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Synthesis of a strained, air-sensitive, polycyclic aromatic hydrocarbon by means of a new 1,4-benzadiyne equivalent

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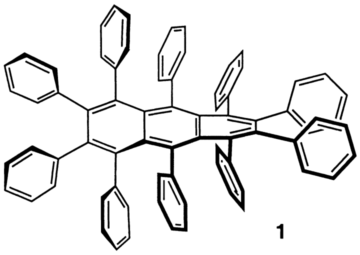
Abstract—9,11,20,22-Tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**4**) was prepared by the pyrolysis of 1,4-bis(phenyliodonio)benzene-2,5-dicarboxylate (**9**), a new 1,4-benzadiyne equivalent, in the presence of phencyclone. Although stable as a solid, solutions of **4** must be handled in the dark; otherwise, ambient light promotes its oxygenation to the 10,21-endoperoxide (**10**). The X-ray structures of both **4** and **10** were determined, as well as the stuctures of two dihydrophencyclones isolated as byproducts of the pyrolysis. Compound **4** adopts a conformation with approximate C_{2h} symmetry in the solid state, in contrast to the results of gas-phase calculations, which uniformly predict a twisted, D_2-symmetric ground state structure. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) of extraordinary size or shape have received increased attention from chemists, perhaps stimulated by the structures of the fullerenes, during the last decade.[1,2] Of the many new compounds prepared, PAHs with helical conformations are among the most aesthetically pleasing,[3] none more so than the longitudinally twisted derivatives of acenes. These molecules are essentially twisted aromatic ribbons, but thus far only one acene derivative has been reported with an end-to-end twist greater than 70°: 9,10,11,12,13,14,15,16-octaphenyl-dibenzo[*a*,c]naphthacene[4] (**2**, 105° twist). This molecule is formally derived from decaphenylanthracene[5] (**1**, 63° twist) by joining two phenyl groups with a carbon–carbon bond to yield the naphthacene core.

The greater twist in **2** results from the steric conflict of the benzo hydrogens with the faces of the adjacent phenyl groups. If two more phenyl groups on the opposite end of the molecule were to be joined, the result would be the pentacene derivative **3**, which is calculated (AM1[6]) to have a 143° twist. A less crowded, but perhaps more easily accessible molecule is 9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**4**), in which the two central phenyl groups have been removed. Semiempirical and ab initio molecular orbital calculations of **4** at a wide variety of levels yield helical geometries with end-to-end twists ranging from 82° to 95°, with the higher-level calculations all predicting twists in excess of 90° (Table 1). The large calculated twist of **4** and the existence of several reasonable synthetic precursors made this hydrocarbon an attractive target, and its synthesis and structure are the subject of this paper.



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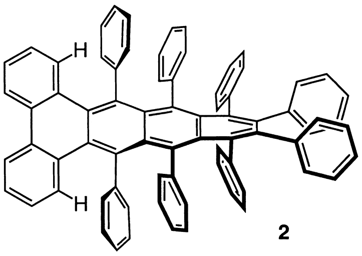

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2. Results and discussion

2.1. Synthesis of 4

Two short synthetic routes to compound **4** may be proposed. The simplest is the reduction of the readily available quinone **5**[7] to its parent hydrocarbon **4**. In a closely related case, we recently prepared 1,2,3,4,5,6,7,8-octaphenyl-

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Keywords: polycyclic aromatic hydrocarbon; endoperoxide; 1,4-benzadiyne equivalent.

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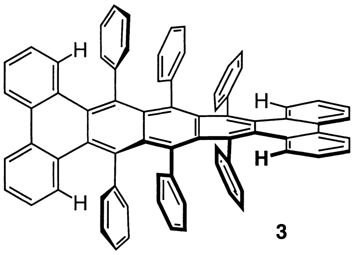
Table 1. Computational data for the D_2 and C_{2h} conformations of compound **4**

Level	E (D_2, au[a])	Twist[b] (deg.)	E (C_{2h}, au[a])	Half-twist[b] (deg.)	ΔE[c] (kcal/mol)
AM1	0.493344	84.5	0.496425	38.3	+1.9
HF/STO-3G	−2341.204399	82.4	−2341.200673	36.9	+2.3
HF/3-21G	−2356.797109	86.6	−2356.792761	39.0	+2.7
HF/6-31G(d)	−2370.029798	94.7	−2370.024263	42.4	+3.5
B3PW91/6-31G(d)	−2384.647171	92.8	−2384.641431	39.9	+3.6
B3PW91/cc-pVDZ	−2384.803559	91.6	−2384.797820	39.3	+3.6
B3LYP/6-31G(d)	−2385.549854	92.2	−2385.545221	40.2	+2.9
B3LYP/6-311G(d,p)	−2386.079867	92.4	−2386.074395	40.4	+3.4

[a] 1 au=627.503 kcal/mol.

[b] Using the crystallographic numbering scheme (Fig. 2), for the D_2 conformation the 'twist' is the torsion angle C(10)–C(11)–C(11A)–C(10A); for the C_{2h} conformation, the twist is 0° by symmetry; the half-twist is the torsion angle C(10)–C(11)–C(1A)–C(1). The experimental value for the latter is 36.7°.

[c] $\Delta E = E(C_{2h}) - E(D_2)$.



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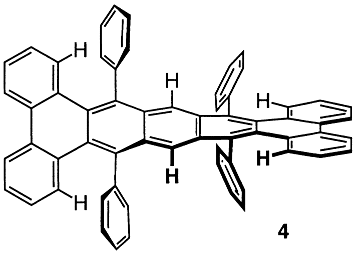
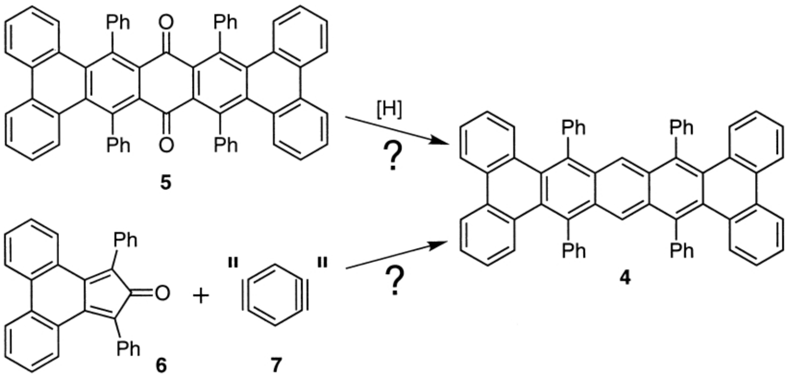


4

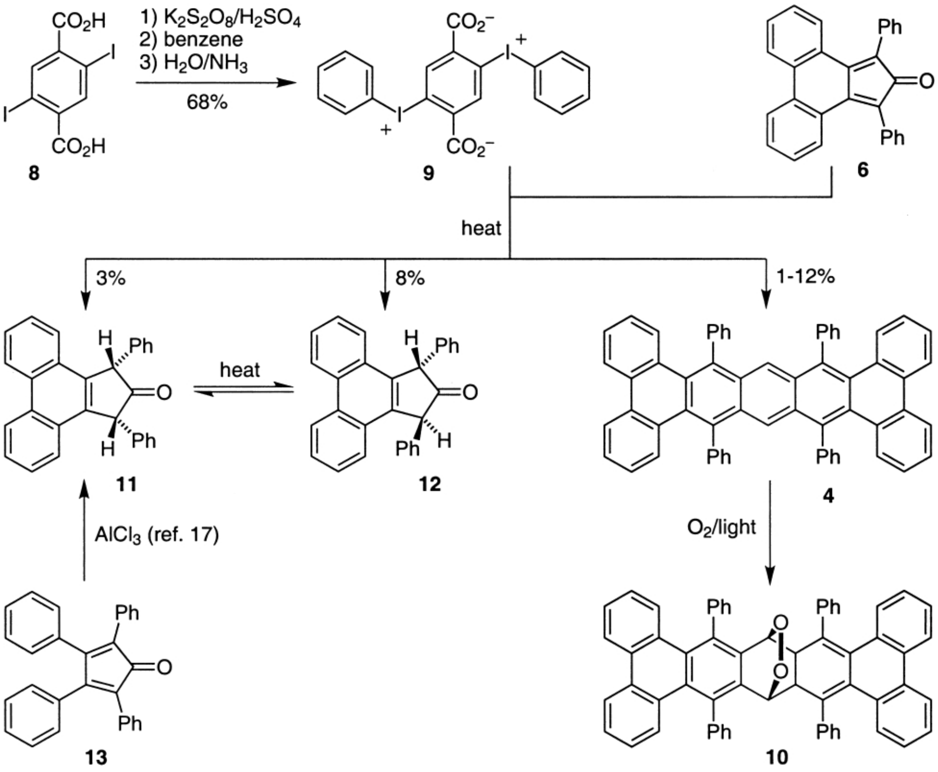
anthracene by reducing octaphenylanthraquinone with HI in refluxing acetic acid.[8] Unfortunately, this very useful method for quinone reduction[9] is somewhat compromised by steric hindrance: anthraquinone is completely reduced in 15 h,[9] but octaphenylanthraquinone requires two weeks' reduction for a 30% yield of the anthracene.[8] Compound **5** proved to be even more resistant; no reduction was observed at all. Reduction of **5** with hydride reagents has been shown to give partially reduced and isomerized products,[10] so we turned to the second approach to **4** (Scheme 1).

Reaction of two molecules of phencyclone (**6**) with a 1,4-benzadiyne equivalent (**7**) should give **4** directly. Hart and co-workers have developed a variety of 1,4-benzadiyne equivalents for the synthesis of anthracene derivatives. The simplest precursors are the 1,2,4,5-tetrahalobenzenes,[11] but these are unsuitable for our purpose because the alkyllithium reagents used in such reactions are incompatible with phencyclone. A more elegant 1,4-benzadiyne equivalent is Hart and Ok's 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d′*]bistriazole,[12] but its synthesis had frustrated us in the past. A neutral, thermally activated 1,4-benzadiyne equivalent might be the best precursor of **4**, and after examining several possible candidates we decided to prepare 1,4-bis(phenyliodonio)benzene-2,5-dicarboxylate (**9**, Scheme 2). 2-(Phenyliodonio)benzoate is a well-known thermal benzyne precursor.[13] At temperatures above 160°C, benzyne, iodobenzene, and carbon dioxide are the major products of its decomposition,[13b] and the bisiodonium dicarboxylate **9** should undergo similar reactions. Compound **9** was prepared from 2,5-diiodoterephthalic acid (**8**) by using a standard method.[14] The doubly zwitterionic **9** is extremely insoluble; this property facilitates its purification (impurities can be washed away with hot solvents) but hinders its characterization and further reaction. Nevertheless, a clean, if noisy, proton NMR spectrum and a satisfactory FAB mass spectrum were obtained for **9**, and we turned to the synthesis of **4**.

Compounds **6** and **9** and a small amount of γ-butyrolactone (the preferred solvent for such reactions[13b]) were mixed in a screw-capped tube and heated to 270°C for 1.5 h. After cooling, the reaction mixture was dissolved in CH_2Cl_2 and fractionated by silica gel preparative TLC, ultimately yielding a small amount of a pale yellow material with



Scheme 1.



Scheme 2.

proton NMR and EI mass spectra seemingly consistent with compound **4**. Slow evaporation of the NMR sample gave single crystals, and X-ray analysis revealed this material to be the endoperoxide **10** (Fig. 1). Undoubtedly compound **4** had been formed, but it had subsequently reacted with oxygen. It was then recalled that during chromatography an initially red band of product had turned yellow. No doubt this event was the oxygenation in progress! The endoperoxide is quite stable (crystals of **10** were unchanged after six months), but it gave no molecular ion in either EI or FAB mass spectra; however, its MALDI-TOF mass spectrum clearly showed an M+H ion (*m/z* 815).

The pyrolysis of **6** and **9** was then repeated with greater attention paid to the extraction and fractionation of the products. Once again, the endoperoxide **10** was the only high molecular weight product observed, but the *cis*- and *trans*-dihydrophencyclones **11** and **12** were also isolated. It was noted that the dark red organic extracts faded to yellow in a matter of hours in ambient light, but no bleaching was observed when they were kept in the dark. Thus **4** probably acts as a sensitizer for its own photooxygenation. The pyrolysis was again performed, but this time precautions were taken to exclude light during the isolation and purification of the products. The initial fractions from

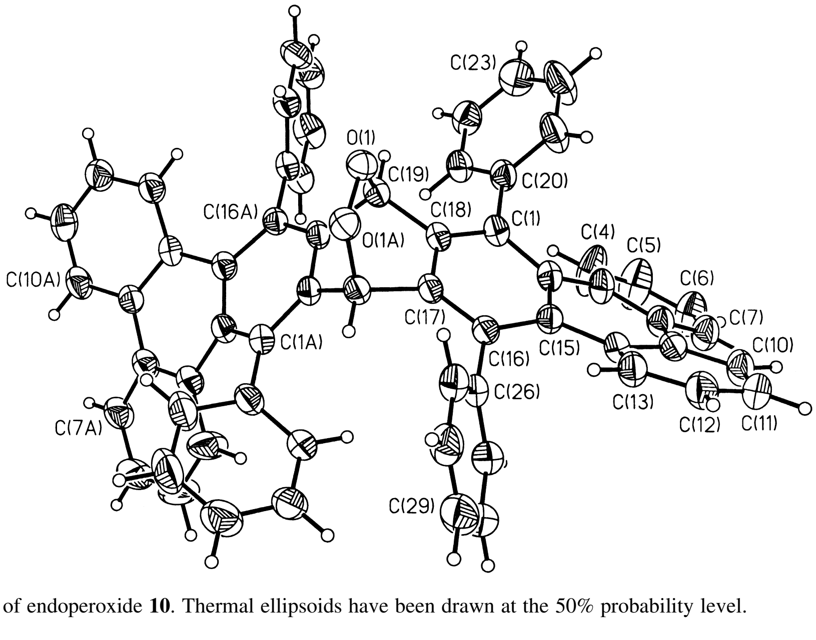


Figure 1. Molecular structure of endoperoxide **10**. Thermal ellipsoids have been drawn at the 50% probability level.

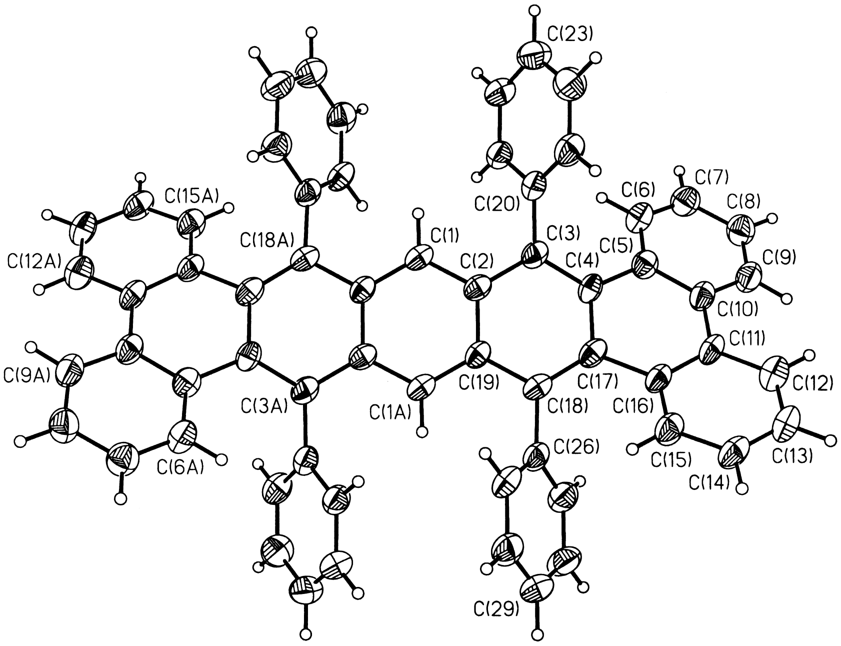


Figure 2. Molecular structure of hydrocarbon **4**. Thermal ellipsoids have been drawn at the 50% probability level.

column chromatography (silica gel, 1:1 hexanes–benzene) were red, and upon evaporation of the solvent and addition of chloroform they deposited a red precipitate of **4**, which was collected and dried in the dark. The proton NMR spectra of **4** and **10** are easily distinguished by the location of the singlet due to the central ring protons; in **4** this falls at δ 8.46, in **10** at δ 6.79.

The low yields in the syntheses of **4** and/or **10** from **9** (usually only 1–2% of the purified product) persuaded us to 'bite the bullet' and carry out the seven-step synthesis of 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*′]bistriazole[12] which we had previously avoided. Unfortunately, the yields of **4**/**10** obtained when using this 1,4-benzadiyne precursor were no better than those from **9** (data not shown).

Recrystallization of **4** from toluene in the dark gave bright red-orange, single crystals, which proved to be stable indefinitely to air and light. However, dilute solutions of **4** in chloroform, initially red-orange, faded to pale yellow in ambient light within one hour. None of twisted acenes that we have previously prepared, even the exceptionally twisted compound **2**, exhibit such air sensitivity, but unlike those molecules, compound **4** lacks phenyl groups on the central aromatic ring to shield its carbon atoms from contact with oxygen.

2.2. Structure of 4

The X-ray structure of compound **4** is illustrated in Fig. 2. To our surprise (and, in truth, disappointment), this molecule is not a continuously twisted acene ribbon such as **1** and **2**, but rather it possesses crystallographic C_i symmetry and approximate C_{2h} symmetry. The overall twist for the molecule is 0° (by symmetry), although the twist from one end of the molecule to the center [C(10)–C(11)–C(1A)–C(1)] is 36.7°. The observed C_{2h} conformation is in contradistinction to the calculated D_2-symmetric, twisted, gas-phase conformation of **4**, which is favored by 2–4 kcal/mol by a wide variety of computational methods (Table 1). In the crystal, packing forces must provide the energy needed to populate the less stable C_{2h} conformation. However, the higher-level calculations favor the D_2 conformation by as much as 3.6 kcal/mol, which is, in our experience, a large energy difference to overcome for the appearance of a less stable conformer in a hydrocarbon

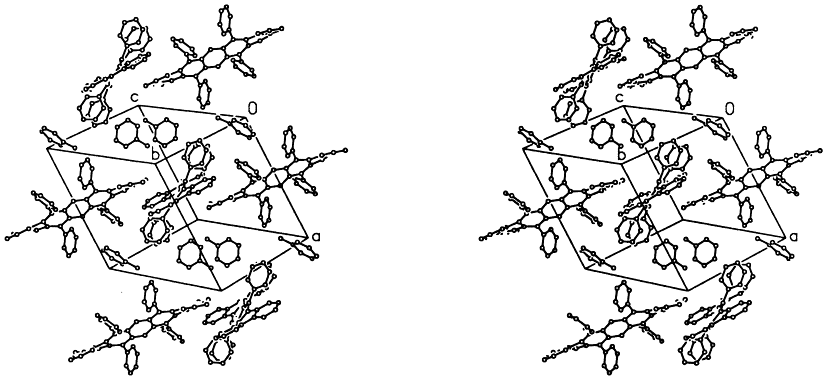
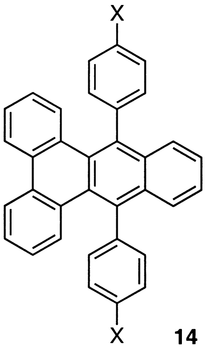


Figure 3. Stereo view of the unit cell and crystal packing of hydrocarbon **4**.

crystal structure. The crystals contain two molecules of toluene per molecule of **4**, which fit nicely into small clefts between the tilted phenyl groups of the larger hydrocarbon (Fig. 3). These interactions and a favorable stacking of the toluenes may provide the needed stabilization of the C_{2h} conformation.



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In a closely related example, we have reported 12 crystal structures of simple derivatives of 9,14-diphenylbenzo[*b*]-triphenylene (**14**) which differ only in the identity of the X-substituents.[15] Compound **14** has two low-energy conformations of C_2 and C_s symmetry, and the twisted C_2 conformation is calculated to be 2–3 kcal/mol more stable than the C_s by a variety of methods. One might expect the C_s conformation to occur frequently in crystal structures of this class of molecules. However, although several packing arrangements were observed for **14**, in only one of 12 structures was the C_s conformation observed.[15] It is notable that the average twist of the derivatives of **14** possessing the C_2 conformation is 38.3°,[15] almost the same as the 36.7° 'half-twist' for compound **4**. In the case of **4**, additional crystal structures would be required in order to determine whether the high energy, C_{2h} conformation observed here is an anomaly or a structure generally favored in the solid state.

Evidence for the D_2 conformation of **4** in solution might be obtained by means of NMR in the presence of a chiral solvent or chiral shift reagent, but the success of such an experiment requires that racemization of **4** be slow on the NMR time scale. This is extremely unlikely. A single transition state for the conversion of the D_2 to the C_{2h} conformation was located at the AM1 level, but the barrier for this process is only 4.5 kcal/mol. Since racemization merely requires the reaction sequence $(+)$-$D_2 \rightarrow C_{2h} \rightarrow (-)$-$D_2$, the detection of the D_2 conformation would be impossible under normal conditions.

2.3. Concerning dihydrophencyclone

Two dihydrophencyclones (**11** and **12**) are by-products of the synthesis of **4**. Their mechanism of formation is unclear, but surely some transhydrogenation can occur under the high temperatures and concentrations of this reaction. The structures of **11** and **12** were unambiguously determined by X-ray analysis (Fig. 4); the colorless compound **11** is the *cis* isomer, and the bright yellow **12** is the *trans* isomer.

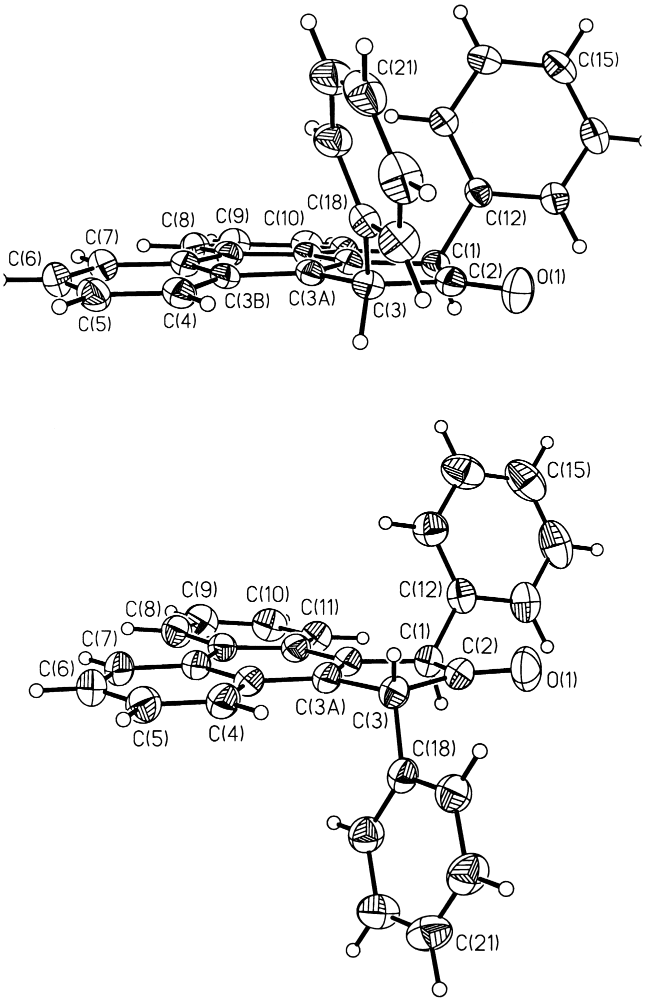

Figure 4. Molecular structures of the *cis*-dihydrophencyclone **11** (top) and the *trans*-dihydrophencyclone **12** (bottom). Thermal ellipsoids have been drawn at the 50% probability level.

Interestingly, 'dihydrophencyclone' has been reported on several previous occasions,[16–18] but the stereochemistry of the phenyl groups has not been specified. This compound has been described in the literature as 'schöne weisse Krystalnadeln'[16] and 'pearly colorless flakes';[17] thus we suspect that this material was the *cis* isomer. However, the reported melting points of these samples were invariably sharp (314–315°C,[16] 320–323°C,[17] and 313°C[18]) with no reference made to any unusual behavior or decomposition. This is inconsistent with our own experience; both **11** and **12** exhibit broad melting point ranges, color changes upon heating, and slow decomposition accompanied by gas evolution. Upon heating to temperatures near 300°C, compound **11** becomes quite yellow, and NMR analysis of material recovered from a melt, before decomposition is too far advanced, shows it to be a roughly 1:1 mixture of **11** and **12**. Compounds **11** and **12** are stable in chloroform solution at room temperature, but in DMSO solution each also isomerizes into a mixture of the two. The interconversion is easily monitored by NMR; the separate resonances for each isomer change in intensity over a period of several hours, although the rate is variable and may reflect the presence of some trace catalyst. No sample of either **11** or **12**, including the crystals used for X-ray analysis, was found with a melting point range of less than 10°C.

For comparison, we prepared an authentic sample of dihydrophencyclone by the method of Sonntag et al.[17] Treatment of tetraphenylcyclopentadienone (**13**) with AlCl$_3$ smoothly gave the colorless *cis*-dihydrophencyclone **11**. This material was judged to be very clean by NMR, and its properties proved to be identical in all respects to those of our own samples, including a broad melting point range and a propensity for isomerization to **12**.

3. Conclusion

9,11,20,22-Tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**4**) has two surprising properties: it is air-sensitive, and it adopts the 'wrong' conformation, at least in the solid state. Given the stability of our previously prepared polyphenylacenes and related hydrocarbons to air, light, heat, acids, and bases,[4,5,19] the sensitivity of **4** to air was unexpected. This reactivity can be rationalized in terms of a lack of steric protection at the central ring, but 1,2,3,4,5,6,7,8-octaphenylanthracene, which is similarly unencumbered, does not seem to be air-sensitive.[8] A somewhat analogous situation exists for the polymethylanthracenes. Meador and Hart[20] studied the photochemistry of many of these molecules and observed that 'several somewhat less methylated analogues… had to be prepared and isolated in the dark since even laboratory fluorescent lights were sufficient to bring about their [photooxidation].' The unexpected preference for the C_{2h} conformation of **4** in the solid state is probably due to a crystal packing effect. However, in two other studies where we have compared the crystal conformations of a series of related polycyclic aromatics with their computational geometries, the higher energy structure was very seldom found in the crystalline state.[15,21] In order to establish the intrinsic conformational preference of **4**, one would need to devise an experimental method which could elucidate the geometry of **4** in solution or in the gas phase.

4. Experimental

4.1. Data for compounds

4.1.1. 1,4-Bis(phenyliodonio)benzene-2,5-dicarboxylate (9). Potassium persulfate (3.00 g, 11.1 mmol) was added in small portions to a solution of 2,5-diiodoterephthalic acid[22] (**8**, 0.96 g, 2.3 mmol) in concentrated sulfuric acid (10 mL) at −10°C. The resulting mixture was stirred for 5 min at −10°C, and then it was allowed to warm to room temperature. After 20 min stirring, the mixture was again cooled to −10°C, benzene (2.5 mL) was added, and the mixture was stirred for 1 h below 10°C. The reaction mixture was then cooled to −15°C, and ice water (22 mL) was added slowly so that the temperature did not exceed 10°C. The pH was adjusted to 9 by the dropwise addition of concentrated ammonia (ca. 27 mL). The resulting precipitate was collected by filtration, washed with water, and dried overnight under vacuum. The yield of the gray product **9** was 0.89 g (1.6 mmol, 68%). Further purification of this material was achieved by leaching the solid with hot methanol followed by hot acetone; mp >400°C (but becomes dark). ^{1}H NMR (DMSO-d_6) δ 7.52 (s, 2H), 7.65 (t, J=8 Hz, 4H), 7.83 (t, J=8 Hz, 2H), 8.19 (d, J=8 Hz, 4H); MS (FAB), *m/z* 571 (M+H, 8), 495 (M+H−C$_6$H$_4$, 75), 465 (M−CO−C$_6$H$_5$, 100).

4.1.2. 9,11,20,22-Tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene 10,21-endoperoxide (10). Compound **9** (0.26 g, 0.46 mmol), phencyclone[16] (**6**, 0.45 g, 1.18 mmol), and γ-butyro-lactone (1.5 mL) were heated in a screw-capped Pyrex tube at 250°C for 3 h. After cooling, methanol was added to precipitate a brown solid which was collected by filtration. This material (0.25 g) was subjected to column chromatography (silica gel, 1:1 hexanes–benzene). Several early fractions (R_f 0.6–0.8, alumina TLC, 1:1 hexanes–benzene) contained the peroxide **10**, and these were combined and further fractionated by preparative TLC (silica gel GF, 1:1 hexanes–benzene) to give the pure endoperoxide **10** (4.1 mg, 0.0050 mmol, 1.1%). Further elution of the silica gel column gave a white solid (R_f 0.2, alumina TLC, toluene) which proved to be *cis*-dihydrophencyclone **11** (15.1 mg, 0.039 mmol, 3%). The original methanol filtrate gradually deposited a yellow solid upon standing, the *trans*-dihydrophencyclone **12** (36.4 mg, 0.095 mmol, 8%). A second preparation gave a 1.6% yield of **10**.

For **10**, mp 220°C; ^{1}H NMR (CDCl$_3$) δ 6.79 (s, 2H), 6.94–7.00 (m, 8H), 7.14 (t, J=8 Hz, 4H), 7.35–7.41 (m, 20H), 8.39 (d, J=8 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 74.6, 123.1, 125.4, 126.6, 127.5, 129.2, 129.5, 129.8, 130.3, 130.5, 131.38, 131.44, 131.50, 134.0, 134.6, 139.6 (16 of 16 expected resonances under conditions of slow phenyl rotation); MS (MALDI-TOF), *m/z* 815 (M+H); MS (FAB), *m/z* 782 (M−O$_2$); MS (EI), *m/z* 782 (M−O$_2$, 9), 503 (5), 429 (15), 369 (38), 355 (38), 295 (55), 281 (48), 221 (100), 207 (63); exact mass 782.2936, calcd for C$_{62}$H$_{38}$ (M−O$_2$) 782.2975. Single crystals of **10** were obtained by the slow evaporation of a CDCl$_3$ solution.

For **11**, mp behavior: ca. 295°C becomes distinctly yellow and shrinkage occurs; 309–322°C melts with slow gas evolution [lit. (see text) 314–315°C,[16] 320–323°C,[17] 313°C[18]]; ^{1}H NMR (CDCl$_3$) δ 5.20 (s, 2H), 7.19–7.28 (m, 10H), 7.49 (ddd, J=8, 7, 1 Hz, 2H), 7.58 (dd, J=8, 1 Hz, 2H), 7.68 (ddd, J=8, 7, 1 Hz, 2H), 8.82 (d, J=8 Hz, 2H); MS (EI), *m/z* 384 (M$^+$, 100), 382 (M−H$_2$, 15), 356 (M−CO, 19), 354 (M−H$_2$−CO, 18), 279 (M−CO−C$_6$H$_5$, 87). Single crystals of **11** were obtained from CHCl$_3$–acetone.

For **12**, mp behavior: ca. 240°C partly melts to give a resinous semisolid; ca. 270°C darkens; 300–310°C melts completely with slow gas evolution; ^{1}H NMR (CDCl$_3$) δ 5.24 (s, 2H), 7.14–7.16 (m, 4H), 7.25–7.29 (m, 6H), 7.48 (ddd, J=8, 7, 1 Hz, 2H), 7.58 (dd, J=8, 1 Hz, 2H), 7.67 (ddd, J=8, 7, 1 Hz, 2H), 8.80 (d, J=8 Hz, 2H); MS (EI), *m/z* 384 (M$^+$, 100), 382 (M−H$_2$, 25), 370 (M−CH$_2$, 50), 356 (M−CO, 21), 354 (M−H$_2$−CO, 26), 279 (M−CO−C$_6$H$_5$, 97). Single crystals of **12** were obtained from CH$_2$Cl$_2$–acetone.

4.1.3. 9,11,20,22-Tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (4). Compound **9** (0.259 g, 0.455 mmol), phencyclone (0.451 g, 1.18 mmol), and γ-butyrolactone (1.5 mL) were

Table 2. Crystallographic data for compounds **4**, **10–12**

	10	**11**	**12**	**4**
Chemical formula	$C_{62}H_{38}O_2 \cdot CHCl_3$	$C_{29}H_{20}O \cdot C_3H_6O$	$C_{29}H_{20}O$	$C_{62}H_{38} \cdot 2C_7H_8$
Formula weight	934.29	442.53	384.45	967.19
Crystal size (mm)	0.22×0.17×0.11	0.21×0.14×0.10	0.32×0.25×0.12	0.15×0.14×0.02
Space group	*Pbcn* (No. 60)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	13.7466(5)	10.1687(3)	10.2497(3)	13.7224(7)
b (Å0	17.9472(6)	10.3813(3)	10.5972(4)	14.5041(7)
c (Å)	18.6378(7)	12.6836(4)	11.2543(4)	14.3718(7)
α (deg.)	90	110.809(1)	109.198(1)	90
β (deg.)	90	101.383(1)	105.151(2)	117.077(2)
γ (deg.)	90	101.647(1)	110.492(2)	90
V (Å^3)	4598.2(3)	1171.68(6)	978.57(6)	2546.9(2)
Z	4	2	2	2
ρ_{calcd} (g/cm^3)	1.350	1.254	1.305	1.261
μ (mm^{-1})	0.248	0.077	0.077	0.071
T (K)	200(2)	200(2)	200(2)	200(2)
θ_{max} (deg.)	25.0	27.5	27.5	22.5
Reflections				
Total	25263	13699	11893	11281
Unique	4033	5344	4470	3315
Observed [$I>2\sigma(I)$]	2688	3819	3143	1861
$R(F)$ (obs. data)[a]	0.082	0.050	0.048	0.063
$wR(F^2)$ (obs. data)[a]	0.218	0.124	0.120	0.133
S (obs. data)[a]	1.13	1.04	1.04	1.121
$R(F)$ (all data)[a]	0.120	0.077	0.082	0.1315
$wR(F^2)$ (all data)[a]	0.246	0.145	0.151	0.1648
S (all data)[a]	1.03	1.02	1.02	0.999

[a] $R(F)=\sum||F_o|-|F_c||/\sum|F_o|$; $wR(F^2)=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; S=goodness-of-fit on $F^2=[\sum w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

heated in a screw-capped Pyrex tube at 265°C for 2.25 h. After cooling, methanol was added to precipitate 0.184 g of a brown solid which was collected by filtration, and the filtrate deposited an additional 0.023 g upon standing. The combined solids (0.207 g) were air dried while protected from light. This material was then chromatographed on a silica gel column (1:1 hexanes–benzene), with both the column and receiving flasks wrapped in aluminum foil to protect them from light. The initial fractions from the column were red in color, and after concentration and then addition of chloroform, they deposited a red precipitate. This material was collected and dried in the dark to yield pure compound **4** (4.3 mg, 0.0055 mmol, 1.2%), mp >300°C. Concentration of the remaining solution to dryness left a mixture of **4** and **10** (41.2 mg, ~0.0515 mmol, 11.4%), which indicates that the yield of the double aryne addition was at least 12%. ^{1}H NMR ($CDCl_3$) δ 6.87 (t, J=8 Hz, 4H), 7.22–7.40 (m, 24H), 7.46 (d, J=8 Hz, 4H), 8.12 (d, J=8 Hz, 4H), 8.46 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 123.3, 125.3, 125.9, 127.0, 127.3, 128.3, 128.7, 128.8, 130.5, 130.9, 131.7, 132.3, 135.5, 141.5 (14 of 14 expected resonances); MS (EI), *m/z* 782 (M^+, 100), 391 (M^{2+}, 10); exact mass 782.2943, calcd for $C_{62}H_{38}$ 782.2975.

Compound **4** is an air- and light-stable solid, but in solution in the presence of air under ambient room light it is rapidly oxygenated to give **10**. Single crystals of **4** were obtained by the evaporation of a toluene solution in the dark.

4.2. General X-ray crystallographic procedures

X-Ray data were collected by using graphite monochromated Mo Kα radiation (0.71073 Å) on a Nonius KappaCCD diffractometer. The diffraction data were processed by using the program DENZO.[23] All structures were solved by direct methods using Siemens SHELXTL,[24] and all were refined by full-matrix least-squares on F^2 using SHELXTL. All nonhydrogen atoms were refined anisotropically, and hydrogens were included with a riding model. Specific crystal, reflection, and refinement data are contained in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 187845-187848. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.3. Computational studies

All semiempirical (AM1[6]), ab initio [HF/STO-3G, HF/3-21G, HF/6-31G(d)[25]], and hybrid density functional [B3PW91/6-31G(d), B3PW91/cc-pVDZ, B3LYP/6-31G(d), B3LYP/6-311G(d,p)[26–30]] calculations were performed by using GAUSSIAN 98.[31] The built-in default thresholds for wave function and gradient convergence were employed. Transition states for the conformational interconversions were located by using the QST3 function in GAUSSIAN 98.

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