Is Schleyer’s Predicted All-Cis [10]Annulene an Unstable Framework?

Karnjit Parmar, Christa Blaquier, Sydnie Gengler, Brianna Lukan, Michel Gravel*

The initial quantum mechanical description of aromaticity\(^1\) by Hückel\(^2\) spawned decades worth of experimental studies into aromaticity, resulting in the synthesis of nearly all annulenes up to and including [30]annulene.\(^3\) Amongst those prepared, [18]annulene\(^4\) and [20]annulene\(^5\) are especially notable structures as some configurations enable near planar ground state structures, resulting in diatropic ([18]annulene) and paratropic ([20]annulene) ring currents upon exposure to an external magnetic field. However, other annulenes such as [8],\(^6\) [10],\(^7\) [12],\(^8\) and [14]annulene\(^9\) are more challenging to study due to the absence of accessible planar ground states and/or kinetic instability. Various planar dehydro and benzannulated derivatives have also been prepared.\(^10\)

The parent [10]annulene (1, Figure 1a) was initially prepared by Masamune and coworkers and confirmed to be non-aromatic by the lack of downfield resonances (>6.5 ppm) in the $^1$H NMR spectrum.\(^7\) This observation was later corroborated by theoretical investigations, which found that the lowest energy structure was not planar.\(^11\) Though there is some
computational evidence that mono-trans[10]annulene can adopt a planar and aromatic conformation,\textsuperscript{11-12} such a conformation has not been observed experimentally.

In order to understand the effect of ring size on aromaticity, it is highly desirable to access a kinetically stable planar, aromatic [10]annulene. Various strategies have been employed towards obtaining such compounds. Notably, the bridged 1,6\textsuperscript{13} and 1,5-methano[10]annulenes\textsuperscript{14} were found to be aromatic, though some contaminating homoaromaticity has been suggested to exist.\textsuperscript{15} The highly aromatic 3 was also successfully prepared by Myers and coworkers,\textsuperscript{16} but it is kinetically unstable and degrades above -40 °C due to cross-ring orbital interactions of the cumulene and alkyne orbitals orthogonal to the aromatic system (Figure 1b).
Later theoretical investigations by Schleyer, Schaefer, and coworkers predicted that cyclopropanes or cyclobutanes fused to the [10]annulene framework (5-7) induce planarity due in part to the incentive to expand bond angles of the sp² hybridized carbon atom from 120° up to 150° (Figure 1c).¹⁷ This expansion resulted in planar minima using B3LYP, suggesting these molecules could exist as planar aromatic structures. Recently, we also described the successful preparation of the highly aromatic dehydro[10]annulene 8 based on the assumption that monocyclopropanation would stabilize the previously known and unstable 3 by eliminating the cross-ring orbital interactions leading to Bergman-like¹⁸ cyclizations (3 to 4).¹⁹ We hoped that monocyclopropanation (8) would retain the essence of the previously theorized [10]annulenes
(5-7). To our delight, the structure was found to be planar and kinetically stable, as evidenced by its notable bench stability.\textsuperscript{19} The dehydro[10]annulene 8 was also found to be heavily delocalized despite the presence of the alkyne and ultimately displayed all the hallmarks of a highly aromatic annulene.

However, there was still a great interest in preparing one of the original [10]annulene frameworks (5-7) computed by Schleyer and Schaefer\textsuperscript{17} in order to study experimentally a planar all-cis [10]annulene. Both 6 and 7 were considered but were eventually rejected as targets due to a lack of functionalizable aromatic ring sites and synthetic tractability. We instead directed our attention towards 5, which was the result of a formal cyclopropanation of our previously prepared 8. In addition to the reasonably small departure from the kinetically and thermodynamically stable 8, it was the only theorized [10]annulene that had degenerate Kekule resonance structures, which we hypothesized would force a delocalized state. Thus we believed that the synthesis of 5 would enable us to access a highly aromatic, true all-cis planar[10]annulene system.
The original synthetic strategy towards \( \textbf{5} \) involved ozonolysis and reduction of a suitably cyclopropanated tetrahydrohydronaphthalene \( \textbf{9} \) to generate a cyclodecane derivative \( \textbf{10} \) (Scheme 1).\(^{19}\) A dehydration and elimination sequence would afford a tetraene \( \textbf{11} \) that may undergo facile or spontaneous oxidation to the final annulene framework, from which the carbon atoms could be de-halogenated to yield \( \textbf{5} \). Analogous oxidations of protoaromatic benzenoids are well described in the literature.\(^{20}\) It was also presumed that the chlorinated annulene may be stable enough for analysis, due to the previous preparations of the analogous 7,7-dichlorocyclopropabenzene framework.\(^{21}\) However, we believed that the material may be amenable to a mild reduction\(^{22}\) to afford the parent dicyclopropanated [10]annulene. Substitution of the chlorine atoms also seemed plausible and a good opportunity for functionalization of the aromatic system.\(^{23}\)
The synthesis began with the Diels-Alder reaction between diene 13 (Scheme 2) and tetrachlorocyclopropene (14), the former being readily prepared from the bicyclic anhydride 12. The reaction proceeded smoothly to yield a mixture of cis and trans adducts (15a/15b). The cis adduct (15a) was formed preferentially (ca. 3:1 dr), presumably due to the favoured exo approach of 14 from to the least hindered face of the diene 13. The mixture of adducts (15) could be ozonolyzed smoothly on a small scale to afford the diketone 16 but scale up typically afforded large amounts of undesired transannular aldol products, with 17 being the major isomer. The problem could be circumvented by carrying out a reductive quench of the ozonolysis mixture with NaBH4 at low temperature, affording the diol 18 directly as a single diastereomer. Only 15a underwent ozonolysis under the optimized conditions and attempts to induce 15b to react by increasing the temperature or by prolonging reaction times resulted in complex mixtures of products. Mesylation of the diol (18) proceeded to generate dimesylate 19, which could conceivably be induced to undergo a four-fold elimination to afford the tetraene 22 (analog of 11). However, attempts to induce elimination with NaOH or NaHMDS resulted in material degradation whereas the use of the weaker DBU resulted in no reaction. A mono-elimination of 19 was observed when using potassium tert-butoxide, which only further degraded upon exposure to higher temperature or prolonged reaction time. To our delight, attempts to invert the diastereomeric diol 18 under Mitsunobu conditions resulted in the near exclusive formation of diene 21, which is likely favoured over the substitution product due to the hindered nature of the 10-membered ring. However, our excitement at the formation of the diene was soon stunted by its utter recalcitrance to the introduction of additional unsaturations. Indeed, a number of
attempted eliminations resulted in either no product formation or complete material degradation.

Scheme 2: Initial attempts towards the synthesis of a cyclopropanated [10]annulene.

Our initial suspicion was that the tetraene 22 was forming as a number of new olefinic signals were observed, but the final oxidation to 23 was slower than the degradation of 22. It was also possible that a double elimination/isomerization sequence (involving the dichlorocyclopropene moiety) occurred more rapidly on 21 than the intended tetraene formation, leading to an unstable non-aromatic material. Therefore, in order to mitigate these issues, a suitably oxidized cyclodecane precursor was sought, so that direct elimination to the potentially stable aromatic annulene 23 was possible (Scheme 3a). The chlorinated annulene (23), ideally stabilized kinetically due to aromaticity, could then be subjected to a reduction to
afford 5. The synthesis using this revised strategy began with a Diels-Alder reaction between 2-chlorobutadiene and maleic anhydride to generate the chlorinated bicyclic anhydride 26 (Scheme 3b). The subsequent steps proceeded uneventfully, with only minor modifications relative to the initial route using butadiene. However, the Diels-Alder adduct 24 failed to undergo ozonolysis, likely due to the enhanced steric bulk introduced by the additional chlorine atom. Further oxidation attempts on the tetrasubstituted alkene using various reagents also failed to yield any useful materials for advancing the synthesis, prompting us to reassess our tactics.
a. First revised strategy towards a suitably oxidized cyclodecane precursor:

**Scheme 3**

The correct oxidation state is shown in the figure.

b. Synthetic efforts towards cyclodecane 25

In continuation of this strategy, we sought to directly oxidize the previously obtained diene 21 to afford a formal equivalent of the oxidized cyclodecane 25. Dozens of oxidations were
attempted to almost no avail, likely due to the rigidity of the system. Trace amounts of enone 33 were eventually observed using sublimed SeO$_2$ as the oxidant, but the low material availability and its facile degradation suggested an alternative route was necessary (Scheme 3c).

**Reassessing the strategy**

Previously, we have shown that exposure of the diene 21 to MeLi in diethyl ether and quenching the reaction with water resulted in didechlorination and hydrolysis of the putative dichlorocyclopropene intermediate (35) to ultimately yield the bench stable cyclopropenone 36 (Scheme 4).$^{19}$ The chemoselectivity of the transformation is somewhat unclear, but presumably occurs due to the strong electrophilicity of the tetrachlorocyclopropane ring. Interestingly, possible Skattebøl rearrangement$^{24}$ products were not detected in the crude reaction mixture. Ring opening products derived from carbene intermediates were not observed either.$^{25}$ Nevertheless, the formation of the cyclopropenone 36 represented a significant milestone in the synthetic efforts towards 8 as it was the first step that successfully introduced strain in the cyclodecane framework. Upon exposure to UV light, 36 could be decarbonylated to obtain the cis,cis-dienyne 37,$^{26}$ which could be exposed to potassium tert-butoxide in THF$^{27}$ to generate the highly aromatic and unexpectedly volatile [10]annulene 8.$^{19}$ The reaction proceeds through a double endo-to-exo cyclopropene isomerization mechanism (38-40) and is presumably driven by sequential and favourable elimination/isomerization steps rather than incipient aromaticity. As formation of the final product is not dependent on its aromaticity, it seems this route may hold significant promise for the formation of either 5 or a derivative thereof.
Scheme 4: Synthesis of 8 via a double elimination-isomerization procedure. The anisotropy of the induced current density (AICD)\textsuperscript{28} program to generate the plot.

Unfortunately, the analogous double elimination and isomerization on the cyclopropenone 36 resulted in material degradation, possibly due to the sensitivity of the cyclopropenone moiety to basic conditions. As the intermediate between the diene 21 and cyclopropenone 36 was presumed to be the dichlorocyclopropene (35), we sought to intercept it after the didechlorination reaction to form a stable derivative (41-42) that may not succumb to hydrolysis (Scheme 5). We surmised that the formation of a difluorocyclopropene (41)\textsuperscript{29} or an analogous ketal (42)\textsuperscript{30} would afford improved stability. Unfortunately, treatment of the dichlorocyclopropene intermediate with rigorously dried TBAF or even with neopentylglycol only resulted in either degradation or formation of the cyclopropenone 36 after aqueous quench.
As the problem was the ultimate formation of 36 due to hydrolysis of 35, we believed that replacing the offending dichlorocyclopropane in 21 with a dihydrocyclopropane may be feasible. We presumed that this would still allow for a selective didechlorination to yield the corresponding triene (analogous to 41-41). Alkyl or aryl substituted cyclopropanes were explicitly avoided due to their propensity towards carbene formation via ring opening.\textsuperscript{25b} We suspected that a chemoselective reduction of 21 may be possible due to the strong electron withdrawing nature of the tetrachlorocyclopropane group. Various reduction methods were sought, but ultimately treatment of the diene 21 with lithium aluminum hydride resulted in a highly selective abstraction of a chloride to form trichlorocyclopropane 43. Exposure of the mono reduced material (43) to methyl lithium failed to afford the desired triene (44) and resulted in a mixture of products. The failure of the reaction seemed attributable to the likely instability of the chlorocyclopropene moiety in 44, a functional group that is conspicuously absent in the literature. Attempts to further direct the reduction of 43 to the dihydro derivative were met with failure. It seemed plausible that the decreased in electrophilicity resulted in a loss of
regioselectivity. Attempts to induce an analogous reduction on the Diels-Alder adducts (15) also failed to yield any usable materials.

We instead decided to return our attention to the cyclopropenone (36), believing we could transform it directly rather than intercept the intermediate dichlorocyclopropene (35). The presence of a ketal on the [10]annulene framework would also suppress the volatility of the parent [10]annulene, potentially easing its purification on a smaller scale, which was highly problematic for the unexpectedly volatile 8. We also considered that the stability of a ketal to base would allow it to proceed through the aforementioned endo-to-exo isomerization (cf., 37 to 8) with no issues. Proceeding with this plan, the crude cyclopropenone was activated with freshly prepared triethyloxonium tetrafluoroborate (46) and transformed into the ketal by direct addition of neopentyl glycol (47), which was found to be unstable to silica (Scheme 6a). Subjecting the crude material to the final transformation resulted in no observable aromatic species (e.g., 48). In an effort to provide a more stable material that could be purified prior to and after exposure to tBuOK, we opted for the preparation of the more robust thioketal derivative (49). Thus, treating the activated cyclopropenone 46 with 1,3-propanedithiol formed the requisite thioketal 49, which was stable to chromatography. Gratifyingly, when 49 was reacted with tBuOK in THF, we observed signals in the $^1$H NMR spectrum that were consistent with the expected chemical shifts and multiplicities of the desired annulene 50 (Scheme 6b).
a. Protection of the cyclopropenone

36 \[ \text{tBuOK (4 equiv.)} \rightarrow \text{45} \]

36 \[ \text{Et}_2\text{OBF}_4 (0.88 \text{ equiv.})} \rightarrow \text{46} \]

[neopentyl glycol (1 equiv.)]

46 \[ \text{1,3-propanedithiol (1 equiv.)} \rightarrow 15\% \rightarrow \text{49} \]

47 \[ \text{unstable} \]

48 \[ \text{could be purified} \]

49 \[ \text{could be purified} \]

50 \[ \text{traces observed} \]

by $^1\text{H NMR spectroscopy}$

b. Computed and experimental $^1\text{H NMR}$ spectrum of 50

**Simulated**

**Experimental**
The observation of 50 by $^1$H NMR spectroscopy suggested the parent dicyclo[10]propa[10]annulene (5) was in fact aromatic and a thermodynamic minimum as predicted by Schleyer, Schaefer et al. Unfortunately, the material degraded on standing and could not be purified, suggesting a potential kinetic instability. The origin of this instability was unclear, as no degradation products could be isolated or observed. It seemed that there existed two possible scenarios: either the carbon framework itself was inherently unstable or the thioketal initiated some degradation pathway. As the thioketal triene 49 was observed to be stable, it seemed unlikely that the thioketal itself imposed undue strain on the 10-membered ring. However, the slight changes to the framework that occurred after aromatization made this ambiguous. Seeking to resolve this uncertainty, we decided to perform the synthesis anew with a 1,2-dihalocyclopropene (51) in lieu of tetrachlorocyclopropene 14 (Scheme 7). This tactical modification sought to obviate the need to reduce or transform the problematic geminal dichloro group in 21 or 35.
The newly proposed synthetic route involved a key Diels-Alder reaction between a 1,2-dihalocyclopropene (51) and the previously prepared diene 13. Due to the similar nature of the substrates in our previous route and the revised route, we were confident that the Diels-Alder and ozonolysis steps would proceed without much problem. However, we did anticipate some issues during the double elimination and didehalogenation steps, which were potentially dependent on the presence of the strongly electron withdrawing tetrachlorocyclopropane group. Indeed, it was previously shown that the removal of only one chlorine atom (43) had a detrimental effect on chemoselectivity in a LiAlH₄ reduction, likely due to the attenuated electrophilicity. In order to ensure chemoselectivity in the MeLi didehalogenation, it was presumed that at least one bromine atom was necessary to incorporate. Thus, the synthetically accessible 1-bromo,2-chlorocyclopropene was used.
The synthesis began with the preparation of the known 1-bromo,1-trimethylsilyl-2,2-dichlorocyclopropane (55, Scheme 8). Treating the crude cyclopropane precursor with TBAF generated 1-bromo,2-chlorocyclopropene 56 in situ, which was trapped with the previously prepared diene (13) to generate cycloadduct 57 as a 2.5:1 mixture of diastereomers in 25% yield. Gratifyingly, the mixture of cis/trans diastereomers 57 underwent smooth ozonolysis to generate an apparent mixture of diols 58 after an in situ sodium borohydride reduction. As the previous trans Diels-Alder adduct 15b failed to undergo ozonolysis, it was believed that the reduced steric bulk of trans-57 was responsible for its increased reactivity toward ozone. As a consequence of the complete ozonolysis of both diastereomers of starting material 57, a complex mixture of products was obtained. Exposure of this mixture to the previously used Mitsunobu conditions generated a mixture of two dienes (59), which upon exposure to methyl lithium generated triene 60. The triene was stable to work-up but degraded upon exposure to silica. With the small amounts of triene we were able to generate, we could test the final transformation. Attempts to carry out the final elimination/isomerization with tBuOK/THF followed by a standard work-up resulted in mostly degradation products.
As the desired product may be kinetically unstable or highly volatile, the reaction was attempted again in $d_8$-THF and monitored by $^1$H NMR spectroscopy (Scheme 9). The resulting spectrum was quite complex, but to our delight some downfield signals ($>$7.5 ppm) were clearly resolvable. Remarkably, a doublet at 8.32 ppm and a triplet at 7.95 ppm with an integral ratio of 2:1 was observed, which matches the expected multiplicity and integration for the annulene protons in 5. Additionally, a singlet was visible at 2.45 ppm, with an integration consistent with the four cyclopropane protons of 5. To confirm the assignment, the $^1$H NMR chemical shifts and coupling constants for 5 were calculated at the B3LYP/6-311+G(2d,p) and B3LYP/6-31G(d,p) levels respectively, which have been previously found to be successful in the $^1$H NMR calculation for 8.$^{19}$ The bond lengths of the computed structure are all between 1.36 and 1.39 angstroms,
showing considerable delocalization. The calculated spectrum (Figure 2) closely matched that of the experimentally observed spectrum (Scheme 9b). Interestingly, all three signals were also observed to degrade concomitantly while retaining their relative integrations, further demonstrating their association.

Scheme 9: a. Preparation of the final doubly cyclopropanated [10]annulene 5 and an aromatic side product (61). b. $^1$H NMR spectrum of the *in situ* reaction between triene 60 and tBuOK.

Figure 2: Simulated$^{31}$ $^1$H NMR spectrum of 5 using computed chemical shifts and coupling constants (see S2).
In addition to the signals belonging to dicyclopropa[10]annulene 5, a series of multiplets were also apparent in the same region of the $^1$H NMR spectrum. Fortunately, the signals were also well resolved and had a defined first order appearance. This species was also much more kinetically persistent than 5, but unfortunately was also observed to degrade and was not air stable. The chemical shifts initially suggested a naphthalene-based degradation product, but all attempts at matching these signals to various naphthalene derivatives failed. Finally, we considered that another desymmetrized [10]annulene structure may have formed. Inspired by previous theoretical explorations,$^{11}$ we hypothesized that a planar and aromatic [10]annulene structure containing a trans-double bond may exist as a minimum on a potential energy surface if at least one cyclopropane ring is present to favour widened bond angles. The parent mono-trans[10]annulene (non-cyclopropanated) structure can adopt a similar conformation, but is higher in energy and thus not observed experimentally.$^{11}$

To our surprise, we observed that the analogous cyclopropanated structure did in fact adopt a near planar conformation when minimized at the M06-2X/6-31+G(d,p) level and that the computed $^1$H NMR spectrum was a close match to the signals observed in the aromatic region (Table 1), suggesting a potentially very rigid structure. This prompted us to experimentally re-acquire the $^1$H NMR spectrum with an expanded window, which allowed us to observe a highly shielded doublet corresponding to the aromatic ring’s inner proton. Although the chemical shifts of the downfield signals match much more closely to the computed shifts than that of the inner proton, this discrepancy is most likely due to the scaling factors used in the calculations being derived from empirical datasets that do not include such highly shielded protons. The
observation of the aromatic trans [10]annulene 61 is significant for several reasons. In contrast to the parent mono-trans [10]annulene structures previously prepared, 7b 61 is aromatic and nearly planar in its lowest energy conformer, with only a slight pucker to accommodate the inner hydrogen atom. The inner hydrogen atom is also perfectly sized to engage in stabilizing non-covalent interactions across the inside of the ring (see SI). This appears to be a rare example of an in-plane transannular H-π interaction and may play a role in the kinetic stabilization of the trans [10]annulene isomer relative to the all-cis dicyclopropa[10]annulene 5.

![61]

Figure 3: The $d_8$THF NMR spectrum of 61 visible after the degradation of 5.

Table 1: Comparison of experimental $^1$H NMR shifts of 61 to a computed structure. Geometry minimization: M06-2X/6-31+G(d,p), NMR computation: B3LYP/6-311+G(2d,p). ND = not determined.

<table>
<thead>
<tr>
<th>proton</th>
<th>Experimental (ppm)</th>
<th>Computed (ppm)</th>
<th>Absolute error (Δppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haa</td>
<td>2.76</td>
<td>2.82</td>
<td>0.06</td>
</tr>
<tr>
<td>Hab</td>
<td>8.06</td>
<td>8.00</td>
<td>0.06</td>
</tr>
<tr>
<td>Hac</td>
<td>7.61</td>
<td>7.79</td>
<td>0.18</td>
</tr>
<tr>
<td>Had</td>
<td>8.24</td>
<td>8.19</td>
<td>0.05</td>
</tr>
<tr>
<td>Hae</td>
<td>-1.23</td>
<td>-2.18</td>
<td>0.95</td>
</tr>
<tr>
<td>Haf</td>
<td>ND</td>
<td>5.11</td>
<td>ND</td>
</tr>
</tbody>
</table>
To our knowledge, this represents the smallest reported aromatic compound featuring a trans double bond and the first such demonstration of the stabilizing effect of a fused cyclopropane on a mono-trans [10]annulene, which has clearly demonstrated to be an effective strategy to rigidify expanded conjugated systems. The mechanism of its formation is currently unknown but may proceed via a ring opening of the cyclopropane to the vinyl carbene that can intercept tBuOK or a direct attack of the tBuOK onto the cyclopropane ring followed by isomerization to the trans alkene.

The successful observation of both 5 and 61, as confirmed by the computed $^1$H NMR spectra, prompted us to further investigate their aromaticity. Our initial hypothesis was that the symmetry of 5 would enhance the aromaticity when compared to 8 due to the degeneracy of the Kekulé structures. Ignoring the endocyclic bond of the cyclopropane moiety, both 5 and 61 demonstrate significant bond equalization with bond lengths ranging between 1.38-1.39Å and 1.37-1.42Å respectively (Figure 4a and b). However, the systems don’t appear to be significantly more bond equalized than the previously prepared 8 (Figure 4c). As bond length equalization is a poor indicator of aromaticity, and potentially highly dubious in the presence of small ring annihilations,\textsuperscript{32} we sought to further explore the electronic structure of the aromatic systems and compare them to the still theoretical 6 (Figure 4d).

<table>
<thead>
<tr>
<th></th>
<th>1.33</th>
<th>1.36</th>
<th>0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hah</td>
<td>8.15</td>
<td>8.16</td>
<td>0.01</td>
</tr>
<tr>
<td>Hai</td>
<td>7.74</td>
<td>7.80</td>
<td>0.06</td>
</tr>
<tr>
<td>Haj</td>
<td>7.83</td>
<td>8.17</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Mean absolute error 0.19

The nucleus-independent chemical shift (NICS) was first explored,[33] where it was demonstrated that diatropic ring current exists to varying degrees in 5, 6 and 8. Notably, 61 was omitted from the analysis due to the slight pucker and the asymmetry of the system. The largest NICS value is apparently exhibited by 5 (NICS(1)zz = -32.9) and 8 (NICS(1)zz = -31.9), both being
larger than that exhibited by 6 (NICS(1)zz = -23.4). However, there are numerous problems with the NICS method, especially with rings of varying sizes or composition. Furthermore, comparisons of non-planar structures are challenging. In order to ascertain the extent to which each system is delocalized, the number of delocalized electrons per atom was measured by the electron distribution of delocalized bonds (EDDB) method.\textsuperscript{34} The natural bond orbital resonance energy (NBO-RE) was also used to probe the extent to which $\pi_{\text{NBO}}\rightarrow\pi_{\text{NBO}*}$ interactions contribute to the total energy of the system.\textsuperscript{35,36} Using both methods, 5 ranks as the most aromatic with 0.97 delocalized electrons per atom in the aromatic ring (EDDB\textsubscript{F}) and an NBO-RE of 17.8 kcal/mol/$\pi$e\textsuperscript{-}. The mono-trans 61 is equally aromatic (EDDB\textsubscript{F} = 0.96e\textsuperscript{-}; NBO-RE = 17.8 kcal/mol/$\pi$e\textsuperscript{-}) while 8 is apparently less delocalized (EDDB\textsubscript{F} = 0.76e\textsuperscript{-}, NBO-RE = 17.1 kcal/mol/$\pi$e\textsuperscript{-}). Finally, the pentacyclopropanated 6 appears to be the least aromatic (EDDB\textsubscript{F} = 0.55e\textsuperscript{-}; NBO-RE = 15.2 kcal/mol/$\pi$e\textsuperscript{-}). The correlation between EDDB\textsubscript{F} and NBO-RE is quite apparent, and seemingly consistent with the initial hypothesis. The degeneracy of the Kekulé structures in 5 quite clearly increased its aromaticity compared to 8. Furthermore, the highly attenuated aromaticity of 6 strongly supports this and demonstrates how favourable the exomethylene electronic structure is. The strongly aromatic 61 is highly unexpected and quite peculiar, suggesting that one fused cyclopropane may not be sufficient to induce strong bond length alternation or localize the electronic structure in the absence of higher symmetry.
We have shown that cyclopropanation is a feasible strategy for the planarization of [10]annulene systems. In a previous report, we demonstrated that 8 was synthetically accessible, isolable, and remarkably bench stable. The general design included inhibiting the degradation pathway of the kinetically unstable didehydro[10]annulene 3 by eliminating a cross-ring interaction via cyclopropanation. We believed that the key successful feature of the route was the final double elimination-isomerization sequence of transformations triggered by tBuOK, which was driven by strain formation and release rather than incipient aromaticity (37 to 8, Scheme 4). The success of the strategy, the effectiveness of the route, and the remarkable stability of 8 improved our confidence that other cyclopropanated derivatives could also be prepared. After several route modifications, we eventually identified a feasible pathway towards the putative penultimate material 60, which upon exposure to tBuOK in d8-THF generated signals that were consistent with and computed to be the desired doubly cyclopropanated material 5. We observed the material to degrade quite rapidly, which was also noted to occur with the
dithiane derivative 50. Interestingly, when the final transformation was tested with triene 60 we also observed the novel and never previously identified [10]annulene 61. Curiously, the material seems to be the first ever identified stabilized mono-trans[10]annulene system. Thus, in pursuit of the aromatic [10]annulene theorized by Schleyer we found that it is not kinetically stable and ultimately uncovered a novel never before theorized structure.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, computational methods, and compound characterization data.

DATA AVAILABILITY STATEMENT

The data underlying this study are available in the online supplementary material.

AUTHOR INFORMATION

Corresponding Author

*michel.gravel@usask.ca

Author Contributions
All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

We thank the Government of Saskatchewan for an Innovation and Opportunity Scholarship (to K.P.), the Deutscher Akademischer Austauschdienst for a scholarship (to K.P.), the Natural Sciences and Engineering Research Council of Canada for a Discovery Grant (RGPIN-2017-06230 to M.G.), Compute Canada for computing resources, and the Canada Foundation for Innovation. We thank Prof. Dr. Peter R. Schreiner, Prof. Dale Ward, and Dr. Steven Langdon for helpful discussions. We would also like to thank the Saskatchewan Structural Sciences Centre (SSSC).

REFERENCES


32. Benzocyclopropene is highly aromatic despite the presence of compressed bonds.


35. Parmar, K.; Gravel, M. ChemRxiv 2022. This content is a preprint and has not been peer-reviewed.