)aromaticity, (ii) ring strain release, and (iii) changes in the bonding character at the Si atom as it goes from sp³ to sp² hybridized. Formation of a Si=C double bond is an unfavorable process which is not sufficiently compensated by relief of ring strain in the least ring strained of the compounds (3a(S₀)). Indeed, the ring opening of the all-carbon congener (allC-3(S₀)), where a C=C double bond is formed instead, was exergonic by 6.4 kcal/mol (see Figure S13).

For 2 and allC-2, the S₀ electrocyclic ring-opening transition states were conrotatory, as expected for a thermal reaction with 4π electrons. In T₁, this was reversed to a disrotatory fashion. In contrast, for 3 and allC-3, both the S₀ and T₁ transition states were conrotatory. The conrotatory mode in T₁ could be explained by the fact that the spin density is delocalized both over the eight-membered and four-membered rings in the TS (Figures S44 and S45). This is consistent with a 10-electron electrocyclic ring-opening with Möbius orbital topology which would be allowed in T₁. Indeed, the ACID plots for 3 and allC-3 supported this interpretation, as the ring current went over all 10 atoms (Figures S54 and S55). However, the difference of mechanism in T₁ with 10-electron conrotatory for 3 and 4-electron disrotatory for the other molecules was not sufficiently large to prevent application of the Bell–Evans–Polanyi principle, as they all fell on the same correlation line (Figure S40, vide infra).

In addition to the SCB ring fused to aromatic and antiaromatic annulenes, we also analyzed it when fused to the non-aromatic reference compounds cyclobutene, cyclohexene, and cyclohexadiene. When going from 4 to 6 over 5, the reaction energies in the T₁ state became gradually less strongly exergonic, while the activation energies increased slightly. Compounds 4 and 5 both have nonconjugated C=C double bonds, yet, the cycloalkene ring was larger in 5, leading to less ring-strain than in 4, as well as a T₁ state SCB ring-opening reaction energy which was lower by 11.3 kcal/mol. When going from 5 to 6, the reaction energy further decreased by 12.1 kcal/mol, revealing that the length of the conjugated path also had an impact. An indication that T₁ state antiaromaticity was alleviated in 2a(T₁) was the fact that the energy released when going from 2a(T₁) to 2b(T₁) (Figure 3) was larger than when going from 5a(T₁) to 5b(T₁) (Figure 4). Indeed, the ring-closed 2a(T₁) was at an even higher energy than 5a(T₁) where the triplet biradical was confined to an essentially planar olefin bond. This clarified that the benzene ring in the T₁ state was strongly destabilized. The destabilized nature of T₁ state benzene became obvious when regarding compound 6, where the ring-closed isomer has a SCB moiety with its C=C double bond being part of a conjugated, yet, nonaromatic segment because the T₁ energy of 2a(T₁), was substantially higher than that of 6a(T₁) (78.0 vs. 47.5 kcal/mol,
respectively). Moreover, the activation energy for SCB ring-opening of \(2a(T_1)\) was 6.6 kcal/mol lower than that of \(6a(T_1)\), which indicated an influence of \(T_1\) antiaromaticity in \(2a(T_1)\).

![Figure 4. Relative reaction and activation free energies (kcal/mol) for the SCB ring-opening when fused to non-aromatic rings. The energies for transition states are given in bold. Black energy levels represent the \(S_0\) state and red ones represent \(T_1\) states at (U)B3LYP/6-311G(d,p) level.](image)

2.2. Changes in \(T_1\) State (Anti)aromaticity upon Ring-Opening

2.2.1. Harmonic Oscillator Model of Aromaticity (HOMA) Values

Bond length equalization is one indicator of aromaticity, and we chose the geometric HOMA index as one of the indices used (Table 1). The large negative HOMA values in \(1a(S_0)\), \(1b(S_0)\) and \(1b(T_1)\) corresponded to antiaromaticity, while the small HOMA value of \(1a(T_1)\) suggested that this structure is non-aromatic. Ring-opening of \(1a(T_1)\) to \(1b(T_1)\) led to an increase in antiaromaticity (\(\Delta\)HOMA\((T_1) = -0.69\)).

| Compounds | \(S_0\) a | \(S_0\) b | \(T_1\) a | \(T_1\) b | \(\Delta\)HOMA \(S_0\) | \(\Delta\)HOMA \(T_1\) |
|-----------|-----------|-----------|-----------|-----------|----------------|----------------|
| 1         | -4.04     | -1.11     | 2.93      | 0.10      | -0.59          | -0.69          |
| 2         | 0.97      | 0.07      | -0.90     | -0.32     | 0.83           | 1.15           |
| 3         | 0.08      | -0.21     | -0.13     | 0.89      | 0.21           | -0.68          |

Compound 2, in comparison, was aromatic in structures \(2a(S_0)\) and \(2b(T_1)\) while it was non-aromatic in structures \(2a(T_1)\) and \(2b(S_0)\). Since \(2a(T_1)\) is non-aromatic, ring-opening to \(2b(T_1)\) was favored, as aromaticity was gained (\(\Delta\)HOMA\((T_1) = 1.15\)). Benzene in the \(T_1\) state can adopt several different conformers depending on the starting geometry; (i) it can have a quinoidal structure with two unpaired electrons in the para-positions and two double bonds parallel to the \(C_2\)-axis \((^3Q)\), (ii) it can have an anti-quinoidal structure with two allyl radical segments \((^3AQ)\), or (iii) it can be described as a combination of a pentadienyl and a methyl radical \((^3PM)\) [55] (Figure 5). Isomer \(2a(T_1)\) is geometrically most similar to \(^3AQ\) since it has two long CC bonds and two allylic segments (see Figure S9).

The small HOMA values of \(3a(S_0)\), \(3b(S_0)\) and \(3b(T_1)\) indicate that these are nonaromatic while a high positive value of \(3a(T_1)\) suggests aromatic character. Thus, ring-opening of 3 in the \(T_1\) state entails an unfavorable reduction in aromaticity as \(\Delta\)HOMA\((T_1) = -0.68\). Taken together, the HOMA
values support our hypothesis that T\textsubscript{1} state aromaticity is lost in SCB ring-openings of 1\textsubscript{a} and 3\textsubscript{a}, while the T\textsubscript{1} state antiaromaticity of 2\textsubscript{a} is alleviated in this reaction.

![Figure 5](image)

**Figure 5.** The quinoid (Q), anti-quinoid (AQ), and pentadienyl-methyl (PM) conformers of T\textsubscript{1}-state benzene.

2.2.2. Nucleus Independent Chemical Shift (NICS) Scans

NICS is a magnetic indicator of aromaticity. The chemical shifts of NICS probe are scanned over a certain distance (0–5 Å) above the center of the molecular plane. The out-of-plane component obtained is then plotted against the distance. The NICS scans of 1–3 in their T\textsubscript{1} states in ring-closed and ring-opened isomers are shown in Figure 6, while those in the S\textsubscript{0} states are found in Figure S1. With regard to 1\textsubscript{a}(T\textsubscript{1}), the out-of-plane component in the NICS scan had a negative value (−14.4 ppm; 1.1 Å) suggesting that this structure is significantly aromatic. Conversely, a high positive value of the out-of-plane component in 1\textsubscript{b}(T\textsubscript{1}) shows that this structure had antiaromatic character. For 2, it was found instead to be 2\textsubscript{a}(T\textsubscript{1}), as it had a high positive value for the out-of-plane component (90.9 ppm; 0 Å) revealing that this structure was T\textsubscript{1} antiaromatic. This T\textsubscript{1} antiaromaticity changed back to aromaticity when the SCB ring opened, because a value of −19.8 ppm at 1.1 Å was calculated for 2\textsubscript{b}(T\textsubscript{1}). With regard to 3, the NICS scan showed 3\textsubscript{a}(T\textsubscript{1}) to be aromatic with a value of −30.4 ppm at 0.9 Å, yet, 3\textsubscript{b}(T\textsubscript{1}) was non-aromatic. Because of the non-planarity of the COT of 3\textsubscript{b}(T\textsubscript{1}) a small kink was observed in its NICS scan, in contrast to that of 3\textsubscript{a}(T\textsubscript{1}) (Figure 6 and Figure S1). Discontinuities in NICS-XY scans due to non-planarities were earlier observed by Schaffroth and co-workers for tetraazaacenes [56]. Thus, based on NICS, we have support for our hypothesis that T\textsubscript{1} (anti)aromaticity influences the reaction energies for the ring-openings of 1, 2, and 3. This led to loss of T\textsubscript{1} aromaticity in 1 and 3, whereas it leads to alleviation of T\textsubscript{1} antiaromaticity in 2. This reversal when going from 1 to 2, and then to 3 was also viewed clearly in Figure 6, since the structures with negative (aromatic) NICS values were successively 1\textsubscript{a}(T\textsubscript{1}), 2\textsubscript{b}(T\textsubscript{1}) and 3\textsubscript{a}(T\textsubscript{1}).

![Figure 6. Cont.](image)
Figure 6. Nucleus independent chemical shifts (NICS) scans of (a) 1a(T₁) and 1b(T₁); (b) 2a(T₁) and 2b(T₁); as well as (c) 3a(T₁) and 3b(T₁) at the GIAO-(U)B3LYP/6-311+G(d,p)//(U)B3LYP/6-311G(d,p) level. Only the out-of-plane components are displayed.

2.2.3. Anisotropy of the Induced Current Density (ACID) Plots

ACID is a magnetic indicator of aromaticity for visualizing ring-currents and electron delocalization. The ACID plots (Figure 7) of compounds 1, 2, and 3 corroborated the results of the NICS scans. Clockwise ring-currents for 1a(T₁), 2b(T₁) and 3a(T₁) indicated aromaticity, while counter-clockwise ring-currents in 1b(T₁) and 2a(T₁) represented antiaromaticity. Yet, the ring-currents in 1b(T₁) suggested this structure to be only weakly antiaromatic. The 3b(T₁) structure was non-aromatic. Clearly, 2a(T₁) opened the SCB ring to alleviate T₁ antiaromaticity (a favorable process), while 1a(T₁) and 3a(T₁) lost aromaticity upon ring-openings (unfavorable processes).

2.2.4. Isomerization Stabilization Energy (ISE) Values

ISE is an energetic index of aromaticity and it is based on the energy difference between the calculated total energy of fully aromatic methyl isomer to that of the non-aromatic exocyclic methylene isomer. We also utilized the isomerization stabilization energy (ISE) index of Schleyer [32] to estimate either the aromaticity or antiaromaticity in ring-closed structures in the T₁ state. Here, we examined only 1 and 2, and only in their T₁ states. With regard to the smallest compounds, the 4- and 5-methyl substituted 1a(T₁) derivatives showed negative ISE values (ISE_{avg} = -10.1 kcal/mol, Figure 8), indicative of some T₁ aromatic stabilization. With regard to 2, the methyl-substituted 2a(T₁) structures showed positive ISE values from 10.1 to 12.6 kcal/mol, indicative of T₁ antiaromatic destabilization. Structure 2a(T₁) is highly destabilized, evident from the computed ISE values. On the other hand, the ISE values
reported for benzene in $S_0$ state is $-33.2$ kcal/mol \[57\]. Thus, the ISE values support our hypothesis that $2a(T_1)$ is destabilized to the same extent as $1a(T_1)$ is stabilized.

**Figure 7.** Anisotropy of the induced current density (ACID) plots at (U)B3LYP/6-311+G(d,p)//(U)B3LYP/6-311G(d,p) level. Broken arrows in $1b(T_1)$ indicate weaker ring-currents. Aromatic = A, antiaromatic = AA, weakly antiaromatic = WAA, and non-aromatic = NA.

**Figure 8.** Isomerization stabilization energy (ISE) values (kcal/mol) of the 4- and 5-methyl substituted $1a(T_1)$ derivatives, and the 5-, 6-, 7-, and 8-methyl substituted $2a(T_1)$ derivatives at the UB3LYP/6-311G(d,p) level. ISE$_{avg}$ is the average ISE value for the various methyl substitutions.
2.3. Five- and Seven-Membered Carbocyclic Anions and Cations Fused to SCB

In order to explore if the findings on 1–3 can be extended to other \([4n]-\) and \([4n+2]\) annulenyl-SCBs, we examined the potential energy surfaces of 5- and 7-membered annulenyl cations and anions fused to SCB rings (7–9, Figure 9). This also allowed us to evaluate how the reaction energies depend on the annulene size. It should be noted that we only investigated energy and geometry changes, and we predicted 7 and 9 to resemble 1 and 3, respectively, while 8 should resemble 2. The SCB-fused Cp- was excluded as its calculated \(T_1\) state was of \(\pi\sigma^*\) and not of \(\pi\pi^*\) character.

The 7a(S\(_0\)) structure was a transition state; being a 4\(\pi\)-electron species it is strongly singlet state antiaromatic, it showed large CC bond length alternations (Figure S11), and it was unstable to SCB ring-opening, leading to singlet state antiaromaticity alleviation. On the other hand, 7a(T\(_1\)) in the \(T_1\) state was a minimum on the \(T_1\) PES; its geometry met the aromaticity criterion of bond length equalization, and the spin density was uniformly distributed over the cyclopentadienyl fragment (Figure S12). Interestingly, it was 2.9 kcal/mol lower in energy than 7a(S\(_0\)), similar to the parent cyclopentadienyl cation which has a triplet ground state [58–61]. The ring-opening of 7a(T\(_1\)) to 7b(T\(_1\)) was endergonic by 3.8 kcal/mol, opposite to the ring-opening of 1a(T\(_1\)) to 1b(T\(_1\)) which was exergonic by 17.5 kcal/mol. The reason why 1a(T\(_1\)) does not behave similar to 7a(T\(_1\)) and 3a(T\(_1\)) could be explained by the ring-strain in the CBD ring.

With regard to 9a(T\(_1\)), it was merely 4.2 kcal/mol higher in energy than 9a(S\(_0\)), and its geometry indicated a completely delocalized cycloheptatrienyl anion. This delocalization of the triplet biradical character was also confirmed through its spin density (Figure S12). The ring-opening of 9a(T\(_1\)) to 9b(T\(_1\)) was energetically unfavorable, yet, not equally unfavorable as the ring-opening of 3a(T\(_1\)) to 3b(T\(_1\)). Thus, when going to gradually larger annulenes the SCB ring-opening energies in the \(T_1\) state were −17.5 (1), 3.8 (7), 12.2 (9), and 22.2 (3) kcal/mol, respectively. i.e., only the most ring-strained compound (1) displayed an exergonic reaction energy. The activation energies in the \(T_1\) state also increased gradually and they were 9.5 (1), 21.7 (7), 24.6 (9) and 31.6 (3) kcal/mol, respectively. Hence, the SCB ring, when fused with \([4n]\) annulenes will in general not open in the \(T_1\) state, a feature that stems from \(T_1\) aromaticity. When an SCB ring is attached to an annulene ring, the absence of a photochemical ring-opening should therefore indicate \(T_1\) aromaticity. Only when ring-strain is high, as in 1a(T\(_1\)), will \(T_1\) state ring-opening occur in such species.

**Figure 9.** Free energy changes in 5- and 7-membered annulenyl cations and anions fused with SCB rings upon ring-openings at (U)B3LYP/6-311G(d,p) level. Compound 7a(S\(_0\)) is not a minimum in the \(S_0\) state. The black energy levels represent \(S_0\) and those of red indicate \(T_1\) state and energies for transition states are given in bold.
Compound 8 showed the opposite behavior to that found for 7 and 9. Structure 8a(T1) was highly skewed and its ring-opening to 8b(T1) was exergonic by 17.6 kcal/mol. Also, the ring-opened 8b(T1) isomer was planar and had a CC bond delocalized structure. Thus, 8 having a [4n + 2]annulene moiety, displayed similar characteristics as 2. Yet, the smaller the ring, the higher the exergonicity of the ring-opening, explained by relief of ring-strain in addition to the relief of T1 antiaromaticity. Taken together, the T1 state ring-opening reactions were markedly uphill for compounds 3, 7, and 9, and downhill for 2 and 8. Compounds 3, 7, and 9 showed T1 aromaticity similar to [4n]annulenes, while compounds 2 and 8 showed T1 antiaromaticity analogous to [4n + 2]annulenes, suggesting that loss of T1 aromaticity was observed in ring-openings of [4n]annulenes while T1 antiaromaticity of [4n + 2]annulenes is alleviated through such reactions. Finally, the T1 state activation energies for SCB rings of the T1 aromatic compounds 3, 7, and 9 were higher than those of the non-aromatic reference compounds 4–6 (Figure 10), allowing the SCB ring to function as a T1 state aromaticity indicator. For the (4n + 2)π-electron annulenoSCBs, the activation energies were similar or lower than those of the nonaromatic references. Overall, the height of the activation barriers in the T1 state were, to a significant extent, correlated with the reaction energies (R² = 0.762, Figure S40), in accordance with the Bell–Evans–Polanyi principle. This correlation was even stronger for the S0 state (R² = 0.872).

Figure 10. Activation free energies (kcal/mol) of all compounds 1–9 at the (U)B3LYP/6-311G(d,p) level in the S0 (unfilled circles) and T1 (filled circles) states.

2.4. Polycyclic Structural Units Fused to SCB

In order to test the generality of the hypothesis, the reaction and activation energies for the ring-opening of an SCB ring when fused to polycyclic moieties (10 and 12π-electrons) were also explored (Scheme S1). With 10 π-electrons, naphthalene is T1 antiaromatic, and we found that the SCB ring-openings of all three isomers of naphtho-SCB (10a–10c) were exergonic, in line with our hypothesis. However, the activation energy for 10a (23.3 kcal/mol) is significantly higher than observed for the cPr-naphthalenes previously studied (8–11 kcal/mol) [34], suggesting that the SCB ring will remain closed when fused to naphthalene. With regard to biphenylene, a 12π-electron compound which is T1 state Baird-aromatic, the SCB ring-opening energies of 11a–11c were modestly exergonic. Moreover, the activation barrier for SCB ring-opening was nearly the same as that of naphthalene (24.2 kcal/mol). Yet, it should be noted that polycyclic systems are more complex than monocycles because the SCB ring-opened products can adopt aromaticity in some of the rings leading to stabilization, a feature already observed for the ring-openings of the corresponding cPr substituted systems. Clearly, the SCB ring should remain closed for T1 aromatic polycyclic compounds, however, it may also not open for polycyclic T1 antiaromatic species, leading to limitations of its usage.
3. Computational Methods

All calculations were performed with Gaussian 09 revision D.01 [62]. The structures were optimized at the (U)B3LYP and (U)OLYP density functional theory levels [63–66], with the 6–311G(d,p) basis set [67,68]. Frequency calculations were carried out at the same level to confirm stationary points with real frequencies. Single-point energy calculations were performed at the (U)CCSD(T)/6-311G(d,p)//(U)B3LYP/6-311G(d,p) level and thermal corrections at the B3LYP level were added to get the free energies. Structural, magnetic and energetic indices were used to assess the extent of aromaticity [69]. The harmonic oscillator model of aromaticity (HOMA) [70] values were calculated at the (U)B3LYP/6-311G(d,p) level. Positive values approaching 1.0 correspond to aromatic compounds, negative values to antiaromatic compounds, and values close to zero indicate nonaromatic compounds. Nucleus independent chemical shift (NICS) scans along an axis perpendicular (z-axis) to the ring planes were generated with the Aroma package 1.0 [71–73], using the Gauge-Independent Atomic Orbital (GIAO) method [74] at the GIAO-(U)B3LYP/6-311+G(d,p)//(U)B3LYP/6-311G(d,p) level. Scans were performed starting at the centre of the annulene to 5.0 Å above the ring plane with increments of 0.1 Å. For aromatic compounds, the out-of-plane components show relatively deep minima. For non-aromatic compounds, the values close to the molecular plane are positive, decreases asymptotically and approach zero as the distance is increased. The antiaromatic compounds display high positive values for the out-of-plane components which go to zero with increasing distance. The anisotropy of the induced current density (ACID) calculations [75,76] were used to analyze the ring-currents with the CGST method [77] at (U)B3LYP/6-311+G(d,p) level with AICD 2.0.0 software package. The ACID plots were generated using (NMR = CGST IOp(10/93 = 1) and ultrafine grid (integral = grid = ultrafine). Clock-wise ring-currents indicates aromaticity and counter clock-wise ring-currents indicates antiaromaticity. Isomerization stabilization energies (ISE) [32,33,57] were calculated at the (U)B3LYP/6-311G(d,p) level.

4. Conclusions

We have shown that the ring-opening ability of the SCB ring in the T1 state can be used to sense for T1 aromaticity of a [4n]annulene to which it is fused, as its ring-opening disrupts the T1 aromaticity of the [4n]annulene, an unfavorable (endergonic) process. Conversely, it should open regardless if fused to a T1 non-aromatic or T1 antiaromatic ring. By usage of a variety of (anti)aromaticity indices, we link the shapes of the T1 PES to changes in T1 (anti)aromaticity. Consequently, the SCB ring could be used as a T1 aromaticity probe, in contrast to the all-carbon cyclobutene or disilacyclobutene rings which are either too photoresistant or too labile. Moreover, as the silacyclobutene ring when fused does not π-conjugate with the annulene, it has a benefit when compared to strained four-membered rings with Group 15 and 16 elements. The SCB ring also has a benefit over the cPr group examined earlier by us in the context of excited state aromaticity indicators [34] because the transient intermediate formed upon SCB ring-opening, in contrast to the ring-opened cPr intermediate, is easily trapped by alcohols to yield photostable silylethers. Yet, the SCB ring is likely of limited applicability in polycyclic systems as it may remain closed regardless of whether the ring system is T1 aromatic or T1 antiaromatic. Still, our study can be interesting from an applications perspective as it reveals situations when the SCB ring as a part in a larger molecule could lead to photoinstability of compounds used for various applications in organic electronics [78].

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/5/4/91/s1, NICS scans, ACID plots, geometries, spin densities, and Cartesian Coordinates.

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