Synthesis and Structure of Longitudinally Twisted Polycyclic Aromatic Hydrocarbons

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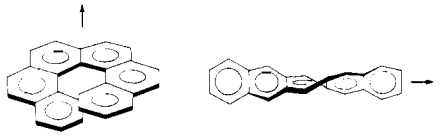
Abstract: The syntheses of 9,18-diphenyl-, 9,18-bis(4-chlorophenyl)-, 9,18-bis[4-(trifluoromethyl)phenyl]-, and 9,18-bis(4-isopropylphenyl)tetrabenz[*a,c,h,j*]anthracene as well as 9,18-diphenyltetrabenz[*de,jk,op,uv*]pentacene are described. X-ray crystallographic analyses of the first three compounds show them to be highly distorted from planarity, with the end-to-end twists of the anthracene moieties ranging from 60.8° to 69.7°. Variable-temperature NMR experiments using the bis(isopropylphenyl) derivative indicate that the barrier to twist inversion is approximately 16.7 kcal/mol.

The planarity of polycyclic aromatic hydrocarbons is often taken for granted, and the synthesis of molecules which are at variance with this structural truism is an enterprise which has attracted many organic chemists. Their efforts have been rewarded with the preparation and characterization of a variety of aromatic hydrocarbons exhibiting exceptional nonplanar deformations. The convex polycycle corannulene ([5]circulene)[1] and the saddle-shaped [7]circulene[2] are prominent examples, but nonplanar aromatic rings are much more frequently observed in certain cyclophanes[3] and in the helicenes.[4]

The cylindrical spiral structures of the helicenes [e.g., hexahelicene[5] (**1**)] arise from nonbonded repulsions between the faces of the repeatedly ortho-annelated aromatic rings, and in such

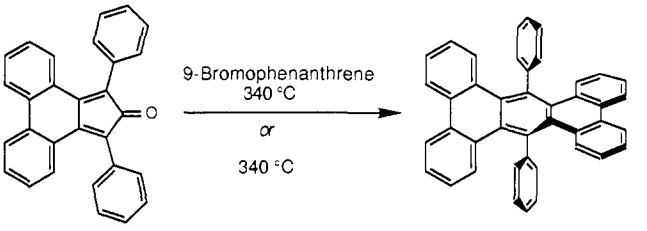


1 2

compounds the propagation axis of the molecular helix is roughly perpendicular to the mean planes of the constituent rings. However, one can also imagine a twisted hydrocarbon ribbon (**2**), in which the helix propagates in a direction parallel to the aromatic ring planes. Since simple linear acenes are planar, such a helical geometry must be enforced by properly chosen substituents. In this paper we report the syntheses of several longitudinally twisted derivatives of anthracene and pentacene, the X-ray crystallographic characterization of three of these molecules, and a study of the conformational stability of such compounds in solution.[6]

Results and Discussion

Synthesis of 9,18-Diphenyltetrabenz[*a,c,h,j*]anthracene. Preliminary molecular mechanics calculations (MMPI[7]) suggested that 9,18-diphenyltetrabenz[*a,c,h,j*]anthracene (**4**) would be twisted by more than 60° along the long axis of the anthracene nucleus. In principle, **4** could be prepared by the addition of 9,10-phenanthryne to phencyclone[8] (**3**) followed by the loss of carbon monoxide. We attempted to carry out this cycloaddition



3 4

by treating 9-bromophenathrene with strong bases (potassium, *tert*-butoxide, sodium amide, sodium bis(trimethylsilyl)amide, and lithium diisopropylamide) in the presence of **3** in various solvents, but all such reactions were unsuccessful, apparently due to the relatively rapid decomposition of **3** under basic conditions. However, 9-bromophenanthrene has been employed as a phenanthryne equivalent in cycloadditions conducted at over 300 °C in the absence of base.[9] On the assumption that **4** would survive such drastic conditions, we pyrolyzed a 1:1 mixture of **3** and 9-bromophenanthrene at 340 °C for 4 h. TLC analysis (solvent 2:1 hexane–benzene) of the resulting black solid showed it to be an exceptionally complex mixture, but the desired product **4** was located easily due to the similarity of its chromatographic mobility (R_f 0.59) with that of the structurally related 1,2,3,4-tetraphenyltriphenylene[8] (R_f 0.63). Continuous extraction of the solid reaction mixture with hexane followed by silica gel column chromatography yielded pure **4** as yellow crystals in 4% yield.[10] Ironically, in light of our efforts to generate 9,10-phenanthryne for this synthesis, compound **4** was also formed when phencyclone was heated *alone* at 340 °C (2.3% yield[10]), suggesting that **3** decomposes at high temperatures to yield phenanthryne and other, as yet uncharacterized, products.[11]

The existence of multiple reaction pathways for the formation of **4** was suggested by a crossed condensation experiment. A 1:1 mixture of pyrene and phencyclone was pyrolyzed, and compound **4** was isolated as before. However, the resulting crystals of **4** were orange-red, rather than yellow as observed previously. Examination by ^{1}H NMR spectroscopy showed the material to be essentially pure **4**, but a mass spectrometric analysis clearly indicated

(1) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730–1745.
(2) Yamamoto, K.; Harada, K.; Nakazaki, M.; Naka, T.; Kai, Y.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 7171–7172.
(3) Keehn, P. M. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983; Vol. 1, pp 69–238.
(4) Meurer, K. P.; Vogtle, F. *Top. Curr. Chem.* **1985**, *127*, 1–76.
(5) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770.
(6) A part of this work has been reported previously in a preliminary communication: Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653.
(7) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907.
(8) Dilthey, W.; Henkels, S.; Schaefer, A. *Ber. Dtsch. Chem. Ges. A* **1938**, *71*, 974–979.
(9) Grutzmacher, H.-F.; Lohmann, J. *Justus Liebigs Ann. Chem.* **1969**, *726*, 47–56.
(10) When 9-bromophenanthrene was present in the reaction mixture, calculated yields were based on the assumption that each molecule of **4** was derived from one molecule of **3** and one of 9-bromophenanthrene. In the absence of 9-bromophenanthrene, it is obvious that each molecule of **1** must be derived from *two* molecules of **3**.
(11) A plausible mechanism for the formation of 9,10-phenanthryne from **3** may be drawn in which carbon monoxide and diphenylacetylene are by-products. Unfortunately, we have failed to isolate either diphenylacetylene or 1,2,3,4-tetraphenyltriphenylene (the product of the reaction of diphenylacetylene and **3** under these conditions) from any of our reaction mixtures.

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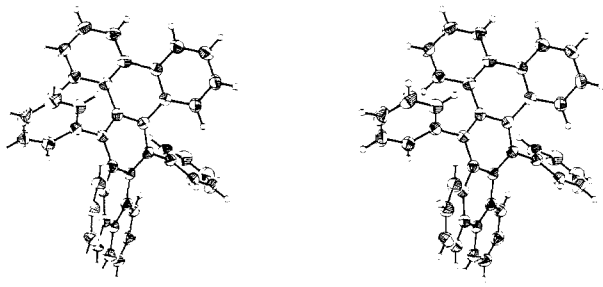
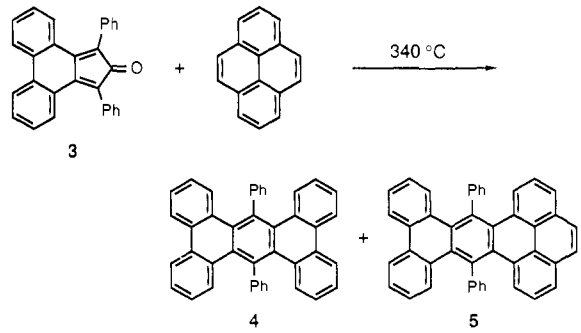


Figure 1. Stereoview of the X-ray structure of 9,18-diphenyltetrabenz-[*a,c,h,j*]anthracene (**4**).

Figure 2. Stereoview of the X-ray structure of compound **4** looking down the long axis of the anthracene nucleus.

the presence of a small amount of 9,18-diphenyltetrabenz[*a,c,hi,mn*]naphthacene (**5**),[12] which must have been formed by the



addition of pyrene to phencyclone followed by the loss of carbon monoxide and hydrogen. It seems probable that the dimerization pathway for the formation of **4** is the predominant one, but higher yields of **4** are consistently obtained when the reaction mixture contains 9-bromophenanthrene.

Structure of 9,18-Diphenyltetrabenz[*a,c,h,j*]anthracene. The molecular structure of **4** was determined by X-ray analysis.[13] The crystals are monoclinic, space group $P2_1/n$; the unit cell contains four molecules which therefore occupy general positions in the lattice. Two stereoviews of the structure are illustrated in Figures 1 and 2, and the crystallographic numbering scheme is given in Figure 3. Compound **4** adopts a highly twisted conformation in order to relieve severe hydrogen–carbon nonbonded interactions. As shown in Figure 1, a pair of hydrogens "clamps" each of the proximal carbons of the phenyl substituents. These measured H–C distances range from 2.33 to 2.43 Å, although the actual internuclear H–C nonbonded distances may be slightly shorter, since X-ray crystallography tends to underestimate the length of C–H bonds.[14] The anthracene nucleus is twisted by 65.7° end to end. Each anthracene ring exists in a shallow twist-boat conformation, and the overall twist is shared rather evenly among them, with the three nuclear rings contributing 22.5°, 23.6°, and 19.6°, respectively. The C–C bond lengths of the central ring are almost uniform (average 1.416 Å), but the two adjacent rings show substantial bond alternation, with long bonds averaging 1.475 Å and the short bonds 1.411 Å. As might be expected from the twist, the four external angles of the type C(1)–C(2)–C(7) are significantly greater than the usual 120° (average 124.6°) while the internal angles of the types C(3)–C(2)–C(7) (average 117.1°) and C(1)–C(2)–C(3) (average 118.3°) are slightly contracted.

(12) MS, *m/z* (relative intensity) 554 (M^+ of **5**, 5), 530 (M^+ of **4**, 100). No *m/z* 554 ion was observed in samples prepared in the absence of pyrene.
(13) Crystallographic data and final atomic parameters are listed in the Experimental Section.
(14) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

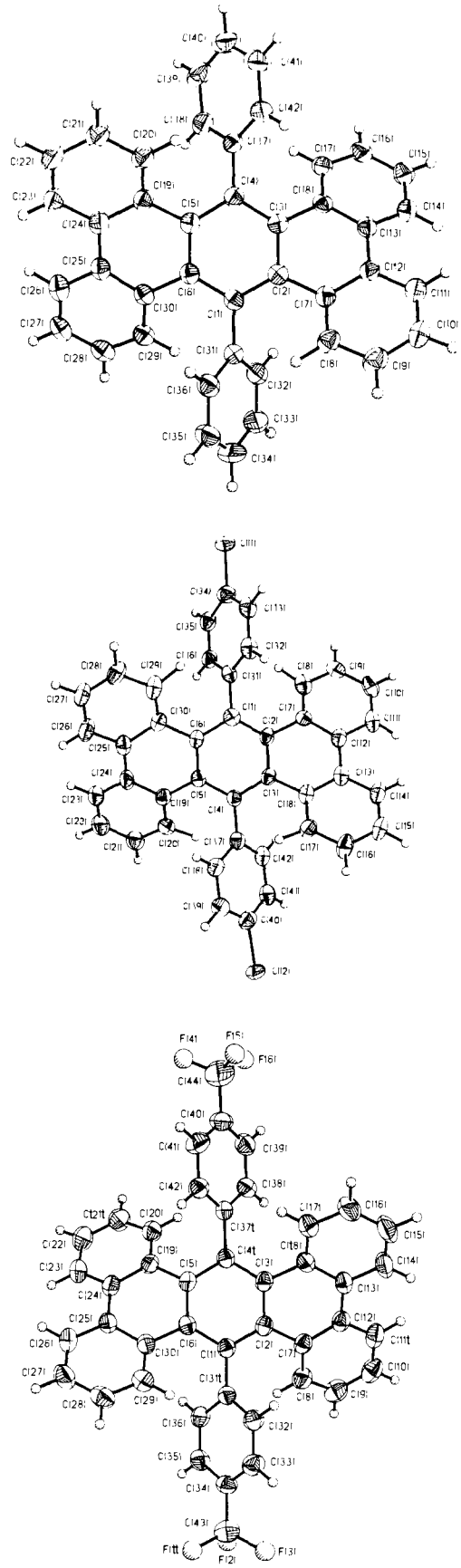
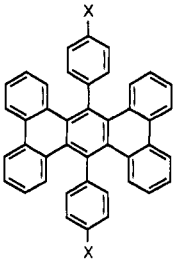


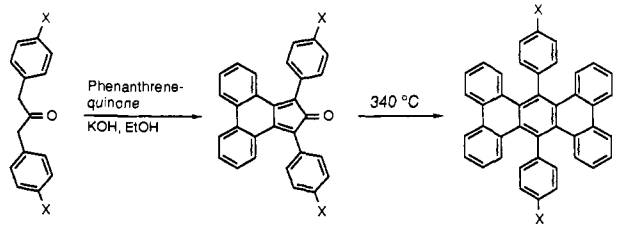
Figure 3. X-ray structures and *crystallographic* numbering schemes of (top to bottom) 9,18-diphenyl- (**4**), 9,18-bis(4-chlorophenyl)- (**7**), and 9,18-bis[4-(trifluoromethyl)phenyl]tetrabenz[*a,c,h,j*]anthracene (**8**). The thermal ellipsoids for carbon and chlorine atoms are drawn at the 50% probability level; hydrogen and fluorine atoms are shown as spheres of arbitrary diameter. The two trifluoromethyl groups of **8** are highly disordered; only the most highly populated rotamer of each is shown.

Synthesis and Structure of Phenyl-Substituted Derivatives of 9,18-Diphenyltetrabenz[a,c,h,j]anthracene. The exceptionally high nuclear twist observed in the X-ray structure of compound **4** is almost exclusively due to the four very close hydrogen–aromatic carbon (hereafter H–C_{ar}) nonbonded interactions. We wondered if the H–C_{ar} distance, and hence also the nuclear twist, would be sensitive to the electron density in the phenyl substituents. Derivatization of the phenyl substituents of **4** at their para positions would alter the electron density of the aromatic rings, or at least their polarizability, without introducing greater steric congestion; perhaps a Hammett correlation of ring twist with σ would be observed. We hypothesized that electron-withdrawing substituents, by removing electron density from the aromatic rings, might reduce the H–C_{ar} nonbonded repulsions and favor smaller nuclear twists, while electron-donating substituents might increase the twist. The para substituents of compounds **6–9** cover a broad range of Hammett σ_p values (OMe, −0.28; Cl, 0.24; CF_3, 0.53; NO_2, 0.81),[15] and the preparation and X-ray structure determination of these compounds, in conjunction with the data for **4** (H, 0.00), would provide an interesting test of this hypothesis. We report here the synthesis and X-ray crystallographic characterization of compounds **7** and **8**; compounds **6** and **9** have proven elusive thus far.



6 X = OMe
7 X = Cl
8 X = CF_3
9 X = NO_2

9,18-Bis(4-chlorophenyl)tetrabenz[*a,c,h,j*]anthracene (**7**) was prepared by the pyrolysis of 1,3-bis(4-chlorophenyl)cyclopenta[*l*]phenanthren-2-one[16] (**10**) in a manner analogous to that described for the preparation of compound **4**. Similarly, pyrolysis of 1,3-bis[4-(trifluoromethyl)phenyl]cyclopenta[*l*]phenanthren-2-one (**12**) yielded 9,18-bis[4-(trifluoromethyl)phenyl]tetrabenz[*a,c,h,j*]anthracene (**8**). The phencyclone derivatives **10** and **12** are readily prepared from the diphenylacetones **11** and **13**, which in turn are derived from commercially available substituted phenylacetic acids. It is noteworthy that the synthetic yield of compound **8** was *much* higher (31%) than for any other twisted aromatic described in this paper (yields 0.9–4.0%). The pyrolysis was carried out for a shorter time at a higher temperature than before (2 h, 395 °C), and at first we thought that a temperature increase might improve the yields in all cases. Unfortunately, no improvement in the conversion of **3** to **4** was noted when the reaction was carried out under the conditions used for the preparation of **8**.



11 X = Cl
13 X = CF_3
16 X = Me_2CH

10 **12** **15**

7 **8** **14**

The molecular structure of **7** was determined by X-ray analysis.[13] As with compound **7**, the crystals are monoclinic, space group $P2_1/n$, $Z = 4$. The structure of **7** is illustrated in Figure 3, and the gross features of this structure are very similar to those of compound **4**. The most notable difference is the significantly reduced twist of the anthracene nucleus in **7** (60.8° ± 1.5°)[17] when compared with that of **4** (65.7° ± 0.4°).[17] The central ring of **7** was the most highly distorted in the molecule with a twist (along the axis of the anthracene) of 22.3°.

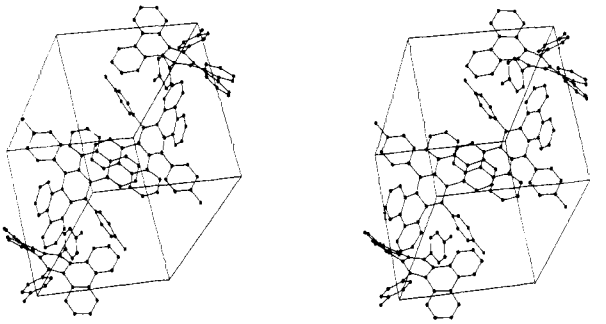


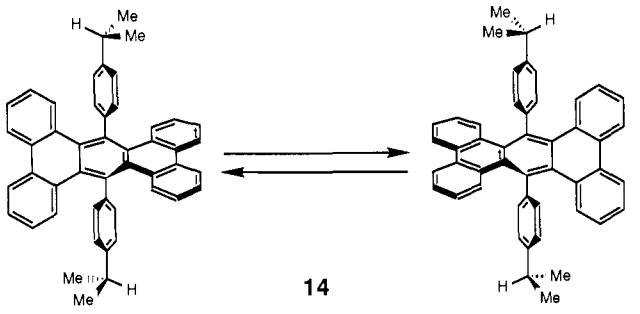
Figure 4. Stereoview of the unit cell of 9,18-bis[4-(trifluoromethyl)-phenyl]tetrabenz[*a,c,h,j*]anthracene (**8**). Hydrogen and fluorine atoms have been omitted for clarity.

The molecular structure of **8** also was determined by X-ray analysis.[13] Again the crystals are monoclinic, space group $P2_1/c$, $Z = 4$. The structure of **8** is illustrated in Figure 3, and a stereoview of the unit cell is shown in Figure 4. The reduced twist of compound **7** with respect to **4** was in accord with our original hypothesis that electron-withdrawing groups on the phenyl substituents should permit the H–C_{ar} nonbonded distance to shrink. We were therefore quite surprised when the X-ray analysis of compound **8** showed it to be the most highly twisted (69.7° ± 0.8)[17] of the three compounds! The three rings of the anthracene nucleus are highly distorted, with individual twists of 22.4°, 24.9°, and 22.4°.

The observed difference in the nuclear twist angles of compounds **4** and **8** (4.0°) may not be significant; the substituents on the phenyl groups of these molecules (H and CF_3) are quite different in steric bulk, and it is difficult to know to what degree the twist angle might be influenced by crystal packing forces. On the other hand, the marked difference in the twists of compounds **7** and **8** (8.9°) is much more noteworthy, since the substitution of a chlorine by a trifluoromethyl group is, in terms of steric requirements, a small change. Inasmuch as the crystals of compounds **4**, **7**, and **8** fall in the same space group $P2_1/c$ ($P2_1/n$ is a nonstandard setting of this space group) and exhibit similar unit-cell dimensions, we consider it more likely that the observed differences in geometry between these molecules are due to real differences in electronic structure and not to crystal packing forces. However, in the absence of additional crystallographic data, it would be unwise to speculate on the precise origins of these structural differences.

Synthesis of 9,18-Bis(4-isopropylphenyl)tetrabenz[a,c,h,j]-anthracene and Estimation of the Activation Energy for Twist Inversion. The helical geometries of compounds **4**, **7**, and **8** are fully established by our X-ray crystallographic measurements; however, although the individual molecules are chiral, only the racemates have been prepared thus far. Before attempting a resolution into enantiomers, we decided to measure the barrier to twist inversion in a dynamic NMR experiment. For this purpose we prepared 9,18-bis(4-isopropylphenyl)tetrabenz[*a,c,h,j*]-anthracene (**14**) by pyrolysis of 1,3-bis(4-isopropylphenyl)cyclopenta[*l*]phenanthren-2-one (**15**). If compound **14** adopts a helical conformation, then the methyls of the isopropyl groups would be

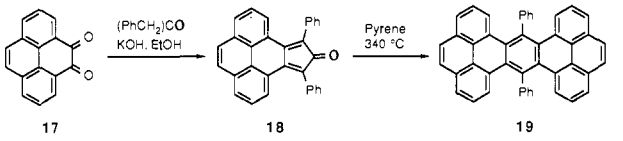
(15) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 244.
(16) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261–367.
(17) The twists of the anthracene moieties of these molecules were determined in the following manner. The centroids of carbons 12 and 13 [X(1)] and 24 and 25 [X(2)] were located, and dummy atoms were assigned to these positions. The nuclear twist is the dihedral angle of the type C(12)–X(1)–X(2)–C(25). The estimated standard deviations for the nuclear twist angles were calculated by the method of Stanford and Waser.[18]
(18) Stanford, R. H.; Waser, J. *Acta Crystallogr.; Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1972**, *A28*, 213–215.



diastereotopic, and two sets of doublets should be observed in the ^{1}H NMR spectrum of **14**, barring accidental isochrony or rapid interconversion of the two enantiomers. Measurement of the coalescence temperature for these resonances would permit the estimation of the activation energy for the interconversion of the enantiomers.[19]

The dynamic NMR experiment is illustrated in Figure 5. In the 250-MHz ^{1}H NMR spectrum of **14** in 1,2-dichloro[1,1,2,2-$^2H_4$]ethane at room temperature (293 K) and below, the diastereotopic methyl resonances are clearly resolved. This result is in agreement with our expectation that compound **14** should adopt a chiral, presumably helical conformation in solution. Coalescence of these resonances is observed upon heating to 300 K. Given that the peak separation in the absence of exchange is 1.9 Hz, the enantiomerization rate at the coalescence temperature can be calculated by using the Gutowsky–Holm approximation,[20] and assuming a transmission coefficient of 1, $\Delta G_c^{\ddagger}$ for the inversion process is 16.7 kcal/mol.[19] Unfortunately, this barrier to enantiomerization is too low to permit even a partial resolution of enantiomers at temperatures much above −60 °C.[21]

Synthesis of 9,18-Diphenyltetrabenz[*de*,*jk*,*op*,*uv*]pentacene. As a first example of the preparation of a longer, perhaps more highly twisted, polycyclic aromatic ribbon, we synthesized 9,18-diphenyltetrabenz[*de*,*jk*,*op*,*uv*]pentacene (**19**) by an approach



analogous to that employed for the tetrabenzanthracene derivatives above. Pyrene-4,5-quinone[22] (**17**) was condensed with diphenylacetone to give 1,3-diphenylcyclopenta[*e*]pyren-2-one (**18**). Pyrolysis of **18** and fractionation of the reaction mixture as described for **4** gave compound **19** in low (0.9%) yield. Although fully characterized by spectroscopic methods, we have been unable to obtain satisfactory crystals of compound **19** for X-ray analysis.

Conclusion

All of the helical polycyclic aromatic hydrocarbons described above are remarkably stable compounds despite their distorted geometries. The central aromatic rings of **4**, **7**, and **8** are twisted by 22–25°, yet these compounds are quite unreactive. Their melting points lie above 350 °C, and their solutions are insensitive to air, light, acids, and bases at normal temperatures (although prolonged heating with strong acids in air does cause some degradation). We had hoped that these molecules would also exhibit sufficient *conformational* stability to permit the isolation of pure enantiomers; unfortunately, the barrier to racemization is too low to carry out this experiment at room temperature. However, because of the high chemical stability of these compounds, we have every expectation that polycyclic aromatic ribbons of much greater length and overall twist can be synthesized. It is probably also possible, by judicious choice of substituents, to prepare similar molecules with increased helical pitch and conformational stability.

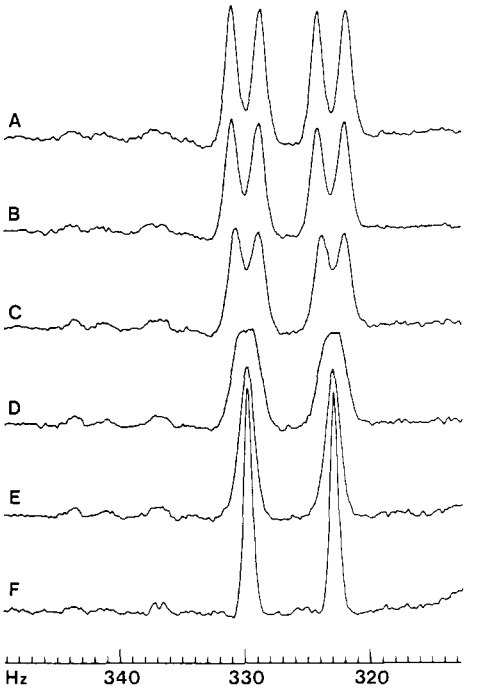


Figure 5. ^{1}H NMR spectra of 9,18-bis(4-isopropylphenyl)tetrabenz[*a*,*c*,*h*,*j*]anthracene (**14**) recorded at various temperatures. Only the isopropyl methyl resonances are shown. The spectra were recorded at 273 (spectrum A), 283 (B), 293 (C), 300 (D), 311 (E), and 333 K (F). Further details are given in the Experimental Section.

Experimental Section

Phencyclone (1,3-diphenylcyclopenta[*l*]phenanthren-2-one),[8] 1,3-bis(4-chlorophenyl)cyclopenta[*l*]phenanthren-2-one,[16] 1,2,3,4-tetraphenyltriphenylene,[8] pyrene-4,5-quinone,[22] and (4-isopropylphenyl)acetic acid[23] were prepared as described previously. Phenanthrenequinone, diphenylacetone, 9-bromophenanthene, pyrene, and [4-(trifluoromethyl)-phenyl]acetic acid were purchased from Aldrich.

9,18-Diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene (4). Procedure A (Presence of 9-Bromophenanthene). Phencyclone (0.40 g, 1.05 mmol) and 9-bromophenanthrene (0.40 g, 1.56 mmol) were placed in a Pyrex screw-capped tube and heated to 340 °C (metal bath) for 4 h. The resulting black solid was crushed, and it was continuously extracted with hexane for 12 h. The extract was concentrated and applied to a silica gel column packed in hexane. The unreacted 9-bromophenanthrene was eluted with hexane, and the solvent was changed to 97:3 hexane–benzene to elute the desired product, which exhibited R_f 0.59 on TLC (2:1 hexane–benzene). Recrystallization of this material from CH_2Cl_2–MeOH yielded compound **4** (22 mg, 0.042 mmol, 4% yield based on the assumption that each product molecule was derived from one molecule of phencyclone and one molecule of 9-bromophenanthrene): mp >350 °C; ^{1}H NMR δ 6.96 (ddd, 4 H, J = 8, 7, 1 Hz, 2,7,11,16-H$_4$), 7.18 (dd, 4 H, J = 8, 1 Hz, 1,8,10,17-H$_4$), 7.39 (m, 14 H), 8.35 (dd, 4 H, J = 8, 1 Hz, 4,5,13,14-H$_4$); UV (cyclohexane) λ_{max} (log ε) 324 (5.1), 350 (shoulder, 4.6), 390 (shoulder, 3.2), 413 (3.0); MS, m/z (relative intensity) 530 (M^+, 100), 451 (M − H − C_6H_6, 18), 450 (M − H_2 − C_6H_6, 17); exact mass 530.2036, calcd for $C_{42}H_{26}$ 530.2034.

Procedure B (Absence of 9-Bromophenanthrene). Phencyclone (1.00 g, 2.62 mmol) was placed in a Pyrex screw-capped tube and heated to 340 °C for 4 h. The resulting black solid was crushed, and it was continuously extracted with hexane for 12 h. The extract was fractionated as described above to yield 16 mg of compound **4** (0.030 mmol, 2.3% yield), identical in all respects with that obtained in procedure A.

9,18-Bis(4-chlorophenyl)tetrabenz[*a*,*c*,*h*,*j*]anthracene (7). 1,3-Bis(4-chlorophenyl)cyclopenta[*l*]phenanthren-2-one (1.35 g, 2.99 mmol) was placed in a Pyrex screw-capped tube and heated to 340 °C for 4 h. The resulting black solid was crushed, and it was continuously extracted with hexane overnight. The extract was concentrated and applied to a silica gel column packed in hexane. The column was eluted successively with 100:0, 98:2, and 96:4 hexane–benzene solutions. The fractions containing the desired product, which exhibited R_f 0.61 on TLC (2:1 hexane–benzene), were combined and concentrated to dryness. Recrystallization

(19) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; pp 93–123.
(20) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; pp 77–92.
(21) The half-life for racemization would be 6 h at −60 °C.
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of the product from CH_2Cl_2–MeOH yielded compound **7** (12 mg, 0.020 mmol, 1.3%): mp >350 °C; ^{1}H NMR δ 7.03 (ddd, 4 H, J = 8, 7, 1 Hz, 2,7,11,16-H_4), 7.14 (dd, 4 H, J = 8, 1 Hz, 1,8,10,17-H_4), 7.36 (s, 8 H, chlorophenyl-H_8), 7.42 (ddd, 4 H, J = 8, 7, 1 Hz, 3,6,12,15-H_4), 8.36 (dd, 4 H, J = 8, 1 Hz, 4,5,13,14-H_4); MS, m/z (relative intensity) 598 (M^+, 100), 451 (M – Cl – C_6H_5Cl, 31), 450 (M – HCl – C_6H_5Cl); exact mass 598.1256, calcd for $C_{42}H_{24}Cl_2$ 598.1255.

1,3-Bis[4-(trifluoromethyl)phenyl]acetone (13). Triethylamine (8 mL) was added dropwise to a stirred solution of [4-(trifluoromethyl)-phenyl]acetic acid (5.0 g, 24.5 mmol) in acetic anhydride (25 mL). After 2 h the mixture was poured into cold 4 N HCl (200 mL), and the resulting mixture was extracted with methylene chloride. Removal of the solvent gave the crude enol acetate derivative of the desired ketone (5 g). This material was hydrolyzed by refluxing overnight in a mixture of THF (30 mL) and 9 N sulfuric acid (60 mL). After the mixture cooled, water was added, and the mixture was extracted with ether. The organic extract was washed with saturated $NaHCO_3$ and water, and it was dried over anhydrous Na_2SO_4. evaporation of the solvent left a low-melting yellow solid (3.75 g). This was purified by steam distillation to give white crystals of the desired ketone **13** (2.09 g, 6.04 mmol, 49%): mp 63–67 °C; ^{1}H NMR δ 3.82 (s, 4 H), 7.28 and 7.59 (AA′BB′ system, 8 H); MS, m/z (relative intensity) 346 (M^+, 20), 327 (M – F, 20), 187 (86), 160 (63), 159 (100); exact mass 346.0799, calcd for $C_{17}H_{12}F_6O$ 346.0792.

1,3-Bis[4-(trifluoromethyl)phenyl]cyclopenta[*l*]phenanthren-2-one (12). Phenanthrenequinone (0.285 g, 1.38 mmol) and 1,3-bis[4-(trifluoromethyl)phenyl]acetone (0.475 g, 1.38 mmol) were suspended in warm ethanol (10 mL). Three drops of a solution of KOH (2.0 g) in ethanol (8 mL) were added to dissolve all of the quinone. As the flask was heated with stirring in a hot water bath, two more drops of ethanolic KOH were added. After 5 min, the reaction mixture was cooled and placed in the freezer. Dark-green crystals of compound **12** soon formed and were collected by filtration (0.317 g). The mother liquor was treated with an additonal five drops of ethanolic KOH, and after it was chilled a second crop of crystals was obtained. After drying, the combined crops of **12** totaled 0.392 g (0.76 mmol, 55%): mp 290–310 °C dec; ^{1}H NMR δ 7.01 (t, 2 H, J = 8 Hz, 5,10-H_2), 7.34 (t, 2 H, J = 8 Hz, 6,9-H_2), 7.48 (d, 2 H, J = 8 Hz, 4,11-H_2), 7.54 and 7.72 (AA′BB′ system, 8 H, CF_3–phenyl-H_8), 7.85 (d, 2 H, J = 8 Hz, 7,8-H_2); MS, m/z (relative intensity) 518 (M^+, 67), 490 (M – CO, 95), 141 (100); exact mass 518.1089, calcd for $C_{31}H_{16}F_6O$ 518.1105.

9,18-Bis[4-(trifluoromethyl)phenyl]tetrabenz[*a*,*c*,*h*,*j*]anthracene (8). 1,3-Bis[4-(trifluoromethyl)phenyl]cyclopental[*l*]phenanthren-2-one (300 mg, 0.58 mmol) and 9-bromophenanthrene (150 mg, 0.58 mmol) were mixed in a Pyrex screw-capped tube and heated to 395 °C for 2 h. After the mixture cooled, the residue was extracted with warm benzene; concentration of the extract gave an orange oil. This material was chromatographed on a silica gel column packed in hexane. The column was eluted successively with hexane and 100:2 hexane–benzene. The desired product, which exhibited R_f 0.49 on TLC (2:1 hexane–benzene), eluted as a bright-yellow band. Concentration of these fractions yielded pure compound **8** (117 mg, 31%): mp >320 °C; ^{1}H NMR δ 7.02 (m, 8 H, 1,2,7,8,10,11,16,17-H_8), 7.43 (ddd, 4 H, J = 8, 8, 2 Hz, 3,6,12,15-H_4), 7.60 and 7.65 (AA′BB′ system; 8 H, CF_3–phenyl-H_8), 8.40 (d, 4 H, J = 8 Hz, 4,5,13,14-H_4); MS, m/z (relative intensity) 666 (M^+, 100), 519 (M – $C_6H_5CF_3$, 29), 450 (M – $C_6H_5CF_3$ – CHF_3, 42); exact mass 666.1774, calcd for $C_{44}H_{24}F_6$ 666.1782.

1,3-Bis(4-isopropylphenyl)acetone (16). A solution of (4-isopropylphenyl)acetic acid (25 g, 140 mmol), acetic anhydride (70 mL), and pyridine (70 mL) was heated to reflux for 6 h. The excess acetic anhydride and pyridine were distilled away, and the residue was taken up in benzene and washed with two 150-mL portions of 10% NaOH. The organic layer was separated, dried, and concentrated to yield a dark oil. Most of the undesired byproduct of the condensation, (4-isopropylphenyl)acetone, was distilled away under vacuum (bp 90–120 °C, 0.5 mm). The undistilled residue was subjected to chromatography on silica gel (solvent 1:1 hexane–toluene). The appropriate fractions were combined and concentrated to yield compound **16** as an orange–brown oil (4.7 g, 16 mmol, 23%), which was used without further purification.

1,3-Bis(4-isopropylphenyl)cyclopenta[*l*]phenanthren-2-one (15). Phenanthrenequinone (1.10 g, 5.3 mmol) and 1,3-bis(4-isopropylphenyl)-acetone (1.80 g, 6.1 mmol) were mixed in ethanol (30 mL). A solution of KOH (0.25 g) in ethanol (1 mL) was added dropwise until all of the quinone had dissolved. The reaction mixture then was heated in a hot water bath, and the remainder of the base was added. Green–black crystals began to form on the sides of the flask, and after a brief reflux, the mixture was cooled to 0 °C. The product **15** was collected by vacuum filtration and dried (0.99 g, 2.1 mmol, 40%): mp 188–190 °C; ^{1}H NMR δ 1.29 (d, 12 H, J = 7 Hz, isopropyl–Me_4), 2.95 (septet, 2 H, J = 7 Hz, isopropyl methine-H_2), 6.95 (t, 2 H, J = 8 Hz, 5,10-H_2), 7.3 (m, 10 H), 7.62 (d, 2 H, J = 8 Hz, 4,11-H_2), 7.79 (d, 2 H, J = 8, 7,8-H_2); MS m/z (relative intensity) 466 (M^+, 96), 438 (M – CO, 54), 397 (100); exact mass 466.2299, calcd for $C_{35}H_{30}O$ 466.2296.

Table I. Crystallographic Data for Compounds **4**, **7**, and **8**

	4	**7**	**8**
formula	$C_{42}H_{26}$	$C_{42}H_{24}Cl_2$	$C_{44}H_{24}F_6$
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	14.851 (3)	14.953 (3)	12.092 (3)
b (Å)	10.136 (3)	9.705 (2)	14.495 (6)
c (Å)	18.425 (4)	20.256 (5)	18.454 (6)
β (deg)	96.55 (2)	100.35 (2)	95.27 (2)
Z	4	4	4
V (Å^3)	2755 (1)	2892 (1)	3221 (1)
D_{calcd} (g cm^{-3})	1.28	1.38	1.37
crystal size (mm)	0.22 × 0.25 × 0.50 0.20 × 0.25 × 0.46	0.04 × 0.07 × 0.56	0.20 × 0.30 × 0.35
μ (Cu Kα) (cm^{-1})	5.6	22.6	8.9
2θ range (deg)	3–110	3–110	3–114
reflections measured	$+h,+k,\pm l$	$+h,+k,\pm l$	$\pm h,+k,+l$
unique reflections	3470	3637	4336
observed reflections[a]	3016	2916	3869
parameters	395	397	472
least-squares refinement	blocked cascade	blocked cascade	blocked cascade
R (R_w)	0.041 (0.047)	0.080 (0.086)	0.071 (0.087)
goodness of fit	1.57	2.49	2.65

[a] Reflections were considered to be observed if $|F_o| > 3\sigma(F_o)$.

9,18-Bis(4-isopropylphenyl)tetrabenz[*a*,*c*,*h*,*j*]anthracene (14). 1,3-Bis(4-isopropylphenyl)cyclopenta[*l*]phenanthren-2-one (0.21 g, 0.45 mmol) and 9-bromophenanthrene (0.24 g, 0.93 mmol) were placed in a Pyrex screw-capped tube and heated to 340 °C for 4 h. The resulting black solid was crushed, and it was continuously extracted with hexane overnight. The extract was concentrated and applied to a silica gel column packed in hexane. The column was eluted successively with 100:0, 98:2, and 97:3 hexane–benzene solutions. The fractions containing the desired product, which exhibited R_f 0.7 on TLC (2:1 hexane–benzene), were combined and concentrated to dryness. Recrystallization of the product from acetone yielded compound **14** (2.5 mg, 0.004 mmol, 0.9%): ^{1}H NMR (20 °C) δ 1.31 (d, 6 H, J = 7 Hz, isopropyl–Me_2), 1.32 (d, 6 H, J = 7 Hz, isopropyl–Me_2), 2.98 (septet, 2 H, J = 7 Hz, isopropyl methine-H_2), 6.95 (ddd, 4 H, J = 8, 7, 1 Hz, 2,7,11,16-H_4), 7.28 (m, 16 H), 8.35 (d, 4 H, J = 8 Hz, 4, 5,13,14-H_4); MS, m/z (relative intensity) 614 (M^+, 100), 571 (M – Me_2CH, 12), 528 (M – 2Me_2CH, 13), 452 (M – 2Me_2CH – C_6H_4, 25), 451 (M – 2Me_2CH – C_6H_5, 38), 450 (M – 2Me_2CH – C_6H_6, 33); exact mass 614.2978, calcd for $C_{48}H_{38}$ 614.2974.

1,3-Diphenylcyclopenta[*e*]pyren-2-one (18). Pyrene-4,5-quinone (0.438 g, 1.89 mmol) and 1,3-diphenylacetone (0.44 g, 2.1 mmol) were mixed in ethanol (13 mL). A solution of KOH (90 mg) in ethanol (4 mL) was added dropwise until all of the quinone had dissolved. The solution then was heated in a hot water bath, and the remainder of the base was added. Red-brown crystals began to form on the sides of the flask, and after a brief reflux, the mixture was cooled to 0 °C. The crystalline product **18** was collected by vacuum filtration and dried (406 mg, 1.00 mmol, 53%): mp 235–239 °C; ^{1}H NMR δ 7.25 (t, 2 H, J = 8 Hz, 5,10-H_2), 7.45 (m, 10 H, phenyl-H_{10}), 7.66 (s, 2 H, 7,8-H_2), 7.73 (dd, 2 H, J = 8, 1 Hz, 4,11-H_2), 7.87 (dd, 2 H, J = 8, 1 Hz, 6,9-H_2); MS, m/z (relative intensity) 406 (M^+, 100), 378 (M – CO, 59), 376 (M – H_2 – CO, 31); exact mass 406.1333, calcd for $C_{31}H_{18}O$ 406.1357.

9,18-Diphenyltetrabenz[*de*,*jk*,*op*,*uv*]pentacene (19). 1,3-Diphenylcyclopenta[*e*]pyren-2-one (0.30 g, 0.74 mmol) and pyrene (0.30 g) were placed in a Pyrex screw-capped tube and heated to 340 °C for 4 h. The resulting black solid was crushed, and it was continuously extracted with hexane overnight. The extract was concentrated and applied to a silica gel column packed in hexane. The column was eluted successively with 100:0, 98:2, and 96:4 hexane–benzene solutions. The fractions containing the desired product, which exhibited R_f 0.6 on TLC (2:1 hexane–benzene), were combined and concentrated to dryness. Recrystallization of the product from $CHCl_3$–MeOH yielded compound **19** (2 mg, 0.0035 mmol, 0.9%): mp >350 °C; ^{1}H NMR δ 7.36 (m, 14 H), 7.48 (dd, 4 H, J = 8, 1 Hz, 1,8,10,17-H_4), 7.91 (dd, 4 H, J = 8, 1 Hz, 3,6,12,15-H_4), 7.96 (s, 4 H, 4,5,13,14-H_4); MS, m/z (relative intensity) 578 (M^+, 45), 500 (M – C_6H_6, 17), 499 (M – H – C_6H_6, 22), 498 (M – H_2 – C_6H_6,

30), 247 (100); exact mass 578.2025, calcd for $C_{46}H_{26}$ 578.2034.

Variable-Temperature NMR Measurements on Compound 14. Compound **14** (2 mg) was dissolved in 1,1,2,2-tetrachloro[1,2-$^2H_2$]ethane (0.8 mL), and 250-MHz ^1H NMR spectra were recorded at a variety of temperatures from 273 to 333 K. The sample was allowed to equilibrate at each of the chosen temperatures for 15 min prior to the recording of the spectrum. Temperatures were measured by means of a thermocouple mounted in the NMR spectrometer probe. Coalescence of the diastereotopic isopropyl methyl resonances of compound **14** was observed at 300 K (see Figure 5). This temperature was verified by measurement of the separation of the hydroxyl and methylene proton resonances in a spectrum of ethylene glycol recorded under the same conditions.[24] The coalescence temperature is considered to be accurate to ±2 K. Given that the peak separation in the absence of exchange is 1.9 Hz, and assuming a transmission coefficient of 1, $\Delta G_c^{\ddagger}$ for the exchange process is 16.7 kcal/mol.[19,20]

X-ray Crystallography. Single crystals of compound **4** were formed upon slow evaporation of a chromatographic fraction containing **4** (solvent, 97:3 hexane–benzene). Single crystals of compound **7** were obtained by recrystallization of chromatographically purified **7** from CH_2Cl_2–MeOH; similarly, chromatographically purified **8** was crystallized by slow evaporation of a hexane–benzene solution. Crystallographic measurements were made by using graphite monochromated Cu Kα radiation (λ = 1.541 78 Å) on a Nicolet R3m difractometer. The data for compounds **4** and **7** were collected at 175 K, but the data for **8** were obtained at room temperature (295 K). The crystallographic data and details of data collection are reported in Table I.

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Supplementary Material Available: X-ray data for **4**, **7**, and **8**, including atomic coordinates, bond lengths and angles, and anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

The Effect of Divalent Metal Ions on the Rate and Transition-State Structure of Phosphoryl-Transfer Reactions[1]

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Abstract: The divalent metal ions, Mg^{2+} and Ca^{2+}, catalyze the reaction of *p*-nitrophenyl phosphate dianion (PNPP) with substituted pyridines but do not increase the associative character of the transition state, as indicated by values of β_{nuc} in the range 0.17–0.21 for PNPP and for its metal ion complexes. The reactions of phosphorylated morpholinopyridine (MPP) are inhibited approximately twofold by Mg^{2+} and Ca^{2+}. This shows that there is no electrophilic catalysis from the interaction of a metal ion with the phosphoryl oxygen atoms and is consistent with electron donation from the phosphoryl oxygen atoms in a dissociative transition state. The constant value of $\beta_{lg} = -1.02$ to -1.05 for the hydrolysis of three phosphorylated pyridines in the presence and absence of 0.33 M Mg^{2+} and the constant ratio of the rate constants for the reactions of two pyridines with MPP and MPP·Mg also provide no indication of a significant change in transition-state structure upon binding of the metal ion. The dependence of the observed rate constants on the concentration of the metal ions and substrates at ionic strength 1.0 indicates the formation of 1:1 complexes with K_a(PNPP·Mg) = 14.8 M^{-1} and K_a(PNPP·Ca) = 7.5 M^{-1} at 39.2 °C and K_a(MPP·Mg) = 4.4 and 9.1 M^{-1} at 25.1 and 52.3 °C, respectively. The three- to sixfold catalysis by Mg^{2+} and Ca^{2+} of the reaction of PNPP with pyridines contrasted, with the inhibition of reactions with uncharged leaving groups, suggests that the bound metal ion interacts with the phenoxide ion leaving group as well as the phosphoryl oxygen atoms in the transition state. 2,4-Dinitrophenyl phosphate dianion (DNPP) binds Ca^{2+} and Mg^{2+} with kinetically determined association constants of 6.0 and 6.2 M^{-1}, respectively, at 39.1 °C and ionic strength 1.0, and DNPP·Ca reacts with pyridines sevenfold faster than free DNPP. The constant value of β_{nuc} for the reactions of DNPP and DNPP·Ca with two substituted pyridines again gives no evidence for a significant change in nucleophilic participation upon complexation with a divalent metal ion. The reactions of DNPP·Mg with pyridines are at least eightfold slower than the reactions of free DNPP because of an unfavorable interaction of Mg^{2+} and the ortho nitro group of DNPP in the transition state. The effects of Mg^{2+} and Ca^{2+} on the rate constants for hydrolysis follow the same trends as for the reactions with pyridines, except that the hydrolysis of PNPP·Mg is 20% slower than that of PNPP.

The mechanisms employed by enzymes to catalyze phosphoryl-transfer reactions are not understood. It has often been suggested that complexation with a metal ion could change the mechanism of phosphoryl transfer from the largely dissociative mechanism observed in the absence of a metal ion to an associative mechanism, with more nucleophilic involvement in the transition state.[2-4] A change from a dissociative to an associative mechanism would allow a larger potential advantage from catalysis by induced intramolecularity in an enzymatic reaction because reactions with "tight" transition states have stricter requirements for alignment than reactions with "loose" transition states.[5] In addition, a change to an associative mechanism would give a greater potential advantage from general base catalysis due to the increased bond formation to the nucleophile in the transition state and concomitant charge development on the nucleophile. We have used a nonenzymatic system to test whether or not complexation with a metal

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