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Synthesis and properties of polycyclic quinones condensed with 1,6-methano[10]annulene

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Abstract

Two types of polycyclic quinones condensed with 1,6-methano[10]annulenes as type A: 1,6-methanonaphtho[2,3-*c*][10]annulene-7,12-dione **5a**, and type B: 1,6-methanonaphtho[2,3-*c*][10]annulene-5,14-dione **18**, bis(1,6-methano[10]annuleno[3,4-*b*; 3,4-*g*])anthracene-10,21-dione **20**, 1,6-methanoanthraceno[2,3-*c*][10]annulene-5,16-dione **22**, 1,6-methanotetraceno[2,3-*c*][10]annulene-6,17-dione **23**, and 1,6-methano phenanthreno[2,3-*c*][10]annulene-5,6-dione **24** have been synthesized. The acene derivative **6** corresponding to that of **5a** was synthesized by the reduction of quinone **5a**. The physical, spectral, and chemical properties of these new compounds have been investigated.

Keywords: Bridged [10]annulene; Poly condensed quinone; Condensed acene; Rearrangement; Fluorescence; Reduction potentials

1. Introduction

Polycyclic quinones and quinodimethanes (**D**), known as electron acceptors [1], are of interest in their utility of dichroic dyes [2], dyes as textile colorants [3], paints [4], organic transistors [5] and so on. For example, the acenes (**E**), especially pentacene, are mostly used in organic thin film transistors [6]. Anthracene derivatives were also used in blue light emitting materials [7]. These utilities deeply related with their structure and electronic states. We have studied the relation between structure and electronic states in π-conjugated polycyclic compounds such as quinones and related acenes containing 1,6-methano[10]annulene (bridged annulene). This is because bridged annulenes, an isoelectronic isomer of naphthalene, are expected to be good electron current compounds than naphthalene by delocalization of electron over the ring for the use of organic materials, and ^{1}H NMR chemical shifts of the methylene protons of bridged annulenes are good indicators for the estimation of the ring current related with electronic states. We synthesized such new polycyclic quinone compounds containing bridged annulene types **A**, **B**, and acene **C** as shown in Fig. 1 and examined their properties by spectral measurements. Details of the results are described as follows.

2. Synthesis and identification of quinone type A and acene

2.1. Synthesis and identification of quinone 5a; type A

The synthesis of quinone **5a** [8] as type **A** has previously been reported in our paper; however, the detailed properties were not described, and the yield was not satisfactory. Although the synthetic key compound of dione **4** has been known, the yield was low (25%) [9]. We developed a new synthetic method and improved the yield as follows. The reaction of **1** [8] with morpholine in the presence of a three molar excess of $TiCl_4$ and a 12 molar excess of NEt_3 in

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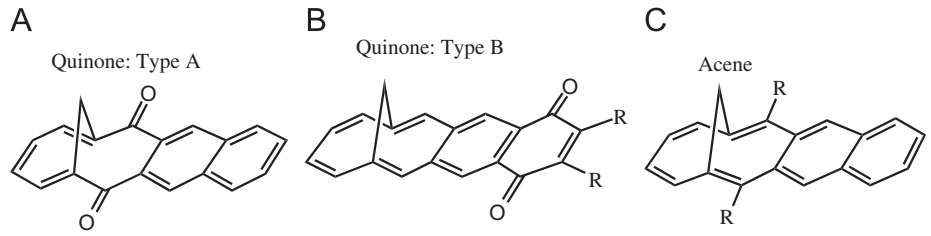
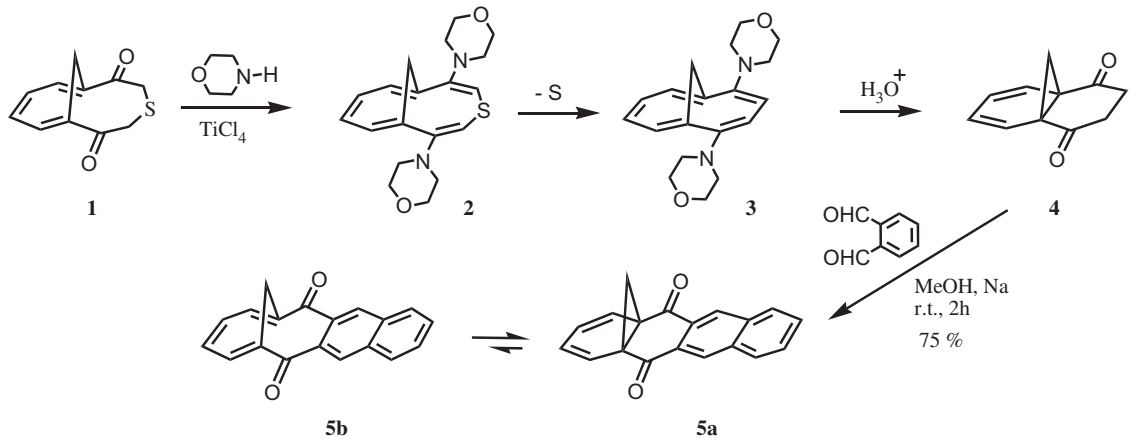


Fig. 1. Newly synthesized polycyclic quinone compounds containing bridged annulene types **A**, **B**, and acene **C**.



Scheme 1.

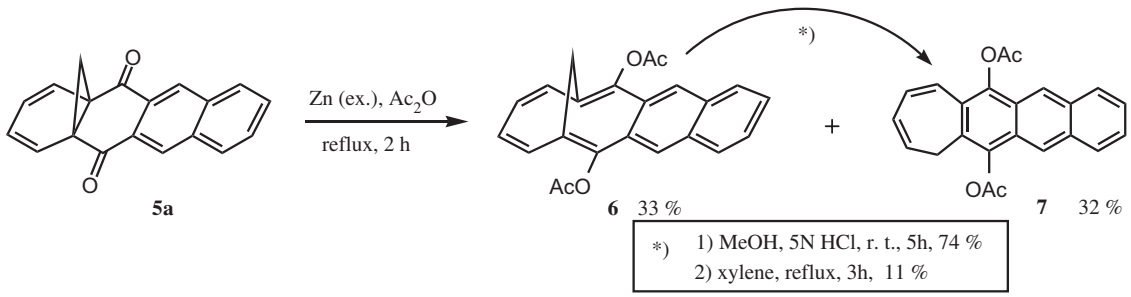
toluene at 40 °C for 2 h gave 2,6-morpholino-1,7-methano-4-thio[11]annulene **2** as an unstable compound under air moisture with 76% yield. Desulfurization of **2** easily occurred at over 40 °C to give 2,5-morpholino-1,6-methano[11]annulene **3** as stable compound with 95% yield. The hydrolysis of **3** in acidic media gave key intermediate **4** in over 78% yield. The reaction of **4** with *o*-phthalaldehyde in the presence of NaOMe in dry MeOH at 40 °C for 4 h gave condensed compound **5a** with 67% yield. The identification of **5a** was done as follows. The IR spectrum of **5a** showed that the strongest absorption band appearing at 1680 cm^{-1} was assigned as carbonyl groups of a typical quinone compound. The ^1H NMR signals at δ 8.65, 8.05, and 7.68 ppm were assigned as protons on the naphthalene moiety, and the signals at δ 7.06 and 6.19 ppm were assigned as protons of the bridged annulene moiety. The signals at δ 2.62 and 0.92 ppm were assigned as bridged methylene protons. The coupling constants ($J = 4.4$ Hz) of methylene protons and ^{13}C chemical shift of the methylene carbon (δ 24.4 ppm) indicate that the bridged annulene moiety of **5a** is a norcaradiene form rather than a cycloheptatriene form **5b**. The mass spectrum of **5a** shows that the parent peak appeared at m/z 272 corresponding to the assigned structure (Scheme 1).

2.2. Synthesis of acene derivative *6* by reduction of *5a*

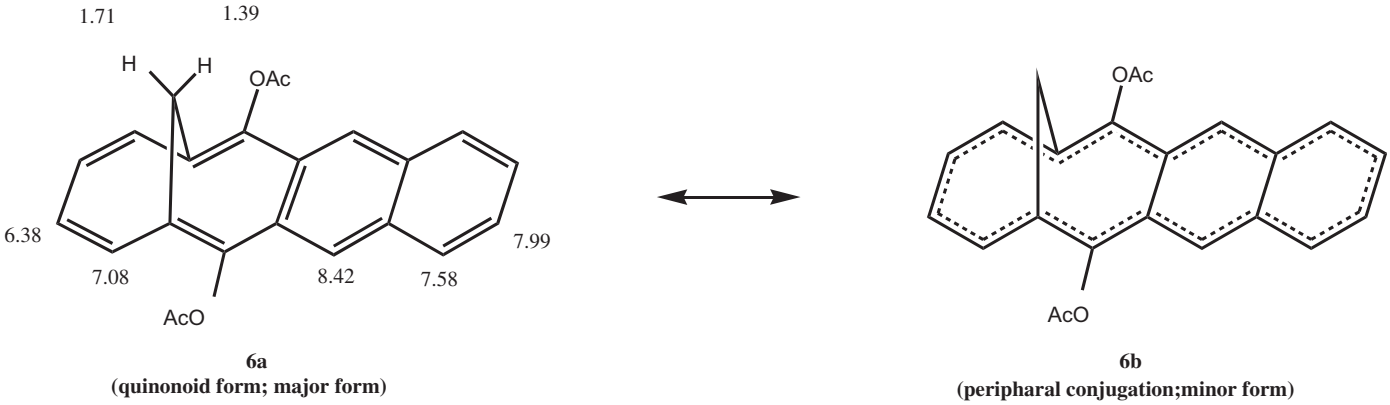
Acene **6** corresponding to quinone **5a** was synthesized by the reductive acetyloxylation of **5a** as follows. As expected from its reduction potentials, 0.61 and 1.10 eV measured by the cyclic voltammetry (CV) method, reduction of **5a** with Zn in acetic anhydride at reflux for 1 h gave acene derivative **6** and its rearranged compound **7**, in 33% and 32% yields, respectively, as shown in Scheme 2. The structures of these compounds were confirmed by the physical and spectral data as described in the next section.

2.3. Structure of acene derivatives *6* and *7*

The structure of the new acene **6** was confirmed by the spectral data. The IR spectrum of **6** showed that the strong absorption band at 1750 cm^{-1} was assigned to acetate as typical ester groups. The structure of **6** was identified by the ^1H-, ^{13}C-NMR spectra, which were assigned by the ^1H–^1H, ^1H–^{13}C, two-dimensional methods, HMBC, HMQC methods, etc. The ^1H-NMR spectrum of acene type compound **6** is shown in Fig. 2 and the signals observed at δ 1.71 ppm ($J = 8$ Hz, 1H) and 1.39 ($J = 8$ Hz, 1H) are assigned as bridged methylene protons. They are lower fields than those of parent 1,6-methano[10]annulene **7** [10] and also benzannelated 1,6-methano[10]annulene **8** [11] rather similar to those of thiophen-condensed 1,6-methano[10]annulene **9** [12]. This suggests that the contribution of the conjugation in the bridged annulene moiety is quinodimethane form **5a** rather than 18π electron peripheral conjugation as **5b**. This phenomenon may depend on the number of condensed rings as mentioned



Scheme 2.



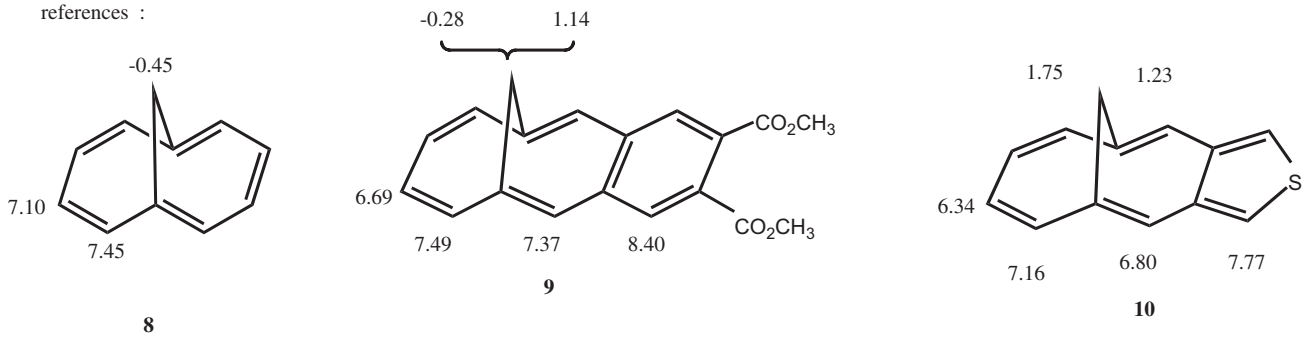
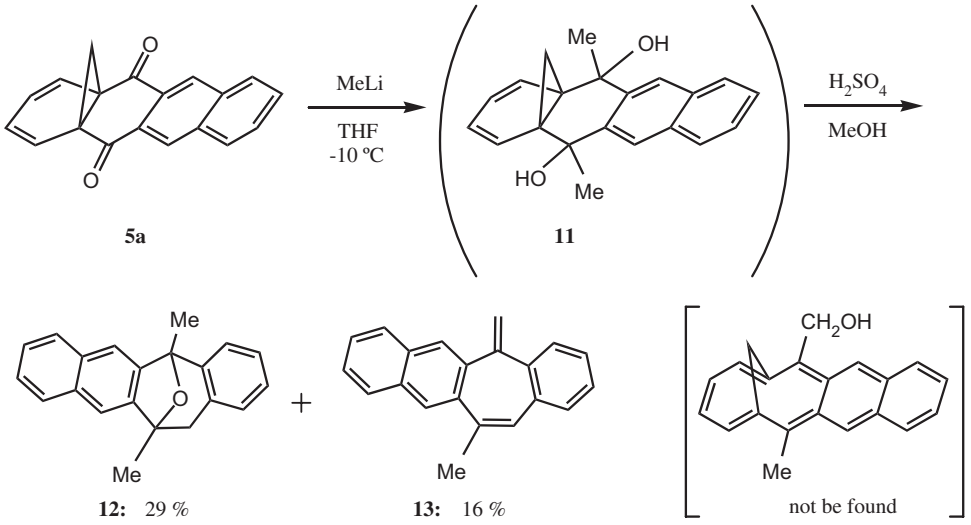


Fig. 2. The ^{1}H chemical shifts of **6** and related compounds.

above and may be due to its substituents. The IR spectrum of **7** showed that the strongest band appearing at 1754 cm^{-1} was assigned to acetate as typical ester groups. The ^{1}H NMR spectrum of **7** showed no bridged methylene protons, but the signals appeared at 7.49–7.46 ppm (2H), and 7.14 (1H), 6.52 (1H), and 6.38 ppm (1H) showed typical benzannelated cycloheptatriene. This indicates that the bridged annulene moiety was rearranged to cycloheptatriene. The ^{1}H NMR signals at δ 2.63 and 2.59 ppm were assigned to two methyl groups of acetate groups. Then the parent peak of the mass spectrum of **7** was observed at m/z 268 as base peak. Based upon these data, the structure of **7** was assigned as shown in Scheme 2.

2.4. Some reactions of *5a* aimed at acene derivatives

During the course of the synthesis of acene fused with bridged [10]annulene, some new and interesting reactions were found as illustrated in Scheme 3. The reaction of **5a** with MeLi in dry THF afforded dimethyl-diol **11** as an unstable compound; then it was treated with H_2SO_4



Scheme 3.

in methanol at r.t. for 30 min and gave rearranged compounds **12** with 29% yield and heptafulvene derivative **13** with 16% yield, respectively, as shown in Scheme 3. The IR spectrum of **12** showed no significant strong band such as a carbonyl group except for 750 cm^{-1}. The mass spectrum showed that the parent peak appeared at m/z 286, and its exact mass was 286.1339, which indicates the formula as $C_{21}H_{18}O$. The ^1H NMR signals of δ 2.13 and 1.89 ppm showed the two methyl groups, and the signals at δ 3.38 and 2.86 ppm were assigned as germinal methylene protons. Based on the above spectral data, the structure of **12** was determined as shown in Scheme 3. Also the structure of **13** was confirmed by a similar method. The IR spectrum of **13** showed a strongest band at 750 cm^{-1} and no other characteristic band such as carbonyl group. The ^1H NMR spectrum of **13** showed that signals at δ 7.91,7.84–7.82, 7.45–7.43, 7.28–7.26 ppm were assigned to aromatic ring protons, those at δ 5.38 and 5.33 ppm were assigned to germinal vinyl protons, and that at δ 2.53 ppm (3 H) was assigned to methyl group. The ^{13}C NMR spectrum and the mass spectrum are consistent with the assigned structure as shown in Scheme 3.

2.5. Mechanism of the formation of *12* and *13*

Methylation occurred at carbonyl groups and then the yielded dialcohol rearranged by protonation on hydroxyl groups in sulfuric acid. The dehydration of one alcohol occurred to yield carbocation at the methyl substituted carbon. It was followed by the shifting of cyclopropane ring to carbocation and then it opened to a seven membered ring. The rearrangement proceeded via two pathways. One was dehydrogenation to give the double bond and then dehydration of the other hydroxyl group by the action of acid to give heptafulvene **13**. The other was that the carbocation was attacked by the other hydroxyl group to give ether **12** as shown in Scheme 4.

3. Synthesis and structures of quinone type B

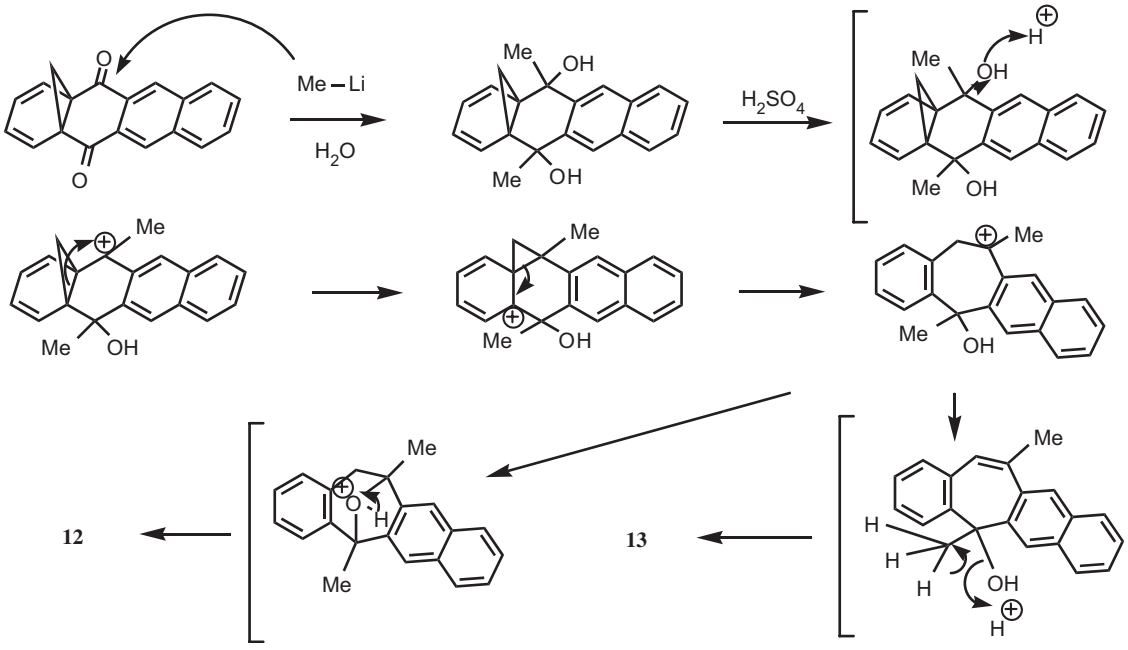
3.1. Synthesis of quinone *18* as type B

The reaction of reactive quinodimethane intermediate **15** formed by thermolysis of **14** [10] with *p*-benzoquinone **16** gave fully conjugated polycyclic quinone **18** as pale yellow crystals and sulfone **19** in 51% and 15% yields, respectively, as shown in Scheme 5. Quinone **18** was formed by the dehydrogenation of cycloadduct **17** with excess benzoquinone under the reaction conditions. Compound **19** was formed by the recombination of the generated **15** with sulfur dioxide, and is similar to that of the reported reaction of **15** [11] as shown in Scheme 5.

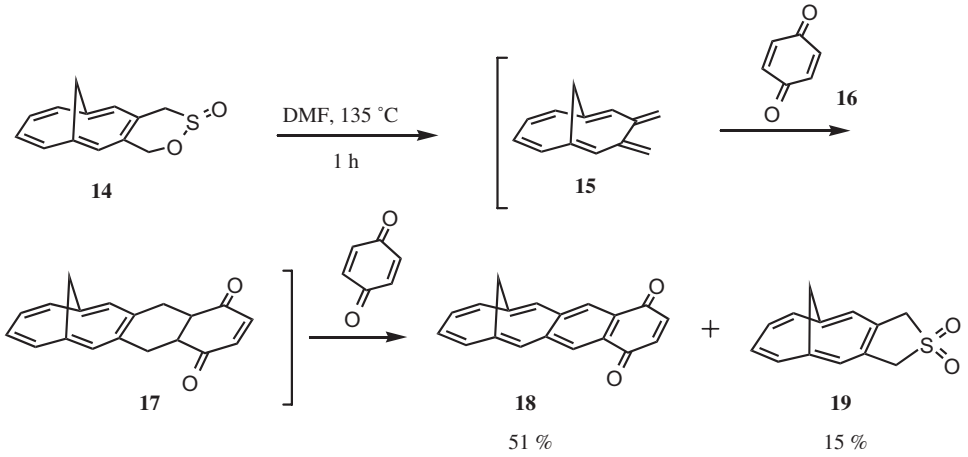
The reaction of **15** with **18** again gave a very long straight ring chain system of bis(1,6-methano[10]annuleno) [2,3-*b*; 6,7-*i*] anthraquinone **20** in 31% yield. When left in the NMR sample tube at r.t. for 2 days, the ^1H NMR spectrum was completely changed. The spectrum indicates the cycloadduct of oxygen at both bridged [10]annulene moiety **21** as shown in Scheme 6.

3.2. Synthesis of quinones type B: *22, 23, and 24*

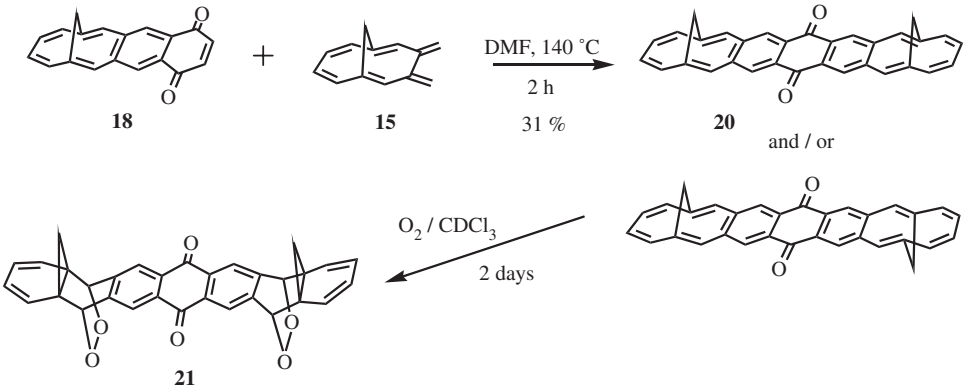
In a similar way, the reaction of **15** with 1,4-naphthoquinone, 1,4-anthraquinone, and 1,2-naphthoquinone gave fully conjugated polycyclic quinones **22**, **23**, and **24** in 54%, 33%, and 15% yields, respectively, along with sulfone **19** in each case. Furthermore, the reaction of 1,2-quinone **24** with *o*-phenylenediamine gave phenazine derivative **25** condensed with 1,6-methano[10]annulene as yellow needles in 64% yield as shown in Scheme 7, Fig. 3.



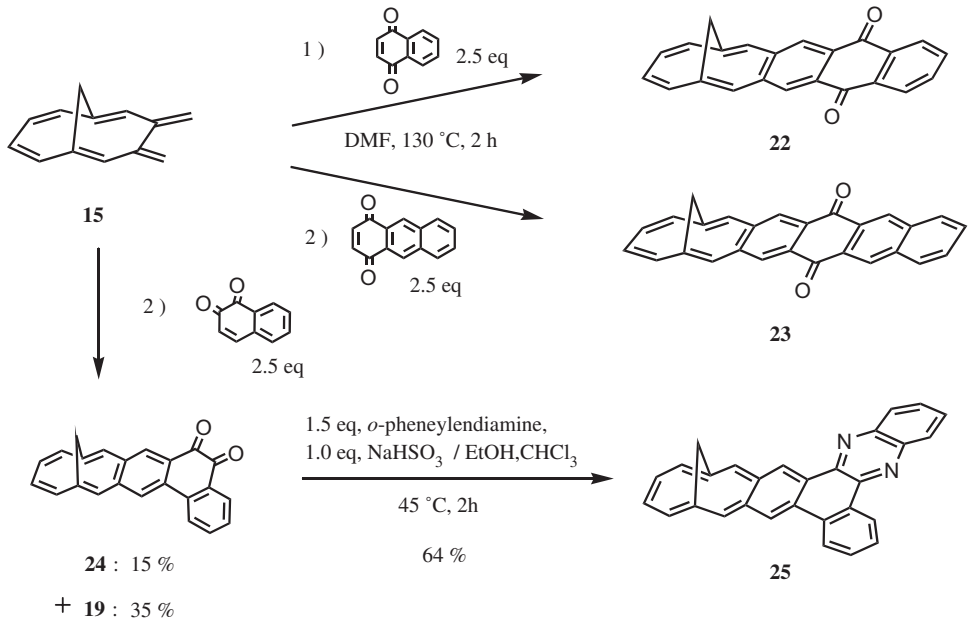
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

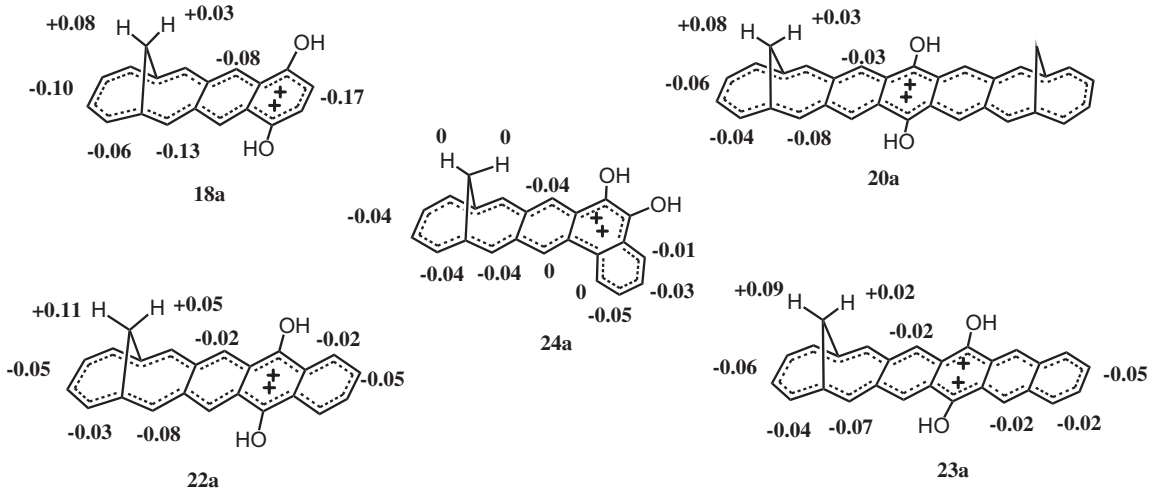


Fig. 3. The ^{1}H chemical shifts differences in $CDCl_3$ and containing 6 wt% trifluoroacetic acid-*d* in $CDCl_3$.

3.3. Structures of the polycyclic quinones **18**, **20**, **22**, **23**, and **24**

The ^{1}H chemical shifts of the outer ring protons of all new quinones are similar to those of corresponding benzenoid quinones. However, the ^{1}H chemical shifts of the methylene protons of **18**, **20**, **22**, **23**, and **24** are shifted to lower fields in the order of **18**, **20**, **22**, **23**, and **24** as shown in Fig. 4. It suggests that the ring currents of these compounds decrease in this order, and it depends on the number of condensed benzene ring and the condensed position of benzene ring. Generally, the protonation on carbonyl groups of quinones in strong acidic media yields cationic species. Then the protonated cationic species are of interest in their electronic state, and the ^{1}H chemical shifts of quinones in the presence of 6 vol% of trifluoroacetic acid-*d* were observed as shown in Fig. 3. Since the ring rearrangement of the bridged annulene moiety occurred at a higher concentration of acid, 6 vol% of acid concentration has been used for measuring the ^{1}H NMR spectra. The ^{1}H chemical shifts of the outer ring protons of the bridged [10]annulene moiety of **18a**, **20a**, **22a**, **23a**, and **24a** are shifted to little lower fields. However, the methylene protons of all these quinones are observed at a little higher fields. The concentration of acid is so low that it could not be protonated completely; however, it could be concluded by the partial formation of cationic species.

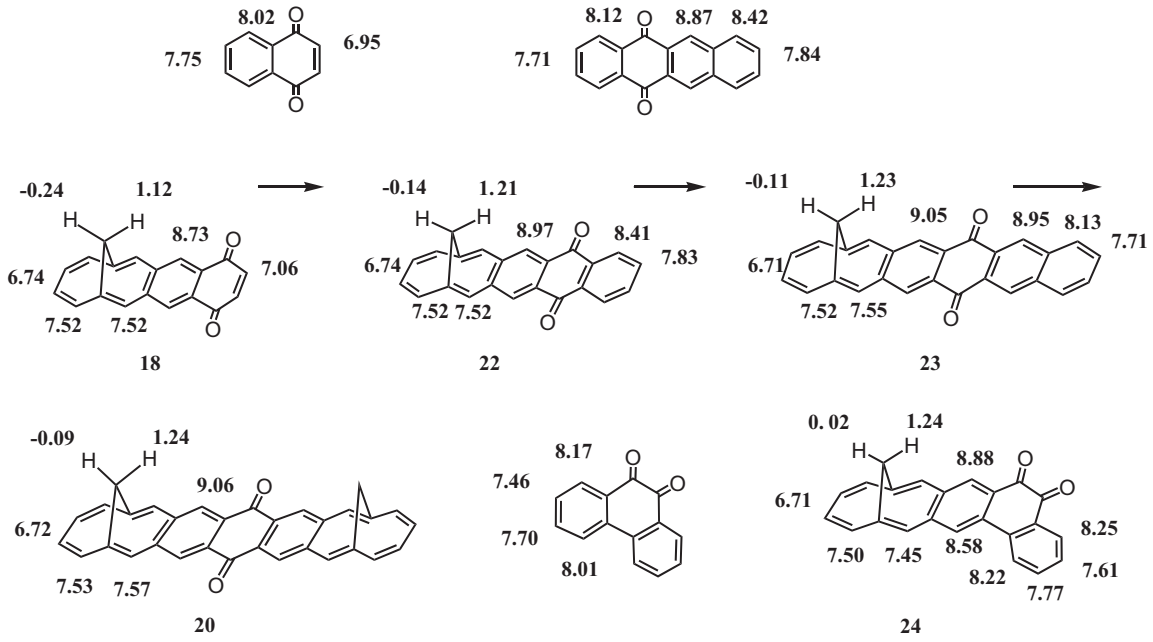
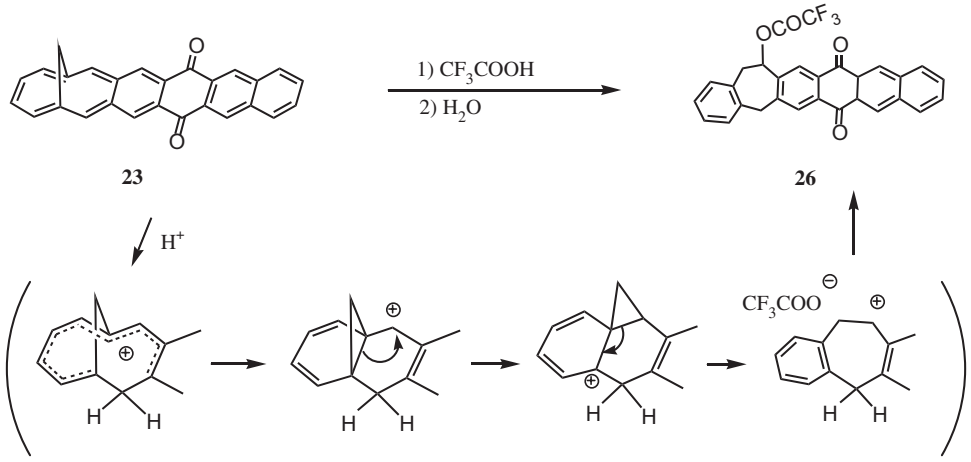


Fig. 4. The ^{1}H NMR chemical shifts of quinone compounds (400 MHz, δ ppm).



Scheme 8. Mechanism of the formation of quinone **26** in CF_3COOH.

*3.4. Rearrangement of quinones **23–26***

As described above, the partial formation of dicationic species was expected by the protonation of carbonyl groups of these quinones. Actually, the absorption maxima of these quinones in the presence of 6 vol% of trifluoroacetic acid were observed at longer wavelength than those in neutral media. At higher concentration over 6 vol% trifluoroacetic acid, the absorption maxima of these quinones changed to shorter wavelength. It suggests that some change has occurred in quinone compounds. Then treatment of **23** as a typical example with trifluoroacetic acid gave rearranged compound **26** quantitatively. The mechanism of this reaction was explained as follows. First protonation occurred at carbonyl groups of quinone in a low concentration of acid, although at higher concentrations than 6 vol% of acid, protonation occurred at the bridged annulene moiety. The protonated cationic species rearranged along with the skeletal rearrangement finally to give cation, and then trifluoroacetate anion reacted with the cation on the carbon of the seven-membered ring to give **26** as shown in Scheme 8.

4. Spectra of the new quinones

4.1. ^{1}H NMR spectra of the new polycyclic quinones

All the signals of the ^{1}H- and ^{13}C-NMR spectra were assigned by the ^{1}H–^{1}H, ^{1}H–^{13}C, two-dimensional methods, HMBC, HMQC methods, etc. The ^{1}H chemical shifts of all new quinines and reference quinone compounds are shown in Fig. 2. The outer ring protons of all quinines are similar

to those of corresponding known quinines. However, the ^{1}H chemical shifts of the methylene (bridge) protons placed over the condensed benzene ring moiety of the new quinones are almost similar regions (δ 1.12–1.24 ppm). The other side of the methylene protons is shifted to lower field in the order of **18**, **22**, **23**, **20**, and **24**. It shows that the ring current effect of the diene moiety decreases in this order. It also corresponds to the results of the other spectral results.

4.2. UV–vis spectra of the new quinones

The absorption maxima of the UV–vis spectra of the new quinones show longer wavelength than those of benzenoide quinones, and these results are shown in Table 1. The absorption maxima of poly condensed quinones shortened in the order of **23**, **18**, **20**, **22**, and **23** by increasing the number of benzene ring. It suggests that the condensation of benzene ring shortened the absorption maxima. The longer absorption maxima of **24** than those of other quinones may be explained as follows: that the outer benzene ring and carbonyl group are co-planar with the bridged annulene moiety and, as a result, the π conjugation is expanded over all rings. The solvent effects observed in these quinines, except for **22**, indicate that the contribution of the dipolar structure is large.

4.3. Reduction potentials of new quinones (CV method)

The reduction potentials of the quinones are a good index of the electron acceptor, and they are generally reduced to dianionic species and were measured by an electrochemical method such as the CV method. The first reduction potentials of these new quinones become greater in the order of **24**, **22**, **18**, **23**, and **20** as the condensed ring was increased as shown in Table 2. Also, they are higher than that of **5a**. It suggests that the ability of the reduction and the electron acceptance decreases in the above order, which corresponds to the difficulty of the reduction of these compounds. Actually these quinones could not be reduced.

4.4. Fluorescence of the new quinones

Fluorescence is an important property of quinone compounds for the use of organic materials. The fluorescences of these compounds were measured and observed, except for **18** and **24**. The reason for the absence of fluorescence in **18** and **24** is not clear now. The fluorescence of phenazine derivative **25** was observed at 533 nm (MeOH) and 554 nm (CH_2Cl_2), respectively. The fluorescences of these compounds were observed at longer wavelength than those of corresponding benzenoid quinones listed in Table 3. Since the fluorescences of new quinones were observed at longer wavelength, it suggests that these compounds are potential candidates for new organic materials.

Table 1
UV-vis

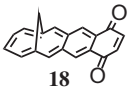
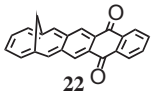
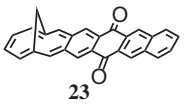
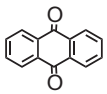
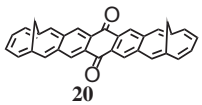
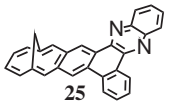
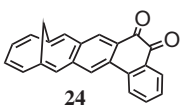
Compound	(1) CH_3OH (nm)	(2) CH_2Cl_2 (nm)	(3) Δ (2−1)
18	489	497	+8
20	470	485	+15
22	472	472	0
23	457	465	+8
24	522^{sh}	529^{sh}	+7

Absorption maxima of the new quinones in MeOH and CH_2Cl_2.

Table 2
Reduction potentials of the new and related quinones (CV)

Quinone	$-^1E_{1/2}$ (V)	$-^2E_{1/2}$ (V)	Quinone	$-^1E_{1/2}$ (V)	$-^2E_{1/2}$ (V)
Benzoquinone	0.48		22	0.77	1.42
1,4-naphthoquinone	0.71	1.63	18	0.91	1.36
9,10-anthraquinone	0.82	1.44	23	0.91	1.46
9,10-phenanthroquinone	0.70		20	1.00	1.35
24	0.70		5a	0.61	1.32

Table 3
Fluorescenes of the quinones and related compounds

Quinone	(1) MeOH (nm)	(2) CH_2Cl_2 (nm)	Quinone	(1) MeOH (nm)	(2) CH_2Cl_2 (nm)
	—	—	 **18**	—	—
	400	403	 **22**	570	565
			 **23**	560	543
	472	493	 **20**	560	543
 **25**	533	554	 **24**	—	—

5. Summary

(1)New types of quinone type A and type B were synthesized. (2) The new acene derivatives were synthesized by the reduction of quinone type A. Its conjugation form is a quinonoid form in bridged [10] annulene moiety. (3) Quinones type B are a potential candidate for new organic materials by their longer wavelength absorptions of UV–vis spectra and their longer wavelength fluorescence. (4) The reduction potentials of quinone type B are larger than those of benzenoid quinones and type A.

6. Experimental section

6.1. General

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrum RX I spectrometer. UV spectra were measured on a Shimadzu UV-1600 spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 Hz) were recorded with tetramethylsilane as an internal standard on a JEOL α 400. Mass spectra were measured on JEOL GC-Mate and JMS-700 mass spectrometers using electron impact ionization at 70 eV. UV photoelectron spectra were measured on a Riken-Keiki AC-2 instrument. Cyclic voltammogram was recorded on a Yanako P1100 instrument. Column chromatography was done with Merck Kieselgel 60 Art 7734. Toluene and *N*, *N*-dimethylformamide were purified by distillation from calcium hydride under nitrogen atmosphere. Triethylamine and titanium tetrachloride were purchased from Tokyo Kasei Ind. Co., 1,2-naphthoquinone was purchased from Aldrich Co., and *p*-benzoquinone was purchased from Wako Chem. Co. and were used without purification.

6.2. Synthesis of 2, 5-dimorpholino-1,6-methano[10] annulene *3* from *1*

To a solution of 100 mg (0.48 mmol) of keto-sulfide **1** and 250 mg (2.88 mmol) of morphorine in 5 mL of dry toluene, 182 mg (0.48 mmol) of $TiCl_4$ in 3 mL of toluene was added dropwise and then heated at 50 °C for 4 h with stirring. The reaction mixture was filtered and the filter cake was washed three times with 5 mL of toluene. The combined filtrate was evaporated to dryness. The residue was column chromatographed on silica gel eluted by AcOEt–hexane (7:3) to give 109 mg (73% from **1**) of **3** as orange needles.

3: orange needles; mp 130–132 °C; IR (KBr) ν_{max} 3419 s, 3018m, 2960m, 2934m, 2884m, 2853m, 2828s,1655m, 1638m, 1619m, 1546s, 1448m, 1393m, 1241s, 1202m, 1162w, 1066 w, 1026m, 926s, 890m, 840w, 807m, 767m, 733m cm^{-1}; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 7.3 (m, 2H), 7.2 (m, 2H), 5.9(s, 2H), 3.7–3.8 (m, 12H), 3.1 (m, 2H), 0.8 (d, J = 9.6 Hz, 1H), −0.7(d, J = 10 Hz, 1H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 32.9, 53.3, 67.4, 108.6, 117.8, 125.4, 127.3, 147.3; MS (70 eV) m/z (rel int) 312 (M^+, 100%), 226 (87), 196 (41), 195 (54), 141 (36); EA found: *C* 73.02%; *H* 7.80%; *N* 8.84%, calcd. for $C_{19}H_{24}O_2$: C, 73.05; H, 7.74; N, 8.97.

6.3. Hydrolysis of 2,5-dimorpholino-1,6-methano[10] annulene *3* to *4*

The solution of 100 mg (0.37 mmol) of **3** in 5 mL of 3 M of HCl and 3 mL of dioxane solution was refluxed for 30 min. The resulting solution was extracted with 5 mL of ether three times. The organic layer was washed with 3 mL of saturated $NaHCO_3$ solution three times and 3 mL of saturated NaCl solution three times and dried over anhydrous $MgSO_4$. The ether was removed by evaporation to give a yellow residue. The residue was column chromatographed on silica gel eluted with AcOEt–hexane (8:2) to give pure **4** in 78% yield.

4: pale yellow needles, mp 143–145 °C [11].

6.4. Synthesis of *4a, 12a-methano-naphthacene-5,12-dione* **5a**

To a solution of 20 mL of dry methanol, 28 mg (1.25 mmol) of Na metal was added and 308 mg (2.3 mmol) of *o*-phthalaldehyde and 400 mg (2.3 mL) of **4** was added dropwise under N_2 atmosphere at room temperature and then heated at 40 °C for 4 h with stirring. The reaction mixture was filtred and the filterate was neutralized by the addition of 3 M of HCl solution. The solution was extracted with 5 mL of $CHCl_3$ three times, the filter cake was dissolved in 5 mL of $CHCl_3$, and the combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by the evaporation, and the residue was column chromatographed on silica gel eluted by AcOEt–hexane (8:2) to give 418 mg (67%) of **5a** as pale yellow needles.

5a: pale yellow solid; mp 215–220 °C; IR (KBr) ν_{max} 3045w, 2369w, 2344w, 1680vs, 1620s, 1453m, 1298s, 1166m, 1001s, 706s, 565m cm^{-1}; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 8.65 (s, 2H), 8.05 (dd, J = 3.2, 6.0 Hz, 2H), 7.68 (dd, J = 3.2, 6.0 Hz, 2H), 7.06 (dd, J = 2.8, 8.0 Hz, 2H), 6.19 (dd, J = 2.8, 8.0 Hz, 2H), 2.62 (d, J = 4.4 Hz, 1H), 0.92 (d, J = 4.4, 1H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 191.9, 135.1, 129.7, 129.3, 129.3, 127.7, 122.1, 121.3, 44.6, 24.4; UV–vis (MeOH) λ_{max} 221 (log ε = 4.45), 268 (4.48), 363 nm (3.66); MS (70 eV) m/z (rel int) 272 (M^+, 66%), 271 (60), 244 (32), 243 (37), 216 (24), 215 (1 0 0), 213 (28).

6.5. 6,13-Diacetoxy-6,12-methano[10]annulene[*b*] naphthalene *6* and 6,12-diacetoxy-7h-cyclohepta[*b*] anthracene *7*

To a solution of 50 mg (0.18 mmol) of **5a** in 15 mL of AcOH, 500 mg of zinc powder was added and heated at 140 °C for 2 h. The solution was neutralized by the addition of saturated $NaHCO_3$ solution. The solution was extracted

by 5 mL of $CHCl_3$ three times. The combined organic layer was washed with saturated NaCl solution three times and dried over anhydrous $NaSO_4$. The solvent was removed by evaporation and the residue was column chromatographed on silica gel eluted by AcOEt–hexane (95:5) to give **6** as yellow needles in 33% (21 mg, 0.06 mmol) yield and also **7** as yellow needles in 32% (20 mg, 0.06 mmol) yield.

6: yellow solid; IR (KBr) ν_{max} 3420m, 2924s, 2853s, 1750s, 1626m, 1459m, 1184s, 804w cm^{-1}; ^1H NMR ($CDCl_3$-TMS) δ ppm = 8.42 (s, 2H), 7.99 (dd, J = 3.0, 6.2 Hz, 2H), 7.58 (dd, J = 3.2, 6.4 Hz, 2H), 7.09–7.06 (m, 2H), 6.38 (dd, J = 3.2, 8.4 Hz, 2H), 2.21 (s, 6H), 1.71 (d, J = 12.0 Hz, 1H), 13.9 (d, 12.0, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 169.1, 136.1, 131.6, 129.8, 128.9, 128.1, 127.1, 126.4, 125.7, 60.4, 29.2; UV–vis (MeOH) λ_{max} 204 (log ε = 3.87), 286 (3.95), 385 (2.79), 411sh nm (2.69); MS (70 eV) m/z (rel int) 268 (M^+, 100%), 267 (18), 265 (14), 253 (26), 252 (35).

7: pale yellow solid; mp 218–223 °C; IR (KBr) ν_{max} = 3447m, 2963m, 2365m, 1754s, 1428m, 1195s, 1039s, 794s cm^{-1}; ^1H NMR ($CDCl_3$-TMS) δ ppm = 8.33 (s, 1H), 8.32 (s, 1H), 7.98 (t, J = 5.0 Hz, 2H), 7.49–7.46 (m, 2H), 7.14 (d, J = 12.0 Hz, 1H), 6.52 (dd, J = 5.2, 12.0 Hz, 1H), 6.15 (dd, 5.2, 10.0 Hz, 1H), 5.98 (dt, J = 10.0, 6.8 Hz, 1H), 3.26 (d, J = 6.8 Hz, 2H), 2.63 (s, 3H), 2.59 (s, 3H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 169.4, 169.0, 141.4, 139.4, 131.9, 131.7, 130.4, 130.0, 129.0, 128.4, 128.4, 127.4, 126.8, 126.4, 126.3, 126.2, 126.1, 124.6, 27.8, 21.1, 20.8; UV–vis (MeOH) λ_{max} 202 (log ε = 4.40), 217 (4.14), 250sh (4.91), 256 (4.92), 265 (4.93), 293 (4.71), 345sh (3.65), 367 (3.89), 386 (4.02), 408 nm (3.95); MS (70 eV) m/z (rel int) 268 (M^+, 100%), 267 (18), 265 (14), 253 (26), 252 (35).

6.6. Rearrangement of diol *11*

To a solution of 50 mg (0.18 mmol) of **5a** in 20 mL of dry THF solution, three equivalents of MeLi in hexane solution were added under N_2 atmosphere and stirred at −10 °C for 30 min; H_2O was added to the solution and neutralized by 3 M of HCl solution. The solution was extracted by 5 mL of $CHCl_3$ three times. The combined organic layer was washed with saturated NaCl solution three times and dried over anhydrous $NaSO_4$. The solvent was removed by evaporation and the residue was column chromatographed on silica gel eluted by AcOEt–hexane (95:5) to give **12** as yellow needles in 29% (15 mg, 0.05 mmol) yield and also **13** as yellow needles in 16% (8 mg, 0.03 mmol) yield.

12: pale yellow solid; mp 161–168 °C; IR (KBr) ν_{max} = 2974w, 1637w, 1456m, 1375m, 1080m, 884m, 750s, 730s, 475m cm^{-1}; ^1H NMR ($CDCl_3$-TMS) δ ppm = 7.80 (dd, J = 3.6, 6.0 Hz, 1H), 7.75 (dd, J = 3.6, 6.0 Hz), 7.59 (s, 1H), 7.42 (s, 1H), 7.04 (dd, J = 3.2 Hz, 1H), 7.39 (dd, J = 3.2 Hz, 1H), 7.33 (dd, J = 2.0, 6.4 Hz, 1H), 7.12-7.08 (m, 2H), 6.93 (dd, J = 2.0, 6.4 Hz, 1H), 3.38 (d, J = 16.3 Hz, 1H), 2.86 (d, J = 16.3 Hz 1H), 2.13 (s, 3H), 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 148.6, 144.7, 142.6, 133.1, 132.9, 129.4, 128.0, 127.3, 126.1, 125.8, 125.6, 121.5, 118.7, 116.1, 82.5, 81.5, 40.8, 24.8, 19.9; MS (70 eV) m/z (rel int) 286 (M^+, 38%), 271 (28), 268 (26), 244 (46), 243 (100); HRMS observed: 286.1339; calcd. for $C_{21}H_{18}O$: 286.1358.

13: colorless solid; mp 109–113 °C; IR (KBr) ν_{max} 2925w, 2343w, 1820w, 1620m, 1088s, 903s, 772m, 750s, 476m cm^{-1}; ^1H NMR ($CDCl_3$-TMS) δ ppm = 7.91 (s, 1H), 7.84–7.82 (m, 3H), 7.45–7.43 (m, 2H), 7.41–7.39 (m, 1H), 7.28–7.26 (m, 1H), 7.25–7.22 (m, 1H), 6.88 (s, 1H), 5.38 (d, J = 2.0 Hz 1H), 5.33 (d, J = 2.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 151.6, 141.7 140.9, 136.4, 135.0, 134.0, 133.4, 132.5, 129.4, 128.2, 127.9, 127.8, 127.4, 127.3, 127.0, 126.1, 126.0, 125.1, 118.4, 25.6; UV–vis (MeOH) λ_{max} 206sh (log ε = 2.52), 219 (4.55), 245 (4.64), 279 (4.21), 314 nm (4.18); MS (70 eV) m/z (rel int) 268 (M^+, 100%), 267 (18), 265 (14), 253 (26), 252 (35); HRMS observed: 268.1246; calcd. for $C_{21}H_{16}$: 268.1252.

6.7. 1,6-Methano[10]annuleno[3,12-b]-6,9-naphthoquinone *18*

A solution of 80 mg (0.34 mmol) of sulfinate **14** and 130 mg (1.2 mmol) of *p*-benzoquinone in 2 mL of dry DMF was heated at 135 °C for 2 h with stirring. Then 30 mL of 3 M HCl solution was added and extracted with $CHCl_3$ (30 mL × 3). The solution was washed with saturated $NaCO_3$ and saturated NaCl solution (two times) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was column chromatographed on silica gel eluted by chloroform to give **18** as red crystals in 51% (47 mg, 0.17 mmol) yield.

18: red crystals; mp 143–145 °C; ^1H NMR ($CDCl_3$-TMS) δ ppm = 8.71 (2H, s), 7.50 (4H, s), 7.05 (2H, s), 6.73 (2H, dm, J = 9.2 Hz), 1.15 (1H, d, J = 10.0 Hz), −0.25 (1H, d, J = 10.0 Hz); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 184.7, 139.9, 137.0, 132.6, 131.9, 128.8, 126.9, 126.6, 126.3, 32.0. IR (KBr) ν_{max} 2925m, 1661s, 1590s, 1351m, 1297s, 1055m, 940w, 848s cm^{-1}; UV–vis (CH_3OH) λ_{max} 203sh (log ε = 4.20), 219sh (4.13), 247 (4.27), 284 (4.53), 327 (3.85), 343 (3.90), 489 nm (3.62); UV–vis (CH_2Cl_2) λ_{max} 252 (log ε = 4.16), 287 (4.23), 346(3.62), 497 nm (3.30); MS (70 eV) m/z (rel int) 272 (M^+, 19.7%), 149 (70.1), 77 (71.8), 57 (100); HRMS (M^+) observed: 272.0831; calcd. for $C_{19}H_{12}O_2$: 272.0837.

6.8. Bis1,6-methano[10]annuleno[2,3-b;6,7-i]-9,10-anthraquione *20*

A solution of 16 mg (0.07 mmol) of sulfinate **14** and 14 mg (0.05 mmol) of **4** in 2 mL of dry DMF was heated at 140 °C for 2 h with stirring. Then 30 mL of 3 M HCl solution was added and extracted with $CHCl_3$ (30 mL × 3). The solution was washed with saturated Na_2CO_3 and saturated NaCl solution (two times) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was column chromatographed on silica gel eluted

by chloroform to give **20** as orange crystals in 31% (7 mg, 0.016 mmol) yield.

20: orange crystals; mp 143–145 °C; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 9.06 (4H, s), 7.55 (8H, m), 6.72 (4H, dm, J = 8.0 Hz), 1.24 (1H, d, J = 10.0 Hz), −0.09 (1H, d, J = 10.0 Hz); IR (KBr) ν_{max} 2926m, 2853m, 1673s, 1579m, 1346m, 1285s, 692s cm^{-1}; UV–vis (CH_3OH) λ_{max} 203 (log ε = 5.96), 224 (5.77), 264 (5.85), 289 (5.81), 470 (4.96) nm; UV–vis (CH_2Cl_2) λ_{max} 231 (log ε = 3.93), 270 (4.03), 297 (4.06), 343sh (3.76), 485 nm (3.09); MS (70 eV) m/z (rel int) 436 (M^+, 51%), 250 (32), 149 (42), 69 (84), 55 (100); HRMS observed: 436.1475; calcd. for $C_{32}H_{20}O_2$: 436.1463.

6.9. 1,6-Methano[10]annuleno[2,3-b;6,7-i]-9,10-anthraquinone 22

A solution of 100 mg (0.43 mmol) of sulfinate **14** and 237 mg (1.50 mmol) of 1,4-naphthoquinone in 2 mL of dry DMF was heated at 140 °C for 2 h with stirring. Then 30 mL of 3 M HCl solution was added and extracted with $CHCl_3$ (30 mL × 3). The solution was washed with saturated Na_2CO_3 and saturated NaCl solution, (two times) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was column chromatographed on silica gel eluted by chloroform to give **22** as orange crystals in 54% (75 mg, 0.23 mmol) yield.

22: orange crystals; mp 233–235 °C; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 8.97 (s, 2H), 8.41 (m, 2H), 7.83 (m, 2H), 7.55 (s, 2H), 7.52 (m, 2H), 6.72 (dd, J = 6.8, 3.2 Hz, 2H), 1.21 (d, J = 9.6 Hz, 1H), −0.14 (d, J = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 183.0, 137.5, 134.6, 134.1, 132.7, 132.6, 129.2, 128.3, 127.4, 126.5, 126.2, 32.1; IR (KBr) ν_{max} 3024m, 2950m, 1671s, 1584s, 1285s, 702s cm^{-1}; UV–vis (CH_3OH) λ_{max} 204 (log ε = 3.30), 285 (3.66), 328 (3.19), 472 nm (2.80); UV–vis (CH_2Cl_2) λ_{max} 259sh (log ε = 3.48), 290 (3.74), 339 (3.23), 472 nm (2.81); MS (70 eV) m/z (rel int) 322 (M^+, 100), 321 (32), 149 (50) 57 (42); HRMS observed: 322.0963; calcd. for $C_{23}H_{14}O_2$: 322.0994.

6.10. 1,6-Methano[10]annuleno[2,3-b]benz[6,7]-9,10-anthraquione 23

A solution of 90 mg (0.39 mmol) of sulfinate **14** and 160 mg (0.77 mmol) of 1,4-anthraquinone in 2 mL of dry DMF was heated at 140 °C for 1 h with stirring. Then 30 mL of 3 M HCl solution was added and extracted with $CHCl_3$ (30 mL × 3). The solution was washed with saturated $NaCO_3$ and saturated NaCl solution (two times) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was column chromatographed on silica gel eluted by chloroform to give **23** as orange crystals in 33% (48 mg, 0.13 mmol) yield.

23: orange powder; mp 237–240 °C; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 9.05 (s, 2H), 8.95 (s, 2H), 8.13 (m, 2H), 7.72 (m, 2H), 7.55 (s, 2H), 7.53 (m, 2H), 6.72 (dd, J = 4.4, 2.8 Hz, 2H), 1.23 (d, J = 9.6 Hz, 1H), −0.11 (d, J = 9.6 Hz, 1H); IR (KBr) ν_{max} 2928m, 1674s, 1456m, 1281s, 990 m, 761 m cm^{-1}; UV–vis (CH_3OH) λ_{max} 205 (log ε = 3.63), 233 (3.82), 249 (3.72), 288 (3.60), 296 (3.60), 406 (2.99), 457 (2.99), 515sh nm (2.73); UV–vis (CH_2Cl_2) λ_{max} 235 (log ε = 3.21), 302 (3.45), 338sh (3.11), 396sh (2.65), 465 nm (2.58); MS (70 eV) m/z (rel int) 372 (M^+, 100), 315 (33), 158 (52), 129 (70), 91 (72); HRMS observed: 372.1273; calcd. for $C_{27}H_{16}O_2$: 372.1284.

6.11. 1,6-Methano[10]annuleno[3,4-b]phenanthroline-5,6-dione 24

A solution of 115 mg (0.49 mmol) of sulfinate **14** and 154 mg (0.98 mmol) of 1,2-naphthoquinone in 2 mL of dry DMF was heated at 140 °C for 2 h with stirring. Then 30 mL of 3 M HCl solution was added and extracted with $CHCl_3$ (30 mL × 3). The solution was washed with saturated Na_2CO_3 and saturated NaCl solution (two times) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was column chromatographed on silica gel eluted by chloroform to give **24** as orange crystals in 15% (23 mg, 0.07 mmol) yield.

24: purple powder; mp 205–210 °C; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 8.88 (s, 1H), 8.58 (s, 1H), 8.25 (m, 2H), 8.22 (m, 2H), 7.50 (m, 3H), 7.41 (d, J = 7.2 Hz, 2H), 6.71 (dd, J = 10.0, 4.0 Hz, 2H), 1.24 (d, J = 10.0 Hz, 1H), 0.02 (d, J = 10.0 Hz, 1H); IR (KBr) ν_{max} 2926m, 1666s, 1585s, 1326s, 1287s, 1247m, 1209m, 773m cm^{-1}; UV–vis (CH_3OH) λ_{max} 203 (log ε = 4.35), 252 (4.41), 298 (4.13), 3.55 (3.75), 522 nm (4.01); UV–vis (CH_2Cl_2) λ_{max} 228sh (log ε = 4.18), 255 (4.52), 301 (4.22), 352 (3.87), 492 (3.14) 529 nm (3.20); MS (70 eV) m/z (rel int) 322 (M^+, 42%), 294 (100), 265 (53), 69 (36), 57 (32). HRMS observed: 322.0989; calcd. for $C_{23}H_{14}O_2$: 322.1005.

6.12. 1,2-Benzo[a]-(1,6-methano[10]annuleno[3,4-b]benzo)[2,3-c]phenazine 25

A solution of 18 mg (0.06 mmol) of quinone **24**, 9.0 mg (0.09 mmol) of *o*-phenylenediamine, and 6 mg of $NaHSO_3$ in 1 mL of ethanol and $CHCl_3$ was heated at 140 °C for 2 h with stirring. Then 30 mL of 3 M HCl solution was added and extracted with $CHCl_3$ (30 mL × 3). The solution was washed with saturated $NaCO_3$ solution, saturated Na_2Cl and (two times) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was column chromatographed on silica gel eluted by chloroform to give **25** as orange crystals in 64% (14 mg; 0.04 mmol) yield.

25: yellow crystals; mp 205–210 °C; ^{1}H NMR ($CDCl_3$-TMS) δ ppm = 9.91 (s, 1H), 9.33 (d, J = 8.0 Hz, 1H), 9.05 (s, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.32 (m, 2H), 7.84 (t, J = 4.0 Hz, 2H), 7.79 (t, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.47 (m, 3H), 7.39 (s, 1H), 6.60 (dd, J = 6.8, 4.0 Hz, 2H), 1.39 (d, J = 10.0 Hz, 1H), 0.25 (d, J = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$-TMS) δ ppm = 143.1, 142.9, 142.1, 136.2, 134.2, 133.0, 132.7, 132.2, 130.5, 130.5, 130.4, 129.8, 129.7, 129.6, 129.4, 129.3, 129.3, 128.3, 128.1, 127.1, 126.4, 125.7, 125.4, 124.8, 123.9, 123.0, 32.2;

IR (KBr) ν_{max} 2923m, 1345m, 1058m, 762m, 487s cm^{-1}; UV–vis (CH_3OH) λ_{max} 205 (log $\varepsilon = 4.11$), 221 (4.06), 277 (4.27), 310 (4.42), 375 (3.88), 443 nm (3.40); UV–vis (CH_2Cl_2) λ_{max} 279 (log $\varepsilon = 4.60$), 3.14 (4.76), 377 (4.23), 446 nm (3.73); MS (70 eV) m/z (rel int) 394 (M^+, 100%), 196 (13).

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