On the Nature of Nonplanarity in the [N]Phenylenes

Daniel Holmes, Sriram Kumaraswamy, Adam J. Matzger, and K. Peter C. Vollhardt*[a]

Abstract: The [N]phenylenes display marked deformation from planarity in the crystalline state. In order to probe the generality of this phenomenon, several derivatives were synthesized and their single-crystal X-ray structures were obtained. All new compounds displayed some degree of nonplanarity. Thus, for example, the parent triangular [4]phenylene (**4b**) has a median bend angle at the ring junction of 1.5° and a range of 0.3° to 3.5°, whereas hexakis[triisopropylsilyl(ethynyl)] triangular [4]phenylene (**4c**) possesses the bulkiest appendages and the largest median bend angle and range (3.8° and 1.7°–5.6°, respectively). A detailed analysis of the bending and twisting angles at the ring junctions, however, revealed that the magnitude of deformations were independent of topology, molecular size, and substituent type. In contrast to the phenylenes, a Cambridge Structural Database (CSD) search of unsubstituted and non-*peri*-substituted naphthalenes and anthracenes shows these molecules to be virtually planar in the solid state. A comparison of the single-point energies (HF/6-31G*) of the phenylenes with the acenes calculated for molecules possessing a fixed bend angle at the ring fusion of 3°, 6°, 9°, and 12° reveals the former to be 26% to 45% easier to deform than the latter. Based on these results, the nonplanarity seen for the phenylenes is most likely a consequence of crystal-packing forces deforming particularly flexible molecules.

Keywords: ab initio calculations · acenes · nonplanarity · phenylenes · polycycles · solid-state structures

Introduction

The [N]phenylenes, where N denotes the number of benzene rings, are a new class of [4*n*]annuleno[4*n*+2]annulenes[1] in which the arrangement of opposing aromatic and antiaromatic π circuits and σ strain leads to decidedly nonaromatic character, which includes bond localization in the central benzenoid ring of the branched phenylenes with N ≥ 3 and the corresponding olefinic reactivity as demonstrated by their facile hydrogenation,[2] cyclopropanation, and epoxidation.[3] They have also been the subject of many theoretical analyses over the last several years, which have generally focused on the determination of the relative geometric and energetic properties of the various isomers of the [N]phenylenes.[4] All such treatments have yielded planar lowest energy structures, although both our calculations[5b, d] and those of Schulman et al.[4i, k] have shown these molecules to be quite flexible with respect to deplanarization. This finding is noteworthy in connection with the intriguing experimental observation that hexakis(trimethylsilyl) triangular [7]phenylene (**1**) adopts a bowl-shaped structure in the absence of any intramolecular restrictions to planarity.[5b] This result prompted us to revisit previous X-ray structural determinations of phenylenes. Indeed, while angular [3]phenylene (**2a**) is essentially planar,[6a] the molecules biphenylene (**3**),[7] hexakis(trimethylsilyl) triangular [4]phenylene (**4a**),[5a] and tetrakis(trimethylsilyl) linear [3]phenylene (**5a**)[5c] displayed curvature in the crystalline state (Figure 1). Consequently, the questions presented themselves as to the origin of this deformability and whether such deplanarization persisted in solution.

The ease of deformation may be a consequence of σ and/or π effects, both of which feature prominently in this class of hydrocarbons.[1–6] Thus, for example, the σ strain may be relieved by adoption of a nonplanar structure. Calculations and experiment have shown that olefins which possess bonding angles of less than 100°, as in bicyclobutene-$\Delta^{1,3}$, prefer a puckered structure.[8] Such pyramidalization of alkenes can also result from steric interactions,[9] as typified by the sesquinorbornenes.[10] Pyramidalization occurs as a consequence of rehybridization in strained olefins as a means of regaining some stabilization lost due to reduction of π bonding.[11, 12] For the phenylenes, reduction of π-antiaromatic overlap, which has been implicated as dominating the electronic interactions within the molecules,[4j] may be an additional driving force for deplanarization. The deviation from planarity of tetrafluorocyclobutadiene[13] and the cyclobutadiene dication[14] is noteworthy in this regard.

The preference of the benzene nuclei in the phenylenes to adopt a planar configuration might, on first sight, be expected to oppose the deplanarizing influence of the fused cyclo-

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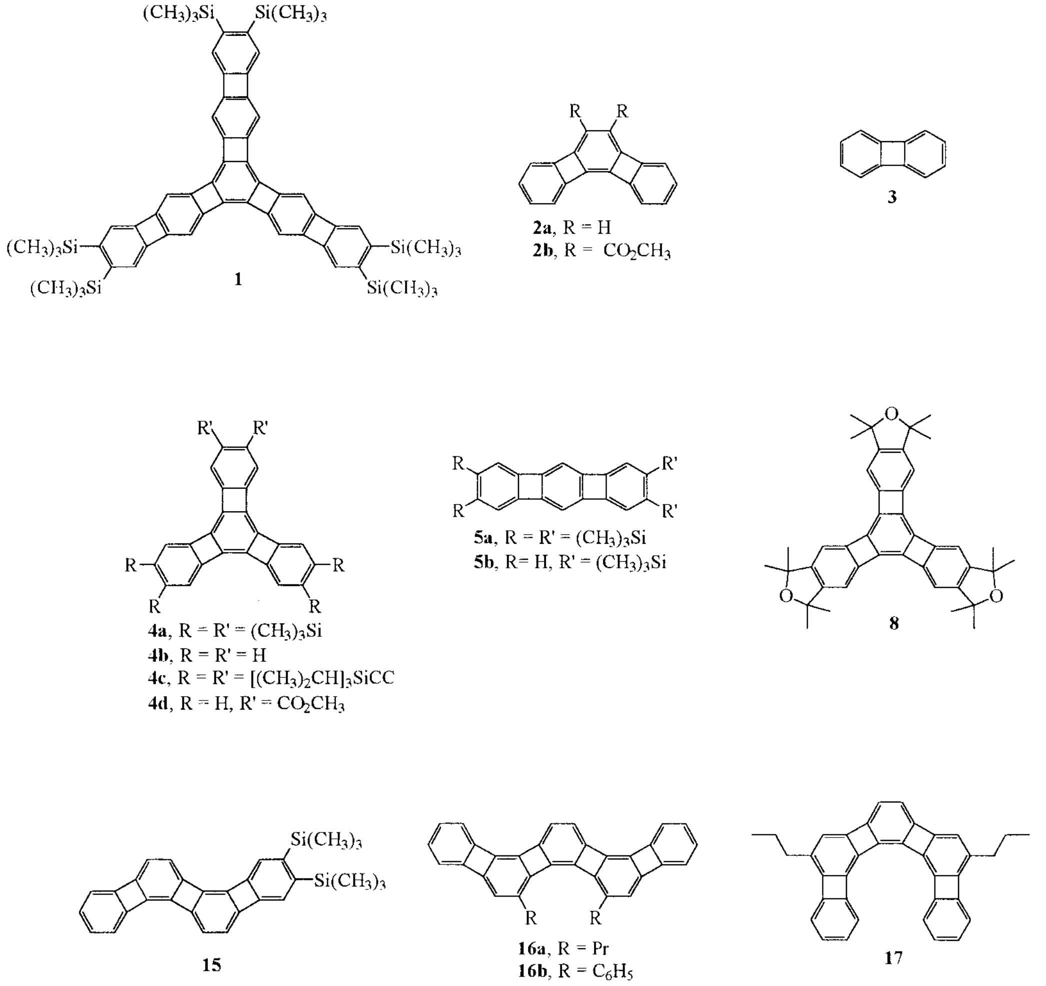

2a, R = H
2b, R = CO_2CH_3

4a, R = R' = $(CH_3)_3Si$
4b, R = R' = H
4c, R = R' = $[(CH_3)_2CH]_3SiCC$
4d, R = H, R' = CO_2CH_3

5a, R = R' = $(CH_3)_3Si$
5b, R = H, R' = $(CH_3)_3Si$

16a, R = Pr
16b, R = C_6H_5

Figure 1. List of [N]phenylene derivatives used in this study.

butadienes. However, it should be noted that benzene itself has been shown to be quite flexible.[15] In fact, Herndon pointed out that the majority of polycyclic benzenoids capable of existence will exhibit highly nonplanar structures due to nonbonded interactions.[16] Sterically induced deformations from planarity can be seen in many polycyclic aromatic hydrocarbons,[17, 18] including *peri*-substituted acenes[19] and, most notably, the helicenes.[20] Also, there exists a plethora of stable nonplanar geometrically constrained aromatic molecules; this class is exemplified by the cyclophanes,[21] buckminsterfullerene, the semibuckminsterfullerenes, and corannulene.[22] In a recent review on the subject, Herndon examined 38 examples of crystal structures of unsubstituted acenes.[17] He found that 12 were planar, 9 nearly planar, and 17 highly nonplanar. Deplanarization was ascribed to either special geometric constraints or steric interactions, the only exceptions were perylene[23] and quaterrylene.[24]

In this paper, we address the following questions by use of theory and experiment: Are the phenylenes intrinsically nonplanar? Is there a relationship between molecular topology, size, degree of substitution, and the extent of deplanarization? How do the deformations seen in the phenylenes compare with those of the appropriate acene models? To this end, we present the synthesis of two new [N]phenylenes, an improved route to 2,3-bis(trimethylsilyl) linear [3]phenylene (**5b**), six new crystal structures of [N]phenylene derivatives, a Cambridge Structural Database (CSD) search of substituted and unsubstituted acenes possessing no intramolecular interactions, a redetermination of the X-ray crystal structures of tetracene and pentacene, a quantitative analysis of deformation at the ring junctions for both the acenes and the phenylenes, and high-level ab initio calculations on the energetics of deformation in these compounds.

Results

Synthesis: Triangular [4]phenylene (**4b**)[5a] and hexakis-2,3,6,7,10,11-[(triisopropylsilyl)ethynyl] triangular [4]phenylene (**4c**)[5b] were prepared according to our literature procedure. Dimethyl triangular [4]phenylene-2,3-dicarboxylate (**4d**) was prepared in a manner analogous to the synthesis of the butyl carboxylate derivative.[25]

*Synthesis of dimethyl angular [3]phenylene-5,6-dicarboxylate (**2b**)*: Originally, angular [3]phenylene was synthesized by intramolecular CpCo-mediated cyclization of bis(2-ethynylphenyl)ethyne.[6] The present strategy allows a more efficient access to the substituted angular [3]phenylene framework and involves an intermolecular Co-mediated [2+2+2] cyclization

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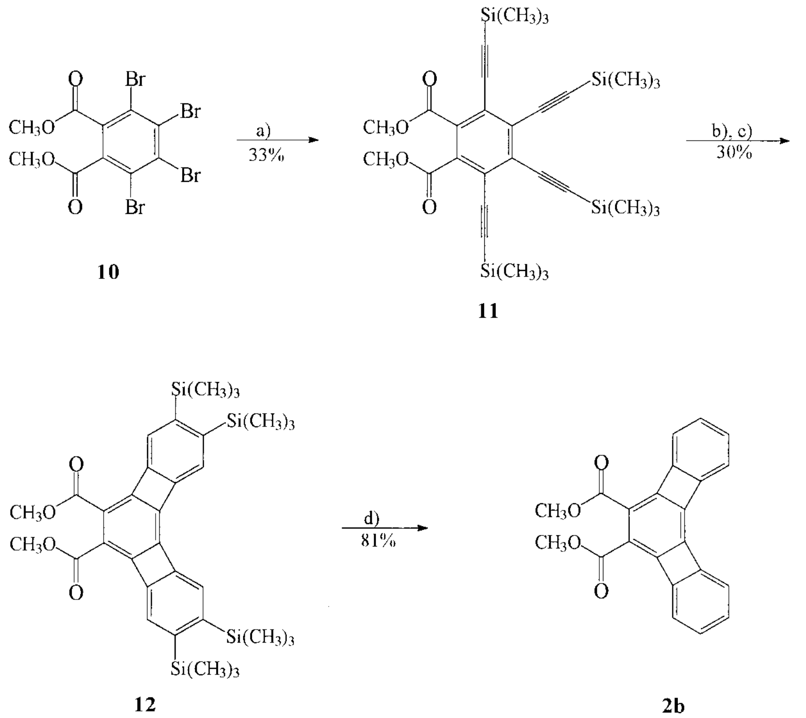
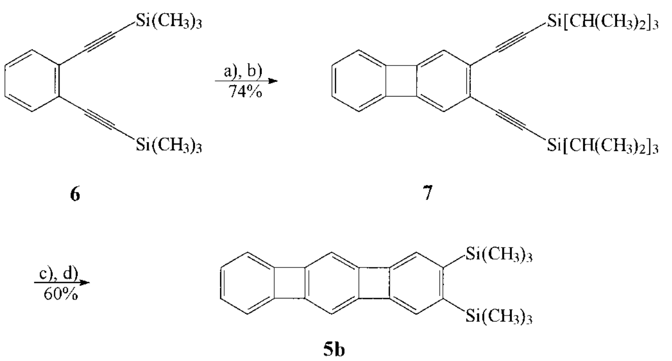


Scheme 1. a) $(CH_3)_3SiC_2H$, $[Pd(PPh_3)_2Cl_2]$, CuI, NEt_3, 20 h; b) $KF\cdot2H_2O$, [18]crown-6, DME, 23 °C; c) $[(CH_3)_3Si]_2C_2$ (solvent), $[CpCo(CO)_2]$, Δ, $h\nu$, 14 h; d) CF_3COOH, $CHCl_3$, 23 °C, 18 h.

of 1,2,3,4-tetraethynylarenes with bis(trimethylsilyl)acetylene. Scheme 1 depicts an application to the synthesis of **2b**.

Thus, fourfold coupling of (trimethylsilyl)acetylene to dimethyltetrabromophthalate (**10**)[26] with standard Pd^0/Cu^I conditions[27] gave tetrayne **11** in 75% yield. Compound **11** was desilylated by the use of $KF\cdot2H_2O$ and [18]crown-6 to furnish the free tetrayne, which was cyclized with bis(trimethylsilyl)acetylene using $[CpCo(CO)_2]$ to afford **12** in 30% yield. Final desilylation with trifluoroacetic acid gave **2b** in 81% yield.

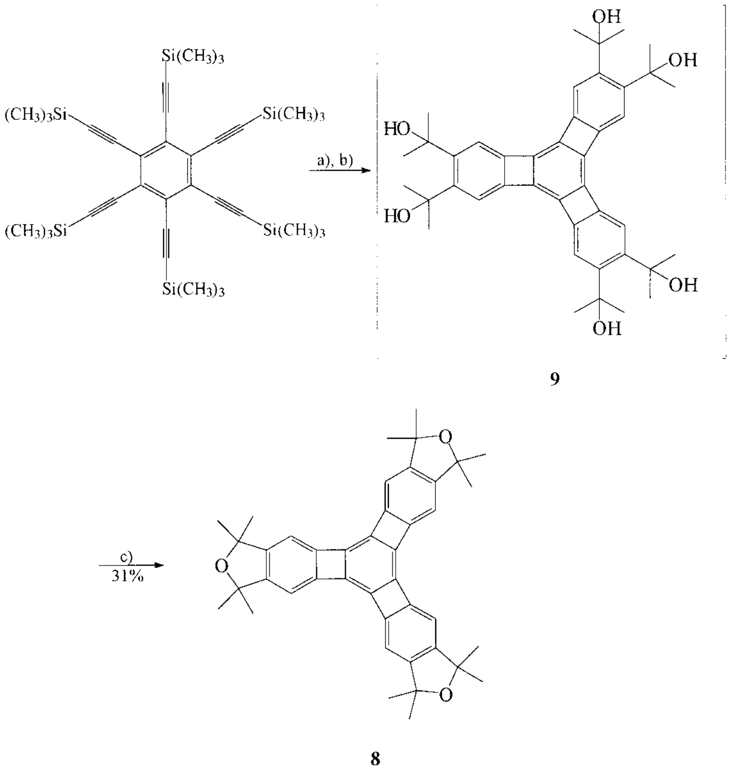
*Synthesis of 2,3-bis(trimethylsilyl) linear [3]phenylene (**5b**)*: Scheme 2 outlines the synthetic strategy for the formation of **5b**, improved over that employed previously,[5c] by exploiting the utility of 1,6-bis(triisopropylsilyl)-1,3,5-hexatriyne in the Co-mediated [2+2+2] cyclization to directly access *o*-diethynyl arenes.[5b, 28]



Scheme 2. a) $KF\cdot2H_2O$, [18]crown-6, DME, 23 °C; b) 1,6-bis(triisopropylsilyl)-1,3,5-hexatriyne (3 equiv), $[CpCo(CO)_2]$, xylenes, Δ, $h\nu$, 16 h; c) $Bu_4N^+F^-$, THF, 23 °C; d) $[(CH_3)_3Si]_2C_2$ (solvent), $[CpCo(CO)_2]$, Δ, $h\nu$, 13 h.

Thus, 1,2-bis[(trimethylsilyl)ethynyl]benzene (**6**)[5c] was desilylated by the use of $KF\cdot2H_2O$ and [18]crown-6 and then subjected to cyclization with 1,6-bis(triisopropylsilyl)-1,3,5-hexatriyne[28, 29] in the presence of $[CpCo(CO)_2]$ to afford 2,3-bis[(triisopropylsilyl)ethynyl] biphenylene (**7**) in 74% yield. Subsequent desilylation with $[Bu_4N]^+F^-$, followed by $[CpCo(CO)_2]$-catalyzed cyclization with bis(trimethylsilyl)acetylene as solvent and cyclization partner provided **5b** in 60% yield.

*Synthesis of tris(2,2,5,5-tetramethyldihydrofurano) triangular [4]phenylene (**8**)*: Compound **8** was obtained by the route shown in Scheme 3, modeled on the synthesis of hexakis(trimethylsilyl) triangular [4]phenylene (**4a**); this route has as its cornerstone a remarkable threefold CpCo-mediated alkyne trimerization to provide six rings in one step in a yield of 53%.[5a] Thus, hexakis[(trimethylsilyl)ethynyl]benzene[30] was desilylated by the use of $KF\cdot2H_2O$ and [18]crown-6 to



Scheme 3. a) $KF\cdot2H_2O$, [18]crown-6, DME, 23 °C; b) 2,5-dimethyl-3-hexyne-2,5-diol (6 equiv), $[CpCo(CO)_2]$, xylenes, Δ, $h\nu$, 16 h; c) p-$CH_3C_6H_4SO_3H$, benzene, 4 Å sieves, 12 h.

afford the free hexayne, which was cyclized with 2,5-dimethyl-3-hexyne-2,5-diol in the presence of [CpCo(CO)$_2$]. The crude hexaol **9** was then subjected to acid-catalyzed ether formation by treatment with *p*-toluenesulfonic acid in benzene at reflux to furnish **8** in 31 % yield.

X-ray crystallography: In all cases, X-ray quality crystals were grown by slow evaporation of solutions at room temperature with the exception of **5b**, which required slow cooling. Bond length and bond angle values for **2b**, **4b–d**, **5b**, and **8** are very similar to those of **2a**, **4a**, and **5a**, respectively, reported and discussed in some detail previously. Significantly, all the new structures exhibited nonplanarity in the solid state. Crystal data and data collection parameters are presented in Tables 1 and 2.

Table 1. Details of the crystal structure analyses for **2b** and **4b–d**.

	2b	**4b**	**4c**	**4d**
formula	$C_{22}H_{14}O_4$	$C_{24}H_{12}$	$C_{90}H_{132}Si_6 \cdot 1.5\,C_4H_8O_2$	$C_{28}H_{16}O_4$
M_r	342.35	300.36	1514.70	416.43
crystal system	triclinic	orthorhombic	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$Pna2_1$(no. 33)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	10.2837(2)	14.562(1)	14.0766(2)	12.7620(4)
b [Å]	11.4673(4)	18.398(2)	19.6157(2)	7.4295(2)
c [Å]	14.8844(5)	5.5274(4)	20.4719(3)	21.3289(7)
α [°]	98.906(1)		118.372(1)	
β [°]	99.567(1)		96.750(1)	99.686(1)
γ [°]	106.521(1)		90.182(1)	
V [Å^3]	1621.03(13)	1480.9(2)	4927.96(15)	1993.48(9)
Z	4	4	2	4
ρ_{calcd} [g cm^{-1}]	1.403	1.347	1.021	1.387
$F(000)$	712.00	624.00	1656.00	864.00
μ [cm^{-1}]	0.96	0.76	1.28	0.93
T [°C]	− 131	− 118.0	− 96	− 145
crystal size [mm^3]	0.34 × 0.09 × 0.08	0.40 × 0.15 × 0.04	0.28 × 0.20 × 0.15	0.21 × 0.20 × 0.15
2θ range [°]	3–52°	4–45°	4–42°	3–45°
total no. reflns	7684	6670	20484	9377
independent reflns	5341 ($R_{int} = 0.025$)	2608 ($R_{int} = 0.062$)	13696 ($R_{int} = 0.051$)	3791 ($R_{int} = 0.027$)
observed reflns [$I > 3\sigma(I)$]	3161	1606	6983	2701
parameters	470	216	946	353
abs. correction	ellipsoidal	ellipsoidal		
min./max. trans. ratio	0.844/1.000	0.840/0.990		
min./max. residual elec. density [e Å^{-3}]	− 0.26/0.25	− 0.29/0.25	− 0.40/0.52	− 0.20/0.21
extinction coefficient	0.000000679	0.00000105		
GOF	1.60	1.93	2.74	1.71
R[a]	0.047	0.052	0.077	0.033
R_w[b]	0.048	0.054	0.090	0.043

[a] refined against F_o. [b] $w = 1/\sigma^2(F_o)$.

Table 2. Details of the crystal structure analyses for **5b**, **8**, **13**, and **14**.

	5b	**8**	**13**	**14**
formula	$C_{24}H_{26}Si_2$	$C_{42}H_{42}O_3 \cdot 2\,C_7D_8$	$C_{18}H_{12}$	$C_{22}H_{14}$
M_r	370.64	795.07	228.29	278.35
crystal system	monoclinic	orthorhombic	triclinic	triclinic
space group	Cc (no. 9)	$Pna2_1$ (no. 33)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	15.8100(1)	15.3797(8)	6.0565(9)	6.2753(8)
b [Å]	15.7992(2)	34.083(2)	7.8376(11)	7.7138(10)
c [Å]	34.5802(6)	8.7252(4)	13.0104(18)	14.4424(19)
α [°]			77.127(2)	76.752(2)
β [°]	96.277(1)		72.118(2)	88.011(2)
γ [°]			85.792(2)	84.524(2)
V [Å^3]	8585.87(26)	4573.6(3)	572.97(24)	677.32(26)
Z	16	4	2	2
ρ_{calcd} [g cm^{-1}]	1.15	1.153	1.323	1.365
$F(000)$	3168.00	1672.00	240.00	292.00
μ [cm^{-1}]	1.70	0.68	0.75	0.77
T [°C]	− 96	− 117	− 98	− 93
crystal size [mm^3]	0.35 × 0.30 × 0.02	0.36 × 0.31 × 0.19	0.43 × 0.40 × 0.01	0.35 × 0.25 × 0.01
2θ range [°]	3–45°	4–45°	3–52°	3–52°
total no. reflns	18160	18951	2721	3186
independent reflns	6439 ($R_{int} = 0.055$)	5465 ($R_{int} = 0.033$)	1899	2235
observed reflns [$I > 3\sigma(I)$]	3320	4129	985	1199
parameters	453	531	163	199
abs. correction	ellipsoidal		ellipsoidal	ellipsoidal
min./max. trans. ratio	0.792/0.978		0.721/0.986	0.826/0.987
min./max. residual elec. density [e Å^{-3}]	− 0.36/0.49	− 0.19/0.42	− 0.22/0.17	− 0.23/0.20
extinction coefficient		0.000000732		
GOF	2.05	2.04	2.66	2.68
R[a]	0.067	0.045	0.057	0.054
R_w[b]	0.070	0.053	0.070	0.066

[a] refined against F_o. [b] $w = 1/\sigma^2(F_o)$.

*Crystal structure of dimethyl angular [3]phenylene-5,6-dicarboxylate (**2b**)*: Unlike the crystal structure of **2a**, which is exceptional among those of the other phenylenes in exhibiting a virtually planar molecule,[6a] the X-ray structure of **2b** revealed a nonplanar frame. As shown in Figure 2, there are two inequivalent molecules of **2b** in the unit cell. One displays a bow-shaped structure, the other a sinusoidal structure. There are 32 intermolecular contacts within the sum of the van der Waals radii between neighboring molecules in the unit cell.

*Crystal structure of triangular [4]phenylene (**4b**)*: This structure is significant, because **4b** is the parent triangular [4]phenylene, and the structure exhibits a completely localized central cyclohexatriene. As can be seen in Figure 3, the crystal structure of **4b** revealed a hydrocarbon with a slightly bowl-shaped topology accompanied by some twisting. The molecules pack as sheets of inter-

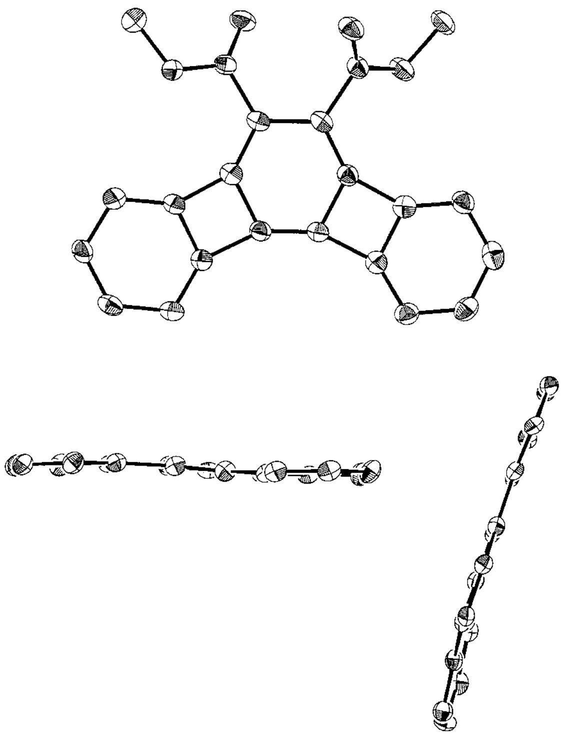


Figure 2. Structure of **2b** in the crystal: views of one of the two molecules in the unit cell from above (top) and both of them from the side, methyl ester groups omitted for clarity (bottom).

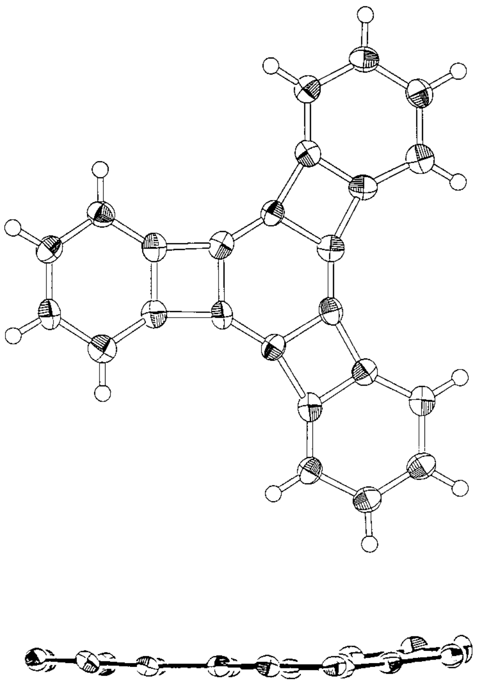


Figure 3. Structure of **4b** in the crystal: views from above (top) and the side (bottom).

locking units with an acute angle between them of approximately 70°. There appear to be no π-stacking or edge-π interactions. Twelve intermolecular contacts exist between carbon atoms below the sum of their van der Waals radii. Except for the local perturbations that originate from the trimethylsilyl substituents in **4a**, the structural features of **4a** and **4b** are quite similar, especially the extent of bond alternation: the difference between the average long and short bonds of the central rings of **4a** and **4b** are 0.159 and 0.154 Å, respectively.

*Crystal structure of hexakis[(triisopropylsilyl)ethynyl] triangular [4]phenylene (**4c**)*: As revealed in Figure 4, compound **4c** exhibits a marked bowl shape. In the unit cell, two molecules stack in a staggered cofacial manner with their centers offset, which is also seen in the structure of hexakis(trimethylsilyl) triangular [7]phenylene (**1**).[5b] Interestingly, as with **1**, there are close contacts (~3.3 Å) between the convex faces of the phenylene cores. There are two highly disordered ethyl acetate molecules in the unit cell. Each of these has contacts of less than 3.50 Å with the phenylene core. One molecule of ethyl acetate is held between the concave faces of two **4c** molecules.

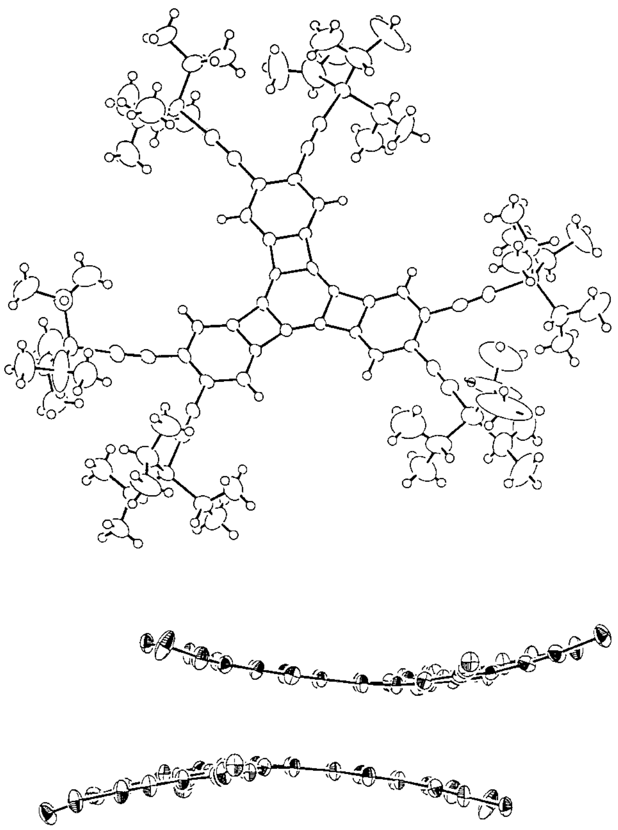


Figure 4. Structure of **4c** in the crystal: views of one molecule in the unit cell from above (top) and two of them from the side, triisopropylsilyl groups omitted for clarity (bottom).

*Crystal structure of dimethyl triangular [4]phenylene-2,3-dicarboxylate (**4d**)*: As Figure 5 demonstrates, **4d** has adopted a slightly nonplanar structure in which two benzocyclobutadiene "arms" bend in the same direction, while the last arm containing the ester groups remains basically flat. The molecules are stacked in columns with an inversion center between neighboring units. There are close-contacts (3.22, 3.27, and 3.29 Å) between the carbons of the phenylene cores of adjacent molecules.

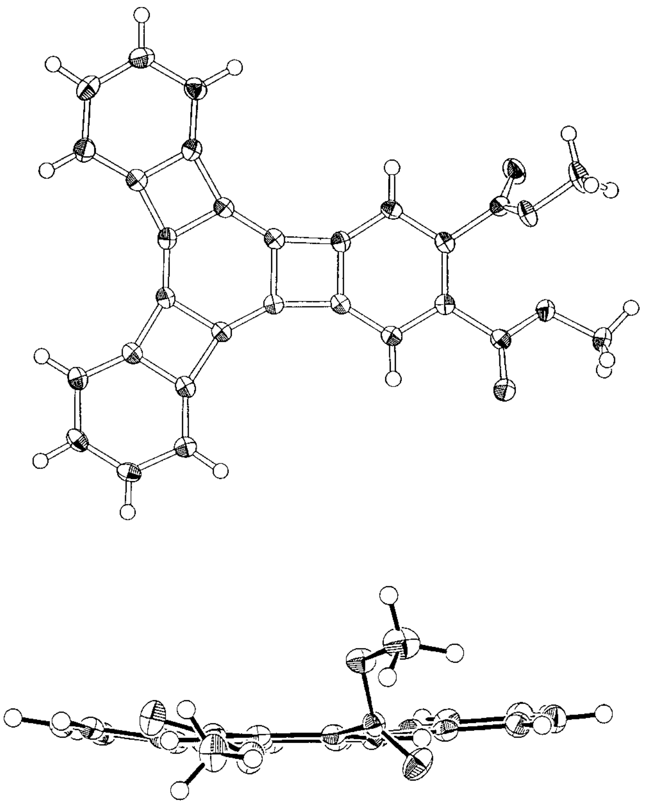


Figure 5. Structure of **4d** in the crystal: views from above (top) and the side (bottom).

*Crystal structure of 2,3-bis(trimethylsilyl) linear [3]phenylene (**5b**)*: Compound **5b** exhibits a slightly bowed topology (Figure 6). There are four inequivalent molecules in the unit cell, which necessitated the use of isotropic refinement. They pack in staggered pairs in which the trimethylsilyl groups are kept distant. The two pairs are related by a pseudoinversion center. There are no nonbonded contacts of less than 3.40 Å, the closest contact of 3.43 Å occuring between carbons of the phenylene core.

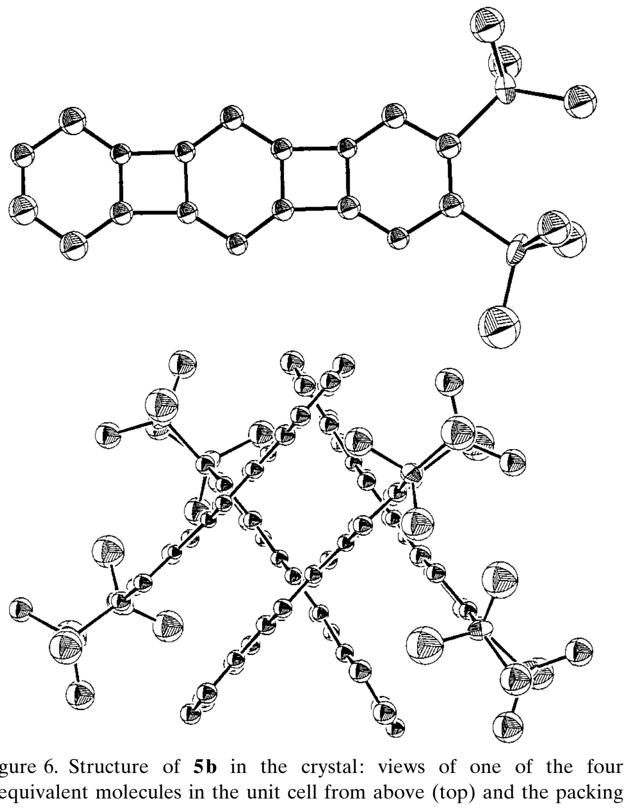


Figure 6. Structure of **5b** in the crystal: views of one of the four inequivalent molecules in the unit cell from above (top) and the packing of all four from the side (bottom).

*Crystal structure of tris(2,2,5,5-tetramethyldihydrofurano) triangular [4]phenylene (**8**)*: As seen in Figure 7, compound **8** is nonplanar with the three "arms" showing varying amounts of twisting and bending. Inspection of the displacements of the atoms from the mean plane of the central ring shows that one arm bends in the opposite direction to the other two. There are two toluene molecules per unit cell. Packing occurs without π-stacking or edge-π interactions. The closest contact is between a furano oxygen and a carbon of the toluene solvate (3.35 Å).

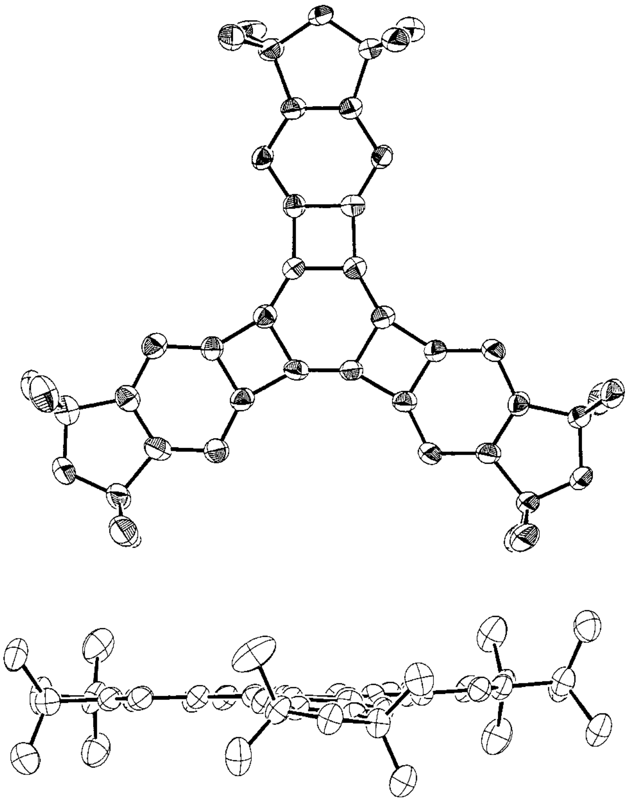


Figure 7. Structure of **8** in the crystal: views from above (top) and the side (bottom).

*Redetermination of the crystal structure of tetracene (**13**)*: The original structural determination of tetracene was found to be of insufficient quality to pinpoint subtle deformations.[31] Our redetermined unit cell data were in accord with the previous study and a more recent powder diffraction study.[32] However, although the average bond lengths agreed well with the earlier data, the individual bond lengths differed significantly in the unit cell. This discrepancy is probably owing to the older data collection technique, in which two-dimensional film data were used. The increased quality of the new structure also manifested itself in reduced uncertainty in atomic positions. As shown in Figure 8, **13** exhibits a virtually planar structure.

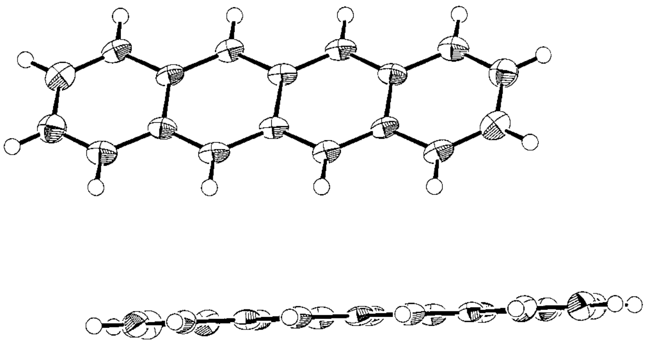


Figure 8. Structure of **13** in the crystal: views from above (top) and the side (bottom).

*Redetermination of the crystal structure of pentacene (**14**)*: Although the crystallization solvent was the same as that used in the previous study, the unit cell parameters were in disagreement with those previously determined.[33] However, this factor did not affect the gross structural features and good agreement was found for the average bond lengths of the two inequivalent molecules in the unit cell. As seen in Figure 9, the X-ray structure revealed an essentially planar molecule.

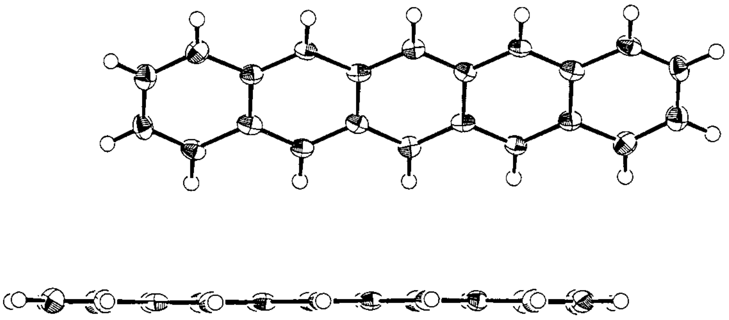


Figure 9. Structure of **14** in the crystal: views from above (top) and the side (bottom).

Cambridge Structural Database (CSD) search of naphthalenes and anthracenes: The CSD search was conducted according to the parameters defined in the Experimental Section. Initially, it was directed towards unsubstituted naphthalenes and anthracenes (the effect of substitution was investigated separately). The search retrieved 24 unsubstituted naphthalenes and 25 unsubstituted anthracenes, typically solvates or charge-transfer complexes. From the torsion angles so obtained, the bend and twist angles at the ring junctions were calculated as described in the Data Analysis section. The distribution of the bend and twist angles is displayed in Figure 10.

The effect of non-*peri*-substitution was investigated in the same manner. In order to conform with the substitution pattern of the available [N]phenylene structures, only di- and tetrasubstituted acenes were included. The CSD search retrieved 139 inequivalent 2,3-di- and 2,3,6,7-tetrasubstituted naphthalene molecules and four inequivalent 2,3-di- and 2,3,7,8-tetrasubstituted anthracenes. The distribution of the twist and bend values is displayed in Figure 11.

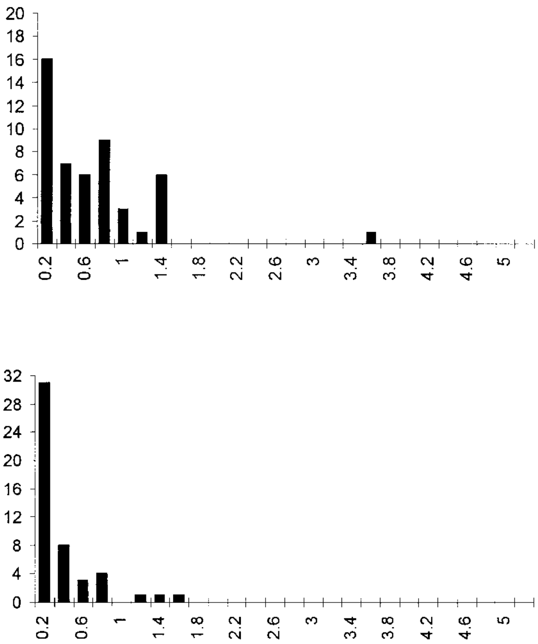


Figure 10. Distribution of deformation angles at the ring junction in unsubstituted acenes with bin sizes of 0.2° increments: twist angles (top) and bend angles (bottom).

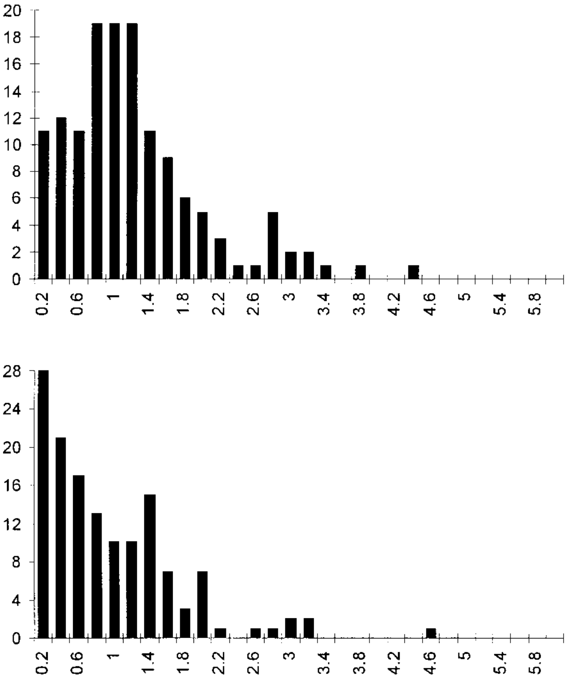


Figure 11. Distribution of deformation angles at the ring junction in substituted acenes with bin sizes of 0.2° increments: twist angles (top) and bend angles (bottom).

Discussion

Nonplanarity in naphthalene and anthracene in the absence of intramolecular interactions: Naphthalene and anthracene represent ideal compounds on which to investigate the effects of crystal packing on traditionally planar molecules. As can be seen in Figure 10, intramolecular interactions induce slight deviations from planarity in naphthalene and anthracene. A mean bend angle of 0.24° was found for these unsubstituted acenes. The median value was slightly lower at 0.09°. The search gave eleven structures with bend values of 0.0°. These data indicate the presence of an inversion center within or a mirror plane containing the molecule. The effect of imposing one of these symmetry elements on a molecule is to reduce the computed deformation angle to 0°. With these values eliminated from the data set, the average becomes 0.30° and the median becomes 0.17°. The mean twist for the set is 0.56° with a median value of 0.48°. The anomalously high value of 3.56° belongs to an anthracene molecule in a complex with 3,3′,5,5′-tetrachlorodiphenoxinone.[34] Apparently, the presence of a torsion angle of 4.06° between the six-membered rings in this molecule induces an artificially high twist in the anthracene.

The redetermined structures of tetracene and pentacene reveal that larger molecular size and hence, the extent of conjugation, does not lead to increased nonplanarity for the acenes. For tetracene, the angles between least-squares planes of adjacent benzene rings are 0.28 and 0.91°; for pentacene, they are 0.18, 0.30, 0.54, and 0.69°. It is clear from the data that crystal-packing forces induce very small deformations on the parent acenes, most of them within instrumental error.

As shown in Figure 11, substitution in the non-*peri*-positions of naphthalene and anthracene leads to increased distortions. The mean bend value for this set was 0.84° with a range of 4.4°. Its median is 0.67°, indicating the presence of a few relatively highly deformed molecules. The mean twist for the set is somewhat larger, 1.1°, and the range slightly narrower, 4.2°. The median twist is 0.97°, again due to the presence of some "abnormal" molecules in the set. Careful examination of the original experimental data for these "abnormal" molecules did not reveal any potential flaws.[35] There does not appear to be any correlation between substituent size or electron donating/withdrawing ability of the substituent on the degree of nonplanarity. As in the case of the parent acenes, the data suggest that the minimal deformations that occur are the result of crystal-packing forces; however, the overall extent of deformation is increased with substitution and the range of values is significantly larger.

Specific examples of nonplanarity in the [N]phenylenes: Figure 1 displays the molecules used in this analysis. Bend and twist angles were extracted from these structures using the method described in the Data Analysis section.

The already available and herein reported X-ray structures of [N]phenylene molecules represent all the currently accessible topologies; namely, linear, angular, zigzag, and triangular, and possess a variety of substituents ranging from the relatively small alkyl to the bulky triisopropylsilyl group. Table 3 lists the median values and range for the twist (T) and bend (B) angles in each compound.

The average degree of deformation in the parent compounds **2a**, **3**, and **4b** is minimal relative to their substituted counterparts. Compound **4b** is the most nonplanar in this group, with a large range of deformation values (0.3–3.5°), whereas **2a** remains virtually planar (0.0–1.0°). Substitution leads to increased deplanarization; however, there is no obvious correlation between its extent and the size of the substituent. For example, compound **4c** possesses the most bulky appendages, triisopropylsilyl, and does indeed show the largest median bend value of 3.8°, yet both the trimethylsilyl substituted **5a** and methyl ester **2b** exhibit equally large deformations ($B_m = 3.5$ and 3.0°, respectively). One could have expected that extended conjugation and decrease in the HOMO–LUMO gap could have lead to (roughly) increased nonplanarity.[36] However, this does not seem to be the case for the phenylenes, as can be seen for **4a** and its tris(benzocyclobutadieno) homologue **1** (Table 3), which show a similar degree of deformation.

Table 3. Deformation angles [°] for the [N]phenylenes.[a]

	B_m	B_r	T_m^{four}	T_r^{four}	T_m^{six}	T_r^{six}
1	2.0	0.1–5.1	0.7	0.1–1.5	1.4	0.2–5.3
2a(m1)	0.5	0.4–0.9	0.4	0.2–0.5	0.4	0.1–1.1
2a(m2)	0.2	0.0–0.8	0.2	0.1–1.0	0.2	0.1–0.4
2a(m3)	0.6	0.3–1.0	0.2	0.1–0.6	0.2	0.1–1.4
2b(m1)	3.1	2.3–3.7	1.2	0.9–1.4	0.8	0.3–2.1
2b(m2)	2.9	1.0–6.0	0.3	0.2–0.3	0.4	0.2–0.5
3(m1)	0.1	0.1	0.0	0.0	1.1	1.1
3(m2)	0.8	0.0–1.6	0.6	0.6	1.0	1.0
4a	2.5	0.3–3.28	0.6	0.1–2.6	1.5	0.3–7.0
4b	1.5	0.3–3.5	0.5	0.3–1.3	1.2	0.2–3.8
4c	3.8	1.7–5.6	1.4	0.6–1.6	1.8	0.1–4.5
4d	1.9	0.6–3.9	0.8	0.6–3.1	1.8	0.3–4.8
5a	3.5	3.2–3.8	1.3	1.3	0.9	0.7–1.1
8	1.2	0.4–3.1	0.6	0.1–1.2	2.6	0.1–4.8
15	2.8	0.2–5.3	0.7	0.6–1.0	1.2	0.8–2.6
16a	1.2	0.2–1.5	1.2	0.4–2.1	1.4	0.6–4.0
16b	0.5	0.1–1.8	1.0	0.0–1.9	2.0	0.5–4.1
17	1.0	0.0–4.1	0.6	0.4–1.8	1.7	0.1–3.2

[a] The subscripts m and r refer to the median and the range respectively.

The extent and direction of the deplanarization appear to be random and independent of molecular topology, perhaps with the exception of the triangular phenylenes, in which the sense of curvature of the inner and outer junctions is generally the same (see, however, **8**), thereby contributing to their bowl-shaped structures, as exemplified by compound **4c** (Figure 3), which has bend angles of 5.6, 3.9, and 3.7° around the central ring and 4.2, 2.4, and 1.7° for the outer junctions. Interestingly, the least deplanarized benzocyclobutadiene unit of **4c** exhibits the largest degree of six-membered ring twist in the molecule (4.5 and 3.6°). The extent of deformation may be attributed to the numerous intermolecular close contacts. For **1**, two of the arms bend in the same direction. The bend values from the center outward are 2.30, 0.65, 2.20, and 1.7° for one arm, and 4.30, 1.35, 5.10, and 3.60° for the other. For the third, the inner ring fusions are distorted in the same direction as the other arms (0.10, 2.30°), while the two outermost junctions are bent slightly in the opposite direction (−0.4° each). Also, the latter exhibit the largest degree of twisting in the four- (1.5°) and six-membered ring (5.3°). Compound **8** does not exhibit the typical bowl-shaped structure, rather the molecule has one arm slightly bent in the opposite direction to the rest of the molecule (0.7°, 1.3° compared with −1.8°, −3.1° and −1.2°, −0.4° for the other arms).

The so far only published crystal structure of a linear phenylene, tetrakis(trimethylsilyl) linear [3]phenylene (**5a**),[5c] shows a molecule that adopts a sinusoidal shape. In contrast, the crystal structure of the bis(trimethylsilyl) derivative **5b** reveals a curved structure. In both cases the packing diagrams indicate that the trimethylsilyl groups play a significant role in enforcing the shape of the molecule in the solid state (Figure 6). Indeed, another molecule possessing identical substitution, namely bis(trimethylsilyl) zigzag [4]phenylene (**15**),[37] exhibits a similar packing pattern and, most notably, **15** has a similar, albeit much greater, degree of curvature (bend angles of 2.8, 2.9, 5.1, and 5.3° are present in the molecule).

Compound **2a** is the only phenylene structure obtained thus far that is planar. In light of the results presented here, the flatness of **2a** may be fortuitous. Indeed, disruption of the packing efficiency by the introduction of substitution as in **2b** leads to significant deviation from planarity. Here, one of the inequivalent molecules adopts a bow shape with bend values from the center outward of −5.95 and −2.95° for one arm, and 0.95 and −2.85° for the other. The remaining molecule exhibits a sinusoidal shape with bend values (from the central ring) of 3.70 and 3.35° for one arm, and −2.85 and −2.25° for the other. There are several intermolecular interactions below 3.40 Å and these close contacts may contribute (but not in a readily explainable manner) to deplanarization in this molecule. The fact that **2b** displays two modes of deformation within the same crystalline environment is also suggestive of the influence of crystal-packing forces.

In the [5]phenylene series, there are crystal structures of three compounds; the dipropyl and diphenyl zigzag [5]phenylene (**16a** and **16b**, respectively),[37] and the dipropyl angular [5]phenylene (**17**).[38] For **16a** and **16b**, there is only minor bending (the largest value being 1.8°); however, there does exist significant twisting, a maximum of 4.0° for each, presumably due to steric interactions of the substituents. Compound **17** possesses a helical structure in which most of the deplanarization originates from the central portion of the molecule (central bend values of 2.3 and 4.1° versus 1.0° for the outer junctions).

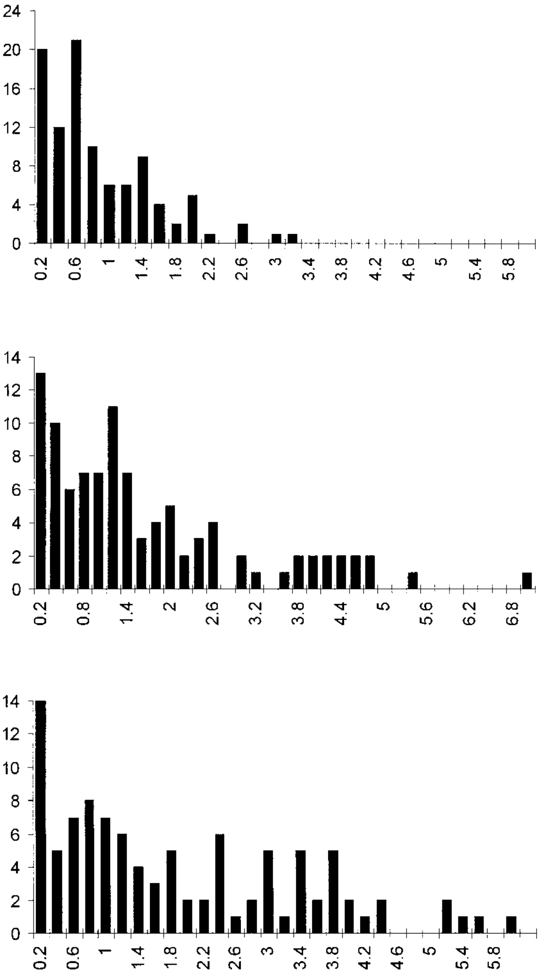


Figure 12. Distribution of deformation angles in the [N]phenylenes with bin sizes of 0.2° increments: twist angles in the four-membered rings (top), in the six-membered rings (middle), and bend angles at the ring junctions (bottom).

Comparison of the nonplanarity in the phenylenes and the acenes: Figure 12 displays the distribution of deformation values for the entire set of [N]phenylene molecules. The pattern of bend angles is indicative of a random distribution. The range of values is 5.95° and the median is 1.3°. The distribution of twist values in the four-membered rings is centered at 0.60° with a few surprisingly large angles (>2.4°). The distribution of twist values in the six-membered rings is centered at 1.1° and has a greater range than the four-membered rings (a range of 6.9° compared with 3.1°, respectively), demonstrating the greater flexibility of the six-membered rings. If one removes the unsubstituted phenylenes from the distribution, there is no appreciable increase in the median twist angles ($T^{four} = 0.7$ and $T^{six} = 1.4°$ for substituted phenylenes). There is, however, an increase in the median bend angle from 1.3 to 1.8° for substituted phenylenes. A possible explanation for the last observation is that substituents disrupt packing efficiency and that the phenylene frames are curving to accommodate them.

A comparison of the distribution of deformation angles for the acenes and the phenylenes reveals that the overall bending in the latter is greater than in the former, as evident in the larger median and range of values for the phenylenes. Whereas the acenes show a relatively peaked distribution of bend angles (kurtosis = 3.4), the phenylenes show an even distribution over the entire range (kurtosis = −0.2). The twisting in the six-membered rings is essentially the same for both classes of molecules with a few high values (>4.2°) for the phenylenes. Interestingly, while there is a slight preference for twisting over bending for the substituted acenes (1.1° to 0.77°, respectively), the phenylenes display basically no preference for bending over twisting (1.3 to 1.4°, respectively). This finding may be due to restriction of torsional deformation in the phenylenes by the four-membered ring annulation. If one assumes that, on average, the crystal-packing forces are of similar magnitudes for the acenes and the phenylenes, then the data suggest that the phenylenes are more flexible.

Compound **8** was synthesized in order to probe the issue of deplanarization in solution. However, a variable temperature ^1H NMR experiment showed no change in the singlet resonance for the methyl groups on cooling to −93 °C; this is consistent with a barrier to bowl-to-bowl interconversion too low to measure experimentally or with the presence of a planar molecule. Our attention, therefore, turned to computational techniques to elucidate the (unencumbered) ground state geometry of these molecules.

Energetics of deformation: Initial efforts utilized molecular mechanics and semiempirical approaches, since these have been shown by Herndon to effectively predict the geometry of the acenes.[17] When applied to linear [3]phenylene (**18**), biphenylene (**3**), and triangular [4]phenylene (**4b**), all these systems emerged with a planar most stable structure. This result was also obtained with ab initio methods on **4b** at the HF/6-31G* level. The addition of electron correlation, HF/6-31G(2d), and the use of both density functional (Becke3LYP/6-31G*) and MP2/6-31G* optimizations of **4b** did not change this feature.

In light of these calculational results, it seems likely that crystal-packing forces are responsible for the deplanarization observed in the solid state. Here, close packing often goes in tandem with the adoption of higher energy conformations than would be observed in the absence of close neighbors.[39] An example of this phenomenon is seen in the crystal structure of biphenyl (and some derivatives), which reveals preference for a relatively more coplanar arrangement that is more energetic (ca. 1.4 kcal mol^{-1}) than the minimum energy conformation.[40] Molecules can also crystallize in various polymorphic modifications which exhibit significantly differing molecular conformations that possess energy differences of several kcal mol^{-1}. Bernstein has referred to this phenomenon as "conformational polymorphism".[41] While such polymorphs are not encountered with the [N]phenylenes, two or three molecular conformations within a single unit cell can be found, as described above. To obtain an estimate of the energy of the observed deplanarizations in the solid state, calculations (HF/6-31G*) were carried out by employing the X-ray structural parameters found for **4b**. For carbon, these were kept fixed, while the hydrogens were allowed to optimize. The resulting energy of this structure was 3.55 kcal mol^{-1} above the planar form. To place this number in perspective, when packing is dominated by van der Waals forces, the difference in energy between the observed (solid state) and calculated lowest energy conformation is typically in the range of 1–2 kcal mol^{-1}.[42] The higher value obtained for **4b** might be attributed to the lack of electron correlation in the calculation (vide infra).

Since the experimental results suggest that, on average, the [N]phenylenes exhibit a greater deformability relative to naphthalene and anthracene, ab initio calculations were performed to determine the relative energetic cost of incremental deformation. The potential that results from bending can be fit to a quadratic function (Figure 13).

Thus, the energetics of a given deformation can be estimated given the coefficient. The calculations show that while not much energy is required to deform naphthalene and anthracene, even less is required for the phenylenes. The potential wells of **3**, **4b**, and **18** are more shallow than those of the acenes (Figure 13). Thus, **3** and **18** are 26% and **4b** 45% more readily deplanarized than the acenes. The effect of electron correlation on the bending potentials was also explored. Optimization of **4b** at a fixed angle (3°) at the Becke3LYP/6-31G* level showed a shallowing of the potential well by 19% relative to the Hartree-Fock result. The corresponding change for naphthalene (6°) was only 9%, which suggests a greater "softening" of the phenylenes relative to the acenes on addition of electron correlation. An alternative approach to the inclusion of electron correlation based on second-order Møller–Plesset perturbation theory resulted in the corresponding values of 28% for **4b** and 26% for naphthalene. It remains to be seen whether higher level calculations will lead to a further reduction in the energy of deformation. However, the use of very high-level correlation methods which were required to reproduce the conformations of other hydrocarbon systems may be prohibited by size.[43]

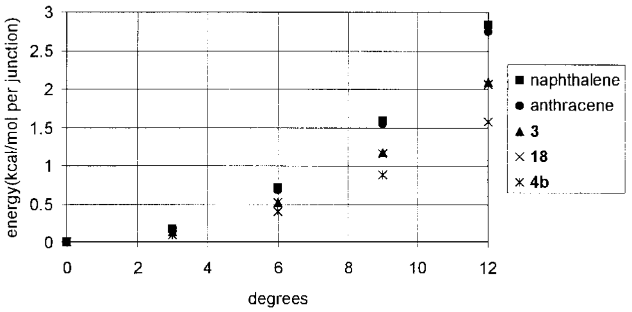


Figure 13. Normalized deformation energies for naphthalene, anthracene and the phenylenes, **3**, **4b**, and **18**.

Conclusion

Based on calculations and experiment, the [N]phenylenes appear to prefer planar most stable structures in the absence of intermolecular interactions. The nonplanarity observed in the solid state is generally independent of molecular topology, size, and nature of substitution, and is presumably a result of crystal-packing forces. Furthermore, calculations show that the phenylenes are more readily deformable than naphthalene and anthracene. While the [N]phenylenes are apparently not intrinsically nonplanar, the increased flexibility of this class of molecules over the acenes is encouraging for the stability and hence synthetic accessibility of cyclobutadienoid fullerenes, in particular the spherical phenylenes described by a truncated cuboctahedron, C_{48},[44] and a truncated icosidodecahedron, C_{120} ("archimedene").[4b, i, l]

Experimental Section

General details: All commercially available reagents and solvents were used without further purification unless otherwise noted. Dimethoxyethane (DME) and tetrahydrofuran (THF) were distilled from sodium/benzophenone, and triethylamine was distilled from calcium hydride just prior to use. All reactions involving air-sensitive materials were carried out under an inert atmosphere. Thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254}. Flash column chromatography was performed on ICN silica gel (32–63 μm, 60 Å). IR spectra (KBr method) were recorded on a Perkin–Elmer System 2000 FT-IR. UV/Vis spectra were measured on a Hewlett–Packard Model 8450A UV/Vis diode array system. NMR spectra were obtained on Bruker AM and AMX spectrometers; the operating frequencies are given with the data. Mass spectral data were provided by the UCB Mass Spectrometry Laboratory. Elemental analyses were carried out by the UCB Microanalytical Laboratory. Melting points were observed in sealed glass capillaries on a Thomas Hoover Melting-Point Apparatus and are uncorrected.

Dimethyl 1,2,3,4-tetrakis[(trimethylsilyl)ethynyl]phthalate (11): Dimethyl 1,2,3,4-tetrabromophthalate (**10**) (6.466 g, 12.68 mmol), $[PdCl_2(PPh_3)_2]$ (0.688 g, 0.979 mmol), CuI (0.185 g, 0.969 mmol), and NEt_3 (100 mL) were added to a Fischer–Porter bottle. This solution was degassed and (trimethylsilyl)acetylene (22.0 mL, 0.156 mol) was added. The bottle was sealed and heated for three days at 125 °C. Salts were filtered off and the solvents removed by evaporation. The residue was dissolved in ether (250 mL) and washed with water (250 mL), HCl (1M; 250 mL), and aqueous saturated NaCl solution (250 mL), and dried over Na_2SO_4. The solvent was removed by evaporation, and purification by column chromatography (14% ethyl acetate/hexanes) gave **11** as a brown solid. Recrystallization from methanol/water afforded **11** (2.427 g, 33%) as off-white needles. M.p. 141.5–142.5 °C; IR (KBr): $\tilde{\nu} = 2961$, 2900, 2159, 1752, 1726, 1439, 1403, 1322, 1249, 1227, 1181, 980, 968, 885, 903, 844, 760 cm^{-1}; UV/Vis (hexanes): λ_{max} ($\log\varepsilon$) = 283 (4.77), 314 (4.25) nm; MS (70 eV): m/z (%): 579 (12) [M^+], 563 (100), 459 (33), 309 (39), 73 (74); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.85$ (s, 6H), 0.26 (s, 9H), 0.23 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 166.2$, 134.4, 130.7, 124.0, 106.5, 106.3, 100.4, 99.5, 52.6, −0.1, −0.2; $C_{30}H_{42}O_4Si_4$ (579.00): calcd C 62.23, H 7.31; found C 61.83, H 7.26.

Dimethyl 2,3,8,9-tetrakis(trimethylsilyl) angular [3]phenylene-5,6-dicarboxylate (12): $KF \cdot 2H_2O$ (5.4 g, 63 mmol) was added to a solution of **11** (0.500 g, 0.864 mmol) and [18]crown-6 (0.14 g, 0.52 mmol) in DME (100 mL). The mixture was stirred for 30 min, and the solution was decanted from solids and subsequently degassed with N_2. $[CpCo(CO)_2]$ (217 µL, 1.70 mmol) was added, and the resulting solution was added through a syringe to a boiling solution of degassed bis(trimethylsilyl)acetylene (100 mL) over a period of 6 h with magnetic stirring. During the reaction, the flask was irradiated with a slide projector lamp. Heating to reflux and irradiation was continued for 8 h after addition was complete. The reaction mixture was then cooled and the solvent evaporated via vacuum transfer. Purification by column chromatography (10% CH_2Cl_2/hexanes) afforded **12** as a yellow powder (0.100 g, 18%). M.p. 178–180 °C; IR (KBr): $\tilde{\nu} = 3002$, 2951, 2926, 1725, 1717, 1629, 1440, 1365, 1295, 1251, 1199, 1136, 1071, 852, 755 cm^{-1}; UV/Vis (hexanes): λ_{max} ($\log\varepsilon$) = 241 (4.96), 248 (4.96), 293 (5.11), 303 (5.21), 337 (5.15), 389 (4.08), 414 (4.06), 440 (3.89) nm; MS (70 eV): m/z (%): 630 (100) [M^+], 615 (7), 599 (5), 511 (10), 73 (10); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$ (d, $J = 1.1$ Hz, 2H), 7.37 (d, $J = 1.1$ Hz, 2H), 3.90 (s, 6H), 0.38 (s, 18H), 0.36 (s, 18H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 165.4$, 154.0, 150.9, 150.0, 147.4, 147.3, 136.5, 126.4, 125.6, 116.5, 52.02, 2.16, 2.09; $C_{34}H_{46}O_4Si_4$ (631.08): C 64.70, H 7.30; found C 64.31, H 7.47.

Dimethyl angular [3]phenylene-5,6-dicarboxylate (2b): CF_3CO_2H (3.0 mL) was added to a solution of **12** (0.150 g, 0.238 mmol) in $CHCl_3$ (15 mL), and the mixture was stirred for 18 h. The solution was diluted with Et_2O, washed successively with H_2O and aqueous saturated $NaHCO_3$, dried over $MgSO_4$, and the solvents evaporated. Purification by column chromatography (10% ethyl acetate/hexanes) afforded **2b** as a yellow powder (0.066 g, 81%). M.p. 170–172 °C; IR (KBr): $\tilde{\nu} = 3070$, 2993, 2948, 1722, 1709, 1455, 1437, 1375, 1292, 1271, 1199, 1148, 1115, 1037, 748 cm^{-1}; UV/Vis (hexanes): λ_{max} ($\log\varepsilon$) = 231 (4.47), 240 (4.46), 274 (4.49), 287 (4.64), 325 (4.53), 380 (3.46), 404 (3.46), 431 (3.41) nm; MS (70 eV): m/z (%): 342 (100) [M^+], 311 (32), 237 (8), 224 (70), 212 (28), 198 (8), 59 (18); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.09$–7.05 (m, 3H), 7.01–6.99 (m, 1H), 3.87 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 165.5$, 153.0, 148.4, 148.3, 135.2, 130.5, 130.1, 121.1, 120.0, 116.5, 52.1; high-resolution MS for $C_{22}H_{14}O_4$: calcd 342.0892; found 342.0895.

Dimethyl triangular [4]phenylene-2,3-dicarboxylate (4d): A solution of 5,6-bis[(trimethylsilyl)ethynyl] angular [3]phenylene[5b] (0.200 g, 0.478 mmol) and $Bu_4N^+F^-$ (1.0 mL of a 1.0M solution, 1.0 mmol) in toluene (50 mL) was stirred at room temperature for 2 h. The reaction mixture was washed with H_2O, dried over $MgSO_4$, filtered, and flushed with argon. Dimethylacetylene dicarboxylate (DMAD) (800 µL, 7.50 mmol) and $[CpCo(CO)_2]$ (130 µL, 1.02 mmol) was added to this solution, and the total was injected over an 8 h period into boiling degassed toluene (100 mL) that contained additional DMAD (200 µL, 1.63 mmol). During addition, and for an additional 8 h, the reaction mixture was irradiated with a slide projector lamp, while boiling. After cooling, the solvents were removed by evaporation. Purification by chromatography on silica (solvent gradient 20% CH_2Cl_2/hexanes to CH_2Cl_2) gave crude **4d**. Crystallization from pentane gave pure **4d** as a yellow powder (0.036 g, 18%). M.p. 205–208 °C (decomp); IR (KBr): $\tilde{\nu} = 2944$, 2892, 1729, 1712, 1591, 1438, 1273, 1252, 1101, 765, 739 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 230sh (4.64), 239 (4.77), 246 (4.83), 276sh (4.75), 290 (4.90), 305 (5.05), 329sh (4.57), 340 (4.51), 359sh (4.36), 396 (3.91) nm; MS (70 eV): m/z (%): 416 (16) [M^+], 385 (8), 370 (8), 298 (14), 277 (10), 262 (26), 221 (10), 183 (40), 133 (34), 111 (48), 97 (70), 83 (66), 71 (100); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.39$ (s, 2H), 7.14 (ABCDm, 8H), 3.90 (s, 6H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta = 167.9$, 150.5, 148.6, 147.7, 132.8, 132.2, 130.8, 129.3, 128.9, 127.9, 120.1, 120.0, 119.2, 52.7; high-resolution MS for $C_{28}H_{16}O_4$: calcd 416.1048; found 416.1039.

2,3-Bis[(triisopropylsilyl)ethynyl]biphenylene (7): $KF \cdot 2H_2O$ (5.00 g, 53.1 mmol) was added to a solution of 1,2-bis[(trimethylsilyl)ethynyl]benzene[5c] (0.289 g, 1.07 mmol) and [18]crown-6 (0.142 g, 0.535 mmol) in DME (50 mL). The mixture was stirred for 30 min, decanted from solids, and subsequently degassed with N_2. $[CpCo(CO)_2]$ (164 µL, 1.28 mmol) was added, and the resulting solution added through a syringe to 1,6-bis(triisopropylsilyl)-1,3,5-hexatriyne[29] (1.24 g, 3.21 mmol) in boiling, degassed xylenes (100 mL) over a period of 8 h with magnetic stirring. During the reaction, the flask was irradiated with a slide-projector lamp. Heating to reflux and irradiation was continued for 5 h after addition was complete. The reaction mixture was then cooled and the solvent evaporated. Purification by column chromatography (hexanes) gave **7** as a yellow solid (0.405 g, 74%). M.p. 105–106 °C; IR (KBr): $\tilde{\nu} = 2943$, 2892, 2865, 2143, 1463, 1425, 1272, 996, 882, 805, 739, 712, 677, 660, 628 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 215 (4.15), 273 (4.84), 283 (4.85), 288 (4.81), 347 (3.65), 367 (3.89), 384 (4.09), 418 (3.16) nm; MS (70 eV): m/z (%): 512 (100) [M^+], 427 (19), 385 (10), 343 (8), 315 (6), 301 (8), 73 (9); ^1H NMR (400 MHz): $\delta = 6.81$ (BB′ m, 2H), 6.69 (s, 1H), 6.68 (AA′ m, 2H), 1.11 (s, 21H); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta = 150.1$, 150.0, 129.1, 125.8, 121.0, 118.3, 106.4, 96.1, 18.8, 11.4; high-resolution MS for $C_{34}H_{48}Si_2$: calcd 512.3295; found 512.3293.

2,3-Bis(trimethylsilyl) linear [3]phenylene (5b):[5c] TBAF (1.56 mL, 1.56 mmol, 1M in THF) was added to a solution of **7** (0.400 g, 0.780 mmol) in THF (20 mL). The mixture was stirred for 30 min, passed through a silica plug, diluted additional THF (10 mL), and degassed with N_2. $[CpCo(CO)_2]$ (100 µL, 0.783 mmol) was added, and the resulting solution added through a syringe to boiling bis(trimethylsilyl)acetylene (45 mL) over a period of 8 h with magnetic stirring. During the reaction, the flask was irradiated with a slide-projector lamp. Heating to reflux and irradiation was continued for 5 h after addition was complete. The reaction mixture was then cooled, and the solvent removed by vacuum transfer. The resulting residue was dissolved in Et_2O and adsorbed on alumina (activity III). Column chromatography (pentane) with alumina (III) gave **5b** as deep red needles (0.172 g, 60%). M.p. 171–173 °C; ^1H NMR (400 MHz, C_6D_6): $\delta = 6.84$ (s, 2H), 6.19 (BB′ m, 2H), 6.45 (AA′ m, 2H), 6.07 (s, 2H), 0.30 (s, 18H).

Tris(2,2,5,5-tetramethyldihydrofurano) triangular [4]phenylene (8): $KF \cdot 2H_2O$ (1.92 g, 20.4 mmol) was added to a solution of hexakis(trimethylsilylethynyl)benzene[30] (0.303 g, 0.462 mmol) and [18]crown-6 (0.063 g, 0.237 mmol) in DME (50 mL). The mixture was stirred for 30 min, decanted from solids, and subsequently degassed with N_2. $[CpCo(CO)_2]$ (207 µL, 1.62 mmol) was added, and the resulting solution added through a syringe to 2,5-dimethyl-3-hexyne-2,5-diol (0.406 g, 2.86 mmol) in boiling degassed *m*-xylene (100 mL) over a period of 8 h with magnetic stirring. During the reaction, the flask was irradiated with a slide-projector lamp. Heating to reflux and irradiation was continued for 8 h after addition was complete. The reaction mixture was then cooled, and the solvent evaporated. The dark residue was passed through a short silica plug (10% CH_3OH/CH_2Cl_2). Solvents were evaporated, the residue dissolved in benzene (250 mL), and *p*-toluenesulfonic acid (1 mg) was added. The mixture was heated to reflux over 4 Å molecular sieves for 16 h. After cooling, the solvents were evaporated, and the product purified by column chromatography (25% ethyl acetate/hexanes) to yield **8** as a yellow solid (0.086 g, 31%). M.p. >315 °C; IR (KBr): $\tilde{\nu} = 2970$, 2924, 1437, 1361, 1291, 1256, 1175, 1122, 1077, 989, 871, 545 cm^{-1}; UV/Vis (hexanes): λ_{max} ($\log\varepsilon$) = 238 (4.96), 248 (5.12), 277 (4.95), 289 (5.17), 304 (5.35), 345 (4.91), 362

(4.90), 397 (4.42) nm; MS (70 eV): m/z (%): 594 (44) [M^+], 579 (100), 549 (8), 282 (31), 267 (7); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.93$ (s, 6H), 1.53 (s, 36H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 147.9$, 146.4, 128.5, 112.9, 84.3, 30.8; high-resolution MS for $C_{42}H_{42}O_3$: calcd 594.3134; found 594.3128.

X-ray crystal structure analyses: All data were obtained on a Siemens SMART diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Area detector frames were collected from ω scans of 0.3°. The structures were solved by direct methods,[45] expanded with Fourier techniques,[46] and subjected to full-matrix least-squares refinement by means of the teXsan crystallographic software package.[47] The data were corrected for Lorentz and polarization effects.

*Dimethyl angular [3]phenylene-5,6-dicarboxylate (**2b**)*: Crystals were obtained as yellow needles by slow evaporation from hexanes.

*Triangular [4]phenylene (**4b**)*: Very thin yellow blades resulted on slow evaporation from CH_2Cl_2.

*Hexakis[triisopropylsilyl(ethynyl)] triangular [4]phenylene (**4c**)*: Suitable crystals precipitated as yellow blades by slow evaporation from ethyl acetate.

*Dimethyl triangular [4]phenylene-2,3-dicarboxylate (**4d**)*: Orange blades were formed on slow evaporation of ethyl acetate.

*2,3-Bis(trimethylsilyl) linear [3]phenylene (**5b**)*: Crystals were obtained as red plates by slow cooling of a diethyl ether/methanol solution.

*Tris(2,2,5,5-tetramethyldihydrofurano) triangular [4]phenylene (**8**)*: Crystals were collected as yellow blades by slow evaporation from [D_8]toluene.

*Tetracene (**13**)*: Crystals in the form of extremely thin orange plates formed on evaporation of 1,2,4-trichlorobenzene.

*Pentacene (**14**)*: Crystals suitable for X-ray crystallography were obtained as large, thin blue plates from 1,2,4-trichlorobenzene in a sealed tube under vacuum.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114444 (**2b**), 114440 (**4b**), 114442 (**4c**), 114443 (**4d**), 114445 (**5b**), 114441 (**8**), 114446 (**13**), 114447 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Database search: The 1996 version of the Cambridge Structural Database was used to search for unsubstituted and 2,3-di- and 2,3,6,7-tetrasubstituted naphthalene and 2,3-di- and 2,3,7,8-tetrasubstituted anthracene molecules. *Peri*-substituted derivatives were avoided because of the large deformations induced by sterics.[19] Angularly fused acenes were not used in this search, since nonbonded interactions in the bay region are known to induce nonplanarity.[17] Structures with the following characteristics were also excluded: crystallographic agreement factor R greater than 0.10, fragments with metal coordination, charged fragments, and geometrically constrained molecules (i.e. cyclophanes). The four dihedral angles around the C–C bond at the site of ring fusion were extracted with the CSD programs QUEST and VISTA.

Data analysis: The analyses of the CSD data and the X-ray crystal structures are based primarily on the structure-correlation method.[48] Inspection of the deformation at the ring junction is a size consistent procedure for examining the nonplanarity in the acenes and [N]phenylenes. There are four torsion angles that fully describe a ring fusion and these are denoted as DD($\varphi_{1,2,3,4}$), DC($\varphi_{5,2,3,6}$), DS($\varphi_{4,3,2,5}$), and DZ($\varphi_{1,2,3,6}$), in which the second letter refers to the shape described by the angle, see Figure 14. As a reference frame, the z axis is chosen as pointing along the $C_{2,3}$ bond. Any displacement in the xy frame represents a deformation. For present purposes, all torsion angles were appropriately adjusted so that they were less than 90°, while still maintaining their sign. Two parameters were defined to represent the possible modes of deformation: a twist T and a bend B. In the simplest case, the twist would arise from a rotation about the $C_{2,3}$ bond. The bend can be achieved by holding $C_{2,3}$ in place and pulling on C_1, C_4, C_5, and C_6 (Figure 14). For the acenes, which have adjacent six-membered rings, $T = (|DD| + |DC|)/2$. For the phenylenes, which have adjacent four- and six-membered rings, there are two twist values (T^{four} and T^{six}), which are simply the dihedrals within the respective rings. The bend value for both classes is defined as $B = [(DS + DC) + (DS + DD)]/2$. For example, from a single ring junction in triangular [4]phenylene one obtains the torsion angles $DS = -175.4°$, $DZ = 177.8°$, $DD = 1.90°$, $DC = 0.40°$. DS and DZ are adjusted to be relative to 0.0°, which gives $DS = -4.6°$ and $DZ = 2.20°$. Applying the equation for B, one obtains a bend angle of $-3.45°$ (the negative sign denotes the relative directionality of the deformation; a positive value indicates a bend in the opposite direction). The twist values, T^{six} and T^{four}, are simply the torsion angles 1.9° and 0.4°, respectively. Absolute values were used for generation of the histograms. An approach similar to this one was used to delineate the out-of-plane deviation in the methoxyphenyl group.[49]

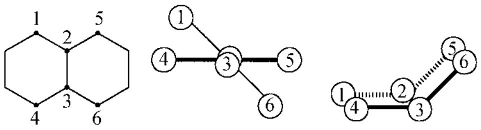


Figure 14. Numbering scheme for the description of deformation at a ring junction: Top view of a ring junction (left), side view of a twist (middle), and side view of a bend (right).

Computation: All geometry optimizations were performed with the GAUSSIAN 92[50] or GAUSSIAN 94[51] packages. Constrained geometry optimizations were carried out at the HF/6-31G* level of theory by use of dihedral angles between planes fixed in the Z-matrix and allowing full relaxation of the hydrocarbon frame at each point. Some calculations included electron correlation through a Møller–Plesset correlation energy correction, truncated at the second order (MP2), and employing the frozen-core approximation.[52] To compare varying treatments of these molecules, some calculations were carried out at the 6–31G* level with a density functional model based on Becke's three-parameter hybrid method, which uses the correlation functional of Lee, Yang, and Parr (Becke3LYP).[53] For naphthalene, anthracene, biphenylene (**3**), and linear [3]phenylene (**18**), D_{2h} symmetry was assumed for the planar and C_{2v} symmetry for the bent structures. Triangular [4]phenylene (**4b**) was constrained to either D_{3h} or C_{3v} symmetry.

In order to compare the energetic cost of deforming the [N]phenylenes relative to the acenes, it was necessary to make some approximations to simplify modeling the phenomenon. First, bending was induced only at the junctions between rings and, second, its magnitude was made equal at all junctions. Thus, the calculations were carried out by keeping the four- and six-membered rings completely planar and fixing the angles between planes at 0, 3, 6, 9, and 12°. Symmetric bending was employed to raise the symmetry of the systems and thus decrease computational cost. Finally, to normalize the calculated energy changes for molecular size, the total deformation energy was divided by the number of junctions present to give a "normalized deformation energy", an index independent of molecular size.

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