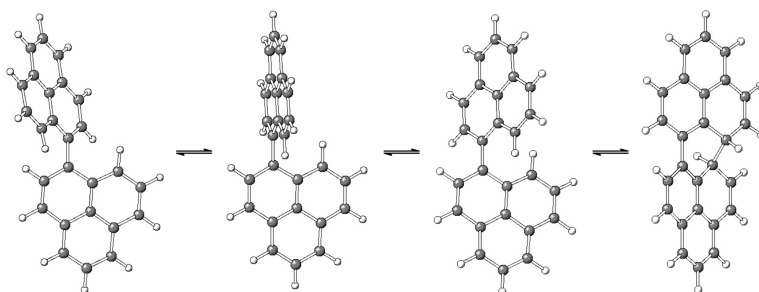


Biphenalenylidene: The Forgotten Bistricyclic Aromatic Ene. A Theoretical Study

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Biphenalenylidene: The Forgotten Bistricyclic Aromatic Ene. A Theoretical Study

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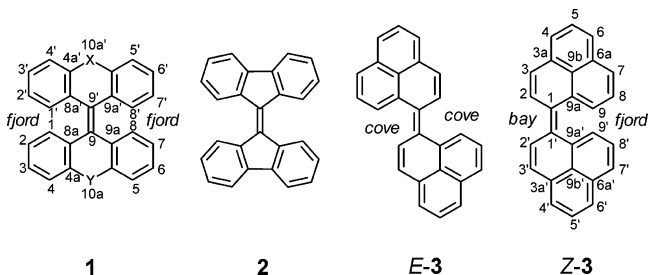
Abstract: The Lawesson reagent and P₂S₅ mediated reductive coupling of phenalenone (**6**) gives LPAH peropyrene (**5**) in 47% and 54% yields. The mechanism of the reaction involves the formation of phenalenethione (**10**), *Z*- and *E*-1,1'-biphenalenylidene (**3**), and **9** as intermediates. The electrocyclization reaction of *Z*-**3** to **9**, followed by aromatization, gives **5**. The results of an ab initio and DFT study of **3** and 2,2'-biphenalenylidene (**12**) are reported. *E*-**3** and *Z*-**3** have a diradical character with twist angles of 44.8° and 57.8° (at UB3LYP/6-311G**). $\Delta E_{\text{Tot}}^{\ddagger} = 10.2$ kJ/mol and $\Delta G_{298}^{\ddagger} = 10.6$ kJ/mol for *E*-**3** \rightleftharpoons *Z*-**3** diastereomerization. These unusually low energy barriers are due to the ground-state diradical destabilization and the aromatic stabilization of the transition state TS-**3**. Triplet *Z*-**3** is higher in energy than singlets *E*-**3** and *Z*-**3** by 10.4 and 3.1 kJ/mol. In the concealed non-Kekulé **12**, singlet **12** is more stable than the triplet by 1.3 kJ/mol. Singlet **12** is more stable than singlet *E*-**3** by 2.0 kJ/mol, and orthogonal singlet TS-**12** is lower in energy than singlet TS-**3** by 6.0 kJ/mol. The energy barriers for the hexatriene-cyclohexadiene electrocyclization *Z*-**3** \rightarrow **9** are $\Delta E_{\text{Tot}}^{\ddagger} = 94.8$ and $\Delta G_{298}^{\ddagger} = 98.3$ kJ/mol (at (U)B3LYP/6-31G*). The reaction occurs thermally in a conrotatory mode.

Introduction

The bistricyclic aromatic enes (BAEs) (**1**) are representatives of the more general class of overcrowded polycyclic aromatic enes (PAEs).^{1,2} These systems are convenient substrates for the study of the ground state conformations and dynamic stereochemistry of overcrowded PAEs. Thermochromic and photochromic BAEs serve as candidates for potential molecular switches,^{3,4} whereas 9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene (**2**), the parent BAE, and related BAEs serve as potential starting materials for the preparation of buckybowls.^{5–9} The syntheses of the fullerene fragment diindeno[1,2,3,4-*defg*:1',2',3',4'-*mnp*]-chrysene from **2** and its 1,1'-dibromo derivative by FVP have been reported.^{10,11} The topic of BAEs has been reviewed.^{1,2,12,13}

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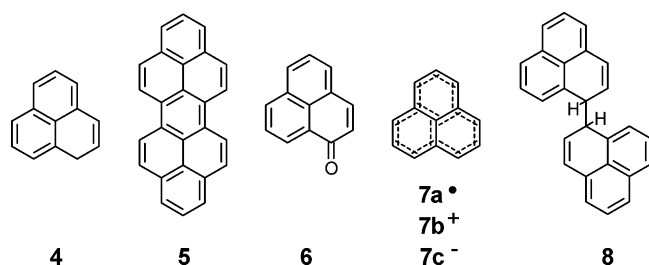
Chart 1



BAEs were perceived as bridged tetraarylethylenes or tetra-benzofulvalenes and were classified into homomeric BAEs (**1**, $X = Y$) and heteromeric BAEs (**1**, $X \neq Y$).² 1-(1*H*-phenalen-1-ylidene)-1*H*-phenalene (**3**), a constitutional isomer of **2**, has eluded the attention of the explorers.¹⁴ Formally, **3** is a BAE, but has a different topology than **1**. It is composed of two units of 1*H*-phenalene (**4**), known for its unusual chemistry.^{15–17} BAE **3** may also be regarded as phenalenofulvalene. BAE **3**, contrary to **2**, can exist as two diastereomers, *E*-**3** and *Z*-**3**. Both are

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Chart 2



overcrowded: *E*-**3** has two *cove* regions, whereas *Z*-**3** has a *ffjord* region and a *bay* region. The overcrowding in *Z*-**3** and *E*-**3** leads to out-of-plane deformations and to a variety of conformations, whereas close carbon–carbon nonbonding distances at the *ffjord* region of *Z*-**3** could facilitate an aromatization process, leading to dibenzo[*cd,lm*]perylene (peropyrene, **5**), a large polycyclic aromatic hydrocarbon (LPAH). LPAH **5** was identified as a component of coal tar pitch,¹⁸ of diesel particulate extract,¹⁹ and as a product of bituminous coal volatiles pyrolysis.²⁰ It was synthesized from 1*H*-phenalen-1-one (phenalenone, **6**) by the Clar reaction, a reductive coupling of phenalenone-type polycyclic aromatic ketones, using Zn dust in a melt of NaCl and ZnCl₂ at 300 °C.^{21,22} Peropyrene (**5**) can also be formed from phenalenyl radical (**7a**), which is reported to undergo σ -dimerization to form its dimer 1,1'-biphenalenyl (**8**) in an equilibrium reaction.^{15,16} At ≤ -25 °C **7a** exists only in the dimeric form.²³ It has also been shown to form a staggered “dimeric pair”, with weak or intermediate covalent bonding between two molecules of **7a**.²⁴ Dimer **8** disproportionates slowly at room temperature and rapidly in boiling benzene, yielding **5** and an unidentified hydroaromatic product.¹⁵ It has also been mentioned as a possible intermediate in the formation of **5** from 1-(1-hydroxy-1*H*-phenalenyl)-1*H*-phenalen-1-ol under acidic catalysis.^{15,16} The reductive dimerization of phenalenium perchlorate with Zn dust in diethyl ether at 25 °C via radical **7a** yields **5**.²⁵ Radical **7a** can also be generated from **6**.^{15,16} Dimer **8** has neither been isolated nor characterized and the mechanism of the formation of **5** from **8** has not been elucidated.

The phenalene system has gained a special status in Novel Aromatic Chemistry.^{16,17} Consider the odd-alternant phenalenyl $D_{3h}\text{-C}_{13}\text{H}_9$ system. Phenalenyl radical $D_{3h}\text{-C}_{13}\text{H}_9^\bullet$ (**7a**), phenalenium cation $D_{3h}\text{-C}_{13}\text{H}_9^+$ (**7b**), and phenalenide anion $D_{3h}\text{-C}_{13}\text{H}_9^-$ (**7c**) all possess special thermodynamic stability.¹⁷ This extraordinary picture stems from the Hückel diagram of molecular π -orbitals. The HOMO/LUMO of the odd-alternant species **7a**, **7b**, and **7c** is a nonbonding orbital (NBMO), lying above three degenerate bonding orbitals. Phenalenium cation (**7b**) is a truly closed shell species,²⁶ with an empty NBMO, whereas in radical **7a**, and anion **7c** this orbital is singly and

doubly occupied, respectively. This is not expected to introduce a significant destabilizing effect. Thus, TREPE values, calculated for **7a-c**, are positive and almost identical, indicating similar aromatic stabilization.²⁷ The unusual thermodynamic stability of **7a** is noted.^{16,17} The problem of kinetic instability of **7a** due to σ -dimerization to **8**, leading to **5**, was overcome by introducing bulky substituents in **7a**. 2,5,8-Tri-*tert*-butylphenalenyl radical and perchlorophenalenyl radical were synthesized and their X-ray structures were determined.^{28,29}

We report here the Lawesson reagent and P₂S₅ mediated reductive coupling of phenalenone (**6**) leading to peropyrene (**5**) and the mechanism of the reaction, including the formation of 1*H*-phenalene-1-thione (**10**) and of *Z*-**3** and *E*-**3** as intermediates. The results of an ab initio and DFT study of the conformational space of *Z*-**3** and *E*-**3** and related species are presented. Special emphasis is drawn to the electrocyclization of *Z*-**3** in the multistep transformation of **6** to **5**. We note the very low barriers for *E* \rightleftharpoons *Z* diastereomerization of **3**.

Results and Discussion

Synthesis of Peropyrene (5) by Reductive Coupling of Phenalenone (6). We have previously reported an attempted synthesis of **3**³⁰ by a low-valent titanium-induced reductive carbonyl coupling reaction, a convenient synthetic method for preparation of aromatic and aliphatic enes from carbonyl compounds, referred to in the chemical literature as the McMurry reaction.^{31–33} Treatment of **6** with low-valent titanium species generated from TiCl₄ and LiAlH₄ did not produce *Z*-**3** and *E*-**3**, but gave LPAH **5** in a relatively low yield (15%).³⁰ The possibility of converting **6** into phenalenethione (**10**), with the subsequent application of Barton's 2-folded extrusion diazo/thione coupling method^{34–36} with **10** and 1-diazo-1*H*-phenalene to give **5**, was considered. Alternatively, **10** could be converted to **5** by a reductive coupling with copper.

Treatment of **6** with P₂S₅ in boiling benzene under argon atmosphere for 10 h did not give the expected thione **10**, but afforded LPAH **5** in 54% yield. The reaction of **6** with Lawesson reagent under similar conditions for 2.5 h gave LPAH **5** in 47% yield. Neither *Z*-**3** nor *E*-**3** were found in the product mixture. To explore the reaction further, ¹H NMR spectra were recorded 5, 30, and 60 min from the beginning of the reaction of **6** with P₂S₅. In addition to **5** and **6**, signals ascribed to two unknown compounds I and II were recorded. After 5 min, the reaction mixture contained 70–95% of Compound I, 0–20% of **6**, and small amounts of **5** and Compound II. After 30 min, the reaction mixture contained 30–40% of Compound II, 15–40% of **5**,

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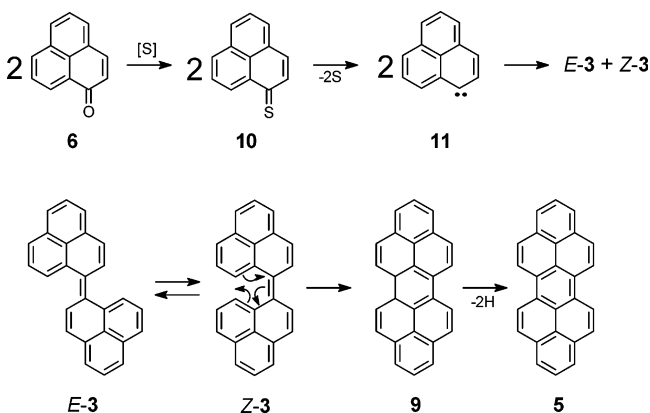
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Scheme 1. Proposed Mechanism of the Reductive Coupling of Phenalenone (**6**) to Form Peropyrene (**5**)



0–30% of Compound I, but no traces of **6**. After 60 min, the reaction mixture contained 30–50% of **5**, 35% of Compound II, and trace amount of Compound I. The ^1H NMR spectrum of the latter sample recorded after a week showed 70–95% of **5**. The UV–vis spectrum of the dark orange solution (Compound I), resulting from the reflux of **6** with P_2S_5 in benzene (5 min), demonstrated signals at 470, 444, 418, 394, 375, 356, 340, 328, and 315 nm. The ^1H NMR spectrum of this orange solution (Compound I) resembled the ^1H NMR spectrum of **6**, with a slight shift to a lower field. After evaporating the solvent in a vacuum and dissolving the residue again, the color of the solution changed from dark orange to green. The UV–vis spectra showed a broad band at 647 nm with the intensity rapidly decreasing in time and disappearing after 50 min, whereas the intensities of the characteristic bands belonging to LPAH **5** (438, 409, 382, and 354 nm) were consistently increasing. It was concluded that the orange Compound I is phenalenethione (**10**). The signal of aliphatic protons in the ^1H NMR spectrum of Compound II could be ascribed to **4**, **9**, or another intermediate product of the phenalenone coupling reaction, leading to **5**. The band at 647 nm in UV–vis spectrum is ascribed to **Z-3** and/or **E-3**.

The proposed mechanism of the coupling reaction is depicted in Scheme 1. Thione **10** is formed first. Thiones of aromatic ketones can undergo dimerization, including carbon–carbon bond formation.^{37,38} Thione **10** then undergoes dimerization and desulfurization, via carbene **11** or, alternatively, via 2,4-bis-(1*H*-phenalenylidene)-1,3-dithiane, leading to BAE **3**. (*E*)-**3** readily isomerizes to (*Z*)-**3** (vide infra), which then undergoes a hexatriene–cyclohexadiene electrocyclic cyclization, to give heptacyclic hydrocarbon **9**. Subsequent aromatization of **9** yields **5**.

This reaction may be compared with the reductive coupling of 7*H*-benz[*de*]anthracen-7-thione with copper powder in boiling toluene, to give LPAH tetrabenz[*a,cd,j,lm*]perylene as the sole reductive dimerization product in 14% yield.³⁹ The reductive coupling of **6** to **5** with P_2S_5 or with Lawesson reagent requires a moderate heating (80 °C), but does not require high temperatures as the Clar reaction. The depicted mechanism (Scheme 1) differs considerably from the reported transformation of **7a**

via **8** into **5**.^{15,16} The conditions of the reductive coupling of **6** mediated by Lawesson reagent and by P_2S_5 rule out the formation of **8** as an intermediate.

Conformational Space of 1,1'-Biphenalenylidene (3). The conformational space of BAE **3** was studied by ab initio HF and MP2 and DFT B3LYP methods. DFT can be successfully used to probe the aromaticity of large molecular systems, in a cost-effective way, using the different energetic, geometrical and magnetic criteria of aromaticity.⁴⁰ Lately, B3LYP hybrid functional was successfully employed to treat BAEs,⁴¹ LPAHs,⁴² fullerenes, and fulvalenes.⁴³ Table S1 and Table S2 give HF, MP2, and B3LYP relative and total energies of BAE **3**. Table S3 gives selected geometrical parameters of **3**. The global minimum of **3** is twisted *E-3* ($\omega = 37.5^\circ$), with twisted *Z-3* ($\omega = 38.9^\circ$) being less stable by 15.4 kJ/mol (at RB3LYP/6-31G*). These twist values are similar to the pure twist of **2**, 34.0° .⁴¹ Both twisted conformations of **3** are slightly overcrowded, having nonbonding distance $\text{C}^{2\cdots}\text{C}^{9'}$ = 305.6 pm (11% penetration; the van der Waals radii of carbon is 171 pm⁴⁴) and $\text{C}^{9\cdots}\text{C}^{9'}$ = 313.9 pm (8% penetration). The *anti*-folded *E-3* conformation is a local minimum, 27.5 kJ/mol less stable than *E-3*. *Syn*-folded *Z-3*, which is 78.1 and 62.7 kJ/mol higher than *E-3* and *Z-3*, respectively, is a transition state. It is overcrowded, with nonbonding distances $\text{H}^9\cdots\text{H}^{9'}$ = 171.5 pm (25% penetration; the van der Waals radii of hydrogen is 115 pm⁴⁴) and $\text{C}^{9\cdots}\text{C}^{9'}$ = 301.7 pm (12% penetration). For comparison, *anti*-folded and *syn*-folded **2** are 39.0 and 74.3 kJ/mol less stable than twisted **2**.⁴¹ Planar *E-3* and *Z-3* are third-order saddle points and are located 104.1 and 147.3 kJ/mol above *E-3*, respectively.

Spin unrestricted treatment of *E-3* and *Z-3* lowers their relative energies by 3.1 and 10.7 kJ/mol, respectively, with *Z-3* being less stable than *E-3* by 7.8 kJ/mol (at UB3LYP/6-31G*). At UB3LYP/6-311G**, the energy difference is 7.3 kJ/mol. Both *E-3* and *Z-3* have a diradical character,^{45,46} which is reflected in higher twist angles as compared to spin restricted geometries: 45.1° and 55.6° , respectively. The transition state for *E* \rightleftharpoons *Z* diastereomerization, the orthogonally twisted TS-**3** conformation ($\omega = 88.5^\circ$), is located 12.0 and 4.2 kJ/mol above *E-3* and *Z-3*, respectively (at UB3LYP/6-31G*). Figure 1 shows the relative energies of the important, twisted conformations of **3**. Figure 2 shows the three-dimensional views of twisted *E-3*, *Z-3*, and TS-**3**. The *E,Z*-diastereomerization barrier is remarkably low: $\Delta E^\ddagger_{\text{Tot}} = 12.0$ kJ/mol (UB3LYP/6-31G*) and 10.2 kJ/mol (UB3LYP/6-311G**). The enthalpy of activation of the reaction $\Delta H^\ddagger_{298} = 7.4$ and 5.5 kJ/mol, respectively. Gibbs activation energy ΔG^\ddagger_{298} is 12.5 and 10.6 kJ/mol, respectively. For comparison, the experimental ΔG^\ddagger for thermal *E,Z*-diastereomerization of disubstituted bifluorenylidene are in the range of 79.5–104.6 kJ/mol.²

The unusually low energy barrier for *E,Z*-diastereomerization of **3** is ascribed to a combination of a ground state destabilization of this BAE, possessing a diradical character, high torsion angles and significantly weakened central double bond, and of an

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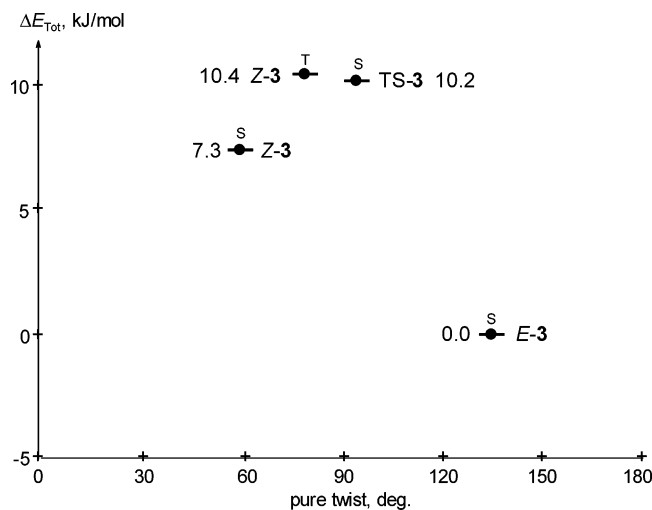


Figure 1. DFT relative energies (ΔE_{Tot} , kJ/mol) of the twisted conformations of BAE **3** (at UB3LYP/6-311G**); $\Delta E_{\text{Tot}}(E-3) = 0$; S: singlet, T: triplet).

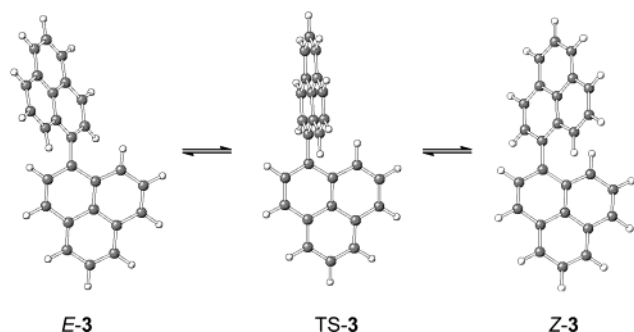


Figure 2. Three-dimensional representations of twisted *E*-**3** and *Z*-**3** and of the transition state for *E,Z*-diastereomerization of **3** (singlets, at UB3LYP/6-311G**).

aromatic stabilization of the orthogonally twisted transition state TS-**3**. The degree of this stabilization could be estimated by a comparison of TS-**3** with the analogous transition state for enantiomerization of twisted **2**.⁴¹ TS-**3** is more stable than TS-**2** by 101.3 kJ/mol (at UB3LYP/6-31G*). Hence, the experimental *E,Z*-diastereomerization barriers in derivatives of **2** are substantially higher (vide supra). The results of HF and MP2 methods are in agreement with the results of DFT. At UHF/6-31G*, *E*-**3** ($\omega = 61.5^\circ$) is more stable than *Z*-**3** ($\omega = 66.4^\circ$) by 0.4 kJ/mol, and TS-**3** is less stable than *E*-**3** and *Z*-**3** by only 2.0 and 1.6 kJ/mol, respectively. At UMP2/6-31G**/UHF/6-31G*, the energy difference between *E*-**3** and *Z*-**3** is 0.2 kJ/mol, whereas TS-**3** is less stable than *E*-**3** and *Z*-**3** by 3.0 and 2.8 kJ/mol, respectively. However, the high spin contamination of the resulting open shell singlets ($\hat{S}^2 = 3.68\text{--}3.69$) should be noted.

Kekulé versus Non-Kekulé Biphenalenylidenes. Triplet *Z*-**3** ($\omega = 77.0^\circ$) is a minimum, being higher in energy than singlets *E*-**3** and *Z*-**3** by 10.4 and 3.1 kJ/mol (at UB3LYP/6-311G**). A similar picture was revealed in Clar Goblet⁴⁷ (4*H*,13*H*-diphenaleno[2,1,9,8-*defg*:2',1',9',8'-*opqr*]pentacene-4,13-diyl). However, Clar Goblet is a planar concealed non-Kekulé LPAH,⁴⁸ in contrast to **3**, which is obviously a Kekulé hydrocarbon. Non-Kekulé molecule is a fully conjugated

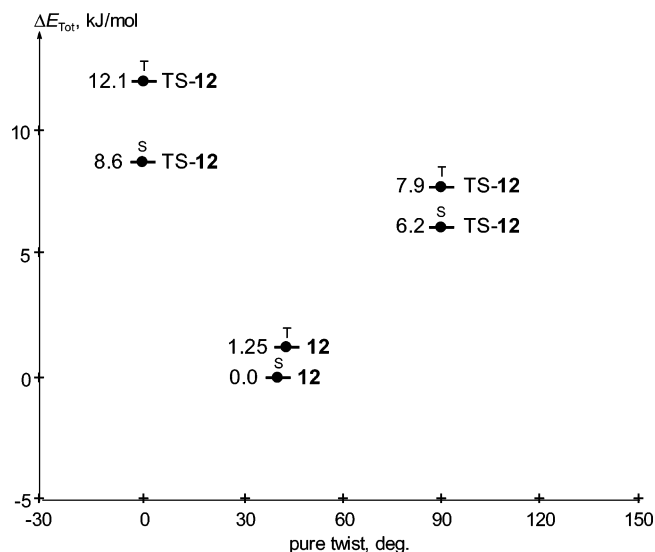
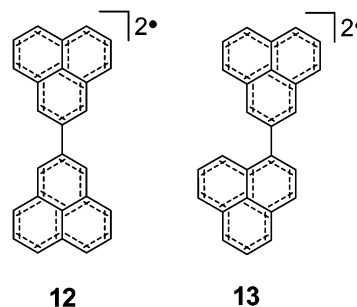


Figure 3. DFT relative energies (ΔE_{Tot} , kJ/mol) of the optimized conformations of diradical **12** (at UB3LYP/6-311G**); ΔE_{Tot} of twisted singlet **12** = 0; S: singlet, T: triplet).

Chart 3



molecule, each of whose Kekulé structures contains at least two atoms that are not π -bonded.^{49–51} A distinction has been made between concealed and nonconcealed (obvious) non-Kekulé hydrocarbons.^{52–56} In a concealed non-Kekulé hydrocarbon, the numbers of starred and unstarred carbon vertexes are equal.^{54,55}

In contrast to **3**, its constitutional isomers 2,2'-biphenalenylidene (**12**) and 1,2'-biphenalenylidene (**13**) diradicals are concealed and nonconcealed non-Kekulé hydrocarbons, respectively.⁵⁷ The AM1-ROHF CI calculations of diradicals **12** and **13** (Chart 3) have been reported:⁵⁸ the triplet of nonconcealed **13** ($\omega = 50^\circ$) was more stable than the singlet ($\omega = 80^\circ$) by 10.4 kJ/mol, whereas the singlet of concealed **12** ($\omega = 44^\circ$) was more stable than the triplet ($\omega = 44^\circ$) by 7.2 kJ/mol.⁵⁸ Figure 3 shows the relative energies of the optimized conforma-

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tions of **12**. The DFT relative and total energies of **12** are given in Table S1 and Table S2 (see the Supporting Information). The DFT calculations showed that singlet **12** ($\omega = 41.1^\circ$) is the global minimum and is lower in energy than triplet **12** ($\omega = 42.9^\circ$) by 1.3 kJ/mol (at UB3LYP/6-311G**). Note that the POMOs 86α and 86β of singlet **12** as well as singlets **E-3** and **Z-3** are disjoint and localized on the upper and the lower phenalenylidene unit, respectively (Figure S1 and Figure S2). Orthogonally twisted singlet and triplet **12** are transition states for the enantiomerizations of the respective twisted conformations: (*M*)-**12** \rightleftharpoons TS-**12** (orthogonal) \rightleftharpoons (*P*)-**12**. They are located 6.2 and 6.6 kJ/mol higher than the corresponding singlet and triplet twisted **12**. Planar singlet and triplet **12** are also transition states for the enantiomerizations: (*P*)-**12** \rightleftharpoons TS-**12** (planar) \rightleftharpoons (*M*)-**12**. They are located 8.6 and 10.8 kJ/mol higher than singlet and triplet **12**, respectively. All of these transition states are achiral. The conformations of **12** are slightly more stable than the respective conformations of **3**. Thus, singlet **12** is more stable than singlet **E-3** by 2.0 kJ/mol, and triplet **12** is lower in energy than triplet **Z-3** by 11.0 kJ/mol (at UB3LYP/6-311G**). Orthogonally twisted singlet TS-**12** is more stable than orthogonally twisted singlet TS-**3** by 6.0 kJ/mol. The increased stability of **12** can be explained by the different topologies of these $C_{26}H_{16}$ species (vide infra).

Table S4 gives the eigenvalues of the seven highest occupied (80–86), the seven highest vacant (87–93) π -MOs of **3** and **12**, and the relevant MOs of the parent **7a**. The degeneracy of the three highest doubly occupied and the three lowest vacant MOs of D_{3d} -**7a** is lifted, lowering the MO symmetry to C_{2v} . The HOMO–LUMO gaps in singlets **E-3**, **Z-3**, and **12** are 1.81, 1.84, and 1.90 eV, respectively (at UB3LYP/6-31G*).

Table S5 and Figure S3 give the total atomic spin density at the carbon atoms of **7a**, twisted conformations of **3**, and **12** (at UB3LYP/6-311G**). In **7a**, the calculated spin density is concentrated mainly at the *peri* C^1 , C^3 , C^4 , C^6 , C^7 and C^9 positions (0.309). This pattern is maintained in **3** and **12**. In singlets **E-3**, **Z-3**, TS-**3**, **12**, and TS-**12**, the highest positive and negative values of spin density are located at the *peri* positions C^1 , C^3 , C^4 , C^6 , C^7 and C^9 of one phenalenylidene unit and at $C^{1'}$, $C^{3'}$, $C^{4'}$, $C^{6'}$, $C^{7'}$ and $C^{9'}$ of the other phenalenylidene unit, respectively. The positive spin density in triplets **Z-3**, **12**, and orthogonal TS-**12** is delocalized mainly through all the *peri* positions. The spin density at the central C^{9b} and $C^{9b'}$ atoms are low for all the species. These results are consistent with the literature spin density distribution for **7a** and **12**.⁵⁸ The absolute values of spin density in singlet **E-3** ($\omega = 44.8^\circ$) at the *peri* positions are considerably lower than the respective values in radical **7a** (0.226–0.201 vs 0.309), except for the bridgehead C^1 and $C^{1'}$ atoms (0.284 vs 0.309). Increasing the pure twist in singlets **Z-3** (57.8°) and TS-**3** (87.5°) and in triplet **Z-3** (77.0°) breaks the π -conjugation along the C^1 – $C^{1'}$ bond, thus eliminating the spin exchange between two halves of the molecules. In **12**, the bridging C^2 – $C^{2'}$ bond lies in a nodal plane of the spin active POMOs 86α and 86β , and the spin density values are very close to those in **7a**. The calculated spin density pattern in the singlets of **3** and **12** suggests that each of the two electrons of opposite spin occupies one of the degenerate POMOs, which are disjoint and located on different phenalenylidene units. Obviously, the net spin of these singlets is zero. Due to the different topology of **3** and **12**, the spin density is high at the

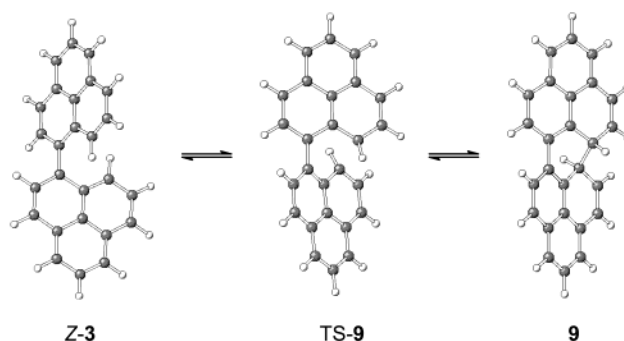


Figure 4. Three-dimensional representations of **Z-3**, **9**, and the transition state TS-**9** for **Z-3** \rightarrow **9** electrocyclization (singlets, at (U)B3LYP/6-311G**).

bridgehead C^1 and $C^{1'}$ atoms of **3**, whereas it is low at the bridgehead C^2 and $C^{2'}$ atoms of **12**, thus reducing spin exchange between two phenalenyl units of **12**. This difference may account for the lower energy of **12** relative to **3**.

Reductive Coupling of Phenaleneone (6) to Peropyrene (5)—A Computational Approach. The transformation of **6** into **5** is described as a multistep process, including formation of the intermediate enes **E-3** and **Z-3** with subsequent electrocyclization followed by aromatization, leading to **5** (Scheme 1). The latter steps include the formation of heptacyclic hydrocarbon **9** as an intermediate. Table S6 and Table S7 gives DFT relative and total energies of **9**. It may exist as (*R,R/S,S*) and (*R,S*) diastereomers, with the two C_{sp^3} –H hydrogens located on the same side or on the different sides of the plane of the aromatic skeleton of **9**, respectively. Twisted **9** is the global minimum, with torsion angle around the former double bond 21.0° . Folded **9** is a local minimum, 48.9 kJ/mol higher in energy than twisted **9** (at B3LYP/6-311G**). Folded TS-**9** lies 59.6 kJ/mol higher than twisted **9**, and, according to IRC calculations, serves as a transition state for diastereomerization of folded **9**, with an energy barrier of 10.7 kJ/mol. Singlet twisted TS-**9** ($\hat{S}^2 = 0.21$) is a transition state for the hexatriene-cyclohexadiene electrocyclization of **Z-3** to **9**, and lies 119.7 kJ/mol higher in energy than twisted **9** (at UB3LYP/6-31G*). Figure 4 shows three-dimensional representations of **Z-3**, TS-**9**, and **9**. Table S8 gives selected geometrical parameters of the central C^9 – C^{9a} – C^1 – $C^{1'}$ – $C^{9a'}$ – $C^{9'}$ ring in **Z-3**, TS-**9**, and **9**. In the course of the **Z-3** \rightarrow TS-**9** \rightarrow **9** electrocyclization, the nonbonding $C^9 \cdots C^{9'}$ distance shortens from 328.5 via 219.1 to 155.5 nm, and the C^{9a} – C^1 – $C^{1'}$ – $C^{9a'}$ torsion angle changes from 59.9° via 37.5° to 21.0° . The length of the central ethylene bond hardly changes.

The energy barrier for the electrocyclization of **Z-3** ΔE_{Tot}^\ddagger is 94.8 kJ/mol. The enthalpy of activation of the reaction ΔH_{298}^\ddagger is 92.4 kJ/mol, whereas ΔG_{298}^\ddagger is 98.3 kJ/mol (at (U)B3LYP/6-31G*). For comparison, the experimental ΔG^\ddagger for the *tZt*-1,3,5-hexatriene (*tZt*-HT) \rightarrow 1,3-cyclohexadiene (CHD) electrocyclization is 123.8 ± 1.3 kJ/mol,⁵⁹ whereas the calculated energy barrier for the *tZt*-HT \rightarrow *cZc*-HT diastereomerization is 47.1 kJ/mol.⁶⁰ Thus, the energy barrier for the reaction *cZc*-HT \rightarrow CHD, which corresponds to the reaction **Z-3** \rightarrow **9**, is 76.7 kJ/mol. The higher value of the barrier for the latter electrocyclization could be ascribed to a more rigid structure of **Z-3** and to the temporary loss of aromatic stabilization during the

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reaction. The central ring of TS-9 has a twisted chair conformation, and its geometry differs considerably from the geometry of the transition structures for the disrotatory and conrotatory ring closure of *tZt*-HT.^{61–68} Table S8 (see the Supporting Information) gives the calculated and experimental energy barriers and selected geometrical parameters in the hexatriene region of the reagents, the transition states and the product of the electrocyclizations of **3** and CT.

The *tZt*-CT → CHD reaction occurs thermally in a disrotatory fashion, in accordance with the Woodward–Hoffmann rules.^{69–70} By contrast, the displacements of the atoms of the central aromatic ring of TS-9 along the normal mode of the imaginary frequency correspond to the conrotatory course of the thermal Z-3 → 9 electrocyclization. The reaction, however, obeys the conservation of orbital symmetry rule: the symmetry of the two degenerate π -POMOs of Z-3 implies an overlap between orbital envelopes on opposite sides of the hexatriene C⁹–C^{9a}–C¹–C^{1'}–C^{9a'}–C^{9'} system to form the C⁹–C^{9'} σ -bond (*antara* fashion), thus requiring a conrotatory motion. This *antara* fashion closure is facilitated by a significant twist around the central C¹–C^{1'} bond: the torsion angle C^{9a}–C¹–C^{1'}–C^{9a'} in Z-3 is 59.9° (at UB3LYP/6-311G**). The respective torsion angle in *cZc*-CT is 0–10° (Table S8).

Conclusions

1,1'-Biphenalenylidene (**3**), a BAE with a topology different from that of the conventional BAEs (**1**), is found to have a diradical structure. Despite this, singlets *E*-3 and Z-3 are more stable than BAE **2** by 21.9 and 14.1 kJ/mol, respectively (at UB3LYP/6-31G*). On the other hand, **3**, a Kekulé hydrocarbon, is found to be less stable than the non-Kekulé hydrocarbon **12**. Singlet **12** is more stable than singlet *E*-3 by 2.0 kJ/mol, and triplet **12** is lower in energy than triplet Z-3 by 11.0 kJ/mol (at UB3LYP/6-311G**). BAE **3** readily undergoes *E,Z*-diastereomerization: $\Delta E^{\ddagger}_{\text{Tot}} = 10.2$ kJ/mol and $\Delta G^{\ddagger}_{298} = 10.6$ kJ/mol (at UB3LYP/6-311G**). TS-3 is lower in energy than TS-2 by 101.3 kJ/mol, due to the aromatic stabilization of its phenalenyl units. The electrocyclization of Z-3 to **9** has the energy barriers $\Delta E^{\ddagger}_{\text{Tot}} = 94.8$ kJ/mol and $\Delta G^{\ddagger}_{298} = 98.3$ kJ/mol, and occurs under modest heating (80 °C). The experimental and computational results do not, in principle, rule out the possibility of synthesizing kinetically stable derivatives of *E*-3, Z-3, and **12**.

Experimental Section

General. Melting points are uncorrected. All NMR spectra were recorded with Bruker DRX 400. UV–vis spectra were recorded with Kontron UVIKON 860. ¹H NMR spectra were recorded at 400.1 MHz

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using CDCl₃ as solvent and as internal standard ($\delta(\text{CHCl}_3) = 7.26$ ppm). ¹³C NMR spectra were recorded at 100.6 MHz using CDCl₃ as solvent and as internal standard ($\delta(\text{CHCl}_3) = 77.01$ ppm). Complete assignments were made through 2-dimensional correlation spectroscopy (DQF-COSY, NOESY, and HSQC). The literature procedure^{37,38} for converting aromatic ketones to thiones was slightly modified to afford the maximal yields of the product. The reactions were carried out under Ar; benzene was dried over sodium and freshly distilled.

Reaction of Phenalene (6) with Lawesson Reagent in Benzene.

To a magnetically stirred boiling solution of **6** (0.509 g, 2.82 mmol) in benzene (35 mL), Lawesson reagent (875 mg, 2.16 mmol) was added. The color of the mixture changed rapidly from yellow via orange to dark brown. The mixture was refluxed for 2.5 h. Column chromatography of the reaction mixture (SiO₂ dried, diethyl ether/petroleum ether 40–60, 1:1) afforded 377 mg of a yellow solid containing ca. 47% of **5**. The crude product was purified by sublimation (250 °C, 0.4 mmHg): 19.6 mg of crude **5** yielded 10.6 mg (54%) of pure **5** as yellow crystals, mp 380–385 °C decomp. (lit.²¹ mp 374–375 °C); ¹H NMR: $\delta = 9.27$ (d, *J* = 8.1 Hz, H⁵, H⁶, H¹², H¹³), 8.44 (d, *J* = 9.3 Hz, H⁴, H⁷, H¹¹, H¹⁴), 8.38 (d, *J* = 7.6 Hz, H¹, H³, H⁸, H¹⁰), 8.18 (t, *J* = 7.4 Hz, *J* = 7.6 Hz, H², H⁹); ¹³C NMR: $\delta = 130.95$ (C^{3a}, C^{7a}, C^{10a}, C^{14a}), 127.66 (C^{4c}, C^{7c}, C^{11c}), 126.01 (C^{2c}, C^{9c}), 125.15 (C^{5a}, C^{5b}, C^{12a}, C^{12b}), 125.19 (C^{1c}, C^{3c}, C^{8c}, C^{10c}), 125.20 (C^{10b}, C^{14b}), 122.95 (C^{12b}, C^{14c}), 122.88 (C^{5c}, C^{6c}, C^{12c}, C^{13c}) (cf. ref 30,71); UV–vis (C₆H₁₄, nm): 436, 411, 387, 366, 323, 310 (cf. ref 21, 25). An analogous reaction conducted at 25 °C for 24 h afforded only the starting ketone **6**.

Reaction of 6 with Phosphorus Pentasulfide in Benzene.

To a magnetically stirred boiling solution of **6** (2.00 g, 0.111 mol) in benzene (100 mL), P₂S₅ (4.93 g, 0.222 mol) was added. The color of the mixture changed from yellow via orange to dark brown. The mixture was refluxed for 10 h. The reaction mixture was cooled and filtered, the residue was extracted seven times with cold chloroform. The joint extracts were evaporated in a vacuum. Recrystallization of the solid residue from toluene yielded 983 mg (54%) mg of **5** as a dark brown powder, mp 376–380 °C. The ¹H NMR and ¹³C NMR spectra of the product were identical with those of the product of the reaction of **6** with Lawesson reagent. The UV–vis spectrum was recorded for the orange solution before and after its evaporation and dissolving again (the green solution). The orange solution: UV–vis (C₆H₆, nm): 656 (very weak), 470, 444, 418, 394, 375, 356, 340, 328, 315. The green solution: UV–vis (C₆H₆, nm): 647, 465, 438, 409, 382, 354.

Reaction of 6 with Phosphorus Pentasulfide in Chloroform-*d*.

To a magnetically stirred boiling solution of **6** (50 mg, 0.277 mmol) in chloroform-*d* (15 mL), P₂S₅ (185 mg, 0.832 mmol) was added. The mixture was refluxed for 1 h. The samples of the reaction mixture were taken 5, 30, and 60 min after the beginning of the reaction, filtered, and ¹H NMR spectra of resulting dark orange solution were recorded immediately and after a week. The following signals were observed:

- (1) 9.24 (d, 2H), 8.39 (d, 2H), 8.36 (d, 2H), 8.15 (t, 1H)—assigned to **5**;
 (2) 8.66 (d, 1H), 8.23 (d, 1H), 8.05 (d, 1H), 7.76–7.84 (m, 3H), 7.62 (t, 1H), 6.78 (d, 1H)—assigned to **6**.
 (3) 8.87 (br. s., 1H), 8.26 (br. s., 1H), 8.04 (br. s., 1H), 7.87 (br. s., 1H), 7.68 (tr, 1H), 7.55–7.48 (m, 3H)—assigned to **10** (Compound I).
 (4) 7.82–7.70 (m), 7.54–7.49 (m), 7.38–7.33 (m), 6.99 (d, 1H), 6.59 (br. d, 1H), 6.04 (dd, 1H), 4.07 (br. s., 2H)—Compound II.

Swift decomposition of Compound I and low concentration of the samples made it impossible to record ¹³C NMR spectra.

Computational Methods. The ab initio and DFT calculations were performed using the Gaussian98⁷² package. The RHF Hamiltonian was used for the closed shell systems, whereas RHF and/or UHF Hamiltonian were used to treat the twisted conformations of **3** and open-shell systems. Becke's three parameter hybrid density functional

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B3LYP,⁷³ with the nonlocal correlation functional of Lee, Yang, and Parr^{74–76} was used. The basis sets STO-3G, 6-31G*, and 6-311G** were employed. MP2 single point calculations were carried out at the HF/6-31G* optimized geometries. All structures were fully optimized using symmetry constrains as indicated. Vibrational frequencies were calculated to verify minima, transition states or higher order saddle points (at B3LYP/STO-3G or B3LYP/6-31G*). Nonscaled thermal energy corrections calculated at (U)B3LYP/6-31G* were used. Intrinsic reaction coordinates (IRC) for reactions and for diastereomerization

processes were calculated for selected transition states. The dummy atoms and symmetry constrains were removed, and two IRC calculations for each transition state were run to follow the normal mode with imaginary frequency in both directions.

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Supporting Information Available: The ab initio and DFT relative and total energies and the optimized geometries of **3**, **9**, and **12**, selected geometrical parameters of **3**, **9**, HT, and CHD, selected MOs of **3**, **7a**, and **12**, total atomic spin densities in **3**, **7a**, and **12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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