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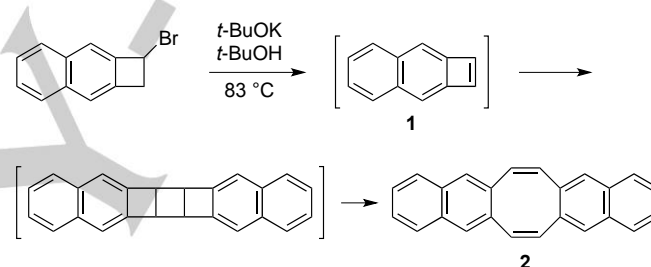
Serendipitous Rediscovery of the Facile Cyclization of Z,Z-3,5-Octadiene-1,7-diyne Derivatives to Afford Stable, Substituted Naphthocyclobutadienes

Joshua E. Barker,^[a] Takuya Kodama,^[a] Min K. Song,^[b] Conerd K. Frederickson,^[a] Tanguy Jousselin-Oba,^[c] Lev N. Zakharov,^[d] Jérôme Marrot,^[c] Michel Frigoli,^[c] Richard P. Johnson,^[b] and Michael M. Haley^{*[a]}

Dedicated to Prof. Ed Billups (Rice University) on occasion of his 80th birthday.

Abstract: The serendipitous isolation of very small amounts of two naphthocyclobutadiene (NCB) derivatives has led to the computational reexamination of the electrocyclization of Z,Z-3,5-octadiene-1,7-diyne as well as the experimental and computational study of diethynylindeno[2,1-a]fluorene derivatives that contain the 3,5-octadiene-1,7-diyne motif as part of a larger π -framework. In both cases the calculated potential energy surface strongly implicates two successive electrocyclic reactions to afford the antiaromatic products. With the octadienediyne fragment locked in the reactive conformation, the postulated diethynylindeno[2,1-a]fluorene intermediates afford the NCBs in modest to good yields. X-ray crystallography of four NCBs as well as NICS-XY scan calculations show that the paratropic motif is located primarily in the benzocyclobutadiene fragment within the larger π -scaffold.

imparts the molecules with inherently low HOMO/LUMO energy levels and small energy gaps, making PAAHs ideal counterparts to acenes in material science applications.^[3] Although antiaromatic compounds tend to be rather unstable, including them within a much larger conjugated system tends to afford isolable, stable, and well-characterized structures. Recent examples have included a variety of molecules based on the paratropic cyclobutadiene,^[4] pentalene,^[5] and indacene motifs.^[6]



Scheme 1. Formation and Dimerization of Naphthocyclobutadiene

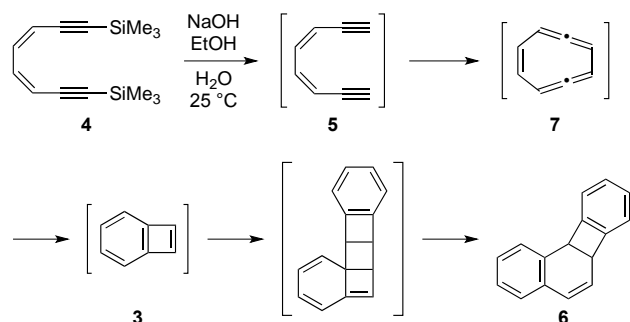
Introduction

The past 10-12 years have seen a resurgence of interest in antiaromatic molecules. In particular, expanded structures that contain a paratropic subunit, namely polycyclic antiaromatic hydrocarbons (PAAHs), have attracted considerable attention as potential small molecule semiconductors for use in organic electronics.^[1] Compared with the intensively studied polycyclic aromatic hydrocarbons (PAHs),^[2] inclusion of a paratropic core

In a large majority of these systems, the antiaromatic unit is “buried” within the larger structure and not contained on the periphery of the molecule because of the high propensity to undergo dimerization, a well-know reactivity pathway of paratropic compounds. Comparison of constitutional isomers biphenylene vs. naphthocyclobutadiene (**1**) illustrates this point clearly: whereas the former is stable to over 300 °C,^[7] the latter readily dimerizes in a linear fashion and the intermediate then ring-opens to give dinaphthocyclooctatetraene (**2**) under the elimination reaction conditions (Scheme 1).^[8] Benzocyclobutadiene (**3**) is even more reactive. This was first prepared by Cava in 1956, also by dehydrobromination at elevated temperature.^[9] Sondheimer discovered in 1969 a remarkable reaction cascade presumably involving three different C₈H₆ isomers, as shown in Scheme 2.^[10] Desilation of compound **4** with ethanolic NaOH proceeded rapidly at room temperature to furnish the parent Z,Z-3,5-octadiene-1,7-diyne (**5**), which then rearranged ($t_{1/2}$ ~10 min) to give a spectrum attributable to tetracycle **6**, the known angular dimerization product of **3**. The authors postulated that **5** underwent extremely fast electrocyclic closure to **7** then **3**, followed by dimerization/ring-opening to yield **6**. Conclusive evidence of the intermediacy of **3** was provided by isolation of its Diels-Alder adduct (60% yield) if the desilation reaction was performed in the presence of excess cyclopentadiene.^[10]

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Scheme 2. Formation and Dimerization of Benzocyclobutadiene

This is not to say all benzocyclobutadienes and naphthocyclobutadienes are unstable. Toda and coworkers in the 1970s prepared numerous stable, well-characterized derivatives of both types of structures provided there was sufficient steric protection (*t*-Bu and/or aryl groups) to inhibit dimerization.^[11] Interestingly, the initial precursor molecule in the Toda studies was also generated by the cyclization of a *Z,Z*-3,5-octadiene-1,7-diyne analogue to yield a substituted benzocyclobutadiene.^[12] More recently, Fukazawa, Yamaguchi, and co-workers have utilized a similar cyclization pathway to generate a number of substituted biphenylene derivatives; however, the 3,5-octadiene-1,7-diyne unit was part of a bigger π -conjugated circuit and the resultant cyclobutadiene motif was “buried” within the larger structure.^[13] Herein we report the synthesis and characterization of stable naphthocyclobutadienes (NCBs) **8–12** (Figure 1) via the facile cyclization of diethynylindeno[2,1-*a*]fluorene intermediates.

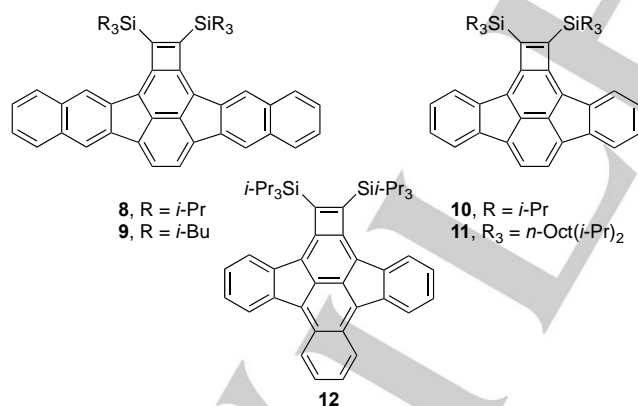
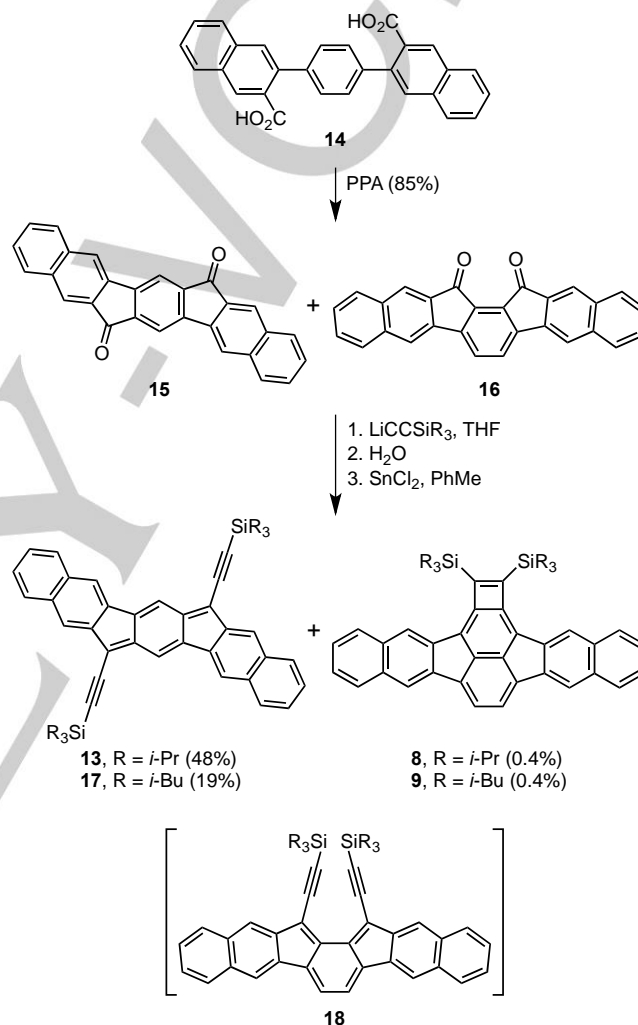


Figure 1. Naphthocyclobutadiene molecules **8–12** reported in this study.

Results and Discussion

Serendipitous Synthesis. Since 2010 the Haley group has investigated a class of PAAHs based on the fully conjugated indenofluorene (IF) scaffold.^[14] The molecules could also be thought of as ‘dibenzo-*s*-indacenes’, and as such, their overall $4n$ π -electron count makes these compounds formally

antiaromatic. Inclusion of the indacene subunit enhances the electron-accepting capabilities of the molecules,^[3b] leading to the examination of IFs and their congeners as possible *n*-type or ambipolar organic semiconductors (OSCs).^[6c,15] We recently published an extensive study on closely related dinaphthoindacenes (DNIs, e.g., **13**)^[6b] and were interested in exploring their OSC performance in OFETs, which required scaling up their preparation.



Scheme 3. Synthesis of DNIs **13** and **17** and Serendipitous Discovery of NCBs **8** and **9**

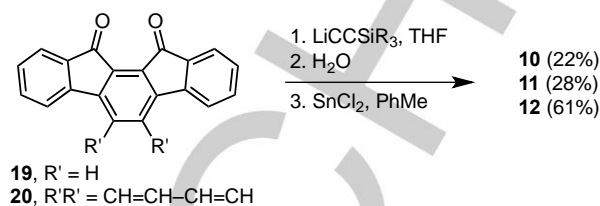
As shown in Scheme 3, Friedel-Crafts acylation of diacid **14** gave primarily highly insoluble diene **15**, which was carried forward through the three-step sequence to generate previously reported DNI **13**.^[6b] Interestingly, TLC analysis of the recrystallization mother liquor after removal of **13** indicated the presence of a second compound. Concentrating the filtrate and digesting the resultant solid with hexanes afforded an orange material. ¹H NMR analysis revealed that this compound possessed essentially the same splitting pattern and integral

values, with two of the singlets now down in the 8.2-8.3 ppm range. The ^{13}C NMR spectrum showed that the alkyne carbon signals in the 100-110 ppm range were absent and instead a new peak at ~ 177 ppm was present; however, the IR spectrum was missing a telltale carbonyl stretching mode. As a whole, the spectral data suggested that the material could be a structural isomer of **13**. Fortunately, orange crystals suitable for diffraction were obtained and the x-ray structure was secured (*vide infra*), confirming the formation of isomer **8**, albeit it in a low 0.4% yield. Repetition of the reaction sequence with (triisobutylsilyl)-acetylene furnished new DNI **17** along with a similar very low yield of NCB **9**, whose spectral characteristics were similar to those outlined above for **8**.

While puzzling initially, the cyclobutadiene ring in **8** and **9** must come from a formal [2 + 2] cyclization of the alkynes in a transient indeno[2,1-a]fluorene (i.e., **18**), which in turn means that diketone **16** must be formed in low yield during the Friedel-Crafts acylation step. The poor solubility of diones **15** and **16**, along with the smaller scale reactions we had previously performed, is what allowed NCBs **8** and **9** to go undetected. In spite of the bulky silyl groups, the enforced proximity of the diynes once the [2,1-a]IF geometry of **18** is generated in the SnCl_2 reduction step allows the cyclization to form **8** and **9** to occur rapidly.

Intentional Synthesis. To support our hypothesis that a diethynyl[2,1-a]IF intermediate was indeed what led to formation of the naphthocyclobutadienes, we set out to deliberately synthesize such molecules from the known [2,1-a]IF diones **19**^[16] and **20**^[17] (Scheme 4). Addition of lithium (triisopropylsilyl)acetylide followed by SnCl_2 -mediated reduction afforded NCBs **10** and **12** in moderate to good yield. Switching to (n-octyldiisopropylsilyl)acetylide ultimately furnished NCB **11**, whereas use of (trimethylsilyl)acetylide or (triethylsilyl)acetylide

afforded a fully desilated diol intermediate. Unfortunately, attempts to convert the diethynyldiol into the purely hydrocarbon NCB gave only intractable materials.



Scheme 4. Intentional Synthesis of NCBs **10–12**

Cyclization Computations. To help understand this facile cyclization, we performed calculations on a simplified analogue of **18** ($\text{R} = \text{Me}$, **SM**) as well as on the parent hydrocarbon **5**. Computations at the B3LYP/6-31+G(d,p) level of theory (Figure 2) show a low free energy barrier ($13.0 \text{ kcal mol}^{-1}$) for cyclization to the cyclic bisallene **I1** that has a modestly twisted structure. This cyclization is best characterized as an 8π -electron conrotatory process. The second ring closure might be described as either 6π -electron (disrotatory) or 4π -electron (conrotatory), both of which are symmetry allowed. This proceeds to **¹P**, with a second predicted barrier of $16.8 \text{ kcal mol}^{-1}$. All stationary points along this path were found to be stable relative to becoming open shell. Attempts to locate a stepwise diradical mechanism for this cyclization failed, with optimizations leading to closed shell stationary points. The calculated triplet state of the NCB product (**³P**) is ca. $26.2 \text{ kcal mol}^{-1}$ higher than that of the singlet state (**¹P**).

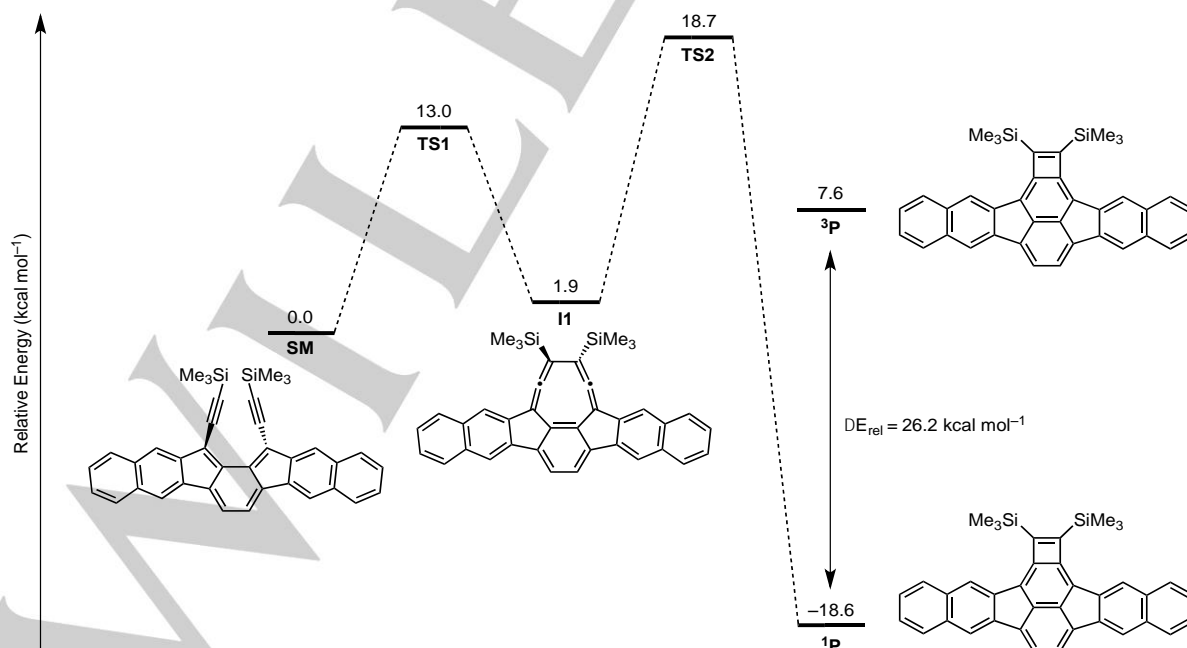


Figure 2. Calculated (B3LYP/6-31+G(d,p)) free energy surface for the electrocyclization of **18** ($\text{R} = \text{Me}$).

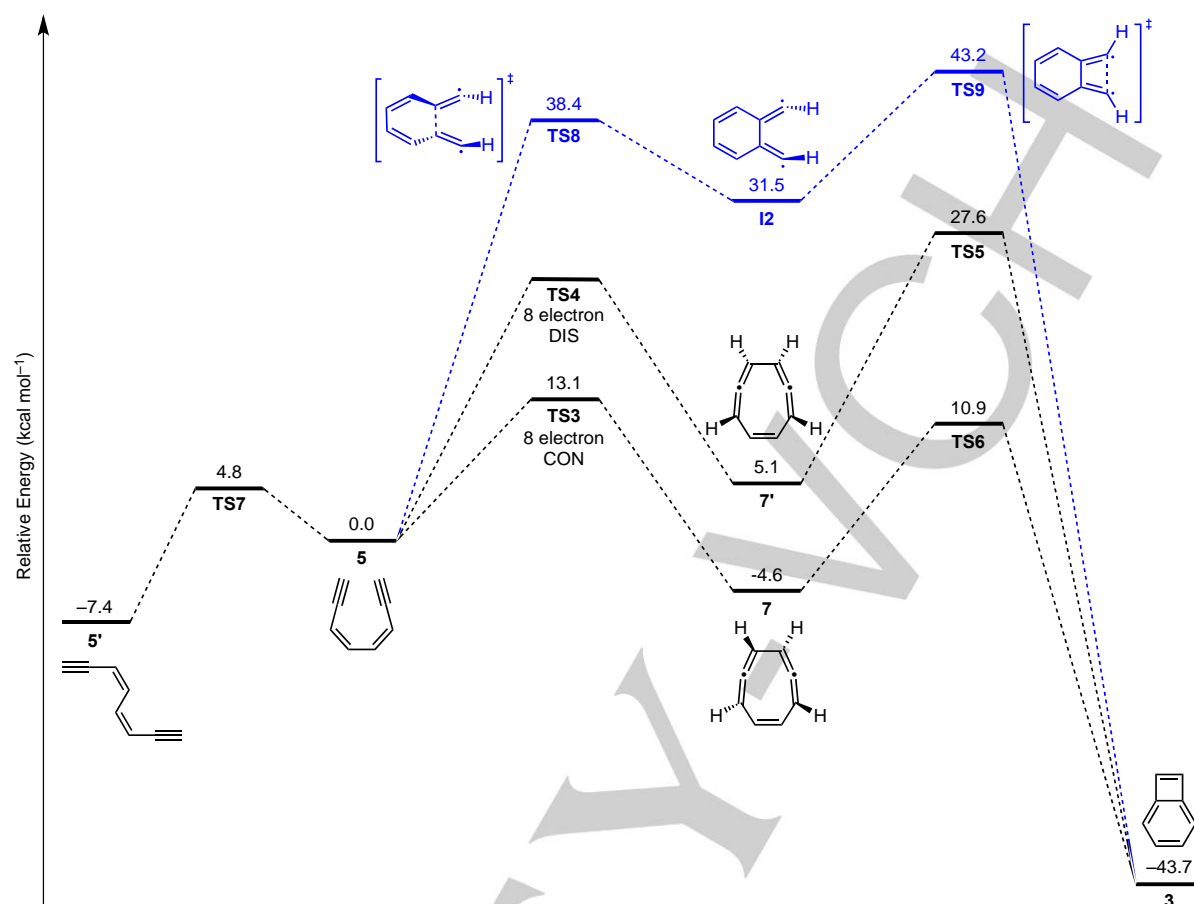


Figure 3. Calculated (B3LYP/6-31+G(d,p)) free energy surface for the electrocyclicization of **5** to **3**. The calculated diradical pathway (UB3LYP/6-31+G(d,p)) is shown in blue.

Z,Z-3,5-Octadiene-1,7-diyne (**5**) was used as a simplified model system to better understand diethynylindeno[2,1-*a*]fluorene electrocyclicization (Figure 3). As noted earlier, cyclization of **5** to generate benzocyclobutadiene (**3**) has been reported previously (Scheme 2).^[10] Because of increased flexibility, the initial cyclization can yield two diastereomers of the cyclic bisallene (**7** and **7'** in Figure 3), which can then cyclize further to furnish **3**. As above, the lowest energy path is expected to be an 8π -electron conrotatory process that leads to the C_2 symmetric *d*-allene **7**. Disrotatory closure to the *meso* cyclic allene **7'** should be symmetry forbidden. A stepwise diradical cyclization (in blue) is also possible.

DFT computations at the B3LYP/6-31+G(d,p) level of theory easily located the expected conrotatory path via **TS3** but failed to locate the symmetry forbidden disrotatory transition state. In Figure 3, the *s-cis* conformer of **5** was arbitrarily assigned as the reference point, $E_{\text{rel}} = 0.0$ kcal mol⁻¹. The reactive *s-cis* conformer (**5**) has a 4.8 kcal mol⁻¹ isomerization barrier (**TS7**) to the *s-trans* conformer (**5'**) and a barrier of 13.1 kcal mol⁻¹ (**TS3**) for the 8π conrotatory electrocyclicization to intermediate bisallene **7**. Similar to **I1** in Figure 2, **7** can undergo either 6π disrotatory or 4π conrotatory cyclization (**TS6**, 15.5 kcal mol⁻¹ from **7**) to afford the product **3**. As expected, the 8π disrotatory transition

state (**TS4**) could not be located (energy shown is only an estimate) but it was found that **7'** can undergo cyclization through **TS5** to the product but with a considerably higher barrier (27.6 kcal mol⁻¹). In this case, a stepwise diradical mechanism could be located (Figure 3, blue) using UBLYP/6-31+G(d,p) theory. The calculated barriers for the diradical mechanism are significantly higher, where **5** proceeds through **TS8**, **I2**, and **TS9** to the closed shell product with relative energies of 38.4, 31.5 and 43.2 kcal mol⁻¹, respectively. Based on the relative energetics, the expected cyclization of **5** to **3** through **TS3** and **TS6** via bisallene **7** is indeed the favored reaction pathway, thus corroborating Sondheimer's proposed reaction cascade in Scheme 2.^[10]

NICS-XY Scan Calculations. To examine the strength of the aromaticity/antiaromaticity within the polycyclic skeleton, we performed nucleus independent chemical shift (NICS) computations on the model structures shown in Figure 4 using the NICS-XY scan methods that account only for π -electron contributions.^[18] Parent versions of each compound without the silyl groups on the four-membered ring were used to simplify comparisons as well as make the most efficient use of computational resources; prior results have shown that inclusion of these groups in the computed structures has minimal effect

on the outcome of the NICS-XY scans.^[6b,c,15b] The resultant plots are shown in Figure 5 and the NICS_{πZZ} values for each ring are summarized in Table 1.

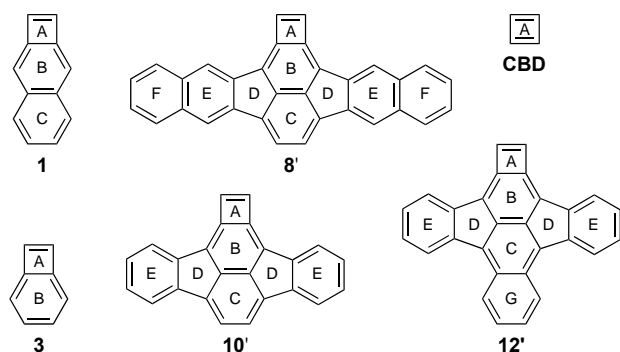


Figure 4. Structures for comparison in the NICS-XY scan computations; lettering corresponds to ring assignments in Figure 5 and Table 1.

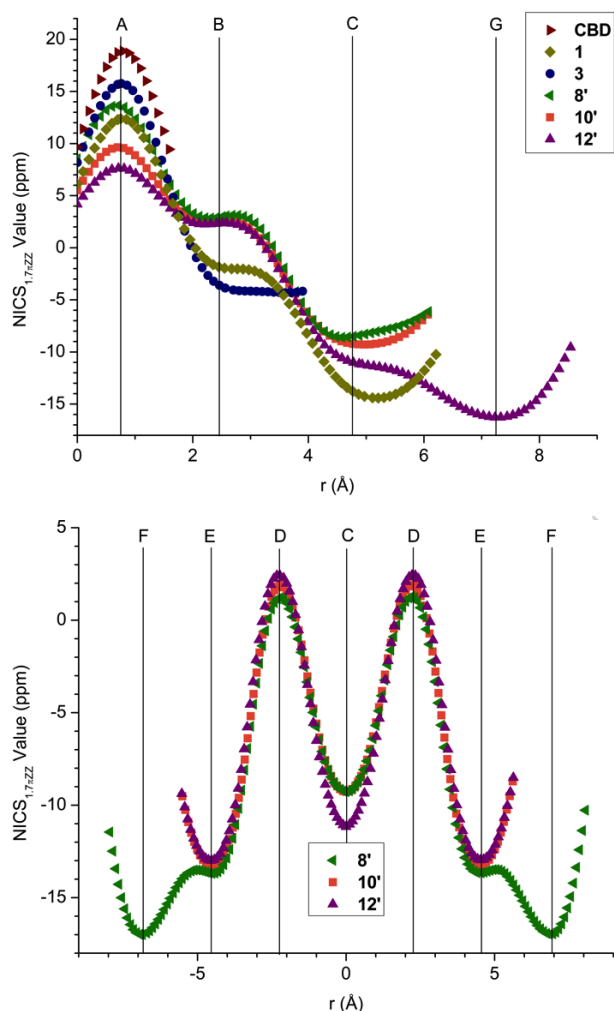


Figure 5. NICS-XY scans of (top) cyclobutadienes **1**, **3**, **8'**, **10'** and **12'** along the axis of four-membered ring fusion, and of (bottom) **8'**, **10'** and **12'** along the axis of the indenofluorene motif.

Table 1. Summary of NICS_{1,7πZZ} Values

Cmpd	Ring ^[a]					
	A	B	C	D	E	F/G
CBD	19					
1	12	-2	-14			
3	16	-4				
8'	14	3	-9	1	-14	-17
10'	10	2	-9	2	-13	
12'	8	2	-11	2	-13	-16

[a] Ring assignments shown in Figure 4.

As shown in Figure 5a, the NICS-XY scans reveal that cyclobutadiene (**CBD**) is strongly paratropic at 19 ppm and that each additional benzo-fusion along the axis of four-membered ring fusion reduces the paratropicity of ring A by 3–4 ppm, dropping to 8 ppm in **12'**. Interestingly, while ring B is slightly diatropic (–2 to –4 ppm) in **1** and **3**, it converts to slightly paratropic (2–3 ppm) upon introduction of rings D/E/F in **8'**, **10'**, and **12'**. The values of ring C are typical of a benzene (–9 to –11 ppm) fused to a ring that is weakly paratropic (**8'**, **10'**, **12'**) or of a benzene (–14 ppm) fused to a ring that is weakly diatropic (**1**); this latter argument also applies to ring G (–16 ppm) in **12'** and is analogous to the NICS-XY scan findings in the dinaphthoindacene (DNI) studies.^[6b] Figure 5b shows that rings C/D/E along the indenofluorene axis exhibit little variation between **8'**, **10'** and **12'** (only 1–2 ppm difference), with the outer naphthalene ring (ring F) more diatropic (–17 ppm) than ring E, again in agreement with the DNI results. While it is possible to envision an antiaromatic pyracylene resonance contributor within rings B/C/D as recently reported by Murata et al.,^[20] the very low NICS values in ring D (1–2 ppm) suggest such a contribution to be minimal.

X-ray Analysis. Single crystals of **8–10** suitable for X-ray diffraction were obtained via slow recrystallization from toluene; crystals of **12** were grown from CH₂Cl₂ and CH₃CN.^[20] The resultant molecular structures (Figures 6a and S2) show that the compounds possess distinct bond length alternation in the antiaromatic 8π-electron benzocyclobutadiene unit (Table 2), with bonds a (1.384–1.404 Å), d (1.360–1.374 Å) and f (1.364–1.378 Å) more double-bond like and bonds b (1.504–1.524 Å) and e (1.437–1.450 Å) much more single-bond like. The remaining variations of bond lengths (ca. 0.015–0.025 Å) in between the structures can be attributed to differences that typically arise from benzo- vs. naphtho-fusion.^[6b,21] The π-frameworks of **8–10** and **12** are essentially flat, with the central heptacyclic core common to all four compounds planar to within 0.035–0.049 Å. Nonetheless, the close proximity of the bulky triisopropylsilyl groups forces them to deviate from planarity, with Si–C–C–Si torsion angles ranging from 8.3° (**8**) to 14.0° (**10**), and as large as 22.4° (**12**); this same angle is a more modest 4.2° for the less bulky triisobutylsilyl derivative **9**.

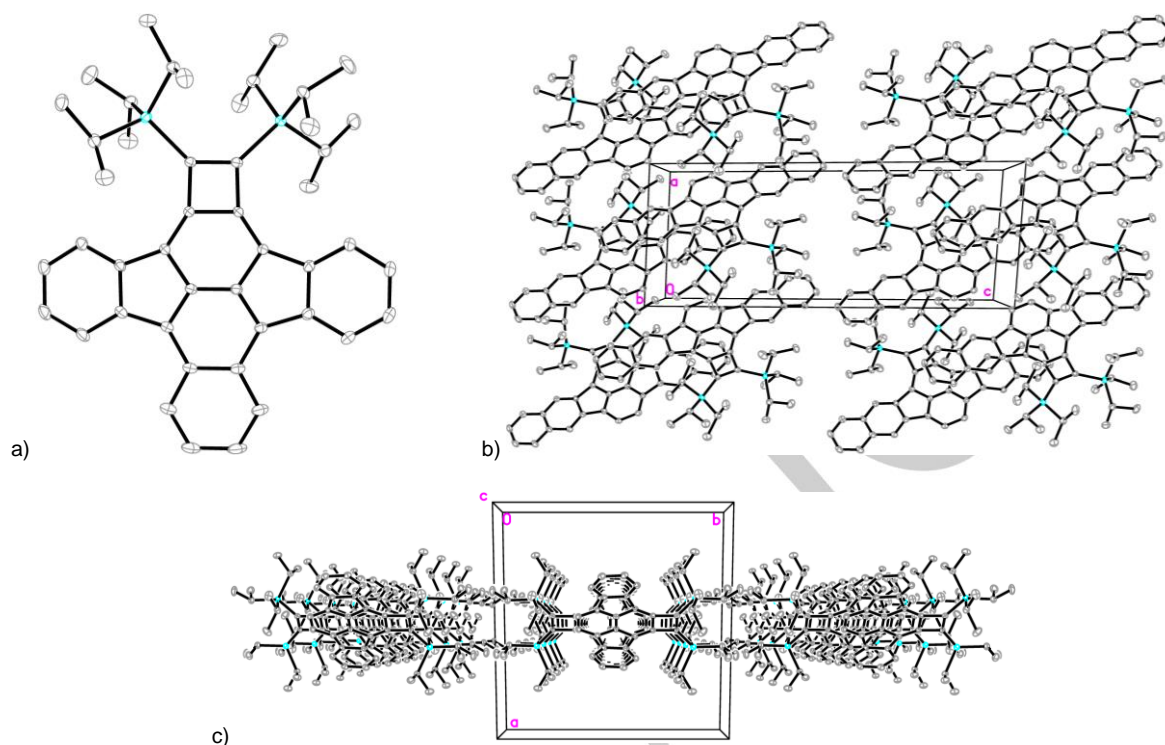


Figure 6. (a) Molecular structure of **12** with hydrogens omitted for clarity; ellipsoids drawn at the 30% probability level. (b) Solid-state packing of **8** showing that the molecule stacks as isolated dimeric pairs. (c) Solid-state packing of **10** showing that the molecule packs as 1D stacks.

Table 2. Select Bond Lengths (Å) of NCBs **8–10** and **12**

The chemical structure of the NCBs is shown with labels a through i and a' through i' indicating specific bond lengths. The structure features a central core with four phenyl rings and two silyl groups (R₃Si and SiR₃).

bond	8	9	10	12
a	1.384(4)	1.392(3)	1.389(3)	1.404(2)
b	1.516(4)	1.524(3)	1.519(2)	1.508(2)
b'	1.522(4)	1.521(3)	1.519(2)	1.504(2)
c	1.476(4)	1.474(3)	1.487(3)	1.489(2)
d	1.367(5)	1.367(3)	1.370(2)	1.364(2)
d'	1.367(4)	1.374(3)	1.370(2)	1.360(2)
e	1.439(4)	1.448(3)	1.443(2)	1.447(2)
e'	1.448(4)	1.437(4)	1.443(2)	1.450(2)
f	1.364(5)	1.371(3)	1.367(3)	1.378(2)
g	1.389(5)	1.394(4)	1.390(2)	1.383(2)

g'	1.395(4)	1.389(3)	1.390(2)	1.379(2)
h	1.396(5)	1.403(4)	1.395(2)	1.427(2)
h'	1.400(5)	1.395(4)	1.395(2)	1.432(2)
i	1.415(5)	1.413(4)	1.411(3)	1.450(2)
j	1.491(4)	1.484(3)	1.492(2)	1.478(2)
j'	1.494(4)	1.484(3)	1.492(2)	1.477(2)
k	1.453(5)	1.457(3)	1.431(2)	1.434(2)
k'	1.451(4)	1.452(4)	1.431(2)	1.435(2)
l	1.470(4)	1.472(4)	1.476(2)	1.480(2)
l'	1.469(4)	1.474(4)	1.476(2)	1.477(2)

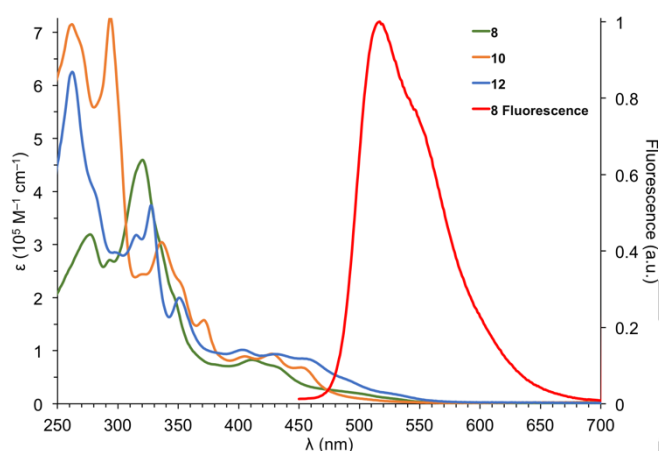
In the solid state molecules **8** and **9** pack as dimeric pairs; for NCB **8** (Figure 6b) the distances are 3.48 and 6.30 Å between the average planes of the central groups of the pairs and between the pairs, respectively, and these distances are roughly the same in **9** (Figure S3). On the other hand, NCBs **10** and **12** form a 1D structure in the crystal (Figures 6c and S4) with distances of 3.56 and 6.24 Å, respectively, between the average planes of the overlapping π -frameworks.

Electronic Absorption and Emission Data. The UV-Vis spectra of **8**, **10** and **12** (Figure 7) display strong absorbances in the higher energy range and multiple low-energy absorbances

Table 3. Summary of Optical and Electrochemical Data of NCBs **8**, **10** and **12**

Cmpd	electrochemical						optical		
	E_{red}^1 (V) ^a	E_{red}^2 (V) ^a	E_{ox}^1 (V) ^a	E_{ox}^2 (V) ^a	E_{LUMO} (eV)	E_{HOMO} (eV) ^b	E_{gap} (eV)	λ_{max} (nm)	E_{gap} (eV) ^b
8	-2.13	—	0.92	—	-2.67	-5.72	3.05	320, 411, 430 (sh), 506 (sh)	2.21
10	-2.07	—	0.85	1.56	-2.73	-5.65	2.92	335, 372, 404, 427, 452	2.26
12	-2.16	-2.55	0.47	1.37	-2.64	-5.27	2.63	315, 327, 351, 403, 431, 456, 525 (sh)	2.16

^a CV recorded using 1-5 mM of analyte in 0.1 M TBAPF₆/CH₂Cl₂ using a scan rate of 100 mV s⁻¹. The working electrode was a glassy carbon electrode (3 mm diameter) with a Pt-coil counter electrode and Ag wire pseudoreference. The Fc/Fc⁺ couple (0.46 V) as an internal standard. Potential values were re-referenced based on the redox potential of Fc/Fc⁺ being 4.8 eV vs. vacuum level; see reference [25]. ^b The optical HOMO-LUMO energy gap was determined as the intersection of the x-axis and a tangent line that passes through the inflection point of the lowest energy absorption.

**Figure 7.** Electronic absorption spectra of NCBs **8**, **10** and **12** and emission spectrum of **8**, all in CH₂Cl₂.

stretching out to 525-575 nm.^[22] Interestingly, inclusion of one (as in **12**) or two (as in **8**) additional benzenes as part of the basic π -skeleton of **10** seems to have only minimal effect on λ_{max} in the low-energy region; the emission spectra, however, tell a different story. Whereas **10–12** are non-emissive, NCBs **8** and **9** surprisingly are emissive, with a CH₂Cl₂ solution of **8** glowing bright yellow (λ_{em} 517 nm, Figure 7) with a quantum yield of 18%. Although most PAAHs are “dark” because of rapid non-radiative decay via a conical intersection,^[23] this clearly is not the case for **8** and **9**.^[24]

Electrochemistry. Cyclic voltammograms of **8**, **10** and **12** are shown in Figure S2 and the results compiled in Table 3. All three systems exhibit one or two irreversible oxidations and one reversible reduction, with NCB **12** showing a second quasireversible reduction. These data are similar to other cyclobutadienoid-containing systems, where the resultant HOMO-LUMO energy gaps are in the 2.6-3.0 eV range,^[4,13] with **12** showing the smallest energy gap in both the electrochemical (2.63 eV) and optical data (2.16 eV).

Conclusions

In summary, we have shown that the SnCl₂-mediated reduction of diethynylindeno[2,1-*a*]fluorenediols (generated serendipitously or intentionally) can be used to prepare naphthocyclobutadiene derivatives via a formal [2+2] cyclization within the transient diethynylindeno[2,1-*a*]fluorene intermediates. DFT calculations provide evidence that two successive, symmetry allowed electrocyclic reactions are what lead to the formation of the PAAH products. X-ray crystallography of four NCBs as well as NICS-XY scan calculations show that the paratropic portion of the molecules is located primarily in the benzocyclobutadiene fragment within the larger π -framework and that the remainder of the skeleton is typical of fused, fully aromatic benzenes and/or naphthalenes.

Acknowledgements

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Keywords: indenofluorene • cyclobutadiene • antiaromaticity • NICS calculations • electrocyclic reactions

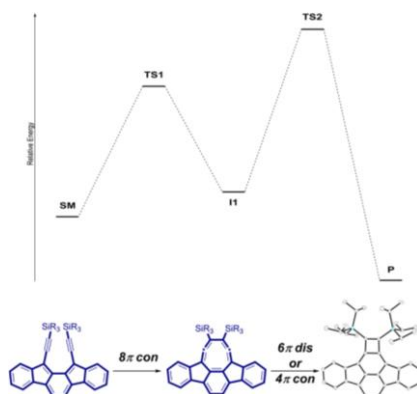
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Entry for the Table of Contents

FULL PAPER

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Page No. – Page No.

Serendipitous Rediscovery of the Facile Cyclization of Z,Z-3,5-Octadiene-1,7-diyne Derivatives to Afford Stable, Substituted Naphthocyclobutadienes





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