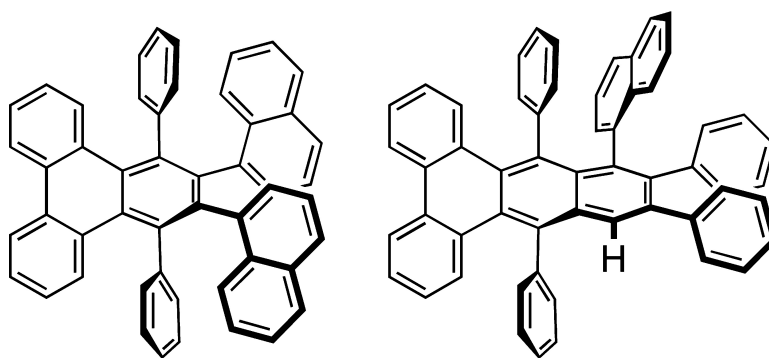


Configurationally Stable Longitudinally Twisted Polycyclic Aromatic Compounds

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J. Am. Chem. Soc., **2008**, 130 (48), 16435-16441 • DOI: 10.1021/ja806958x • Publication Date (Web): 08 November 2008

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Configurational Stability of Longitudinally Twisted Polycyclic Aromatic Compounds

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Abstract: Two strategies for the synthesis of configurationally stable twisted polycyclic aromatic compounds (PACs) were pursued. The first approach employed dissymmetrically positioned 1-naphthyl substituents to bias the direction of twist in highly substituted PACs. 2,3-Bis(1-naphthyl)-1,4-diphenyltriphenylene (**7**) was prepared, and its meso *cis*-dinaphthyl and enantiomeric *trans*-dinaphthyl isomers were resolved by preparative supercritical fluid chromatography (SFC) on chiral supports. Similarly, several naphthyl-substituted derivatives of the more highly twisted 9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene (**2**) were prepared. Of these, 10-(1-naphthyl)-9,11,12,14-tetraphenylbenzo[*b*]triphenylene (**13**) was resolved by SFC on a chiral support. The pure enantiomers of *trans*-**7** showed moderately large specific rotations ($[\alpha]_D^{25} = -330$ and $+320^\circ$), but the specific rotations for the enantiomers of **13** were unexpectedly small ($[\alpha]_D^{25} = -23$ and $+23^\circ$). Computational studies suggest that the latter result is due to presence of a minor conformation of **13** possessing a larger rotation of opposite sign than the major conformation. Both **7** and **13** showed strong circular dichroism and moderately strong circularly polarized luminescence. A byproduct of these syntheses was 9,10,19,21-tetraphenyldiphenanthro[9,10-*b*:9,10-*h*]carbazole (**15**), a very crowded carbazole that exhibits an 81° end-to-end twist but is not resolvable. In the second approach, the large, twisted, polycyclic aromatic ligand 9,10,11,12,13,14-hexaphenylbenzo[*h*]naphtho[2,3-*f*]quinoline (**21**, an aza-**2**) was used to prepare the chiral, cyclometallated iridium(III) complex **4**. The ligand **21** was prepared via an unusually stable benzannulated norbornadienone, for which the free energy of activation for decarbonylation was a remarkable 33.5 kcal/mol. The iridium complex **4** proved to be configurationally stable and resolvable by analytical HPLC on chiral supports, but the low solubility of **4** prevented its resolution on a preparative scale. A much more soluble dibutyl analogue of **4** (complex **28**) was then prepared, but it was not resolvable on any of the available media.

Introduction

Longitudinally twisted polycyclic aromatic compounds (PACs) have been objects of our attention for over 20 years,^{1,2} but only recently have any of these highly strained, strongly helical molecules been resolved into pure enantiomers. Pentacene **1**, which has a 144° end-to-end twist, has been resolved by chromatography on a chiral support, and its pure enantiomers display exceptionally high specific rotations ($[\alpha]_D^{25} = 7400^\circ$).^{3,4} However, **1** racemizes with a half-life of 9.3 h at 25 °C ($\Delta G_{\text{rac}}^\ddagger = 23.8$ kcal/mol)^{3,4} and thus is less than ideal for extensive studies of its chiroptical properties and certainly unsuitable for any materials applications that depend upon enantiomeric purity.

All of the other acene derivatives that are known to possess end-to-end twists of 60° or more^{5–9} undergo rapid racemization at room temperature. These stand in contrast to the helicenes, which have comparable specific rotations (hexahelicene, $[\alpha]_D^{24} = 3640^\circ$; [13]helicene, $[\alpha]_D^{24} = 8840^\circ$) but generally high barriers to racemization ($\Delta G_{\text{rac}}^\ddagger = 36–44$ kcal/mol).¹⁰

How might longitudinally twisted PACs be made configurationally stable?¹¹ The most direct approach is to extend the structure of **1** to give even more highly twisted molecules, for which the transition state(s) for racemization would be extremely

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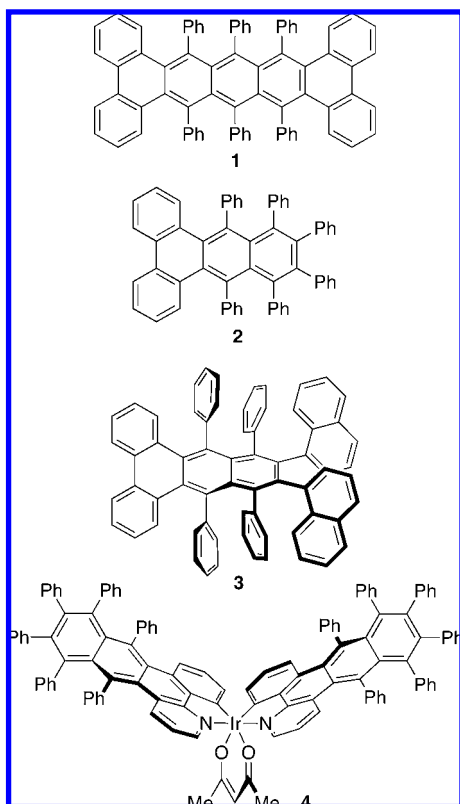
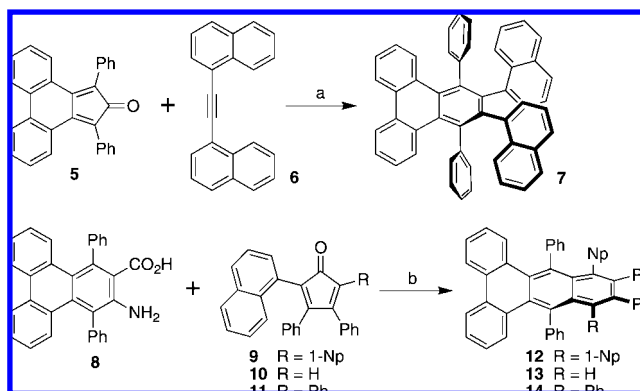
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(11) This and related questions are without a doubt the most frequent queries after lectures on twisted acenes by R.A.P.

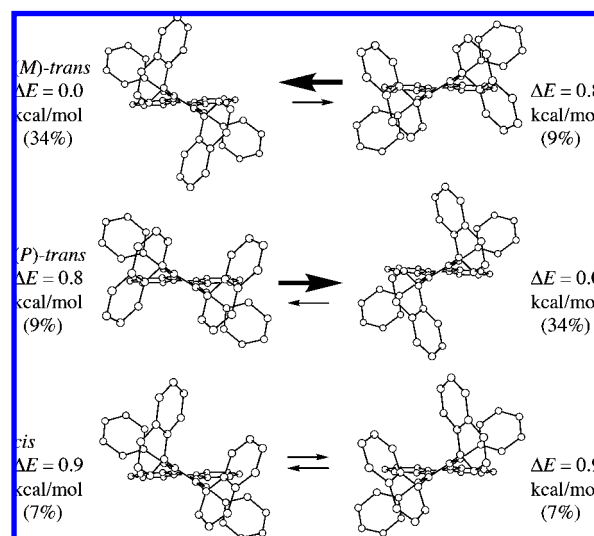
crowded and likely ensure a high barrier.¹² However, the synthesis of such molecules is most challenging. Perhaps a better question is, “Can *easily prepared* twisted PACs be made configurationally stable?” Compound **2** provides an excellent framework from which to build such molecules: it possesses a 60° end-to-end twist⁷ and is easily prepared by the reaction of a bulky aryne with a cyclopentadienone,⁷ and its precursors contain easily modified structural elements; however, **2** does racemize rapidly at room temperature. In this paper, we explore two methods for conferring configurational stability to twisted PACs related to **2**.

The first strategy is to attach bulky groups to a twisted PAC in a dissymmetric orientation. For example, the benzo[*b*]triphenylene core of compound **3**, like **2**, has a low barrier for twist inversion, but the two “twistomers” are diastereomeric because the naphthyl-group rotations are impossible at room temperature. A significant difference in the energies of the diastereomers would yield a preferred twist direction. The second approach is to use twisted PACs as ligands for chiral metal complexes. Thus, a configurationally stable iridium complex might have cyclometalating ligands elaborated into highly twisted PACs, as in **4**. The twistomers of **4** are diastereomeric, and once again, any energy difference leads to a preferred twist orientation. In this paper, we report examples of both approaches.

Scheme 1^a

^a Conditions: (a) Ph₂O, 300 °C, 26%; (b) isoamyl nitrite, 1,2-dichloroethane, reflux. Yields in (b): **12**, trace; **13**, 0.6%; **14**, 0.1%.

Scheme 2



that enforces the twist, and more complex substituents have been avoided because of problems that arise when slow aryl rotation results in conformational diastereomerism. However, if the rotation of aryl substituents is frozen at room temperature, then the resulting stereoisomerism can be used to advantage.

Consider the case of 2,3-bis(1-naphthyl)-1,4-diphenyltriphenylene (**7**) (Scheme 1). The triphenylene core of the corresponding all-phenyl-substituted compound, 1,2,3,4-tetraphenyltriphenylene, is twisted by ~30°,¹³ and it exists as a rapidly interconverting set of two enantiomeric conformations. However, with two naphthyl groups in place of phenyls, compound **7** possesses six conformations, whose B3LYP/6-31G(d)-optimized structures and relative energies are illustrated in Scheme 2.

The rotation of 1-naphthyl groups in crowded polyarylenebenzenes is extremely slow—at least as slow as the rotation barriers for *o*-tolyl groups in similar compounds, which range from 33 to 38 kcal/mol.^{14–16} For this reason, compound **7** under normal conditions exists as a mixture of *cis* and *trans* isomers with respect to the orientation of the two naphthyl groups, and the

Results and Discussion

Twist Bias by Dissymmetrically Disposed Naphthyl Substituents. Approximately 10 acene derivatives have been prepared with end-to-end twists in excess of 60°,^{2–9} but all of them undergo twist inversion (enantiomerization) on time scales ranging from microseconds to hours at room temperature. In most of these compounds, phenyl groups provide the steric bulk

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C_2 -symmetric trans isomer possesses enantiomeric M and P forms. These three isomers cannot interconvert at room temperature, but the inversion of the twist of their triphenylene cores remains rapid. In the case of the cis isomer, twist inversion rapidly interconverts enantiomeric conformations of equal energy. At room temperature, the time-averaged structure is C_s -symmetric; thus, the cis isomer is a meso compound. However, twist inversion in the trans isomers interconverts diastereomeric conformations of unequal energy; thus, the orientation of the naphthyl groups determines the principal direction of the twist of the triphenylene core. In the case of compound **7**, the Boltzmann distribution of the various conformations indicates that the compound should exist at equilibrium at 298 K as a 17:3 mixture of trans and cis isomers, and the direction of the twists in the trans isomers should be biased by roughly 4:1 in favor of the more stable conformation (Scheme 2).

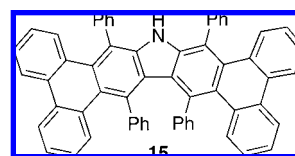
A similar analysis can be performed for 10,13-bis(1-naphthyl)-9,11,12,14-tetraphenylbenzo[*b*]triphenylene (**12**). B3LYP/6-31G(d) calculations again find six conformations for compound **12**. In this case, the energy differences between the conformations are greater than for **7**, so at equilibrium at 298 K, compound **12** should be an 8:1 mixture of trans and cis isomers, and the direction of the twists in the trans isomers should be biased by more than 80:1 in favor of the more stable conformation. The related compounds **13** and **14** contain only one naphthyl group each, and thus, the twist bias is somewhat smaller than for **12**, but there is also no possibility of cis/trans isomerism, which is a distinct advantage.

Synthesis and Resolution of Triphenylene 7. The crowded triphenylene **7** was chosen as the first “twist bias” target because its synthesis (Scheme 1) was expected to be trivial. The two starting materials, phenyclone^{13,17} (**5**) and dinaphthylacetylene **6**,¹⁸ were in hand, and warming them in diphenyl ether at 300 °C gave compound **7** as a mixture of cis and trans isomers in 26% yield. Although inseparable by ordinary chromatography, the cis (meso) and trans (chiral) isomers were cleanly separated by supercritical fluid chromatography (SFC) on a Chiralcel OD-H column (see the Supporting Information). A 7:3 trans–cis ratio was observed, which is lower than the calculated 17:3 Boltzmann distribution for 298 K. However, the synthesis was carried out at 573 K, where the calculated distribution would be 77:23, which is much closer to the observed ratio (and certainly well within reasonable errors for the B3LYP/6-31G(d) calculations), and the conformational distribution would have been frozen upon rapid cooling. A high barrier to naphthyl-group rotation was demonstrated by heating pure *cis-7* in DMSO at 180 °C for 24 h without detectable isomerization to the trans isomer. This establishes a lower limit of ~39 kcal/mol for the $\Delta G_{\text{rot}}^{\ddagger}$ of **7**. The purified *trans-7* was resolved by SFC on a Chiralpak AD-H column to give (+)- and (–)-enantiomers with specific rotations ($[\alpha]_{\text{D}}^{25}$) of +320 and –330°, respectively.

Synthesis of Naphthyl-Substituted Benzo[*b*]triphenylenes. The syntheses of compounds **12–14** are direct but inefficient. The preparation of the cyclopentadienone precursor of **12**, 2,5-bis(1-naphthyl)-3,4-diphenylcyclopentadienone (**9**), is not fully

described in the open literature but only outlined in a review.^{19–21} Its synthesis from 1,3-bis(1-naphthyl)acetone²² is reported in Experimental Procedures (see the Supporting Information). Diazotization of the anthranilic acid **8**⁷ (to give a crowded aryne) in the presence of **9** provided only traces of compound **12**, as judged by mass spectrometry, and all of the samples were contaminated with the giant carbazole **15**. The low yield of **12** was discouraging; furthermore, only the *cis*-dinaphthyl isomer was likely to have been formed under the mild conditions of this reaction, because both naphthyl groups of cyclopentadienone **9** must be oriented away from the approaching aryne for the cycloaddition and the temperature is not high enough to equilibrate the naphthyl orientations. The necessity to perform an extra thermolysis and purification to obtain the *trans*-dinaphthyl isomer from an already problematic reaction led us to abandon **12** and turn to the synthesis of the mononaphthyl compounds **13** and **14**, for which there is less steric hindrance to the cycloaddition and no cis/trans isomerism.

Compound **13** was prepared in a manner analogous to that



used for **12**. The requisite cyclopentadienone **10** was formed by double aldol condensation of (1-naphthyl)acetone²³ with benzil followed by dehydration. Diazotization of **8** in the presence of **10** gave compound **13** in 0.6% yield; thus, even one naphthyl group appears to strongly inhibit the aryne addition, as judged by comparison with the synthesis of the all-phenyl-substituted **2** (24% yield). However, the low yield is also due in part to the difficulty of separating **13** from carbazole **15**; the two compounds coelute in many chromatographic systems. Thus, when compound **8** was diazotized in the absence of a cyclopentadienone, carbazole **15** was isolated relatively easily in 8% yield. All such diazotization reactions, with or without a diene, produce numerous byproducts.²⁴ With **8**, the most abundant of these is 1,4-diphenyltriphenylene, which is formed in 10–15% yield.

Though inefficient, the synthesis described above provided sufficient compound **13** for its resolution by means of SFC on a Chiralpak AD-H column. The pure (+)- and (–)-enantiomers, although configurationally stable, exhibited only modest specific rotations ($[\alpha]_{\text{D}}^{25}$) of +23 and –23°, respectively. Given that compound **1** and its derivatives, with end-to-end twists of 138–144°, display $[\alpha]_{\text{D}}$ values ranging from 5200 to 7400°⁴ and compound **7**, with a B3LYP/6-31G(d)-calculated end-to-end twist of 32°, shows an $[\alpha]_{\text{D}}$ value of 330°, the small rotations of **13** were quite a surprise for a compound with a calculated end-to-end twist of 58°. However, calculations of the specific rotations of these molecules at the B3LYP/6-31G(d) level (using the dipole electric field polarizabilities) were able to shed some light on this result. In the case of compound **7**, the two M-trans twistomers (top row of Scheme 2) were calculated to have

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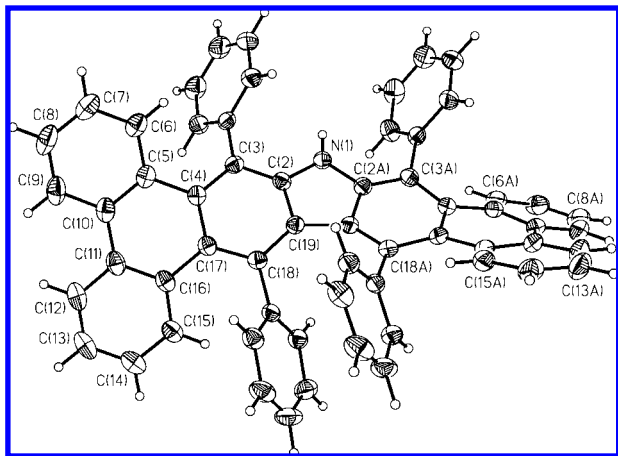


Figure 1. Molecular structure of compound **15**. Thermal ellipsoids are drawn at the 50% probability level.

specific rotations of $+526$ and -342° for the major and minor conformations, respectively. The Boltzmann-weighted sum of the two rotations is approximately $+344^\circ$, in remarkable agreement with the experimental rotation measurements. However, for compound **13**, the major and minor twistomers were calculated to have specific rotations of $+184$ and -238° , respectively; thus, the absolute magnitudes of the rotations are smaller than for **7** and the minor component has the stronger rotation. In this case, the calculated energy difference is 1.1 kcal/mol (for an 84:16 ratio of twistomers), yielding a Boltzmann-weighted sum of the rotations of 116° . This is higher than the experimental value, but the results provide a reasonable explanation for the observed low rotation.

The final member of this series, compound **14**, was isolated in a dismal 0.1% yield from the reaction of **8** and cyclopentadienone **11**. This inexplicably low yield, combined with the disappointing results for **13**, discouraged any attempts to resolve compound **14** on a preparative scale.

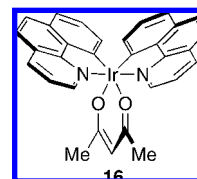
Molecular Structure of Carbazole 15. We have frequently observed octaphenylcarbazole²⁴ as a byproduct of the diazotization of tetraphenylanthranilic acid (**19**); thus, the isolation of the giant carbazole **15** upon diazotization of **8** was not a surprise. However, this polycycle is quite crowded, and molecular mechanics calculations indicated that it should have a very large end-to-end twist. Fortunately, compound **15** crystallized easily, so its X-ray structure could be determined; its molecular structure is shown in Figure 1.

Carbazole **15** crystallized in the space group $C2/c$, and since the molecule lies on a special position, it possesses crystallographic C_2 symmetry. The twisted polycyclic core of **15** resembles a two-bladed propeller with the N–H bond as the “axle”. The C(10)–C(11)–C(11A)–C(10A) torsion angle is 80.8° , which is larger than the end-to-end twists of all but three other twisted acenes.^{3,4,9} However, all attempts to resolve **15** by chromatography on chiral supports, even at 0°C , were unsuccessful, and thus, its barrier to racemization is likely to be less than 20 kcal/mol.

Twist Bias by Fusion to a Configurationally Stable Metal Complex. A second way to confer configurational stability to a twisted acene is to attach it to a chiral metal complex. As in the cases of compounds **7** and **13**, the barrier to twist inversion remains low, but the resulting twistomers are diastereomeric; thus, one twistomer must be preferred to a greater or lesser degree. The specific choice of metal complex hinged on two

other criteria. Strong circularly polarized luminescence (CPL) is one of the properties of interest for these compounds, so a strongly luminescent metal complex is to be preferred. In addition, preliminary studies showed that cationic chiral metal complexes, such as derivatives of ruthenium(II) tris(phenanthroline), were much more difficult to resolve chromatographically than neutral metal complexes such as iridium(III) bis(benzo[*h*]quinolino-*N,C*¹⁰)acetylacetonate (**16**).²⁵

Our prior experience with these and related cyclometalated



iridium complexes^{26–28} led to the choice of compound **16** as the parent for a family of configurationally stable metal complexes bearing twisted acene ligands. For use as a reference, a sample of the highly luminescent **16** was prepared and resolved by preparative HPLC on a Chiralpak AD column, giving (–)– and (+)–enantiomers with specific rotations ($[\alpha]_D^{25}$) of -340 and $+360^\circ$, respectively. The relative ease of this endeavor encouraged us to prepare similar complexes with highly twisted ligands.

Synthesis of Iridium Complex 4. The initial synthetic target was compound **4**, a derivative of compound **16** in which the benzo[*h*]quinoline ligands have been replaced by 9,10,11,12,13,14-hexaphenylbenzo[*h*]naphtho[2,3-*f*]quinoline (**21**) (Scheme 3). As noted above, the hydrocarbon 9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene (**2**) (Scheme 1), which is isosteric with **21**, possesses a 60° end-to-end twist.⁷ The synthesis of **21**, like those of many twisted hydrocarbons, requires the addition of a crowded aryl to a crowded cyclopentadienone. First, aldol condensation of benzo[*h*]quinoline-5,6-dione²⁹ (**17**) and 1,3-diphenylacetone gave cyclopentadienone **18**. This material was used without purification for the cycloaddition of **18** and tetraphenylbenzynes, generated by diazotization of tetraphenylanthranilic acid (**19**),⁸ to form the adduct **20** in 18% yield from compound **17**.

This “norbornadienone” adduct **20** was quite unexpected because the decarbonylation of such compounds almost always occurs rapidly at the temperature of the tetraphenylbenzynes addition (80°C). However, X-ray analysis of a crystal of compound **20** unambiguously confirmed the result, and the molecular structure of **20** is illustrated in Figure 2. Compound **20** possesses evenly distributed, moderate strain, as judged by the observed bond distances in the norbornadiene core, all of which were roughly 0.04 \AA longer than the canonical sp^3 – sp^2 C–C bond distance of 1.51 \AA : C(9)–C(8B), $1.545(4)\text{ \AA}$; C(9)–C(9A), $1.552(4)\text{ \AA}$; C(9)–C(15), $1.548(4)\text{ \AA}$; C(14)–C(13A), $1.550(4)\text{ \AA}$; C(14)–C(14A), $1.545(4)\text{ \AA}$; and C(14)–C(15), $1.550(4)\text{ \AA}$.

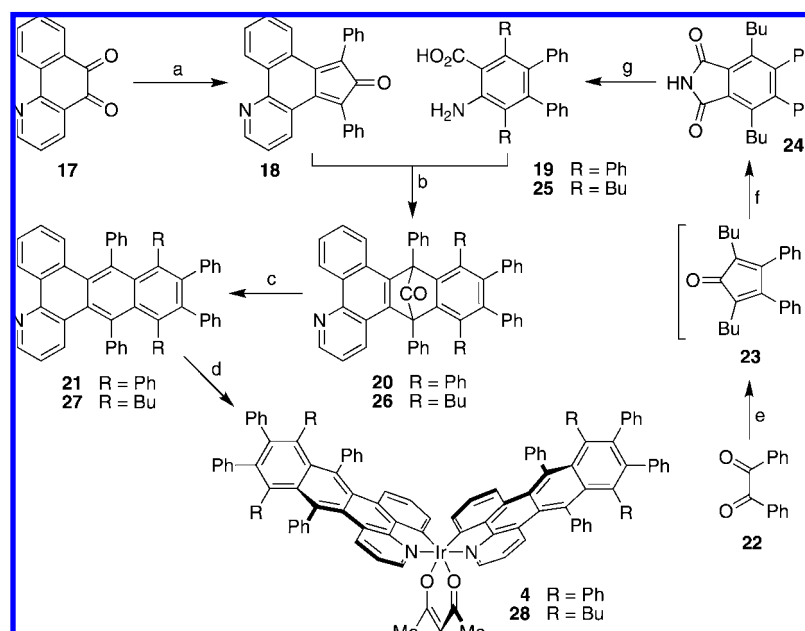
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Scheme 3^a

^a Conditions: (a) 1,3-diphenylacetone, KOH, MeOH; (b) isoamyl nitrite, DCE (yields from **17**: **20**, 18%; **26**, 21%); (c) PhNO₂, 200 °C (yields: **21**, 77%; **27**, 37%); (d) IrCl₃, 2-methoxyethanol, H₂O followed by 2,4-pentanedione, Na₂CO₃, 2-ethoxyethanol (yields: **4**, 8%; **28**, 4%); (e) 6-undecanone, KOH, EtOH followed by Ac₂O, H₂SO₄; (f) maleimide, PhNO₂, 210 °C (yield: 36% from **22**); (g) NaOCl, NaOH, MeOH followed by KOH, *n*-PrOH, reflux (yield: 90%).

Only a handful of even moderately stable norbornadienones are known, and the Cambridge Structural Database³⁰ contains only three crystallographically characterized examples of such compounds, all of which are crowded molecules.^{31–33} Compound **20** is perhaps the most robust norbornadienone thus far observed; it is completely stable at room temperature and decarbonylates with a half-life of 40 min at 180 °C to give the desired twisted ligand **21**. The kinetics of decarbonylation were determined by monitoring the ¹H NMR spectrum of **20** in DMSO-*d*₆ at various temperatures; the relative concentrations of **20** and **21** were followed by integration of their characteristic aromatic resonances. The reaction was first-order with rate constants $k_{433\text{K}} = 3.47 \times 10^{-5} \text{ s}^{-1}$, $k_{443\text{K}} = 1.00 \times 10^{-4} \text{ s}^{-1}$, and $k_{453\text{K}} = 2.86 \times 10^{-4} \text{ s}^{-1}$ (see the Supporting Information). From these data the following parameter values were calculated: $E_a = 41.5 \pm 1.5 \text{ kcal/mol}$, $\Delta H^\ddagger_{443\text{K}} = 40.6 \pm 1.5 \text{ kcal/mol}$, $\Delta S^\ddagger_{443\text{K}} = 16 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1}$, and $\Delta G^\ddagger_{443\text{K}} = 33.5 \pm 1.5 \text{ kcal/mol}$.

The preparative decarbonylation of **20** was conducted in nitrobenzene at 200 °C, giving **21** in 77% yield. The ¹H and ¹³C NMR spectra of compound **21** possess numerous highly broadened resonances resulting from dynamic exchange processes at room temperature, a feature that complicates the interpretation of the spectra. Fortunately, a single crystal of compound **21** was obtained, and X-ray analysis revealed the molecular structure shown in Figure 2. As expected, compound **21** possesses an end-to-end twist of 56°. Proton NMR spectra of **21** were recorded in toluene-*d*₈ at a variety of temperatures from 223 to 363 K, and several coalescence events occur

between 283 and 303 K (see the Supporting Information). Although the pairs of exchanging resonances cannot be conclusively identified, these data give a limiting range of free energies of activation for the dynamic processes involved (almost certainly phenyl rotations and probably the twist inversion as well) of 12–15 kcal/mol.

With ligand **21** in hand, the preparation of complex **4** was relatively straightforward. Initial reaction of 2 equiv of **21** with 1 equiv of IrCl₃ gave an intermediate μ -chloro-bridged iridium dimer, and treatment of this material with 2,4-pentanedione and base gave complex **4** in 8% overall yield after purification by preparative TLC. Although no X-ray structure of **4** was obtained, its constitution was confirmed by the expected NMR resonances for both the acetylacetonate and twisted ligands (including broadening of the latter), the molecular ion in the MALDI mass spectrum, and the characteristic UV spectrum of this brilliant-orange compound. Compound **4** is soluble in chlorinated organic solvents but quite insoluble in the alcohols and hydrocarbons that are permissible solvents for the available chiral chromatographic media. Thus, it proved possible to resolve complex **4** *analytically* on a Chiralcel OD column (see the Supporting Information), but its *preparative* resolution was out of the question because of the low solubility.

Synthesis of Butyl-Substituted Iridium Complex 28. The low solubility of compound **4** led us to consider a variety of more soluble alternatives, and we speculated that perhaps the addition of alkyl groups to complex **4** would enhance its solubility. First, the reaction of **21** with IrCl₃ and 2,2,6,6-tetramethyl-3,5-heptanedione (in order to place two *tert*-butyl groups on the enolate ligand) was examined, but none of the desired complex was formed in several attempts, perhaps because of steric hindrance. Second, an analogue of compound **21** with *tert*-butyl groups at the para positions of the C9 and C14 phenyl groups was prepared (data not shown), but this ligand inexplicably failed to give the desired iridium complex, even though the *tert*-

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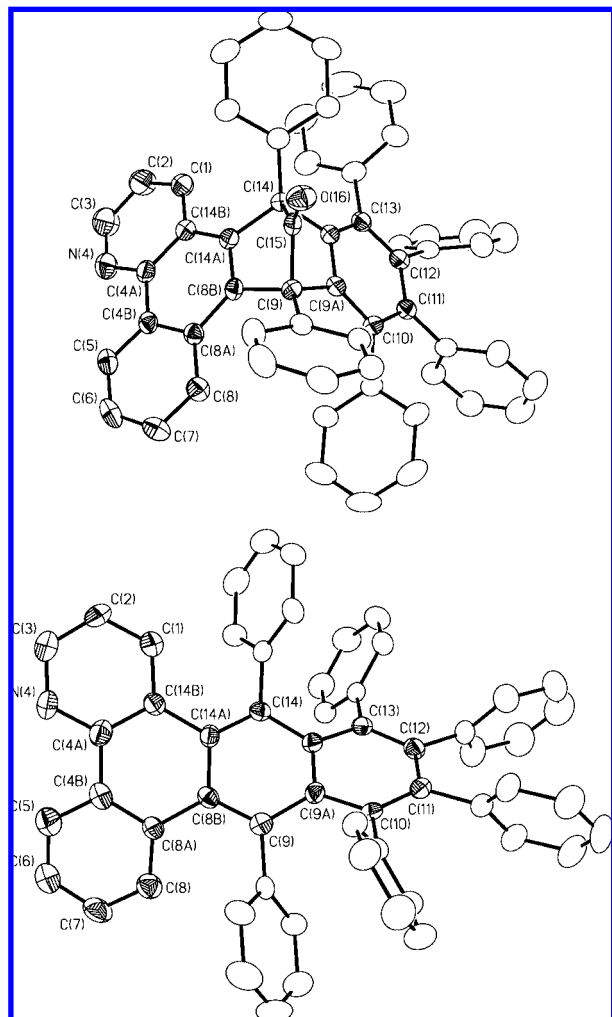


Figure 2. Molecular structures of (top) **20** and (bottom) **21**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

butyl groups are far from the metal. In a third, ultimately successful approach, compound **27**, an analogue of compound **21** having *n*-butyl groups in place of the C10 and C13 phenyls, was prepared and then used to prepare complex **28** (Scheme 3).

The key intermediate is 3,6-dibutyl-4,5-diphenylanthranilic acid (**25**), which was prepared in a manner analogous to that for **19**.⁸ The aldol condensation of benzil (**22**) and 6-undecanone gave 2,5-dibutyl-3,4-diphenylcyclopentadienone (**23**) as a red oil. The Diels–Alder reaction of **23** with maleimide and the dehydrogenation of the adduct were achieved by heating the two starting materials in refluxing nitrobenzene; the product imide **24** was obtained in 36% overall yield from benzil. Hofmann degradation of **24** followed by a stringent base hydrolysis then gave the desired amino acid **25** in 90% yield. Diazotization of **25** in the presence of cyclopentadienone **18** formed adduct **26** (23%), and decarbonylation of this norbornadienone in hot nitrobenzene gave the ligand **27** (37%). Finally, the two-step reaction of **27** with IrCl₃ and 2,4-pentanedione produced complex **28** in a low 4% yield.

Compound **28** proved to be quite soluble in many organic solvents. However, although its solubility properties are nearly ideal, all attempts to resolve it by chromatography (both HPLC and SFC) on a chiral support proved unsuccessful.

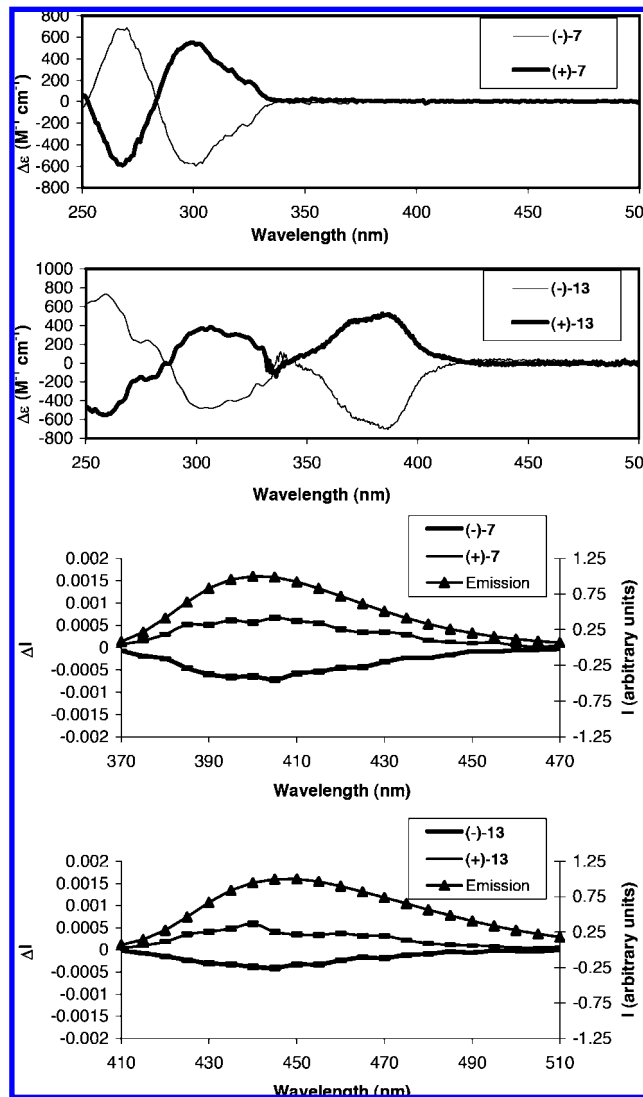


Figure 3. (top) CD and (bottom) CPL spectra of compounds **7** and **13**. All of the spectra were recorded in chloroform solution.

Chiroptical Properties of Twisted Acenes 7 and 13. In addition to the conventional specific rotation measurements for compounds **7** and **13**, their circular dichroism (CD) and CPL spectra were measured (Figure 3).³⁴ The CD results display the mirror-image spectra expected for the two enantiomers of each compound as well as large values of $\Delta\epsilon$, as high as 5% of ϵ ($\Delta\epsilon \approx 700 \text{ M}^{-1} \text{ cm}^{-1}$ vs $\epsilon = 14\,000 \text{ M}^{-1} \text{ cm}^{-1}$) in the case of the 370 nm absorption band of compound **13**.

Circularly polarized luminescence^{35,36} (emission having different intensities for the left and right circularly polarized components) is of increasing interest because of its *potential* application in stereoscopic displays³⁷ if only a material with a large enough emission dissymmetry could be prepared. In the present examples, the luminescence maxima for compounds **7** and **13** occur at 400 and 445 nm, respectively, with correspond-

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ing emission dissymmetries [$g_{em} = 2(I_{left} - I_{right})/(I_{left} + I_{right})$] of 1.4×10^{-3} and 0.8×10^{-3} . While it is easy to understand that the longer-wavelength emission occurs in the larger π system (**13**), the differences in emission dissymmetry cannot be easily rationalized. However, the magnitudes of the CPL for **7** and **13** are comparable to those of other large polycyclic aromatic compounds³⁸ but not nearly so large as the CPL sometimes observed in lanthanide-containing systems.³⁹

Conclusion

Two synthetic approaches were investigated that might confer configurational stability to polyphenyl, polycyclic aromatic compounds with large longitudinal twists. Both were successful: two configurationally stable twisted hydrocarbons (**7** and **13**) and two chiral metal complexes containing twisted polycyclic aromatic ligands (**4** and **28**) were prepared. However, some problems arose during chromatographic resolution of the racemates. In each case, numerous chromatographic media and solvent combinations were examined to find one (if any) that gave satisfactory resolution. Furthermore, the resulting resolutions were idiosyncratic: the successful resolution of a compound by one method provided little insight into the best method for the resolution of a closely related molecule. Ultimately, the two twisted hydrocarbons (**7** and **13**) were resolved preparatively, and their chiroptical properties were examined; however, the preparative resolution of the chiral metal complex **4** was confounded by solubility problems, and no conditions were found for resolving its more highly soluble derivative **28**.

Interestingly, the chiroptical properties of compounds **7** and **13** did not obviously parallel their structures. The modestly

twisted compound **7** (calculated end-to-end twist: 32°) exhibited a reasonably large specific rotation ($[\alpha]_D = 330^\circ$) and strong circular dichroism, but the more highly twisted **13** (58°) showed a small specific rotation ($[\alpha]_D = 23^\circ$) but a strong CD spectrum. Similarly, the emission dissymmetry of the less-twisted **7** was significantly stronger than that of the more-twisted **13**.

Clearly, a great deal of information is needed for the truly effective *design* of materials with exceptional chiroptical properties. Apart from the accurate prediction of the chiroptical properties themselves, one must find stable molecules that can be easily synthesized, easily dissolved, and easily resolved. At present, no twisted polycyclic aromatic compound meets all of these criteria, but the present studies show that some such molecules should exist.

Acknowledgment. This work was supported by National Science Foundation Grants CHE-0614879 (to R.A.P.), CHE-0449755, and DMR-0605621 (to S.B.), which are gratefully acknowledged.

Supporting Information Available: Experimental Procedures, containing full details of the syntheses of compounds **4**, **7**, **9**, **13–15**, **20**, **21**, and **24–28** as well as procedures for the chromatographic resolution of **4**, **7**, **13**, and **16**, measurement of the kinetics of decarbonylation of **20**, and dynamic NMR studies of **21**; ^1H and/or ^{13}C NMR spectra of compounds **4**, **7**, **13**, **15**, **20**, **21**, and **24–28**; CIF files for the structure determinations of compounds **15**, **20**, and **21**; chromatograms illustrating the resolution of compounds **4**, **7**, and **13**; kinetic data for the decarbonylation of compound **20**; and dynamic NMR data for compound **21**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA806958X

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