# Twisted Acenes

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## Contents

Robert A. Pascal, Jr., was born in New Orleans in 1954. He attended Louisiana State University where he ran track (primarily the long sprints, 440 yard and 600 yard dashes) and ultimately received his B.S. in 1976 (Biochemistry). Entering Rice University on an NSF Predoctoral Fellowship, he studied demethylation reactions in cholesterol biosynthesis under the direction of George Schroepfer, Jr., and he received his Ph.D. in 1980 (Biochemistry). Joining Christopher Walsh's group at MIT as an NIH Postdoctoral Fellow, he spent two years on the isolation and mechanistic studies of dihydroorotate oxidase from parasitic protozoa. He joined the Chemistry faculty at Princeton in 1982 and soon began the synthesis of strained organic molecules as a diversion from biochemical research. Professor Pascal's principal research interests have been in the areas of biochemistry (enzyme mechanisms, design of enzyme inhibitors, and natural product biosynthesis) and physical organic chemistry (strained aromatic molecules, kinetic isotope effects, molecular association, and crystal engineering) with a recent emphasis on the latter. His chief pastimes are reading, running, cycling, shooting, photography, and amateur astronomy.

## 1. Introduction

The IUPAC definition of "acenes" is the following: polycyclic aromatic hydrocarbons consisting of fused benzene rings in a rectilinear arrangement.[1] Naphthalene is the smallest acene, followed by anthracene, tetracene (naphthacene), pentacene, etc. To most chemists, the term "acene" calls to mind a flat, rigid molecule. This is frequently *not* the case, because the energy required to bend or twist most polycyclic aromatic hydrocarbons (PAHs) is quite modest, and the crystal structures of most acenes and their derivatives show some deviations from planarity. This review is a survey of the structures of acenes with a *substantial* degree of twisting deformation. The most extreme examples challenge the usual chemists' prejudices concerning the shape and stability of molecules; the lesser ones are merely beautiful.

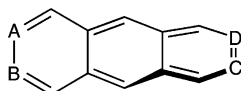In this review, the term "twist" refers to the torsion angles ABCD and BADC for the acene in question (Figure 1).[2] In

**Figure 1.**

molecules of low symmetry, these need not be identical; the larger value is always reported, and it is rounded to the

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nearest degree. But what should be considered a "significant" or "substantial" twist? At the B3LYP/6-31G(d) level of theory,[3,4] a mere 3.2 kcal/mol is required to twist naphthalene by 20°. As shall be seen, there are a number of acene derivatives that adopt conformations (in a crystal) that are 3−4 kcal/mol above the ground state (in a gas-phase calculation). For this reason, a molecule normally must meet a higher standard for inclusion in this review: it must contain an acene substructure with a 30° twist (7.2 kcal/mol is needed to twist naphthalene to this degree; less energy is required for longer acenes). Molecules with smaller twists (or no twist) are included when they serve to illustrate some interesting structural point, but the review is comprehensive only for acenes meeting the 30° criterion.

As stated above, this review is a survey of the *structures* of twisted acenes. For most of the compounds cited, the prospect of an unusual geometry was not even a consideration to the maker (for example, compounds **36** and **85** were synthesized almost 50 years before their X-ray structures

were determined), and their syntheses and reactions are relatively unaffected by the nonplanar distortion. For the most highly twisted molecules, however, the syntheses, reactions, and properties may be of interest and are discussed.

Only molecules with atomic coordinates deposited in the Cambridge Structural Database[5] (CSD) have been included, and the author makes no apology for omitting reports for which the crystallographic data have not been deposited. Experimental structures should be readily accessible to the reader, and failure to deposit the structural data is a form of negligence. After all, one cannot easily search the literature for the shape of a molecule in a figure! To depict clearly the unusual features of these molecules, the twisted acene moiety in the more complex structures is highlighted with bold bonds in the conventional chemical drawing. For many compounds, the molecular structure from the crystallographic coordinates is plotted as well, with the twisted acene highlighted by solid atoms. Finally, the CSD refcode for each of the cited structures has been appended to the reference for its crystal structure determination.

## 2. "Simple" Twisted Acenes

The conceptually simplest way to deform an acene is to attach several bulky substituents to its periphery by single bonds. Such molecules are usually (but not always) twisted, because it is easier to twist torsion angles (even in PAHs) than to distort bond angles or to compress or stretch C—C bonds. In the absence of benzannulation (to be considered later), the highly substituted acenes may retain most of the characteristic chemical or spectroscopic properties of the parent, although perturbed to varying degrees by structural deformation and steric crowding.

## 2.1. Highly Substituted Naphthalenes

Substitution of naphthalene with eight identical substituents usually leads to a twisted structure. Octabromonaphthalene (**1**) is typical (Figure 2). The sum of the van der Waals radii
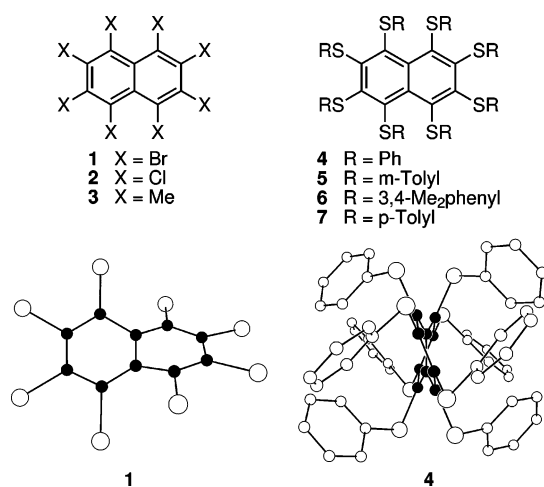


**Figure 2.**

of two bromine atoms is ca. 3.8 Å, but the distance between C1 and C8 in naphthalene is only 2.5 Å, so there must be some distortion in the substituted compound. In this case, **1** exhibits a 31° end-to-end twist.[6] Octachloro- (**2**, 24°) and octamethylnaphthalene (**3**, 26°), with slightly smaller substituents, are less twisted.[7,8] A number of octakis(arylthio)-

naphthalenes (**4**–**7**) have been prepared by MacNicol and others as eight-legged "spider" hosts,[9–13] and these also show substantial distortions from planarity. In various crystal structures, the phenyl, tolyl, and xylyl compounds **4**–**6** have exact or approximate $D_2$ symmetry and twists ranging from 29° to 44°, but, interestingly, the *p*-tolyl compound **7** possesses crystallographic $C_i$ symmetry, no twist, and a mildly undulating ring.[10] This must be a crystal packing effect, and it is discussed in section 2.4.

Even a compound with the relatively modest steric crowding of **1** can be challenging to synthesize. Conventionally rigorous brominations of naphthalene are said to give only hexabromonaphthalene, and an exotic mercuration/bromination procedure was required to prepare **1**.[6] In contrast, the fully encapsulated naphthalenes **4**–**7** are easily prepared by the reaction of octafluoronaphthalene with excess sodium arenethiolates.[9,10]

Substitution by eight aromatic rings can also twist a naphthalene, but octapyrrolylnaphthalene **8** (Figure 3) has a
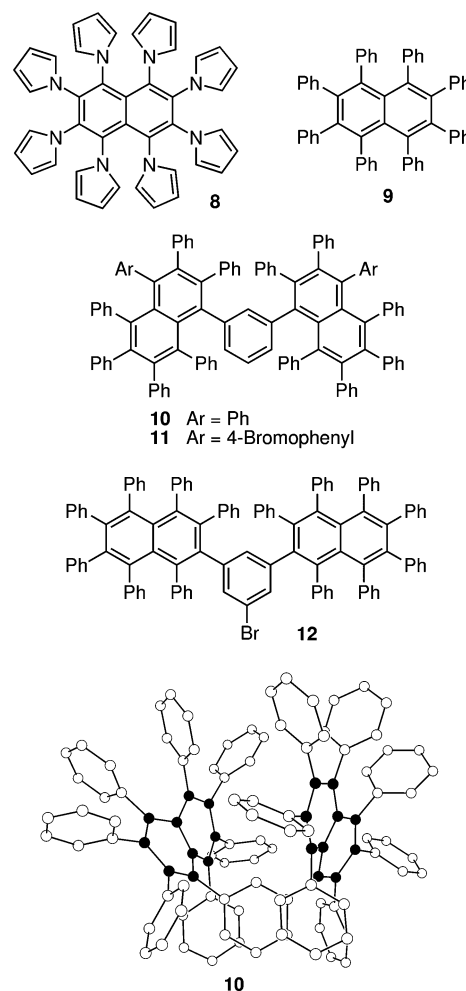


**Figure 3.**

modest 22° twist,[14] and octaphenylnaphthalene (**9**) is an essentially untwisted structure with approximate $C_{2h}$ symmetry in the solid state.[15] The latter finding must also be the result of crystal packing, because all other structures of octaphenylnaphthalenes, including the cleft-containing "albatrossenes" **10**–**12**,[16,17] are twisted. The largest twist in an octaarylnaphthalene is found in the relatively crowded compound **10** (35°).[16]

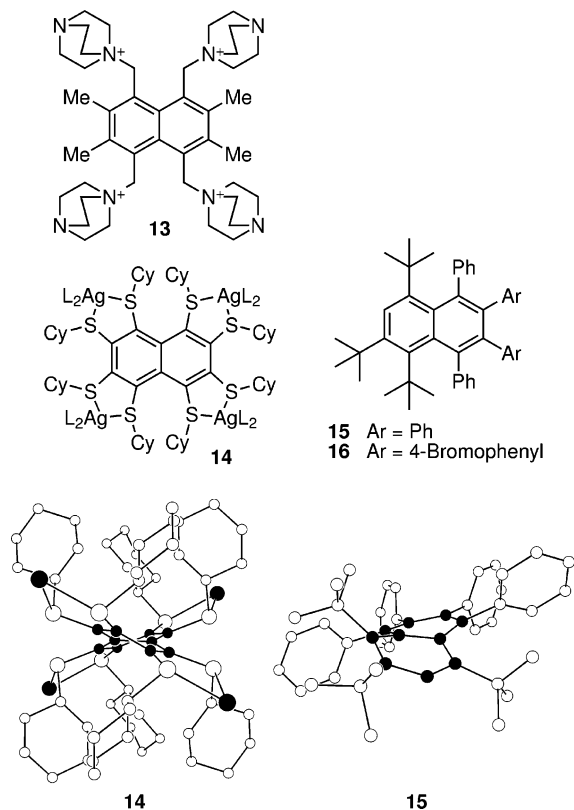Other octasubstituted naphthalenes are compounds **13** (Figure 4), a bulked-up octaalkylnaphthalene with a 34°



**Figure 4.**

twist,[18] and **14**, where silver complexation of the already large cyclohexylthio substituents gives maximal crowding and the greatest twist (52°) of the "simple" crowded naphthalenes.[19] Fewer but larger substituents can also give significant distortions, as in the tri(*tert*-butyl)tetraphenylnaphthalenes **15** (31°) and **16** (30°).[20] Compounds **15** and **16**, as well as all of the octaphenylnaphthalenes, were prepared by the reaction of crowded cyclopentadienones with tetraphenyl-benzyne generated by the diazotization of tetraphenylan-thranilic acid.[15−17,20,21]

## 2.2. Naphthalenes Constrained by Cyclophanes

An alternative method for inducing twist, but one rarely observed, is the incorporation of acenes into cyclophanes with diagonal straps. The triple-decker cyclophane **16** (Figure 5) is the finest crystallographically characterized example; the central naphthalene has a 32° twist.[22]

The single bridge in **17** (29°) is nearly as effective as the two in **16**, but **17** is especially interesting because the pyridine ring is held perpendicular to the naphthalene so that the nitrogen−carbon nonbonded contact distance is only 2.73 Å,[23] one of the closest such contacts known.[24]

A very different sort of structure is the giant cyclophane **18** that incorporates two twisted (24°) octaphenylnaphthalene moieties.[25] However, because the bridge is not diagonal (between C1 and C4, rather than C1 and C5 or C2 and C6), the twist of the naphthalenes is not enhanced; if anything, it is reduced from the generally larger twists observed in **10**−**12**.
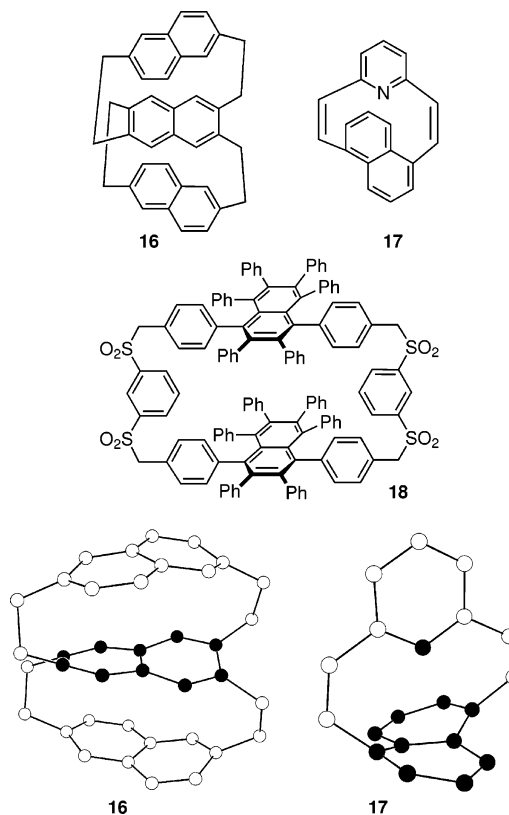


**Figure 5.**

## 2.3. Highly Substituted Anthracenes and Tetracenes

X-ray structures of anthracenes with many singly bonded peripheral substituents are very uncommon. The premier example is decaphenylanthracene (**19**, Figure 6), a molecule
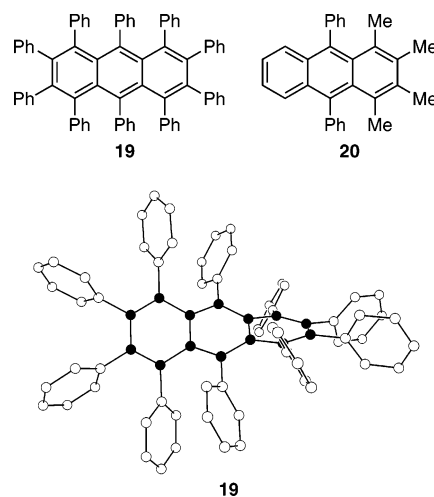


**Figure 6.**

with a 63° end-to-end twist,[15] but the next most twisted "simple" anthracene is compound **20** with a mere 28° twist.[26]

Despite its great distortion from planarity, decaphenylan-thracene in many ways retains the characteristics of a "normal" anthracene. Its carbon NMR resonances fall squarely in the aromatic region, its UV absorption is shifted 60 nm to the red of anthracene itself (as is expected from the addition of many aryl groups), and the characteristic anthracene vibrational fine structure is still visible.[6] Com-

pound **19** is also highly fluorescent, and the anthracene core is well protected by the "picket fence" of phenyl rings, so that it displays reversible electrochemistry and a very stable electrogenerated chemiluminescence.[27]

Tetracenes with large substituents at the peri positions of the central rings (C5, C6, C11, and C12) may also be highly twisted. Compound **21** (Figure 7) has a 40° end-to-end
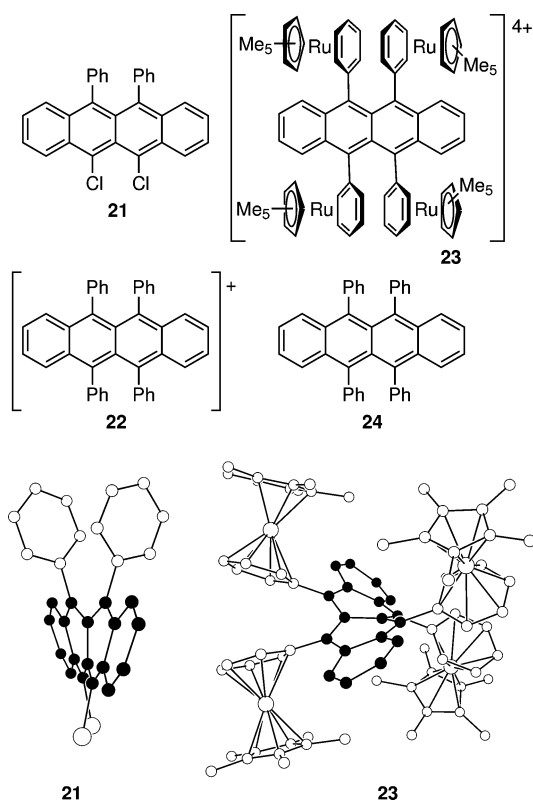
**Table 1. Calculated Energies of Twisted and Achiral Conformations of Some Highly Substituted Acenes**

| compound | $E$ [B3LYP/6-31G(d), au] | $\Delta E$ (kcal/mol) |
|---|---|---|
| $C_i$-**4** | −5419.694 696 | +2.5 |
| $D_2$-**4** | −5419.698 701 | 0.0 |
| $C_{2h}$-**9** | −2234.257 398 | +3.7 |
| $D_2$-**9** | −2234.263 243 | 0.0 |
| $C_{2h}$-**24** | −1617.329 463 | +3.8 |
| $D_2$-**24** | −1617.335 486 | 0.0 |
| $C_s$-**70** | −1717.898 567 | +3.9 |
| $C_2$-**70** | −1717.904 803 | 0.0 |
| $C_{2h}$-**77** | −2385.545 221[a] | +2.9 |
| $D_2$-**77** | −2385.549 854[a] | 0.0 |
| $C_{2h}$-**81** | −2538.014 502[b] | +2.8 |
| $D_2$-**81** | −2538.018 900[b] | 0.0 |

[a] Reference 76. [b] Reference 77.

centrosymmetric structure of rubrene (**24**) and the twisted structure of its cation radical (**22**) illustrated in Figure 8.

Are these apparent structural discrepancies the products of crystal packing forces, or do they reveal an unexpected ground-state structure for these compounds? Table 1 gives the calculated energies, at the B3LYP/6-31G(d) level,[3] for the twisted and achiral conformations of several of the molecules mentioned in this review that display such a dichotomy. In every case, it appears that the twisted $D_2$ or $C_2$ conformation is 2−4 kcal/mol more stable than the corresponding achiral conformation in the gas phase. Significantly, however, both the twisted and achiral structures are potential minima at this level of theory. Thus it seems that the achiral conformations of these compounds, present in solution in amounts ranging from 0.1% to 2% of the total, are sometimes able to form more favorable interactions in the solid state. As the minor component crystallizes, it is replaced in solution by the rapid equilibration of the conformers.

No case was found where a twisted conformer crystallized in preference to a more stable achiral conformer. This possibility cannot be excluded, but it may simply be more difficult to pack helical molecules than flat ones.



**Figure 7.**

twist,[28] and the rubrene cation radical (**22**) has a 27° twist.[29] The most impressive distortion occurs upon complexation of the four phenyl groups of rubrene with very bulky RuCp* groups; the resulting tetracation **23** exhibits a twist of 69°.[30] However, in the crystal structure of rubrene (**24**) itself, the molecule adopts a conformation with strict $C_{2h}$ symmetry.[31]

Several other highly substituted anthracenes and tetracenes, including decamethylanthracene and dodecamethyltetracene, have been prepared by Hart and co-workers.[32] These compounds are likely to be greatly distorted from planarity, but none have been crystallographically characterized.

### 2.4. To Twist or Not To Twist?

In the preceding sections, the molecular structures of compounds **7**, **9**, and **24** were found to be untwisted in the solid state, even though, in each case, other very similar molecules were observed to be twisted. A typical pair is the
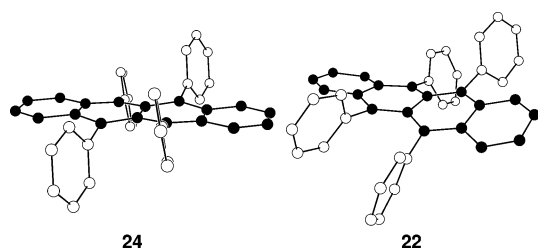
### 3. Benzannulated Acenes

The fusion of benzo groups to simple acenes is another way to induce distortion from planarity. Devoid of other substituents, the molecules in this section might be passed over as flat and uninteresting, but in fact, they have quite a conformational diversity. However, they are distinct from the compounds in section 2 in that the benzo groups are intimately united with the acene cores. For example, tetrabenzonaphthalene (**25**, Figure 9) is no longer just a substituted naphthalene, or even a true naphthalene at all, but instead an entirely different PAH with its own characteristic spectra and reactivity. However, for the purpose of this review, the central ten-carbon unit, composed of two fused six-membered rings, will remain a "naphthalene".

The highlighted naphthalene cores of compounds **25** and **26** have twists of 35° and 37°, respectively.[7,33] This cannot be a surprise; these molecules are analogous to compounds **1**−**3** in the steric requirements of the peripheral groups. Indeed, the structures of **2** and **25** are described in the same paper![7] On the other hand, the saddle-shaped [7]circulene (**27**) contains an unexpectedly twisted (30°) naphthalene in its periphery.[34,35]
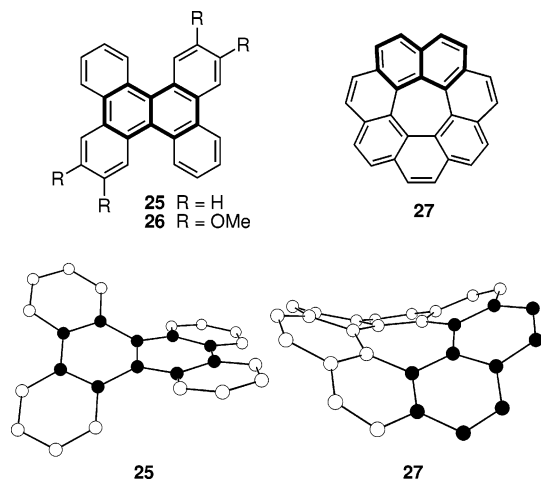


**Figure 8.**

**Figure 9.**

A remarkable conformational dichotomy is present in hexabenzotriphenylene (**28**, Figure 10). This molecule was
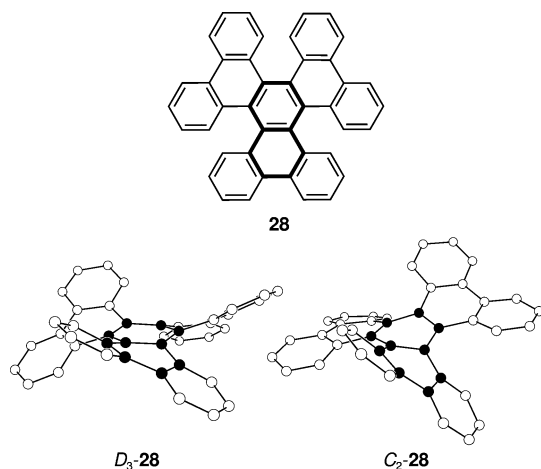


**Figure 10.**

first unambiguously prepared by Hacker et al. by the cyclotrimerization of 9,10-dehydrophenanthrene ("9,10-phenanthryne") formed by pyrolysis of cyclobuta[*l*]phenanthrene-1,2-dione at 700 °C.[36] A subsequent pyrolysis of phenanthrene-9,10-dicarboxylic acid anhydride also gave **28**, and an X-ray structure showed it to be a $D_3$-symmetric propeller.[37] However, computational studies at the B3LYP/cc-pVDZ level revealed a $C_2$-symmetric conformation 5.0 kcal/mol less stable than the ground state.[37] Shortly thereafter, in a surprising development, compound **28** was synthesized by the palladium-[38,39] or nickel-promoted[40] cyclotrimerization of 9,10-phenanthryne at room temperature or below, but the $C_2$ conformation was isolated instead! The structure was established by X-ray analysis,[40] and, upon heating, $C_2$-**28** was smoothly converted to the thermodynamically preferred $D_3$ conformer with a free energy of activation of 26.2 kcal/mol.[39] The naphthalene subunit in $D_3$-**28** is much less twisted (24°)[37] than that in $C_2$-**28** (56°),[40] and a likely explanation for the preference for $D_3$-**28** is the preservation of conjugation in the central aromatic ring.[37]

A number of benzannulated anthracenes, tetracenes, and pentacenes display substantial distortions, but none have end-to-end twists even as great as the naphthalene in $C_2$-**28**. The anthracene moieties embedded in **29** and **30** (Figure 11) have twists of 37° and 38°, respectively.[41,42] The tetrabenzotetracene **31** is similar to the tetrabenzonaphthalenes **25** and
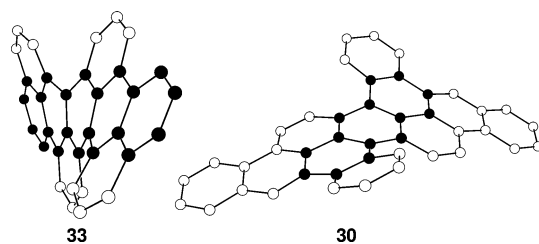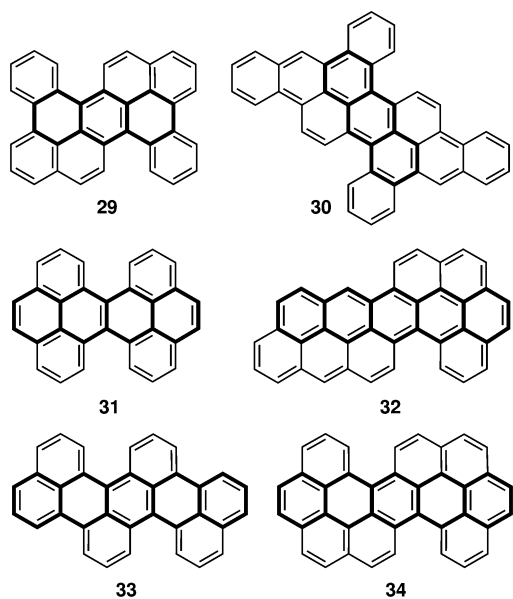




**Figure 11.**

**26** but less twisted at 34° (and the central naphthalene twist is only 27°).[43] Finally, given their length, the benzannulated pentacenes **32** (23°), **33** (41°), and **34** (43°) have only moderate distortions.[44−48]

## 4. Twisted Acenes with Mixed Substituents

The greatest distortions of acene substructures are observed in molecules that possess some benzannulation in conjunction with bulky substituents. In contrast to the majority of the compounds in sections 2 and 3, for which the twists were incidental to their syntheses, many or most of these compounds have been constructed with the express intent of generating nonplanar aromatic molecules, and some of the results are astounding.

### 4.1. Crowded Naphthalenes

Triphenylene is a dibenzonaphthalene, and the addition of peripheral substituents usually produces significant out-of-plane distortions. Even 1,4-dimethyltriphenylene[49] (**35**, Figure 12) has a 29° twist, and 1,2,3,4-tetraphenyltriphenylene[50] (**36**) has a 31° twist. Much more impressive are the fully substituted triphenylenes. Perfluorotriphenylene[51,52] (**37**), perchlorotriphenylene[53,54] (**38**), and the aryloxytriphenylene **39**[55] have naphthalene twists of 40°, 56°, and 45°, respectively, and the fluorinated molecule **40** has a 42° twist.[56]

The most crowded of these molecules, **38**, cannot be prepared by direct chlorination of triphenylene (rearranged compound **41** is obtained instead[57]), and several alternative syntheses were unsuccessful.[54,58] Ultimately, cyclotrimerization of tetrachlorobenzyne generated by pyrolysis of tetrachlorophthalic anhydride produced **38** in 2% yield.[53,54]
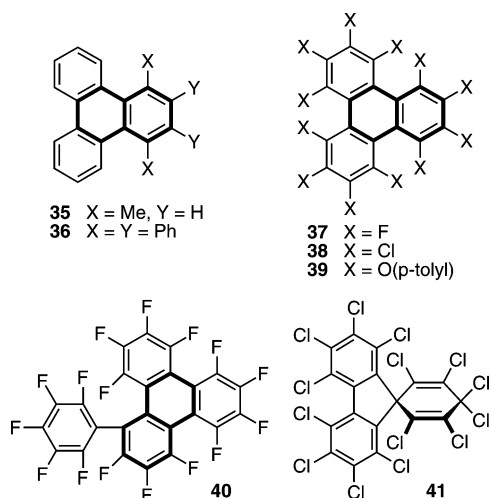
**Figure 12.**

*All* of these molecules possess triphenylene cores with exact or approximate $C_2$ symmetry (Figure 13). In contrast
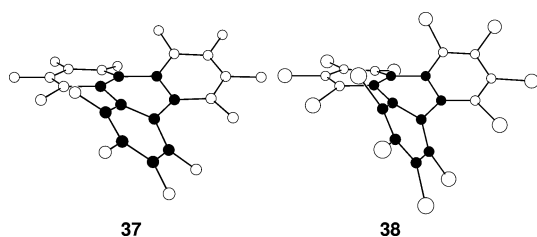


**Figure 13.**

to hexabenzotriphenylene (**28**), the $C_2$ conformation is thermodynamically preferred to the $D_3$,[37] because triphenylenes are, in some sense, just three benzene rings connected by single bonds. The $C_2$ conformation better preserves the planarity of the three outer rings while sacrificing the central ring to greater deformation; whereas, in the case of **28**, it is the central ring that is most benzene-like, and so the $D_3$ conformation is favored.[37]

The helicenes and other substituted phenanthrenes also contain embedded naphthalene substructures. It is surprising that no simple helicenes contain naphthalene subunits with large twists; other substituents must also be present. Only two of these have naphthalenes with twists greater than
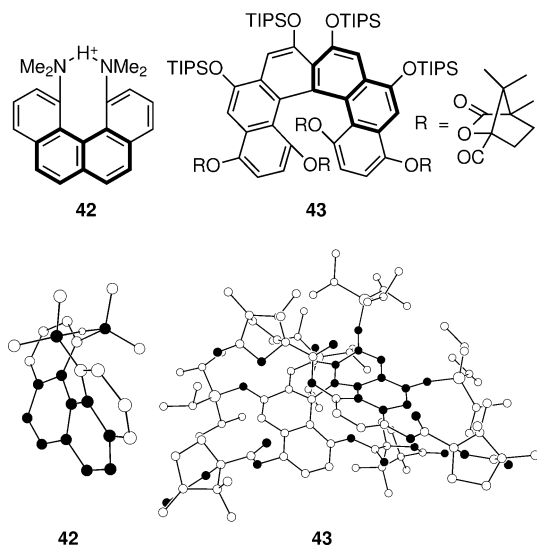


**Figure 14.**

30°: the bridged ammonium ion **42** (31°) and the almost dendrimeric **43** (32°) (Figure 14).[59,60]

Other twisted phenanthrene-containing structures are compound **44** (31°),[61] the "molecular spiral staircase" **45** (33°),[62] and the chromium tricarbonyl complex **46** (31°) (Figure 15).[63]
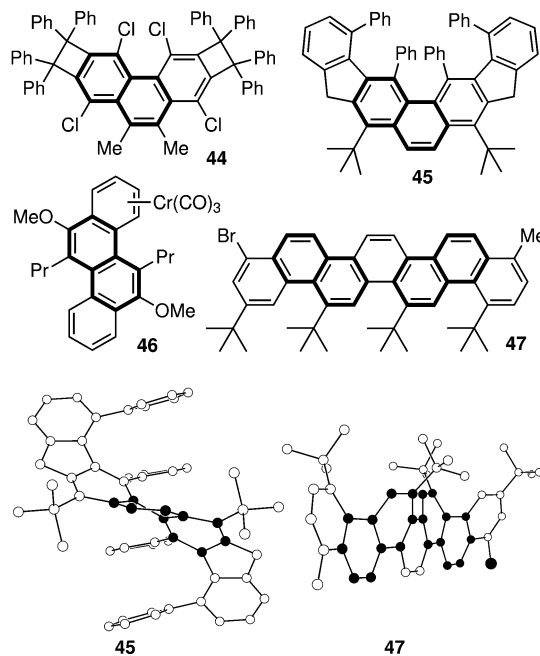




**Figure 15.**

The synthesis of the "spiral staircase" is interesting in that a linear phenylene ethynylene containing four alkynes was sewn together to make heptacycle **45** in a single step.[62]

Mallory's "[7]phenacene" **47** also contains several distorted naphthalenes, but the molecule "missed a chance" to form a continuous twist in one direction rather than alternating back and forth.[64] However, this does not appear to be a case of selective crystallization of the less stable conformer. Calculations at the B3LYP/6-31G(d) level indicate that the alternating conformation is preferred to that with a continuous twist by 12 kcal/mol.[3]

Coronenes contain six pairs of peri positions, and when these are fully substituted, the molecule cannot be planar. Neither compound **48** nor compound **49** (Figure 16) is twisted—the coronene cores have exact or approximate $C_i$ symmetry—but significantly twisted naphthalenes (26° and
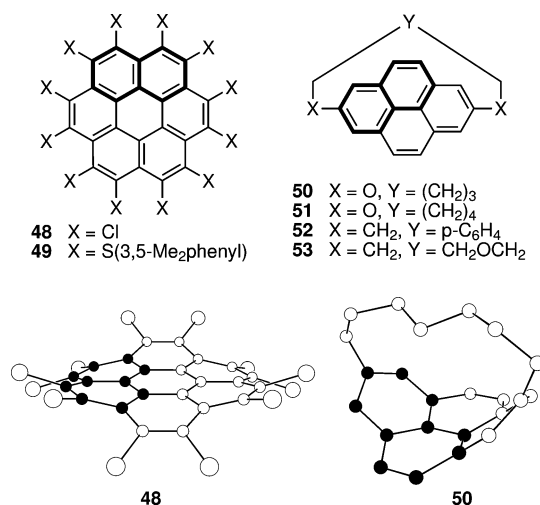




**Figure 16.**

36°, respectively) are embedded in the polycycles.[65,66] Similarly, the pyrenes in Bodwell's pyrenophanes **50−53** are dramatically bent, but they also contain naphthalene substructures with twists ranging from 30° to 37°.[67−70]

## 4.2. Crowded Anthracenes

Benzannulated acenes with phenyl groups positioned to clash with the benzo hydrogens give molecules with the largest end-to-end twists. The author's interest in this area began with the synthesis of the diaryltetrabenz[a,c,h,j]-anthracenes **57**, **58**, and **59** (Figure 17), which at the time
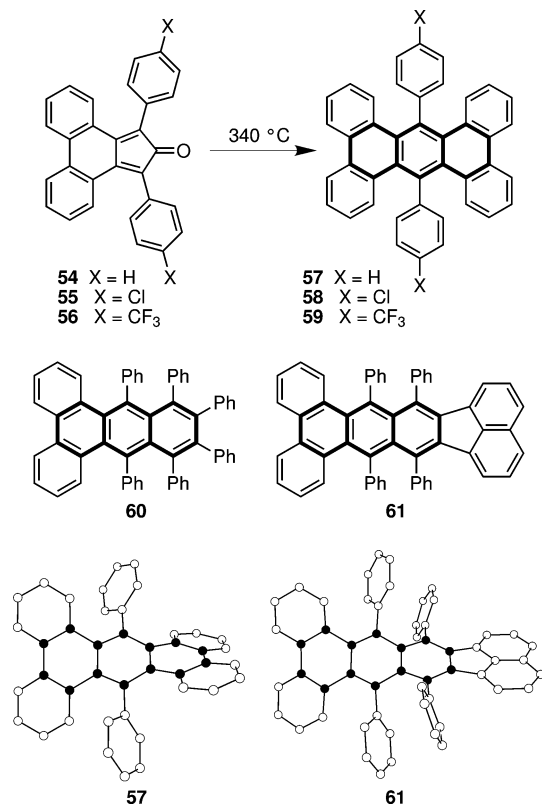
**Figure 17.**

possessed the largest twists of any PAHs (66°, 61°, and 70°, respectively).[71,72] The synthesis of these compounds is unusual; they are obtained in yields of 2−31% by pyrolysis of phencyclones **54−56**.[72]

Despite the large distortion from planarity, these chiral molecules are not configurationally stable. Variable temperature NMR studies with a diisopropyl derivative of **57** revealed only a moderate barrier to enantiomerization ($\Delta G^{\ddagger} = 16.7$ kcal/mol).[72] Two other highly twisted anthracenes are compounds **60** (60°) and **61** (57°), prepared in a more conventional manner by the addition of a crowded benzyne to crowded cyclopentadienones.[73] All of the above compounds are perfectly stable under ordinary conditions.

The series of diarylbenzo[b]triphenylenes **62−70** (Figure 18) was prepared subsequently to test whether electron-donating or -withdrawing groups on the aryl substituents influence the degree of distortion.[74] No obvious correlation was found among the twists, which ranged from 33° to 43°, but one molecule, the dinitro derivative **70**, adopted an untwisted, $C_s$-symmetric conformation. That this is a crystal packing effect (as is, presumably, the 10° variation in the twists of **62−69**) was established by the X-ray structure of compound **71**. The extra methyl is electronically innocuous,
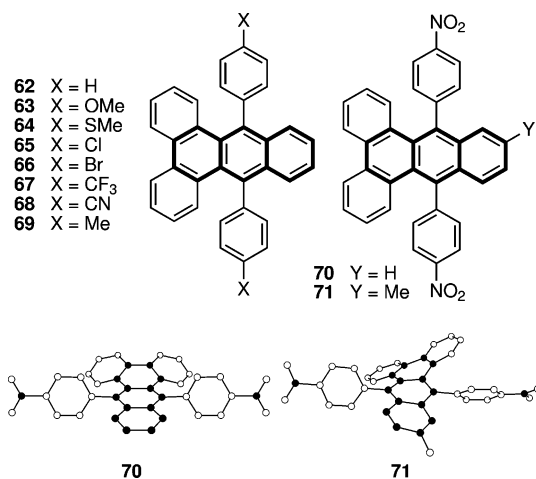
**Figure 18.**

but it alters the crystal packing, and **71** was found to have a conventional 40° twist.[74]

## 4.3. Crowded Higher Acenes

Larger benzannulated acenes with many phenyl groups at last provide structures that are strongly twisted ribbons. The first acene to possess an end-to-end twist of more than 90° is the octaphenyldibenzo[a,c]naphthacene **74** (105°, Figure 19).[75] This molecule was prepared by diazotization of the
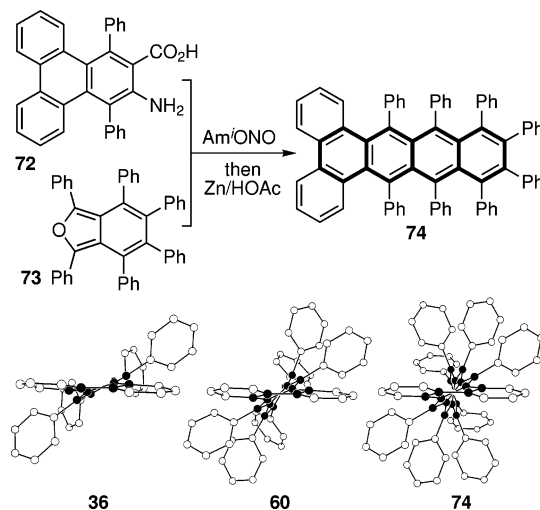
**Figure 19.**

crowded anthranilic acid **72** in the presence of hexaphenyl-isobenzofuran (**73**), followed by deoxygenation of the aryne−furan adduct. End-on views of the structures of three generations of similar twisted acenes, tetraphenyltriphenylene **36** (31°),[50] hexaphenylbenzo[b]triphenylene **60** (60°),[73] and compound **74** (105°),[75] show how much the pitch of the helix increases with each additional ring. However, there is no apparent interruption of π-conjugation: compound **36** is white, **60** bright yellow, and **74** orange.

For the formation of longer twisted acenes, it has been necessary to employ bisaryne equivalents as the key precursors. Pentacene **77** was prepared by the thermolysis of the bis(iodonium carboxylate) **76** in the presence of phencyclone (**54**),[76] and heptacene **81** was made by treatment of the bis-(silyl triflate) **80** with fluoride ion in the presence of cyclopentadienone **79**.[77] These compounds were anticipated to have twists in excess of 90° on the basis of a variety of

calculations. Indeed, a preference for a twisted conformation for **77** was indicated by eight methods ranging from AM1 to B3LYP/6-311G(d,p).[76] However, *both* **77** and **81** formed crystals in which the acene resides on a crystallographic center of inversion.[76,77] Thus, in the solid state, they have 0° net twists, but they are far from planar (Figure 20).
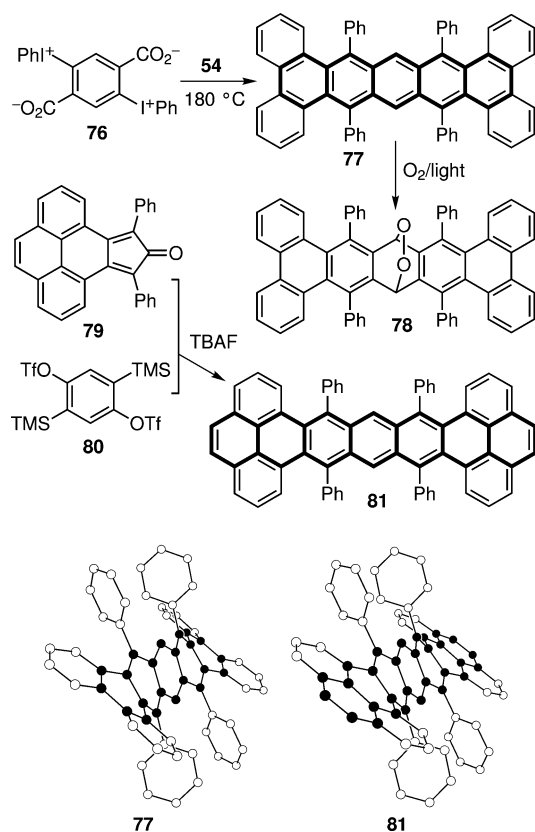




**Figure 20.**

Compound **77**, unlike any of the preceding molecules, is sensitive to air and light in solution (it is stable as a solid or in the dark), forming the endoperoxide **78** with a half-life of 30 min in room light. Interestingly, no such sensitivity has been reported for compound **81**, and it has even been used to make "efficient single-layer twistacene-doped polymer white light-emitting diodes".[78]

The acenes **77** and **81** have both $D_2$ and $C_{2h}$ low-energy conformations, but when phenyl groups are added to the central ring to give the hexaphenyltetrabenzo[*a,c,l,n*]pentacene **84** (Figure 21), only the $D_2$ conformation is accessible (the $C_{2h}$ conformation is 19.7 kcal/mol higher at the B3LYP/6-31G(d) level[3]). This molecule was synthesized by the treatment of the tetrabromide **82** with *n*-butyllithium in the presence of furan **83**, followed by deoxygenation of the double adduct.[79] The product **84** forms ruby red crystals, and the X-ray structure shows that it has a 144° end-to-end twist.[79] The pitch of the helical core is great, almost 30° per ring, and **84** contains the most highly twisted naphthalene (60°), anthracene (86°), tetracene (116°), and pentacene (144°) substructures known. With the added protection of the phenyl groups on the central ring, compound **84** is much more robust than **77**. It is completely stable in the dark or in the solid state, but it decomposes to unknown products in bright room light in solution with a half-life of 36 h.[79]

Some twisted acenes (for example, **68**[74]) crystallize in chiral space groups with only one enantiomer present in each crystal. Unfortunately, when a crystal is dissolved, the acene
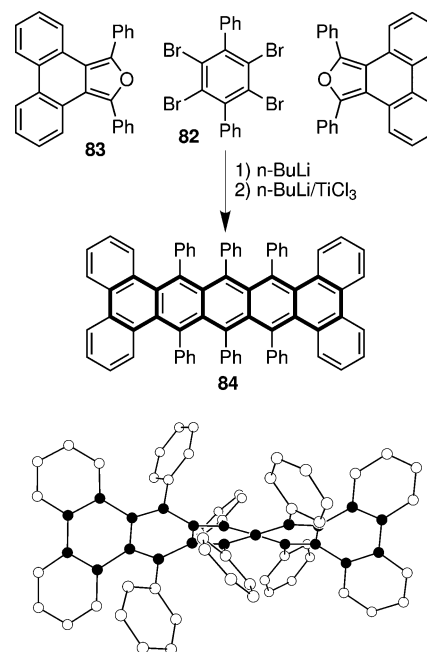


**Figure 21.**

racemizes almost instantly. Pentacene **84** appears to be the first twisted acene to be resolved into relatively stable enantiomers; they have very large specific rotations of $[\alpha]_D^{25} = +7440° \pm 150°$ and $[\alpha]_D^{25} = -7420° \pm 150°$.[79] However, this compound is not quite configurationally stable, racemizing with a half-life of 9 h at room temperature ($\Delta G^{\ddagger} = 23.8$ kcal/mol).[79]

## 5. Twisted Quinones

Benzannulated quinones are not proper acenes, but, as polycyclic ring systems containing only sp[2] hybridized carbons, they have similar structural characteristics, and there are several notably twisted examples.

The crystal structure of pentacenequinone **85** is entirely analogous to that of pentacene **77**: the molecule lies on a crystallographic center of inversion and possesses no net twist, but it contains naphthalene substructures twisted by 40°.[80] Interestingly, when **85** was reduced with sodium borohydride, upon aqueous workup the *cis*-dihydro compound **86** (Figure 22) was recovered in which the 1,4-
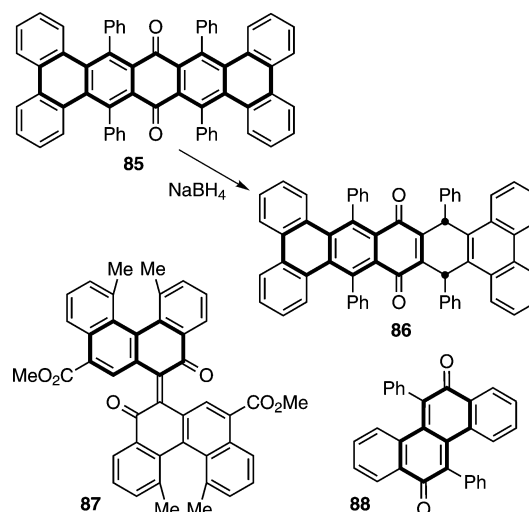


**Figure 22.**

anthracenedione substructure possesses a 43° twist.[81] AM1 calculations find this molecule to be 6 kcal/mol lower in energy than the hydroquinone corresponding to **85**; presumably the hydroquinone relieves strain by tautomerization to **86**.[81]

The quinoid double helicene **87** contains twisted naphthalene moieties (33°),[82] and the 2,6-naphthoquinone in **88** is much more strongly twisted (45°) than the naphthalene in the closely related compound **46** (31°) mentioned previously.[63] However, perhaps the most aesthetically pleasing twisted quinone is the $D_2$-symmetric, colossal **89** (Figure 23); the central anthraquinone is twisted by 51°.[83]
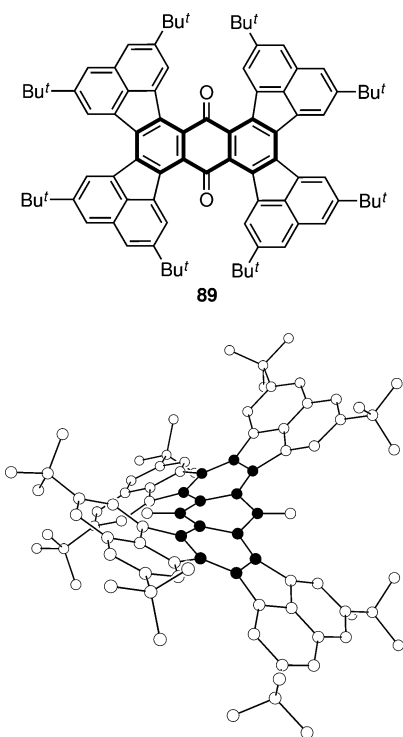


**89**



**Figure 23.**

## 6. Naturally-Occurring Twisted Acenes?

The most twisted natural "acenes" are all quinoid structures, and they display only modest distortions from planarity. Hypocrellin (**90**), cercosporin (**91**), and their simple derivatives contain anthracene substructures with 26−27° twists,[84−86] and the next most twisted natural product seems to be hypericin (**92**) with a mere 21° twist (Figure 24).[87]

One may hope that there exist natural products as yet undiscovered, or at least not yet crystallographically characterized, that are more highly twisted. However, at present, those of us "Designing the Molecular World" have little competition from Mother Nature in the arena of twisted acenes!

## 7. Prospects

Acenes even more highly twisted than those prepared thus far should be stable. AM1 calculations, which reproduce well the experimental structures of the most highly twisted acenes **74** and **84**,[75,79] indicate that hexacene **93** (Figure 25) should have a 178° twist.[75] A synthesis similar to that used for **84** may succeed for **93**, and if so, then it is easy to imagine a sequence yielding the fanciful Möbius band **94**!
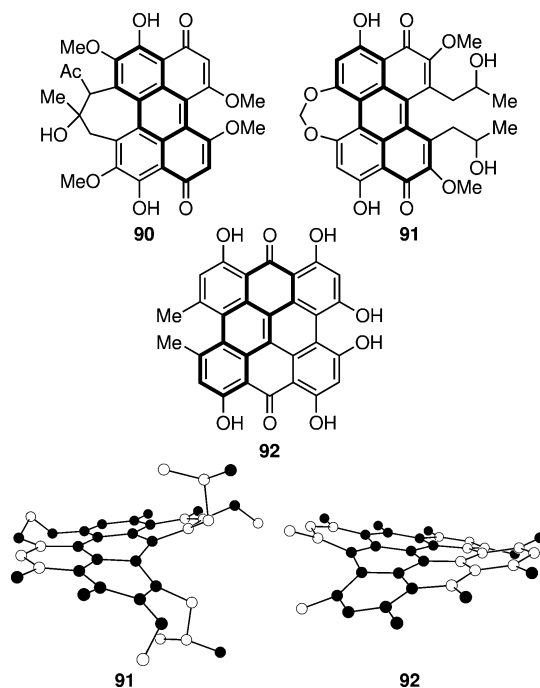


**90**



**91**



**92**



**91**                    **92**

**Figure 24.**

The author does not think that the limit to the degree of twist possible in these molecules is governed by any intrinsic instability, because the bulky groups that induce the twist also serve to protect the potentially reactive acene cores. Instead, the precursors of these acenes will become so sterically encumbered that it will no longer be possible to carry out the final ring closure or substitution. This limit has not yet been reached.

Most interest in the twisted acenes arises from their unusual structures, but these molecules may have significant practical applications. Many twisted acenes are highly fluorescent, and their most obvious potential applications are for the construction of light-emitting devices. The favorable characteristics of decaphenylanthracene (**19**) for electrogenerated chemiluminescence[27] and the use of compound **81** in light-emitting diodes have been mentioned.[78] A second, less obvious, potential application of the twisted acenes is for
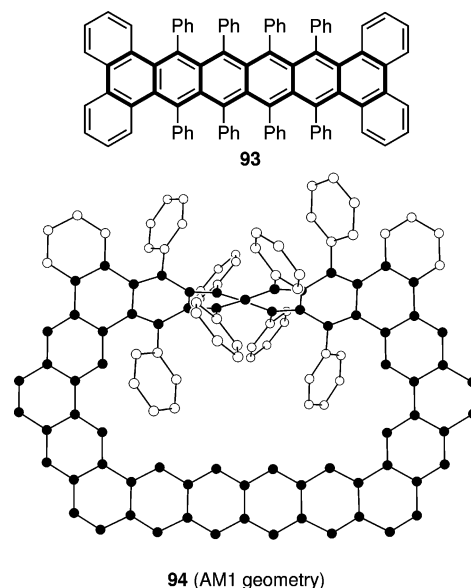


**93**



**94** (AM1 geometry)

**Figure 25.**

the construction of porous solids. The octakis(arylthio)-naphthalenes **4**−**7** readily form clathrates with a wide variety of solvents,[9−13] and several polyphenyl-substituted twisted acenes cited in this review, including compounds **11**, **12**, **18**, and **19**, have crystal structures containing large solvent channels.[15,16,25] This is a property shared by many large polyphenyl aromatics,[88,89] but with twisted acenes one may have a better chance to form porous solids with *chiral* channels (as indeed occurred with compound **11**), thus increasing the opportunities for their application in separations technologies. Finally, as stated above, the same bulky substituents that impart the strain and twist to these molecules also protect the acene cores from attack by external reagents. The resulting high (kinetic) stability of the twisted acenes can only enhance their value in materials applications.

## 8. Acknowledgments

## 9. References

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