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Rotation of Aryl Groups in 9,10-Diarylphenanthrenes: Does the Rotational Barrier Become Lower as the Backbone Becomes More Crowded?

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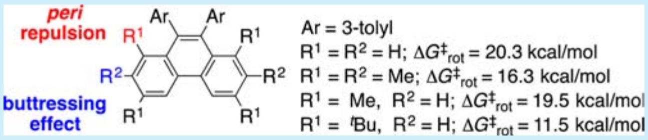
Supporting Information

ABSTRACT: A series of 9,10-diarylphenanthrenes was prepared, and their structures and dynamic behaviors were both theoretically and experimentally investigated. A more twisted and crowded phenanthrene backbone was associated with a lower barrier to the rotation of an aryl group.



Recently, the rotational behaviors of pendant aryl groups in 1,2,3,6,7,8-hexamethyl-9,10-di(3-tolyl)phenanthrene (**1**) were examined to elucidate the pseudorotation of persubstituted [8]circulene **2** (Figure 1).[1] The measured barrier for **1** (16.3 kcal/mol) is smaller than those for 9,10-di(3-tolyl)-phenanthrene (**3**) (20.3 kcal/mol) and 9,10-bis[(3-bromomethyl)phenyl]phenanthrene (**4**) (21.5 kcal/mol).[2] However, methyl groups at the C-1/8 and C-2/7 positions in the phenanthryl framework of **1** would contribute to *peri* repulsions[3] and buttressing effects,[4] respectively, increasing steric hindrance and the barrier to the aryl rotation. This statement is supported by the fact that 2,7-diisopropoxy-1,8-diarylnaphthalene[5] and 2,7-dimethyl-1,8-diarylanthracene[6] have higher barriers to rotation than 1,8-diarylnaphthalene[7] and 1,8-diarylanthracene,[6b,c] respectively. Additionally, the rotation of an aryl group in 9,10-di(2-tolyl)phenanthrene (**5**) requires much more energy (around 37 kcal/mol)[2a] than in **3**. To understand the unusually low rotational barrier exhibited by **1**, a series of 9,10-diarylphenanthrenes was structurally analyzed, and their dynamic behaviors were systematically studied.

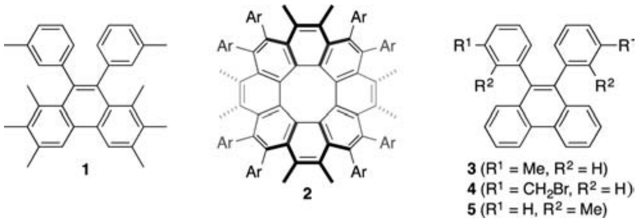
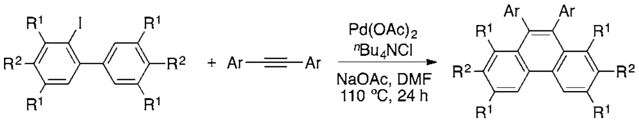


Figure 1. 9,10-Diarylphenanthrenes and [8]circulene.

Numerous 9,10-diarylphenanthrenes were synthesized by the palladium-catalyzed benzannulation of 2-iodobiphenyl with 1,2-diarylethyne (Table 1), following Larock's protocol.[8] The prepared compounds contained *syn*- and *anti*-rotamer, depending on the relative position of two substituents in the pendant aryl groups. Additional conformers are associated with a nonplanar backbone. In most cases, the products contained only two conformers as an inseparable mixture in nearly equal amounts, and **9** was observed as a single conformer, based on its NMR spectra recorded at room temperature. In contrast, the chromatogram of 9,10-di(2-chlorophenyl)phenanthrene (**10**) included two clearly separated spots. The first fraction (with a higher R_f value) and the second fraction were identified as *anti*-**10** and *syn*-**10** on the basis of X-ray crystallography. A very small amount of one conformer, which was assumed to be *anti*-1,2,3,6,7,8-hexamethyl-9,10-di(2-tolyl)phenanthrene (*anti*-**11**), with >95% isomeric purity was obtained by collecting the first 10% of the eluate. Notably, the methyl signal of the 2-tolyl group in *syn*-**11** (1.33 ppm in CDCl$_3$) was extremely upfield in the ^{1}H NMR spectrum, in contrast to those of the corresponding in *anti*-**11** (2.31 ppm) and **5**[2a] (2.04 and 1.94 ppm). Strong ring-current shielding should be responsible for the high-field shift of *syn*-**11**.[9]

Table 1. Synthesis of Phenanthrenes[a]



phenanthrene	substituents	yield (%)
3	R^1 = R^2 = H; Ar = 3-CH$_3$C$_6$H$_4$	95
6	R^1 = R^2 = Me; Ar = 3-^{t}BuC$_6$H$_4$	58
7	R^1 = R^2 = OMe; Ar = 3-CH$_3$C$_6$H$_4$	78
8	R^1 = Me, R^2 = H; Ar = 3-CH$_3$C$_6$H$_4$	68
9	R^1 = ^{t}Bu, R^2 = H; Ar = 3-CH$_3$C$_6$H$_4$	57
10	R^1 = R^2 = H; Ar = 2–Cl-C$_6$H$_4$	91[b]
11	R^1 = R^2 = Me; Ar = 2-CH$_3$–C$_6$H$_4$	72

[a] The reaction was conducted on a 0.5 mmol scale. [b] The reaction was conducted with LiCl, instead of ^{n}Bu$_4$NCl, for 3 days, and two rotamers *syn*-**10** and *anti*-**10** (ratio 44:56) were obtained.

X-ray-quality crystals of *anti*-**1**, *syn*-**10**, *anti*-**10**, and *syn*-**11**[10] were obtained by slow evaporation of a mixed CH$_2$Cl$_2$/MeOH solvent (Figure 2). The phenanthrene moieties in both *syn*-**10**

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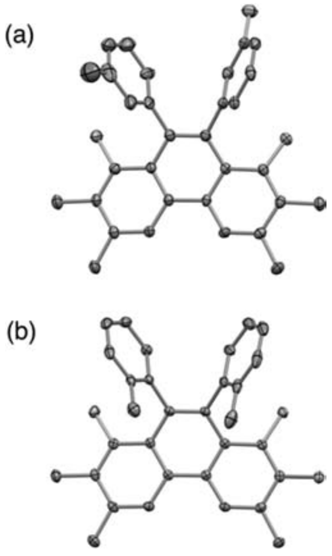

Figure 2. Crystallographic structures of (a) *anti*-**1** and (b) *syn*-**11**. Only carbon atoms are shown for clarity, and the thermal ellipsoids are set at 50% probability.

and *anti*-**10** are nearly planar, whereas *anti*-**1** contains a C_s-symmetric phenanthryl framework, which is highly distorted from planarity with a torsion angle θ_1 (Ca−C9−C8a−C8) of 20.7° (Figure 3). The two 3-tolyl groups align in parallel with each other, with a torsion angle θ_2 (Ca−C9−C10−Cb) of only 2.0°. Notably, the 9,10-diarylphenanthrenyl subunit in the saddle-shaped [8]circulene **2** exhibits C_2-symmetry, different from **1**. Like *anti*-**1**, *syn*-**11** contains a C_s-symmetric phenanthrene backbone with similar torsion angles θ_1 and θ_2.

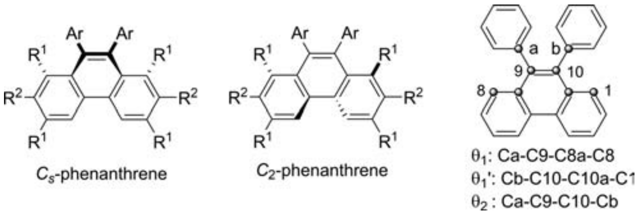

Figure 3. C_s- and C_2-symmetric phenanthrene backbone.

The optimized geometries of the aforementioned compounds were calculated at the B3LYP/6-31G** level using Gaussian 09 (Table 2),[11] and the C_s-symmetric phenanthrene was found to be more stable than its C_2-conformer (see below), consistent with the X-ray crystallographic results. Therefore, the structure of the twisted phenanthrene with C_s-symmetry was analyzed herein, except where otherwise specified. The *syn*- and *anti*-rotamers, except **5** and **10**, have practically identical potential energies in the ground state with an energy difference (ΔE_{sa}) of less than 0.5 kcal/mol. The *peri*-repulsion between a pendant aryl ring and its neighboring group at the C-1/8 positions causes deplanarity. Their torsion angles θ_1 follow the order **9** > **1** ≈ **6** ≈ **11** > **8** > **7** > **3** ≈ **5** ≈ **10**, consistent with the effective van der Waals' radii of the substituents [^{t}Bu (3.60 Å) > Me (1.80 Å) > OMe (1.52 Å) > H (1.20 Å)].[12] Although **7** contains six methoxy groups, its framework is slightly more twisted than those of the parent series, including **3**, **5**, and **10**. The buttressing effect of substituents at the C-2/7 positions also contributes remarkably to the twisting of the framework, as revealed by the fact that θ_1 in **1** exceeds that in **8**. Notably, replacing the methyl group in the 3-tolyl substituent with a *tert*-butyl group did not further deform the backbone because **1** and **6** have almost equal torsion angles θ_1 of about 24°.

The dynamic behaviors of numerous 9,10-di(3-tolyl)-phenanthrenes in suitable solvents were examined using a 500 MHz ^{1}H NMR instrument and variable-temperature (VT) techniques.[13] The frequent rotation of 3-tolyl groups is revealed by coalescence of their methyl signals. The height of the rotational barrier ($\Delta G^{\ddagger}_{rot}$) depends strongly on the substituents on the phenanthrene backbone, and its values follow the order **3** ≈ **7** > **8** > **1** > **9** (Table 2). 1,3,6,8-Tetra-*tert*-butylphenanthrene **9** with bulky substituents at the C-1/8 positions has the lowest barrier of 11.8 kcal/mol (11.5 kcal/mol based on *tert*-butyl signals). 1,2,3,6,7,8-Hexamethylphenanthrene **1**, whose structural rigidity is supported by substituents at the C-2/7 positions, demonstrates a lower barrier (16.3 kcal/mol) than 1,3,5,7-tetramethylphenanthrene **8** (19.5 kcal/mol). Less twisted phenanthrene **3** and hexamethoxyphenanthrene **7** exhibit comparable rotational barriers of around 20 kcal/mol. The role of the substituent at the C-3 position of the phenyl pendant group is not critical to effect rotation of the aryl group, as revealed by the fact that **1** and **6** (15.5 kcal/mol) have similar barriers to rotation. The results of all of the aforementioned experiments demonstrate that a crowded and rigid phenan-

Table 2. Selected Physical and Structural Data of 9,10-Diarylphenanthrenes[a]

	$\Delta G^{\ddagger}_{rot}$ (kcal/mol)			structural analysis				
				ground state		transition state		
	exptl	B3LYP	ΔE_{sa} (kcal/mol)	θ_1, θ_1' (deg)	θ_2 (deg)	θ_1, θ_1' (deg)	θ_2 (deg)	$\Delta\theta_1$, $\Delta\theta_1'$ (deg)
1	16.3[b]	15.3	0.2	24.4, 24.4 (20.7, 19.1)[d]	0 (2.0)[d]	55.7, 18.5	25.0	31.3, −5.9
3	20.3 (20.3)[c]	20.6	0.0	1.6, 1.3	0.1	39.7, 2.4	27.8	38.1, 1.1
5	37.8[c]	39.3	1.1	2.2, 2.2	1.2	46.4, 4.7	31.9	44.2, 2.5
6	15.8, 15.5	15.2	0.0	24.7, 24.2	0.4	56.1, 18.3	25.4	31.4, −5.9
7	20.0	22.1	0.3	9.5, 8.6	0.5	55.4, 16.1	26.0	45.9, 7.5
8	19.5	18.1	0.0	18.1, 18.1	0	54.9, 18.2	25.1	36.8, 0.1
9	11.8, 11.5	11.2	0.0	39.6, 39.4	0.7	60.4, 29.7	21.8	20.8, −9.7
10		39.4	2.3	0.6, 0.6 (5.3, 0.1)[d]	0 (0.6)[d]	46.6, 8.4	34.9	46.0, 7.8
11	33.8	33.1	−0.4	25.3, 15.9 (24.1, 18.4)[d]	7.1 (4.2)[d]	66.4, 13.6	31.6	41.1, −2.3

[a] Theoretical studies were calculated at the B3LYP/6-31G** level implemented with zero-point energy corrections. The structure of the most stable conformer with a C_s-symmetric backbone was analyzed. ΔE_{sa} (= $E_{syn} - E_{anti}$) is the difference between the potential energies of the *syn*- and *anti*-rotamers. $\Delta\theta_1$ (= $\theta_{1,TS} - \theta_{1,GS}$) is the deformation angle between $\theta_{1,GS}$ and $\theta_{1,TS}$. [b] Reference 1a. [c] Reference 2a. [d] X-ray structural data.

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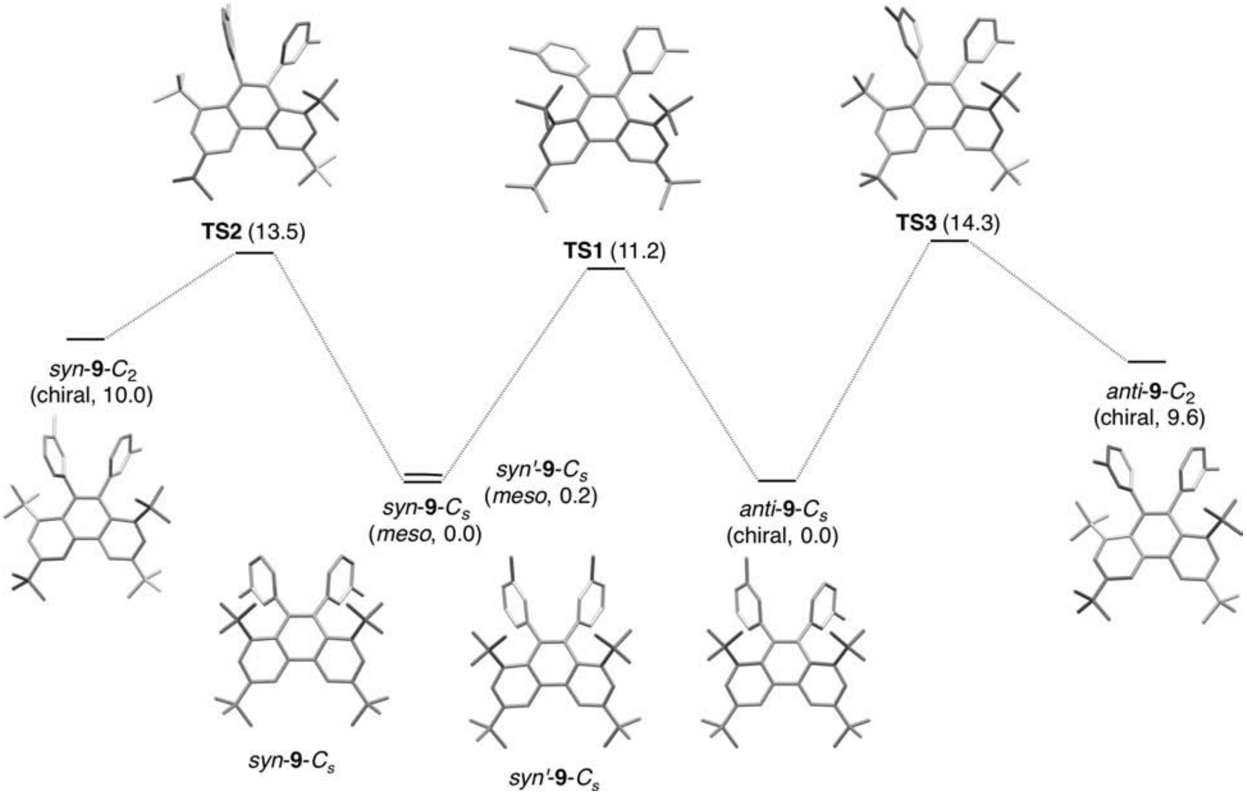

Figure 4. Energy profile for dynamic behaviors of phenanthrene **9**. Values in parentheses refer to the relative energies in kcal/mol.

threne framework lowers the barrier to rotation of a 3-tolyl group.

The high rotational barrier of 1,2,3,6,7,8-hexamethyl-9,10-di(2-tolyl)phenanthrene (**11**) cannot be determined by performing VT ^{1}H NMR experiments because the interconversion between two conformers is very slow and the coalescence of methyl signals (δ = 1.33 and 2.31 ppm) cannot be observed even at 433 K. Therefore, the kinetic diastereomerization of a solution of *anti*-**11** in 1,2-dichlorobenzene-d_4 at 160 °C was investigated and found to have a barrier ($\Delta G^{\ddagger}_{\mathrm{rot}}$) of 33.8 kcal/mol, which is around 4 kcal/mol smaller than that of **5** (see Table 2 and the Supporting Information). The equilibrium constant [(*syn*-**11**)]/[(*anti*-**11**)] was 1.56 (after 110 min), indicating that the former is more stable than the latter by about 0.4 kcal/mol, which is consistent with theory. The calculated barriers to the *syn*−*anti* interconversion of **5** and **10** are almost equal because the substituents methyl group and chlorine (1.75 Å)[12] have very similar van der Waals' radii.

Notably, a new conformer of 1,3,6,8-tetra-*tert*-butyl-9,10-di(3-tolyl)phenanthrene (**9**) was observed at low temperature, in addition to *syn*-**9** and *anti*-**9**. Upon cooling of the sample to 193 K, a highly broad methyl band, centered at 2.12 ppm (303 K), was progressively split into four sharp peaks with an integral ratio of 1:1:1:2. The new conformer was assigned as *syn'*-**9** (Figure 4), in which both methyl groups are arranged in a *syn*-manner and directly face two *tert*-butyl groups at C-1/8 positions, in contrast to their backward alignment with the *tert*-butyl groups in *syn*-**9**. The ratio of the amounts of *syn*-**9** to *anti*-**9** to *syn'*-**9** was 2:2:1, agreeing closely with the theoretical results that *syn*-**9** and *anti*-**9** are more stable than *syn'*-**9** by 0.2 kcal/mol. The above results suggest that two bulky *tert*-butyl groups create a highly twisted phenanthrene backbone, making *syn'*-**9** distinguishable from two other rotamers. The ^{1}H NMR spectra of a solution of mixed *syn*-**11** and *anti*-**11** in CD_2Cl_2 at 183 and 298 K are nearly identical, suggesting that these signals correspond to an equilibrium structure of C_s- and C_2-symmetric backbones because the barriers to the interconversion among several conformers are lower than the thermal energy in this temperature range (see below). This statement also explains why the ^{1}H NMR spectra of most nonplanar phenanthrenes, such as **1**, **6**, **8**, and **11**, at room temperature simply include signals from only two conformers.

At the B3LYP/6-31G** level of theory, the mechanism of *syn*−*anti* interconversion by aryl rotation was studied and verified using the pseudo-intrinsic reaction coordinate (pseudo-IRC). This dynamic process involves a C_1-symmetric transition state (TS1), in which the aryl substituents are bent away from each other, preventing clashes (Figure 4), and the highly twisted structure can be easily described in terms of its torsion angles θ_1, θ_1', and θ_2. The calculated barriers to the aryl rotation agree closely with the experimental outcomes (Table 2). The heights of the barriers to the rotations for both the 2-tolyl- and 3-tolyl-substituted subseries correlate closely with $\Delta\theta_1$ (= $\theta_{1,\mathrm{TS}} - \theta_{1,\mathrm{GS}}$), which is an indicator of the structural deformation of the transition state relative to the ground state. A compound with a high rotational barrier has a high $\Delta\theta_1$. For example, $\Delta\theta_1$ and $\Delta G^{\ddagger}_{\mathrm{rot}}$ for **3** and **9** were evaluated as 38.1°/20.2 kcal/mol and 20.6°/11.5 kcal/mol, respectively. This relationship demonstrates that the formation of a twisted transition state from an almost planar phenanthrene ($\theta_{1,\mathrm{GS}}$ = 1.6° in **3**) requires more energy than that for the essentially nonplanar compound **9** ($\theta_{1,\mathrm{GS}}$ = 39.8°). Similarly, less twisted phenanthrenes **7** and **8** have higher values of $\Delta\theta_1$ and $\Delta G^{\ddagger}_{\mathrm{rot}}$. Therefore, a bulky substituent at the critical position on the dynamic behaviors "destabilizes" the potential energy in the ground state,[14] lowering the barrier to the aryl rotation.[15]

Figure 4 presents the dynamic behaviors of **9**, and its most stable conformers are denoted as *syn*-**9**-C_s and *anti*-**9**-C_s that the point symmetry refers to the C_s-symmetric backbones, not the geometry of the whole molecule. The interconversions among *syn*-**9**-C_s, *anti*-**9**-C_s, and *syn*′-**9**-C_s proceed via the transition state TS1 with a barrier of around 11 kcal/mol. *syn*-**9**-C_s and *anti*-**9**-C_s were observed to be more stable than *syn*-**9**-C_2 and *anti*-**9**-C_2 by 10.0 and 9.6 kcal/mol, respectively. The interconversion between C_s- and C_2-symmetric backbones involved the bending of an aryl ring or its neighboring *tert*-butyl group via a transition state (TS2 or TS3) in which these two substituents align in an almost coplanar manner. The barriers to the conversions of *anti*-**9**-C_s to *anti*-**9**-C_2 and *syn*-**9**-C_s to *syn*-**9**-C_2 were thus theoretically evaluated as 14.3 and 13.5 kcal/mol, respectively. In contrast, less bulky substituents at C-1/8 positions in other examples strongly lowered the potential energies of their C_2-conformers and the barriers to C_s-to-C_2 conversion. For instance, *syn*- or *anti*-**1**-C_2 are approximately 1.9 kcal/mol less stable than their C_s-conformers.

In conclusion, the syntheses, structures, and dynamic properties of highly substituted 9,10-diarylphenanthrenes have been systematically and comprehensively investigated both theoretically and experimentally. The steric hindrances that were caused by the pendant aryl groups and the phenanthrene backbone oppositely affected the barrier to the rotation of the pendant aryl groups. As expected, a sterically congested aryl group destabilizes the transition state in its rotation, raising the barrier to rotation. A highly substituted 9,10-diarylphenanthrene with a crowded and nonplanar core has a low barrier to the rotation of an aryl substituent owing to its high-strain ground state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03343.

Complete ref 11, experimental procedures, characterization data, and computational studies (PDF)
X-ray crystallographic data for *anti*-**1** (CIF)
X-ray crystallographic data for *syn*-**10** (CIF)
X-ray crystallographic data for *anti*-**10** (CIF)
X-ray crystallographic data for *syn*-**11** (CIF)

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Notes

The authors declare no competing financial interest.

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