

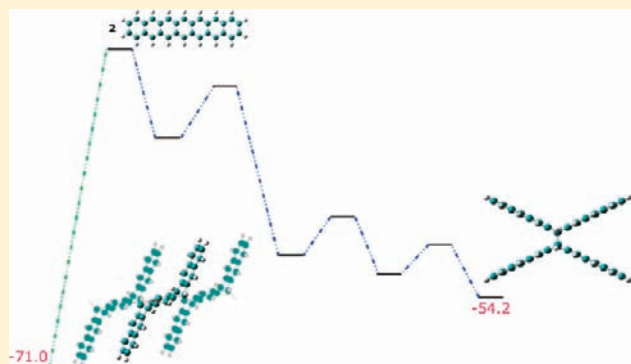
Products and Mechanism of Acene Dimerization. A Computational Study

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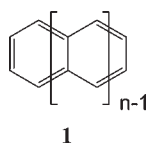
 Supporting Information

ABSTRACT: The high reactivity of acenes can reduce their potential applications in the field of molecular electronics. Although pentacene is an important material for use in organic field-effect transistors because of its high charge mobility, its reactivity is a major disadvantage hindering the development of pentacene applications. In this study, several reaction pathways for the thermal dimerization of acenes were considered computationally. The formation of acene dimers via a central benzene ring and the formation of acene-based polymers were found to be the preferred pathways, depending on the length of the monomer. Interestingly, starting from hexacene, acene dimers are thermodynamically disfavored products, and the reaction pathway is predicted to proceed instead via a double cycloaddition reaction (polymerization) to yield acene-based polymers. A concerted asynchronous reaction mechanism was found for benzene and naphthalene dimerization, while a stepwise biradical mechanism was predicted for the dimerization of anthracene, pentacene, and heptacene. The biradical mechanism for dimerization of anthracene and pentacene proceeds via syn or anti transition states and biradical minima through stepwise biradical pathways, while dimerization of heptacene proceeds via asynchronous ring closure of the complex formed by two heptacene molecules. The activation barriers for thermal dimerization decrease rapidly with increasing acene chain length and are calculated (at M06-2X/6-31G(d)+ZPVE) to be 77.9, 57.1, 33.3, -0.3, and -12.1 kcal/mol vs two isolated acene molecules for benzene, naphthalene, anthracene, pentacene, and heptacene, respectively. If activation energy is calculated vs the initially formed complex of two acene molecules, then the calculated barriers are 80.5, 63.2, 43.7, 16.7, and 12.3 kcal/mol. Dimerization is exothermic from anthracene onward, but it is endothermic at the terminal rings, even for heptacene. Phenyl substitution at the most reactive meso-carbon atoms of the central ring of acene blocks the reactivity of this ring but does not efficiently prevent dimerization through other rings.



INTRODUCTION

Acenes (**1**) are polycyclic aromatic hydrocarbons consisting of linearly fused benzene rings. These compounds are currently the subject of great interest from both fundamental and applied perspectives.^{1,2} The smallest acenes—benzene, naphthalene, and anthracene—are among the most studied organic molecules, while pentacene has received much attention as an active semiconducting material in organic field effect transistors (OFETs) because of its unusually high charge-carrier mobility.^{2,3}



Therefore, significant efforts have been devoted to the preparation of acenes with a low HOMO–LUMO gap that are stable

enough for applications in organic electronics. Recently, significant progress⁴ has been achieved in this regard, with the synthesis of longer acenes such as hexacene, heptacene,⁵ and, very recently,⁶ even octacene and nonacene. The reactivity of acenes has been studied intensively.^{1,2,7–9} It is well recognized that, as the number of rings increases, the members of the acene family become increasingly reactive^{7–9} and more difficult to synthesize and isolate.^{4–6,10} Indeed, in order to prepare acenes longer than pentacene that are stable under ambient conditions, very bulky protecting groups must be used to prevent dimerization. Recently, a dimerization reaction of hexacene with relatively bulky substituents was reported even during storage in the solid state in the dark.¹¹ The central ring of anthracene undergoes Diels–Alder reactions,^{7b,12} protonation,^{7c} and other reactions, while very few reactions have been reported for tetracenes and

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pentacenes.^{2,13,14} Only a few reactions of oligoacenes have been studied computationally.^{8,9,14,15}

Acenes are commonly known for their photoreactivity,¹⁶ with the most important photoreactions being oxidation by molecular oxygen and dimerization.¹⁷ Photodimerization of anthracene is one of the oldest known photochemical reactions,^{17a} and tetracene was the first photochromic organic compound¹⁸ described in the literature. Several photochemical studies¹⁷ of acene dimerization were undertaken, and it was assumed that the [4+4] cycloaddition occurred through a concerted mechanism. For 6,13-bis(trimethylsilyl)ethynyl-substituted pentacene,¹⁹ dimerization through the second pentacene ring was found to be the main photoinduced path leading to degradation.²⁰

Thermal reactions of long acenes are much less studied. Wudl's group¹⁴ discovered the first reaction of a substituted pentacene molecule as a dienophile. A surprisingly clean Diels–Alder self-coupling reaction of 2,3,9,10-tetrachloropentacene leads to a novel ladder acene-based polymer, poly(iptycene). In poly(iptycene)s, as well as in similar acene-based polymers, the intramolecular cavities allow strong, noncovalent binding to suitably sized species, which makes such materials suitable for use in gas separation²¹ or as sensors, e.g., for nitric oxide.²² Due to the low solubility and instability of long acenes, most reactions have been performed on anthracene and its derivatives.

The reactivity of acenes can reduce their potential applications in the field of molecular electronics. Although pentacene is an important material for use in OFETs, its reactivity (oxidation and dimerization) is a major disadvantage hindering the development of pentacene applications.^{2,3} The formation of peripentacene was observed during thermal activation of pentacene,²³ and this simple procedure for the fusion of two polyacenes to give a larger graphene fragment¹⁵ could be a general way to synthesize graphenes. Currently, graphene²⁴ attracts intense interest as an electronic material²⁵ due to its properties, such as an abnormal quantum Hall effect, massless Dirac fermions, and great stiffness and structural stability.²⁶ Since long oligoacenes can be considered the building blocks of carbon nanotubes and graphene, the study of oligoacene reactivity is important to understanding the stability and decomposition mechanisms of graphene and carbon nanotubes.

Here, we report a computational study of the thermal dimerization of acenes, which can be viewed as a formally thermally symmetry-forbidden [4+4] reaction.^{16c} To understand the reactivity of acenes, we explored the mechanism of dimerization for benzene, naphthalene, anthracene, pentacene, and heptacene, and the stability of acene dimers from benzene to nonacene. Interestingly, we found an alternative favorable route for the dimerization of longer acenes (hexacene onward): the formation of an acene-based polymer. For the dimerization of benzene and naphthalene, only a concerted asynchronous pathway was found, while for the dimerization of anthracene and pentacene, a multistep biradical mechanism is preferred. Dimerization of heptacene proceeds via multistep collapsing of the complex formed by two heptacene molecules to form the product.

COMPUTATIONAL METHODS

The Gaussian 09²⁷ series of programs were used. Some benchmark studies were performed using ORCA program.²⁸ The molecules were fully optimized using density functional theory²⁹ at the M06-2X level,³⁰ and, since the studied systems are quite large, the economical basis set 6-31G(d) was used (denoted as M06-2X/6-31G(d)). When the restricted

wave function was unstable, calculations were performed using the broken-symmetry unrestricted DFT (UDFT) method, and the species were optimized at the UM06-2X/6-31G(d) level of theory. Frequency calculations were performed at the M06-2X/6-31G(d) level for all stationary points (except of polymers) to differentiate them as minima or saddle points. The energies reported in this paper are at the M06-2X/6-31G(d) level of theory unless otherwise stated. Where frequency calculations were performed, unscaled zero-point vibrational energies (ZPVE) at M06-2X/6-31G(d) were added to the calculated relative energies. The calculations for polymers were performed using the periodic boundary conditions (PBC) approximation as implemented in Gaussian 09.³¹ Gibbs free energies (ΔG) were calculated at 298 K/1 atm using frequency calculations at M06-2X/6-31G(d). Originally, all stationary points were optimized at the B3LYP/6-31G(d) level of theory, and intrinsic reaction coordinate (IRC)³² calculations were performed for several representative cases.

For large systems, DFT has been shown to perform exceedingly well in studies of biradicals³³ and, especially, in predicting the competition between the biradical and concerted pathways in Diels–Alder reactions. Recent discussion in the literature regarding the applicability of DFT as a tool for studying biradicals concluded that UDFT is the best method for studying large systems where high-level *ab initio* calculations are impractical.³⁴ The problem of dispersion interactions in DFT-based methods, in general, and in B3LYP, in particular, is well known and is expected to be especially severe for systems such as acene dimers.³⁵ Recently, the M06-2X functional has been introduced as a method of choice for studying the kinetics and thermodynamics of systems that are expected to suffer from large dispersion errors, and it was shown that the M06-2X functional performs very well for the dimerization of anthracene.³⁶ It was also reported that the M06-2X method yields very good activation barriers and reaction energies for the reaction of benzene and maleic anhydride and that the M06-2X method also succeeds in describing dispersion interactions between π – π systems.³⁷

To the best of our knowledge, there are two experimental values related to acene dimerization that can serve as benchmarks for the current study. The best estimation for the relative energy of an anthracene dimer relative to two anthracene molecules is -9 ± 3 kcal/mol, as suggested by Grimme et al.³⁵ The value obtained in the current paper at M06-2X/6-31G(d)+ZPVE is -5.4 kcal/mol, which agrees nicely with the best estimated value. We note that the B3LYP/6-31G(d)+ZPVE values for this reaction have very significant errors (the anthracene dimer is calculated to be $+19.5$ kcal/mol less stable than two anthracene molecules in this work at B3LYP/6-31G(d)+ZPVE), as was also reported previously by Grimme et al.³⁵ and by Zhao and Truhlar.³⁶ The second benchmark comes from Greene,³⁸ who obtained an experimentally measured activation energy for thermal anthracene dimer dissociation of 36.3 kcal/mol. The activation barrier calculated at M06-2X/6-31G(d)+ZPVE in this paper is 38.7 kcal/mol, which again nicely agrees with the experimental result.

We have also performed benchmark calculations at *ab initio* levels of theory (see Supporting Information for details). The dimerization of benzene was calculated at the MP2/6-31G(d), MP2/6-311G(2d,p), and CBS-QB3 levels of theory. In addition, anthracene complexation energy was calculated at the MP2/6-31G(d) and MP2/6-311G(2d,p) levels,²⁷ and at the SCS-MP2/def2-TZVP and LPNO-CEPA1/def2-TZVP levels.^{28,39} The best estimates of anthracene complexation energy, -12.0 and -12.4 kcal/mol, obtained at LPNO-CEPA1/def2-TZVP and at LPNO-CEPA1 (extrapolated to basis set limit using 2/3 scheme as implemented in ORCA program)²⁸ levels, compare very favorably with those obtained at M06-2X/6-31G(d) (-10.8 kcal/mol). Based on these benchmark comparisons, it can be concluded that the M06-2X/6-31G(d) level of theory is appropriate for studying the kinetics and thermodynamics of acene dimerization. Unfortunately, MP2-based methods are not well suited to studying the diradical intermediates, so the

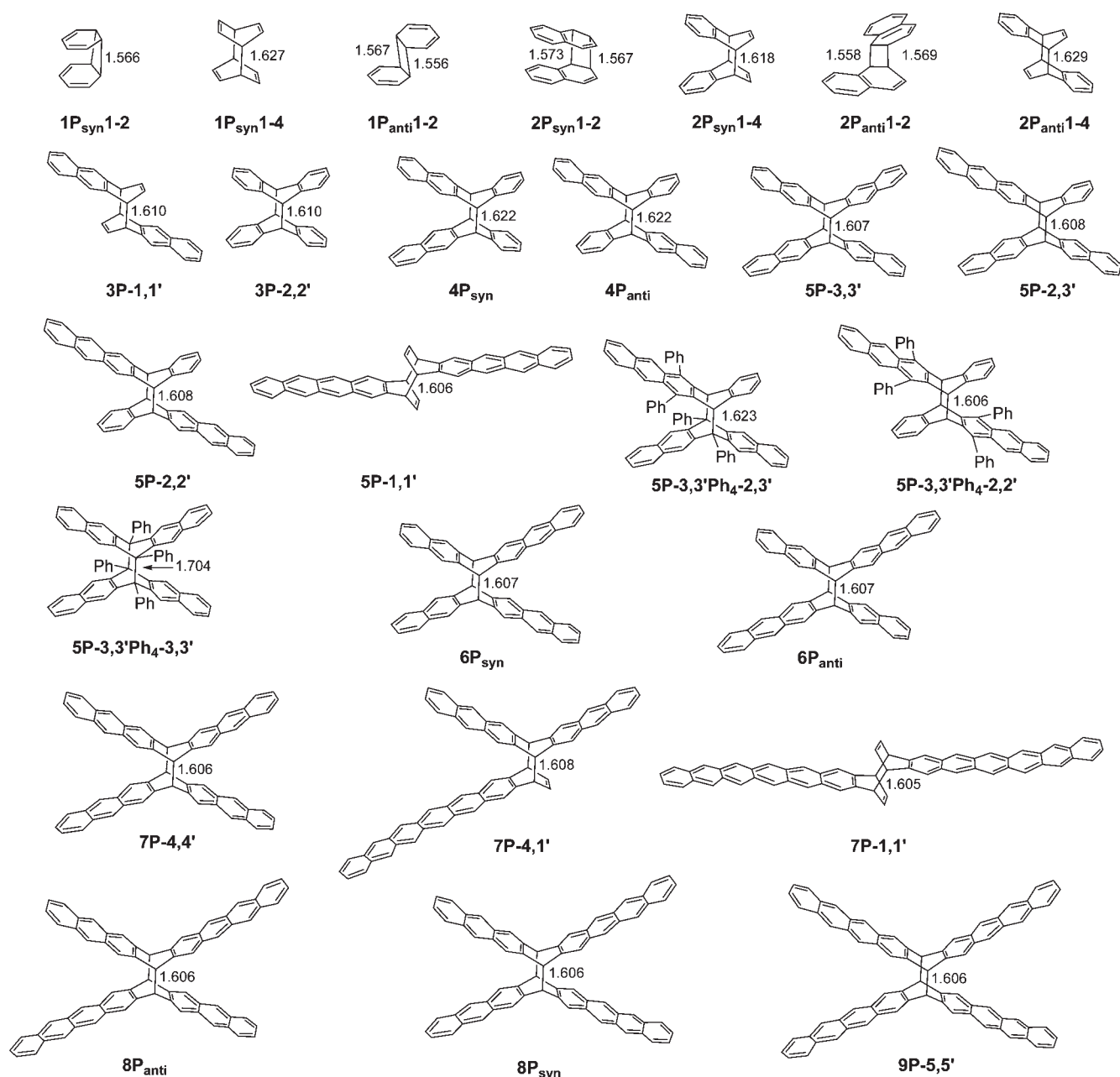


Figure 1. Structures of the studied dimerization products (P) with the forming C–C bond lengths (Å) calculated at the M06-2X/6-31G(d) level of theory. The first digit refers to the number of fused benzene rings in the corresponding acene monomer.

benchmark calculations are limited to the closed-shell intermediates and transition states. The CBS-QB3 level of theory, which is still feasible for studying benzene dimerization from a computer power/time perspective, uses B3LYP optimization (which does not include dispersion interactions), and the B3LYP and M06-2X levels of theory yield somewhat different potential energy surfaces for benzene dimerization (see Table S3 and Table S9 in the Supporting Information for details).

RESULTS AND DISCUSSION

1. Dimerization Products. We have considered the products of the dimerization of acenes from benzene to nonacene. Dimerization is expected to proceed most favorably through the most reactive central rings, and this was considered in all cases. Other

dimerization pathways using different connections between the two acene molecules and different stereochemical orientations (syn and anti) were also considered in some cases. The structures (at M06-2X/6-31G(d)) of the dimers are presented in Figure 1, with calculated forming bond lengths (i.e., the bond length between the two reacting molecules) given in Å. The forming C–C bond length is always exceptionally long for a single C–C bond, decreasing from 1.627 Å for the benzene dimer $1P_{\text{syn}}1-4$ to 1.606 Å for pentacene and longer dimers through to the nonacene dimer. Optimization of the anthracene dimer at the M06-2X/6-31G(d) level yields a forming C–C bond length of 1.610 Å, which is slightly shorter than the value obtained at B3LYP/6-31G(d) (1.623 Å). Several dimers of linear oligoacenes, including dianthracene,⁴⁰

Table 1. Calculated Dimerization Energies at M06-2X/6-31G(d)+ZPVE (Relative to the Two Molecules of the Respective Ground-State Acenes, in kcal/mol) for the Acenes in Figure 1^a

	ΔE	ΔG		ΔE	ΔG
benzene			naphthalene		
1P _{syn} 1-2	49.5 (47.3)	59.8	2P _{syn} 1-2	24.1 (21.2)	36.2
1P _{syn} 1-4	62.1 (60.1)	74.3	2P _{syn} 1-4	31.7 (28.8)	45.3
1P _{anti} 1-2	47.4 (45.4)	57.5	2P _{anti} 1-2	23.9 (21.2)	36.2
			2P _{anti} 1-4	31.2 (28.1)	44.7
anthracene			tetracene		
3P-2,2'	-5.4 (-9.6)	10.7	4P _{syn}	-19.3 (-23.8)	-5.0
3P-1,1'	20.3 (17.0)	35.6	4P _{anti}	-19.3 (-23.7)	-5.7
pentacene			hexacene		
5P-3,3'	-34.3 (-39.1)	-19.9	6P _{syn}	-41.4 (-46.5)	-25.8
5P-2,3'	-30.1 (-34.6)	-15.7	6P _{anti}	-41.8 (-46.5)	-26.3
5P-2,2'	-25.6 (-30.2)	-10.8			
5P-1,1'	13.0 (9.6)	27.5			
heptacene			octacene		
7P-4,4'	-49.1 (-54.3)	-33.9	8P _{syn}	-53.2 (-58.5)	-37.6
	-46.4 (-54.2)	-31.2		-46.7 (-54.9)	-31.2
7P-4,1'	-19.2 (-23.5)	-4.4	8P _{anti}	-53.4 (-58.6)	-38.0
	-16.5 (-23.4)	-1.7		-47.0 (-55.0)	-31.7
7P-1,1'	10.9 (7.5)	26.2			
	13.6 (7.6)	28.9			
nonacene			substituted pentacenes		
9P-5,5'	-57.4 (-63.0)	-41.5	5P-3,3'Ph ₄ -3,3'	18.6 (40.7)	14.4
	-45.8 (-54.5)	-30.0	5P-3,3'Ph ₄ -2,3'	-23.9 (-28.5)	-4.1
			5P-3,3'Ph ₄ -2,2'	-30.4 (-35.1)	-12.8

^a The energy values given in italics are at UM06-2X/6-31G(d)+ZPVE for cases where the reactants have open-shell electronic structures. Values in parentheses are without ZPVE.

s-dipentacene,⁴¹ and the syn and anti forms of ditetracene,⁴² have been prepared and the crystal structures of dianthracene,^{40b-f} dipentacene,⁴¹ and other acene photodimers^{42a,43,44} have been reported. The experimental C–C central bond length of dianthracene ranges from 1.599(3) Å^{40c} to 1.618(3) Å,^{40d} and that of dipentacene⁴¹ is 1.58(4) Å. Thus, our calculated values of 1.610 Å and 1.607 Å are within the experimentally measured C–C bond lengths for anthracene and pentacene dimers, respectively. Recently, Anthony's group reported X-ray structures of dimers of substituted hexacenes that have a C–C central bond length of about 1.59–1.60 Å,¹¹ which is again in agreement with our value of 1.607 Å for hexacene dimer. A classical steric argument should make a significant contribution to understanding the exceptionally long single C–C bond in acene dimers, as the proximal atoms of the π systems lie only 2.8 Å apart, which is well within the sum of their van der Waals radii (3.55 Å).⁴⁵

At the M06-2X/6-31G(d)+ZPVE level of theory, the calculated energy of the anthracene dimer is 5.4 kcal/mol lower than that of the two reacting anthracene molecules (Table 1), and thus the dimer is more stable than the monomers. As was mentioned in the Computational Methods section, this value compares well with the best estimate for the relative energy of the anthracene

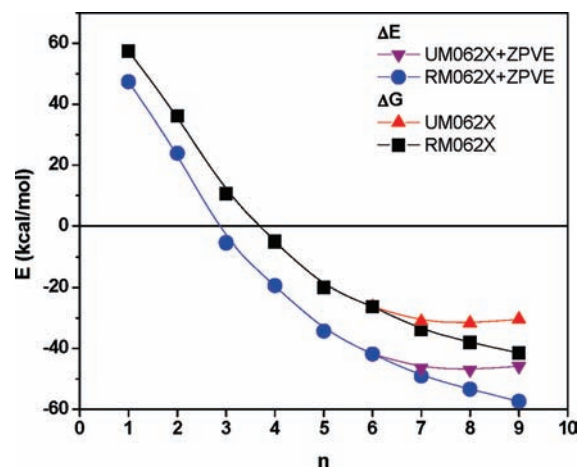


Figure 2. Dimerization energies (ΔE) and Gibbs free energies (ΔG) for acenes calculated at the RM06-2X/6-31G(d)+ZPVE and UM06-2X/6-31G(d)+ZPVE levels of theory as a function of the number of fused benzene rings.

dimer (-9 ± 3 kcal/mol).^{35,46} The pentacene dimer is 34.3 kcal/mol more stable than the reactants. According to our computational results, dimerization is more favorable at the central ring (i.e., to form 5P-3,3'), which is in line with previous observations (Table 1).^{7c} Dimerization at a terminal ring (Figure 1 and Table 1) causes the reaction energy to increase (from -5.4 to 20.3 kcal/mol for anthracene and from -46.4 to 13.6 kcal/mol for heptacene, at UM06-2X/6-31G(d)+ZPVE). The dimerization energies and Gibbs free energies for the series from benzene to nonacene are plotted in Figure 2. Dimerization is exothermic from anthracene onward, but it is endothermic at the terminal rings, even for heptacene (Table 1). For acenes longer than hexacene,⁴⁷ the dimerization energies calculated using the spin-unrestricted wave function are always higher (less exothermic) than those calculated using the restricted wave function as a result of stabilization of acene by consideration of the open-shell structures with biradical character.^{48,49} Consequently, the exothermicity of acene dimerization barely changes with the size of the acene from heptacene onward (Figure 2). This is a consequence of the unusual biradical ground state of the acenes.⁴⁸ Thus, if only dimer formation is considered, then very long acenes are as stable toward dimerization as heptacene. However, as we will discuss below, other decomposition pathways (such as polymerization) are possible for long oligoacenes.

The substituent effect has been studied by considering phenyl substitution at the 6,13 (meso, 3,3') positions of pentacene (Figure 3). Such substitution causes a very significant change in the stability of the 3,3'-dimer, which decreases from -34.3 kcal/mol in the unprotected pentacene dimer (5P-3,3') to $+18.6$ kcal/mol in 5P-3,3'Ph₄-3,3' (Table 1). However, if dimerization through the second rings (5P-3,3'Ph₄-2,2') is considered, the product is exothermic by -30.4 kcal/mol, which is similar to the unprotected dimer. This suggests that aryl substitution at the central ring effectively protects against dimerization only at the central rings; however, dimerization through other rings remains possible (for example, via the 2,2' positions of pentacene). For the asymmetric dimer 5P-3,3'Ph₄-2,3', the formation energy is moderate (-23.9 kcal/mol, Table 1). Indeed, in the experimentally obtained long oligoacenes, several protecting groups were used, which prevented dimerization through other rings around the center of the molecule.^{4,5,6a} It was suggested that the

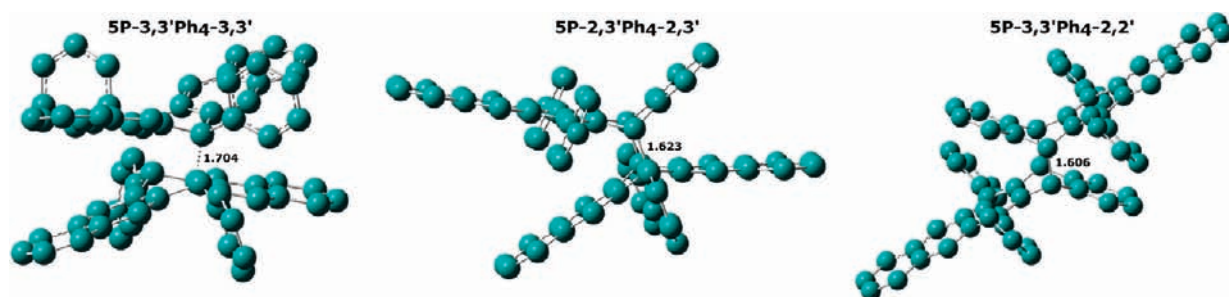


Figure 3. Optimized structures (at M06-2X/6-31G(d)) of 6,13-diphenyl pentacene dimers. Bond lengths are given in Å. Hydrogens are omitted for clarity.

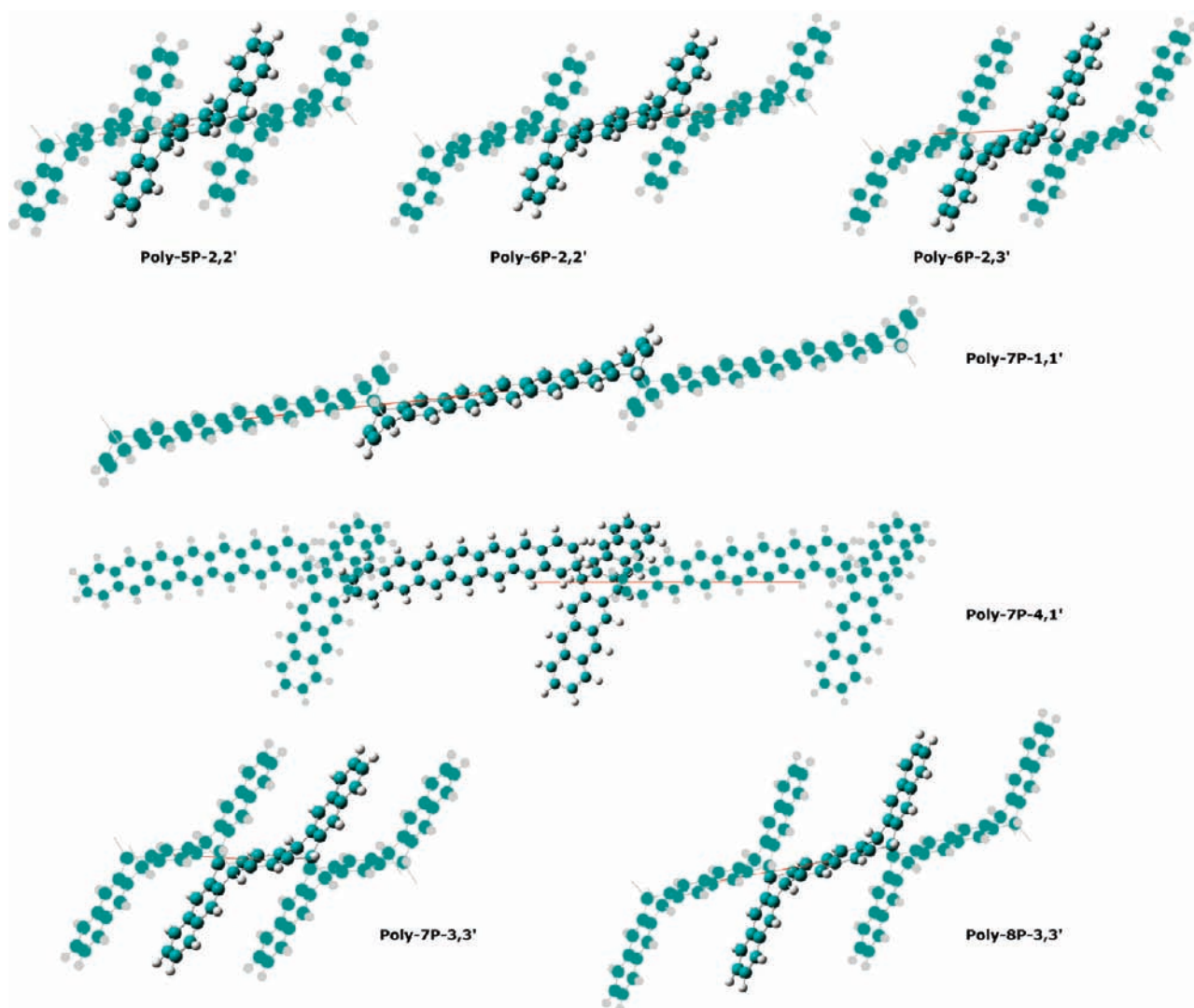


Figure 4. Representative optimized structures (PBC/M06-2X/6-31G(d)) of the acene-based polymers (for relative energies see Table 2). Red line shows a unit cell vector.

substituents should have a diameter equivalent to 30–50% of the length of the acene in order to protect the central ring from photooxidation and dimerization in larger acenes.^{5a,50}

2. Formation of Acene-Based Polymers.⁵¹ We have considered pathways other than dimerization for the self-reaction of acenes, in particular, the double dimerization (polymerization) of long acene molecules to form acene-based polymers (Figure 4) that

are poly(iptycene) analogues. Poly(iptycene)s, polymers composed of iptycene scaffolds, are rare; however, recently several examples of such polymers were obtained by Swager's and Wudl's groups.^{14,52,53} Poly(iptycene)s are of interest partly because of their molecular organization in liquid crystals and polymer matrices.^{52a–c}

At the M06-2X/6-31G(d) level of theory, pentacene dimerization to form the most stable dipentacene (5P-3,3') is 2.1 kcal/mol more

Table 2. Calculated Energies of Acene Dimers (Taken from Table 1) and Polymers (Relative to the Two Molecules of the Respective Ground-State Acenes, in kcal/mol, at M06-2X/6-31G(d) without ZPVE) for Pentacene, Hexacene, Heptacene, and Octacene^a

	ΔE	$\Delta\Delta E^b$		ΔE	$\Delta\Delta E^b$
5P-3,3'	-39.1		6P _{anti}	-46.5	
poly-5P-3,1'	10.9	50.0	poly-6P-2,3'	-41.4	5.1
poly-5P-2,2'	-37.0	2.1	poly-6P-2,2'	-55.6	-9.1
7P-4,4'	-54.2		8P _{anti}	-55.0	
poly-7P-4,1'	6.2	60.4	poly-8P-3,3'	-86.5	-31.5
poly-7P-3,3'	-71.0	-16.8			
poly-7P-1,1'	16.3	70.5			

^a For heptacene and octacene, the energies of the reactants were calculated at UM06-2X/6-31G(d), and the corresponding dimerization and polymerization energies are given in italics at UM06-2X/6-31G(d).

^b $\Delta\Delta E = \Delta E(\text{polymer}) - \Delta E(\text{dimer})$.

favorable than the formation of the most stable acene-based polymer (poly-5P-2,2') (Table 2). However, the acene-based polymers obtained from hexacene (poly-6P-2,2') and heptacene (poly-7P-3,3') monomers are 9.1 and 16.8 kcal/mol, respectively, more stable than the corresponding dimers, which shows that the formation of acene-based polymers from long oligoacenes is thermodynamically preferred over dimerization. Polymerization through the terminal rings, such as in poly-7P-1,1' (Figure 4 and Table 2), is endothermic (even in long acenes) and is strongly disfavored compared to polymerization through the central rings (e.g., poly-7P-3,3' is 87.3 kcal/mol more stable than poly-7P-1,1'). This supports earlier findings that the central ring of the acene backbone is the most reactive, with reactivity reducing toward the termini.⁸ Competition between the formation of dimers and acene-based polymers shifts toward the formation of acene-based polymers as acene chain length increases. Indeed, for octacene, the formation of the acene-based polymer poly-8P-3,3' is favored over the formation of the dimer by as much as 31.5 kcal/mol. Therefore, we suggest that acene-based polymers are the thermodynamically preferred polymerization products for higher acenes (Table 2). These computational results call for experimental reinvestigation of the dimerization of long unsubstituted acenes.

We note that the activation energy for the formation of acene-based polymers should be somewhat higher than that for the formation of acene dimers, since cycloaddition does not occur at the central ring.⁵⁴ So, for long acenes, acene-based polymers are a thermodynamically controlled product while acene dimers are a kinetically controlled product. We also note that the presence of sterically bulky substituents should somewhat disfavor the formation of acene-based polymers compared to acene dimers, since in acene-based polymers the substituted acene skeleton is sandwiched between similarly substituted molecules, while in an acene dimer it has only one neighbor with a substituted acene skeleton. So, although hexacene dimerization is 9.1 kcal/mol less favorable than the formation of the most stable acene-based polymer, formation of hexacene-based polymers might not be expected. Indeed, very recently, Anthony's group reported the formation of dimers of hexacene with bulky substituents.¹¹

Formation and decomposition of unsubstituted heptacene was reported.⁵⁵ Examination of Figure 9 in ref 55, which describes the annealing of photogenerated heptacene in an Ar matrix, revealed

the formation of peaks around 280–320 nm with relatively sharp shoulders at longer wavelengths. Considering that the UV spectrum of anthracene shows peaks around 310–380 nm and the UV spectrum of naphthalene shows peaks around 250–300 nm, we can assume that the annealing of unsubstituted heptacene leads to the formation of a compound comprising only naphthalene units (substituted by benzyl groups). So, formation of heptacene dimer 7P-4,4', which has substituted anthracene units, is not supported by Figure 9 in ref 55. On the other hand, formation of acene polymers such as poly-7P-3,3' or other similar polymers, which have only naphthalene units, could be supported by Figure 9 in ref 55.

3. Dimerization Mechanism. The thermal dimerization of acenes is usually viewed as a formally thermally symmetry-forbidden [4+4] reaction; however, to the best of our knowledge, the mechanism of this reaction was never studied in detail computationally. The experimentally determined activation energy for the dissociation of the anthracene dimer was reported, and it was proposed that this reaction occurs through a stepwise C–C bond-breaking process.³⁸ In the present computational study, we considered both concerted (synchronous or asynchronous) and stepwise biradical mechanisms for acene dimerization and explored the mechanistic pathway for benzene, naphthalene, anthracene, pentacene, and heptacene.

A concerted asynchronous reaction mechanism was found for benzene and naphthalene (Figures 5 and 6, respectively). Dimerization of benzenes can lead to an anti-[2+2] product (1P_{anti} 1-2), a syn-[2+2] product (1P_{syn} 1-2), or a [4+4] product (1P_{syn} 1-4) (Figure 5). The reaction starts with the exothermic ($\Delta E = -2.6$ kcal/mol) formation of a complex of two benzene molecules (1-complex) separated by 3.353 Å. The lowest energy pathway for benzene dimerization (Figure 5a) is endothermic by 47.4 kcal/mol, with a very large activation energy of 77.9 kcal/mol (at M06-2X/6-31G(d)+ZPVE), such that dimerization of benzene is not expected to occur under reasonable conditions; indeed, benzene is not known to dimerize under any conditions (Table 3). This path for benzene dimerization is calculated to proceed through an asynchronous concerted biradical transition state (TS) in which the two benzene molecules are in an anti position, one above the other (Figure 5a). The dihedral angles between the two forming 1,1' and 2,2' bonds are 74.9° and 155.5°, and the C–C forming bond lengths are 1.542 and 2.246 Å, respectively (Figure 5a).⁵⁶ The TS for benzene dimerization has significant biradical character (spin contamination, $\langle S^2 \rangle = 0.75$, $\langle S^2 \rangle$ after annihilation of the first contaminant is 0.23). Alternatively (Figure 5b), the formed 1-complex can dimerize in a syn fashion via TS 1T_{syn} 1-2 with an even higher activation energy of 84.7 kcal/mol (which has biradical character of $\langle S^2 \rangle = 0.77$) leading to a syn minimum product 1P_{syn} 1-2, which is 49.5 kcal/mol less stable than the reactants (two benzene molecules). The [2+2] syn product 1P_{syn} 1-2 can rearrange into a [4+4] product 1P_{syn} 1-4, however the latter is significantly less stable than 1P_{syn} 1-2 (62.1 kcal/mol less stable than the reactants). Formation of 1P_{syn} 1-4 can go from 1P_{syn} 1-2 via 1T_{syn} 2-4 or directly from 1-complex via 1T_{syn} 1-4, both having very high activation energies of 88.4 and 89.1 kcal/mol, respectively (Figure 5b). We note that 1T_{syn} 1-4 also has some biradical character ($\langle S^2 \rangle = 0.49$). Attempts to find a stepwise mechanism for this reaction failed (see Figure S5).⁵⁷

Dissociation of benzene dimers to produce two benzene molecules was extensively studied, and there is consensus in the

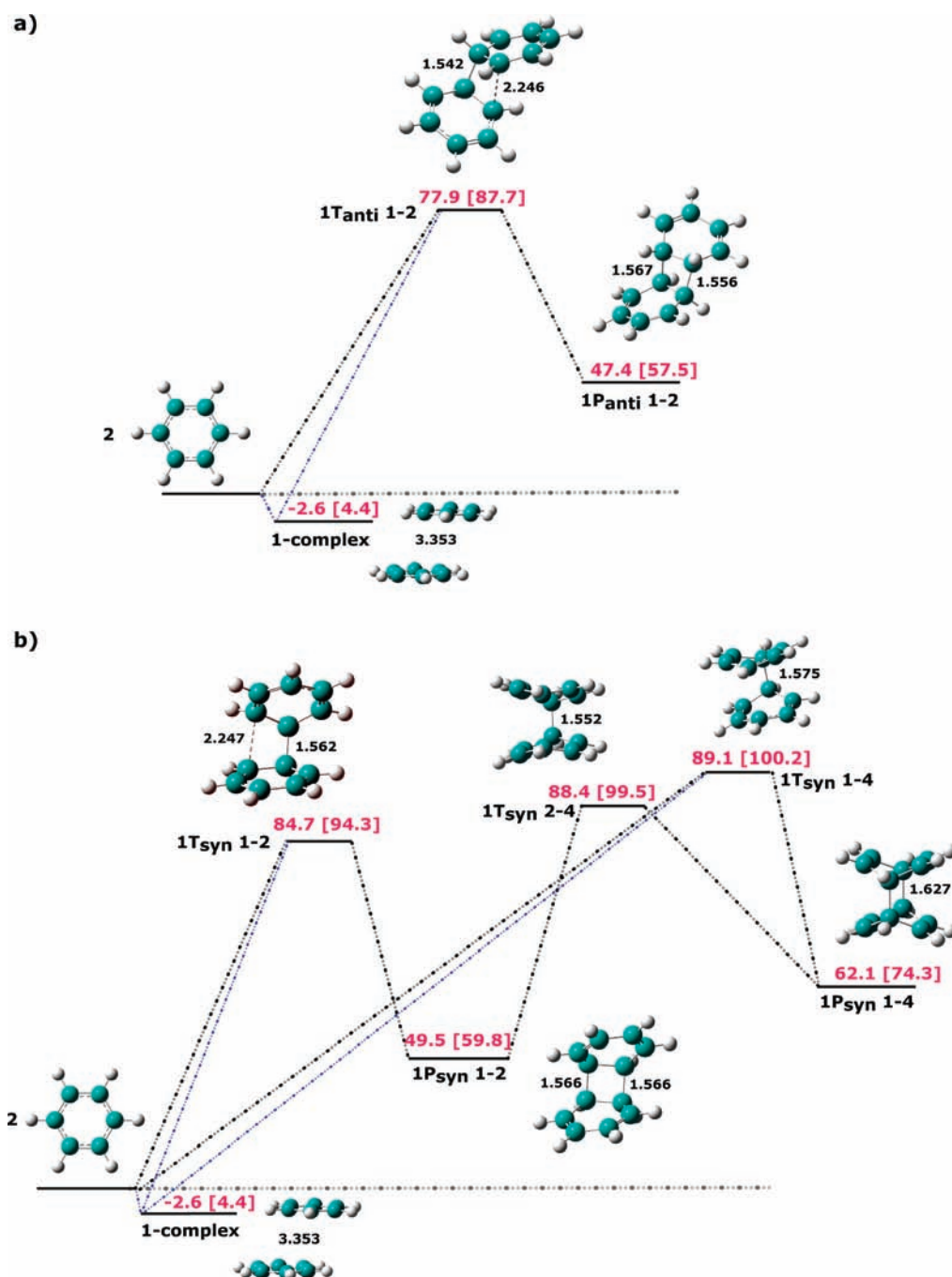


Figure 5. Reaction path for the dimerization of benzene (a) leading to an anti product and (b) leading to a syn products at M06-2X/6-31G(d)+ZPVE. Calculated energies (in kcal/mol, red) and bond lengths of newly forming C–C bonds (in Å, black) are shown. The Gibbs free energy (ΔG , in kcal/mol) values are given in brackets.⁵⁹

literature that this reaction proceeds via formation of biradical intermediates.⁵⁸ Interestingly, our extensive computational search for such an intermediate at M06-2X/6-31G(d) did not find any biradical intermediate, and the computationally obtained mechanism for benzene dimerization has only TSs connecting the reactants and products, as shown in Figure 5.

The dimerization of naphthalene can lead to both syn and anti products (Figure 6), and we found an asynchronous concerted pathway for the dimerization, similar to the mechanism of benzene dimerization. As for benzene dimerization, the lowest energy pathway for naphthalene dimerization includes formation

of an anti [2+2] product (Figure 6a). The reaction starts by formation of a complex (**2-complex**) between two naphthalene molecules. The complex is 6.1 kcal/mol more stable than the reactants. However, ΔG for such a complex is positive, +3.8 kcal/mol. The lowest energy pathway includes an anti [2+2] TS (**2T_{anti}1-2**) with an activation barrier of 57.1 kcal/mol and leads to an anti [2+2] product (**2P_{anti}1-2**) that is 23.9 kcal/mol less stable than two naphthalene molecules.⁵⁷ Another anti addition leads to an anti [4+4] product (**2P_{anti}1-4**) that is 31.2 kcal/mol less stable than the reactants and requires overcoming an activation barrier (**2T_{anti}1-4**) of 64.7 kcal/mol (Figure 6a). Syn

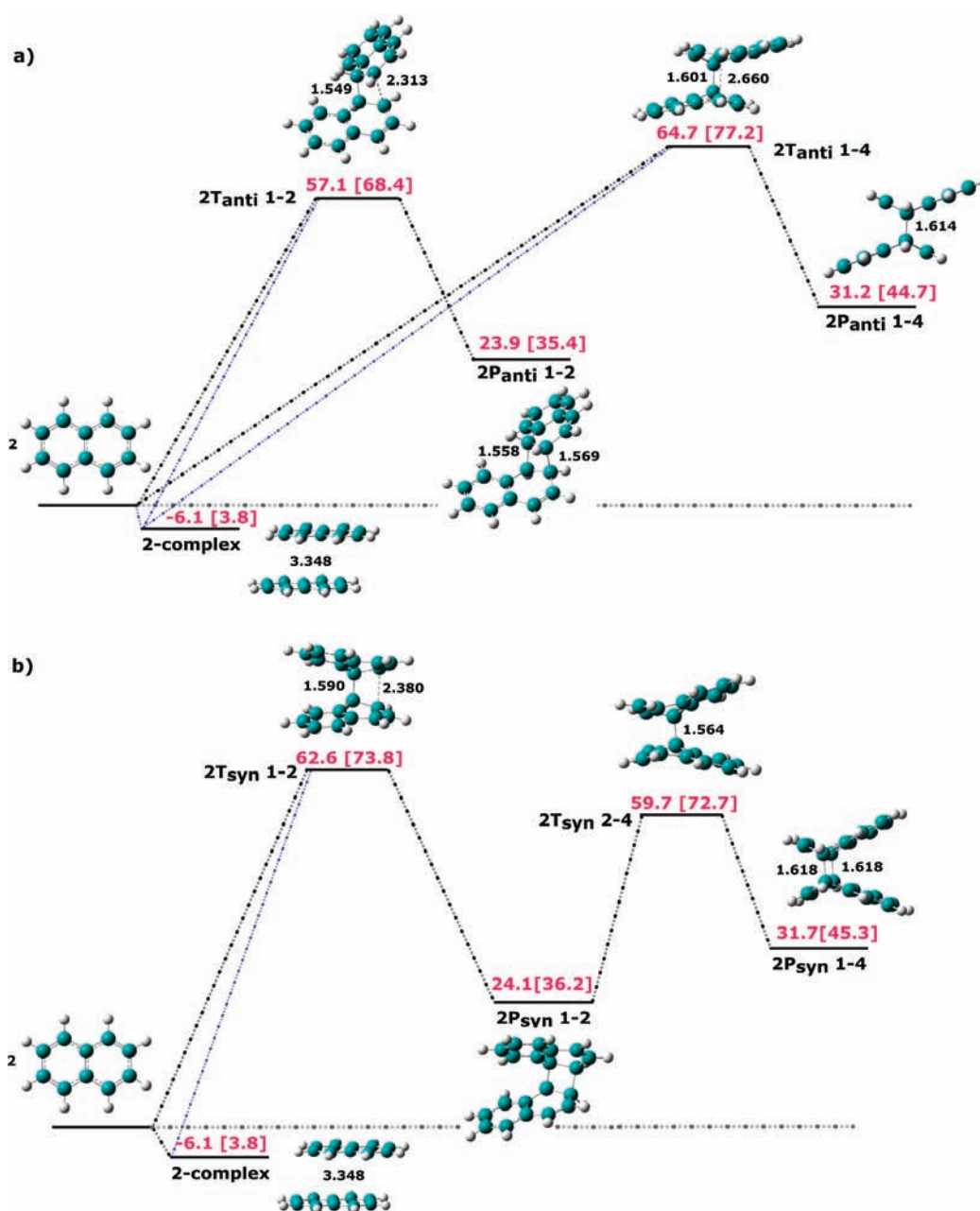


Figure 6. Reaction path for the dimerization of naphthalene (a) leading to anti products and (b) leading to syn products at M06-2X/6-31G(d)+ZPVE. Calculated energies (in kcal/mol, red) and bond lengths of newly forming C–C bonds (in Å, black) are shown. The Gibbs free energy (ΔG , in kcal/mol) values are given in brackets.⁵⁹

dimerization (Figure 6b) proceed by [2+2] addition, which can be followed by [1,3] rearrangement, however, syn [2+2] addition requires overcoming a higher activation energy (62.6 kcal/mol), and leads to a syn dimers, with slightly higher relative energy (24.1 and 31.7 kcal/mol, respectively).^{57,60} While the activation energy for the dimerization of naphthalene is 20.8 kcal/mol lower than that of benzene, the activation energy is still very high. We note that both the anti TSs and one syn TS have biradical characters ($\langle S^2 \rangle = 0.76$ for $2T_{\text{anti}}1-2$, $\langle S^2 \rangle = 0.69$ for $2T_{\text{anti}}1-4$, and $\langle S^2 \rangle = 0.72$ for $2T_{\text{syn}}1-2$) that are similar to those of the TSs for benzene dimerization ($\langle S^2 \rangle = 0.75-0.77$). Similarly to the case of benzene dimerization, $2T_{\text{syn}}2-4$ does not have biradical character.⁵⁶

Attempts to find a concerted TS without symmetry constraints for the dimerization of anthracene and pentacene yielded the biradical pathway, which involves addition in an anti fashion (T_{anti} and M_{anti}), rotation (T_{rot}) to a syn minimum (M_{in}), and closure of the ring (T_{form}) to give the respective dimer product (P) (Figures 7 and 8). Alternatively, syn attack is possible through T_{in} , and, thereafter, the same pathway is followed from M_{in} to T_{form} and dimer (P). We note that the change in the acene dimerization mechanism from concerted to stepwise is consistent with the prediction of increasing biradical character in longer acenes.^{48,49} Similarly, we expect that formation of the acene-based polymers from the long acenes will also proceed via biradical stepwise mechanism.

Table 3. Calculated Energies (ΔE) of the Transition States (T), Local Minima (M), and Products (P) and Gibbs Free Energies (ΔG) (Relative to the Two Molecules of the Respective Ground-State Acenes, in kcal/mol) at M06-2X/6-31G(d)+ZPVE for Dimerization Reactions of Benzene, Naphthalene, Anthracene, Pentacene, and Heptacene^{a,59}

	ΔE	ΔG		ΔE	ΔG
benzene			naphthalene		
1-complex	-2.6 (-3.3)	4.4	2-complex	-6.1 (-7.0)	3.8
1T _{syn} 1-2	84.7 (86.1)	94.3	2T _{syn} 1-2	62.6 (63.2)	73.8
1T _{syn} 1-4	89.1 (90.1)	100.2	2T _{syn} 2-4	59.7 (58.3)	72.7
1T _{syn} 2-4	88.4 (87.9)	99.5	2T _{anti} 1-2	57.1 (57.6)	68.4
1T _{anti} 1-2	77.9 (79.3)	87.7	2T _{anti} 1-4	64.7 (65.0)	77.2
1P _{syn} 1-4	62.1 (60.1)	74.3	2P _{syn} 1-2	24.1 (21.2)	36.2
1P _{syn} 1-2	49.5 (47.3)	59.8	2P _{syn} 1-4	31.7 (28.8)	45.3
1P _{anti} 1-2	47.4 (45.4)	57.5	2P _{anti} 1-2	23.9 (21.3)	35.4
			2P _{anti} 1-4	31.2 (28.1)	44.7
anthracene			pentacene		
3-complex	-10.4 (-10.8)	2.7	5-complex	-17.0 (-18.8)	-2.3
3T _{anti}	28.6 (28.6)	42.2	5T _{anti}	3.2 (2.6)	17.9
3M _{anti}	25.4 (24.0)	39.6	5M _{anti}	-6.1 (-8.1)	6.2
3T _{rot}	30.3 (30.2)	44.7	5T _{rot}	1.5 (0.1)	15.7
3M _{in}	21.4 (20.9)	35.4	5M _{in}	-6.8 (-8.9)	6.6
3T _{form}	33.3 (32.6)	47.7	5T _{form}	-0.3 (-1.5)	16.1
3T _{in}	21.4 (21.7)	35.7	5T _{in}	-1.1 (-1.4)	13.3
3P 2-2'	-5.4 (-9.6)	10.7	5P 3-3'	-34.3 (-39.1)	-19.9
heptacene					
7-complex	-24.4 (-27.0)	-6.7			
7T ₁	-12.1 (-14.6)	6.3			
7M ₁	-43.3 (-50.5)	-25.3			
7T ₂	-41.9 (-49.4)	-23.6			
7M ₂	-44.3 (-51.9)	-27.4			
7T ₃	-43.4 (-51.0)	-26.6			
7P-4,4'	-46.4 (-54.2)	-31.2			

^a Values in parentheses are without ZPVE.

The optimized TSs and intermediates of the dimerization of anthracene with selected structural parameters (in Å and degrees) are given in Figure 7.⁵⁶ Formation of the **3-complex** created by two anthracene molecules is exothermic by 10.4 kcal/mol (for benchmark calculations of anthracene dimers, see Supporting Information). The initial step for anthracene dimerization involves an anti attack, resulting in a TS **3T_{anti}** with an activation energy of 28.6 kcal/mol. The spin contamination of **3T_{anti}** ($\langle S^2 \rangle = 0.80$) indicates the significant biradical character of the TS. This TS is followed by the minimum **3M_{anti}**, which is 25.4 kcal/mol above the reactants ($\langle S^2 \rangle = 0.86$). **3M_{anti}** then undergoes rotation via the TS **3T_{rot}** which is 30.3 kcal/mol higher in energy than the reactants and which has a $\angle C_{10}-C_5-C_5'-C_{10}'$ dihedral angle of 118° and C_5-C_5' bond length of 1.648 Å ($\langle S^2 \rangle = 1.04$), to form a new minimum **3M_{in}**, which is 21.4 kcal/mol above the reactants ($C_5-C_5' = 1.651$ Å, $\angle C_{10}-C_5-C_5'-C_{10}' = 55^\circ$, $\langle S^2 \rangle = 0.86$). From **3M_{in}**, the reaction proceeds via **3T_{form}**, which has an activation energy of 33.3 kcal/mol ($\angle C_{10}-C_5-C_5'-C_{10}' = 0.0^\circ$, $\langle S^2 \rangle = 0.85$), to obtain the product **3P-2,2'**, which is 5.4 kcal/mol more stable than the reactants.

Alternatively, the dimerization reaction can be initiated by a syn attack via a different TS, **3T_{in}** ($\angle C_{10}-C_5-C_5'-C_{10}' = 52^\circ$, $\langle S^2 \rangle = 0.495$), which has an activation energy of 21.4 kcal/mol, followed by **3M_{in}**. Interestingly, the energy of **3T_{in}** is 7.2 and 8.9 kcal/mol lower than those of **3T_{anti}** and **3T_{rot}** respectively, where both the **3T_{anti}** and **3T_{rot}** TSs lie on the anti pathway. Thus, the syn and anti pathways for the dimerization of anthracene shown in Figure 7 are competitive reaction mechanisms; however, the pathway via **3T_{in}** is somewhat preferred. **3T_{form}** is a rate-determining step in the thermal dimerization of anthracene, and the activation energy for this dimerization is 33.3 kcal/mol at M06-2X/6-31G(d)+ZPVE, while the calculated Gibbs free energy is 47.7 kcal/mol. We note that the dimerization mechanism reported in this paper is similar to the mechanism that was calculated for the thermal reaction of the terminal ring of tetrachloropentacene, which leads to halogen elimination and the formation of acene-based polymers (through what is formally a thermal [4+2] cycloaddition).¹⁴

An experimental study of the thermal dissociation kinetics of the anthracene dimer and of anthracene dimers substituted at the 9-position in benzene solution is available.³⁸ The experimentally obtained activation energy for the thermal dissociation of the anthracene dimer is 36.3 kcal/mol.³⁸ This is very similar to the calculated activation barrier we obtained for thermal dissociation of the anthracene dimer (38.7 kcal/mol) and provides further support for the reliability of the M06-2X/6-31G(d)+ZPVE level of theory in the study of the thermal dimerization of acenes. Importantly, the experimental study concluded^{17b,38} that the thermal dissociation of anthracene dimers is a stepwise C-C bond-breaking procedure, in complete agreement with the calculated stepwise biradical mechanism presented in Figure 7.

The mechanism for pentacene dimerization (Figure 8),⁵⁶ similar to that for anthracene dimerization (Figure 7), is a biradical stepwise mechanism, but the relative energies of the intermediates and TSs for pentacene dimerization are ~ 30 kcal/mol lower than those for anthracene dimerization (except for **T_{in}** and **T_{anti}**, where the difference is about 22-25 kcal/mol). Two molecules of pentacene form a relatively strong complex (**5-complex**) with an energy of -17.0 kcal/mol. This strong complexation energy is also responsible for the low solubility of pentacene and other long acenes. The reaction starts with an anti attack, leading to TS **5T_{anti}** with an activation energy of 3.2 kcal/mol ($\langle S^2 \rangle = 1.03$) relative to the reactants (the activation energy relative to **5-complex** is significantly higher, at 20.2 kcal/mol), followed by a minimum **5M_{anti}** ($\langle S^2 \rangle = 1.08$), which is 6.1 kcal/mol more stable than the starting pentacenes. We note that the activation free energy of **5T_{anti}** is 17.9 kcal/mol relative to the reactants and 20.2 kcal/mol relative to **5-complex**. So, the activation free energy of **5T_{anti}** is relatively independent of the reference level (i.e., the two reactant molecules or **5-complex**), while the activation energy of **5T_{anti}** depends strongly on the reference level. **5M_{anti}** then undergoes rotation via **5T_{rot}** ($\angle C-C-C-C = 118^\circ$, $\langle S^2 \rangle = 1.07$), with an activation energy of 1.5 kcal/mol relative to the reactants (the activation energy of **5T_{rot}** is 7.6 kcal/mol relative to **5M_{anti}**), to form a minimum, **5M_{in}** ($\angle C-C-C-C = 52^\circ$, $\langle S^2 \rangle = 0.97$), which is 6.8 kcal/mol more stable than the starting material. Alternatively, the reaction can proceed from pentacene through the syn pathway via **5T_{in}** ($\angle C-C-C-C = 44^\circ$, $\langle S^2 \rangle = 0.22$), which is 1.1 kcal/mol more stable than the starting pentacene (but 15.9 kcal/mol higher in energy than the complex of two pentacene molecules, **5-complex**), followed by the minimum, **5M_{in}**. From **5M_{in}**, the reaction

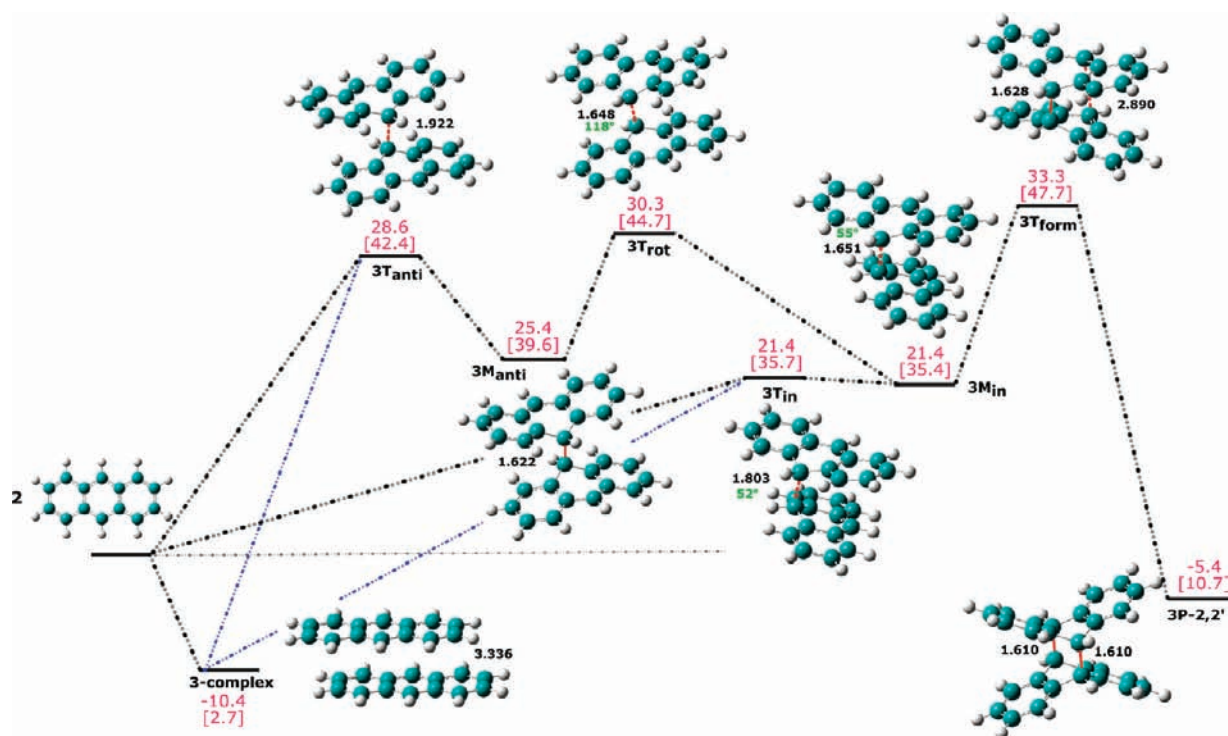


Figure 7. Reaction path for the dimerization of anthracene at M06-2X/6-31G(d)+ZPVE. Calculated energies (in kcal/mol, red), bond lengths of newly forming C–C bonds (in Å, black), and dihedral angles (green) are shown. The Gibbs free energy (ΔG , in kcal/mol) values are given in brackets.⁵⁹

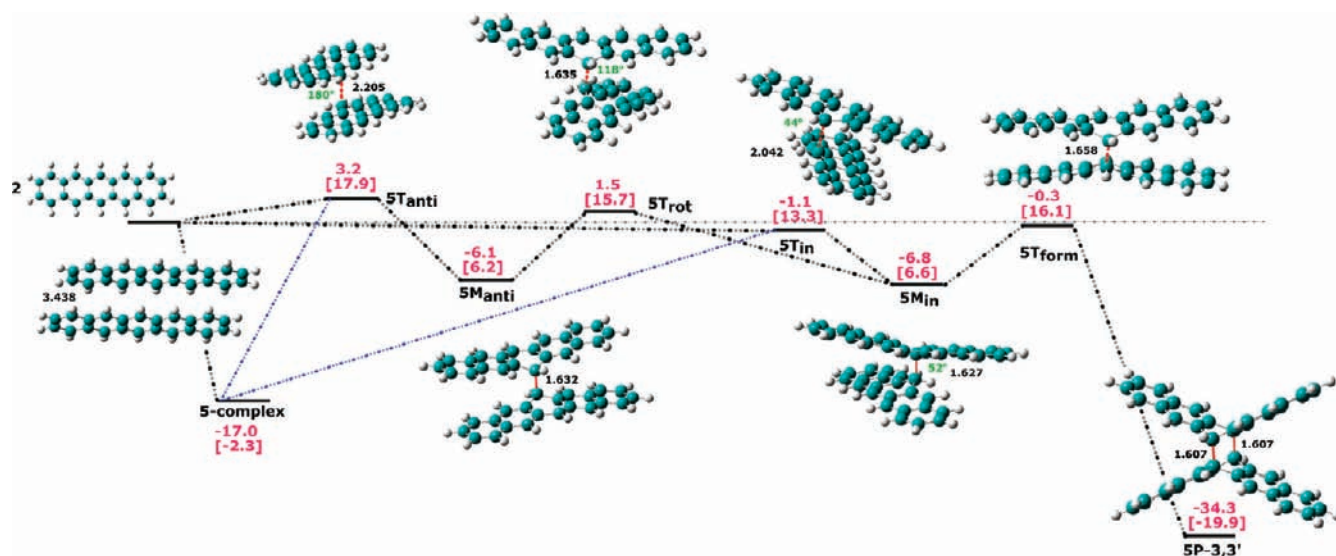


Figure 8. Reaction path for the dimerization of pentacene at M06-2X/6-31G(d)+ZPVE. Calculated energies (in kcal/mol, red), bond lengths of newly forming C–C bonds (in Å, black), and dihedral angles (green) are shown. The Gibbs free energy (ΔG , in kcal/mol) values are given in brackets.⁵⁹

proceeds via $5T_{\text{form}}$ ($\angle \text{C}-\text{C}-\text{C}-\text{C} = 0^\circ$, $\langle S^2 \rangle = 0.76$), with an activation energy of -0.3 kcal/mol relative to the starting material (and an activation energy of 6.5 kcal/mol relative to $5M_{\text{in}}$), to obtain the product $5P-3,3'$, which is 34.3 kcal/mol more stable than the two pentacene molecules. In the case of pentacene dimerization, the lowest energy pathway includes direct syn addition via $5T_{\text{in}}$ and $5T_{\text{form}}$, while anti addition via $5T_{\text{anti}}$ has higher activation barrier. In the case of anthracene dimerization, $3T_{\text{form}}$ is the highest energy stationary point (rate-determining step) for both syn and anti additions.

The mechanism for heptacene dimerization (Figure 9) is significantly different from the dimerization mechanisms for anthracene and pentacene. Heptacene dimerization is calculated to have negative activation energy relative to two heptacene molecules at M06-2X/6-31G(d)+ZPVE, which is in agreement with the literature data regarding the instability of unsubstituted heptacene even at low temperature.⁵⁵ Formation of a complex of two heptacene molecules, **7-complex**, is exothermic by 24.4 kcal/mol. The formation of **7-complex** is followed by a TS, $7T_1$ ($\langle S^2 \rangle = 1.06$), which is 12.1 kcal/mol lower than the

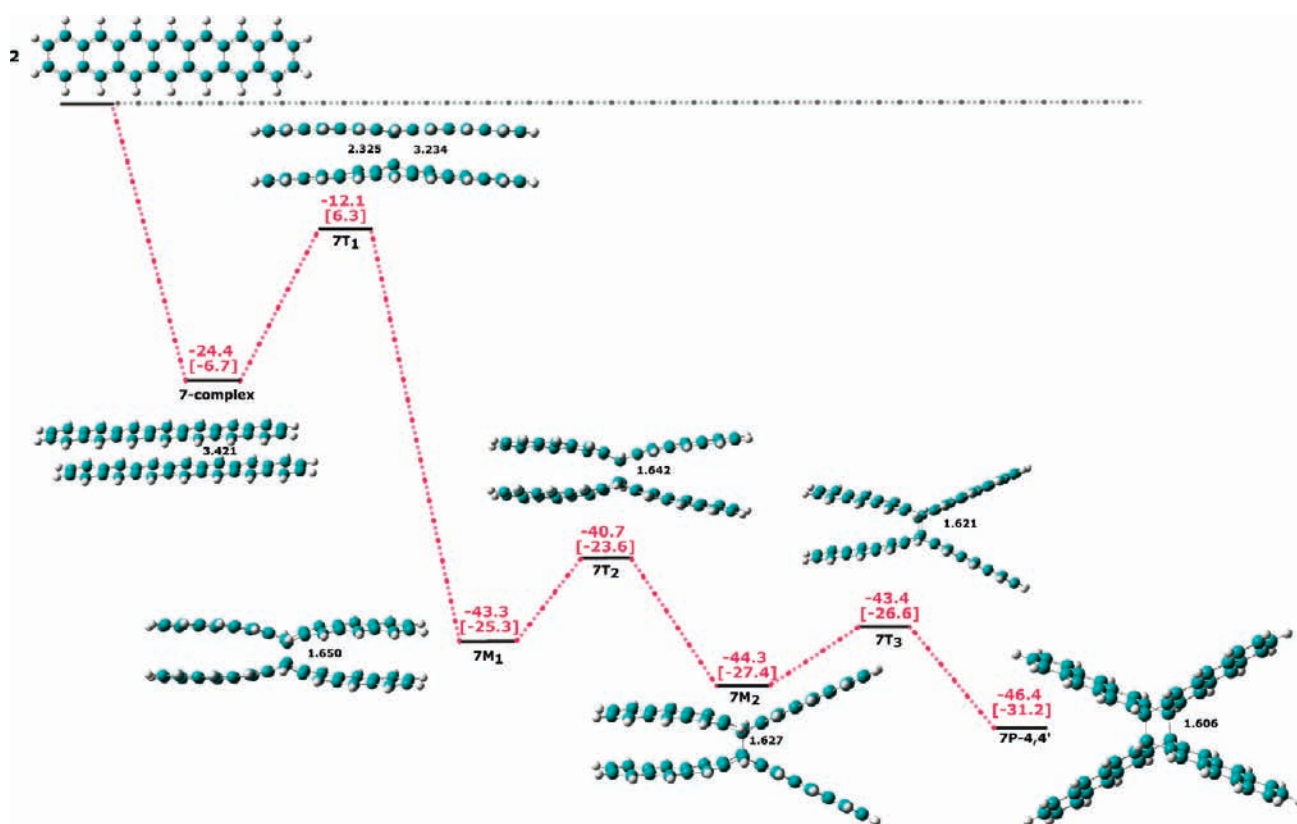


Figure 9. Reaction path for the dimerization of heptacene at M06-2X/6-31G(d)+ZPVE. Calculated energies (in kcal/mol, red), the bond lengths of newly forming C–C bonds (in Å, black) are shown. The Gibbs free energy (ΔG , in kcal/mol) values are given in brackets.⁵⁹

reactants (with activation free energy of 6.3 kcal/mol) and 12.3 kcal/mol higher than 7-complex. C–C bond formation in 7T₁ is an asymmetric process, with one of the forming C–C bonds being significantly shorter than the other (2.325 Å cf. 3.234 Å). 7T₁ leads to the minimum 7M₁, which has strong π – π interactions between the acene tails (Figure 9). This intermediate is 43.3 kcal/mol more stable than the reactants and only 3.1 kcal/mol less stable than the final product 7P-4,4'. The pathway from 7M₁ to 7P-4,4' requires an activation energy of only 2.6 kcal/mol relative to 7M₁ and proceeds via stepwise breaking of π – π interactions between the benzene units from one side of the molecule (as in 7M₂, which is obtained via 7T₂), followed by breaking of the π – π interactions on the other side of the molecule (via 7T₃). We note, however, that formation of the heptacene dimer 7P-4,4' is not thermodynamically preferred (see the section above about the formation of acene-based polymers).

We note that pentacene is very poorly soluble in organic solvents, with a solubility of $<10^{-3}$ M (at room temperature), which is at least 2 orders of magnitude lower than the reagent concentration usually used in organic reactions. Since the dimerization rate is proportional to the square of the monomer concentration $[A]$, and assuming that the monomer concentration is 3 orders of magnitude lower than a usual concentration of 0.1–0.5 M, this is the equivalent of increasing the activation barrier by 8.3 kcal/mol (at room temperature, considering that $k \propto [A]^2 e^{-\Delta G^\ddagger/RT}$) compared to second-order reactions performed at normal concentrations. Since the calculated ΔG^\ddagger of pentacene dimerization is 16.1 kcal/mol vs two isolated pentacene molecules (18.4 kcal/mol vs the complex consisting of two pentacene molecules), and considering the

low concentrations of the pentacene solution, dimerization is not expected to proceed rapidly at room temperature in solution. In the solid state, crystals of pentacene exhibit tight packing, which should significantly raise the activation barrier for dimerization because the planar structure of pentacene needs to bend strongly to form the dimerization product. Hexacenes with substituents that are not too bulky are known to undergo rapid dimerization in the dark,¹¹ in agreement with the results reported here.

In summary, the energetic barriers for acene dimerization decrease markedly as the length of the acene increases and are predicted to be 77.9, 57.1, 33.3, –0.3, and –12.1 kcal/mol, vs two isolated acene molecules, for benzene, naphthalene, anthracene, pentacene, and heptacene, respectively. The dimerization pathway for anthracene and higher acenes proceeds via a stepwise process with at least one biradical minimum. However, there is no such minimum for the dimerization of benzene and naphthalene, and these molecules have a single-step asynchronous TS.⁶¹ The thermal dimerization of acenes is a [4+4] cycloaddition, which is formally symmetry forbidden; however, we note that the activation barriers for long oligoacenes are very low. The acene dimerizations studied here have significant activation entropies (for example, the activation entropy for anthracene dimerization is –56.4 cal/K mol).

CONCLUSIONS

Our computational study of the mechanism and products of the thermal dimerization of acenes reveals several important points. We propose that, for hexacene and higher acenes, polymerization to produce an acene-based polymer is favored over the usual dimerization, and we suggest that acene-based polymers of the

type shown in Figure 4 are formed during the self-reactivity (decomposition) of long unsubstituted acenes. Only the thermodynamics of the formation of the acene-based polymer have been studied here, and they may be kinetically disfavored products compared to acene dimers, so that acene polymers may only form experimentally from long acenes such as heptacene, octacene, and even longer acenes. This computational prediction calls for experimental reinvestigation of the dimerization of long unsubstituted acenes.

For the dimerization of benzene and naphthalene, a single-step asynchronous transition state was found. The dimerization reactions of anthracene and pentacene proceed via syn or anti TSs and biradical minima through stepwise biradical pathways. A different reaction mechanism was found for heptacene dimerization, which includes collapsing of the heptacene dimer complex to the product via a multistep process. The activation barriers for thermal dimerization decrease rapidly with increasing acene chain length and are predicted to be 77.9, 57.1, 33.3, -0.3, and -12.1 kcal/mol, vs two isolated acene molecules, for benzene, naphthalene, anthracene, pentacene, and heptacene, respectively, calculated at M06-2X/6-31G(d)+ZPVE. If the activation energy is calculated vs the initially formed complex of two acene molecules, then the predicted barriers are 80.5, 63.2, 43.7, 16.7, and 12.3 kcal/mol, respectively. Dimerization of heptacene clearly proceeds without any barrier relative to the two heptacene reactant molecules.

Comparison of computational results obtained in this work with scantily available experimental data shows excellent agreement regarding thermodynamics of anthracene dimerization³⁵ and activation energy³⁸ for dissociation of anthracene dimer. Both experimental and computational results agree that the thermal dissociation of anthracene dimer is a stepwise C-C bond-breaking process;^{17b,38} however, our computational results disagree with previous findings³⁸ that predict the presence of a biradical intermediate in dissociation of benzene dimers.

For anthracene and longer acenes, the dimer is more stable than the monomer on the ΔE potential energy surface, and, from tetracene, it is also more stable on the ΔG potential energy surface. Aryl substitution at the most reactive meso-carbon atoms of the central ring (for example, at the 3,3' position of pentacene) protects against dimerization at that ring; however, it cannot protect efficiently against dimerization at rings neighboring the central rings (for example, via the 2,2' positions of pentacene). We believe that this study advances understanding of acene reactivity and will aid in the design and preparation of stable acenes for applications as organic electronic materials.

■ ASSOCIATED CONTENT

S Supporting Information. Calculated absolute energies at different levels of theory for all stationary points mentioned in the paper as well as the coordinates of their optimized structures, additional pictures of TSs and forming C-C bond scans, and complete ref 27. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(60) Our numerous attempts to find the TS from the reactants directly to $2P_{\text{syn}}\mathbf{1-4}$ (which would be $2T_{\text{syn}}\mathbf{1-2}$) failed, in contrast to a similar TS ($1T_{\text{syn}}\mathbf{1-4}$) that was found in the case of benzene dimerization.

(61) It was suggested previously (Navarro-Vázquez, A.; Prall, M.; Schreiner, P. R. *Org. Lett.* **2004**, *6*, 2981–2984) that for Cope-type rearrangements “a nonconcerted reaction takes place when biradical intermediates are stabilized either by allyl or aromatic resonance”. Anthracene and pentacene dimerizations, indeed, have a stabilized benzyl biradical intermediate and proceed via a nonconcerted pathway. However, for the dimerization of benzene and naphthalene, only a concerted pathway was found, even though the dimerization TSs have a stabilized allyl or benzyl biradical. We believe that this is because of the very high activation energies calculated for benzene and naphthalene dimerization.