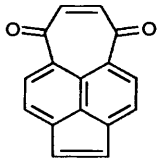
A Five Fused Ring Non-benzenoid Quinone Containing a Seven-membered Ring: Synthesis and Properties of Cyclohept[*f,g*]aceanthrylene-5,8-dione and 1,2-Dihydrocyclohept[*f,g*]aceanthrylene-5,8-dione

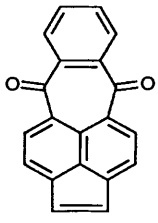
Kiyokazu Morita, Takashi Aida, Kennichi Morinaga and Josuke Tsunetsugu *
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama, Japan 338

Cyclohept[*f,g*]aceanthrylene-5,8-dione **16** and 1,2-dihydrocyclohept[*f,g*]aceanthrylene-5,8-dione **15** have both been synthesized in four steps from aceanthrene **9** in 8 and 7% overall yield, respectively. On the basis of their reduction potentials, the compound **16** was shown to be an [18]annulenedione with a higher reduction potential than the isomeric cyclopenta[*c,d*]pleiadene-5,10-dione **2**. An unsuccessful attempt to synthesize cyclohept[*f,g*]aceanthrylene **21** as well as the efficient synthesis of aceanthrene **9** from anthracene is also described.

Recently it was shown that some non-benzenoid quinones containing a seven-membered ring have higher electrochemical reduction potentials than those of the isomeric benzenoid quinones; azulene quinones[1] and *o*-pleiadiene quinone[2] have almost comparable reduction potentials with those of the naphthoquinones and 9,10-anthraquinone, respectively; and *o*- and *p*-acepleiadylene quinones have higher reduction potentials than the 1,6-, 1,8- and 4,5-pyrenequinones.[3] We have previously reported the syntheses and properties of *o*-pleiadienequinones,[2] dihydrocyclohept[*f,g*]aceanthrylene-5,8-diones,[3] cyclohept-[*f,g*]-acenaphthylene-5,8-diones[3] and a [22]annulenedione, naphtho[2',3':5,6]cyclohept[1,2,3-*f,g*]acenaphthrylene-7,14-dione **3**.[4] Cyclohept[*f,g*]acenaphthrylene-5,8-dione **1**, cyclopenta[*c,d*]pleiadene-5,8-dione **2**[5] and compound **3**[4] form a series of [4*n* + 2]annulenediones (*n* = 3, 4, 5), which have all been previously characterized.



1



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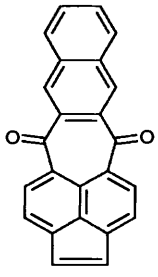
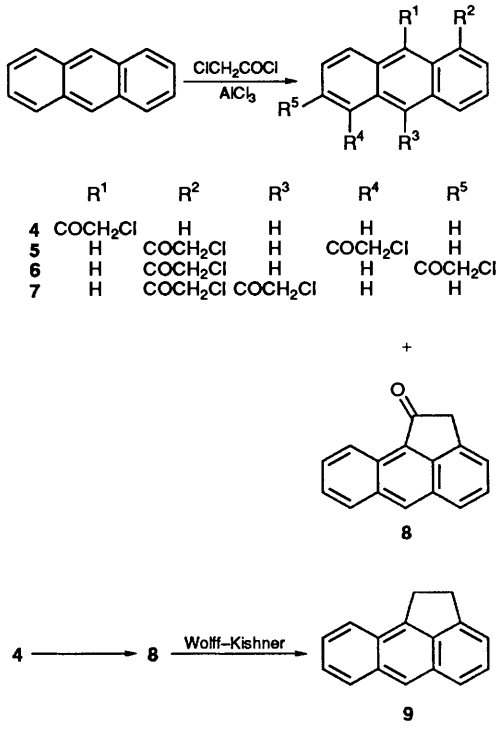


3

We present in this paper the synthesis, characterization and physical properties of the aceanthrylene-5,8-diones **16** and **15**. Compound **16** is an isomer of the quinone **2** and, in contrast with a longitudinal series of those quinones **1**–**3**, can be a member of a series of transverse annulenediones, namely, compounds **1**, **16** and the as yet unsynthesized cyclohepta-[*f,g*]cyclopenta[*o,p*]naphthacene-7,10-dione and so on.

The crucial point in the synthesis of the title compounds **15** and **16** was to build a five- and seven-membered ring into the molecule. Aceanthrene **9** was chosen as the starting material and prepared by an intramolecular Friedel–Crafts cyclization of 9-(chloroacetyl)anthracene **4**. This, in turn, had been synthesized by the controlled Friedel–Crafts acylation of anthracene with chloroacetyl chloride (59%), followed by a Wolff–Kishner reduction (90%) (Scheme 1). Becker reported[6] that aceanthren-1-one **8** was obtained in 38% yield at 0 to −5 °C, together with a mixture of bis(chloroacetyl)anthracenes, but that none of the structures had been determined. The reaction was reinvestigated and found to be delicately temperature dependent. At room



Scheme 1

temperature, disubstituted products of 1,5-, 1,6- and 1,10-bis(chloroacetyl)anthracenes **5**–**7** and aceanthren-1-one **8** were obtained in 6.5, 1.3, 2.2 and 20% yields, respectively. At −50 to −40 °C 9-(chloroacetyl)anthracene **4** was obtained in a satisfactory yield (59%) as a single product. The relationship between the temperature and the product ratio is shown in Table 1.

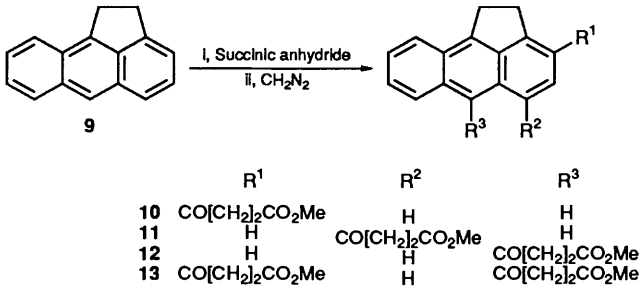
Since the concomitant formation of various polysubstituted products can be a drawback for the Friedel–Crafts reaction, it is noteworthy that in our case, the kinetically rather than the thermodynamically controlled product was preferentially obtained. Comparison of IR, mass spectral and 400 MHz proton NMR data easily elucidated the structures of those compounds **8** and **4**–**7**. Successive intramolecular ring closure of the chloroacetyl **4** to compound **8** by Friedel–Crafts acylation (95%) and Wolff–Kishner reduction (90%) afforded aceanthrene **9** in 54% overall yield, starting from anthracene (Scheme 1). So far as we know, this is the best method for the preparation of aceanthrene. Aceanthrene **9** was then subjected to Friedel–Crafts acylation with succinic anhydride (Scheme 2). Here

Table 1 Friedel–Crafts reaction of anthracene

Temp. (°C)	Products (yield, %) 4	5	6	7	8
0 to 24	—	6.5	1.3	2.2	20
−20 to −16	50	trace	—	trace	—
−50 to −40	59	—	—	—	—

Table 2 Friedel–Crafts acylation of aceanthrene **9**

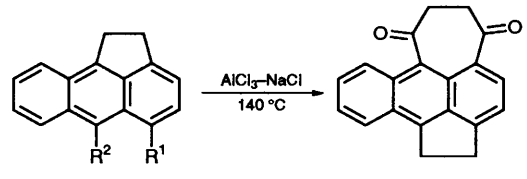
Temp. (°C)	Products (yield, %) 10	11	12	13
−15 to 22	3	25	—	16
−19 to −13	—	7	26	1
−50 to −40	—	—	47	—



	R^1	R^2	R^3
10	$CO[CH_2]_2CO_2Me$	H	H
11	H	$CO[CH_2]_2CO_2Me$	H
12	H	H	$CO[CH_2]_2CO_2Me$
13	$CO[CH_2]_2CO_2Me$	H	$CO[CH_2]_2CO_2Me$

Scheme 2

again, the distribution of the products was very dependent upon temperature and the relationship between the reaction temp. and the distribution of products (as the methyl esters) is shown in Table 2. At −20 °C, the methyl esters **10**, **11** and **13** were obtained in 3, 25 and 16% yields, respectively. At −15 °C the monosubstituted compounds **11**, **12** and the disubstituted compound **13** were obtained in 7, 26 and 1% yields, respectively. Under similar reaction conditions, but at −50 °C, the 6-isomer **12** was formed as a single product from aceanthrene **9** in 47% yield. This compound **12** was intramolecularly cyclized to give the dione **14** (34%), which was also prepared from the 5-isomer **11** (59%), thus proving the structure of the dione **14** (Scheme 3).



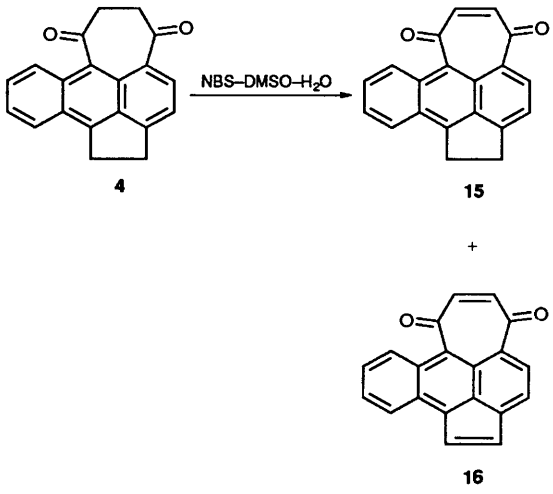
11 $R^1 = CO[CH_2]_2CO_2Me$, $R^2 = H$
12 $R^1 = H$, $R^2 = CO(CH_2)_2CO_2Me$

Scheme 3

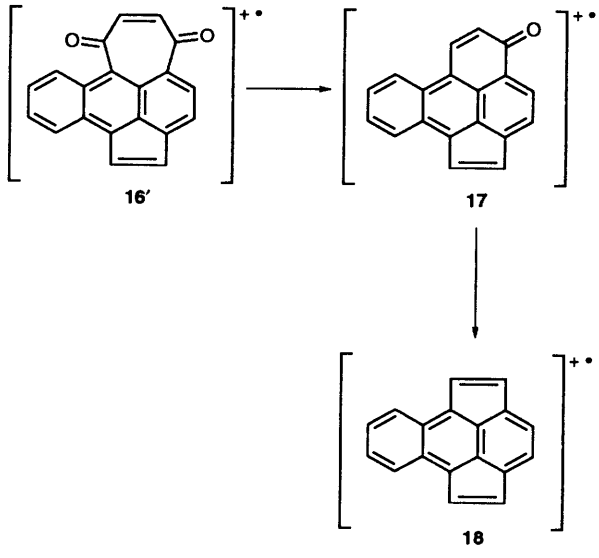
Upon treatment of dione **14** with *N*-bromosuccinimide (NBS) in dimethyl sulfoxide (DMSO), the compounds **15** and **16** were obtained as deep purple and red needles in 18 and 21%, respectively (Scheme 4).

The mass spectrum of the dione **16** showed a weak ($M^+ + 2$) radical ion peak (which is characteristic for quinones), M^+, $M^+ - CO$ and $M^+ - 2CO$ peaks, suggesting that the radical cation **16′** decomposes successively through benz[*f*,*g*]aceanthrylen-5-one **17** and cyclopent[*f*,*g*]aceanthrylene **18** radical cations (Scheme 5).

Physical data for the diones **1**–**2** and **16** are given in Table 3,



Scheme 4



Scheme 5

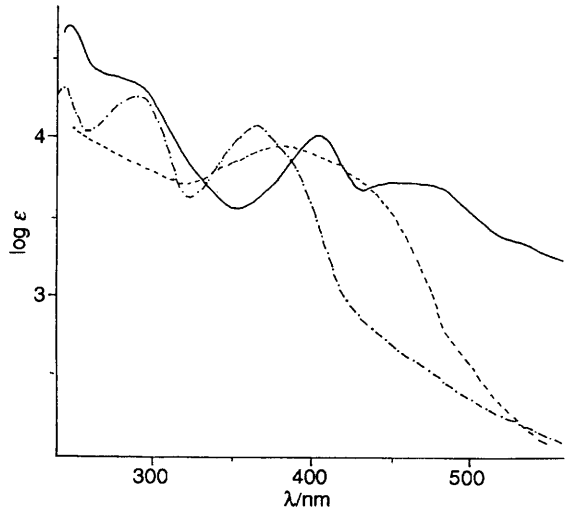


Fig. 1 Electronic spectra of the diones; **2**; —— **16**; - - - - **15**; — · — · — (solution in chloroform)

whilst the electronic spectra of the diones **2**, **15** and **16** are shown in Fig. 1.

The ^{13}C NMR chemical shift values for the carbonyl carbons

Table 3 Physical properties and selected spectral data of the diones **1–2** and **16**

Compound	Appearance	M.p. (°C)	λ_{max}/nm (log ε)	ν_{max}/cm^{-1}	^{13}C NMR (δ) (carbonyl carbons)	^{1}H NMR (δ)
1[a]	Purple needles	186 (decomp.)	337.5 (3.94)	1633	189.3	6.87 (2 H, s, 6- and 7-H), 7.01 (2 H, s, 1- and 2-H), 7.61 (2 H, d, *J* 7.5, 3- and 10-H) and 8.30 (2 H, d, *J* 7.5, 4- and 9-H)
2[b,c]	Orange-red needles	197	363.5 (4.06)	1660	194.4	7.06 (2 H, s, 1- and 2-H), 7.65–7.73 (4 H, m, 6-, 7-, 8- and 9-H), 7.86–7.97 (2 H, m, 3- and 12-H) and 8.35 (2 H, d, *J* 7.3, 4- and 11-H)
16	Deep purple needles	265 (decomp.)	471.5 (3.67)	1646	190.1 195.0	6.81 (1 H, d, *J* 12.6, 7- and 6-H), 7.07 (1 H, d, *J* 5.4, 2- or 1-H), 7.13 (1 H, d, *J* 12.6, 6- or 7-H), 7.54 (1 H, d, *J* 5.4, 1- or 2-H), 7.62 (2 H, m, 10- and 11-H), 7.73 (1 H, d, *J* 7.0, 3-H), 8.17 (1 H, d, *J* 7.9, 12-H), 8.47 (1 H, d, *J* 9.0, 9-H) and 8.57 (1 H, d, *J* 7.0, 4-H)

[a] Ref. 3. [b] Ref. 5. [c] This work.

Table 4 Calculated π-LUMO (pz) coefficients for the quinone **16** (MNDO-PM3). Optimised molecular geometry is non-planar

Compound **16**						
C-1	C-2	C-2a	C-3	C-4	C-4a	C-5
−0.241	0.271	0.287	−0.298	−0.243	0.312	0.073
C-6	C-7	C-8	C-8a	C-8b	C-9	C-10
0.053	−0.063	−0.052	−0.391	0.148	0.188	−0.158
C-11	C-12	C-12a	C-12b	C-12c	C-12d	O-5
−0.183	0.181	0.186	−0.359	0.087	0.083	0.024
O-8						
−0.070						

Table 5 Electrochemical reduction potentials of the diones[a]

Compound	E_1	E_2	$E_1 - E_2$	$E_1 + E_2$
Ferrocene	+0.52			
1,4-Benzoquinone	−0.36	−1.15	0.79	−1.51
Cyclohept[*f*,*g*]aceanthrylene-5,8-dione **16**	−0.44	−0.88	0.44	−1.32
1,4-Naphthoquinone	−0.52	−1.37	0.85	−1.89
Cyclopenta[*c*,*d*]pleiadene-5,10-dione **2**	−0.66	−1.11	0.45	−1.77
9,10-Anthraquinone	−0.82	−1.57	0.75	−2.39
1,2-Dihydrocyclohept[*f*,*g*]acenaphthylene-5,8-dione	−0.82	−1.45	0.63	−2.27
1,2-Dihydrocyclohept[*f*,*g*]aceanthrylene-5,8-dione **15**	−0.90	−1.50	0.60	−2.40
1,2-Dihydrocyclopenta[*c*,*d*]pleiadene-5,10-dione	−1.17	−1.68	0.51	−2.85

[a] At 23.5 °C in dry DMF as described in the text. Potentials measured relative to Ag/AgCl/sat. NaCl electrode.

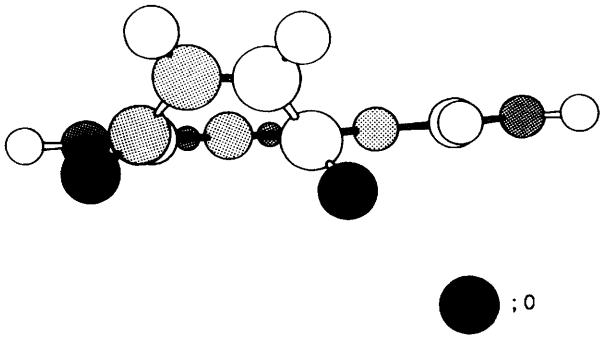


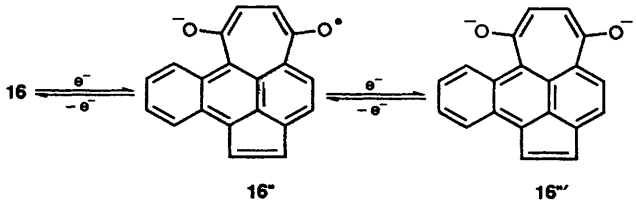
Fig. 2 Optimized PM3 geometries of the dione **16**

of the diketone **16** (δ_{CO} 190.1 and 195.0) are between those of unsaturated ketones and those of quinones. This suggests that the dione **16** might have some degree of quinone character. The molecular orbital calculations by the PM3 method were performed with MOPAC, Ver. 6.02[7] and show that the dione **16** has a non-planar structure, as shown in Fig. 2. The π-LUMO (pz) coefficients suggest the positions most susceptible towards nucleophilic attack (Table 4). The heat of formation was also calculated as 55.48 kcal mol^{-1}.*

* 1 cal = 4.184 J.

The redox potentials of the diones **2**, **15–16** and the related diones were measured by cyclic voltammetry (Fig. 3 and Table 5).

These diones show very good reversible cyclic voltammograms. Interestingly, the potentials E_1, E_2 and $E_1 + E_2$ are all in the order of **16** > **2**. The data obtained show that for the compound **16** in DMF, there is a reversible equilibrium between the radical anion **16″** and the dianion **16‴** (Scheme 6). Since



16″ **16‴**

Scheme 6

the reduction potentials of quinones can be considered as a reflection of the stability of the parent hydrocarbons, the dianion **16‴** must exist in stabilized form as an [18]annulene. This interpretation is supported by the fact that the dihydro dione **15** shows remarkably low reduction potentials. Since the reversibility of the voltammogram is conserved even when measured at slower speed (10 mV s^{-1}), the dianion **16‴** is considered to have a life of at least several minutes in DMF. All

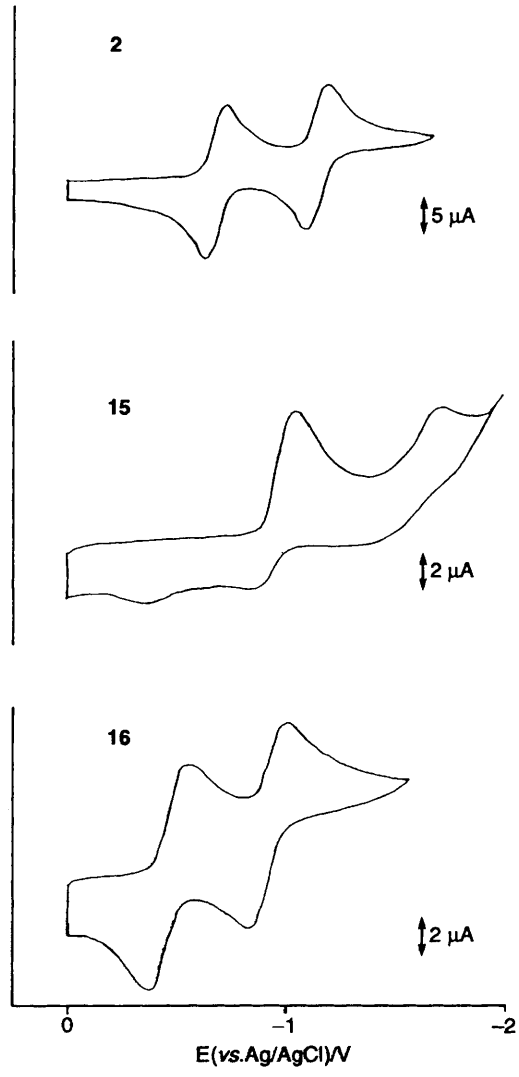
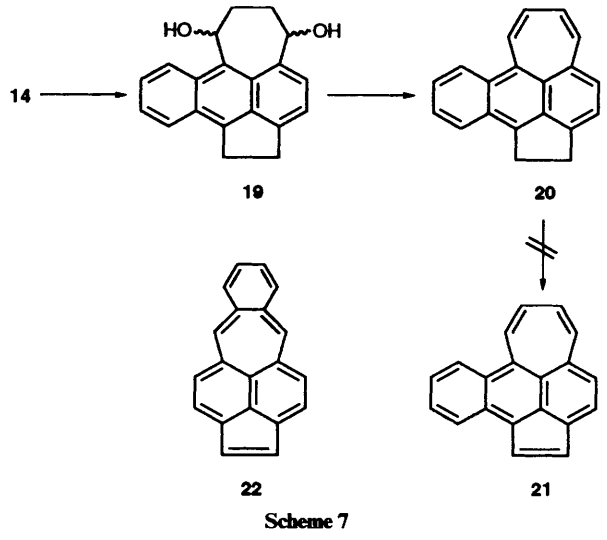


Fig. 3 Cyclic voltammograms of the diones **2**, **15** and **16**

these facts support the identification of the dione **16** as an [18]annulenedione with a vinyl cross link. The difference of E_1 values between compounds **16** and **2** could be ascribed to the difference of the stability between the systems of **21** and **25**. Since the $E_1 - E_2$ values are considered to express the repulsion between two electrons successively entering into the LUMO on a zero-order approximation, it is reasonable that the $E_1 - E_2$ values for the diones **16** and **15** are almost the same, because the area of occupation by the electron does not change.

The compound **14**, when reduced with sodium borohydride, gave the diol **19** as a mixture of diastereoisomers (91%) which was used for the physical measurements and the attempted synthesis of **22** (Scheme 7). The diol **19**, in dry toluene, was refluxed for 30 min with activated neutral alumina to give the dehydrated product **20** (22%) as an unstable red oil. Treatment of this freshly prepared hydrocarbon **20** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) failed to give the unsaturated product **24**, only unidentified and decomposed products.



Scheme 7

Experimental

M.p.s were determined with a Mitamura air-bath apparatus and are uncorrected. ^1H and ^{13}C NMR spectra ($SiMe_4$ as the internal standard) were determined with a JEOL PMX-60si, a JEOL JNM-FX-90Q, and/or a Bruker A-400 spectrometer. IR spectra were determined with a Hitachi 270-50 instrument, electronic spectra were determined with a Hitachi 340 spectrophotometer and mass spectra with a JEOL JMS-01SG-2 and/or a Shimadzu Qp-1000 spectrometer. Unless otherwise stated, the spectra were taken in the following solvents/media: UV/VIS, $CHCl_3$; IR, KBr; ^1H and ^{13}C NMR, $CDCl_3$. The cyclic voltammogram was recorded in the usual manner with a Yanagimoto polarographic analyser P-1100. The progress of most reactions was followed by TLC using Kieselgel 60G (Merck 70–230 mesh). Ether refers to diethyl ether.

Cyclic Voltammetry.—All measurements were performed between 0–100 °C in dry dimethylformamide (DMF) with 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. Voltammograms were determined under a nitrogen atmosphere in a standard three-electrode cell equipped with a silver–silver chloride electrode as reference, and were recorded at a scan rate of 100 mV s^{-1}.

9-(Chloroacetyl)anthracene **4**.—Anhydrous aluminium chloride powder (154 g, 1.16 mol) was added slowly (at −50 to −40 °C) to a stirred mixture of anthracene (100 g, 0.56 mol) and chloroacetyl chloride (380 g, 3.2 mol) in dichloromethane (500 cm^3) and the mixture stirred for a further 12 h under nitrogen. It was then poured into ice–water (1 dm^3) and to this mixture, conc. hydrochloric acid (200 cm^3) was added. Undissolved materials were removed and the filtrate was extracted with dichloromethane. The extract was washed with 5% aq. sodium hydrogen carbonate and saturated brine and then dried ($MgSO_4$) and evaporated. The residue was chromatographed on a silica gel column with benzene as the eluent to give the title compound **4** as pale yellow needles, m.p. 96–97 °C (from cyclohexane); *m/z* (70 eV) 256 (M^+ + 2, 9.6%), 255 (M^+ + 1, 4.2), 254 (M^+, 34.0) and 205 ($M^+ - CH_2Cl$, 100) (Found: C, 75.3; H, 4.4. $C_{16}H_{11}ClO$ requires C, 75.45; H, 4.44%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1727, 1700, 1161, 1095, 910 and 894; δ 4.66 (2 H, s, CH_2), 7.39–7.50 (2 H, m, ArH), 7.55–7.72 (2 H, m, ArH), 7.89–7.99 (2 H, m, ArH) and 8.41 (1 H, s, 6-H).

Aceanthren-1-one **8**.—Anhydrous aluminium chloride powder (58.3 g, 437 mmol) was added over 30 min at 0 °C to a stirred solution of compound **4** (50.6 g, 199 mmol) in dichloromethane (500 cm^3) after which the mixture was allowed gradually to warm to room temperature. After the mixture had been stirred for a further 2 h it was poured into ice–water (1 dm^3) and then treated with conc. hydrochloric acid (100 cm^3). The work-up and purification procedures were similar to

those described for compound **12**. The title compound **8** (41.5 g, 95%) was isolated as yellow needles; m.p. 154–155 °C (from dichloromethane) (lit.,[6] 157–158 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 1691, 1627, 1576, 1388, 1158, 751 and 737; δ 3.87 (2 H, s, CH_2), 7.40–8.20 (6 H, m, ArH), 8.58 (1 H, s, 6-H) and 9.18 (1 H, d, *J* 8.0, 10-H).

Aceanthrene **9**.—A mixture of aceanthren-1-one **7** (20.3 g, 93 mmol), hydrazine monohydrate (32 cm^3, 660 mmol) and diethylene glycol (240 cm^3) was stirred for 2 h at 120 °C under nitrogen. Potassium hydroxide (16.2 g, 29 mmol) was added to the reaction mixture which was then heated at 200 °C for 2 h. After this it was poured into water and the resultant precipitate was filtered off, washed with water and dried. Chromatography of the precipitate on a silica gel column with benzene yielded the title compound **9** (17.1 g, 90%) as pale yellow plates; m.p. 115–116 °C (from benzene) (lit.,[6] 118–119 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 2928, 1622, 1576, 1388, 1158 and 751; δ 3.52 (4 H, m, 1-H and 2-H), 7.10 (1 H, d, *J* 6.0, ArH), 7.23–7.43 (3 H, m, ArH), 7.62 (1 H, d, *J* 8.3, ArH), 7.68–8.04 (2 H, m, ArH) and 8.09 (1 H, s, 6-H).

Methyl 4-(*Aceanthren-6-yl*)-4-*oxobutanoate* **12**.—Anhydrous aluminium chloride powder (27.4 g, 205 mmol) was added slowly at −50 to −40 °C to a stirred mixture of succinic anhydride (11.3 g, 113 mmol) in dichloromethane (300 cm^3) after which the whole was stirred for a further 12 h. It was then poured into ice–water and acidified with conc. hydrochloric acid. The resultant precipitate was collected and dried *in vacuo* to give 4-(aceanthren-6-yl)-4-oxobutyric acid (8.56 g, 50%) as yellow needles; m.p. 208–210 °C (from methanol); *m/z* (70 eV) 305 ($M^+ + 1$, 8.5%), 304 (M^+, 44.7) and 231 ($M^+ - CH_2CH_2CO_2H$, 100) (Found: C, 78.75; H, 5.4. $C_{20}H_{16}O_3$ requires C, 78.93; H, 5.54%); ν_{max}/cm^{-1} 3046, 1699, 1615, 1585, 1245 and 1907; δ([$^2H_6$]-DMSO) 2.82 (2 H, m), 3.29–3.51 (6 H, m), 7.23 (1 H, d, *J* 6.4), 7.41–8.10 (6 H, m) and 12.14 (1 H, br s, OH). To a gently stirred suspension of this keto carboxylic acid (4.92 g, 16 mmol) in ether (50 cm^3) was added an ether solution of diazomethane and the reaction mixture was stirred gently for a further 24 h. After the removal of the solvent, the residue was chromatographed on a silica gel column with dichloromethane as eluent to give the title compound **12** (4.49 g, 87%) as pale yellow needles; m.p. 135 °C; *m/z* (70 eV) 319 ($M^+ + 1$, 11.1%), 318 (M^+, 48.5), 287 (M^+ − OMe, 10.6) and 231 ($M^+ - CH_2CH_2CO_2Me$, 100) (Found: C, 79.3; H, 5.7. $C_{20}H_{14}O_2$ requires C, 79.22; H, 5.73%); $\lambda_{max}(CHCl_3)/nm$ 268 (log ε 5.06), 370 (3.89), 390 (3.99) and 410 (3.91); ν_{max}/cm^{-1} 3010, 2928, 1736 ($CHCl_3$), 1676 ($CHCl_3$), 1569, 1520 and 1267; δ 2.90 (2 H, t, *J* 6.3, 13-H), 3.36 (2 H, t, *J* 6.3, 12-H), 3.51 (2 H, t, *J* 5.5, 2-H), 3.69 (2 H, t, *J* 5.5, 1-H), 3.77 (3 H, s, OMe), 7.22 (1 H, d, *J* 6.6, 3-H), 7.43–7.53 (3 H, m), 7.66 (1 H, d, *J* 9.0, 10-H), 7.96 (1 H, d, *J* 8.2, 5-H) and 7.99 (1 H, d, *J* 8.7, 7-H).

Methyl 4-(*Aceanthren-5-yl*)-4-*oxobutanoate* **11**, *Methyl* 4-(*Aceanthren-3-yl*)-4-*oxobutanoate* **10** *and Dimethyl* 4,4′-(*Aceanthren-4,6-diyl*)-*bis*(4-*oxobutanoate*) **13**.—Anhydrous aluminium powder (1.74 g, 13.0 mmol) was slowly added at −17 °C to a stirred mixture of aceanthrene **9** (0.99 g, 4.9 mmol) and succinic anhydride in dichloromethane (23 cm^3) under nitrogen. The reaction mixture was stirred for 9 h at −17 to −10 °C, and then for 20 h at room temp.; it was then poured into ice–water. After the aqueous mixture had been acidified with conc. hydrochloric acid, the resulting precipitate was filtered off, washed with dichloromethane and then dried *in vacuo*. It was then esterified with diazomethane as described above and the resulting product chromatographed on a silica gel column with dichloromethane as eluent to give the following compounds successively: compound **11** (230 mg, 24.4%) as yellow needles, m.p. 106 °C (from hexane); *m/z* (70 eV) 319 ($M^+ + 1$, 22.8%), 318 (M^+, 99.0), 287 (M^+ − OMe, 10.6) and 231 ($M^+ - CH_2CH_2CO_2Me$, 100) (Found: C, 79.5; H, 5.7. $C_{20}H_{14}O_2$ requires C, 79.22; H, 5.73%); λ_{max}/nm 288 (log ε 4.82), 383 (3.35) and 414 (3.92); ν_{max}/cm^{-1} 3022, 2956, 1736, 1670, 1608 and 1232; δ 2.86 (2 H, t, *J* 6.6, 12-H), 3.36 (2 H, t, *J* 6.6, 13-H), 3.50 (2 H, m, H-2), 3.73 (2 H, m, 1-H), 3.75 (3 H, s, OMe), 7.21 (1 H, d, *J* 8.9), 8.12 (1 H, d, *J* 8.2), 8.19 (1 H, d, *J* 7.1, 4-H) and 9.38 (1 H, s, 6-H).

The ester **10** (380 mg, 1.5%) as yellow needles, m.p. 116 °C (from hexane); *m/z* (70 eV) 318 (M^+, 27.0%), 287 (M^+ − OMe, 11.9), 231 ($M^+ - CH_2CO_2Me$, 42.9) and 203 ($M^+ - COCH_2CH_2CO_2Me$, 100) (Found: C, 79.2; H, 5.8. $C_{20}H_{14}O_2$ requires C, 79.22; H, 5.73%); ν_{max}/cm^{-1} 3025, 2929, 1735, 1675 and 1608; δ 2.84 (2 H, t, *J* 6.6, 12-H), 3.42 (2 H, t, *J* 6.6, 13-H), 3.75 (3 H, s, OMe), 3.81 (2 H, m, 2-H), 3.93 (2 H, m, 1-H), 7.54 (2 H, m), 7.78 (1 H, d, *J* 9.0, 4-H), 7.95 (1 H, d, *J* 9.0, 5-H), 8.07 (2 H, m) and 8.20 (1 H, s, 6-H).

The ester **13** (345 mg, 16.3%) as yellow needles, m.p. 151 °C (from hexane); *m/z* (70 eV) 433 ($M^+ + 1$, 11.9), 432 (M^+, 38.4), 401 (M^+ − OMe, 14.6) and 345 ($M^+ - CH_2CO_2Me$, 48.2) (Found: C, 72.15; H, 5.6. $C_{20}H_{14}O_2$ requires C, 72.21; H, 5.59%); λ_{max}/nm 290 (log ε 4.73), 360 (3.77), 380 (3.95), 416 (373) and 720 (3.71).

1,2,6,7-*Tetrahydrocyclohept*[f,g]*aceanthrylene*-5,8-*dione* **14**.—A melt, prepared by fusing together sodium chloride (18.6 g, 318 mmol) and anhydrous aluminium chloride (104 g, 780 mmol), was allowed to cool to the point of incipient crystallisation (100 °C) when the ester **12** was slowly added to it; the temperature of the melt rose during the addition. The melt was stirred well, brought to 140 °C and kept at that temperature for 30 min. After this it was added, with stirring, to ice–water to afford brown crystals. These were purified by chromatography on a silica gel column, with dichloromethane as eluent, to give the title compound **14** (0.545 g, 34%) as yellow needles (from hexane); *m/z* (75 eV) 286 (M^+, 55), 258 (M^+ − CO, 24), 230 (M^+ − 2CO, 47) and 202 ($M^+ - 2COCH_2CH_2$, 100) (Found: C, 83.7; H, 5.1. $C_{20}H_{14}O_2$ requires C, 83.90; H, 5.13%; λ_{max}/nm 274 (log ε 4.88), 342 (3.48) and 429 (3.95); ν_{max}/cm^{-1} 3010, 2928, 1682, 1603 and 1568; δ 3.26 (2 H, t, *J* 6.6, 6-H), 3.34 (2 H, t, *J* 6.6, 7-H), 3.59 (2 H, m, 2-H), 3.88 (2 H, m, 1-H), 7.36 (1 H, d, *J* 7.1, 3-H), 7.58 (1 H, dd, *J* 6.8 and 8.3, 11-H), 7.65 (1 H, dd, *J* 6.8 and 9.0, 10-H), 8.06 (1 H, d, *J* 8.3, 12-H), 8.30 (1 H, d, *J* 7.1, 4-H) and 8.52 (1 H, d, *J* 9.0, 9-H).

Cyclohept[f,g]*aceanthrylene*-5,8-*dione* **16** *and Cyclohept*[f,g]-*aceanthrylene*-5,8-*dione* **15**.—A mixture of the diketone **14** (445 mg, 1.55 mmol), *N*-bromosuccinimide (407 mg, 2.28 mmol), dimethyl sulfoxide (7.5 cm^3) and water (194 mg) was stirred for 2 h at 40 °C under nitrogen. The reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with 5% aqueous sodium hydrogen carbonate and saturated brine and then dried ($MgSO_4$) and evaporated. The residue was chromatographed on a silica gel column with dichloromethane as eluent to give the title compound **16** from the first fraction and the title compound **15** from the second fraction: compound **16** (92 mg, 21%), deep purple needles (from benzene–hexane), m.p. 265 °C (decomp.); *m/z* (70 eV) 284 ($M^+ + 2$, 2.8), 283 ($M^+ + 1$, 20) and 282 (M^+, 100) (Found: C, 82.4; H, 3.8. $C_{20}H_{10}O_2 \cdot 0.5H_2O$ requires C, 82.46; H, 3.80%); λ_{max}/nm 284 (log ε 4.33), 401 (3.98) and 472 (3.67); ν_{max}/cm^{-1} 2922, 1620, 1564, 1520 and 1288. Compound **15** (77 mg, 18%) as red needles; m.p. 235 °C (decomp.) (from benzene–hexane); *m/z* (70 eV) 286 ($M^+ + 2$, 4.2%), 285 ($M^+ + 1$, 6.4), 284 (M^+, 13.8), 256 (M^+ − CO, 4.3); λ_{max}/nm ($CHCl_3$) 287 (log ε 4.35), 341 (3.51) and 470 (3.88); ν_{max}/cm^{-1} 2922, 1620, 1564, 1520 and 1288; δ 3.66 (2 H, m, 2-H), 3.88 (2 H, m, 1-H),

6.90 (1 H, d, *J* 12.4, 6-H), 7.18 (1 H, d, 12.4, 7-H), 7.50 (1 H, d, *J* 7.0, 3-H), 7.60 (1 H, dd, *J* 8.6 and 6.9, 11-H), 7.70 (1 H, dd, *J* 9.1 and 6.9, 10-H), 8.60 (1 H, d, *J* 9.1, 12-H), 8.66 (1 H, d, *J* 9.0, 9-H) and 8.80 (1 H, d, *J* 7.3, 4-H).

1,2,6,7-*Tetrahydrocyclohept*[f,g]*aceanthryl*-5,8-*diol* **19**.—Sodium borohydride (95 mg, 1 mmol) in methanol (10 cm^3) was added dropwise to a stirred solution of the diketone **14** (211 mg, 0.74 mmol) in benzene (100 cm^3) and the reaction mixture stirred for a further 1 h at room temp., under nitrogen. After removal of the solvent, the residue was washed with 10% aq. sodium hydroxide and water, dried *in vacuo* and recrystallized to give the diol **19** (192 mg, 91%) as yellow crystals (from benzene–hexane), m.p. 105–112 °C; *m*/*z* (eV) 286 (M^+ + 2), 285 (M^+ + 1), 284 (M^+) and 256 (M^+ − CO); ν_{max}/nm 270 (log ε 4.92), 376 (3.70), 392 (3.82) and 410 (3.70); ν_{max}/cm^{-1} 3370, 2928, 1580, 1443, 1089 and 975; δ 1.88–2.55 (6 H, m), 3.43–3.54 (4 H, m), 5.12–5.40 (1 H, m), 5.90 (1 H, m), 7.08–7.64 (1 H, m), 7.65 (1 H, m), 7.80–8.00 (3 H, m) and 8.24 (1 H, m).

1,2-*Dihydrocyclohept*[f,g]*aceanthrylene* **20**.—A mixture of the diol **22**, toluene (22 cm^3) and aluminium oxide (activated at 200 °C for 8 h, 67 hPa, Brockmann neutral Grade 1, 2.02 g) was refluxed for 30 min. The reaction mixture was directly chromatographed on a silica gel column with pentane as eluent to give the title compound **20** (27 mg, 22%) as a red oil; δ 2.30 (2 H, m, 2-H), 3.30 (2 H, m, 1-H), 6.33 (1 H, m), 6.60 (1 H, m), 6.80 (1 H, m), 7.01 (1 H, m), 7.30–7.80 (m) and 8.20–8.50 (m).

Attempted Synthesis of Cyclohept[f,g]*aceanthrylene* **21**.—A mixture of the freshly prepared diene **20** (357 mg, 1.2 mmol) in a solution of toluene and (DDQ) (286 mg, 1.3 mmol) was stirred for 10 min, when the colour of the reaction mixture darkened. The reaction mixture was chromatographed on a silica gel column with pentane as eluent to give a mixture of unidentified, decomposition products.

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