Structure of an Unsymmetrical Isomer from the Attempted Synthesis of 1,8-Dicyclooctatetraenylnaphthalene

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Attempted synthesis of 1,8-dicyclooctatetraenylnaphthalene (**1**) by the palladium(0)-catalyzed coupling of 1,8-dibromonaphthalene with cyclooctatetraenyltrimethylstannane afforded a single unsymmetrical isomer of **1** in 88% yield. Two-dimensional NMR methods and spectral synthesis were employed to assign the structure of the isomer (**2**). AM1 geometry-optimized structures of **2** and its isomers showed that the unexpected unsymmetrical structure of **2** results from the minimization of repulsive inter-ring H−H interactions. Compound **2** is postulated to arise via tandem [2 + 2] cycloaddition and $6\pi \rightarrow 4\pi + 2\sigma$ electrocyclization reactions of **1**.

Introduction

We have been interested in the "gated" transfer of charge (electrons and counterions) in bridged dicyclooctatetraene dianions.[1−4] Reversible charge transfer (CT) in these mixed-valence systems occurs on the NMR time scale as a consequence of a high-energy gating step, i.e., ring flattening and bond length equalization in the neutral cyclooctatetraenyl (COT) ring, that must precede CT.

As an extension of our previous studies of the 1,4- and 1,5-dicyclooctatetraenylnaphthalene dianions,[1,5] we sought to explore the possibility of through-space CT in a system in which the COT rings are constrained in a semirigid face-to-face arrangement with respect to each other and orthogonal to any adjacent π system. One of the compounds of interest to us was 1,8-dicyclooctatetraenylnaphthalene (**1**). Analogous systems with π-electron rings substituted at the 1 and 8 positions of naphthalene (the peri positions) have been extensively investigated.[6] It has been shown by X-ray diffraction that phenyl rings substituted at these positions are highly twisted with respect to the naphthalene ring and cofacially π-stacked with separations that are less than the sum of their van der Waals radii.[7] A similar conclusion has recently been reached for rigid π-stacked porphyrin−spacer−quinone systems,[6c] and this arrangement has been shown to lead to exceptionally fast electron transfer across several stacked π-rings.[8]

In this report, we describe an attempt to synthesize 1,8-dicyclooctatetraenylnaphthalene (**1**). We were especially interested in effect of the sterically compressed environment on the dynamic processes of **1** (ring rotation, ring inversion, and π-bond shift) and its dianion ($\mathbf{1}^{2-}$) (ring rotation, π-bond shift and CT). Furthermore, the study of CT in $\mathbf{1}^{2-}/2M^+$ as a function of M (M = Li, Na, K, Rb, Cs) is expected to provide insight into the role of the counterion in CT in dicyclooctatetraene dianions[3] since the exclusion of M^+ from the inter-ring region may be counterion-size dependent.

We attempted to synthesize **1** by the Stille cross-coupling reaction.[9] However, we were only able to isolate a single *unsymmetrical* isomer of **1** (**2**) in 88% yield (Scheme 1). A number of two-dimensional NMR techniques, as well as spectral synthesis, were employed in the identification of **2**, and semiempirical molecular orbital calculations were performed in order to model the stability of **2** relative to closely related isomers. As reported herein, it is likely that **1** was produced transiently but subsequently isomerized to **2.**

Results

Synthesis. Due to our prior success with the Stille reaction,[1] we attempted to effect the coupling of 1,8-diiodonaphthalene with cyclooctatetraenyltrimethylstannane[10] (**3**) in THF at room temperature (rt) using this methodology. Several reactions using $Pd_2(dba)_3$ as the catalyst and either triphenylphosphine or triphenylarsine[11] as the ligand failed, yielding only small amounts (<5%) of the monosubstituted coupling product (1-cyclooctatetraenyl-8-iodonaphthalene). Unchanged starting material constituted the majority of the mass balance.

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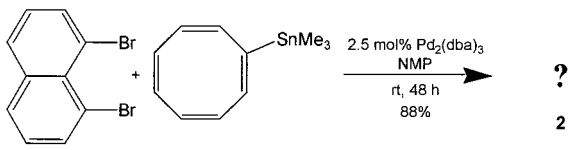
Scheme 1



Similar results were obtained using 1,8-dibromonaphthalene (**4**) as the reactant, *N*-methylpyrrolidinone (NMP) as the solvent, and either triphenylphosphine or triphenylarsine as the ligand. These attempts are summarized in the Experimental Section. However, in NMP with no added ligand, **3** and **4** were consumed at room temperature over 48 h to afford a colorless solid (**2**) in 88% yield (Scheme 1).

NMR Data. The ^{1}H and ^{13}C chemical shifts and couplings for **2** are given in Table 1. The numbering system employed corresponds to the position of each signal in the proton spectrum, starting with the most upfield signal (designated as H_1) and proceeding sequentially to the most downfield signal (H_{20}). NMR assignments are based on vicinal H−H correlations in two-dimensional correlation spectroscopy (COSY) at 300 and 600 MHz. Some of the proton signals exhibited second-order effects, and therefore spectral simulation using the program gNMR[12] was required in order to obtain all of the coupling constants. The initial parameters were determined from the 600 MHz ^{1}H NMR spectrum of **2** in THF-d_8 at room temperature. Excellent agreement was obtained between observed and calculated spectra at both 300 and 600 MHz (Figure 1).

Couplings for directly bonded ^{13}C and ^{1}H were detected by a heteronuclear shift correlation (HETCOR) experiment at 300 MHz and by a heteronuclear correlation through multiple quantum coherence (HMQC)[13] experiment at 600 MHz. A heteronuclear multiple bond correlation (HMBC)[14] experiment at 600 MHz was employed to detect $^3J_{CH}$ couplings in order to assign the quaternary carbons. Finally, nuclear Overhauser effect spectroscopy (NOESY) detected the inter-ring H−H interactions, which are listed in Table 2.

Discussion

Both the elemental analysis and mass spectrum of **2** are consistent with the structure of the target molecule, **1**. However, inspection of the ^{1}H NMR spectrum of **2** (Figure 2) clearly showed that the COT rings had been altered since the integration revealed an aromatic:olefinic:aliphatic ratio of 6:10:4 instead of the 6:14:0 expected for **1**. The naphthalene region appeared to be intact, although the symmetry of precursor **4** had been lost. Four proton signals that would be expected to appear in the olefinic region of **1** appeared in the aliphatic region. This is also seen in the ^{13}C NMR spectrum, which displays six signals in the aliphatic region corresponding to four protonated and two quaternary carbons.

Carbon Framework of 2. H−H coupling constants provided the data required to (a) establish the connectivity for the protonated carbon framework, (b) determine the ring sizes of several subunits, and (c) establish the stereochemistry at some of the ring junctions. The 11.4 Hz doublet for the olefinic H_{14} served as an excellent starting point to establish the connectivity of the carbon skeleton. Its multiplicity indicated that C_{14} is bonded to a quaternary carbon, while its coupling to H_{12} (J = 11.4 Hz) suggested that C_{12} and C_{14} are on the same double bond in an eight-membered ring.[15] The COSY data in Table 1 establish the following connectivity: quaternary C−C_{14}−C_{12}−C_{13}−C_9−C_{11}−C_6−C_2. The values of $J_{9,13}$ and $J_{6,11}$ (11.4 and 12.0 Hz, respectively) confirm the presence of a cyclooctatriene ring. This ring is related to the aliphatic CH groups with connectivity: C_2−C_1−C_3−C_4. The remaining olefinic CH groups bridge C_4 and C_3 as follows: C_4−C_8−C_{10}−C_7−C_5−C_3. The values of $J_{5,7}$ and $J_{8,10}$ (9−10 Hz) and $J_{7,10}$ (5.5 Hz) in the latter fragment are indicative of a cyclohexadiene ring.[15]

At this point, our working hypothesis was that the coupling had been successful, but that compound **1** had subsequently undergone a rearrangement of the carbon skeleton. The proximity of the COT rings to each other[7] and their known propensity to undergo *inter*molecular [2 + 2] cycloaddition[16] (although much more slowly at room temperature) led us to consider structures that would be derived from an analogous *intra*molecular reaction of the COT rings of **1**. Further, the presence of a 1,3-cyclohexadiene ring suggested that one of the cyclooctatriene rings resulting from a [2 + 2] cycloaddition had undergone a $6\pi \rightarrow 4\pi + 2\sigma$ electrocyclic ring closure.[17,18] Accordingly, we postulated the carbon skeleton shown in Figure 3, which is fully consistent with the connectivity given above, and next sought to assign the stereochemistry of this structure.

Stereochemistry of 2. Stereochemical information for organic compounds is commonly derived from vicinal H−H coupling constants. Unfortunately, literature values for vicinal coupling constants of cyclobutanes vary widely, with overlapping ranges for cis (J_{cis} = 4.6−11.5 Hz) and trans (J_{trans} = 2.0−10.7 Hz) orientations.[19] No explicit Karplus-type relationship has yet been formulated for cyclobutane, most likely because of the strong influence of factors such as ring strain and bond angles, which are difficult to assess. However, it is sometimes possible to assess the *relative* magnitude of vicinal couplings in cyclobutanes in terms of configuration.[20] Two of the cyclobutane $^3J_{HH}$ values in **2** are fairly unambiguous. The rather large value of $J_{3,4}$ (11.0 Hz) indicates a cis arrangement. Likewise, $J_{1,3}$ (4.2 Hz) indicates a trans stereochemistry. The coupling between H_1 and H_2 (J = 7.8 Hz) is less straightforward. However, NOEs of H_6 with H_3 and H_4 with H_{14} (Table 2) unambiguously establish the stereochemistry of H_1 and H_2 as cis.

Geometry optimization of **2** at the AM1 level of theory (Figure 4) is strongly supportive of the proposed structure. The nine closest distances between pairs of non-coupled hydrogens in **2** are listed in Table 2. Note that

(12) gNMR 4.0.1; Cherwell Scientific Publishing: The Magdalen Centre, Oxford Science Park, Oxford OX4 4GA, U.K.

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Table 1. NMR Assignments for 2

position	δ ^{1}H[a]	splitting	coupled to[b]	J_{HH} (Hz)[c]	δ ^{13}C[d]
1	2.97	dd	H_2, H_3	4.2 (3), 7.8 (2)	54.74
2	3.50	dddd	H_1, H_6, H_9, H_{11}	1.8 (9), 2.4 (6), 7.8 (1), 3.1 (11)	49.67
3	3.67	ddd	H_1, H_4, H_5	4.2 (1), 5.6 (5), 11.0 (4)	32.48
4	4.11	ddd	H_3, H_8, H_{10}	1.8 (10), 5.0 (8), 11.0 (3)	36.31
5	5.64	ddd	H_3, H_7, H_8	1.0 (8), 5.6 (3), 9.3 (7)	126.14
6	5.70	dd	H_2, H_{11}	2.4 (2), 12.0 (11)	131.59
7	5.79	dd	H_5, H_{10}	5.5 (10), 9.3 (5)	121.18
8	5.90	ddd	H_4, H_5, H_{10}	1.0 (5), 5.0 (4), 9.9 (10)	125.54
9	5.97	ddd	H_2, H_{11}, H_{13}	1.8 (2), 4.4 (11), 11.4 (13)	126.76
10	6.04	ddd	H_4, H_7, H_8	1.8 (4), 5.5 (7), 9.9 (8)	123.4[e]
11	6.09	ddd	H_2, H_6, H_9	3.1 (2), 4.4 (9), 12.0 (6)	128.65[f]
12	6.12	dd	H_{13}, H_{14}	5.1 (13), 11.4 (14)	128.35
13	6.16	dd	H_9, H_{12}	5.1 (12), 11.4 (9)	128.65[f]
14	6.45	d	H_{12}	11.4 (12)	134.46
15	7.42	dd	H_{18}, H_{20}	7.1 (18), 8.0 (20)	127.61[g]
16	7.43	dd	H_{17}, H_{19}	7.1 (17), 8.0 (19)	128.16[g]
17	7.61	dd	H_{16}, H_{19}	7.1 (16), 0.5 (19)}	123.4[e]
18	7.63	dd	H_{15}, H_{20}	7.1 (15), 0.5 (20)	123.4[e]
19	7.65	dd	H_{16}, H_{17}	8.0 (16), 0.5 (17)	118.15
20	7.89	dd	H_{15}, H_{18}	8.0 (15), 0.5 (18)	119.10
21			H_{12}, H_{14}		60.40
22			H_1, H_4		64.85
23			H_{17}, H_{18}		131.71
24					138.82
25			H_{20}		143.57
26			H_{19}		150.39

[a] In THF-d_8. [b] From COSY and HMBC spectra for ^{1}H and ^{13}C ($^3J_{CH}$), respectively. [c] The coupling partner(s) is (are) given in parentheses. [d] In $CDCl_3$; at 75 MHz. [e] Three signals overlapped. [f] Two signals overlapped. [g] The exact assignments for C_{15} and C_{16} are uncertain.

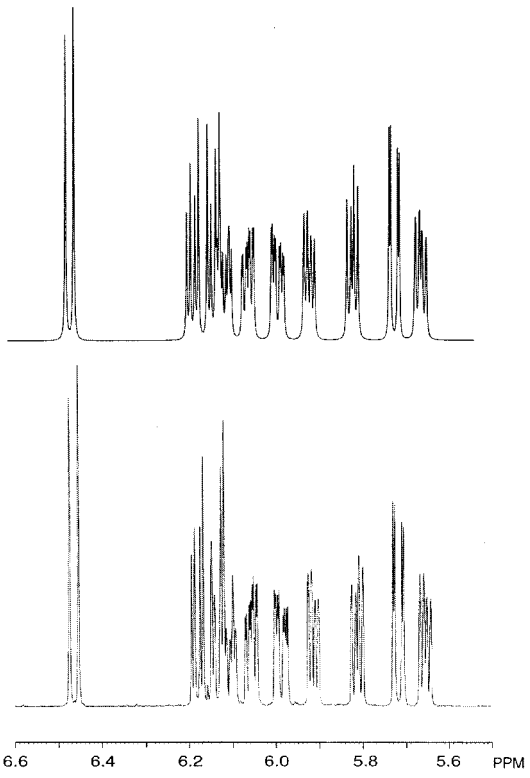

Figure 1. Calculated (top) and experimental (bottom) 600 MHz ^{1}H NMR spectra of the olefinic region of **2** in THF-d_8 at room temperature.

Table 2. Closest Nonbonded H−H Distances from AM1-Optimized Geometry of 2

H−H pairs	r_{H-H}[a]	NOE
H_4−H_{14}	2.026	yes
H_3−H_6	2.106	yes
H_{13}−H_{19}	2.447	yes
H_8−H_{20}	2.615	yes
H_1−H_5	2.903	no
H_{10}−H_{20}	3.159	no
H_2−H_{19}	3.304	no
H_9−H_{19}	3.462	no
H_1−H_{20}	3.763	no

[a] In angstroms.

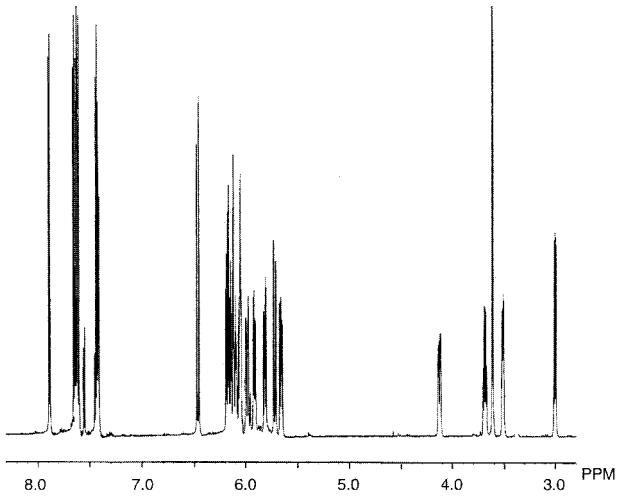

Figure 2. Complete 600 MHz ^{1}H NMR spectrum of **2** in THF-d_8 at room temperature.

the four closest nonbonded pairs (and *only* these pairs) displayed off-diagonal signals in the NOESY contour plots (Supporting Information).

Relative Stability of 2. Why does the reaction not stop at the target molecule **1** or the [2 + 2] cycloaddition isomer **5**? Alternatively, why does only one of the two cyclooctatriene rings undergo a $6\pi \rightarrow 4\pi + 2\sigma$ valence isomerization? The unsymmetrical structure of **2** is one of the most interesting and unexpected features of this reaction. These issues were addressed by examining the AM1 geometry-optimized structures of **2** and its isomers (Figures 4 and 5).

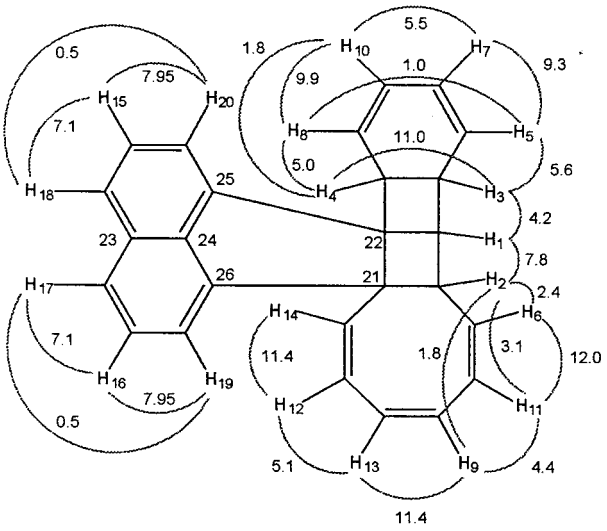

Figure 3. Values of J_{HH} (in Hz) in **2** optimized from spectral synthesis.

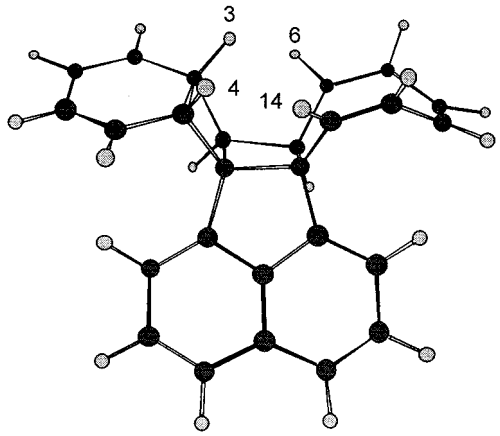

Figure 4. AM1 geometry-optimized structure of **2**.

At the AM1 level of theory, **2** is >2 kcal mol^{-1} more stable than **1** (Table 3). Other isomers that result from only [2 + 2] cycloaddition (**5**) or only one or two $6\pi \rightarrow 4\pi + 2\sigma$ valence isomerizations (**6** and **7**, respectively) are also higher in energy than **2**. The structure resulting from [2 + 2] cycloaddition and double valence isomerization (**8**) is also >2 kcal mol^{-1} less stable than **2**.

The $6\pi \rightarrow 4\pi + 2\sigma$ valence isomerization of *cis*-bicyclo-[6.2.0]deca-2,4,6-triene is thermodynamically unfavorable by 2.3 kcal mol^{-1} at 45 °C.[18] It was therefore somewhat surprising to discover that **2** is formed in preference to **5**. We propose that this is due primarily to the closest inter-ring H−H contact (r_{H4-H14}), which is 2.026 Å in the former but 1.902 Å, in the latter (Table 3). Since any contact less than about 2.4 Å is within the repulsive region,[21] it can be seen that *the H_4−H_{14} distance correlates well with the relative energies of these isomers.*

This also explains why **2** does not isomerize to **8** since, in addition to the factors working against the $6\pi \rightarrow 4\pi + 2\sigma$ valence isomerization of *cis*-bicyclo[6.2.0]deca-2,4,6-triene, the H_4−H_{14} and H_3−H_6 distances *both* decrease on going from **2** to **8** (Table 3). Simply put, the symmetrical structures (**5** and **8**) tend to maximize inter-ring H−H repulsions whereas these interactions are reduced somewhat by valence isomerization of only one of the cyclooctatrienyl rings in **5**.

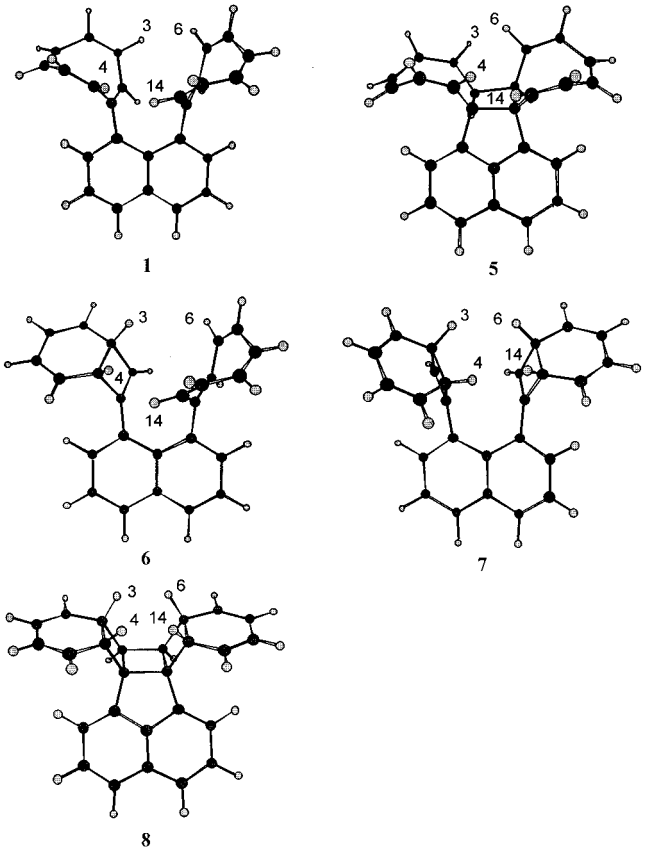

Figure 5. AM1 geometry-optimized structures of isomers of **2**.

Table 3. Smallest Inter-ring H−H Distances and Energies from AM1 Geometry-Optimized Structures of 2 and Its Isomers

compound	H_4−H_{14}[a]	H_3−H_6[a]	H_3−H_{14}[a]	H_4−H_6[a]	E[b,c]	E_{rel}[c,d]
1	2.063	2.241	4.548	5.248	187.89	2.33
2	2.026	2.106	4.505	2.397	185.56	0
5	1.902	2.345	4.298	4.552	188.30	2.74
6	2.176	3.000	3.685	4.700	205.72	20.16
7	2.081	2.412	3.552	3.031	218.26	32.70
8	1.991	1.933	2.413	2.412	187.82	2.26

[a] In angstroms. [b] Heat of formation. [c] In kcal mol^{-1}. [d] Relative energy.

Mechanism of Formation of 2. For the purpose of this discussion, we assume that **1** was initially formed as planned in the Stille coupling. However, we can only speculate on a pathway for the subsequent isomerization of **1** to **2.** This is because we have no information regarding a possible catalytic role for Pd, such as one initiated by complexation of the metal with the π bonds of **1**. Nevertheless, the structure of **2** is consistent with a mechanism (Scheme 2) in which steric crowding at the peri positions of naphthalene causes an intramolecular [2 + 2] cycloaddition of the cyclooctatetraenyl rings in **1** to afford **5**.[16] This reaction would most likely be nonconcerted and proceed via a biradical, as proposed for the [2 + 2] cyclodimerization of COT.[22]

Next, one of the cyclooctatriene rings could undergo a $6\pi \rightarrow 4\pi + 2\sigma$ electrocyclic ring closure analogous to those

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Scheme 2

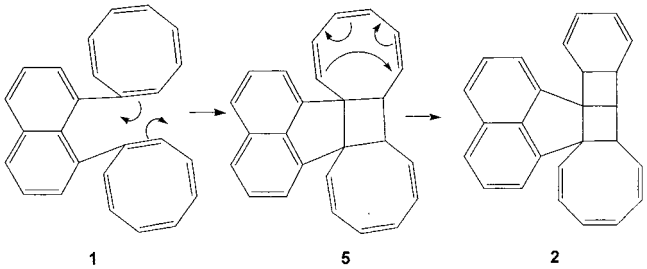

Table 4. Conditions for Palladium(0)-Catalyzed Coupling of Cyclooctatetraenyltrimethylstannane with 1,8-Dihalonaphthalene[a]

halide	ligand, Pd:L	solvent	% yield of monoadduct[b]	% yield of **2**
diiodo	$AsPh_3$, 1:4	THF	2	-
diiodo[c]	PPh_3, 1:2	THF	2	-
dibromo	$AsPh_3$, 1:4	NMP	4	-
dibromo	PPh_3, 1:2	NMP	2	-
dibromo	none	NMP	18	44
dibromo[d]	none	NMP	3	88

[a] Five mol % Pd for 24 h at room temperature unless indicated otherwise. [b] 1-Cyclooctatetraenyl-8-halonaphthalene. [c] From rt to >40 °C. [d] 48 h reaction time.

previously observed in 1,3,5-cyclooctatriene[17] and *cis*-bicyclo[6.2.0]deca-2,4,6-triene.[18] This sequence of isomerizations then stops once the most stable isomer (**2**) has been formed (vide supra). Alternative mechanisms that involve one or two $6\pi \rightarrow 4\pi + 2\sigma$ electrocyclizations *prior to* [2 + 2] cycloaddition are unlikely since the biradical intermediates in the cycloaddition step would be less stable than that arising from **1**. The foregoing mechanism is proposed only to illustrate that a reasonable and precedented pathway exists for the conversion of **1** to **2**.

Experimental Section

General. $CDCl_3$ and THF-d_8 were obtained from Cambridge Isotope Laboratories and used as received in 1 mL ampules. NMP was used as received in Sure-seal bottles from Aldrich Chemical Co.. Hexane and methylene chloride were used as technical grade. Reactions were performed under prepurified nitrogen using oven-dried glassware. TLC was performed on silica gel 60 F_{254}, and preparative column chromatography was performed on 40 μM silica gel. Midwest Microlab, Inc., Indianapolis, IN, performed the elemental analysis.

Preparation of 2. To a stirred solution of 1,8-dibromonaphthalene (0.358 g, 1.25 mmol) and $Pd_2(dba)_3$ (0.057 g, 0.063 mmol) in 15 mL of anhydrous NMP at room temperature was added neat cyclooctatetraenyltrimethylstannane (1.339 g, 5.00 mmol). After 48 h, the reaction mixture was diluted with 50 mL of Et_2O, and 50 mL of 50% satd aq KF was added. The mixture was stirred for 15 min and filtered, and the organic layer was washed with 1 × 50 mL of 50% satd aq KF, 3 × 50 mL of H_2O and 1 × 50 mL of brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on 50 g of SG with 10% CH_2Cl_2/hexane, followed by trituration with acetone to afford 364 mg (88%) of a colorless solid, mp (dec) 141−142 °C; TLC (20% CH_2Cl_2/hexane): $R_f = 0.28$. IR (KBr): 3030, 3002, 2948, 2900, 2883, 1588, 1361, 790, 781 cm^{-1}; UV (cyclohexane): λ_{max} (ϵ) = 205 (24300) 230 (40100) 289 (8000) 299 (8600) 316 (6100) nm; ^1H NMR: see Table 1; ^{13}C NMR: see Table 1. Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.84; H, 6.13. All attempts to grow crystals of **2** suitable for X-ray analysis resulted in discoloration and decomposition. The conditions employed and the results obtained for other attempted syntheses of **2** are given in Table 4.

NMR Experiments. NMR spectra were recorded at ambient temperature on a GE GN300 or a Bruker DRX600B spectrometer. Chemical shifts were referenced to the solvent, $CDCl_3$ (δ $^{13}C = \delta$ 77.70) or THF-d_8 (δ $^1H = \delta$ 3.58). Standard GE and Bruker pulse programs were employed. The experimental details for the 2D NMR experiments are as follows.

COSY. (a) Spectrometer frequency (SF) = 300.10 MHz, spectral width (SW) = 11.6 ppm, pulse width (PW) = 23 μs (90°), acquisition time (AQ) = 0.15 s, relaxation delay (RD) = 0.5 s, number of scans (NS) = 128, number of data points (DP) (in F1) = 1K, DP (in F2) = 1K, digital resolution (DR) = 6.6 Hz/point. (b) SF = 600.33 MHz, SW = 8.0 ppm, PW = 23 μs (90°), AQ = 0.11 s, RD = 1.2 s, NS = 64, DP (in F1) = 1K, DP (in F2) = 1K, DR = 9.4 Hz/point.

NOESY. SF = 600.33 MHz, SW = 8.0 ppm, PW = 7.5 μs, AQ = 3.4 s, RD = 10.0 s, NS = 64, DP (F1) = 32K, DP (F2) = 32K, DR (F2) = 0.29 Hz/point. COSY-type cross-peaks due to *J*-coupling were suppressed as much as possible by including a random 10% variation in τ during the experiment.

HETCOR. SF1 = 75.47 MHz, SF2 = 300.10 MHz, SW (F1) = 40 ppm, SW (F2) = 7.0 ppm, PW = 23.0 μs, NS = 128, DP (F1) = 2K, DP (F2) = 2K, AQ = 0.33 s, DR (F1) = 6.04 Hz/point, DR (F2) = 2.1 Hz/point.

HMQC.[13] SF1 = 150.1 MHz, SF2 = 600.33 MHz, SW (F1) = 200.0 ppm, SW (F2) = 7.0 ppm, PW (^{13}C) = 17.0 μs (90°), PW (^1H) = 23.0 μs (90°), DP (F1) = 1K, DP (F2) = 1K, DR (F1) = 50.0 Hz/point, DR (F2) = 8.4 Hz/point, AQ = 0.12 s, RD = 0.60 s, NS = 128.

HMBC.[14] These spectra, which correlate ^1H with ^{13}C signals via long-range couplings, were obtained by the inverse technique and processed in the magnitude mode. The evolution period for the long-range couplings [0.5/^nJ(CH)] was set at 60 ms, equivalent to ^nJ(CH) = 11 Hz. Couplings involving directly bonded atoms were suppressed as far as possible by a low-pass *J*-filter with a delay of 3.5 ms, corresponding to a *J* value of 145 Hz. SF1 = 150.1 MHz, SF2 = 600.33 MHz, SW (F1) = 200.0 ppm, SW (F2) = 7.0 ppm, PW (^{13}C) = 17.0 μs (90°), PW (^1H) = 23.0 μs (90°), DP (F1) = 1K, DP (F2) = 1K, DR (F1) = 60.0 Hz/point, DR (F2) = 8.33 Hz/point, AQ = 0.12 s, RD = 0.60 s, NS = 128.

Calculational Methods. ^1H NMR spectra of **2** were synthesized with the gNMR[12] software on a Macintosh computer. The olefinic and aliphatic resonances (a total of 14 spins) were calculated as a single spin system, while the six aromatic signals were calculated as a separate spin system. Error analysis was based on a least-squares fit of a final iterative simulation of the experimental spectrum. The maximum errors for the chemical shifts and coupling constants of the olefinic and aliphatic regions were 0.28 ppm and 0.08 Hz, respectively, while those for the naphthalene spin system were 0.26 ppm and 0.10 Hz, respectively.

Semiempirical molecular orbital optimizations of molecular geometries were performed using MOPAC in the CHEM3D Pro[23] series of programs at the AM1[24] level of theory. Fully optimized geometries were shown to have zero imaginary frequencies by analytical frequency analysis.

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Supporting Information Available: COSY, HETCOR, HMQC, HMBC, and NOESY contour plots of **2** in THF-d_8 obtained at 300 and 600 MHz (Figures S1−S10). This material is available free of charge via the Internet at http://pubs.acs.org.

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