

[5]Radialene

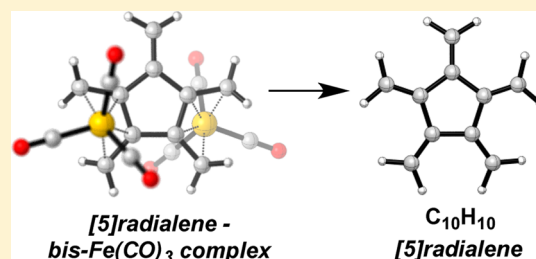
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Supporting Information

ABSTRACT: The $[n]$ radialenes are a unique family of fundamental $[n]$ -membered carbocyclic structures with radiating alkenes, which have attracted significant synthetic and theoretical attention. Whereas [3]-, [4]-, and [6]radialenes have been prepared and studied, all efforts to synthesize the five-membered ring compound have thus far met with failure. Here we describe the first synthesis of the fundamental hydrocarbon [5]radialene, $C_{10}H_{10}$. Our approach was a departure from previous radialene syntheses in that it utilized a low-temperature decomplexation of a stable organometallic compound, rather than high-temperature elimination or rearrangement. Our strategy was guided by analysis of previous radialene syntheses, which indicated rapid decomposition in oxygen, and ab initio calculations, which revealed an extraordinary susceptibility of [5]radialene to undergo Diels–Alder dimerization/polymerization. The origin of this susceptibility was traced to a small distortion energy associated with the formation of the transition structure geometry from the relaxed reactant monomers and to a narrow HOMO–LUMO gap.



INTRODUCTION

The radialenes (Figure 1) are one of the four fundamental classes of hydrocarbons containing only sp^2 -hybridized

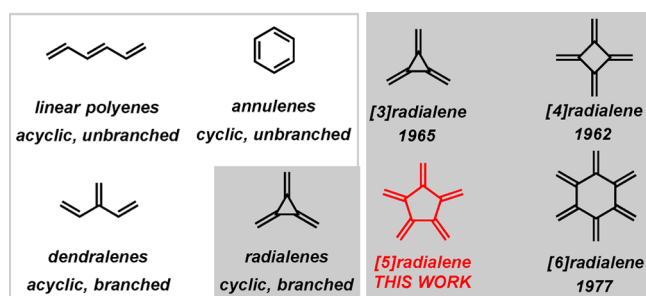


Figure 1. The $[n]$ radialenes. On the left, the four fundamental classes of conjugated oligo-alkenes and, shaded on the right, the first four members of the $[n]$ radialene family. The year indicates the date of the first reported synthesis.

carbons.¹ Radialenes possess a single ring of carbons, each of which is bonded to a methylene group outside of the ring, and have the general molecular formula $C_{2n}H_{2n}$, where $n > 2$ and where n also specifies the number of $C=C$ units. Structures of radialenes are star-like when drawn flat, with $C=C$ bonds radiating outward from the center of the carbocycle.

[3]Radialene,² [4]radialene,³ and [6]radialene⁴ have been previously prepared. These syntheses involved classical eliminations of Hofmann bases, hydrogen halides with bases, and dihalides with zerovalent metals, and high-temperature rearrangements.

Attempts to prepare [5]radialene along similar lines have not been successful.^{1,5} Relatively little is known of the physical and chemical properties of the radialenes, aside from reports of their susceptibility to polymerize when held neat (even at 210 K)⁵ and a propensity to rapidly decompose^{2a–e,3b,c,4a,c} and even spontaneously ignite in air.¹⁴ In contrast to the parent hydrocarbon, substituted [5]radialenes are well-known. The dehydrogenated C_{10} core of [5]radialene is the formal monomer of the sphero-hexameric buckminsterfullerene C_{60} , and other fully substituted [5]radialenes have been prepared.⁶






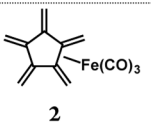


RESULTS AND DISCUSSION

Our significant experience with the related acyclic hydrocarbon family^{6e,7} (Figure 1) led us to devise a preparation of [5]radialene through cyclization of a suitably decorated [5]dendralene. From the very outset, however, accurate high-level G4(MP2) calculations⁸ warned us that [5]radialene should display extraordinarily high reactivity toward Diels–Alder (DA) dimerization or, perhaps, polymerization via a biradical intermediate (Table 1). The G4(MP2) activation enthalpy and free energy of activation for the concerted DA dimerization of [5]radialene are 23.6 and 82.5 kJ/mol, respectively, which are significantly lower than computed values for (a) cyclopentadiene, which is known to dimerize over the course of a couple of days at ambient temperature; (b) [3]dendralene, which has an experimental half-life of 10 h neat at 25 °C;⁹ and (c) 1,1-divinylallene, which has a half-life of 40 h

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Table 1. Gas-Phase G4(MP2) Activation Enthalpies (ΔH^\ddagger), Free Energies (ΔG^\ddagger), and Estimated Relative Rate Constants (k_{rel}) for DA Dimerization of Some Dienes

Diene	ΔH^\ddagger ^a	ΔG^\ddagger	k_{rel} ^b
 cyclopentadiene	49.6	108.5	7.2
 [3]dendralene ^c	54.0	113.4	1.0
 1,1-divinylallene ^c	29.5	91.8	6.1×10^3
 [4]radialene	59.2	106.7	15
 [5]radialene	14.3 (23.6) ^d	73.4 (82.5) ^d	1.0×10^7 (1) ^d
 2	(44.5) ^d	(111.4) ^d	$(8.6 \times 10^{-6})^d$
 [6]radialene	31.5	89.1	1.8×10^4
 3 1,2,3,4-tetramethylene cyclopentane	16.6	76.3	3.2×10^6

^akJ/mol, 298.15K. ^bFrom ΔG^\ddagger and TS theory. ^cCentral double bond is the dienophile. ^dM06-3X/6-31G(d)//B3LYP/6-31G(d) calculations.

as a 20 mM concentration solution in CDCl_3 at 25 °C.¹⁰ G4(MP2) calculations also predict 6 and 3 orders of magnitude increased reactivity for [5]radialene relative to [4]radialene and [6]radialene, respectively (Table 1).

The predicted rate constant for the DA dimerization of [5]radialene is 7 and 4 orders of magnitude greater than that for [3]dendralene and 1,1-divinylallene, respectively. The experimentally determined half-life of 1,1-divinylallene, together with our calculations and other considerations such as statistical factors (which take into account the numbers of equivalent dienophile double bonds, diene units and orientational regioselectivities), leads us to predict a half-life of <5 s for a 20 mM solution of [5]radialene at 25 °C. From these prognostications, it is no surprise that previous synthetic efforts involving elimination processes have been in vain. It would appear that a successful synthesis of [5]radialene should first generate the species as a stabilized organometallic complex. Given the well-established stabilizing effect of the $\text{Fe}(\text{CO})_3$

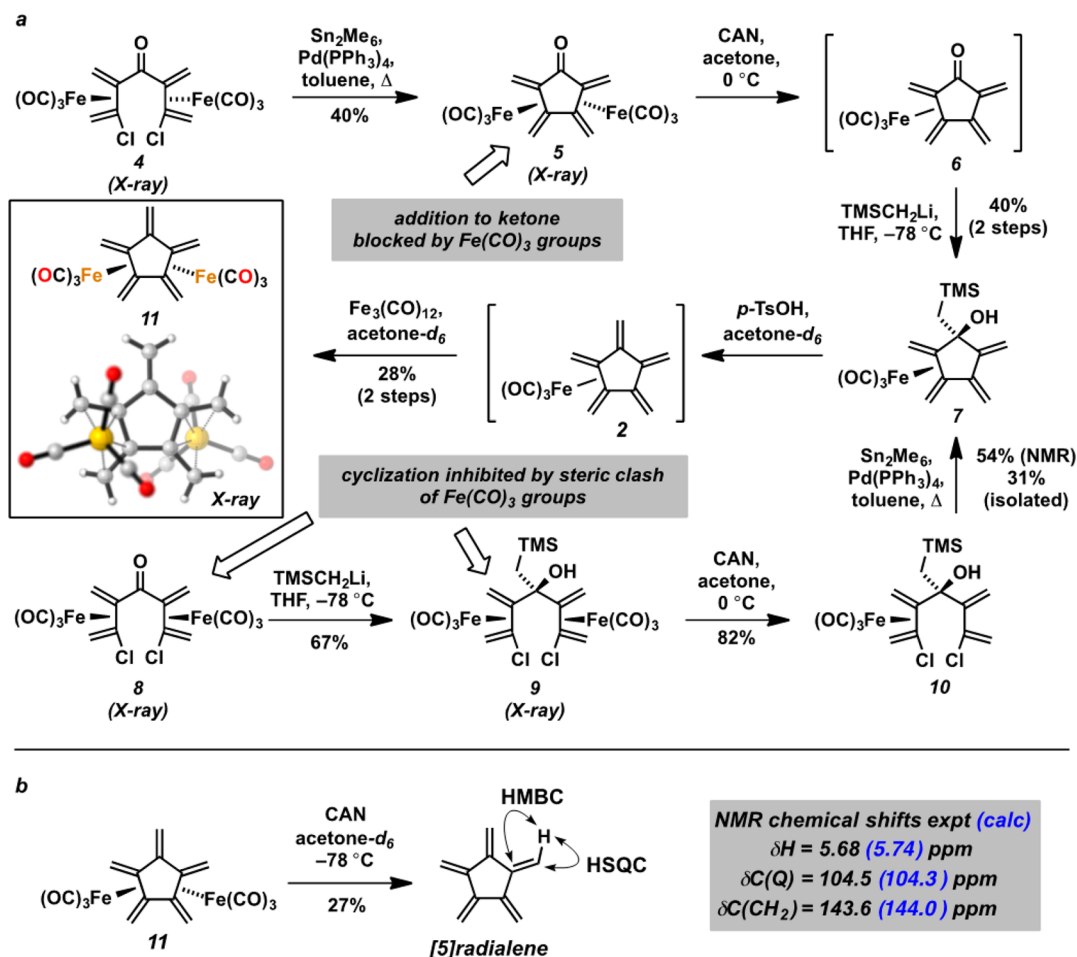
group upon otherwise unstable 1,3-butadiene-containing organic species¹¹ and, more specifically, our successful synthesis of a variety of iron tricarbonyl complexes of [n]dendralenes,¹² $\text{Fe}(\text{CO})_3$ complexes of [5]radialene are attractive synthetic targets. Indeed, we predict the mono- $\text{Fe}(\text{CO})_3$ complex of [5]radialene **2** to be more than 5 orders of magnitude less reactive toward dimerization or polymerization than [5]radialene (Table 1) and the bis- $\text{Fe}(\text{CO})_3$ complex of [5]radialene, lacking a free 1,3-butadiene moiety, would be (presumably) indefinitely stable.

The successful synthesis of a bis- $\text{Fe}(\text{CO})_3$ complex of [5]radialene **11** is depicted in Scheme 1a. We were attracted to the bis- $\text{Fe}(\text{CO})_3$ complex of 2,6-dichloro-3-oxa-[5]dendralene (*anti*-**4** and *syn*-**8**) as a starting point for this synthesis endeavor, due to both its close structural similarity to the requisite precursor for cyclization, and its one step synthesis from 2,3-dichloro-1,3-butadiene.¹³ The reported low yielding protocol was reproducible in our hands, and several 1 g batches of the ketone were prepared. (We obtained a 1:1 mixture of *syn* and *anti* diastereomeric forms **4** and **8**, which was readily separated by flash chromatography. See the Supporting Information (SI) for details.) From here, in principle, only two steps were needed to reach the bis- $\text{Fe}(\text{CO})_3$ complex of [5]radialene, specifically a dechlorinative C–C bond-forming cyclization and a ketone methylenation. In practice, difficulties stemming from the steric burden of the two $\text{Fe}(\text{CO})_3$ groups thwarted all efforts to secure a direct approach.

Ultimately, both diastereomeric forms of the 2,6-dichloro-oxa-[5]dendralene, *anti*-diastereomer **4** and *syn*-diastereomer **8**, were taken through related but nonidentical three step sequences, which were united at cyclized Petersen¹⁴ adduct mono- $\text{Fe}(\text{CO})_3$ complex **7** (Scheme 1a). The *anti*-isomer **4** underwent Stille–Kelly coupling¹⁵ but the resulting oxa-[5]radialene *anti*-bis- $\text{Fe}(\text{CO})_3$ complex **5**, owing to the substantial steric bulk of $\text{Fe}(\text{CO})_3$ groups on both faces of the molecule, could not be methylenated. Evidently, one of these $\text{Fe}(\text{CO})_3$ groups had to be removed. Controlled exposure to ceric ammonium nitrate¹⁶ delivered the sensitive mono- $\text{Fe}(\text{CO})_3$ complex **6**, which, on treatment with (trimethylsilyl)methylolithium, provided 1,2-adduct **7** (only the product of addition *anti*- to the $\text{Fe}(\text{CO})_3$ group was observed). In contrast, the *syn*-diastereomer of dichloroketone **8** could not be cyclized directly (to form the putative oxa-[5]radialene *syn*-bis- $\text{Fe}(\text{CO})_3$ complex). This compound underwent nucleophilic addition to form tertiary alcohol **9** cleanly (only one diastereomer was formed), but once again, all attempts to cyclize were met with failure. Following selective decomplexation, mono- $\text{Fe}(\text{CO})_3$ complex **10** cyclized to form the common key intermediate **7**, thereby setting the scene for the final phase of the synthesis.

Trimethylsilanol was eliminated from Petersen adduct **7** under mildly acidic conditions at ambient temperature to generate a solution of the mono- $\text{Fe}(\text{CO})_3$ complex of [5]radialene **2**. As predicted computationally, this 1,2,3-trimethylene cyclopentane derivative was prone to dimerization/polymerization but nevertheless could be converted directly into the *anti*-bis- $\text{Fe}(\text{CO})_3$ complex of [5]radialene **11**. A single crystal X-ray analysis of the bis- $\text{Fe}(\text{CO})_3$ complex of [5]radialene **11** revealed a broadly in-plane conformation, with the expected pyramidalization at the complexed methylene termini.

Decomplexation and generation of the free hydrocarbon was achieved in dilute (ca. 0.1 mM concentration) solution at –78 °C with cerium ammonium nitrate in acetone (Scheme 1b).

Scheme 1. Chemical synthesis of [5]radialene via bis-Fe(CO)₃ complex 11^a

^a(a) Approach to the bis-Fe(CO)₃ complex of [5]radialene 11 from diastereomeric Fe(CO)₃ complexes 4 and 11, uniting at Petersen adduct 7. (b) Low-temperature decomplexation of bis-Fe(CO)₃ complex 11 provides [5]radialene. Good agreement is found between observed and predicted chemical shifts.

Under these conditions, the hydrocarbon survives long enough for nuclear magnetic resonance (NMR) spectroscopic analysis to be performed. [5]Radialene displays one singlet resonance in the ¹H NMR spectrum at δ 5.68 ppm and two resonances in the ¹³C NMR spectrum at δ 104.5 and 143.6 ppm. Heteronuclear single quantum coherence spectroscopy (HSQC) and heteronuclear multiple-bond correlation spectroscopy (HMBC) cross peaks confirm this structural assignment.

As predicted computationally, [5]radialene exhibits a conspicuous tendency to decompose: a ca. 30 μ M concentration solution of the hydrocarbon generated through this decomplexation method exhibited a half-life of around 16 min at -20 °C, with no new signals discernible in the ¹H NMR spectrum. We presume that the main mode of decomposition is polymerization, perhaps promoted by the decomplexation reagent, although similar observations have been reported for [6]radialene in solutions apparently free of metal salts.^{4a}

The molecular geometry of [5]radialene (Figure 2) is interesting. Several wave function theory and DFT calculations all predict the *D*_{5h} geometry to be a second-order saddle-point, and thus it is not a stable minimum energy structure. This is in contrast to our calculations on [3]- and [4]radialenes, which are predicted to have *D*_{3h} and *D*_{4h} global minimum energy

geometries, respectively. The distance between neighboring methylene carbon atoms in [3]radialene (3.74 Å) and [4]radialene (3.38 Å) lies well beyond the sum of their van der Waals radii, whereas that in *D*_{5h} [5]radialene (3.06 Å) is borderline and appears to destabilize this structure, but barely so.

The minimum energy structure of [5]radialene is calculated to possess *C*₂ symmetry, but where the distance between adjacent methylene carbon atoms has increased by only 0.01 Å, compared to that in the *D*_{5h} structure. The five-membered ring of the *C*₂ structure is fairly flat, with the five dihedral angles between the vicinal ring bonds ranging between 3° and 10° (average value = 6°). The dihedral angles between pairs of contiguous C=C bonds lie between 4° and 14°. The C=C bond lengths in the *C*₂ structure of [5]radialene are equal, to four significant figures, at 1.337 Å, and the C-C bond lengths lie within the narrow range 1.486–1.487 Å; these values are close to those calculated for the *D*_{5h} structure, which are 1.338 and 1.488 Å, respectively. The similarity between the *C*₂ and *D*_{5h} structures of [5]radialene is reflected in their nearly equal energies, which differ by only ca. 0.1 kJ/mol (G4(MP2)). (Although the electronic energy of the *C*₂ structure is lower than that of *D*_{5h}, inclusion of zero-point energy reverses the ordering by 0.3 kJ/mol. However, this is probably due to an

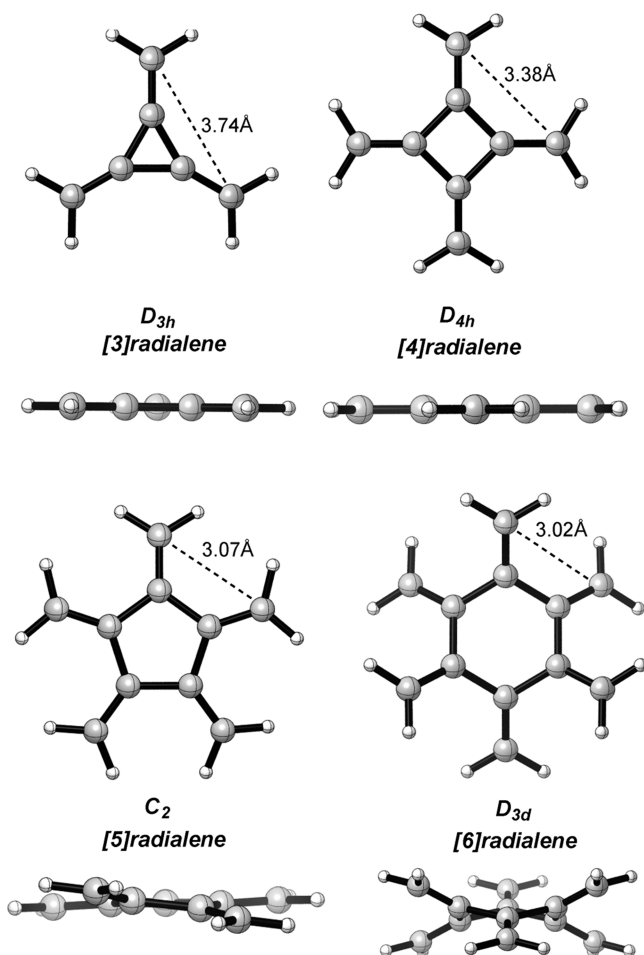


Figure 2. Top and side views of G4(MP2) minimum energy structures of the first four $[n]$ radialenes. D_{3h} [3]radialene, D_{4h} [4]radialene, C_2 [5]radialene, and D_{3d} [6]radialene are shown, with distances between adjacent methylene carbons in Å.

artifact arising from using harmonic frequencies to calculate zero-point energies; see the SI for more discussion.) From this analysis, we conclude that [5]radialene comprises a degenerate set of five C_2 structures that are rapidly interconverting on the NMR time scale, even at very low temperatures, and should give rise to NMR spectra consistent with average D_{5h} symmetry, which was observed experimentally. The ^1H and ^{13}C chemical shifts for C_2 -symmetric [5]radialene were calculated using the procedure of Tantillo et al.¹⁷ The calculated averaged shifts (experimental values in parentheses) are ^1H NMR δ 5.74 (5.68), ^{13}C NMR δ 104.3 (104.5), and 144.0 (143.6) ppm. The good agreement between the calculated and experimental chemical shifts reinforces our conviction that the observed NMR spectra are, in fact, those of [5]radialene.







Parentetically, the lowest energy structure of [6]radialene is predicted to be the D_{3d} chair conformation with a 43° dihedral angle between adjacent $\text{C}=\text{C}$ bonds. This conformation lies 3.2 kJ/mol below the D_2 boat form and a substantial 71.5 kJ/mol below the D_{6h} structure, which is a third-order saddle point. The large energy difference between the chair and D_{6h} forms may be the result of steric compression between neighboring pairs of methylene groups in the latter structure, where the distance between the carbon atoms is only 2.85 Å, compared to 3.02 Å in the chair conformation.

The high degree of reactivity, predicted and observed, for [5]radialene is under active investigation computationally, but our initial results are indicative of this origin. At this stage, we can say that the cause of the high reactivity of [5]radialene is not due to the molecule possessing antiaromatic character arising from the cyclic fully cross-conjugated array of double bonds in the radialene, for the following reasons. First, the radialene shows no sign of any ring current.¹⁸ The computed ^1H NMR chemical shift in [5]radialene (δ 5.74 ppm) has almost the same magnitude as that (δ 5.56 ppm and δ 5.64 ppm) calculated for the two pairs on protons associated with the two internal methylene groups of the (unknown) cyclic interrupted cross-conjugated tetramethylenecyclopentane molecule 3. In addition, the calculated nucleus-independent chemical shift, NICS(1),¹⁹ for the radialene (-2.5 ppm) is small and comparable to that for tetramethylenecyclopentane (-2.0 ppm), thereby signifying negligible ring current in the former molecule. Second, the computed rate constant for the dimerization of tetramethylenecyclopentane 3 is only three times smaller than that for [5]radialene (Table 1). Third, the B3LYP/6-31G(d) highest occupied molecular orbital–lowest occupied molecular orbital [HOMO–LUMO (H–L)] energy gap uniformly decreases by a constant ca. 0.5 eV per additional methylene group along the series n -methylene cyclopentanes: 5.2 eV ($n = 2$), 4.6 eV ($n = 3$), 4.2 eV ($n = 4$), and 3.8 eV for [5]radialene. Thus, there is no anomalous sudden narrowing of the H–L gap in [5]radialene, which would signify the presence of antiaromaticity in that molecule. This conclusion is also consistent with our finding that the H–L gap in the ring-expanded, C_{2v} -constrained, pentamethylenecyclohexane (3.6 eV) is nearly the same as that for [5]radialene.

From the perspective of frontier molecular orbital (FMO) theory, the markedly narrower H–L gap for [5]radialene (3.8 eV), compared to those for cyclopentadiene (5.5 eV), [3]dendralene (5.2 eV), and 1,1-divinylallene (4.6 eV), is consistent with the finding that the former is much more reactive than the latter three molecules. However, the FMO argument is too simplistic because, although the H–L gap for [4]radialene (3.9 eV) is the same as that for [5]radialene, the calculated ΔH^\ddagger for the dimerization of [5]radialene is 45 kJ/mol smaller than that for [4]radialene (Table 1). Resolution of this problem was achieved through the application of the distortion/interaction model.²⁰ In this model, the electronic energy of the transition state (TS), ΔE^\ddagger , is resolved into the sum of the distortion energy, $\Delta E_{\text{dist}}^\ddagger$ and the interaction energy, $\Delta E_{\text{int}}^\ddagger$, where $\Delta E_{\text{dist}}^\ddagger$ is the energy that is required to distort the reactants from their relaxed geometries into the geometries adopted by them in the TS. From the data in Table 2, it is clear that the enhanced dimerization reactivity of [5]radialene, compared to the other cross-conjugated systems listed in Table 2, is due primarily to the comparatively small magnitude of its distortion energy. Thus, even in the case of [6]radialene, for which the interaction energy, $\Delta E_{\text{int}}^\ddagger$ is -11 kJ/mol more stabilizing than that for [5]radialene, this energetic advantage is swamped by a much larger 32 kJ/mol distortion energy for [6]radialene, relative to [5]radialene.

Inspection of the DA dimerization transition structures (TSs) reveals the origin of the variation in $\Delta E_{\text{dist}}^\ddagger$ within these cross-conjugated molecules. The lowest energy TSs for these systems are highly asynchronous, each possessing an advanced, short forming bond of ca. 2 Å and a very long forming bond of 3.3–3.7 Å (represented schematically in Figure 3a). With the exception of [4]radialene, the TSs associated with the

Table 2. Distortion/Interaction Energy Analysis of the Dimerization Reactions of Polyenes^a

Polyene	$\Delta E^{\ddagger}_{\text{dist}}{}^a$	$\Delta E^{\ddagger}_{\text{int}}{}^a$	$\Delta E^{\ddagger}{}^a$
 [4]radialene	102.2	-22.5	79.7
 [5]radialene	63.3	-41.0	22.3
 [6]radialene	95.5	-52.1	43.3
 3 1,2,3,4-tetramethylene cyclopentane	64.7	-41.8	22.9
 [3]dendralene	92.4	-37.5	46.3
 1,1-divinylallene	91.4	-44.0	47.4

^aM06-2X/6-311+G(2df,p)//G4(MP2) energies in kJ/mol.

remaining systems possess C_2 symmetry and are bis-pericyclic, displaying $[4 + 2]/[2 + 4]$ dichotomy which is resolved at the bifurcation point into two enantiomeric product channels.²¹ In fact, the aforementioned longer-forming bond in these TSs is a member of a pair of equivalent very long prebonds, which give rise to either $[4 + 2]$ or $[2 + 4]$ adducts. The [4]radialene dimerization TS (Figure 3d) is asymmetric, with unequal longer-forming bonds of 3.72 and 4.20 Å. The essential structural feature that is shared by all these TSs (including that for [4]radialene dimerization) is that the reaction zone may be regarded as comprising a pair of pentadienyl radical-like moieties (represented schematically in Figure 3b), which enter into a stabilizing through-bond interaction via the shorter forming bond, as has been discussed in detail for the dimerization of [3]dendralene.²² Taking the TS for the dimerization of [3]dendralene as representative of the series of molecules studied here, the two pentadienyl moieties have essentially planar *W*-shaped conformations (Figure 3c), with the two dihedral angles between adjacent formal double bonds in each pentadienyl unit being $<3^\circ$. The methylene carbon atom of each unit associated with the short forming bond is markedly pyramidalized, as assessed by the 144° dihedral angle between the two $C=C-H$ planes of the central $C=CH_2$ group of the pentadienyl fragment (this angle is 180° for planar $C=CH_2$).

The two major contributors to the distortion energy are (a) the planarization of the carbon backbone of a cross-conjugated triene unit in each reactant molecule which becomes a *W*-

shaped pentadienyl component of the TS and (b) the pyramidalization of the central CH_2 group in this unit. Considering the dimerization of [5]radialene (Figure 3e), the planarization distortion energy is negligible, because of the near planarity of the reactant ring (Figure 3). Consequently, $\Delta E^{\ddagger}_{\text{dist}}$ value of 63 kJ/mol for this reaction is attributed to the pyramidalization process. As expected, $\Delta E^{\ddagger}_{\text{dist}}$ and $\Delta E^{\ddagger}_{\text{int}}$ for the dimerization of the nearly planar tetramethylenecyclopentane (Figure 3g) have essentially the same values as the respective quantities for the [5]radialene dimerization.

In contrast to [5]radialene and tetramethylenecyclopentane, [6]radialene (Figure 3f) has a nonplanar chair conformation with 43° dihedral angles between adjacent double bonds. Flattening of a contiguous triene unit in [6]radialene costs 18.5 kJ/mol and is therefore 37 kJ/mol for two [6]radialene molecules. Subtraction of this energy from the total $\Delta E^{\ddagger}_{\text{dist}}$ for the dimerization of [6]radialene (Table 2) gives a pyramidalization distortion energy of 58 kJ/mol, a value comparable to the total distortion energy for the dimerization of [5]radialene. Thus, the cause of the predicted lower dimerization/polymerization reactivity of [6]radialene, compared to [5]radialene, is the planarization distortion energy in the former reaction. Similarly, planarization distortion energy was found to be responsible for the lower reactivities of [3]dendralene and 1,1-divinylallene (Figure 3h), compared to [5]radialene, although a substantial proportion of this energy, 21 and 16 kJ/mol respectively, is required to convert the most stable *anti-gauche-gauche* conformation of these molecules into their reactive *gauche-gauche* forms.

The greater magnitude of $\Delta E^{\ddagger}_{\text{dist}}$ for the dimerization of [4]radialene, compared to that for [5]radialene, is due to an increase in the pyramidalization distortion energy in the [4]radialene reaction, not to planarization distortion energy owing to the planar nature of the former. Possibly on account of the splaying of the double bonds in [4]radialene, compared to [5]radialene (Figure 3), the longer forming bond in the [4]radialene TS (Figure 3d) blows out to 3.72 Å, about 0.33 Å longer than that in the [5]radialene TS (Figure 3e). To compensate for, what must be, the absence of stabilizing interactions in such a long forming “bond”, the short forming bond in the [4]radialene undergoes a significant 0.17 Å contraction, from 2.04 Å, in the [5]radialene TS, to 1.87 Å. This contraction is accompanied by increased pyramidalization of both carbon atoms of the short forming bond and, thus, to an increase in $\Delta E^{\ddagger}_{\text{dist}}$ for [4]radialene dimerization, compared to that for [5]radialene dimerization.

In the above discussion, we were equivocal concerning whether the radialenes dimerized by a concerted mechanism or via a biradical intermediate, which could lead to polymer formation. Our G4(MP2) calculations favor the former mechanism, but this preference may be an artifact arising from our use of the restricted formalism. Our equivocation stems from preliminary unrestricted B3LYP/6-31G(d) calculations on the [5]radialene dimerization reaction. The unrestricted bis-pericyclic TS is about 8 kJ/mol lower in free energy than the restricted TS. Following the former TS, using intrinsic reaction coordinate analysis, led to a C_2 -symmetric biradical intermediate which has a *gauche* arrangement of the radialene moieties about the newly formed bond (Figure 3i). This biradical intermediate may collapse, with an activation free energy of 27.5 kJ/mol, to give either one of the enantiomeric DA adducts, or it may act as a seed for polymer formation. More salient to the polymer production channel is the

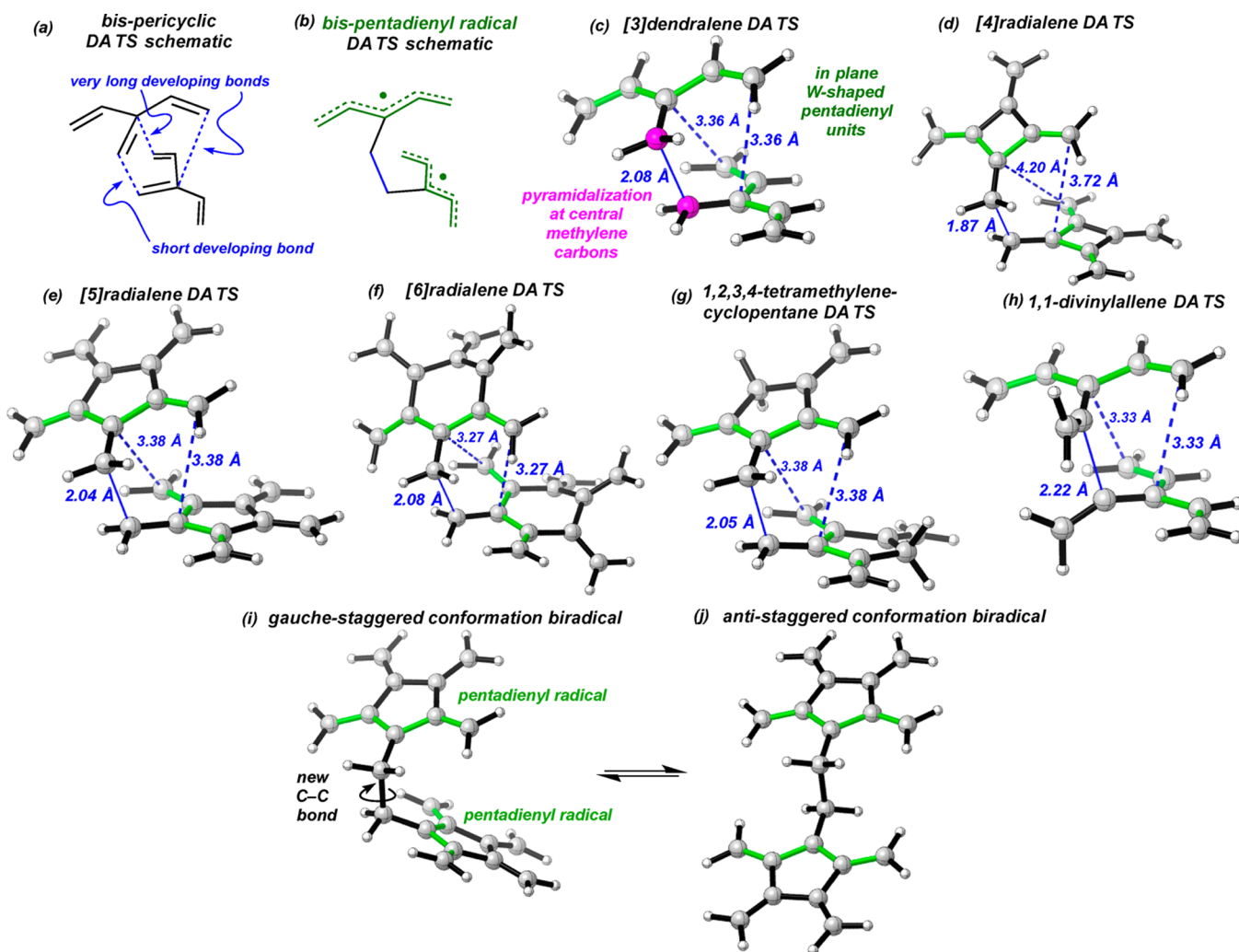


Figure 3. Schematic representations (a,b) and G4(MP2) computed TSs (c–h) of the DA dimerization of polyenes and UB3LYP/6-31G(d) optimized [5]radialene biradical dimers (i,j). Distances are in Å. *W*-shaped pentadienyl radical-like moieties are highlighted in green in the schematic (b), the DA TSs (c–h), as are the pentadienyl radical sections in the biradical species (i, j).

prediction that the activation free energy for the formation of the *anti* conformation of the biradical intermediate (Figure 3j) is favored over the bis-pericyclic (*gauche*) TS by 1.7 kJ/mol. The *anti* biradical is well disposed for initiating polymer production. This prediction of preferred biradical production is consistent with our inability to identify any dimeric adduct arising from the generation of free [5]radialene. A similar prediction was obtained for [4]radialene, with an even stronger energetic preference, of 7.6 kJ/mol, for *anti* addition over *gauche* addition. As for [4]radialene, the unrestricted *gauche* TS led to a *gauche* biradical intermediate, its conversion into the [4 + 2] adduct requiring an activation free energy (48.7 kJ/mol) nearly double that calculated for the *gauche* biradical intermediate formed from [5]radialene dimerization, which reflects the high degree of strain in the [4 + 2] adduct from [4]radialene. In contrast to the behavior of [4]radialene and [5]radialene, the restricted bis-pericyclic TS for the dimerization of [6]radialene is the most stable, lying 5.1 kJ/mol in free energy below the unrestricted TS for formation of the *anti* biradical. Thus, of the three radialenes studied, [6]radialene should offer the best prospect of obtaining a [4 + 2] adduct. A C_2 -symmetry-constrained path from the bis-pericyclic TS, however, led to a C_2 -symmetric unrestricted *gauche* biradical,

which may collapse to a [4 + 2] product with a 21.3 kJ/mol activation free energy. Given the bifurcated nature of bis-pericyclic potential energy surfaces,^{15d} it is unlikely, from a molecular dynamics perspective, that the *gauche* biradical intermediate would participate in radialene dimerization reactions. Nevertheless, the *gauche* biradical is predicted to lie on the Cope rearrangement path, which interconverts the two enantiomeric [4 + 2] adducts. Hence, Cope rearrangements in [4 + 2] adducts from radialene dimerizations are predicted to be nonconcerted, and we also find this to be the case for the Cope rearrangement of the known^{15e} [3]dendralene [4 + 2] dimer. Of course, these provisional results require validation using higher levels of theory.

SUMMARY

In summary, a remarkably reactive hydrocarbon, [5]radialene, has been synthesized for the first time. Computational studies predicted an anomalously high susceptibility of [5]radialene to DA dimerization and polymerization, and these findings prompted the implementation of a synthetic strategy distinct from all previous approaches toward radialenes. The successful approach involved the preparation of a stable $Fe(CO)_3$ complex of [5]radialene, the decomplexation of which led to the

generation of the highly reactive molecule in a controlled fashion. Our initial computational investigations lead us to conclude that the high degree of reactivity of [5]radialene is primarily structural, in that the near planarity of the molecule, together with the strain caused by the enforced *cis*-configured contiguous double bonds, minimizes the distortion energy for dimerization. In addition, the unusually narrow HOMO–LUMO energy gap of 3.8 eV (cf. 5.5 eV for cyclopentadiene) for [5]radialene is expected to further enhance the reactivity of this molecule. This new strategy for [5]radialene synthesis opens the door to this neglected family of hydrocarbons and should permit the first detailed study into their behavior. The reasons for such studies are manifold and include the need for a deeper understanding of fundamental structure and how it relates to properties. Specific applications will most likely involve the applications of radialenes in the rapid generation of structural complexity. Studies with the related *acyclic* cross-conjugated hydrocarbons recently culminated in the shortest total synthesis of important natural products.²³ It would not be surprising if the radialenes were to follow suit.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information is available for synthetic and computational work. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07445.

Crystallographic data (CIF)

Crystallographic data (CIF)

Crystallographic data (CIF)

Crystallographic data (CIF)

Crystallographic data (CIF)

¹H and ¹³C NMR spectra (PDF)

X-ray crystallographic data and computational studies (PDF)

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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