Synthesis of Methylene-Bridged Polycyclic Aromatic Hydrocarbons: An Efficient, Double Friedel–Crafts Cyclization Approach to 11*H*-Benz[*bc*]aceanthrylene

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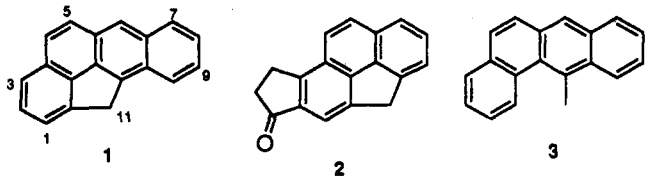
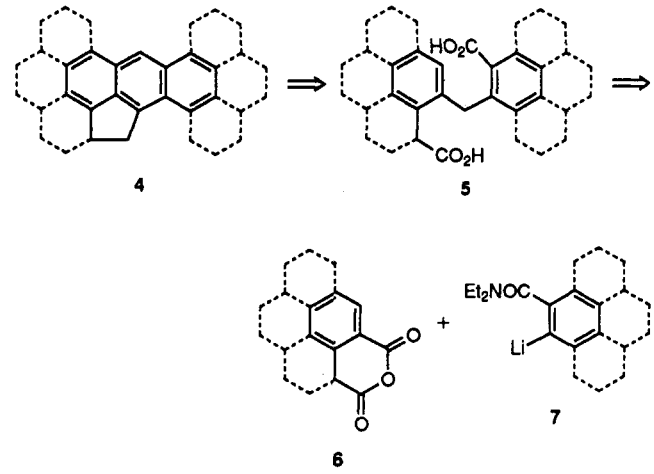
Methylene-bridged polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants[1] that are often found in even higher concentrations than the well-recognized PAHs with bay-region methyl groups.[2] A number of PAHs with a methylene bridge traversing the bay region,[3] see, e.g., 15,16-dihydro-1,11-methanocyclopenta[*a*]phenanthren-17-one (**2**),[4] have been shown to exhibit potent tumorigenic activity. This somewhat unexpected observation has prompted the postulation of alternative modes of metabolic activation of these methylene-bridged PAHs that do not involve the formation of bay-region diol epoxides.[5,6]

The bay-region methylene-bridged PAH 11*H*-benz[*bc*]-aceanthrylene or 1,12-methylenebenz[*a*]anthracene (1,-12-MBA)[7] (**1**) has been tentatively identified as one component of a mixture of high molecular weight PAHs found in cigarette smoke condensate[8] and in sediments from inshore industrial sites in the Great Lakes region.[9] Moreover, this PAH has been shown to be tumorigenic on mouse skin, although its activity is lower than that of the corresponding 12-methyl analogue 12-methylbenz[*a*]anthracene (**3**).[10] An amelioration of the initial synthetic approach[11] to 1,12-MBA was reported by Harvey in 1983[6d] which was followed by the disclosure of a recent, more convenient, albeit lower yielding, modification by the same group.[12] As part of our study directed toward the development of generally applicable synthetic methods of these methylene-bridged PAHs, we sought an approach that could provide a general route for the synthesis of isomeric benzaceanthrylenes.



1 **2** **3**

Scheme I



4 **5** **6** **7**

The construction of the benzaceanthrylene skeleton was envisioned to be readily achieved through double Friedel–Crafts cyclizations of an aryl diacid intermediate, **5** (see Scheme I). The diacid **5**, in turn, should be accessible by the condensation of *ortho*-lithiated arylamides, such as **7**, with reactive aryl anhydrides, such as **6**. While the regiochemical issue of this condensation reaction needs to be addressed when anhydrides **6** and/or the precursor to *ortho*-lithiated arylamides **7** is not symmetrical, in view of its highly attractive nature from practical viewpoints, this one-pot, double Friedel–Crafts cyclization approach was put to the test in connection with the synthesis of 1,12-MBA (**1**). In this report is described a convenient, 5-step synthesis of 11*H*-benz[*bc*]aceanthrylene (1,12-MBA, **1**) starting from 1,8-naphthalic anhydride (**8**) and the *ortho*-lithiated derivative **9** of *N*,*N*-diethylbenzamide, featuring a double Friedel–Crafts cyclization reaction of the diacid intermediate **11**. In addition, a discussion is presented pertaining to verification of the structures of the key pentacyclic ketone intermediates **12** and **13** on the basis of the results of a single crystal X-ray analysis of acetate **13**. Interestingly, the physical and spectroscopic properties of **12** and **13** are in discord with those reported in the literature for compounds to which the same structures had previously been assigned, thus necessitating a reinterpretation of the structures of these literature compounds.

Results and Discussion

The aryl diacid **11** required for the proposed double Friedel–Crafts cyclization was envisioned to be obtainable from spiro-bislactone **10** (Scheme II). Bislactone **10** was, in turn, prepared in 80% overall yield by the addition of *o*-lithio-*N*,*N*-diethylbenzamide (**9**) to a slight excess (1.05

† Correspondence regarding the X-ray crystallographic analysis should be directed to this author.

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(6) (a) Yang, C.; Harvey, R. G. *Tetrahedron* **1992**, *48*, 3735. See, also: (b) Young, R.; Harvey, R. G. *Tetrahedron Lett.* **1989**, *30*, 6603. (c) Lee-Ruff, E.; Kruk, H.; Katz, M. *J. Org. Chem.* **1984**, *49*, 553. (d) Ray, J.; Harvey, R. G. *J. Org. Chem.* **1983**, *48*, 1352. (e) Ribeiro, O.; Hadfield, S. T.; Clayton, A. F.; Vose, C. W.; Coombs, M. M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 87.

(7) This abbreviation 1,12-MBA is used for the PAH **1** throughout the text instead of 11*H*-benz[*bc*]aceanthrylene.

(8) Snook, M. E.; Severson, R. F.; Arrendale, R. F.; Higman, H. G.; Chortyk, O. T. *Beitr. Tabakforsch.* **1977**, *9*, 79.

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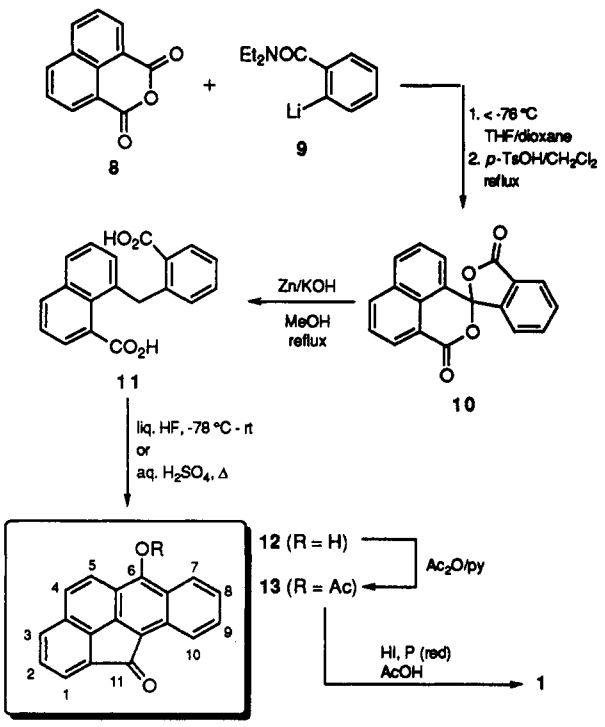
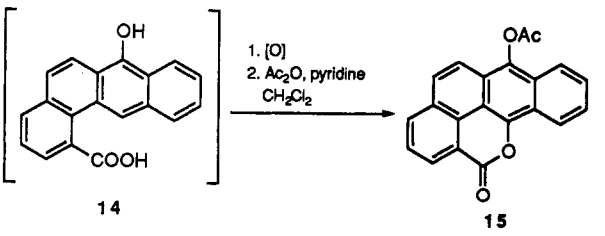
0022-3263/93/1958-5858$04.00/0

Scheme II



molar equiv) of 1,8-naphthalic anhydride (8), which was followed by acid treatment. In an effort to minimize the potential formation of the 1,1-bis-arylation product,[13] *N,N*-diethylbenzamide from which its *ortho*-lithiated derivative **9** was generated was used as the limiting reagent and the temperature of the reaction medium was maintained at below −76 °C throughout the course of the aryl-addition reaction. Reduction of the spiro-bislactone **10** into aryl diacid **11** was effected in 96% yield by refluxing **10** in $MeOH/H_2O$ in the presence of zinc and KOH.

Treatment of aryl diacid **11** with liquid HF from −76 °C to rt resulted in regioselective double Friedel–Crafts cyclization, providing the relatively unstable keto phenol **12** which was isolated after conversion into the corresponding acetate **13** (with Ac_2O/pyridine/DMAP in CH_2Cl_2) in 75% overall yield from **11**. In addition, it was found that this acetate **13** was accompanied by lactone acetate **15**, which was isolated in 12% overall yield from **11**. While lacking in experimental support, this somewhat unexpected formation of lactone **15** may be viewed as the result of adventitious air oxidation of the phenol tautomer of the first Friedel–Crafts cyclization product **14** during the reaction in liquid HF. In an effort to minimize the



formation of lactonic product, it was considered that this cyclization reaction with liquid HF should be carried out under an inert atmosphere. However, since such an experimental setup necessitates the use of an additional

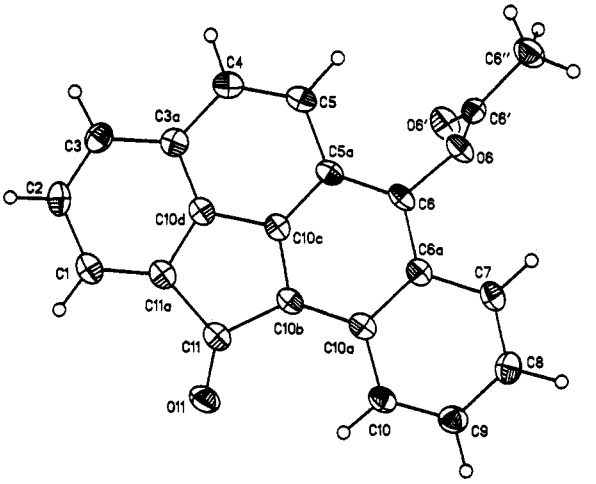


Figure 1. ORTEP view of **13** with atoms represented as 50% thermal ellipsoids.

HF-compatible apparatus, other means for effecting the above Friedel–Crafts cyclization in an inert atmosphere were explored. This was realized most conveniently by heating **11** in aqueous 80% H_2SO_4 at 80 °C for 15 min under a stream of nitrogen, which upon acetylation provided the desired keto acetate **13** in 65% overall yield. Treatment of keto acetate **13** with aqueous HI/red phosphorus in refluxing acetic acid resulted in direct reduction to afford the desired 1,12-MBA (**1**) (48% yield) whose proton NMR data were in complete agreement with those reported in the literature.[14]

Both the above-mentioned ketonic phenol and its acetate to which structures **12** and **13** have been assigned, respectively, are described as intermediates in the previously reported synthesis of **1** by Harvey.[6d] However, the physicochemical properties and spectroscopic data of these compounds obtained in this study were found to be substantially different from those previously reported. The structure of keto acetate **13** obtained here was further corroborated by the observation of two carbonyl stretching absorption bands in its IR spectrum: 1770 (phenolic acetate) and 1704 cm^{-1} (fused 5-membered ketone). However, in view of the strongly acidic nature of the reagent utilized in the Friedel–Crafts cyclization, an unanticipated reaction such as a skeletal rearrangement remained as a distinct possibility. Therefore, it was deemed essential to unequivocally validate the structures of the intermediates **12** and **13**. Single-crystal X-ray analysis of **13**, having a melting point of 233–234 °C, unambiguously confirmed the structure of the acetate of the double Friedel–Crafts cyclization product as being a pentacyclic keto phenol acetate as drawn for **13** (see Figure 1). Accordingly, further verification seems to be warranted for the constitutions of the compounds in the previous synthesis of 1,12-MBA to which structures **12** and **13** have been assigned. Since in this literature synthesis, keto acid **16** was subjected to relatively mildly acidic Friedel–Crafts conditions ($ZnCl_2$/Ac_2O/AcOH), it is tempting to speculate that α-pyrone **17** instead of keto phenol **12** was produced. Moreover, under the strongly acidic reductive conditions with HI/P employed in the subsequent step of this reported synthesis, pyrone **17** could be isomerized to the desired skeleton prior to the reduction. The observed overreduction to **18**

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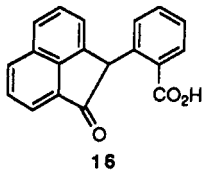
reported in the literature synthesis may also be ascribable to the difference in the skeletal structure of the starting compound since such an overreduction was not observed in our synthesis under identical conditions.



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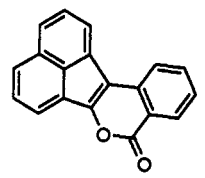

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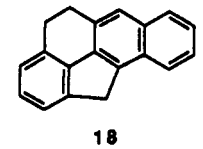

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1,12-MBA (1) has been synthesized from inexpensive 1,8-naphthalic anhydride and *N,N*-diethylbenzamide by a highly efficient (28% overall yield), 5-step sequence. The synthesis features ready access to the pentacyclic ring skeleton by use of a one-pot, double Friedel–Crafts cyclization reaction. Extension of this methodology to the synthesis of other isomeric benzaceanthrylenes is currently under investigation, and the results from this study will be reported in due time.

Experimental Section

Spiro[isobenzofuran-1(3*H*),1′-[1*H*,3*H*]naphtho[1,8-*cd*]pyran]-3,3′-dione (10). To a stirred, cooled (−100 to −105 °C) mixture of 0.741 M *s*-BuLi in cyclohexane (19.3 mL, 14.3 mmol), TMEDA (2.15 mL, 14.3 mmol), and dry THF (80 mL) was added a solution of *N,N*-diethylbenzamide (2.31 g, 13.0 mmol) in 10 mL of dry THF over a 20-min period. The solution was stirred for an additional 30 min while the temperature was raised to −76 °C. The mixture was cannulated to a solution of 1,8-naphthalic anhydride (8) (2.84 g, 14.3 mmol) in 50 mL of dry dioxane. The resulting reddish-brown solution was stirred at −76 °C for 4 h and then quenched with acetic acid (5 mL) at −76 °C and H_2O (100 mL) at 0 °C. The organic solvent was removed by rotary evaporation, and the resulting aqueous solution was acidified with concd HCl and extracted with ether (3 × 100 mL). The combined extracts were washed with brine (100 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation, and the crude product (4.6 g) was dissolved in dry CH_2Cl_2 (20 mL). The solution was then refluxed in the presence of a catalytic amount (10 mg) of *p*-toluenesulfonic acid monohydrate for 4 h, and the mixture was directly concentrated under reduced pressure. The crude product thus obtained was purified by silica gel flash column chromatography using 2:3 ethyl acetate/hexanes as the eluent to afford 3.14 g (80%) of **10** as a white solid (R_f 0.28 1:1 ethyl acetate/hexanes): mp 174–175 °C (white needles from ethyl acetate/hexanes) (lit.[15] mp 173–174 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (dd, 1H, *J* = 7.2, 1.0 Hz, 7′-H), 7.53 (dd, 1H, *J* = 8.3, 7.2 Hz, 8′-H), 7.58 (ddd, 1H, *J* = 7.4, 1.0, 0.9 Hz, 7-H), 7.76 (ddd, 1H, *J* = 7.4, 7.4, 1.0 Hz, 5-H), 7.80 (dd, 1H, *J* = 8.3, 7.4 Hz, 5′-H), 7.82 (ddd, 1H, *J* = 7.4, 7.4, 1.3 Hz, 6-H), 8.03 (ddd, 1H, *J* = 7.4, 1.3, 0.9 Hz, 4-H), 8.06 (dd, 1H, *J* = 8.3, 1.0 Hz, 9′-H), 8.28 (dd, 1H, *J* = 8.3, 1.2 Hz, 6′-H), 8.59 (dd, 1H, *J* = 7.4, 1.2 Hz, 4′-H); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 77.22 (s), 107.15 (s), 119.29 (s), 123.88 (d), 125.73 (d), 125.78 (d), 126.75 (d), 126.88 (s), 127.03 (d), 128.24 (s), 130.28 (d), 131.18 (d), 131.78 (d), 132.06 (s), 134.63 (d), 135.29 (d), 146.17 (s), 161.49 (s), 166.72 (s); IR (KBr) 1794, 1784, 1741, 1235, 912 cm^{-1}.

o-((8-Carboxylnaphthyl)methyl)benzoic Acid (11). To a stirred suspension of Zn (6.6 g) (activated by successive washings with 10% aqueous HCl (50 mL), H_2O (50 mL), 5% aqueous $CuSO_4$ (50 mL), H_2O (5 mL), and MeOH (5 mL)) in MeOH (10 mL) were added KOH (1.02 g, 17.5 mmol) in H_2O (5 mL) and spirobislactone **10** (618 mg, 2.04 mmol) in pyridine (10 mL). The mixture was refluxed for 5 h, diluted with 1 M aqueous NaOH (10 mL), then filtered through Celite, washed with chloroform (10 mL), acidified with concd HCl in an ice bath, and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were washed successively with H_2O (2 × 40 mL) and brine (40 mL) and were dried ($MgSO_4$). Removal of the solvent by rotary evaporation afforded 588 mg (96%) of the diacid **11** (R_f 0.16, 1:9 MeOH/$CHCl_3$): mp 260–262 °C dec (white flakes from ethanol–water); ^{1}H NMR (300 MHz, acetone-d_6) δ 4.95 (s, 2H, Ar_2CH_2), 6.65 (ddd, 1H, *J* = 7.2, 2.3, 1.0 Hz, 2-H), 7.19 (ddd, 1H, *J* = 7.5, 1.4, 0.5 Hz, 6′-H), 7.38 (dd, 1H, *J* = 8.0, 7.2 Hz, 3-H), 7.40 (ddd, 1H, *J* = 7.5, 7.5, 1.4 Hz, 4′-H), 7.51 (ddd, 1H, *J* = 7.5, 7.5, 1.5 Hz, 5′-H), 7.55 (dd, 1H, *J* = 8.2, 7.1 Hz, 6-H), 7.72 (dd, 1H, *J* = 7.1, 1.4 Hz, 5-H), 7.81 (dd, 1H, *J* = 8.0, 1.0 Hz, 4-H), 7.84 (dd, 1H, *J* = 7.5, 1.4 Hz, 3′-H), 8.05 (dd, 1H, *J* = 8.2, 1.4 Hz, 7-H); ^{13}C NMR (75.4 MHz, acetone-d_6) δ 39.32 (t), 125.15 (d), 126.86 (d), 127.38 (d), 128.18 (d), 128.24 (d), 129.34 (d), 129.39 (s), 129.81 (s), 131.72 (s), 131.93 (d), 132.39 (d), 132.97 (d), 133.11 (d), 135.68 (s), 138.90 (s), 143.29 (s), 168.60 (s), 172.72 (s); IR (KBr) 2986, 2884, 1682, 1300, 1262 cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.40; H, 4.65.

Cyclization of the Diacid 11 in Liquid HF. The aryl diacid **11** (306 mg, 1.00 mmol) was dissolved in liquid HF (10 mL) in a 25-mL plastic (Nalgene) bottle with a plastic screw cap, and the resulting solution was cooled at −76 °C. The cold bath was removed, and the solution was allowed to warm up to rt (20 °C) and left to stand at that temperature for 12 h. Evaporation of HF under a nitrogen stream left a purple solid which was dissolved in ethyl acetate (50 mL). The ethyl acetate solution was washed with H_2O (50 mL) and brine (50 mL) and was dried ($MgSO_4$). Removal of the solvent by rotary evaporation provided the crude product (272 mg), which was then dissolved in dry CH_2Cl_2 (7 mL) and pyridine (3 mL). This solution was cooled to 0 °C and treated with acetic anhydride (0.93 mL, 10 mmol) and DMAP (5 mg, 0.04 mmol) at that temperature. The resulting mixture was then stirred at 20 °C for 2 h, at which point the reaction mixture was diluted with ethyl acetate (20 mL). The resulting solution was washed successively with water (2 x 10 mL), saturated aqueous NH_4Cl (2 × 10 mL), and brine (10 mL), and the organic layer was dried (Na_2SO_4). The solvent was removed by rotary evaporation, and the resulting crude product was purified by silica gel flash column chromatography with the use of 4:1 $CHCl_3$/hexanes as the eluent, which afforded 233 mg (75%) of **13** and 41 mg (12%) of lactone **15**. Isolation of pure **13** was aided by the use of this eluent due to the fact that the minor lactone product **15** was unstable and partially decomposed on the column. **For 13** (R_f 0.47, 4:1 $CHCl_3$/hexanes): mp 233–234 °C (orange needles from $CHCl_3$/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.63 (s, 3H, AcO), 7.52 (ddd, 1H, *J* = 8.8, 6.7, 0.8 Hz, 8-H), 7.53 (dd, 1H, *J* = 8.0, 7.0 Hz, 2-H), 7.57 (d, 1H, *J* = 9.2 Hz, 5-H), 7.62 (d, 1H, *J* = 9.2 Hz, 4-H), 7.66 (ddd, 1H, *J* = 8.5, 6.7, 1.2 Hz, 9-H), 7.71 (d, 1H, *J* = 7.0 Hz, 3-H), 7.75 (d, 1H, *J* = 8.0 Hz, 1-H), 7.99 (dd, 1H, *J* = 8.8, 0.8 Hz, 7-H), 8.83 (dd, 1H, *J* = 8.5, 0.8 Hz, 10-H); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 20.75 (q), 118.12 (s), 120.35 (d), 122.77 (d), 122.85 (d), 124.05 (d), 126.13 (d), 126.16 (d), 126.54 (s), 127.20 (s), 129.12 (d), 129.85 (d), 130.41 (s), 130.57 (d), 130.89 (s), 133.33 (s), 138.32 (s), 141.58 (s), 146.95 (s), 168.70 (s), 193.48 (s); IR (KBr) 1770, 1704, 1187, 1088, 1048 cm^{-1}; UV ($CHCl_3$) λ (ε) 234 (50 750), 262 (104 000), 325 (4950), 340 (9500), 357 (10 500), 375 (1200), 424 nm (1050); MS (EI, 70 eV) *m/z* (rel intensity) 312 (M^+, 11), 286 (20), 270 (100), 241 (8), 213 (32). Anal. Calcd for $C_{21}H_{12}O_3$: C, 80.76; H, 3.87. Found: C, 80.61; H, 4.07. **For 15** (R_f 0.40, 4:1 $CHCl_3$/hexanes): mp 278–280 °C dec (softens at 270 °C) (light yelllow plates from $CHCl_3$/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.67 (s, 3H, AcO), 7.74–7.78 (m, 4H, 4-, 5-, 8-, and 9-H), 7.92 (dd, 1H, *J* = 7.8, 7.7 Hz, 2-H), 8.04–8.08 (m, 1H, 10-H), 8.23 (d, 1*H*, *J* = 7.8 Hz, 3-H), 8.63 (d, 1H, *J* = 7.7 Hz, 1-H), 8.78–8.81 (m, 1H, 7-H); IR (KBr) 1744, 1732, 1196, 1161, 1075 cm^{-1}. Anal. Calcd for $C_{21}H_{12}O_4$: C, 76.82; H, 3.68. Found: C, 76.85; H, 3.62.

Cyclization of the Diacid 11 in Aqueous Sulfuric Acid. The diacid **11** (40 mg, 0.13 mmol) was added to 80% aqueous sulfuric acid (2 mL) at 80 °C. The resulting dark solution was stirred at that temperature for 15 min under a nitrogen atmosphere and then poured onto ice (20 mL) with stirring, and the resulting precipitates were collected by filtration, affording **12** (23 mg, 65%) as a purple solid. The crude product thus obtained was either acetylated quantitatively to **13** (*vide supra*) or recrystallized from ethyl acetate to give pure **12** as purple

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microneedles which were used for analytical purposes. **For 12** (R_f 0.28, 3:7 ethyl acetate/hexanes): mp 248–250 °C sublimed; ^{1}H NMR (360 MHz, 1:2.3 DMSO-d_6/acetone-d_6) δ 6.44 (ddd, 1H, J = 8.7, 1.2 Hz, 8-H), 6.55 (dd, 1H, J = 7.8, 6.9 Hz, 2-H), 7.60 (d, 1H, J = 9.4 Hz, 4-H), 7.62 (dd, 1H, J = 6.9, 0.7 Hz, 3-H), 7.67 (ddd, 1H, J = 8.5, 6.7, 1.3 Hz, 9-H), 7.83 (dd, 1H, J = 7.8, 0.7 Hz, 1-H), 8.17 (d, 1H, J = 9.4 Hz, 5-H), 8.52 (ddd, 1H, J = 8.7, 1.3, 0.8 Hz, 7-H), 8.66 (ddd, 1H, J = 8.5, 1.2, 0.8 Hz, 10-H); ^{13}C NMR (90.5 MHz, DMSO-d_6) δ 112.31 (s), 113.92 (s), 121.61 (d), 122.08 (d), 122.53 (d), 123.11 (d), 123.25 (s), 123.74 (d), 124.67 (d), 126.47 (s), 129.82 (d), 130.11 (d), 130.54 (d), 130.93 (s), 133.91 (s), 136.31 (s), 143.23 (s), 157.49 (s), 191.70 (s, observed with the use of Cr^{II}-(acac)$_2$ as a relaxation agent); IR (KBr) 1671, 1602, 1569, 1202 cm^{-1}.

X-ray Crystal Structure Determination of Keto Acetate 13. A single crystal of keto acetate **13** was subjected to X-ray crystallographic analysis. Crystal data for **13**: triclinic, $P\bar{1}$ (No. 2), unit-cell parameters a = 8.363 (2) Å, b = 8.826 (2) Å, c = 10.416 (2) Å, α = 76.61(2)°, β = 71.37(2)°, γ = 89.78(2)°, V = 706.7(3) Å^3, Z = 2, d_c = 1.486 g cm^{-1}, μ(Mo Kα) = 0.88 cm^{-1}, orange rectangular needles, 0.18 × 0.12 × 0.30 mm^3, 6104 data collected with $5° \leq 2\theta \leq 52°$, 2791 unique reflections, 2137 reflections with $|F_o| \geq 4\sigma(F_o)$ used in refinement. Data were collected on a Siemens R3/v equipped with a LT-2 low-temperature device at −90 °C. The structure was solved by direct methods, and all nonhydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively. A total of 266 parameters were refined with a weighting scheme [$w^{-1} = \sigma^2(F) + 0.000191(F)^2$]. Refinement converged with R = 0.0480 and R_w = 0.0454. The program used for the solution and refinement of the structure was Siemens SHELXTL PLUS. Atomic positional coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

11*H*-Benz[*bc*]aceanthrylene (1,12-MBA). A solution of **13** (33 mg, 0.10 mmol), 57% aqueous HI (0.4 mL), and red phosphorus (33 mg) in acetic acid (3 mL) was refluxed for 20 h, then filtered through Celite, and partitioned between ethyl acetate (10 mL) and H_2O (10 mL). The phases were separated, and the organic phase was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL) and dried ($MgSO_4$). Evaporation under reduced pressure and purification of the residue through silica gel flash chromatography, with hexanes as the eluent, afforded 1,12-MBA (**1**) (12 mg, 48%; R_f 0.13, hexanes): mp 122–123 °C (hexanes/acetone) (lit.[11] mp 122.5–123 °C). The ^{1}H NMR data of **1** were in complete agreement with those reported in the literature.[14]

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