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Research Article

Structure and Properties of 9,14,15,16,17,18,19,20-Octahydro-9,14[1′,4′]-benzenobenzo[b]triphenylene

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The compound 9,14,15,16,17,18,19,20-octahydro-9,14[1′,4′]-benzenobenzo[b]triphenylene, $C_{28}H_{24}$, was prepared by hydrogenation of the $4\pi_s + 4\pi_s$ photocycloadduct of dibenz[a,c]anthracene and 1,3-cyclohexadiene with Pt/C in ethyl acetate. The X-ray diffraction analysis shows that the compound crystallizes in the monoclinic space group $P2_1/c$ with the geometric parameters of a = 11.0090(17) Å, b = 13.733(2) Å, c = 13.091(2) Å, and β = 109.583(13)°. In addition to several close intramolecular contacts involving hydrogens derived from the dibenzanthracene moiety, long interannular C–C single bonds of about 1.593 Å are present. These bonds are shorter by about 0.18 Å than the corresponding bonds in the unsaturated precursor, which can be attributed to reduced strain in the more saturated polycyclic ring system. Anisotropic shielding of the four *endo*-methylene hydrogens in the ^{1}H NMR spectrum is larger for the two hydrogens lying above the phenanthrene unit, which resonate at 1.03 ppm, than those above the benzenoid ring, which resonate at 1.24 ppm. Theoretical calculations reproduce the geometry with good agreement.

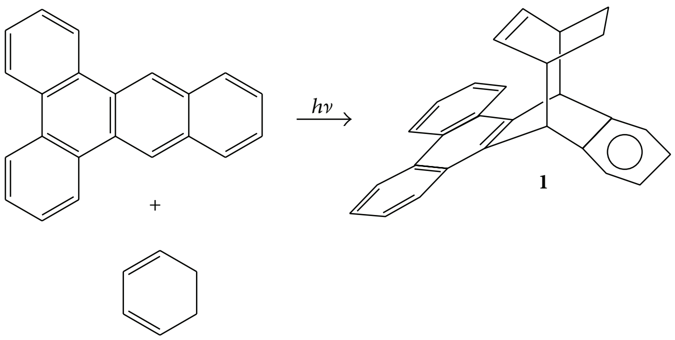
1. Introduction

The photochemical cycloadditions of conjugated dienes to benzenoid aromatic hydrocarbons provide a test of the validity of Woodward-Hoffmann orbital symmetry theory [1]. Employment of naphthalene, benzanthracenes, and dibenzanthracenes has revealed the preferential formation of $4\pi_s + 4\pi_s$ adducts which follow the Alder rule for maximization of secondary orbital overlap, diagnostic of processes involving concerted bond formation (Scheme 1) [2]. Such adducts have been found to contain unusually long interannular carbon-carbon single bonds [3–5], and the *endo*-hydrogens which lie above aromatic moieties in these structures resonate at relatively high field in the ^{1}H NMR spectra [6] due to anisotropic shielding by the subjacent aromatic rings [7–9]. We prepared compound **2**, 9,14,15,16,17,18,19,20-octahydro-9,14[1′,4′]-benzenobenzo[b]triphenylene (Scheme 2), which is free of the disorder associated with other analogues [3, 4], and performed theoretical calculations in order to establish the specific relationships involved.

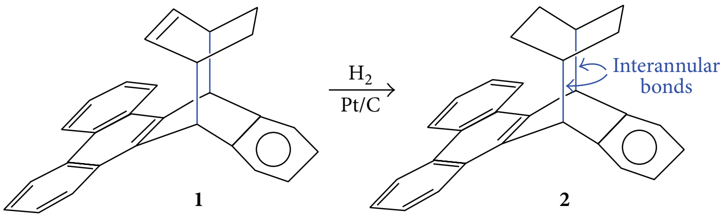
2. Materials and Methods

All reagents and solvents were obtained from commercial sources and used as received. The preparation of the title compound, $C_{28}H_{24}$, followed the literature procedure with the substitution of 5% Pt/C for Adam's catalyst [6]. The ^{1}H-NMR spectrum was recorded on a Bruker AC300 spectrometer in $CDCl_3$ with tetramethylsilane as the internal reference. Crystals suitable for X-ray analysis were obtained by slow evaporation from the dichloromethane-methanol mixed solvent system.

Data collection was performed with an Enraf-Nonius CAD4 single crystal X-ray diffractometer using graphite monochromated Mo radiation (λ = 0.71073 Å) at room temperature in the omega scan mode. Profile analysis was obtained for all collected reflections. Data were corrected for Lorentz and polarization effects and secondary extinction. Cell dimensions were obtained from 25 reflections with 2θ between 30 and 50°. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [10]. Cell parameters, data reduction, and solution and refinement



Scheme 1: $4\pi_s + 4\pi_s$ photocycloaddition of 1,3-cyclohexadiene to dibenz[a,c]anthracene.



Scheme 2: Preparation of 9,14,15,16,17,18,19,20-octahydro-9,14[1′,4′]-benzenobenzo[b]triphenylene (**2**) by catalytic hydrogenation of **1**.

of the structure were achieved with the NRCVAX software suite [11–14]. The structure was solved by direct methods in the space group $P2_1/c$. Crystallographic and refinement parameters are given in Table 1. Molecular graphics were created using ORTEP [15] (Figure 1) and packing diagrams using PLUTO [12] (Figure 2). All carbon atoms were located from the Fourier map and refined anisotropically. The hydrogens could be located in subsequent least-squares refinement cycles but refined to chemically unreasonable positions. This is a common occurrence due to the low electron density about hydrogen nuclei and, in this case, the low ratio of the number of observed reflections to the number of parameters. Therefore, the hydrogens were generated in geometrically idealized positions with aromatic C–H distances fixed at 1.000 Å and aliphatic C–H distances at 1.05 Å and refined with their parent atoms using a riding model. The carbon atomic parameters are given in Table 2.

Ab initio optimizations were performed using Gaussian software [16] through the Ohio Supercomputing Center [17] with both the restricted Hartree-Fock (RHF) and second-order Møller-Plesset (MP2) methods for the isolated molecule. MP2 is a perturbation theory that goes beyond RHF by adding electron-correlation effects. Inclusion of diffuse functions in the 6-31+G(d) basis set is appropriate especially with the elongated bonds in this system.

3. Results and Discussion

Crystallographic and theoretical bond lengths and angles for **2** are in good agreement (Table 3), although experimental results show distortion, discussed below, from the theoretical C_s point-group symmetry of the isolated molecule. A vibrational frequency analysis by RHF showed the optimized geometry to correspond to a potential-energy minimum.

Compound **2** contains a phenanthrene moiety (including carbons C1–C14) and a benzenoid ring (including carbons C16–C21). The aliphatic carbons C15 and C22 derive from the original dibenzanthracene and the remaining six methylene and methine carbons (C1a, C14a, C15a, C16a, C21a, and C22a) derive from the cyclohexadiene addend. Two interannular bonds (C15–C15a and C22–C22a) were formed by the photocycloaddition (Scheme 1). The six carbons of the benzenoid ring are essentially coplanar, and the aromatic bond distances are rather uniform; the shortest at about 1.372 Å involve the distal bonds (C18–C19 and C19–C20) and the longest at 1.395(4) the proximal bond (C16–C21). However, the fourteen carbons of the phenanthrene are less so in both respects (Table 3). Dissecting these atoms into three six-carbon ring systems (two exterior rings including C2–C7 and C8–C13 and an internal ring including C1–C2, C7–C8, and C13–C14), the least-squares planes of the two exterior rings are rotated by 3.41° relative to one another and both rotate about equally towards the cyclohexyl group by about 1.8° from that of the internal ring. This rotation is seen also in the theoretical results and likely is due to unfavorable nonbonded intramolecular interactions involving aromatic and bridgehead hydrogens with distances H3⋯H22 and H12⋯H15 being about 1.93 Å. Similarly the distance between two aromatic hydrogens, H6⋯H9, is 1.97 Å and may account for a chiral twist in the phenanthrene group with a torsion angle of 2.3° for H6–C6–C9–H9. The absence of such a twist in the theoretical geometry, however, suggests that it may be due to a packing effect instead.

Furthermore, significant bond alternation is present. The shortest bond at 1.358(4) Å occurs between the proximal carbons C1–C14, with C3–C4, C5–C6, C9–C10, and C11–C12 also being within 1.37 Å. This is consistent with the structures found for other substituted phenanthrenes [18–20]

Table 1: Crystal and refinement data for compound **2**.

Chemical formula	$C_{28}H_{24}$
Formula weight (g/mole)	360.49
Cell setting	Monoclinic
Space group	$P2_1/c$
a (Å)	11.0090(17)
b (Å)	13.733(2)
c (Å)	13.091(2)
β (°)	109.583(13)
Volume (Å^3)	1864.7(5)
Z	4
Crystal size (mm)	0.47 × 0.41 × 0.23
Density (g/mL)	1.284
$F(000)$	768.22
Temperature (K)	293
Mu	0.07
Number of reflections	3496
R (eq)	0.104
Unique reflections	3315
Reflections (gt)	1972
Extinction coefficient	9800(2600)
Number of reflections used	3315
Number of parameters	254
R (gt)	0.052
wR (gt)	0.071
Goodness of fit	1.05
Shift/su (max)	<0.0005
Residual density (max)	0.17
Residual density (min)	−0.18

Table 2: Atomic parameters for the carbon atoms of compound **2**.

Atom	x	y	z	$B_{\mathrm{iso}}{}^{a}$
C1	0.2553(3)	0.4240(2)	0.8743(2)	2.69(12)
C1a	0.0801(3)	0.2666(3)	0.8227(3)	3.98(16)
C2	0.2495(3)	0.4743(2)	0.9688(2)	2.79(13)
C3	0.1478(3)	0.5362(2)	0.9680(2)	3.51(14)
C4	0.1449(3)	0.5845(3)	1.0579(3)	3.98(16)
C5	0.2468(3)	0.5744(3)	1.1552(3)	4.07(16)
C6	0.3470(3)	0.5136(2)	1.1594(2)	3.35(14)
C7	0.3521(2)	0.4626(2)	1.0687(2)	2.58(12)
C8	0.4564(2)	0.3958(2)	1.0740(2)	2.62(12)
C9	0.5576(3)	0.3779(2)	1.1725(2)	3.30(14)
C10	0.6547(3)	0.3148(2)	1.1775(3)	4.01(15)
C11	0.6561(3)	0.2666(3)	1.0850(3)	4.05(16)
C12	0.5598(3)	0.2818(2)	0.9882(2)	3.42(14)
C13	0.4585(3)	0.3474(2)	0.9801(2)	2.72(12)
C14	0.3554(3)	0.3645(2)	0.8787(2)	2.66(12)
C14a	0.1962(3)	0.2004(2)	0.8303(2)	3.84(16)
C15	0.3528(3)	0.3165(2)	0.7738(2)	2.96(13)
C15a	0.2618(3)	0.2232(2)	0.7473(2)	3.30(14)
C16	0.3157(3)	0.3918(2)	0.6852(2)	3.15(13)
C16a	0.1586(3)	0.2248(2)	0.6349(2)	3.57(14)
C17	0.3779(3)	0.4039(3)	0.6103(3)	4.21(17)
C18	0.3382(4)	0.4753(3)	0.5317(3)	5.10(19)
C19	0.2348(4)	0.5332(3)	0.5265(3)	5.29(19)
C20	0.1731(3)	0.5223(3)	0.6011(3)	4.13(16)
C21	0.2120(3)	0.4520(2)	0.6804(2)	3.19(14)
C21a	0.0437(3)	0.2923(3)	0.6272(2)	3.74(15)
C22	0.1493(3)	0.4343(2)	0.7640(2)	3.05(13)
C22a	0.0534(3)	0.3435(2)	0.7336(2)	3.35(13)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

and indicates electronic localization imparting greater double bond character to the C1–C14 bond. The bond alternation is an intramolecular effect as supported by its agreement with the theoretical results, which pertain to an isolated molecule.

Another unusual feature of the structure concerns the relatively long interannular C–C bonds between C15–C15a and C22–C22a, which average 1.593 Å. An even greater elongation is observed in the adduct **1**, for which the corresponding bond distances average 1.611 Å [5]. This is most likely due to strain [21, 22] rather than to hyperconjugation as proposed for compounds like **1** [23, 24] which contain additional unsaturation, nor can it be ascribed to steric effects involving the methylene carbons, as the *endo*-hydrogens (H1aA and H14aA) lie closer to the subjacent carbons (C1 and C14) in **2** than do the olefinic hydrogens in **1**. Noteworthy is the same distance, 1.593(2) Å, found for the interannular bonds in the corresponding anthracene-derived species containing two benzenoid rings [4]. The nonbonded intramolecular distances in **2** are found to be 2.50 Å for H1aA⋯C1 and 2.45 Å for H14aA⋯C14. Similar distances (2.51 Å for H16aA⋯C16 and 2.45 Å for H21aA⋯C21) are observed for the *endo*-methylene hydrogens lying above the benzenoid ring. The slight differences (~0.05 Å) found in each pair are consistent with the relative skewing of the carbon framework to avoid the unfavorable interactions between neighboring hydrogens. The close contacts between the *endo*-hydrogens and the subjacent aromatic carbons result in diamagnetic shielding of these hydrogens, which are observed to resonate at 1.03 ppm for H1aA and H14aA and at 1.24 ppm for H16aA and H21aA. The greater shielding for the hydrogens lying above the phenanthrene structure is consistent with the presence of a greater aromatic "ring current" in the larger aromatic moiety [7–9]. Knowing the location of the atoms provides assistance in determining the shielding tensors which can be applied to provide information about the aromaticity of molecules with alternating bond lengths [25].

Although large planar aromatic hydrocarbons often pack with parallel-planar stacking [26], **2** is not planar and the phenanthrene moieties do not associate with this fashion. Instead, the benzenoid ring of one molecule orients in a "T"-type interaction [26] with C2, C3, C6, and C7 of the phenanthrene ring of an adjacent molecule, and the saturated ring orients towards the other side near C8, C9, C10, and C13 (Figure 3).

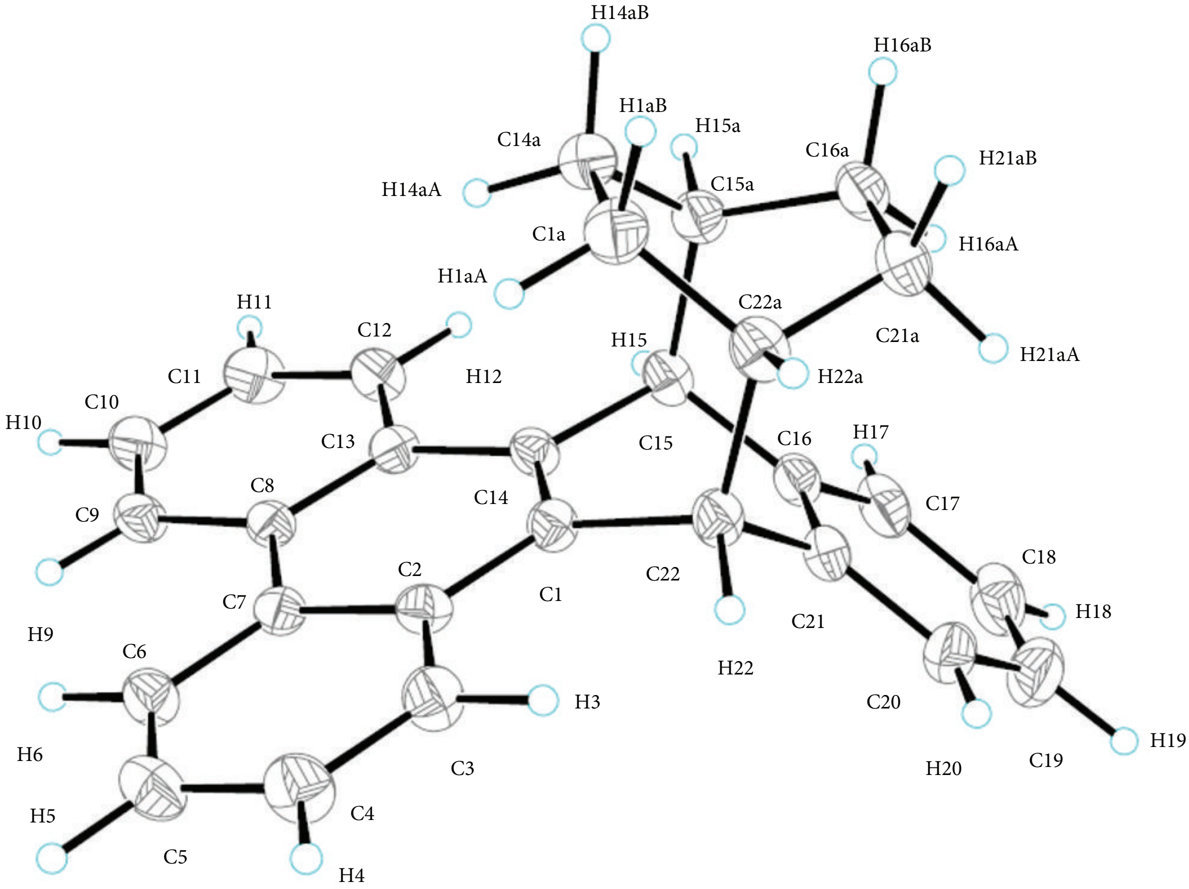


Figure 1: ORTEP (30% probability ellipsoids) of **2** showing the atom labeling scheme.

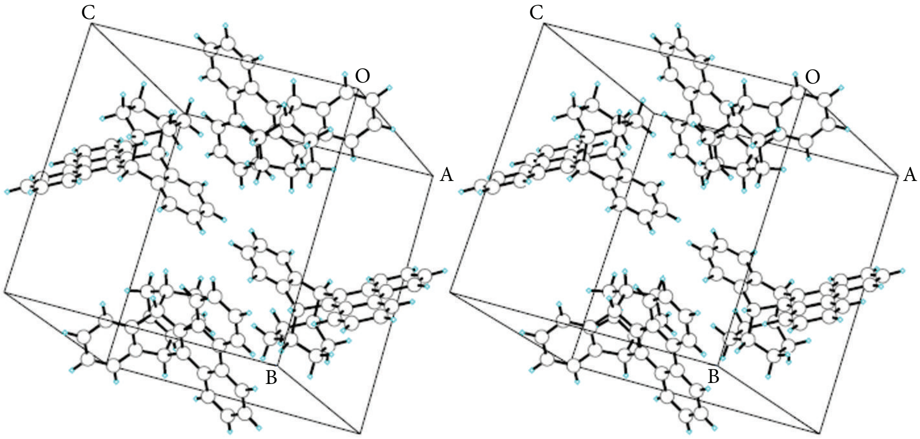


Figure 2: Stereoview of **2** showing the molecular packing in the unit cell.

4. Summary

The solid state structure of 9,14,15,16,17,18,19,20-octahydro-9,14[1′,4′]-benzenobenzo[b]triphenylene **2** was determined by single crystal X-ray diffraction to have no disorder and revealed several close intramolecular nonbonded contacts involving hydrogens derived from the dibenzanthracene moiety. These steric effects produce a symmetric folding in the phenanthrene unit of about 3.4° between the two exterior rings as well as a smaller chiral twisting. Long interannular C–C single bonds of about 1.593 Å also are present due to strain, which is greater in **1** with even longer interannular bonds, rather than steric effects, which would be smaller in **1** than in **2**. The experimental results are in good agreement with calculations using RHF and MP2 theories, confirming that these effects originate mostly from

Table 3: Carbon-carbon bond distances (Å) and angles (°) in compound **2**.

Distance	Observed	RHF^a	MP2^b
C1–C2	1.437(4)	1.452	1.437
C1–C14	1.358(4)	1.349	1.382
C1–C22	1.529(4)	1.528	1.511
C1a–C14a	1.544(5)	1.551	1.550
C1a–C22a	1.527(5)	1.540	1.538
C2–C3	1.403(4)	1.414	1.421
C2–C7	1.422(4)	1.407	1.432
C3–C4	1.361(5)	1.368	1.386
C4–C5	1.393(5)	1.400	1.407
C5–C6	1.370(5)	1.368	1.387
C6–C7	1.395(4)	1.412	1.417
C7–C8	1.454(4)	1.460	1.452
C8–C9	1.414(4)	1.412	1.417
C8–C13	1.405(4)	1.407	1.432
C9–C10	1.360(5)	1.368	1.387
C10–C11	1.386(5)	1.400	1.407
C11–C12	1.368(4)	1.368	1.386
C12–C13	1.410(4)	1.414	1.421
C13–C14	1.447(4)	1.452	1.437
C14–C15	1.516(4)	1.528	1.511
C14a–C15a	1.525(5)	1.540	1.538
C15–C15a	1.591(4)	1.592	1.589
C15–C16	1.504(4)	1.515	1.503
C15a–C16a	1.528(4)	1.540	1.538
C16–C17	1.381(4)	1.384	1.399
C16–C21	1.395(4)	1.389	1.401
C16a–C21a	1.545(5)	1.551	1.550
C17–C18	1.382(6)	1.391	1.400
C18–C19	1.372(7)	1.385	1.401
C20–C21	1.377(4)	1.384	1.399
C21–C22	1.495(4)	1.515	1.503
C21a–C22a	1.532(4)	1.540	1.538
C22–C22a	1.595(4)	1.592	1.589
Angle	Observed	RHF^a	MP2^b
C2–C1–C14	121.5(2)	121.0	121.0
C2–C1–C22	121.9(2)	122.2	122.2
C14–C1–C22	116.6(2)	116.8	116.8
C14a–C1a–C22a	113.6(3)	113.8	113.9
C1–C2–C3	123.4(3)	122.0	121.8
C1–C2–C7	119.1(2)	119.5	119.5
C3–C2–C7	117.5(3)	118.5	118.6
C2–C3–C4	122.6(3)	121.7	121.5
C3–C4–C5	119.8(3)	119.7	119.8
C4–C5–C6	119.2(3)	119.7	119.9
C5–C6–C7	122.2(3)	121.8	121.6
C2–C7–C6	118.7(3)	118.5	118.4
C2–C7–C8	119.1(2)	119.5	119.5
C6–C7–C8	122.2(2)	122.0	122.1
C7–C8–C9	121.4(3)	122.0	122.1
C7–C8–C13	120.1(2)	119.5	119.5
C9–C8–C13	118.5(3)	118.5	118.4
C8–C9–C10	121.4(3)	121.8	121.6
C9–C10–C11	120.1(3)	119.7	119.9
C10–C11–C12	120.3(3)	119.7	119.8
C11–C12–C13	121.0(3)	121.7	121.5
C8–C13–C12	118.8(2)	118.5	118.6
C12–C13–C14	122.0(3)	122.0	121.8
C8–C13–C14	119.2(2)	119.5	119.5
C1–C14–C13	120.8(3)	121.0	121.0
C1–C14–C15	117.0(2)	116.8	116.8
C13–C14–C15	122.1(2)	122.0	122.2
C1a–C22a–C21a	108.2(3)	107.7	108.8
C14–C15–C15a	111.5(2)	113.0	111.9
C14–C15–C16	108.6(2)	107.5	108.3
C15a–C15–C16	113.4(2)	113.7	113.3
C14a–C15a–C15	115.1(2)	115.0	114.3
C14a–C15a–C16a	108.2(3)	107.7	108.8
C15–C15a–C16a	114.2(3)	115.0	114.3
C15–C16–C17	124.0(3)	123.8	123.5
C15–C16–C21	116.6(3)	116.2	116.5
C17–C16–C21	119.4(3)	119.9	120.0
C15a–C16a–C21a	113.5(2)	113.7	113.9
C16–C17–C18	120.4(3)	120.2	120.1
C17–C18–C19	119.9(3)	119.9	120.0
C18–C19–C20	120.1(3)	119.9	120.0
C19–C20–C21	120.8(3)	120.2	120.1
C16–C21–C20	119.5(3)	119.9	120.0
C16–C21–C22	116.3(3)	116.2	116.5
C20–C21–C22	124.2(3)	123.8	123.5
C16a–C21a–C22a	114.2(2)	113.7	113.9
C1–C22–C21	108.2(2)	107.5	108.3
C1–C22–C22a	113.3(2)	113.0	111.9
C21–C22–C22a	111.9(2)	113.7	113.3
C1a–C14a–C15a	114.3(3)	113.8	113.9
C1a–C22a–C22	114.1(2)	115.0	114.3
C21a–C22a–C22	115.1(3)	115.0	114.3

[a] Restricted Hartree-Fock theory with 6-31+G(d) basis set.

[b] Second-order restricted Møller-Plesset theory with the same basis set.

intramolecular interactions, although the twisting may arise from intermolecular packing. Anisotropic shielding of the four *endo*-methylene hydrogens in the ^{1}H NMR spectrum is larger for the two hydrogens lying above the phenanthrene unit than those above the benzenoid ring, as expected for the greater diamagnetic ring current for the larger aromatic moiety.

Data Access

CCDC 1468174 contains the supplementary crystallographic data for the compound 9,14,15,16,17,18,19,20-octahydro-9,14[1′,4′]-benzenobenzo[b]triphenylene. The data can be obtained free of charge via https://summary.ccdc.cam.ac.uk/structure-summary-form by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallography Data Centre, 12 Union Road, Cambridge, CB2 IEZ, UK; Fax: +44(0) 1223-336033.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

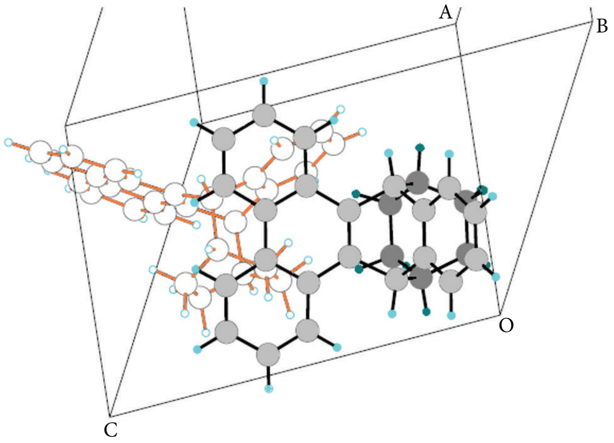


FIGURE 3: Perspective perpendicular to the phenanthrene least-squares plane of one molecule (atoms shaded) showing the orientation of the neighboring subjacent molecule (atoms unshaded) in the unit cell of **2**.

Acknowledgments

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