The Synthesis and Properties of Cyclohepta[*a*]phenalene-6,10-, -6,12-, -7,10-, and -7,12-diones and Their Dicationic and Dianionic Species

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The titled new non linear non benzenoid quinone compounds of cyclohepta[*a*]phenalene-6,10-, -6,12-, -7,10-, and -7,12-diones have been synthesized. The dicationic species formed from quinones by protonation in a strong acid were revealed as diatropic compounds instead of a 16-pi electron system by an examination of spectral measurements, such as the ^{1}H NMR and UV spectra. The stability of these quinones, dicationic species, and dianonic species electrically derived from quinones depends upon the positions of carbonyl groups with both steric and electronic factors.

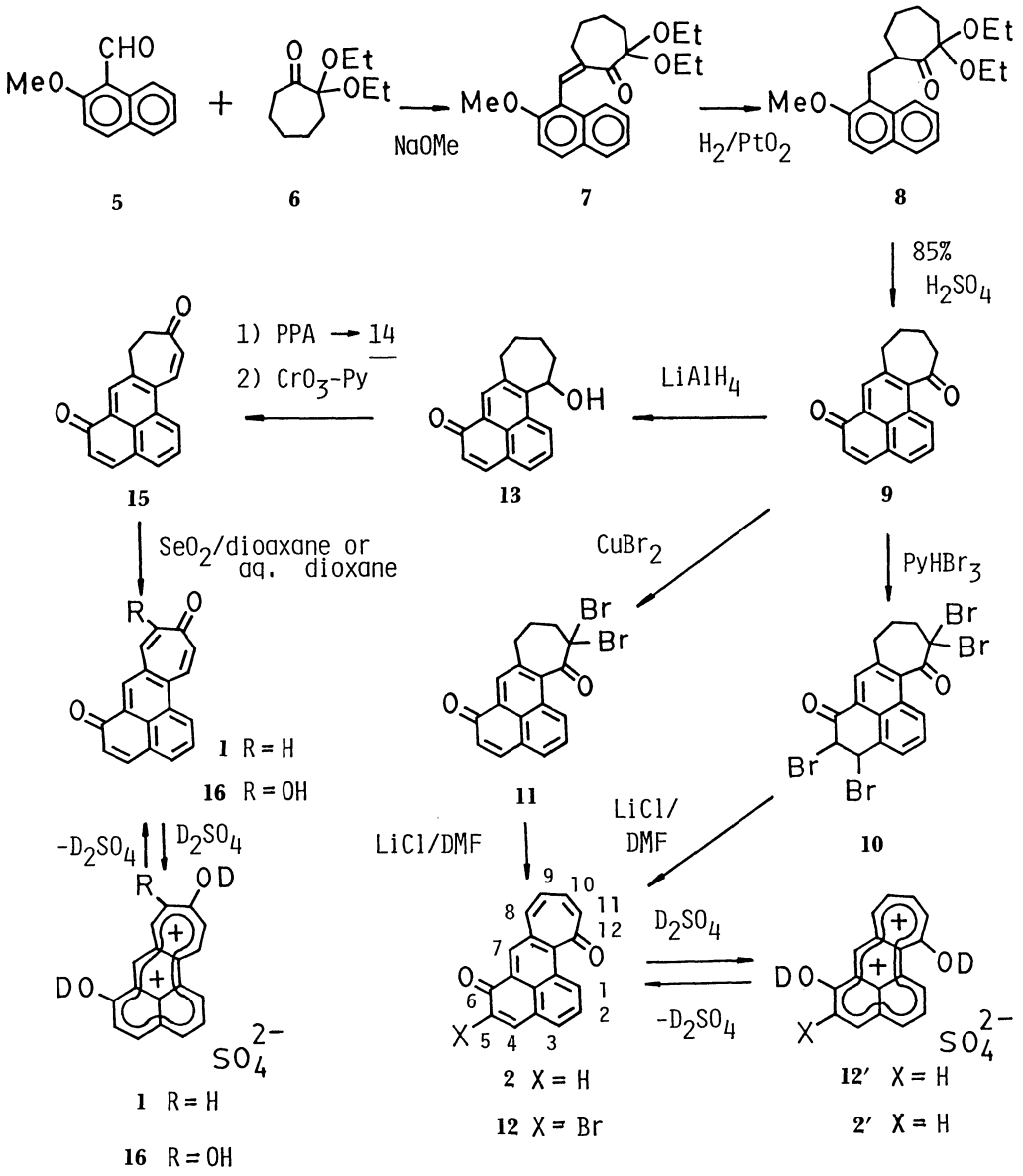
Much attention has recently been focused on quinones and quinodimethane compounds from the viewpoint of advanced materials as organic superconductors by forming CT complexes.[1] Most of these quinones, however, are linear and benzenoid compounds.[2] According to the Trost's definition of quinones,[3] poly condensed nonbenzenoid conjugated dicarbonyl compounds are also included in the quinone category. However, little is known about polycyclic nonbenzenoid quinones containing more than four rings.[4] It is thus of interest to investigate the properties of non linear four-ring-fused quinones of cyclohepta[*a*]phenalenediones as well as their dicationic species expected to be formed by protonation in strong acidic media,[5] with two electrons less than that of the corresponding neutral species of cyclohepta[*a*]-phenalene. Furthermore, to examine the influence of steric and electronic factors of the carbonyl groups on the stability of the quinones and their dicationic species, which is correlated with the planarity of the molecule, quinones having carbonyl groups at the 7- and 12-positions and at positions other than the 7- and 12-positions were required. Because the distances between the peri positions of the 6- and 7-, 7- and 8-positions, as well as the 1- and 12-positions are very close, the proton and the carbonyl group located at these positions are repulsive, causing destabilization by a distortion of the molecule. Furthermore, an electrical reduction of the quinones, measured by cyclic voltammetry, would also be indicative of the stability of their dianionic species.

Herein we wish to report the synthesis and properties of four positional isomers of the quinones of cyclohepta[*a*]phenalene-6,10- (**1**), 6-,12- (**2**)[6], -7,10- (**3**), and -7,12-diones (**4**), their dicationic species **1′**, **2′**, **3′**, and **4′** and dianionic species **1″**, **2″**, **3″**, and **4″**.

Results and Discussion

Synthesis. Syntheses of the four title quinones were successfully carried out as follows, and are illustrated in Schemes 1 and 2. First, the synthesis of a quinone having one carbonyl group at the 6-position, cyclohepta[*a*]phenalene-6,12-dione (**2**), is described. The condensation of 2,2-diethoxycycloheptanone (**6**)[7] with 2-methoxy-1-naphthaldehyde (**5**) in the presence of sodium methoxide in refluxing dry tetrahydrofuran (THF) for 3.5 h gave ketone **7** in 65% yield. When **7** was treated with 85% sulfuric acid, the expected compound **9** was obtained, though in very low yield. It might be considered that one of the isomers (*E*-isomer) around the double bond of the enone moiety does not cyclize, and decreases the yield. This double bond was therefore saturated by catalytic hydrogenation. The reaction of **7** in ethyl acetate (AcOEt) in the presence of PtO_2 under a hydrogen atmosphere at 2.7 atm gave saturated ketone **8** almost quantitatively. Cyclodehydration of **8** with about 10-times excess in weight of 85% sulfuric acid a 45 °C for 30 min successfully furnished phenalenone derivative **9** in 65% yield. To introduce two double bonds to the seven-membered ring for full conjugation, α,α-dibromination and didehydrobromination reactions were carried out. Bromination of **9** with pyridinium tribromide always gave 4,5,11,11-tetrabromo compound **10** as the main product along with a small amount of 4,5,11,-tribromo, 11,11-dibromo compounds. Because 5-bromo derivative **12** is sometime predominant in the following dehydrobromination reaction, an alternative method for bromination was employed. Bromination of **9** with $CuBr_2$[8] in refluxing chloroform for 16 h gave only 11,11-dibromide **11** in 75% yield. Dehydrobromination of **11** with LiCl[9] in DMF at 140 °C for 40 min gave **2** in 95% yield. As mentioned above, 5-bromo derivative **12** was prepared under similar conditions as mentioned above from dione **9** via the tetrabromo compound **10** in 79% yield.

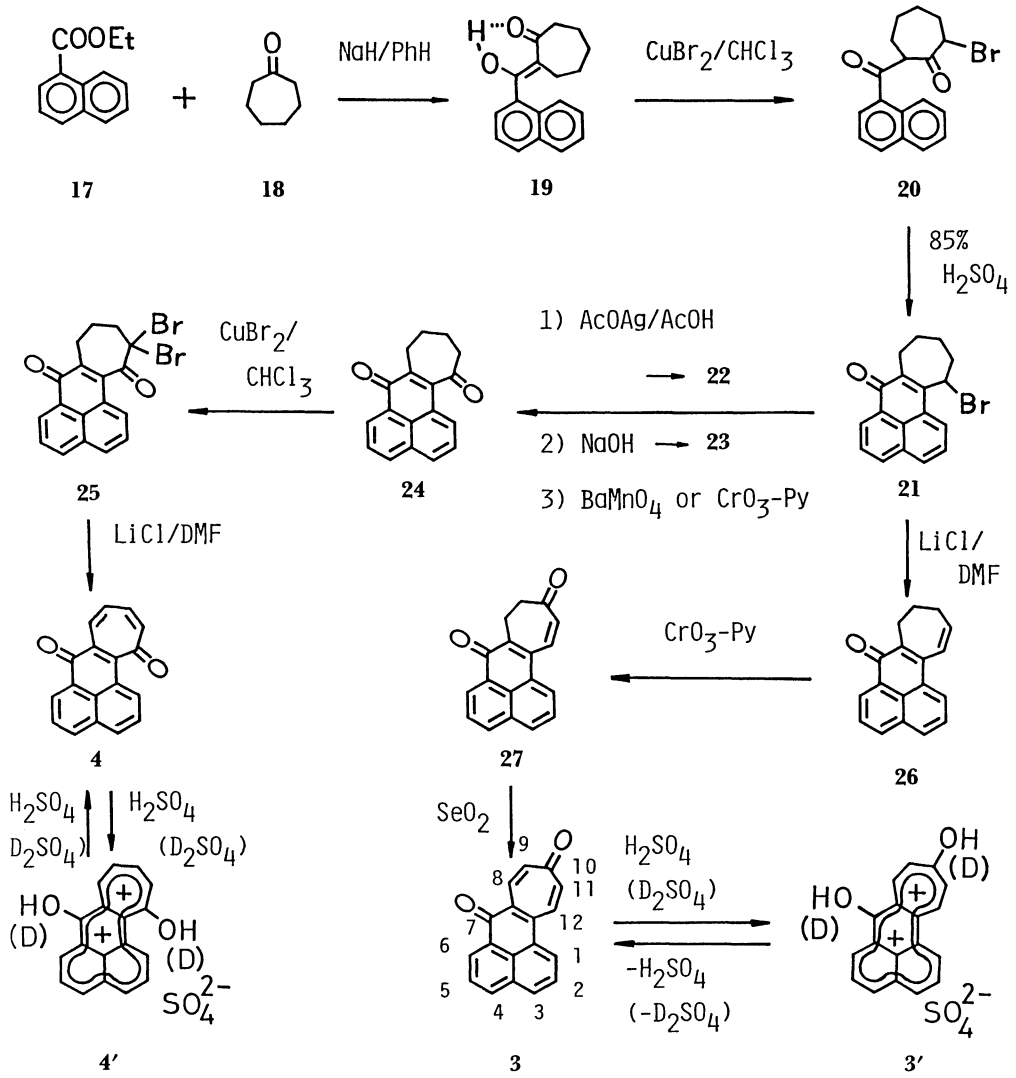
The other isomer, cyclohepta[*a*]phenalene-6,10-dione (**1**), was synthesized by using intermediate **9**. The



Scheme 1.

introduction of a carbonyl group at the 10-position was achieved as follows. The reduction of the carbonyl group at the 12-position of **9** with $LiAlH_4$ gave alcohol **13** in 67% yield. The reaction of **13** with an excess amount of polyphosphoric acid (PPA) at 100 °C for 1 h gave a dehydrated compound **14** in 76% yield. The allylic oxidation of **14** with pyridinium dichromate at room temperature (r. t.) overnight gave dione **15** in 34% yield. Dehydrogenation of **15** was performed by the use of SeO_2 in refluxing dioxane for 3 h to give **1** in 78% yield. When this dehydrogenation was performed[10] by using aqueous dioxane as a solvent, 9-hydroxycyclohepta[*a*]phenalene-6,10-dione (**16**) was obtained in 13% yield.

Two other quinones having one carbonyl group at the 7-position were synthesized as follows. To introduce one carbonyl group at the 7-position, ethyl 1-naphthoate (**17**) was chosen as the starting material. The reaction of **17** with cycloheptanone **18** in the presence of 1.5 equiv of sodium hydride in refluxing dry benzene for 2 h gave dione **19** in 58% yield. The bromination of **19** by using $CuBr_2$ in refluxing chloroform for 5 h furnished **20** exclusively as a colorless oil in 63% yield. The reason for this regioselective bromination is considered to be as follows. Since the ^1H NMR spectrum of **19** showed a signal for an enol proton resonating at δ=16.6, indicating the existence of a table enol form, shown in Scheme 1, a second enolization was induced at the 7-position of the cycloheptanone moiety. Thus, the more reactive 7-position of the cycloheptenone moiety was brominated to give **20**. The cyclodehydration of



Scheme 2.

20 by 90% sulfuric acid at 40—50 °C for 30 min gave a bromo-substituted phenalenone derivative **21** in 81% yield. The reaction of **21** with 1.5 equiv of silver acetate in a solution of acetic acid and acetic anhydride at 110 °C for 24 h gave acetate **22** as a yellow oil in 85% yield. The reaction of **22** with sodium hydroxide in aqueous THF at 50—60 °C for 24 h gave alcohol **23** in 96% yield. Treatment of **23** with pyridinium dichromate[11] of $BaMnO_4$[12] at r. t. for 1 d furnished dione **24** and **23** in 75 and 97% yield, respectively. The bromination of **24** with $CuBr_2$ in refluxing $CHCl_3$ for 1 d gave **25** in 60% yield. The dehydrobromination of **25** was effected by the reaction of LiCl in DMF at 100—110 °C for 3 h to give the desired quinone **4** in over 90% yield.

The synthesis of another isomer of cyclohepta[*a*]-phenalene-7,10-dione (**3**) was started from **21** as follows. The reaction of **21** with LiCl in DMF at 110 °C for 40 min gave a dehydrobrominated compound **26** in 81% yield. An allylic oxidation of **26** with pyridinium dichromate at 50—60 °C for 7 h gave **27** in 16% yield, along with 56% of recovered **26**. The dehydrogenation of **27** was accomplished by using selenium dioxide in refluxing dioxane for 1 h to give cyclohepta[*a*]phenalene-7,10-dione (**3**) in 42% yield.

NMR Spectra of Quinones and Their Dicationic Species. Generally, in the ^1H NMR spectra of four quinones (**1**, **2**, **3**, and **4**) in $CDCl_3$, signals for the protons on the tropone moiety were observed at around δ=7.00,[13] and those of the phenalenone moiety in a range δ=7.10—8.70.[14] Furthermore, in the IR spectra the absorption bands of the carbonyl groups (ν 1595—1585 for tropone moiety and ν 1645—1625 for phenalenone moiety) are similar to those of the corresponding tropone (ν 1582)[15] and phenalenone (ν 1635),[16] respectively. This indicates that these quinones mainly comprise of tropone and phenalenone moieties, though the contribution of the

dipolar structure of quinone was suggested by the electronic absorption spectroscopic measurements. The differences of the ^{1}H-chemical shift averages in $CDCl_3$ from those in D_2SO_4 were evaluated by two methods. In the first one, a comparison was made by using the ^{1}H-chemical shift averages of all protons. In the other one, a comparison was made by using those of selected protons in which protons adjacent to the carbonyl groups were excluded in order to avoid any local anisotropy effects of the carbonyl groups. There was little difference in cases. Further, since these quinones are isomers of the carbonyl groups in the same ring system, the degree of diatropicity of the dicationic species might be estimated by simply making a comparison of the ^{1}H-chemical shifts averages. Since larger values of the ^{1}H-chemical shifts averages of the quinones indicate a greater contribution of the dicationic structures, the order of the stability of the quinones was known to be **3**, **1**, **4**, **2** by a comparison of their ^{1}H-chemical shift averages in $CDCl_3$ (Table 1). Although Wilcox et al. have reported[4a] that the protonated species of cycloocta-[*def*]biphenylene-1,4-dione does not show any significant down-field shift in the ^{1}H NMR spectrum due to a distortion of the molecule as a tab-shaped structure, the ^{1}H NMR spectra of the dicationic species formed from the quinones by protonation in a strong acidic media, such as D_2SO_4 showed large down-field shifts, as listed in Table 1 and can be seen in Figs. 1 and 2, chosen as typical examples. The ^{1}H-chemical shifts of the hydroxytropilium cation (δ=8.50),[13] hydroxyphenalenium cation (δ=8.66),[14] and 6-hydroxy-12-oxo-8,9,10,11-tetrahydrocyclohepta[*a*]phenalenium cation (**9′**) (δ=8.63) formed by protonation of tropone, phenalenone and **9** in strong acid, respectively, are higher than those of the dicationic species: **1′**, **2′**, **3′**, and **4′**. The ^{1}H-chemical shift differences of the dicationic species from the quinones (1.27—1.53 ppm) are larger than those of the evaluated value ($\Delta\delta$=10.6×

Table 1. 90 MHz ^{1}H NMR Chemical Shifts (δ) and the Chemical Shifts Averages of Quinones **1**—**4** (in $CDCl_3$) and Dicationic Species **1′**—**4′** (in D_2SO_4)

H-	**1**	**1′**	**2**	**2′**	**3**	**3′**	**4**	**4′**
1	8.73	10.27	8.67	10.16	8.10	9.17	8.63	10.09
2	7.82	8.52	7.67	8.42	7.68	8.67	7.71	9.06
3	7.82	8.93	7.54	8.90	8.38	9.49	8.18	9.68
4	7.82	9.26	7.70	9.34	8.25	9.69	7.98	8.94
5	6.77	7.84	6.65	7.85	7.80	8.67	7.53	8.52
6	—	—	—	—	8.67	9.79	8.43	9.50
7	8.80	10.21	8.62	10.25	—	—	—	—
8	7.82	9.52	7.48	9.36	8.15	10.10	8.13	9.88
9	7.03	8.38	6.92	8.62	7.17	8.37	6.89	8.52
10	—	—	6.92	8.90	—	—	6.89	8.52
11	7.17	8.52	6.92	8.70	7.02	8.40	6.89	8.52
12	8.68	9.71	—	—	8.44	10.15	—	—
$\delta_{average}$	7.85	9.12	7.51	9.05	7.97	9.24	7.72	9.12

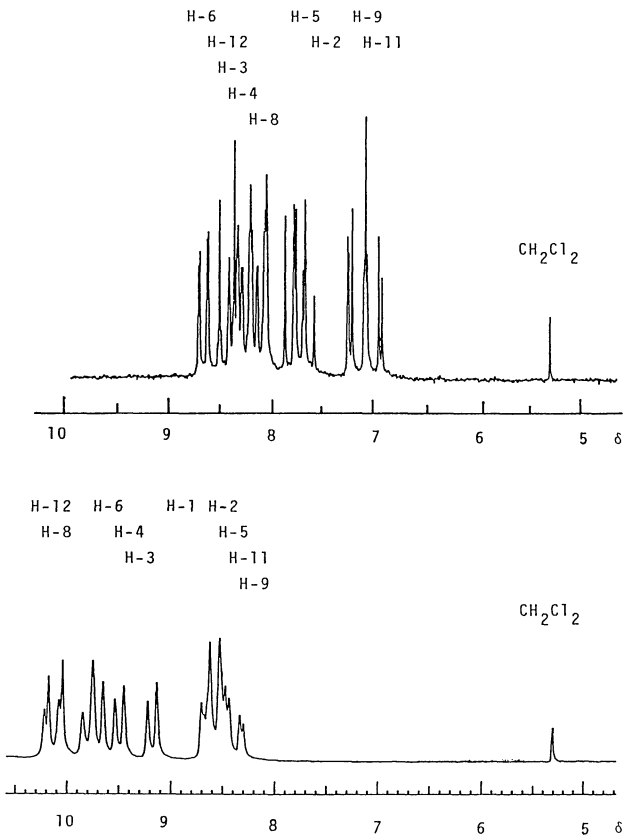


Fig. 1. ^{1}H NMR spectra of **3** in $CDCl_3$ (above) and its dication **3′** in D_2SO_4 (below) at 90 MHz.

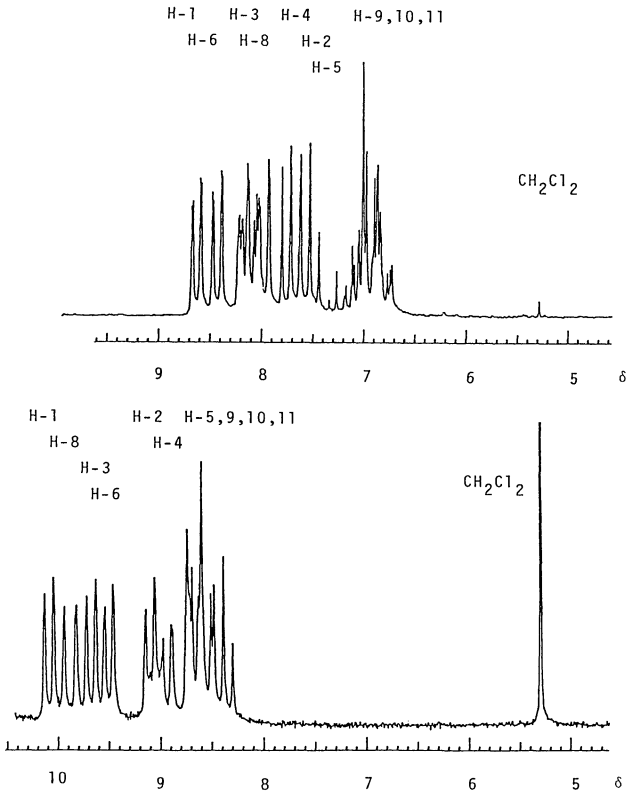


Fig. 2. ^{1}H NMR spectra of **4** in $CDCl_3$ (above) and its dication **4′** in D_2SO_4 (below) at 90 MHz.

2/18=1.18 ppm).[17] In consideration of the above-mentioned results, the larger down-field shifts of these dicationic species are only explained in terms of an induced diatropic ring current with the planarity of the molecule, excluding the structure in which two positive charges are localized at the carbonyl carbons. Based on the ^{1}H-chemical shift averages of dicationic species, the diatropicity falls off in the sequence **3′>1′>4′>2′**, similar to the result obtained for the quinones. The reason for this order might be that a steric repulsion of the carbonyl group at the 12-position and the proton on the 1-position prevents the planarity of the molecules in the formation of dicationic species. This is also supported by the electrochemical results shown later. In the ^{13}C NMR spectra, the chemical shifts of the carbonyl carbons at the 12-position in both **2** and **4** are similar and fairly lower than those of the 10-position in **1** and **3**. Since the positive charge is more localized at the carbonyl carbon in the distorted molecule than that in the planar one,[18] in the ^{13}C NMR spectra the chemical shifts of the carbonyl carbons in the distorted molecules are observed at a lower field than those in the planar molecules. The order of the ^{13}C NMR chemical shifts of both carbonyl carbons in quinones is thus **3**, **1**, **4**, **2** from a high field to a low field, indicating the order of planarity. It is also consistent with the above result obtained by a comparison of the ^{1}H NMR spectra of quinones **1**, **2**, **3**, and **4**, suggesting that the steric repulsion between the carbonyl group at the 12-position and the proton on the 1-position distorts the seven-membered-ring of **2** and **4**. The ^{13}C NMR chemical shifts of the carbonyl carbons of the quinones in D_2SO_4, were observed at a higher field than those in $CDCl_3$ indicating the formation of a dicationic species. Although the ^{13}C NMR chemical shifts of the carbonyl carbons at each of the 12-, 10-, 6-, and 7-positions in the dications are similar, those of the 12- and 7-positions are higher than those of the 10-and 6-positions. The reason for the higher chemial shifts of the 7-positions than those of the 6-positions is conceivablly as follows. The carbonyl group at the 7-positions are forced to maintain coplanarity with the adjacent two rings by a condensation of the two rings through the carbonyl group at the 7-positions. However, no clear explanation could be given for the higher chemical shifts of the 12-positions than those of the 10-positions. The ^{1}H NMR chemical shifts of 5-bromo and 9-hydroxy derivatives of quinones **12** and **16** in $CDCl_3$ are observed at a lower field than those of **2**. Especially, in the 9-hydroxy derivative **16**, though the large ^{1}H–^{1}H coupling constant on the 11- and 12-positions (J=13.0 Hz) are similar to that of 4,5-benzotropone (J=12.8 Hz),[19] indicating a smaller contribution of tautomerization, the larger downfield shift indicates a greater contribution of the dipolar structure of the quinone compared to that of **2** by hydrogen bonding between the hydroxyl and carbonyl groups.[20] Since the ^{1}H NMR chemical shifts of the dicationic species, **12′** and **16′**, are similar to those of **2′**, only slight effects of the substituents on the diatropicity of the dicationic species were noticed. Moreover, the regeneration of the quinones by the addition of a large excess of water to a solution of the dicationic species in conc sulfuric acid indicates the stability of the dicationic species under NMR measurement conditions.

Electronic Absorption Spectra of Quinones and Dicationic Species. The electronic absorption spectra of **1**—**4** in CH_2Cl_2 and conc sulfuric acid are shown in

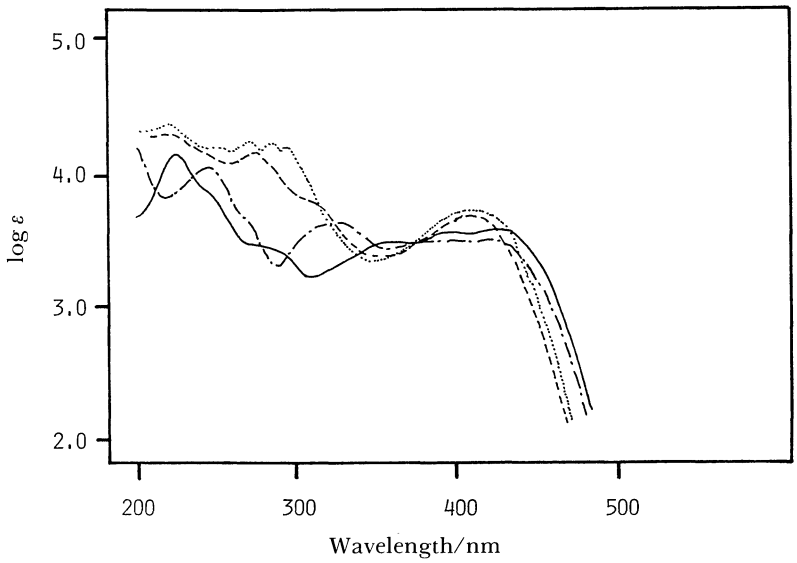


Fig. 3. Electronic absorption spectra of 6,10-dione **1** (·····), 6,12-dione **2** (-----), 7,10-dione **3** (-·-·-·-·), and 7,12-dione **4** (———) in CH_2Cl_2.

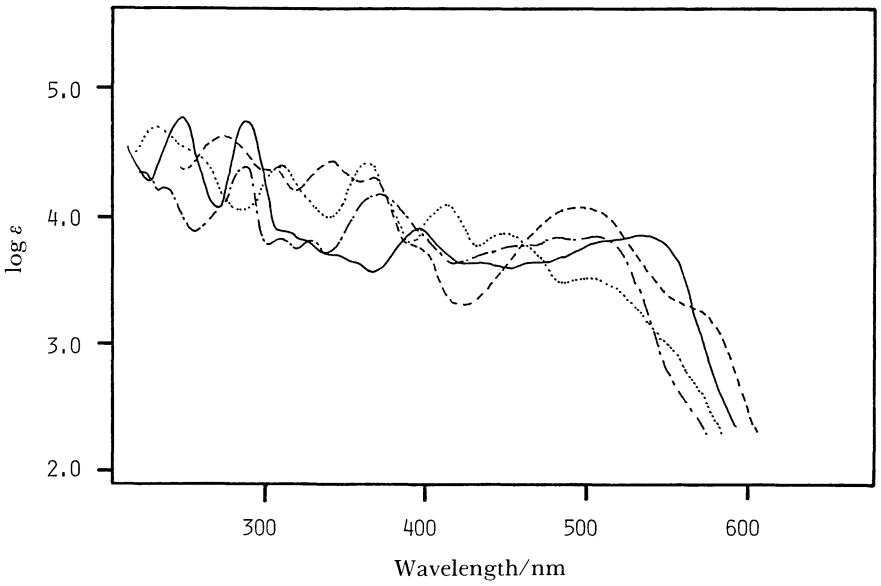


Fig. 4. Electronic absorption spectra of dication **1′** (·····), **2′** (-----), **3′** (-·-·-·-·), and **4′** (———) in conc. H_2SO_4.

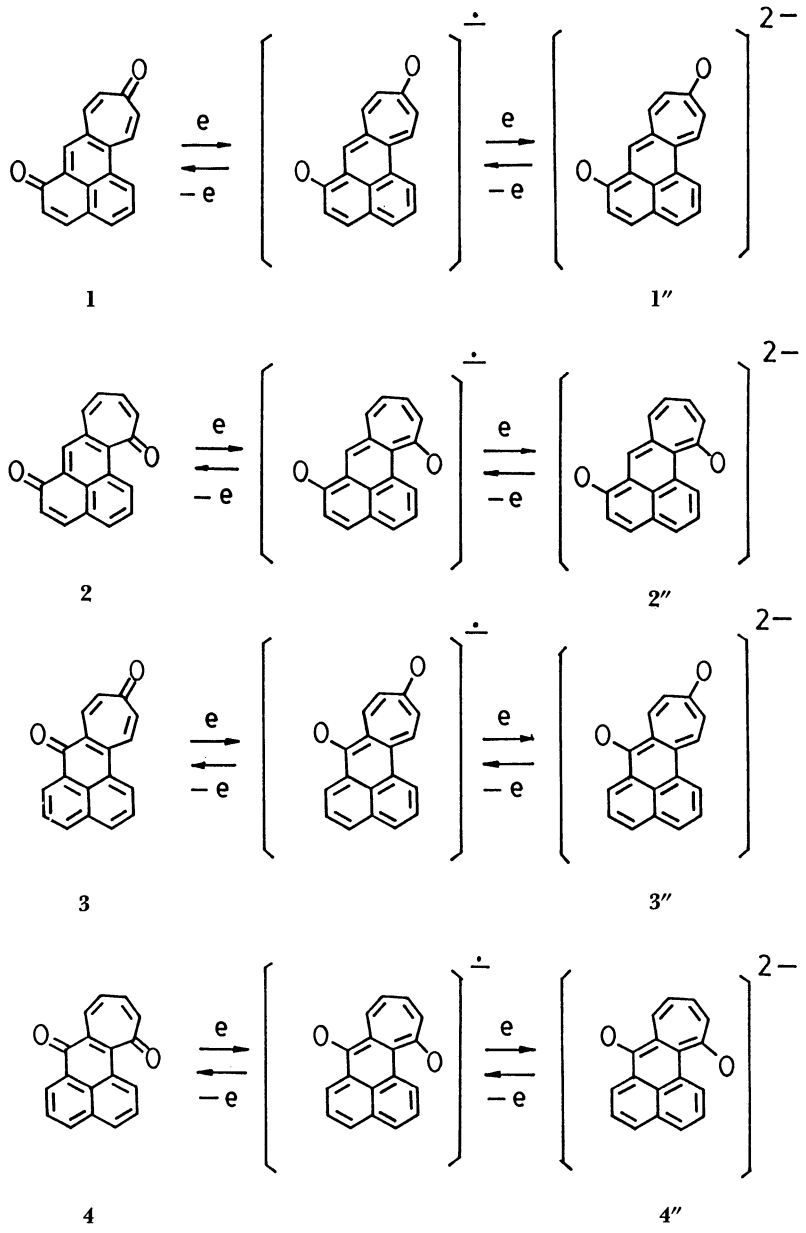
Figs. 3 and 4, respectively. Although they are essentially identical, the spectra of **1** and **2** are quite different from those of **3** and **4**. The longest absorption maxima of **3** and **4** are slightly larger (ca. 10 nm) than those of **1** and **2** in CH_2Cl_2. It should be noted that the longest absorption maxima of **1**—**4** in conc sulfuric acid are larger than those in CH_2Cl_2 by ca. 80—100 nm and that the pK_a values of diones **2** and **4**, chosen as examples, were estimated as −2.3 and −1.4, respectively, by a UV method[21a,21b] in sulfuric acid at various concentrations. Since there were no clear two isobestic points in the UV spectra of **2′** and **4′** protonation to two carbonyl groups does not take place stepwise but gradually. These results indicate the formation of a dicationic species and the existence of equilibrium between the quinone and their dicationic species.[4a,5,22] These pK_a values lie between those of tropone (pK_a=−0.86)[21a] and benzanthrone (pK_a=−3.2),[22] and higher than those of the such quinones as *p*-naphthoquinone, anthraquinone, perylenequinone (their pK_a values are in a range −5.5 to −8.5).[21] This indicates a greater stability of the dicationic species **2′** and **4′** than those of the dicationic species formed by protonation of the corresponding above-mentioned quinones. The longest absorption maxima of dications **2′** and **4′**, having a carbonyl group at the 12-position are larger than those of **1′** and **3′**, having a carbonyl group at the 10-position by ca. 10 nm. It is interesting that the absorption maxima are influenced by the positions of the carbonyl groups, especially at the phenalenone moiety. However, the red shifts of the absorption maxima in sulfuric acid are influenced by the position of the carbonyl group on the seven-membered ring. The influenece of other substituents, such as the 5-bromo and 9-hydroxyl groups, on the absorption maxima are only effected so as to cause a slight red shift.

Table 2. Cyclic Voltammetric Data for Quinones (in Volts vs. SCE)

Quinone	$^1E_{1/2}$	$^2E_{1/2}$	$^1E_{1/2}-^2E_{1/2}$
1	−0.77	−1.11	0.34
2	−0.83 (−1.05)[a]	−1.30 (−1.44)[a]	0.47
3	−0.77	−1.36	0.59
4	−0.81	−1.45	0.64
1,4-Naphthoquinone[23]	−0.58	−1.29	0.71
9,10-Anthraquinone[24]	−0.78	−1.45	0.67

a) The values are measured in acetonitrile.

Electrochemistry (CV Spectra) of Quinones 1—4. These compounds showed two reversible half-wave reduction potentials, indicating the formation of stable radical anions and dianions, as shown in Scheme 3. The first and second half-wave reduction potential values, $^1E_{1/2}$ and $^2E_{1/2}$ (V vs. SCE), of the quinones shown in Table 2 indicate the stability of the reduced radical anion and dianionic species of the quinones. The first reduction potential values of quinones **1** and **3** are similar and more positive than those of **2** and **4**. This can be explained by the higher planarity in the radical anions of **1** and **3** than that of **2** and **4**.[2] The order of the first reduction potentials correlated with the planarity (stability) is **3**=**1**>**4**>**2**, from positive to negative. This relation is similar to that obtained by a comparison of the ^{1}H NMR chemical shift averages described above. A comparison of the second reduction potentials and the



Scheme 3.

differences between $^1E_{1/2}$ and $^2E_{1/2}$ suggest the order of the stability of dianions formed from radical anions to be 6,10-(**1″**)>6,12-(**2″**)>7,10-(**3″**)>7,12-dione (**4″**). This order is different from that of dicationic species. The reason for the smaller stability of dianions having a carbonyl group at the 7-position, compared to those at the 6-position, is considered to be due to the electron-donating oxido-group at the 7-position, which destabilizes the heptafulvene moiety to a greater extent than that at the 6-position. On the other hand, the oxido group at the 12-position destabilizes the seven-membered ring to a greater extent than that at the 10-position due to a steric repulsion, as shown in Fig. 5.

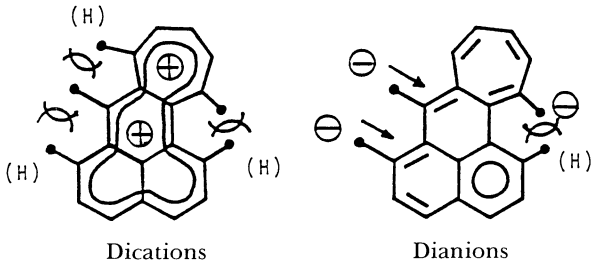


Fig. 5. The steric repulsion and electronic effects of carbonyl, hydroxyl and oxido groups.

Experimental

All melting points are uncorrected. The ^1H NMR spectra were taken on a Hitachi-60 (60 MHz) and on a JEOL-FX90 (90 MHz) spectrometers in chloroform-*d* (TMS as the internal standard) and deuteriosulfuric acid (dichloromethane, δ=5.30, as the internal standard). The ^{13}C NMR spectra were taken on a JEOL-FX90 (23 MHz) spectrometer, in the above two solvents. The mass spectra were taken on a JEOL-OISG-2 mass spectrometer. The UV and IR spectra were taken on a Hitachi EPS-3T spectrometer and on a IR-810 spectrometer, respectively. Cyclic voltammetric measurements were performed on a Yanaco P-1100. A standard three-electrode cell configuration was employed using a glassy carbon disk working electrode, at Pt wire auxiliary electrode, and a Ag wire as a Ag/Ag^+ quasireference electrode. The reference electrode was calibrated at the completion of each measurement to a saturated calomel electrode (SCE). Solvent and supporting electrode for electrochemistry were purified before use. Reduction potentials of quinones were measured by cyclic voltammetry using dimethyl sulfoxide containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) as solvent.

2,2-Diethoxycyloheptanone (6). A solution of 1,2-cycloheptanedione (30 g, 23.8 mmol), ethylorthoformate (105 g, 71.4 mmol) and a catalytic amount of *p*-toluenesulfonic acid (100 mg) in dry ethanol (300 mL) was stirred at room temperature for 12 h. The reaction mixture was poured into 15% sodium hydrogenbicarbonate solution and extracted with ether (200 mL×3). The combined organic layers were washed with water and brine twice each, and dried over anhyd $MgSO_4$. After removal of the solvent by evaporation in vacuo, the residue was distilled to give **6** (45.2 g, 95%): colorless oil, bp 110—115 °C (15 mmHg, 1 mmHg=133.322 Pa); IR (film) 2940s, 1723s, 1138m, 1120m, 997m cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.42 (q, *J*=6.0 Hz, 4H, $-OCH_2-$), 2.46 (bt, *J*=6.0 Hz, 2H, H-7), 1.62 (m, 8H), 1.15 (t, *J*=6.0 Hz, $-CH_3$). MS *m/z* 200 (M^+, 100%).

2,2-Diethoxy-7-[(2-methoxy-1-naphthyl)methylene]cycloheptanone (7). To a suspension of sodium methoxide (1.00 g, 18 mmol) in dry THF (70 mL) were added a solution of **5** (3.00 g, 16 mmol) and **6** (3.22 g, 16 mmol) in dry THF (30 mL). The mixture was refluxed for 3.5 h. After cooling, it was poured into dil HCl (200 mL) and extracted with benzene (50 mL×3). The combined organic layers were washed with brine three times and dried over anhyd $MgSO_4$. The solvent was removed in vacuo, and the residue was chromatographed on silica gel to give **7** (5.23 g, 80%) from benzene elution: pale yellow oil; IR (film) 3027w, 2980w, 1705s, 1258s, 1176m, 1125s, 957m, 803m, 743m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.48 (m, 7H), 3.95 (s, 3H), 3.74 (q, *J*=6.0 Hz, 4H), 2.45 (t, *J*=3.6 Hz, 2H), 1.83 (m, 6H), 1.44 (t, *J*=6.0 Hz, 6H); MS *m/z* 368 (M^+, 85%). Found: *m/z* 360.3856. Calcd for $C_{23}H_{20}O_2$: M, 360.3900.

2,2-Diethoxy-7-[(2-methoxy-1-naphthyl)methyl]cycloheptanone (8). To a solution of **7** (18.3 g, 49.7 mmol) in AcOEt (100 mL) was added a catalytic amount of PtO_2 (10 mg) and the mixture was hydrogenated under hydrogen atmosphere at 2.7 atm for 5 h. The reaction mixture was filtered and the solvent was removed by evaporation to give **8** in an almost quantitative yield: colorless oil; IR (film) 3030w, 2970m, 2930m, 1697s, 1612m, 1584s, 1482s, 1250vs, 951m, 858m, 801m, 743m cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.70 (m, 2H), 7.10 (m, 4H), 3.75 (s, 3H), 3.53 (q, *J*=6.0 Hz, 4H), 2.90—2.30 (m, 5H), 1.70 (m, 6H), 1.27 (t, *J*=6.0 Hz, 6H); MS *m/z* 370 (M^+, 78%). Found: *m/z* 362.4076. Calcd for $C_{23}H_{30}O_4$: M, 362.4048.

8,9,10,11-Tetrahydrocyclohepta[*a*]phenalene-6,12-dione (9). A mixture of 85% sulfuric acid (100 mL) and **8** (10 g) was heated with stirring at 45 °C for 30 min. After cooling, the reaction mixture was poured onto ice (ca. 1 Kg) and extracted with CH_2Cl_2 (200 mL×3). The combined organic layer was washed with water and brine twice each, and dried over anhyd $MgSO_4$. After removal of the solvent by evaporation, the residue was chromatographed on silica gel to give **9** (2.29 g, 32.5%) from CH_2Cl_2 elution: yellow needles, mp 174 °C (CH_2Cl_2–hexane); IR(KBr) 3020w, 2938m, 1678vs, 1626vs, 1580vs, 1400m, 1262s, 1120s, 838s, 762s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.45 (s, 1H), 8.13 (dd, *J*=1.8 & 8.1 Hz, 1H), 7.78 (d, *J*=9.9 Hz, 1H), 7.66 (m, 2H), 6.74 (d, *J*=9.9 Hz, 1H), 3.12 (t, *J*=6.4 Hz, 2H), 2.81 (t, *J*=6.4 Hz, 2H), 1.93 (m, 4H), (D_2SO_4–CH_2Cl_2) δ=9.35 (s, H-7), 9.02 (bd, 9.8 Hz, H-4), 8.82 (bd, *J*=5.4 Hz, H-1), 8.64 (m, H-3), 8.21 (bdt, *J*=5.4 & 5.0 Hz, H-2), 7.73 (bd, *J*=9.8 Hz, H-5), 3.30 (m, H-8), 2.1 (m, H-9 & -10) (signals for 11-position could not be observed by the substitution of deuterium); MS *m/z* 262 (M^+, 100%), 234 (90%); HRMS Found: 262.0956. Calcd for $C_{18}H_{14}O_2$: 262.0991. Found: C, 82.53; H, 5.42%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

Bromination of 9. A) To a solution of **9** (0.20 g, 0.76 mmol) in $CHCl_3$ was added $PyHBr_3$ (3.7 g, 2.28 mmol) and the mixture was stirred at 10 °C for 12 h. The solid of PyHBr was filtered off and the filtrate was washed with water twice and dried over anhyd $MgSO_4$. The solvent was removed by evaporation, and the residue was chromatographed on silica gel to give **10** (0.19 g, 23%) from benzene elution and **11** (0.51 g, 63%) from CH_2Cl_2 elution.

B) To a solution of **9** (2.30 g, 8.7 mmol) in chloroform (30 mL) was added $CuBr_2$ (11.66 g, 5.2 mmol) and the mixture was refluxed for 16 h. After cooling, the solid was filtered off and the filtrate was concentrated by evaporation. The residue was chromatographed on silica gel to give **11** (2.74 g, 75%).

10: Pale yellow plates, mp 158—167 °C (CH_2Cl_2–hexane); IR(KBr) 3030w, 2930w, 1700m, 1684vs, 1608w, 1500w, 1400m, 1222m, 1032m, 892m, 782m, 772m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.22 (s, 1H), 8.02 (dd, *J*=2.0 & 7.7 Hz, 1H), 7.71 (m, 2H), 5.89 (d, *J*=3.1 Hz, 1H), 5.51 (d, *J*=3.1 Hz, 1H), 2.92 (m, 4H), 2.14 (m, 2H); MS *m/z* 422, 420, 418 (M^+-Br_2, 10.2, 19.2, 10.2%), 233 (100%). Found: C, 37.85; H, 2.09%. Calcd for $C_{18}H_{12}O_2Br_4$: C, 37.28; H, 2.17%.

11: Yellow needles, mp 220—223 °C (CH_2Cl_2–hexane); IR(KBr) 3030w, 2951w, 1718s, 1650vs, 1588s, 1420m, 1120m, 912m, 839m, 792m, 771m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.18 (s, 1H), 7.82 (dd, *J*=1.2 & 7.6 Hz, 1H), 7.53 (d, *J*=9.8 Hz, 1H), 7.50 (m, 2H), 6.53 (d, *J*=9.8 Hz, 1H), 2.98 (mt, 2H), 2.69 (mt, 2H), 2.10 (m, 2H); MS *m/z* 422, 420, 418 (M^+, 9.4, 16.9, 9.4%), 233 (100%). Found: *m/z* 421.9077, 419.9102, 417.9172. Calcd for $C_{18}H_{12}Br_2O_2$: M, 421.9163, 419.9183, 417.9202.

Cyclohepta[*a*]phenalene-6,12-dione (2). A mixture of **11** (2.20 g, 5.24 mmol) and lithium chloride (2.40 g, 5.22 mmol) in dry DMF (21 mL) was heated at 100—110 °C with stirring for 3 h. After cooling, the mixture was poured onto ice-

water. The solid was filtered, and then dissolved in CH_2Cl_2. The resulting solution was dried over anhyd $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel to give **2** (1.12 g, 80%) from CH_2Cl_2 elution: yellow needles, mp 209—212 °C (CH_2Cl_2–hexane); IR(KBr) 3040w, 1640s, 1618s, 1580s, 840m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.67 (dd, J=8.5 & 1.5 Hz, 1H), 8.62 (s, 1H), 7.70 (d, J=9.8 Hz, 1H), 7.67 (m, 2H), 7.54 (m, 3H), 7.48 (d, J=10.0, 1H), 6.92 (m, 3H), 6.65 (d, J=9.8 Hz, 1H), (D_2SO_4) δ=10.25 (s, H-7), 10.16 (d, J=8.7 Hz, H-1), 9.36 (bd, J=10.1 Hz, H-8), 9.34 (bd, J=9.3 Hz, H-4), 8.90 (dd, J=10.9 & 8.8 Hz, H-10), 8.90 (d, J=7.8 Hz, H-3), 8.70 (d, J=10.9 Hz, H-11), 8.62 (dd, J=10.1 & 8.8 Hz, H-9), 8.42 (dd, J=8.7 & 7.8 Hz, H-2), 7.85 (d, J=9.3 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ=191.2, 184.7, 143.1, 137.1, 134.5, 133.0, 132.7, 131.9, 130.4, 128.8, 128.4, 127.6, 140.0, 133.4, 130.8, 130.6, 128.4, 128.0, (D_2SO_4–CH_2Cl_2) δ=182.7 (C–OH, C-12), 181.9 (C–OH, C-6), 165.2 (C-4), 154.9 (C-10), 152.5 (C-8), 148.0 (C-1), 146.9 (C-3), 141.8 (C-7), 138.5 (C-5), 132.7 (C-11), 131.4 (C-9), 120.1 (C-2), 140.2, 138.1, 129.7, 127.2, 126.4, 125.0 (quart. C); ES (EtOH) λ_{max} 416 (log ε=3.86), 319 (3.97), 268 nm (4.14), (CH_2Cl_2) λ_{max} 400 (log ε=4.00), 313 (4.09), 290 (4.26), (concd H_2SO_4) λ_{max} 560 sh (log ε=3.26), 490 (3.86), 340 nm (4.18), The pK_a value was measured by UV method. Acidity dependency of the molar extinction coefficients at 486.2 nm in sulfuric acid of various concentrations (97%, 85%, 75%, 62%, 54%, 48%, 45%, 38%, 35%, 28%, and 16%) was measured. The pK_a value was estimated by measuring the inflection point of the sigmoid curve obtained from the above method.[21a,21b]; MS m/z 258 (M^+, 69%), 230 (100%). Found: m/z 258.0672. Calcd for $C_{18}H_{10}O_2$: M, 258.0679. Found: C, 83.79; H, 3.82%, Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%.

5-Bromocyclohepta[*a*]phenalene-6,12-dione (12). 5-Bromo derivative **12** was prepared in 79% yield by the treatment of **10** with LiCl in the similar conditions as in the case of **2**: yellow needles, mp 225 °C (decomp, CH_2Cl_2–hexane); IR(KBr) 3020w, 1655s, 1610s, 1582m, 795m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.85 (s, H-7), 8.67 (dd, J=8.0 & 1.8 Hz, H-1), 8.27 (s, H-4), 7.78 (dd, J=8.0 & 1.8 Hz, H-3), 7.64 (t, J=8.0 Hz, H-2), 7.60 (dd, J=10.5 & 2.0 Hz, H-8), 6.98 (m, H-9, 10, 11), (D_2SO_4–CH_2Cl_2) δ=10.39 (s, H-7), 10.23 (d, J=8.6 Hz, H-1), 9.65 (s, H-4), 9.41 (d, J=10.0 Hz, H-8), 9.03 (md, H-3, H-10), 8.72 (m, H-9 & -11), 8.48 (dd, J=8.5 & 7.5 Hz, H-2); ^{13}C NMR spectrum of **12** colud not be measured owing to its low solubility in many solvents, (D_2SO_4–CH_2Cl_2) δ=182.9 (C–OH, C-12), 176.2 (C–OH, C-6), 165.9 (C-4), 155.6 (C-10), 152.5 (C-8), 150.3 (C-1), 139.0 (C-3), 138.9 (C-7), 132.1 (C-11), 131.9 (C-9), 114.8 (C-2), 140.3, 138.5, 130.0, 127.2, 126.3, 123.9 (quart. C); ES (CH_2Cl_2) λ_{max} 425 (log ε=4.08), 332 (4.08), 295 nm (4.28), (concd H_2SO_4) λ_{max} 588 (log ε=3.62), 504 (4.26), 392 (4.40), 376 (4.46), 350 (4.43), 312 (4.58), 265 nm (4.63); MS m/z 338, 336 (M^+, 91%, 100%), 310 (61%), 308 (53%). Found: C, 64.12; H, 2.70%. Calcd for $C_{18}H_9BrO_2$: C, 64.09; H, 2.67%.

12-Hydroxy-8,9,10,11-tetrahydrocyclohepta[*a*]phenalen-6-(12*H*)-one (13). To a suspension of $LiAlH_4$ (0.343 g, 90.4 mmol) in dry THF (100 mL) was dropwise added **9** (6.321 g, 24 mmol) in dry THF (50 mL) over a period of 1 h under ice cooling. The mixture was allowed to stand for 1 h at room temperature with stirring and then poured slowly into 3M HCl (150 mL, M=mol dm^{-3}). The solution was extracted with CH_2Cl_2 (50 mL×3). The combined organic layers were washed with water and brine twice each and dried over anhyd $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel to give **13** (4.213 g, 66.5%) from CH_2Cl_2–AcOEt (3:1) elution: Yellow needles, mp 171.5—172.5 °C (benzene); IR(KBr) 3380m, 2925m, 1635s, 1582s, 1566s, 1403m, 996m, 829s, 746m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.37 (t, =5.3 Hz, 1H), 7.94 (s, 1H), 7.47 (d, J=5.3 Hz, 1H), 7.33 (d, J=9.7 Hz, 1H), 6.24 (d, J=9.7 Hz, 1H), 6.00 (d, J=6.7 Hz, 1H), 3.77 (t, J=12.3 Hz, 1H), 3.72 (bs, 1H), 2.88 (dd, J=7.0 & 6.1 Hz, 1H), 2.35 (m, 2H), 2.04 (m, 1H), 1.76 (m, 2H), 1.45 (q, J=12.0 Hz, 1H); MS m/z 264 (M^+, 27%), 246 (100%). Found: m/z 264.1095. Calcd for $C_{18}H_{16}O_2$: M, 264.1138. Found: C, 81.76; H, 6.00%. Calcd for $C_{18}H_{16}O_2$: C, 81.81; H, 6.06%.

8,9-Dihydrocyclohepta[*a*]phenalen-6(10*H*)-one (14). A solution of **13** (1.136 g, 4.30 mmol) in PPA (12 mL) was heated at 100 °C for 1 h. The reaction mixture was poured onto ice-water (100 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined organic layer was washed with water, brine twice each and dried over anhyd $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on silica gel to give **14** (0.698 g, 66%) from benezene–CH_2Cl_2 (8:1) elution: yellow needles, mp 120 °C (CH_2Cl_2–hexane); IR(KBr) 3030w, 2840w, 1638vs, 1580vs, 1402m, 1360m, 1278s, 835s, 755m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.47 (s, 1H), 8.25 (dd, J=8.1 & 1.6 Hz, 1H), 7.72 (d, J=9.7 Hz, 1H), 7.60 (m, 2H), 7.29 (d, J=11.5 Hz, 1H), 6.70 (d, J=9.7 Hz, 1H), 6.54 (dt, 11.5 & 5.5 Hz, 1H), 2.90 (m, 2H), 2.25 (m, 4H); MS m/z 246 (M^+, 100%), 231 (69%). Found: C, 87.68; H, 6.10%. Calcd for $C_{18}H_{14}O$: C, 87.80; H, 5.69%.

8,9-Dihydrocyclohepta[*a*]phenalene-6,10-dione (15). To a pyridine solution of pyridinium dichromate prepared by the addition of CrO_3 (1.425 g, 14.2 mmol) to dry pyridine (15 mL) under ice cooling was added **14** (0.701 g, 2.85 mmol) in pyridine (25 mL) with stirring, and the stirring was continued for 22 h at room temperature. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (30 mL×3). The combined organic layers were washed with 3M HCl three times, water twice, brine twice and dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel to give **15** (0.140 g, 19%) from benzene–CH_2Cl_2 (2:3) elution: Yellow needles, mp 179—181 °C (CH_2Cl_2–hexane); IR(KBr) 3039w, 1660vs, 1650vs, 1578vs, 1402s, 1197s, 837s, 759s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.43 (s, 1H), 8.24 (dd, J=7.6 & 2.3 Hz, 1H), 7.90 (d, J=12.9 Hz, 1H), 7.68 (d, J=9.7 Hz, 1H), 7.62 (m, 1H), 6.68 (d, J=9.7 Hz, 1H), 6.55 (d, J=12.9 Hz, 1H), 3.21 (m, 2H), 2.85 (m, 2H); MS m/z 260 (M^+, 68%), 231 (100%). Found: C, 82.92; H, 4.55%. Calcd for $C_{18}H_{12}O_2$: C, 82.06; H, 4.65%.

Cyclohepta[*a*]phenalene-6,10-dione (1). A mixture of **15** (88 mg, 0.338 mmol) and SeO_2 (45 mg, 0.406 mmol) in dioxane (8 mL) was refluxed for 3.5 h. After cooling, the solid of Se was filtered off. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel to gave **1** (65 mg, 74.4%) from CH_2Cl_2 elution: Yellow needles, mp 231.5—233 °C (CH_2Cl_2–hexane); IR(KBr) 3038w, 1650s, 1630s, 1585vs, 1254m, 848m, 766m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.80 (s, 1H), 8.73 (dd, J=7.7 & 2.4 Hz, 1H), 8.64 (d, J=10.0 Hz, 1H), 7.82 (m, 4H), 7.17 (dd, J=10.0 & 3.0 Hz, 1H), 7.03 (dd, J=10.0 & 3.0 Hz, 1H), 6.77 (d, J=10.0 Hz, 1H), (D_2SO_4–CH_2Cl_2) δ=10.27 (bd, J=8.0 Hz, H-1), 10.21 (s, H-7), 9.71 (bd, J=12.5 Hz, H-12), 9.52 (bd, J=12.5 Hz, H-8), 9.26

(bd, J=7.8 Hz, H-4), 8.93 (bd, J=8.0 Hz, H-3), 8.52 (m, H-2 & -11), 8.38 (bd, J=12.5 Hz, H-9); ^{13}C NMR ($CDCl_3$) δ=187.4, 184.6, 142.8, 141.9, 138.5, 137.1, 135.4, 135.2, 132.6, 132.2, 132.1, 130.1, 129.0, 128.4, 128.37, 128.1, 127.2, (D_2SO_4–CH_2Cl_2) δ=184.8, 181.7, 148.4, 148.2, 148.0, 144.7, 138.3, 137.5, 134.4, 132.2, 130.9, 126.9, 126.1, 125.0, 120.6; ES (CH_2Cl_2) λ_{max} 412 (log ε=4.03), 308 (4.34), 295 (4.21), 248 nm (4.34), (concd H_2SO_4) λ_{max} 548sh (log ε=2.88), 518 (3.48) 448 (4.24), 398 (4.32), 338 (4.67), 270 nm (4.35); MS m/z 258 (M^+, 27%), 230 (100%). Found: m/z 258.0686. Calcd for $C_{18}H_{10}O_2$: M, 258.0681. Found: C, 83.75; H, 3.80%. Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%.

9-Hydroxycyclohepta[*a*]phenalene-6,12-dione (16). A mixture of **15** (90 mg, 0.34 mol) and SeO_2 (50 g, 0.56 mol) in aqueous dioxane (2:8) was refluxed for 3.5 h. Compound **16** was obtained by the similar work-up as in the case of **1** in 35% yield: Yellow needles, mp 240—265 °C (decomp, CH_2Cl_2–hexane); IR(KBr) 3298m, 1626s, 1586s, 1499m, 1458m, 1301s, 1223s, 836s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.97 (d, J=13.1 Hz, H-12), 8.84 (s, H-7), 8.73 (d, J=4.8 Hz, H-1), 7.91—7.81 (m, H-2, -3), 7.83 (d, J=9.9 Hz, H-4), 7.54 (d, J=13.1 Hz, H-11), 6.77 (d, J=9.9 Hz, H-5), (D_2SO_4–CH_2Cl_2) δ=10.34 (d, J=12.9 Hz, H-12), 10.18 (s, H-7), 9.69 (d, J=9.0 Hz, H-1), 9.35 (s, H-8), 9.29 (d, J= 8.6 Hz, H-4), 8.91 (d, J=7.7 Hz, H-3), 8.80 (d, J=12.9 Hz, H-11), 8.48 (t, J=7.5 Hz, H-2), 7.83 (d, J=8.6 Hz, H-5); ^{13}C NMR (D_2SO_4–CH_2Cl_2) δ=181.9 (C–OH, C-10), 172.3 (C–OH, C-6), 164.3 (C–OH, C-9), 155.6, 148.8, 145.9, 145.8, 141.0, 139.6, 137.4, 137.0, 132.2, 130.7, 130.4, 126.9, 126.6, 124.0, 120.3; ES (CH_2Cl_2) λ_{max} 430sh (log ε=3.30), 419 (3.46), 348 (3.78), 321 (4.03), 306 (4.10), 252 (3.97), 231 nm (4.16), (concd H_2SO_4) λ_{max} 499 (log ε=3.49), 399 (3.57), 338 (4.25), 286 (4.10), 270 (4.00), 214 nm (3.85); MS m/z 274 (M^+, 54%), 246 (100%). Found: C, 78.78; H, 3.68%. Calcd for $C_{18}H_{10}O_3$: C, 78.83; H, 3.65%.

2-(1-Naphthoyl)cycloheptan-1-one (19). To a suspension of sodium hydride (7.8 g, 160 mmol) in dry benzene (100 mL) was added a mixture of ethyl 1-naphthonate **17** (20 g, 110 mmol) and cycloheptanone **18** (12 g, 110 mmol) in dry benzene (30 mL) dropwise at room temperature with stirring for 30 min. The mixture was refluxed for 3.5 h. After cooling, it was poured into 3M hydrochloric acid (150 mL) and extracted with benzene (30 mL×2). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL×2), brine twice (20 mL), and dried over anhyd $MgSO_4$. After removal of the solvent by evaporation, the residue was chromatographed on silica gel to give **19** (17.0 g, 58%) from benzene elution: Colorless needles, mp 70—71 °C (CH_2Cl_2–hexane); IR(KBr) 3040w, 2920s, 1600s, 1560s, 770s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=16.56 (s, 1H), 7.86 (m, 3H), 7.44 (m, 4H), 2.69 (m, 2H), 2.13 (m, 2H), 1.57 (m, 6H); MS m/z 266 (M^+, 42%), 155 (100%). Found: m/z 266.1305. Calcd for $C_{18}H_{18}O_2$: M, 266.1305. Found: C, 81.02; H, 6.69%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.80%.

2-Bromo-7-(1-naphthoyl)cycloheptanone (20). A solution of **19** (6.0 g, 23 mmol) and $CuBr_2$ (8.9 g, 40 mmol) in chloroform (100 mL) was refluxed with stirring for 3 h. After cooling, the mixture was filtered and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel to give **20** (5.0 g, 63%) from benzene elution: Colorless oil; IR(film) 3050w, 2950s, 1715vs, 1580s, 780s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.84 (m, 3H), 7.53 (m, 4H), 4.88 (dd, J=4.8 & 4.6 Hz, 1H), 2.61—1.48 (m, 9H); MS m/z 346, 344 (M^+, 11.3%, 11.7%), 155 (100%). Found: m/z 346.0252, 344.0233. Calcd for $C_{18}H_{17}BrO_2$: M, 346.0390, 344.0410.

12-Bromo-9,10,11,12-tetrahydrocyclohepta[*a*]phenalen-7(8*H*)-one (21). To 90% sulfuric acid (190 mL) was added **20** (18.9 g, 54.8 mmol) all at once. The mixture stirred at 45—50 °C for 30 min, poured onto ice (ca, 1.5 kg) and extracted with dichloromethane (50 mL×3). The organic layer was washed with water three times, brine twice, and dried over anhyd $MgSO_4$. After removal of the solvent by evaporation in vacuo, the residue was chromatographed on silica gel to give **21** (11.0 g, 61.5%) from CH_2Cl_2 elution: Yellow needles, mp 130—131 °C (CH_2Cl_2–hexane); IR(KBr) 3100w, 2860s, 1640s, 1580s, 790s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.60 (dd, J=7.2 & 1.5 Hz, 1H), 8.13 (dd, J=8.0 & 1.5 Hz, 2H), 7.95 (d, J=7.2 Hz, 1H), 7.69 (dd, J=8.1 & 7.7 Hz, 1H), 7.59 (dd, J=7.9 & 7.2 Hz, 1H), 6.05 (bd, J=5.9 Hz, 1H), 3.55 (dd, J=14.0 & 7.2H, 1H), 2.82 (m, 7H); MS m/z 328, 326 (M^+, 1.2%, 1.2%), 231 (100%). Found: m/z 328.0234, 326.0312. Calcd for $C_{18}H_{15}BrO$: M, 328.0284, 326.0317. Found: C, 66.29; H, 4.7%. Calcd for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62%.

12-Acetoxy-9,10,11,12-tetrahydrocyclohepta[*a*]phenalen-7-(8*H*)-one (22). To a mixture of acetic anhydride (20 mL) and acetic acid (20 mL) were added **21** (3.5 g, 10.7 mmol) and silver acetate (2.7 g, 16.2 mmol), and the resulting mixture was heated at 100—110 °C with stirring for 22 h. After cooling, the solid was filtered off, and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel with CH_2Cl_2–benzene as an eluent to give **22** (2.8 g, 85%): Orange oil; IR(film) 2920w, 1740s, 1630s, 1590s, 780s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.58 (dd, J=7.5 & 1.3 Hz, 1H), 8.13 (d, J=7.6 Hz, 1H), 8.05 (dd, J=7.5 & 1.3 Hz, 1H), 7.87 (d, J=7.6 Hz, 1H), 7.63 (t, J=7.5 Hz, 1H), 7.52 (t, J=7.6 Hz, 1H), 6.71 (d, J=6.4 Hz, 1H), 3.48 (dd, J=15.0 & 6.4 Hz, 1H), 2.86 (m, 1H), 2.13 (s, 3H), 2.40—1.40 (m, 6H); MS m/z 306 (M^+, 6.8%), 246 (100%). Found: m/z 306.1242. Calcd for $C_{20}H_{18}O_3$: M, 306.1253.

12-Hydroxy-9,10,11,12-tetrahydrocyclohepta[*a*]phenalen-7-(8*H*)-one (23). To a solution of **22** (2.77 g, 6.8 mmol) in THF (20 mL) was added a solution of sodium hydroxide (5.44 g, 22.7 mmol) in water (25 mL). The mixture was heated with stirring at 50—60 °C for 24 h. After cooling, it was neutralized with dil HCl, concentrated in vacuo to remove THF, and extracted with CH_2Cl_2 (30 mL×3). The organic layer was washed with water and brine twice each, and dried over anhyd $MgSO_4$. After removal of the solvent by evaporation in vacuo, the residue was chromatographed on silica gel to give **23** (1.73 g, 96%) from CH_2Cl_2 elution: Yellow needles; mp 159—160 °C (CH_2Cl_2–hexane); IR(KBr) 3350m, 2920m, 1620s, 1590s, 780s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.29 (dd, J=8.1 & 1.3 Hz, 1H), 8.14 (d, J=7.5 Hz, 1H), 7.91 (dd, J=8.1 & 1.3 Hz, 1H), 7.78 (d, J=7.5 Hz, 1H), 7.45 (t, J=8.1 Hz, 1H), 7.44 (t, J=7.5 Hz, 1H), 5.59 (d, J=6.1 Hz, 1H), 3.08 (m, 3H), 2.30—1.30 (m, 6H); MS m/z 264 (M^+, 26%), 181 (100%). Found: m/z 264.1111. Calcd for $C_{18}H_{16}O_3$: M, 264.1148. Found: C, 82.16; H, 6.08%. Calcd for $C_{18}H_{16}O_3$: C, 81.82; H, 6.06%.

8,9,10,11-Tetrahydrocyclohepta[*a*]phenalene-7,12-dione (24). A) To a solution of pyridinium dichromate prepared by the addition of chromium trioxide (CrO_3) (5.5 g, 55 mmol) to pyridine (50 ml) was added **23** (2.97 g, 11.3 mmol) in pyridine (10 mL). The mixture stirred at room temperature for overnight, poured onto ice-water, and extracted with

CH_2Cl_2 (50 mL×3). The organic layer was washed with dil HCl three times, brine twice, and dried over anhyd $MgSO_4$. After removal of the solvent by evaporation, the residue was chromatographed on silica gel to give **24** from CH_2Cl_2 elution. Recrystallization from CH_2Cl_2–hexane gave pure **24** (2.22 g, 75%).

B) To a solution of **23** (2.6 g, 9.83 mmol) in CH_2Cl_2 (100 mL) was added $BaMnO_4$ (27 g) and the mixture was refluxed with stirring for 6 h. The solid was filtered, and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel to give **24** (2.5 g, 97%) from CH_2Cl_2 elution: Yellow needles, mp 84—85 °C; IR(KBr) 2920m, 1690s, 1630s, 1570s, 780s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.16 (dd, J=7.6 & 1.3 Hz, 1H), 8.15 (dd, J=7.9 & 1.5 Hz, 1H), 7.95 (dd, J=7.6 & 1.3 Hz, 1H), 7.71 (dd, J=7.9 & 1.5 Hz, 1H), 7.71 (t, J=7.6 Hz, 1H), 7.51 (t, J=7.9 Hz, 1H), 2.84 (m, 4H), 1.95 (m, 4H); MS m/z 262 (M^+, 100%), 219 (87%). Found: m/z 262.0950. Calcd for $C_{18}H_{14}O_2$: M, 262.0991. Found: C, 82.31; H, 5.54%. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.83%.

11,11-Dibromo-8,9,10,11-tetrahydrocyclohepta[*a*]phenalene-7,12-dione (25). To a solution of **24** (2.18 g, 8.32 mmol) in chloroform (50 mL) was added $CuBr_2$ (11.2 g, 49.9 mmol), and the mixture was refluxed for overnight. After cooling, the solid was filtered off and the filterate was evaporated in vacuo. The residue was chromatographed on silica gel to give **25** (3.2 g, 92%) from CH_2Cl_2 elution: Orange needles, mp 157—158 °C (CH_2Cl_2–hexane); IR(KBr) 1710m, 1630s, 1570s, 780m cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.61 (dd, J=7.7 & 1.4 Hz, 1H), 8.18 (dd, J=7.6 & 1.3 Hz, 1H), 8.00 (dd, J=7.7 & 1.4 Hz, 1H), 7.76 (dd, J=7.6 & 1.3 Hz, 1H), 7.72 (t, J=7.7 Hz, 1H), 7.58 (t, J=7.6 Hz, 1H), 3.80—2.30 (m, 2H), 2.02 (m, 2H); MS m/z 422, 420, 418 (M^+, 7%, 12%, 7%). Found: m/z 421.9200, 419.9182, 417.9256. Calcd for $C_{18}H_{12}Br_2O_2$: M, 421.9165, 419.9183, 417.9205. Found: C, 51.50; H, 2.91%. Calcd for $C_{18}H_{12}Br_2O_2$: C, 51.43; H, 2.86%.

Cyclohepta[*a*]phenalene-7,12-dione (4). A mixture of **25** (1.00 g, 2.38 mmol) and lithium chloride (1.00 g, 23.5 mmol) in dry DMF (10 mL) was heated at 100—110 °C with stirring for 3 h. After cooling, the mixture was poured onto ice-water and the solid was filtered. The solid was dissolved in CH_2Cl_2 and dried over anhyd $MgSO_4$. The solvent was evaporated and the residue was chromatographed on silica gel to give **4** (0.70 g, 96%) from CH_2Cl_2 elution: Orange needles, mp 176—177 °C (CH_2Cl_2–hexane); IR(KBr) 3050w, 1640s, 1570s, 760s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.63 (dd, J=7.6 & 1.3 Hz, H-1), 8.43 (dd, J=7.7 & 1.2 Hz, H-6), 8.18 (dd, J=7.6 & 1.3 Hz, H-3), 8.13 (dd, J=10.2 & 1.1 Hz, H-8), 7.98 (dd, J=7.7 & 1.2 Hz, H-4), 7.71 (t, J=7.6 Hz, H-2), 7.53 (t, J=7.7 Hz, H-5), 6.89 (m, H-9, -10, -11), (D_2SO_4–CH_2Cl_2) δ=10.09 (d, J=8.11 Hz, H-1), 9.88 (d, J=10.7 Hz, H-8), 9.68 (d, J=8.1 Hz, H-3), 9.50 (d, J=7.0 Hz, H-6), 9.06 (t, J=8.1 Hz, H-2), 8.94 (d, J=7.0 Hz, H-4), 8.56 (ddd, J=10.7, 9.6, & 2.9 Hz, H-9), 8.54 (m, 10-H), 8.52 (t, J=7.0 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ=190.1 (C-12), 183.3 (C-7), 143.8, 136.1, 133.8, 132.5, 132.4, 131.1, 130.6, 128.0, 127.8, 126.8, 124.4, (D_2SO_4–CH_2Cl_2) δ=181.6 (C-OH, C-12), 178.6 (C-OH, C-7), 156.5 (C-4), 155.6 (C-6), 147.5 (C-5), 146.1 (C-1), 143.6 (C-2), 142.9 (C-3), 140.1 (C-8), 134.2 (C-10), 131.9 (C-11), 130.5 (C-9), 144.6, 134.4, 126.5, 123.7, 120.5 (quart. C); ES (CH_2Cl_2) λ_{max} 432 (log ε=3.72), 382 (3.68), 296sh (3.56), (concd H_2SO_4) λ_{max} 540 (log ε=4.10), 395 (4.12), 307 (4.15), 283 (5.19), 237 nm (5.20), The pK_a value was obtained by the similar manner as **2**; MS m/z 258 (M^+, 100%), 230 (97%). Found: m/z 258.0685. Calcd for $C_{18}H_{10}O_2$: M, 258.0680. Found: C, 83.59; H, 4.09%. Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%.

9,10-Dihydrocyclohepta[*a*]phenalen-7(8*H*)-one (26). A mixture of **21** (9.04 g, 27.6 mmol) and lithium chloride (1.6 g, 41.1 mmol) in DMF (20 mL) was heated at 100—110 °C with stirring for 1 h. After cooling, the mixture was poured onto ice-water and extracted with CH_2Cl_2 (30 mL×3). The organic layer was washed with water and brine twice each and dried over anhyd $MgSO_4$. The solvent was removed by evaporation and the residue was chromatographed on silica gel to give **26** (5.5 g, 81%) from CH_2Cl_2 elution: Yellow needles, mp 73—74 °C (CH_2Cl_2–hexane); IR(KBr) 2920w, 1630s, 1565s, 785s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.65 (dd, J=7.2 & 1.3 Hz, 1H), 8.13 (dd, J=8.1 & 1.3 Hz, 1H), 7.91 (m, 1H), 7.88 (d, J=1.1 Hz, 1H), 7.75 (s, J=8.1 Hz, 1H), 7.63 (t, J=7.9 Hz, 1H), 6.97 (d, J=11.3 Hz, 1H), 6.61 (dt, J=11.3 & 5.9 Hz, 1H), 4.78 (m, 2H), 2.82 (m, 4H); MS m/z 246 (M^+, 40.3%), 219 (100%). Found: m/z 246.1042. Calcd for $C_{18}H_{14}O$: M, 246.1042. Found: C, 87.48; H, 5.77%. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73%.

8,9-Dihydrocyclohepta[*a*]phenalene-7,10-dione (27). To a solution of pyridinium dichromate in pyridine prepared by addition of CrO_3 (17.1 g, 170 mmol) to pyridine (50 mL) at ca. 5 °C was added **26** (8.53 g, 34.7 mmol) dissolved in pyridine (20 mL). The mixture heated at 50—60 °C with stirring for 7 h, diluted with dil HCl (500 mL), and extracted with CH_2Cl_2 (50 mL). The organic layer was washed with dil HCl twice and brine twice, and dried over anhyd $MgSO_4$. The solvent was evaporated and the residue was chromatographed on silica gel to give **27** (0.59 g, 16%) from CH_2Cl_2 elution along with the recovered starting material **26** (4.85 g, 56.8%). Compound **27**: Yellow needles, mp 177—178 °C (CH_2Cl_2–hexane); IR(KBr) 1660s, 1630s, 1570s, 785s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.65 (dd, J=7.2 & 1.3 Hz, 1H), 8.19 (dd, J=7.9 & 1.3 Hz, 1H), 8.01 (d, J=7.9 Hz, 1H), 7.99 (d, J=6.6 Hz, 1H), 7.76 (dd, J=7.5 & 7.0 Hz, 1H), 7.61 (d, J=12.5 Hz, 1H), 7.59 (dd, J=7.9 & 7.7 Hz, 1H), 6.58 (d, J=12.5 Hz, 1H), 3.17 (m, 2H), 2.77 (m, 2H); MS m/z 260 (M^+, 81.5%), 231 (100%). Found: m/z 260.0778. Calcd for $C_{18}H_{12}O_2$: M, 260.0835. Found: C, 82.78; H, 4.72%. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65%.

Cyclohepta[*a*]phenalene-7,10-dione (3). A mixture of **27** (0.64 g, 2.46 mmol) and SeO_2 (0.37 g, 2.95 mmol) in dioxane (30 mL) was refluxed for 3 h. The mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2, washed with saturated aq $NaHCO_3$ twice and brine twice, and dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo and the residue was chromtographed on silica gel to give **3** (0.38 g, 60%) from CH_2Cl_2 elution, along with the recovered starting material **27** (0.15 g, 23%). Compound **3**: Yellow needles, mp 246—247 °C (CH_2Cl_2–hexane); IR(KBr) 3050w, 1640s, 1600s, 1570s, 765s cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.67 (dd, J=13.5 & 1.3 Hz, H-6), 8.44 (d, J=12.9 Hz, H-12), 8.38 (bd, J=7.6 Hz, H-3), 8.25 (dd, J=7.6 & 1.3 Hz, H-4), 8.10 (bd, J=7.6 Hz, H-1), 7.80 (t, J=7.6 Hz, H-5), 7.68 (t, J=7.6 Hz, H-2), 7.17 (dd, J=13.5 & 3.1 Hz, H-9), 7.02 (dd, J=12.9 & 3.1 Hz, H-11), (D_2SO_4–CH_2Cl_2) δ=10.15 (d, J=12.3 Hz, H-12), 10.10 (d, J=12.1 Hz, H-8), 9.79 (d, J=9.0 Hz, H-6), 9.69 (d, J=8.8 Hz, H-4), 9.49 (d, J=7.5 Hz, H-3), 9.17 (d, J=7.7 Hz, H-1), 8.61 (d, J=7.7 & 7.5 Hz, H-2), 8.61 (dd, J=9.0 & 8.8 Hz, H-5), 8.40 (d,

J=12.3 Hz, H-11), 8.37 (d, J=12.1 Hz, H-9); ^{13}C NMR ($CDCl_3$) δ=187.0 (C-10), 182.9 (C-7), 143.2, 142.3, 138.3, 136.1, 134.5, 134.1, 133.2, 132.6, 131.6, 128.9, 128.0, 127.8, 127.6, 127.0, (D_2SO_4) δ=184.7 (C–OH, C-10), 178.7 (C–OH, C-7), 155.4 (C-4), 150.3 (C-3), 147.9 (C-1), 147.4 (C-6), 143.3 (C-8), 143.0 (C-12), 137.2 (C-9 or C-11), 131.4 (C-11 or C-9), 131.4 (C-5), 131.2 (C-2), 150.3, 131.9, 131.3, 126.3, 125.5, 120.9 (quart. C); ES (CH_2Cl_2) λ_{max} 432 (log ε=3.48), 390 (3.46), 340 (3.69), 254 (4.22), 228 nm (4.05), (concd H_2SO_4) λ_{max} 520 (log ε=4.05), 489 (4.01), 370 (3.89), 330 (3.94), 282 (4.58), 230 nm (4.30); MS m/z 258 (M^+, 10.2%), 230 (100%). Found: m/z 258.0702. Calcd for $C_{18}H_{10}O_2$: M, 258.0723. Found: C, 83.49; H, 4.15%. Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%.

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