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Synthesis of Longitudinally Twisted Polycyclic Aromatic Hydrocarbons via a Highly Substituted Aryne

Natalie Smyth, Donna Van Engen, and Robert A. Pascal, Jr.*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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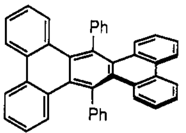
1,4-Diphenyl-3-aminotriphenylene-2-carboxylic acid (7) was prepared in three steps from phencyclone (4). Diazotization of 7 and decomposition of the resulting diazonium salt in the presence of the appropriate cyclopentadienones gave three large, highly substituted, polycyclic aromatic hydrocarbons: 9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene (8), 9,10,17,18-tetraphenylfluorantheno[8,9-*b*]triphenylene (9), and 9,10,19,20-tetraphenyltetrabenzo[*a*,*c*,*j*,*l*]naphthacene (2). Molecular mechanics calculations indicate that all three compounds should have substantial end-to-end twists, and X-ray crystallographic analysis of compounds 8 and 9 showed them to have twists of approximately 60° and 63°, respectively.

We recently reported the synthesis and crystallographic characterization of 9,18-diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene (1) and several of its derivatives, all of which show gross distortions from planarity in the form of longitudinal twists of 61–70°, due to nonbonded interactions between the phenyl substituents and the corner benzo groups.[1] These syntheses employed extreme temperatures (340 °C), and only the remarkable stability of compound 1 and its derivatives permitted their successful isolation. It was this stability which encouraged us to attempt to prepare even more highly strained aromatic hydrocarbons, and subsequent molecular mechanics calculations [MM2(85)[2]] suggested that 9,10,19,20-tetraphenyltetrabenzo[*a*,*c*,*j*,*l*]naphthacene (2) would be an ideal target compound, with a calculated end-to-end twist of more than 90°.



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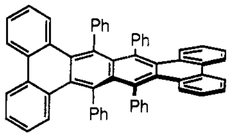
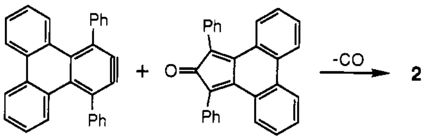
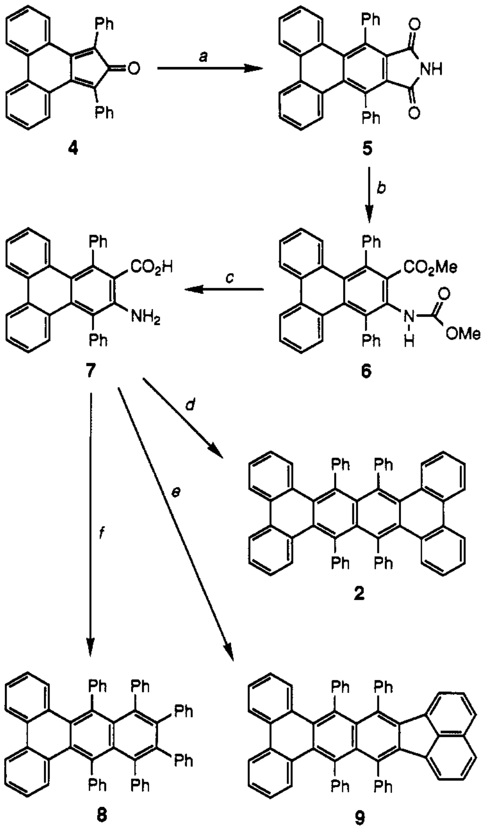


2

Compound 2 should be formed by the cycloaddition of aryne 3 and phencyclone (4), so the problem is reduced to the synthesis of a reasonable precursor of 3. We report herein the synthesis of the aryne precursor 1,4-diphenyl-3-aminotriphenylene-2-carboxylic acid (7), its use for the preparation of 2 as well as two other, related aromatic molecules—9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene (8) and 9,10,17,18-tetraphenylfluorantheno[8,9-*b*]triphenylene (9)—and the crystallographic characterization of 8 and 9 as highly twisted polycyclic aromatic hydrocarbons.



Scheme I[a]



[a] Conditions: (a) maleimide/PhNO$_2$/210 °C; (b) NaOCl/KOH/MeOH/H$_2$O/reflux; (c) KOH/1-propanol/reflux; (d) isoamyl nitrite/phencyclone/1,2-dichloroethane/reflux; (e) isoamyl nitrite/acecyclone/1,2-dichloroethane/reflux; (f) isoamyl nitrite/tetraphenylcyclopentadienone/1,2-dichloroethane/reflux.

Results and Discussion

Our choice of aryne precursor was conditioned by previous experience which indicated that strong bases and phencyclone (1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one, 4) are incompatible.[1b] Thus the generation of 3 by dehydrohalogenation or related reactions was out of the question, and we decided to prepare an anthranilic acid derivative as the precursor of aryne 3. The Diels–Alder reaction of phencyclone[3] with maleimide (in refluxing nitrobenzene to promote in situ decarbonylation and dehydrogenation of the adduct[4]) gave imide 5 in good yield (see Scheme I). Hofmann rearrangement of 5 using NaOCl and KOH in methanol gave the urethane ester 6. Curiously, only the doubly methylated product was observed; little or no urethane acid or free amino acid was formed under these conditions, despite the presence of a

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[1] (a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653. (b) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660–4665.

[2] Allinger, N. L. *QCPE* MM2(85), 1986.

[3] Dilthey, W.; ter Horst, I.; Schommer, W. *J. Prakt. Chem.* **1935**, *143*, 189–210.

[4] Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261–367.

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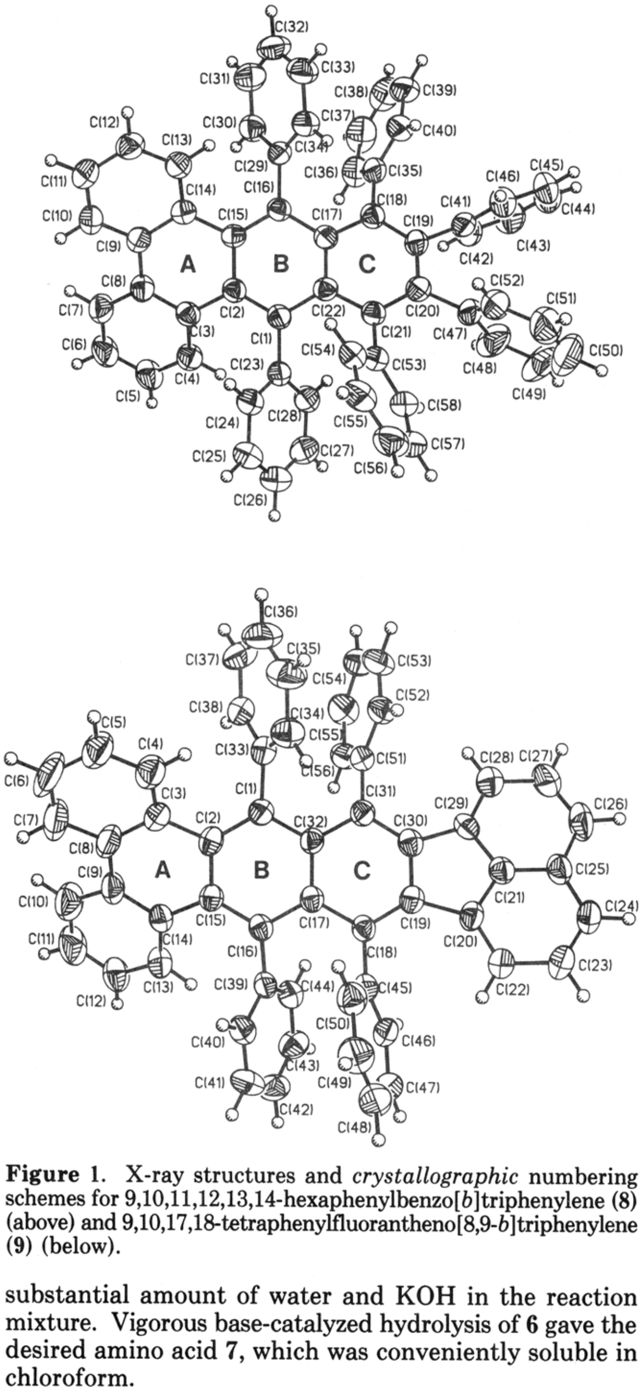

Figure 1. X-ray structures and *crystallographic* numbering schemes for 9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene (**8**) (above) and 9,10,17,18-tetraphenylfluorantheno[8,9-*b*]triphenylene (**9**) (below).

substantial amount of water and KOH in the reaction mixture. Vigorous base-catalyzed hydrolysis of **6** gave the desired amino acid **7**, which was conveniently soluble in chloroform.

The efficacy of compound **7** as a precursor of aryne **3** was tested by diazotization of **7** and reaction with tetraphenylcyclopentadienone in refluxing 1,2-dichloroethane. The desired product, 9,10,11,12,13,14-hexaphenylbenzo[*b*]triphenylene (**8**), was obtained in 24% yield, which, when one considers the steric bulk of the two reactants, is really quite good. Notably, the room temperature ^{1}H NMR spectrum of compound **8** shows a number of very broad resonances, apparently reflecting one or more relatively slow conformational exchange processes (such as twisting of the anthracene and/or phenyl rotation), but at 150 °C the spectrum takes on a normal appearance consistent with the assigned structure. The mass spectrum shows a prominent molecular ion (m/z 734) and relatively few fragments. Compound **8** crystallizes readily from both DMSO and CH_2Cl_2–MeOH. Single crystals were grown from the latter, and an X-ray crystallographic analysis was performed. The crystal structure of **8** is illustrated in Figure 1. The central anthracene moiety is twisted by 60.0 ± 0.7°,[5,6] somewhat more than the twist of 54° predicted by MM2(85). The contributions of rings A, B, and C to the overall twist are 23.0°, 23.3°, and 13.7°, respectively.

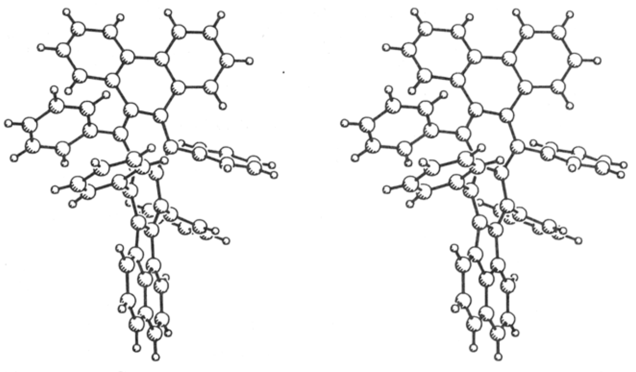

Figure 2. Stereoview of the X-ray structure of compound **9**.

From the above results it was clear that compound **7** is an adequate aryne precursor, but in the several attempts to prepare compound **2** by diazotization of **7** in the presence of **4**, the desired product was obtained in only 1–2% yield. This material was characterized by its ^{1}H NMR spectrum, which is similar to that of **1**, and consistent with the assigned structure **2**. More compelling evidence is the mass spectrum dominated by the molecular ion at m/z 732 and showing very little fragmentation, which is typical of such polycyclic aromatic hydrocarbons. However, compound **2** does not share the stability of **1** and **8**. It decomposes slowly in solution, and a solid sample stored at 0 °C for 3 months showed approximately 30% decomposition. It is likely that the low yield of compound **2** is due at least in part to thermal decomposition in the refluxing reaction mixture, even though this temperature (83 °C) is maintained for only 10 min.

The calculated end-to-end twist [MM2(85)] of the anthracene nucleus in **8** is 54°, and that of the naphthacene nucleus of **2** is 94°.[5] We therefore decided to prepare a compound of intermediate strain which would be stable under the reaction conditions but more highly twisted than compound **8**. 9,10,17,18-Tetraphenylfluorantheno[8,9-*b*]triphenylene (**9**), with a calculated twist of 71°,[5] is the result of this compromise.

Diazotization of **7** and reaction with acecyclone[3] (7,9-diphenyl-8*H*-cyclopent[*a*]acenaphthylen-8-one) gave compound **9** in 10% yield as a brilliant yellow crystalline solid. Like **8**, the ^{1}H NMR spectrum of **9** is highly broadened at room temperature, but sharpens above 100 °C, and the base peak in the mass spectrum is the molecular ion (m/z 706). Fortunately, compound **9** yielded single crystals easily from CH_2Cl_2–MeOH solution, and an X-ray crystal structure was obtained. This structure is illustrated in Figure 1, and a stereoscopic view of the molecule is shown in Figure 2. The smoothly twisted conformation is very similar to that calculated by using MM2(85), but the longitudinal twist of 62.6 ± 0.9°[5,6] is substantially less than predicted (71°). Most of the distortion is localized in the

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(5) The twists in compounds **2**, **8**, and **9** were defined as illustrated in the following examples, which refer to the crystallographic numbering schemes for compounds **8** and **9** shown in Figure 1. To calculate the twist for the anthracene moiety of **8**, the centroids of carbons 8 and 9 [X(1)] and 19 and 20 [X(2)] were located, and dummy atoms were assigned to these positions. The twist is the dihedral angle of the type C(8)–X(1)–X(2)–C(20). The twist angles for linear acene groups in **2** and **9** were calculated similarly. To obtain the *overall* twist of compound **9** dummy atoms were assigned to the centroids of carbons 8 and 9 [X(3)], and 24 and 26 [X(4)]. The end-to-end twist of **9** is the dihedral angle C(8)–X(3)–X(4)–C(26).

(6) The estimated standard deviations for the nuclear twist angles were calculated by the method of Stanford and Waser: Stanford, R. H.; Waser, J. *Acta Crystallogr. A* **1972**, *28*, 213–215.

central anthracene moiety of the molecule, which is twisted by 57.7 ± 1.0°. The rings A, B, and C of the anthracene (see Figure 1) adopt shallow twist-boat conformations, and contribute 21.1°, 22.5°, and 14.1°, respectively, to the overall twist.

The phenyl substituents and deformation from planarity have relatively little effect on the ultraviolet–visible spectrum of compound **9** when compared with the unsubstituted, presumably planar, parent hydrocarbon. The major absorption bands in unsubstituted fluorantheno[8,9-*b*]triphenylene fall at 320 (log ϵ 4.78), 334 (4.76), 350 (4.92), 369 (4.58), 386 (sh, 4.00), 410 (4.14), and 436 nm (4.31),[7] and in the spectrum of **9** all of these features are clearly evident, but shifted to the red by 12–28 nm [$\lambda_{\max}$ 332 (4.4), 352 (sh, 4.3), 366 (4.5), 388 (sh, 4.0), 410 (sh, 3.8), 436 (3.6), 464 (3.7)]. In contrast, the UV spectra of unsubstituted tetrabenzo[*a*,*c*,*j*,*l*]naphthacene [$\lambda_{\max}$ 253 (4.68), 290 (4.58), 301 (4.60), 314 (4.90), 328 (5.30), 368 (4.06), 390 (3.98), 414 (3.50)[8]] and compound **2** [$\lambda_{\max}$ 258 (4.6), 280 (4.6), 320 (sh, 4.1), 344 (sh, 4.0), 428 (sh, 2.3)] are very different. While the reported spectrum of the former compound has numerous features, the spectral bands of **2** are very broad, with no discrete peaks, only shoulders, above 300 nm. However, the UV data for **2** must be interpreted with caution since even our best samples of compound **2** are demonstrably impure by ^{1}H NMR spectroscopy, the identity and UV spectra of the impurities are unknown, and the extinction coefficients are approximate. It is tempting, however, to suggest that the greatly reduced absorption of compound **2** in the visible region of the spectrum, when compared with its unsubstituted parent, is a direct result of a gross molecular distortion which breaks up the naphthacene π system.

Compounds **8** and **9** are only the fifth and sixth polycyclic aromatic compounds with crystallographically documented longitudinal twists of 60° or more. The others are 9,18-diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene (**1**, 65.7°),[1] its bis(trifluoromethyl) (69.7°) and dichloro (60.8°) derivatives,[1b] and a tetrakis[η^5-(pentamethylcyclopentadienyl)ruthenium] complex of rubrene (67.3°).[9] No such compound with a twist of more than 70° has been crystallographically characterized, but it is probable that compound **2** far exceeds this degree of deformation. However, in the absence of a crystal structure, it is fair to ask whether such a complex polycycle might instead adopt some completely different, nontwisted (though certainly nonplanar) conformation.

To address this question, a wide variety of initial geometries for **2** were submitted to MM2(85) for energy minimization. Five optimized geometries were obtained, which represent apparent local minima[10] with D_2, C_i, C_{2h}, C_s, and C_2 symmetry. The D_2 geometry is the familiar twisted conformation, and this exhibits the lowest calculated steric energy by far. The D_2, C_i, and C_{2h} conformations may be compared in Figure 3. Though extremely twisted, the molecular distortion in the D_2 structure is broadly distributed. In the C_i conformation (17.9 kcal/mol higher in energy than D_2), the central naphthacene moiety, which twists in one direction and then back,[11] is more nearly planar, but two carbons (marked a) are highly pyramidalized. In the C_{2h} structure (20.9 kcal/mol higher in energy than D_2), the naphthacene is wavelike rather than twisted, and the corner benzo groups are strongly bent away from the central plane. Even greater distortions are found in the C_s and C_2 conformations, which are ca. 30 kcal/mol higher in energy than the D_2 geometry. Although one cannot be certain that the D_2 conformation is the global minimum, it remains extremely likely that **2** is twisted in this manner.

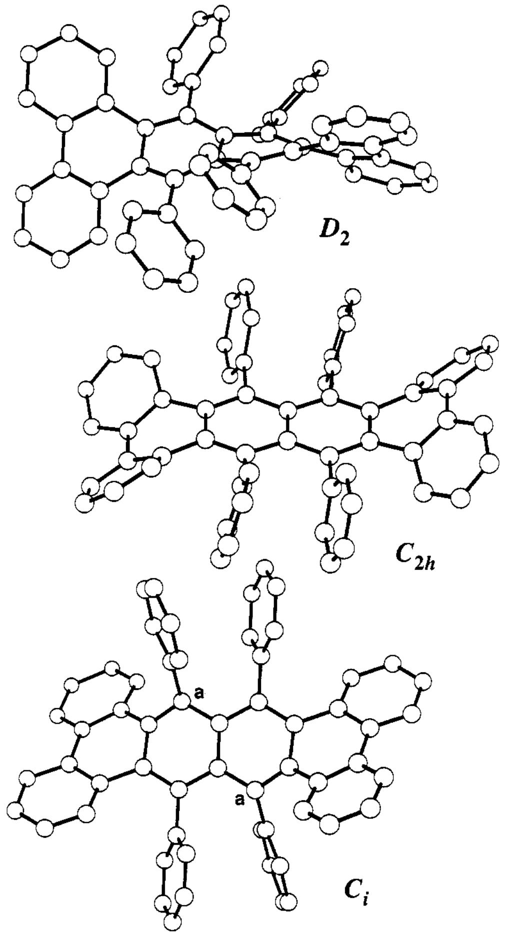

Figure 3. Calculated low-energy conformations of compound **2**.

Experimental Section

Imide of 1,4-Diphenyltriphenylene-2,3-dicarboxylic Acid (5). Phencyclone[3] (8.30 g, 21.7 mmol) and maleimide (2.11 g, 21.7 mmol) were heated in refluxing nitrobenzene (50 mL) for 24 h. After cooling, 300 mL of methanol and 50 mL of water were added to precipitate crude compound **5**, which was dried under vacuum. This material (6.59 g, 67.5% yield) was used in subsequent steps without further purification, but an analytical sample was obtained by recrystallization from chloroform–methanol; mp 399–403 °C dec; ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.08 (t, J = 8 Hz, 2 H), 7.47 (s, 10 H), 7.50 (t, J = 8 Hz, 2 H), 7.68 (d, J = 8 Hz, 2 H), 8.43 (d, J = 8 Hz, 2 H); MS *m/z* 449 (M$^+$, 100), 402 (14), 376 (20), 201 (11), 187 (16); exact mass 449.1444, calcd for $C_{32}H_{19}NO_2$ 449.1416.

Methyl 1,4-Diphenyl-3-[(methoxycarbonyl)amino]triphenylene-2-carboxylate (6). Imide **5** (4.82 g, 10.73 mmol) was mixed with methanol (500 mL) in a large Erlenmeyer flask. While stirring rapidly, a solution of NaOH (1.7 g, 42.5 mmol) in water (3 mL) was added, followed by Chlorox (17 mL, 12 mmol of NaOCl). The mixture was brought rapidly to a boil over an open flame and then refluxed for 20 min on a hotplate. After cooling, the mixture was concentrated to half volume and poured into dilute HCl (400 mL). This mixture was extracted with chloroform (2 × 200 mL), and the combined organic layers were dried over MgSO$_4$ and concentrated. This material was chromatographed on silica gel (solvents: toluene, then 9:1 toluene–ethyl acetate)

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[7] Clar, E.; Stephen, J. F. *Tetrahedron* **1964**, *20*, 1559–1566.

[8] Clar, E.; McCallum, A. *Tetrahedron* **1960**, *10*, 171–174.

[9] Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981–2983.

[10] With the program MM2(85), it is not possible to distinguish true energy minima from very shallow gradients.

[11] We have observed a similar C_i conformation in the crystal structure of the related polycycle 9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene-10,21-dione: Pascal, R. A., Jr.; Van Engen, D. *Tetrahedron Lett.* **1987**, *28*, 293–294.

to give pure urethane **6** (1.57 g, 29%) as an amorphous solid. A similar large-scale reaction gave a 38% yield. Yields were higher but also variable when the reaction was carried out on a smaller scale; two 1-mmol scale reactions, performed using identical proportions of reagents and solvents, gave yields of 46% and 100%: ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.51 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 5.93 (br s, 1 H, NH), 7.04 (t, J = 8 Hz, 2 H), 7.40 (m, 12 H), 7.56 (t, J = 8 Hz, 2 H), 8.40 (d, J = 8 Hz, 2 H); MS m/z 511 (M^+, 5), 479 (M - CH_3OH, 100), 446 (8), 418 (12), 391 (8), 314 (8); exact mass 511.1772, calcd for $C_{34}H_{25}NO_4$ 511.1783.

1,4-Diphenyl-3-aminotriphenylene-2-carboxylic Acid (7). Urethane **6** (0.44 g, 0.86 mmol) and KOH (1.5 g) were heated in refluxing 1-propanol (50 mL) for 45 h. The reaction mixture was poured into water (200 mL), and the pH of this solution was adjusted to between 5 and 6. The resulting mixture, which contained a fine yellow precipitate of the desired product, was extracted with chloroform. The organic phase was dried over Na_2SO_4 and concentrated. The residue was recrystallized from ethanol–water to give bright yellow compound **7** (0.32 g, 85%): mp 220–230 °C (dec with gas evolution); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.98 (m, 2 H), 7.3–7.5 (m, 14 H), 8.33 (t, J = 8 Hz, 2 H); MS m/z 439 (M^+, 80), 420 (M - H - H_2O, 11), 395 (M - CO_2, 39), 393 (24), 392 (31), 391 (22), 376 (15), 188 (16), 121 (28), 83 (100); exact mass 439.1563, calcd for $C_{31}H_{21}NO_2$ 439.1572.

9,10,11,12,13,14-Hexaphenylbenzo[*b*]triphenylene (8). A solution of tetraphenylcyclopentadienone (65 mg, 0.169 mmol) in 1,2-dichloroethane (3 mL) was heated to reflux. A solution of isoamyl nitrite (0.02 mL) in dichloroethane (2 mL) was added, followed by the slow dropwise addition of a suspension of amino acid **7** (25 mg, 0.057 mmol) in dichloroethane (2 mL). The mixture was refluxed for 10 min. The reaction was terminated by addition of ethanol (1 mL) and 1% aqueous NaOH (3 mL). Chloroform was added, and the organic layer was separated and washed with dilute sodium bicarbonate. The organic phase was dried over $MgSO_4$, concentrated, and chromatographed on a preparative TLC plate (silica gel GF; solvent: 3:1 hexanes–benzene). Elution of a yellow band with R_f 0.44 gave pure compound **8**, which was recrystallized from CH_2Cl_2–methanol (10 mg, 24% yield based on **7**): mp 365–365.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) δ 6.2–6.9 (very broad, ca. 16 H), 6.63 (t, J = 7 Hz, 2 H), 6.84 (m, ca. 12 H), 6.99 (t, J = 7 Hz, 2 H), 7.22 (broad, 2 H), 7.27 (t, J = 8 Hz, 2 H), 7.45 (broad, 2 H), 8.16 (d, J = 8 Hz, 2 H); ^{1}H NMR (250 MHz, DMSO-d_6, 150 °C) δ 6.39 (m, 4 H), 6.61 (m, 10 H), 6.81 (m, 10 H), 7.01 (m, 10 H), 7.30 (m, 2 H), 8.23 (d, 2 H); UV (heptane) λ_{max} (log ϵ) 318 (4.8), 328 (4.9), 376 (4.2); MS m/z 734 (M^+, 76), 185 (100); exact mass 734.2991, calcd for $C_{58}H_{38}$ 734.2973.

9,10,19,20-Tetraphenyltetrabenzo[*a,c,j,l*]naphthacene (2). A solution of phencyclone[3] (255 mg, 0.668 mmol) in 1,2-dichloroethane (12 mL) was heated to reflux. A solution of isoamyl nitrite (0.08 mL) in dichloroethane (8 mL) was added, followed by the slow dropwise addition of a solution of amino acid **7** (96 mg, 0.218 mmol) in dichloroethane (8 mL). The mixture was refluxed for 10 min. The reaction was terminated by addition of ethanol (4 mL) and 1.5% aqueous NaOH (12 mL). Chloroform was added, and the organic layer was separated and washed with dilute sodium bicarbonate. The organic phase was dried over $MgSO_4$, concentrated, and chromatographed on four preparative TLC plates (silical gel GF; solvent: 3:1 hexanes–benzene). Elution of a yellow band with R_f 0.69 gave compound **2** (2 mg, 1.3% yield based on **7**). This material could not be crystallized, and was estimated to be >90% pure by TLC but only ca. 80% pure by ^{1}H NMR analysis. After 3 months storage at 0 °C, approximately 30% decomposition had occurred: ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) δ 7.08 (t, J = 8 Hz, 4 H), 7.3–7.6 (m, 24 H), 7.70 (d, J = 8 Hz, 4 H), 8.44 (d, J = 8 Hz, 4 H); UV ($CHCl_3$–heptane) λ_{max} (log ϵ) 258 (4.6), 280 (4.6), 320 (sh, 4.1) 344 (sh, 4.0), 428 (sh, 2.3); MS m/z 732 (M^+, 100), 370 (15); exact mass 732.2828, calcd for $C_{58}H_{36}$ 732.2817.

9,10,17,18-Tetraphenylfluorantheno[8,9-*b*]triphenylene (9). A solution of acecyclone[3] (122 mg, 0.343 mmol) in 1,2-dichloroethane (6 mL) was heated to reflux. A solution of isoamyl nitrite (0.04 mL) in dichloroethane (4 mL) was added, followed by the slow dropwise addition of a solution of amino acid **7** (49 mg, 0.112 mmol) in dichloroethane (5 mL). The mixture was refluxed for 10 min. The reaction was terminated by addition of ethanol (4 mL) and 1.5% aqueous NaOH (6 mL). Chloroform was added, and the organic layer was separated, and washed with water. The organic phase was dried over $MgSO_4$, concentrated, and chromatographed on a preparative TLC plate (silical gel GF; solvent: 3:1 hexanes–benzene). Elution of the bright yellow band with R_f 0.53 gave pure compound **9**, which was recrystallized from CH_2Cl_2–methanol (8 mg, 10% yield based on **7**): mp >400 °C; ^{1}H NMR (500 MHz, DMSO-d_6, 35 °C) δ 6.52 (d, J = 8 Hz, 2 H), 6.74 (dd, J = 8, 1 Hz, 2 H), 6.79 (td, J = 8, 1 Hz, 2 H), 6.8–7.2 (overlapping multiplets and broad peaks, 20 H), 7.29 (td, J = 8, 1 Hz, 2 H), 7.31 (t, J = 8 Hz, 2 H), 7.79 (d, J = 8 Hz, 2 H), 8.25 (d, J = 8 Hz, 2 H); ^{1}H NMR (500 MHz, DMSO-d_6, 155 °C) δ 6.59 (m, 2 H), 6.80 (m, 4 H), 6.92 (m, 4 H), 7.01 (m, 4 H), 7.07 (m, 8 H), 7.11 (m, 2 H), 7.17 (t, J = 8 Hz, 2 H), 7.29 (t, J = 8 Hz, 4 H), 7.75 (d, J = 8 Hz, 2 H), 8.22 (d, J = 8 Hz, 2 H); UV (heptane) λ_{max} (log ϵ) 332 (4.4), 352 (sh, 4.3), 366 (4.5), 388 (sh, 4.0), 410 (sh, 3.8), 436 (3.6), 464 (3.7); MS m/z 706 (M^+, 100), 629 (3), 552 (9), 353 (5), 314 (7), 275 (7); exact mass 706.2684, calcd for $C_{56}H_{34}$ 706.2660.

X-ray Crystallographic Analysis of Compound 8. A single crystal of **8** measuring 0.10 mm × 0.23 mm × 0.40 mm was used for X-ray measurements. Crystal data: $C_{58}H_{38}$; monoclinic, space group $P2_1/n$; a = 13.111 (3) Å, b = 13.131 (4) Å, c = 23.835 (6) Å, β = 99.37 (2)°, V = 4048 (2) Å^3, Z = 4, D_{calcd} = 1.21 g/cm^3. Intensity measurements were made with $3° \leq 2\theta \leq 114°$ by using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at room temperature on a Nicolet R3m diffractometer. A total of 5460 unique reflections were measured, and after Lorentz, polarization, and background corrections were applied, 4117 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods (SHELX86) and refined by using the SHELXTL software. In the final stages of refinement, all non-hydrogen atoms were refined with anisotropic temperature factors, and a riding model with idealized geometry was used for the hydrogens. Refinement converged at R = 0.068, R_w = 0.077. Full details are provided in the supplementary material.

X-ray Crystallographic Analysis of Compound 9. A single crystal of **9**·CH_2Cl_2 measuring 0.10 mm × 0.18 mm × 0.22 mm was used for X-ray measurements. Crystal data: $C_{56}H_{34}$·CH_2Cl_2; monoclinic, space group $P2_1/n$; a = 13.088 (3) Å, b = 11.662 (4) Å, c = 27.048 (6) Å, β = 97.98 (2)°, V = 4088 (2) Å^3, Z = 4, D_{calcd} = 1.29 g/cm^3. Intensity data were collected and processed as described above. Of a total of 5512 unique reflections, 3769 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods using the SHELXTL software. The large temperature factors of the methylene chloride atoms, as well as residual peaks in difference Fourier maps, suggested that the solvent molecule is disordered, but attempts to describe the disorder were not successful. In the final stages of refinement, all non-hydrogen atoms were refined with anisotropic temperature factors, and a riding model with idealized geometry was used for the hydrogens. Refinement converged at R = 0.085, R_w = 0.092. Full details are provided in the supplementary material.

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Registry No. **2**, 125229-51-8; **5**, 125229-52-9; **6**, 125229-53-0; **7**, 125229-54-1; **8**, 125229-55-2; **9**, 125229-56-3; maleimide, 541-59-3; tetraphenyl cyclopentadienol, 479-33-4; phencyclone, 5660-91-3; acecyclone, 641-57-6.

Supplementary Material Available: Crystallographic data and processing descriptions, final atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **8** and **9** (20 pages). Ordering information is given on any current masthead page.