Synthesis and Properties of Cyclohepta[fg]naphth[2,3-a]acenaphthylene-5,12-dione (Naphth[2,3-h]acepleiadylene-5,12-dione)

Josuke Tsunetsugu,* Shinri Tanaka, Seiji Ebine, and Kenichi Morinaga *
Department of Chemistry, Saitama University, Urawa, 338, Japan

Naphth[2,3-h]acepleiadylene-5,12-dione (4) has been synthesized by the cycloaddition of acepleiadylene-5,8-dione (2) and o-dibromoquinodimethane generated in situ from 1,2-bis(dibromomethyl)-benzene and sodium iodide. On the basis of their reduction potentials, determined by cyclic voltammetry, compound (4) and benz[h]acepleiadylene-5,10-dione (3) were shown to be [22]- and [18]-annulenediones, respectively. An unsuccessful attempt to synthesize naphth[2,3-h]acepleiadylene (7) is also described.

Although [4n + 2]annulenediones (n ≠ 1) are of interest because of their physical, chemical, and physiological properties, systematic studies concerning them (n > 3) are still few. As part of a study of the nonbenzenoid quinones (n ≠ 1), we have reported the syntheses of o- and p-acepleiadylene-diones (1) and (2) for which n = 3 and have shown that they are annulenediones with remarkably high reduction potentials.[1] Benz[h]acepleiadylene-5,10-dione (3), which can be regarded as a higher analogue, is also known.[2] In this paper the synthesis and physical properties of the title compound (4), which can be regarded as a higher analogue of compound (3), is reported and compared with compounds (2) and (3).

The parent hydrocarbons of compounds (2) and (3) are acepleiadylene (5) and benz[h]acepleiadylene (6) respectively; the former is a [14]annulene[3] and the latter an [18]annulene.[4] Naphth[2,3-h]acepleiadylene (7), the parent hydrocarbon of compound (4), is considered to be a [22]annulene but has yet to be synthesized. It has been reported that compound (2) is a [14]annulenedione but the evidence for the peri-conjugative character of compound (3) is not sufficient.[2] The synthesis of the dione (4) was carried out by a [2 + 8]cycloaddition of acepleiadylene-5,8-dione (2) and o-dibromoquinodimethane generated in situ from 1,2-bis-(dibromomethyl)benzene and sodium iodide (Scheme 1). The reaction is considered to proceed through the intermediate formation of 6,11-dibromo-5a,11a-dihydronaphth[2,3-h]-acepleiadylene-5,12-dione, followed by dehydrobromination. In order to obtain the optimum reaction conditions, various solvents such as DMF (dimethylformamide), HMPT (hexa-methylphosphoramide), THF (tetrahydrofuran), and 18-crown-6 have been used and temperatures between room and 60 °C have been examined. A reaction period of 2 h at 60 °C in DMF was found to be the best and gave compound (4) as stable orange-yellow needles (8%) after column chromatographic purification (silica gel–benzene) and recrystallization from benzene–hexane. The quinone (2) was recovered unchanged (96%) after attempted reaction with butadiene in acetic acid for 56 h at room temperature. Similarly, attempted reaction of the quinone (2) with 2,3-dimethoxybutadiene in chloroform under reflux for 48 h, or in o-dichlorobenzene at 100 °C for 48 h, gave recovery of starting material, 76.7 or 53.7% respectively, but no addition product.

The mass spectrum of the dione (4) showed a weak $(M^{+\cdot} + 2)$ ion peak which is characteristic for quinones, $M^{+\cdot}$, $M^{+\cdot} - CO$, and $M^{+\cdot} - 2CO$ peaks, suggesting that it decomposes successively through naphtho[2,3-j]-5H-cyclo-penta[cd]phenalen-5-one (8) and naphtho[2,3-a]pyracylene (9) cation radicals (Scheme 2).

(1)

(2)

(3)

(4)

(5)

(6)

(7)

Scheme 1.

Scheme 2.

Figure 1. Electronic spectra of diones: —— dione (4); ———— dihydro dione (10) (solution in chloroform)

Figure 2. Cyclic voltammograms of the diones (2), (3), (4), (10), (13), (14), and (15)

Some physical data for the dione (4) together with the diones (2) and (3) are given in Table 1.

The electronic spectrum of the dione (4), together with that of the dione (10) is shown in Figure 1.

^{1}H N.m.r. data and analytical results (see Table 1) support the proposed structure. The ^{13}C chemical shift value for the carbonyl carbon of the diketone (4), δ_{CO} 194, is between those of unsaturated ketones and those of quinones.[5] This suggests that the dione (4) might have some degree of quinone character.[1,6]

The redox potentials of the diones (2),* (3), and (4), the

related diones (10), (13), and (14), and 1,2-dihydro-benzacepleiadylene-5,10-dione (15) were measured by cyclic voltammetry. The cyclic voltammograms are shown in Figure 2 and the numerical data are shown in Table 2. These diones show

* Careful purification of the sample caused the trough observed[1] at ca. 1 V of the oxidation wave to disappear.

Table 1. Physical properties and spectral data of the diones (2), (3), and (4)

Compound	Appearance	M.p. (°C)	λ_{max}/nm (log ε)	ν_{max}/cm^{-1} (C=O)	^{13}C N.m.r. (C=O) δ (22.5 MHz)	^{1}H N.m.r. δ (90 MHz)
(2)[a]	Purple needles	186.0 (decomp.)	337.5 (3.94)	1 633	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 Hz, 3- and 10-H), 8.30 (2 H, d, J 7.5 Hz, 4- and 9-H)
(3)[b,c]	Orange-red needles	197	363.5 (4.06)	1 660	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), 8.35 (2 H, d, J 7.3 Hz, 4- and 11-H)
(4)[c]	Orange-yellow needles	252.0 (decomp.)	361.5 (4.08), 399.5 (3.96)	1 656	194.3 194.3	7.10 (2 H, s, 1- and 2-H), 7.46—7.78 (4 H, m, 7-, 8-, 9-, and 10-H), 7.90—8.00 (2 H, m, 3- and 14-H), 8.40—8.48 (4 H, m, 4-, 6-, 11-, and 13-H)

[a] Ref. 1. [b] Ref. 2. [c] This work.

Table 2. Electrochemical reduction potentials of the diones (2), (3), (4), (10), (13), (14), (15), and related compounds[a]

Compound	E_1	E_2	$E_1 - E_2$	$E_1 + E_2$
Ferrocene[b]	0.56			
Acepleiadylene-5,8-dione (2)[c]	−0.45	−0.98	0.53	−1.43
Benzacepleiadylene-5,10-dione (3)	−0.66	−1.11	0.45	−1.77
Naphthacepleiadylene-5,12-one (4)	−0.70	−1.12	0.42	−1.82
1,4-Naphthoquinone	−0.53	−1.30	0.77	−1.83
9,10-Anthraquinone	−0.77	−1.46	0.69	−2.23
1,2-Dihydroacepleiadylene-5,8-dione (13)	−0.82	−1.45	0.63	−2.27
6,7-Dihydroacepleiadylene-5,8-dione (14)	−0.79	−1.28	0.49	−2.07
1,2-Dihydrobenzacepleiadylene-5,10-dione (15)	−1.17	−1.68	0.51	−2.85
1,2-Dihydronaphthacepleiadylene-5,10-dione (10)	−1.27	−1.76	0.49	−3.03

[a] At room temperature in dry dimethylformamide as described in the text. Potentials relative to Ag/AgCl/sat. NaCl electrode. [b] G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 462. [c] Ref. 1.

Scheme 3.

very good reversible cyclic voltammograms. $E_1, E_2, E_1 + E_2$ are all in the order of (2) > (3) > (4). Interestingly, the C_{24} compound, (4), has higher reduction potentials than the C_{14} 9,10-anthraquinone, a reverse of the usual trend.[7] The data obtained show that for compound (4) in DMF there is a reversible equilibrium between the anion radical (4') and the dianion (4''). Since the reduction potentials of quinones can be considered as a reflection of the stability of the parent hydrocarbons, the dianion (4'') must exist in stabilized form as peri[22]annulene (Scheme 3).* This interpretation is supported by the fact that the dihydro dione (10) 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 (4'') is considered to have a life of at least several minutes in DMF. Similar arguments to the above have already been made as evidence that the dione (2) is a [14]annulene.[1] The same can also be applied to the dione (3), which, therefore, must be an [18]annulenedione.

Since $E_1 - E_2$ values are considered to express the repulsion between two electrons successively entering into the LUMO on a zero-order approximation, it reasonably explains that the $E_1 - E_2$ values for the diones (2), (3), and (4) progressively

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* Various calculations of the resonance energy seem to indicate that [22]annulene has a certain degree of aromatic stability.[6]

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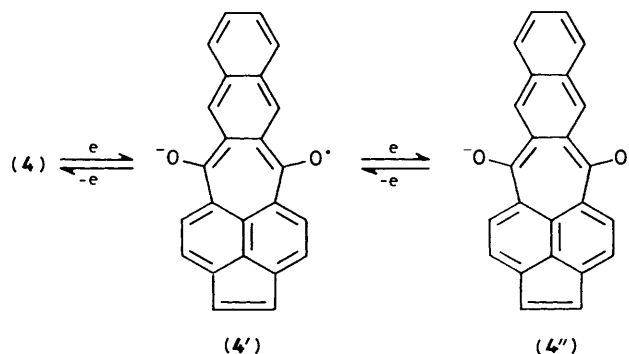
decrease as the area of occupation by π electrons increases. The same trend is observed for the diones (13), (15), and (10).

The dihydroquinone (10) was obtained both by catalytic hydrogenation of the quinone (4) on 5% Pd/C catalyst in benzene solution (69%) (Scheme 4) and also (66%) by cycloaddition of 1,2-dihydroacepleiadylenequinone (13) and o-dibromoquinodimethane generated *in situ* from 1,2-bis(dibromomethyl)benzene and sodium iodide. Compound (10) when stirred with sodium borohydride in benzene–methanol for 1.5 h at room temperature gave the diol (11) as a mixture of diastereoisomers (67.5%) which was used for the physical measurements and subsequent reaction. Since the mass spectrum of compound (11) showed an $M^{+\bullet} - 2H_2O$ ion peak at 302, compound (7) is also assumed to be formed. On the basis that the high reduction potential of the quinone (4) is an indication that the skeleton of [22]annulene is stable, a synthesis of compound (7), the parent hydrocarbon, was attempted by dehydration of compound (11) with concentrated hydrogen chloride for 8 min at room temperature under nitrogen. This afforded pale yellow crystals (m.p. 320 °C, decomp.) and yellow crystals (m.p. 310 °C, decomp.), which showed mass spectral molecular ion peaks at 606 and 320 each, indicating that the former is the dimer of compound (7) and the latter is the monohydric alcohol of compound (7) respectively. A similar experiment in the presence of N-phenylmaleimide gave similar results, no addition product being obtained. In contrast to an earlier report of the detection of the unstable compound (6) in solution,[4] no significant colour change occurred during the reaction. Other spectral data appear to support the proposed structures but a more rigorous study of the reaction and the structures is now being carried out.

Finally, the preparations of the important starting materials, (13) and (2), for the synthesis of the quinone (4) was improved as follows (Scheme 5). Treatment of the dione (12) with NBS in wet
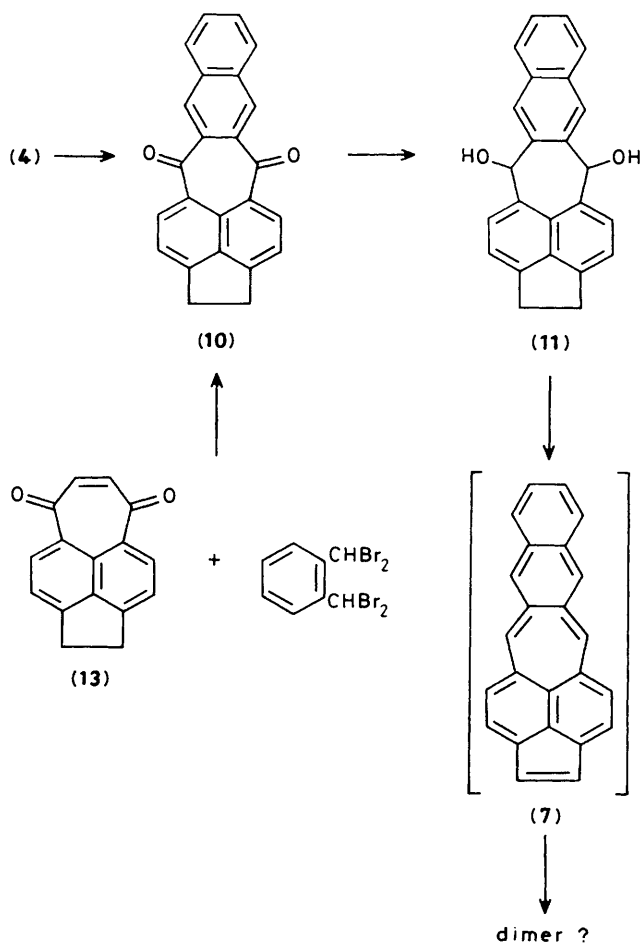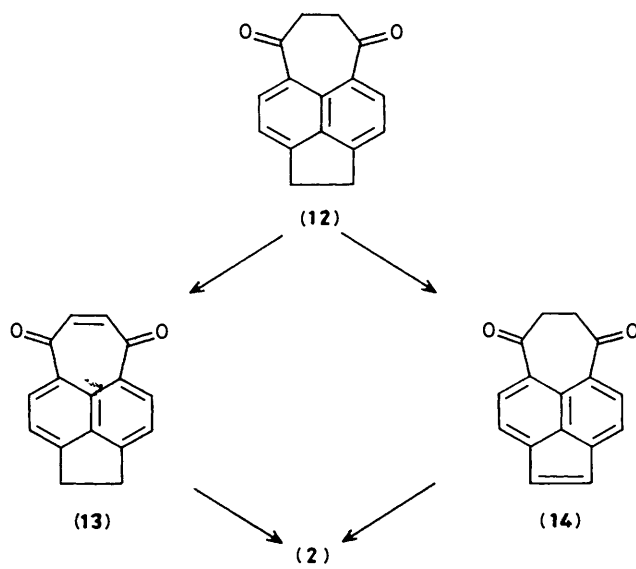
Scheme 4.

Scheme 5.

DMSO at 40 °C afforded the 1,2-dihydroquinone (13) (66%). This method is more convenient and gives higher yields of product than that previously reported in which the dione (12) was treated by NBS in carbon tetrachloride and DBU

successively.[1] The quinone (2) was also obtained in good yield by similar treatment of compound (14) with NBS in wet DMSO.

Experimental

M.p.s were determined with a Mitamura air-bath apparatus and are not corrected. ^1H and ^{13}C N.m.r. spectra (SiMe$_4$ as internal standard) were determined with a JEOL-PMX-60si and/or a JEOL-JNM-FX-90Q spectrometer. I.r. spectra were determined with a JASCO A-2 instrument, electronic spectra (u.v. and vis.) with a Hitachi 340 spectrophotometer, and mass spectra with a JEOL-01SG-2 spectrometer. Unless otherwise stated the spectra were taken in the following solvents/media: u.v. and vis., CHCl$_3$; i.r., KBr; ^1H and ^{13}C n.m.r., 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 t.l.c. using Kieselgel 60G (Merck). Preparative column chromatography was carried out using Kieselgel 60 (Merck 70—230 mesh). Ether refers to diethyl ether.

Cyclic Voltammetry.—All measurements were performed at room temperature between 10—22 °C in dry dimethylformamide with 0.1M tetrabutylammonium perchlorate as supporting electrolyte. Substrates were present at 0.5mM, and the reduction potentials were determined under nitrogen atmosphere in a standard three-electrode cell equipped with a silver–silver chloride electrode as reference. Voltammograms were recorded at a scan rate of 100 mV s^{-1}.

Cyclohepta[fg]naphth[2,3-a]acenaphthylene-5,12-dione (Naphth[2,3-h]acepleiadylene-5,12-dione) (4).—A mixture of the quinone (2) (525 mg, 2.26 mmol), 1,2-bis(dibromomethyl)-benzene (737 mg, 1.74 mmol), sodium iodide (1.713 g, 11.4 mmol), and DMF (8.3 ml) was stirred for 2 h at 60 °C under nitrogen gas. The reaction mixture was poured into 5% aqueous sodium hydrogen sulphite (100 ml) and the brown precipitate was collected and dried. When chromatographed on a silica gel column with benzene as eluant it afforded the *title compound* (4) (59 mg, 8.1%) as orange-yellow needles, m.p. 251.0—252.0 °C (decomp.) (from benzene–hexane); *m/z* (75 eV) 334 ($M^{+\bullet}$ + 2, 1.9%), 333 ($M^{+\bullet}$ + 1, 8.2), 332 ($M^{+\bullet}$, 29), 304 ($M^{+\bullet}$ − CO, 100), and 276 ($M^{+\bullet}$ − 2CO, 59) (Found: C, 85.95; H, 4.2. $C_{24}H_{12}O_2$ requires C, 86.21; H, 4.22%); $\lambda_{max.}$ 303.5 (log ε 4.42), 361.5 (4.08), and 399.5 nm (3.96); $\nu_{max.}$(KBr) 1 656 cm^{-1}; δ 7.10 (2 H, s, 1- and 2-H), 7.46—7.66 (2 H, m, 7- and 10-H), 7.74 (2 H, d, *J* 7.3 Hz, 3- and 14-H), 7.90—8.00 (2 H, m, 8- and 9-H), 8.44 (2 H, d, *J* 7.3 Hz, 4- and 13-H), and 8.46 (2 H, s, 6- and 11-H).

1,2-Dihydrocyclohepta[fg]naphth[2,3-a]acenaphthylene-5,12-dione (1,2-Dihydronaphth[2,3-h]acepleiadylene-5,12-dione) (10).—(*a*) A mixture of compound (4) (197 mg, 0.589 mmol), 5% Pd/C (500 mg), and benzene (50 ml) was shaken under hydrogen gas for 24 h. The catalyst was filtrated off and the solvent was removed. The residue was chromatographed on a silica gel column with dichloromethane as eluant to give the *title compound* (10) (137 mg, 69.2%) as yellow needles, m.p. 251.0—251.5 °C (from benzene); *m/z* (75 eV) 335 ($M^{+\bullet}$ + 1, 18.2%), 334 ($M^{+\bullet}$, 67.8), 306 ($M^{+\bullet}$ − CO, 100), and 276 ($M^{+\bullet}$ − 2CO − H$_2$, 98.8) (Found: C, 85.95; H, 4.2. $C_{24}H_{12}O_2$ requires C, 86.21; H, 4.22%); $\lambda_{max.}$ 252 (log ε 4.78), 296sh (4.18), 384 (4.24), and 398 nm (4.23); $\nu_{max.}$ 1 652 cm^{-1}; δ 3.49 (4 H, s, 1- and 2-H), 7.51 (2 H, d, *J* 7.6 Hz, 13- and 14-H), 7.55—7.67 (2 H, m, 7- and 10-H), 7.95—8.06 (2 H, m, 8- and 9-H), 8.49 (2 H, s, 6- and 11-H), and 8.52 (2 H, d, *J* 7.6 Hz, 4- and 13-H).

(*b*) A mixture of compound (13) (109 mg, 0.466 mmol) and 1,2-bis(dibromomethyl)benzene (218 mg, 0.516 mmol), sodium iodide (351 mg, 2.34 mmol), and DMF (3 ml) was stirred at

60 °C for 2 h under nitrogen gas. The reaction mixture was poured into 5% aqueous sodium hydrogen sulphite (50 ml) and the deposits were filtered off and dissolved in dichloromethane. The dichloromethane solution was dried ($MgSO_4$) and evaporated. The brown residue was purified through a silica gel column with benzene as eluant to give the *title compound* (10) (59 mg, 34.6%) as yellow needles, m.p. 249.5—250 °C (from benzene).

1,2,5,12-*Tetrahydrocyclohepta*[fg]*naphth*[2,3-a]*acenaphthyl-ene-5,12-diol* (1,2,5,12-*Tetrahydronaphth*[2,3-h]*acepleiadylene-5,12-diol*) (11).—A solution of sodium borohydride (41 mg, 1.09 mmol) in methanol (5 ml) was added dropwise to a solution of the compound (10) (94 mg, 0.279 mmol) in benzene (60 ml), and the mixture was stirred for 1.5 h. Work-up afforded the diol (11) (64 mg, 67.5%) as colourless needles, m.p. 191—205 °C (from benzene); m/z (75 eV) 338 ($M^{+\cdot}$, 4.1%), 320 ($M^{+\cdot}$ − H_2O, 47.3), and 302 ($M^{+\cdot}$ − $2H_2O$, 7.1) (Found: C, 85.2; H, 5.25. $C_{24}H_{18}O_2$ requires C, 85.18; H, 5.36%); $\lambda_{max.}$ 230 (log ε 5.21), 294 (4.11), 305 (4.14), and 328 nm (3.94); $v_{max.}$ 3 308 cm^{-1}; δ 3.36 (4 H, s, 1- and 2-H), 5.11 (2 H, s, OH, exchangeable with D_2O), 6.04 (2 H, s, 5- and 12-H), 7.33—7.94 (8 H, m, 3-, 4-, 7-, 8-, 9-, 10-, 13-, and 14-H), and 7.98 (2 H, s, 6- and 11-H).

Attempted Synthesis of Cyclohepta[fg]*naphth*[2,3-a]-*acenaphthylene* (*Naphth*[2,3-h]*acepleiadylene*) (7).—(*a*) Concentrated hydrogen chloride (85 mg) was added dropwise at 26 °C to a stirred mixture of the diol (11) (52 mg, 0.15 mmol), *N*-phenylmaleimide (26 mg, 0.15 mmol), and dioxane (10 ml), and the reaction mixture was stirred for a further 8 min under nitrogen. It was then poured into 5% aqueous sodium hydrogen carbonate and the precipitate was collected and chromatographed on a silica gel column with benzene as eluant to give yellow crystals (11 mg), m.p. 310 °C (decomp.) (from benzene–hexane); m/z (75 eV) 606 ($M^{+\cdot}$, very weak) and 303 ($M^{+\cdot}$ + 2, 100%); $\lambda_{max.}$ 242, 288sh, 322, 335, 352, and 370 nm; $v_{max.}$ 1 100—1 200 cm^{-1}; δ 5.43 (1 H, s), 6.46 (1 H, s), 6.69 (1 H, s), and 7.19—7.61 (8 H, m); successive elution with dichloromethane as eluant gave pale yellow crystals (5 mg), m.p. 320 °C (decomp.) (from benzene–chloroform); m/z (75 eV) 320 ($M^{+\cdot}$, 17.1%) and 302 ($M^{+\cdot}$ − H_2O, 100); $\lambda_{max.}$ 244, 300, 321, 335, and 368 nm; $v_{max.}$ 3 400br, 1 080—1 200, and 720—820 cm^{-1}; δ 5.43 (2 H, s), 6.46 (2 H, s), 6.71 (2 H, s), and 7.06—7.53 (12 H, m).

(*b*) Four small drops of concentrated hydrogen chloride were added to a stirred mixture of the dione (11) (87 mg, 0.257 mmol) and dioxane (20 ml), at 27 °C. After 8 min the reaction was worked up as for that described in (*a*) to give 'the dimer' (11 mg) and 'the monohydric alcohol' (7 mg).

Cyclohept[fg]*acenaphthene-5,8-dione* (13).—A mixture of the diketone (12) (235 mg, 0.994 mmol), NBS (225 mg, 1.27 mmol), DMSO (3.2 ml), and water (89 mg, 4.94 mmol) was warmed for 2 h at 40 °C under nitrogen gas. Dichloromethane (20 ml) was added to this reaction mixture and the organic layer was washed with water, 5% aqueous sodium hydrogen carbonate, and saturated brine, and dried ($MgSO_4$). After removal of the dichloromethane the residue was chromatographed on a silica gel column with dichloromethane as eluant to give the title compound (13) (816 mg, 66.3%) as yellow needles, m.p. 165—168 °C (from benzene–hexane) (lit.,[1] 168—170 °C).

Cyclohept[fg]*acenaphthylene-5,8-dione* (*Acepleiadylene-5,8-dione*) (2).—A mixture of the diketone (14) (1.345 g, 5.75 mmol), NBS (1.226 g, 6.90 mmol), DMSO (17.4 ml), and water (376 mg) was warmed for 3 h at 40 °C under nitrogen gas. Dichloromethane (100 ml) was added to this reaction mixture and the organic layer was washed with water, 5% aqueous sodium hydrogen carbonate, and saturated brine, and dried ($MgSO_4$). After removal of the dichloromethane the residue was chromatographed on a silica gel column with dichloromethane as eluant to give the title compound (2) (839 mg, 62.8%) as purple needles, m.p. 186 °C (decomp.) (from benzene–hexane) [lit.,[1] 186 °C (decomp.)].

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