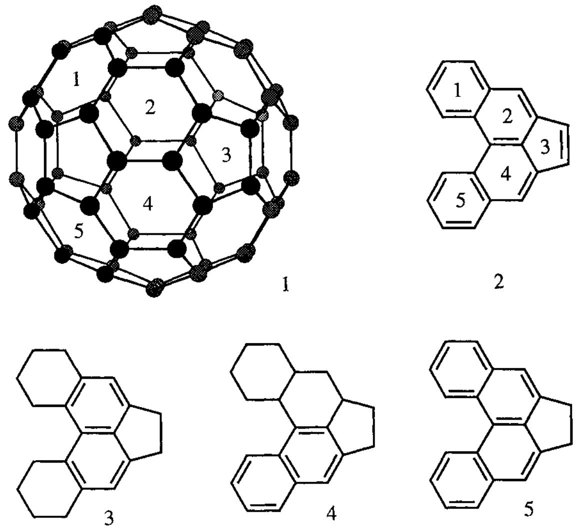
Synthesis of 6,7-Benz[*c*]acephenanthrylene and Its Photodimerization to a Simple Molecular Tweezer

Philip Magnus,* Jonathan C. Morris, Vince Lynch†

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, USA
Fax + 1(512)4717839

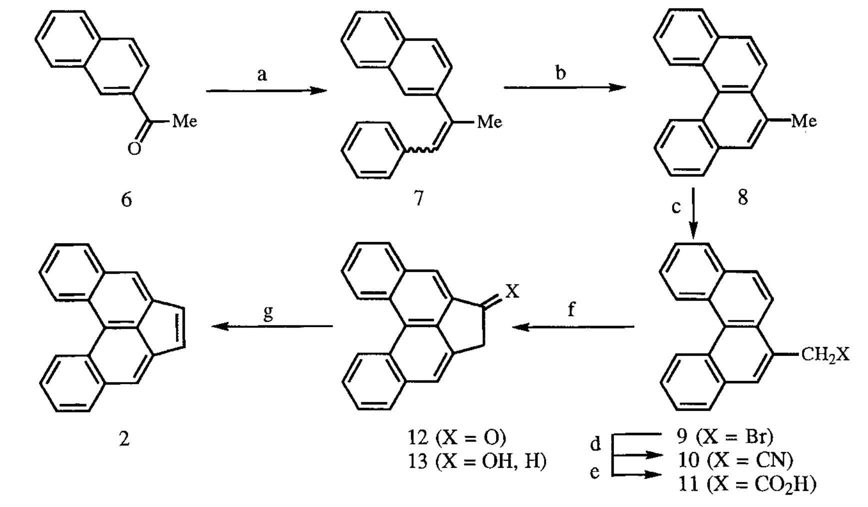
Received 23 August 1996; revised 18 November 1996

A short convenient synthesis of 6,7-benz[*c*]acephenanthrylene (**2**) is described. Solutions of C_{60} (**1**) in toluene exposed to laboratory lighting readily photodimerize to the *cis*-cyclobutane **14**, with a molecule of toluene intercalated inside the molecular cleft.



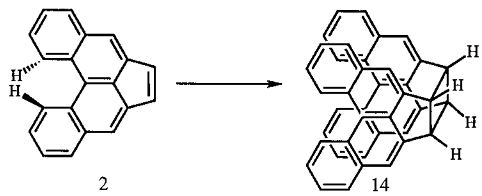
The synthesis of polycyclic aromatic hydrocarbons (PAHs) has witnessed a major renaissance since the discovery of the fullerenes.[1] Much of the renewed effort has been directed towards the synthesis of bowl-shaped PAHs that are segments of buckminsterfullerene (C_{60}, **1**), and derivatives of the parent corannulene.[2,3] As part of our research in this area[4] we required a convenient synthesis of 6,7-benz[*c*]acephenanthrylene (**2**), which is an overlapping and repeating C_{20} substructure of **1**. Surprisingly, while the syntheses of a number of isomers of **2** (benz[*d*], [*j*], [*e*], [*l*] and [*k*]aceanthrylene) have been reported, we could not locate a description of the synthesis of **2**.[5] The only pertinent information is that attempted dehydrogenation of **3** gave an intractable tar,[6] and exposure of **4** to Pd/C at 300 °C gave a low yield of **5**.[7] Consequently, we devised a practical synthesis of **2** that does not require a multiple dehydrogenation step.[8]

6-Methylbenzo[*c*]phenanthrene (**8**)[9] was synthesized using the Katz improvement of the Mallory photocyclization reaction in quantitative yield from **7**.[10] The benzstilbene precursor **7** is available by standard Wittig olefination of **6**.[11] Benzylic bromination of **8** gave **9**, which was immediately treated with aqueous ethanolic sodium cyanide to give **10** (64% from **8**). The nitrile **10** was hydrolyzed to the acid **11** (87%), and cyclized to give the ketone **12** (90%) by treatment with oxalyl chloride followed by $AlCl_3/CS_2$/reflux. Reduction of **12** with $NaBH_4$/MeOH gave **13**, which was dehydrated (PhH/*p*-TsOH/reflux) to provide **2** (95%) as a yellow crystalline material (λ_{max} 401 nm) (Scheme 1).



Scheme 1 Conditions:- a) $PhCH_2PPh_3Br$/NaOEt/EtOH, **7** (80%). b) hv/I_2/C_6H_{12}, **8** (100%). c) NBS/CCl_4/$(PhCO)_2O_2$/hv, **9**. d) NaCN/EtOH/H_2O, **10** (64% from **8**). e) NaOH/$MeOCH_2CH_2OH$, **11** (87%). f) i. $(COCl)_2/CH_2Cl_2$/DMF(cat). ii. $AlCl_3/CS_2$, **12** (90%). g) i. $NaBH_4$/MeOH. ii. *p*-TsOH/PhH, **2** (95%).

It was observed that a yellow solution of **2** in toluene gradually became colorless, and an insoluble white crystalline material was deposited. The ^1H NMR spectrum of the newly formed material exhibited a singlet at δ 4.9 (4H), which immediately suggested the [2 + 2] photodimer structure **14**. This was confirmed by single crystal X-ray analysis, and the Figure shows a Chem 3D representation of **14** from the X-ray coordinates. Interestingly, a molecule of toluene is symmetrically sandwiched into the molecular tweezer.[12] The fjord hydrogen atoms on the 1,5-rings are, as expected, approximately 14° out of plane. Deliberate irradiation of **2** with a tungsten lamp gave **14** (~100%). The exclusive formation of the *cis*-dimer should be contrasted with the irradiation of acenaphthylene which gives a mixture of *cis*- and *trans*-cyclobutanes in the absence of oxygen, and only the *cis*-adduct when oxygen is present.[13]



2 14

Scheme 2

We are currently examining the potential uses of both **2** and **12** for the synthesis of larger curved fragments of the fullerenes.

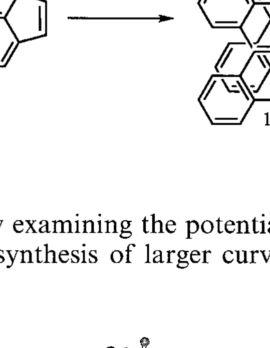


Figure. Chem 3D Representation of **14** from the X-ray Coordinates

Melting points were taken on a Thomas-Hoover capillary tube apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 881 grating spectrophotometer either neat or in $CHCl_3$ as indicated. ^1H NMR spectra were recorded on a GE-300 MHz spectrometer in the indicated solvent, and are reported in ppm downfield from TMS. Low resolution chemical ionization (CI) mass spectra were obtained on a TSQ 70 instrument, and the exact mass determinations were obtained on a VG analytical ZAB2-E instrument. Routine monitoring of reactions was performed by TLC using Merck 60 F_{254} silica gel, aluminum-backed TLC plates. Flash column chromatography was performed with the indicated solvents on Merck 60H F_{254} silica gel. Solvents and commercial reagents were dried and purified before use. Et_2O and THF were distilled from sodium/benzophenone ketyl; CH_2Cl_2 and benzene were distilled from CaH_2 under argon.

6-Methylbenzo[*c*]phenanthrene (8):

Argon was bubbled through a stirred solution of **7** (1.70 g, 6.97 mmol) and I_2 (1.77 g, 6.97 mmol) in cyclohexane (350 mL) for 10 min before propylene oxide (10 mL, 110 equiv) was added. The solution was irradiated with a medium-pressure mercury lamp for 18 h. Upon cooling, the clear solution was evaporated in vacuo, and the residue was purified by chromatography over alumina eluting with hexanes to give **8** as an oil, which slowly solidified (1.69 g, ~100%). The material was identical in all respects to that reported by Nagel and Newman.[9,11]

6-Cyanomethylbenzo[*c*]phenanthrene (10):

A solution of **8** (1.7 g, 7.02 mmol), *N*-bromosuccinimide (1.31 g, 7.36 mmol), and dibenzoyl peroxide (170 mg, 0.70 mmol) in anhyd CCl_4 (350 mL) was irradiated with a tungsten lamp for 3 h. Upon cooling, the solution was evaporated in vacuo and filtered through a plug of silica gel, using CH_2Cl_2 as eluant, to afford **9**, which was immediately dissolved in EtOH (100 mL) and H_2O (10 mL), and NaCN (378 mg, 7.71 mmol) was added. The solution was heated at reflux for 16 h. Upon cooling, the solution was diluted with H_2O, and extracted with CH_2Cl_2 (4 × 20 mL). The extracts were washed with H_2O and dried (Na_2SO_4) and evaporated in vacuo. The yellow oil was purified by chromatography over silica gel eluting with 10% EtOAc/hexanes to remove non-polar impurities, and 25% EtOAc/hexanes to give **10** as a clear gum (1.2 g, 64% overall yield from **8**).

IR (film): ν = 2249 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.26 (2H, s), 7.65–7.75 (4H, m), 7.86 (1H, d, J = 8.5 Hz), 8.00–8.08 (4H, m), 9.07 (2H, t, J = 8.5 Hz).

^{13}C NMR (75.2 MHz, $CDCl_3$): δ = 22.2 (CH_2), 117.6 (C), 120.2 (CH), 123.7 (C), 126.3 (2CH), 126.5 (CH), 127.3 (2CH), 127.9 (CH), 128.0 (CH), 128.1 (2CH), 128.3 (CH), 129.8 (C), 129.9 (C), 132.2 (2C), 132.9 (2C).

HRMS (CI): m/z calcd for $C_{20}H_{13}N$ (M^+ +1) 268.1126. Found 268.1130.

6-Benzo[*c*]phenanthrenylacetic acid (11):

A solution of **10** (876 mg, 3.28 mmol) in 36% aq NaOH solution (5 mL) and 2-methoxyethanol (25 mL) was heated at reflux for 18 h. Upon cooling, the solution was acidified with 6N HCl, and the precipitate extracted with EtOAc (3 × 100 mL). The extracts were washed with H_2O and brine, dried (Na_2SO_4), and evaporated in vacuo to afford a brown solid. Trituration with Et_2O gave the acid **11** as a beige crystalline solid (818 mg, 87%); mp 220–221°C.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.21 (2H, s), 7.58–7.70 (4H, m), 7.83 (1H, s), 7.91–8.03 (4H, m), 9.06 (2H, t, J = 8.9 Hz).

^{13}C NMR (75.2 MHz, $CDCl_3$): δ = 39.4 (CH_2), 122.0 (2 × CH), 126.1 (2 × CH), 127.7 (CH), 128.0 (C), 128.1 (2 × CH), 128.2 (CH), 128.4 (CH), 129.48 (CH), 129.50 (CH), 129.6 (C), 130.0 (C), 130.3 (C), 132.7 (C), 133.0 (2 × C), 176.7 (C).

HRMS (CI): m/z calcd for $C_{20}H_{15}O_2$ (M^+ +1) 287.1072. Found 287.1068.

6-Oxo-6,7-acebenzo[*c*]phenanthrene (12):

Oxalyl chloride (1.64 mL) was added dropwise to a suspension of **11** (700 mg, 2.45 mmol) in CH_2Cl_2 (50 mL) at 25°C, followed by a drop of DMF (gas evolution; solid dissolved), and the solution was stirred for 10 h. The mixture was evaporated in vacuo, and the residue azeotroped with benzene three times. After 2 h under high vacuum, the resulting oil was dissolved in CS_2 (50 mL) and cooled to 0°C. $AlCl_3$ (1.63 g, 5 equiv) was added in one portion to the solution, and the solution was heated at reflux for 3 h. After cooling, the mixture was quenched by the addition of ice and concd HCl (5 mL), and extracted with CH_2Cl_2 (4 × 20 mL). The extracts were washed with H_2O, brine, dried (Na_2SO_4), and evaporated in vacuo to afford a brown solid. Purification over silica gel eluting with 50% EtOAc/hexanes gave **12** as a yellow crystalline solid (590 mg, 90%). A small sample was recrystallized from Et_2O to give pale yellow needles; mp 172–173°C.

IR (film): ν = 1717 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.95 (2H, s), 7.67–7.80 (3H, m), 7.87–7.92 (2H, m), 8.08 (1H, d, J = 7.8 Hz), 8.26 (1H, d, J = 8.2 Hz), 8.46 (1H, s), 9.25 (1H, d, J = 8.2 Hz), 9.33 (1H, d, J = 7.8 Hz).

^{13}C NMR (75.2 MHz, $CDCl_3$): δ = 41.5 (CH_2), 122.7 (CH), 124.0 (CH), 124.1 (CH), 126.1 (2 × CH), 126.3 (2 × CH), 126.5 (CH), 129.0 (C), 129.1 (CH), 129.4 (C), 131.9 (C), 132.2 (CH), 132.9 (C), 133.6 (C), 134.5 (C), 138.6 (C), 203.0 (C).

HRMS (CI): m/z calcd for $C_{20}H_{13}O$ (M^+ +1) 269.0966. Found 269.0966.

6,7-Acebenzo[*c*]phenanthrylene (2):
$NaBH_4$ (65 mg) was added in portions to **12** (330 mg, 1.23 mmol) in MeOH/THF (1:1, 100 mL) at 0 °C under a N_2 atmosphere. The solution was stirred at 0 °C for 1 h, the solvent evaporated in vacuo, and the residue dissolved in H_2O. The aqueous mixture was extracted with CH_2Cl_2 (3 × 20 mL), the extracts were washed with H_2O and brine, dried (Na_2SO_4), and evaporated in vacuo to give **13**. The alcohol **13** was dissolved in benzene (250 mL) and TsOH (330 mg) was added. The solution was heated at reflux for 3 h, and after cooling the mixture it was placed immediately onto basic alumina. Elution with benzene gave **2** as a yellow crystalline solid (295 mg, 95 %); mp 114–116 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.25 (2 H, s), 7.64 (2 H, m), 7.75 (2 H, m), 8.03 (2 H, s), 8.12 (2 H, m), 9.31 (2 H, d, J = 8.5 Hz).

^{13}C NMR (75.2 MHz, $CDCl_3$): δ = 122.3 (C), 124.1 (CH), 125.4 (CH), 126.5 (CH), 126.6 (CH), 130.0 (C), 130.7 (CH), 130.9 (CH), 135.1 (C), 137.5 (C).

HRMS (CI) calcd for $C_{20}H_{13}$ (M^+ +1) 253.1017. Found 253.1016.

UV (cyclohexane): λ = 227, 287, 250, 380, 401 nm.

Photolysis of 6,7-Acebenzo[*c*]phenanthrylene (2):
A solution of **2** (20 mg, 0.79 μmol) in anhyd benzene (3 mL) was irradiated with a 275W tungsten lamp for 8 h under an atmosphere of N_2. The clear yellow solution gradually became colorless and a white precipitate formed. The solvent was evaporated in vacuo to give **14** (20 mg, ~100 %); mp 266–270 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.90 (4 H, s), 7.28–7.32 (8 H, m), 7.53 (4 H, s), 7.70–7.74 (4 H, m), 8.70–8.73 (4 H, m).

^{13}C NMR (75.2 MHz, DMSO-d_6): δ = 45.4, 122.8, 123.3, 125.5, 125.8, 128.2, 128.3, 129.0, 134.5, 139.6, 142.0.

HRMS (CI): m/z calcd for $C_{40}H_{25}$ (M^+ +1) 505.1956. Found 505.1960.

The Texas Advanced Research Program and The Welch Foundation are thanked for financial support.

† Author for inquiries concerning the X-ray data.

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