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SYNTHESIS AND PROPERTIES OF *anti*-6,15-EPITHIA-8,13-METHANOBENZO[*e*][14]ANNULENE-7,14-DIONE, *anti*-5,14-EPITHIA-7,12-METHANOFURO[3,4-*e*]-[14]ANNULENE-5,13-DIONES, AND THEIR IONIC SPECIES

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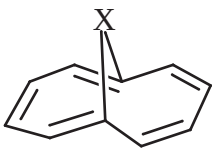
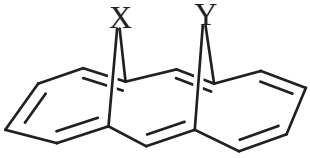
Abstract-The sulfur bridged annulene diones fused with benzene and furan were synthesized, and their ^{1}H and ^{13}C NMR spectra in strong acid media indicated formation of dicationic species in which the positive charges localized on the carbonyl carbons, mainly due to the unfavorable p-orbital overlap.

INTRODUCTION

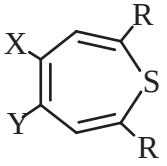
Although many kind of bridged annulenes, the methano-, oxido-, iminoannulenes (**1a~c**) and their higher vinylogues (**2a~c**), have been investigated,[1a-f] none of sulfur bridged annulene has been reported yet. The reason for this may be due to the lability of the sulfur-carbon linkage incorporated π-conjugated systems as seen in thiepins and 1-thia-4,9-methano[11]annulenes (**3a~c**)[2] and the longer bond length of C-S than those of C-C, C-O, and C-N, because the radius of sulfur atom is larger than those of second-low elements in the periodic table such as carbon, oxygen, and nitrogen. It is of interest to know the influence of bridged sulfur atom on the stability of annulene molecule and also of the stereochemical relationship between sulfur and methylene bridges on the peripheral conjugation.[1a] In this paper, we describe the synthesis of *anti*-6,15-epithia-8,13-methanobenzo[*e*][14]annulene-7,14-dione (**7**),[3] anti-3,11-epithia-1,13-methanofuro - [3,4-*e*][14]annulene-2,17-diones (**9**) and (**10**) and their ionic species.



1a ; X = CH_2
1b ; X = O
1c ; X = NH



2a; X = Y = CH_2
2b; X = Y = O
2c; X = Y = NH
2d; X = CH_2, Y = NH



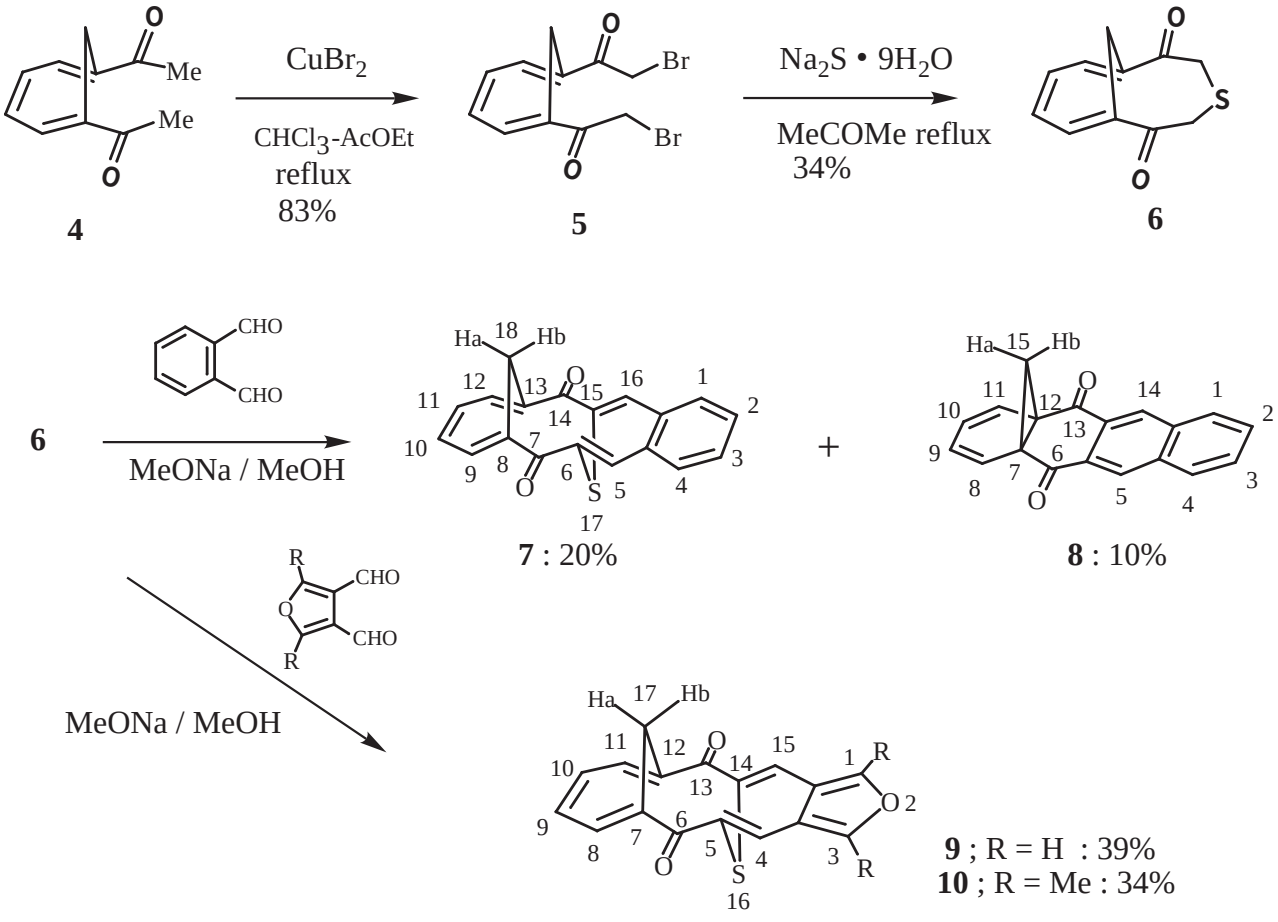
3a; R = X = Y = H
3b; R = COOMe, X = Y = H
3c; R = COOMe, X;Y = -(CH=CH)-

Figure 1

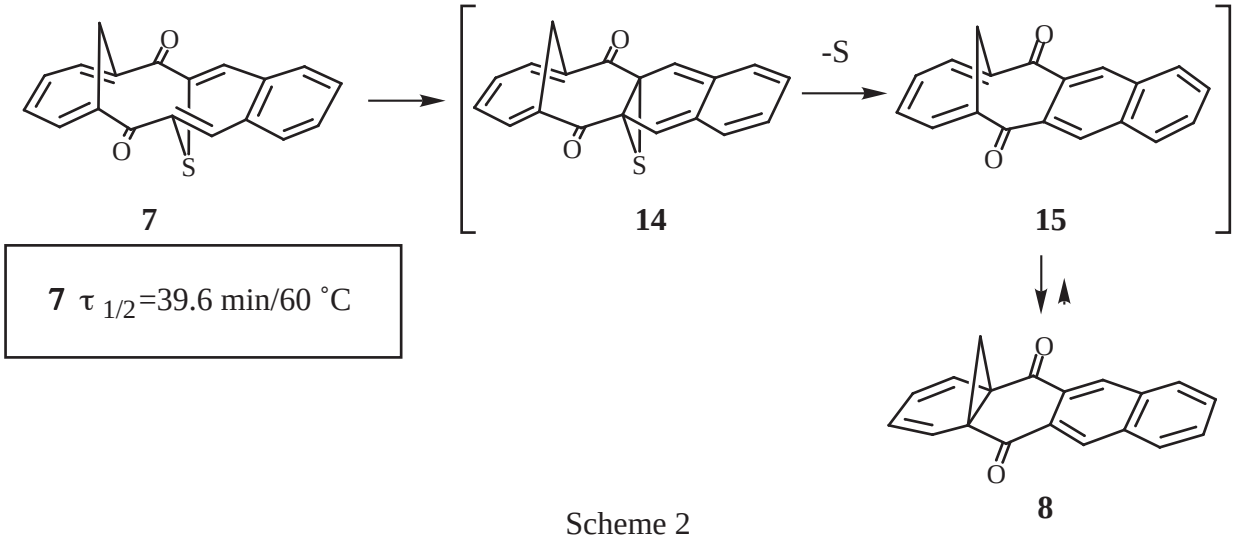
* Dedicated to Prof. Dr. S. Itô on occasion of his 77th birthday.

SYNTHESIS OF 7, 9, AND 10

The bicyclic sulfide (**6**) was prepared from 1,6-diactyl-1,3,5-cyclohexatriene (**4**) in two steps; bromination of **4** with cupric bromide[4a, 4b] gave 1,6-bis(bromoacetyl)cyclohepta-1,3,5-triene (**5**) in 83% yield, and subsequent treatment of **5** with aqueous sodium sulfide gave **6** in 34% yield as shown in Scheme 1. The reaction of the bicyclic sulfide (**6**) with *o*-phthalaldehyde in the presence of sodium methoxide in dry methanol at room temperature[5] gave exclusively one of the possible stereoisomers (**7**) as fairly stable compounds in 20%, accompanied with 10% yield of **8** as pale yellow needles. The furan fused annulenes (**9**) and (**10**) also prepared with 3,4-diformylfuran and 3,4-diformyl-2,5-dimethylfuran under the same conditions in 39% and 34% yields, respectively. In the latter reactions, however, no desulfurized product was detected, probably because the latter furoquinones are hard to form thiiren (*ortho*-quinoidic form) intermediates for desulfurization. The structures of these products were confirmed fully by the spectral data and elemental analyses (*vide infra*). Indepenedent thermolysis of **7** in refluxing benzene gave **8** quantitatively. The thermolysis of **7** was monitered by the ^{1}H NMR spectroscopic measurement of decreasing the integration of the bridged methylene protons of **7** to give a half life (τ) of **7** as 40 min at 60 ˚C, which is comparable to that of benzothiepins (**11**) (58 min/47 ˚C)[6] and their derivatives (**12**) and (**13**) as shown in Table 1. It suggests that the mechanism of the desulfulization of **7** proceeds in the operation of similar mechanism to that of the transformation of **13** to 2-ethoxycarbonylnaphthalene *via* thiiren as benzothianorcaradiene.[7] That is, **7** transform to **15** *via* the thiiren (**14**), and then it equilibriated to **8**, as can be seen in the similar equilibrium system of 1,6-methano[10]annulene-2,5-dione (**16**) and **17**, which the equilibrium inclined toward norcaradiene form.[8]

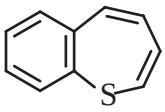
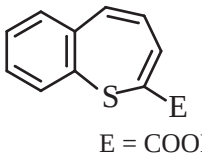
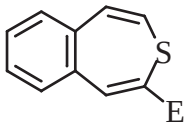


Scheme 1



Scheme 2

Table 1. The half life times (τ) of benzothiepine and its derivatives

	 E = COOEt	
11 $\tau_{1/2}$= 58 min/47 ˚C	**12** $\tau_{1/2}$= 352 min/47 ˚C	**13** $\tau_{1/2}$= 57 min/25 ˚C

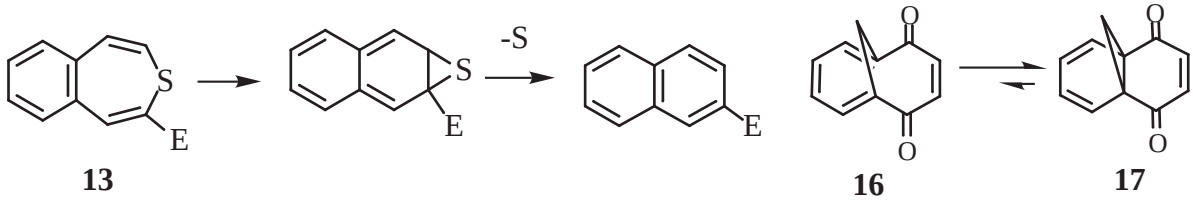


Figure 2

THE DETERMINATION OF THE STRUCTURES OF 7, 8, 9, AND 10 BY THE SPECTRAL DATA AND THE ASSIGNMENTS OF THE ^{1}H- AND ^{13}C- NMR SPECTRA

Although the IR spectra of **7**, **9**, and **10** showed their carbonyl absorption bands at 1657, 1655, and 1655cm^{-1}, respectively, that of **8** was observed at 1678cm^{-1} probably due to less conjugation. While MS spectra of **9** and **10** show their parent peaks with adequite intensity at m/z=294 and 322, respectively, that of **7** at m/z=304 in the same ionization energy displays a 0.12% intensity of its parent peak and relatively large fragment peaks, also indicating easiness of desulfurization in **7**. The bridged methylene protons resonated rises at δ 3.50 and 2.04 with a large geminal coupling constant of 14.2 Hz, clearly indicating that the cycloheptatriene moiety has the open form. The benzene ring protons resonated at δ 7.65 and 7.51, the signal at δ 7.69 is assigned for protons at 5- and 16- positions, similarly to those of 2,7-bis(methoxycarbonyl)benzothiepine.[6] The signals at δ 7.03 and 6.91 are assigned for 9-, 12- and 10-,

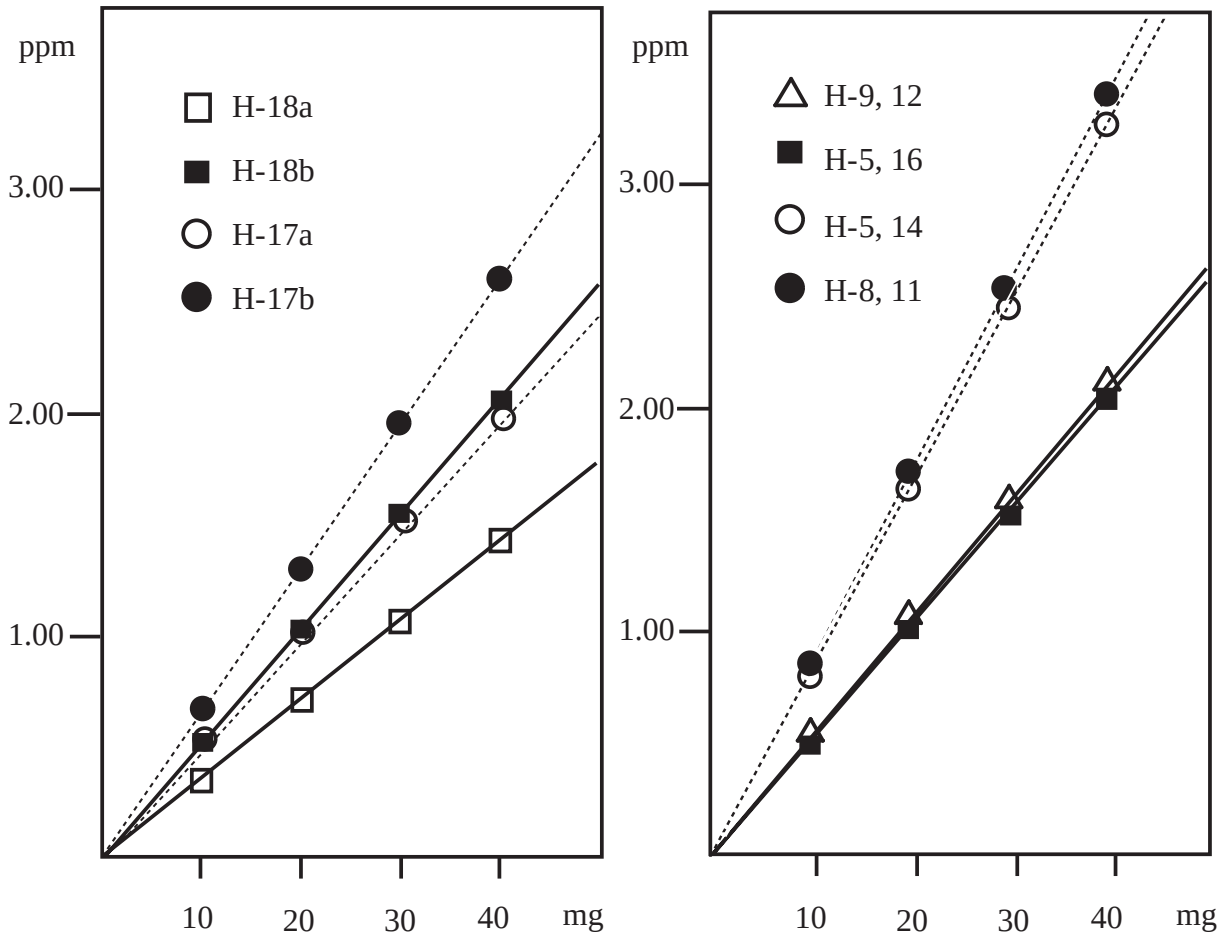
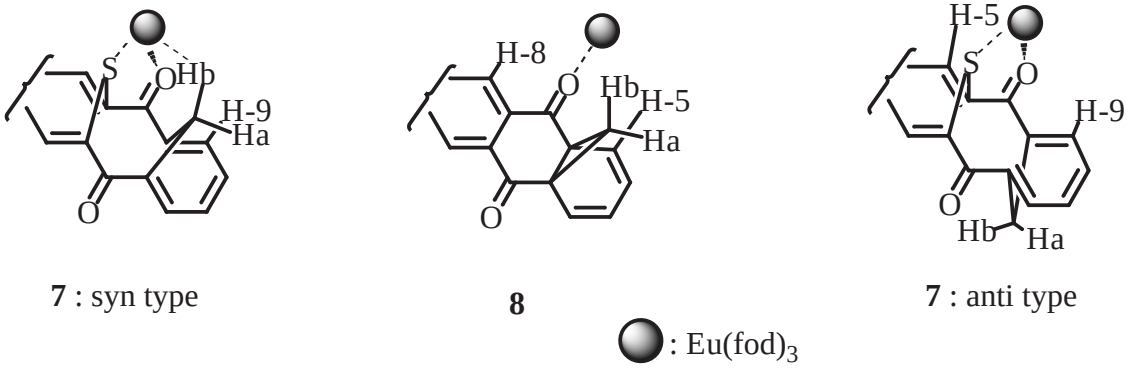


Figure 3 Changes of the ^{1}HNMR chemical shifts of the protons on the methylene and peri-positions of carbonyl groups of **7** (solid line) and **8** (dotted line) by adding $Eu(fod)_3$



7 : syn type **8** **7** : anti type

Figure 4

11-positions, respectively. The ^{13}C NMR spectrum of **7** showed 10 peaks and the carbonyl carbons resonated at δ197.6 which is lower than that of anthraquinone and is similar to those of normal enones.[9] The assignment of all carbons was performed by the C-H COSY and HMBC methods. The *anti* configuration between two bridges of **7** was elucidated by the fact that the chemical shift of the inner protons (H18-b) on the methylene bridge carbon in **7** was observed at higher field (δ 3.50) than that of 4,9-methano-1-thia[11]annulene which has *syn* conformation (δ 6.28).[2] This stereochemical relationship

was also supported by the examination of ^{1}H NMR measurements in the presence of an europium shift reagent. The ^{1}H chemical shifts of methylene protons of **7** and **8** were propotionally shifted to the down field by addition of Eu(fod)$_3$. And the magnitude of the shifts of the methylene protons of **7** are smaller than those of **8** by the comparison of the proportional constants (**7**: 5.77 for H-18b, 3.96 for H-18a, **8**: 7.96 for H-17b, and 5.47 for H-17a, respectively) obtained simply by plotting the shifts values against the amount of Eu(fod)$_3$ as shown in Figure 3. And those of both peri-positions of **7** are less than those of **8**. It indicates that the influence of the anisotropic effect of the shift reagent on the protons on the methylene and peri-positions of carbonyl groups in **8** is greater than those of **7**. It is rationally explained as follows; the influence of the paramagnetic europium complex on the chemical shifts of methylene protons is less when it places rather between the carbonyl oxygen and sulfur atom by its donation charactor[10] in the *anti* configuration of **7** than just on the carbonyl oxygen in **8** otherwise those of syn configuration will be greater than **8** as illustrated in Figure 4. The structure of **8** having a norcaradiene form was confirmed by the spectral data by the similar methods as above and the assignment of ^{1}H NMR signals is shown in Figure 6. Especially, the signals observed at δ 2.62 and 0.92 as doublet were assigned for as methylene protons on the cyclopropane ring with its small coupling constant of 4.8 Hz which is in the range of typical values for cyclopropanes.[11] And the ^{13}C NMR spectrum showed 10 peaks and the carbonyl carbons resonated at δ 192.0 which is rather similar to those of normal enones.[9] The structures of furan fused compounds (**9**) and (**10**) were also confirmed in the similar way as described above. The ^{1}H NMR spectra of **9** showed that the signals observed at δ 3.55 and 2.12 were assigned for the inner and outer protons of bridged methylene respectively with a geminal coupling constant of 14.2 Hz, which is similar value corresponding to that of **7**, showing the cycloheptatriene form. And the signals at δ 7.00 and 6.91 were

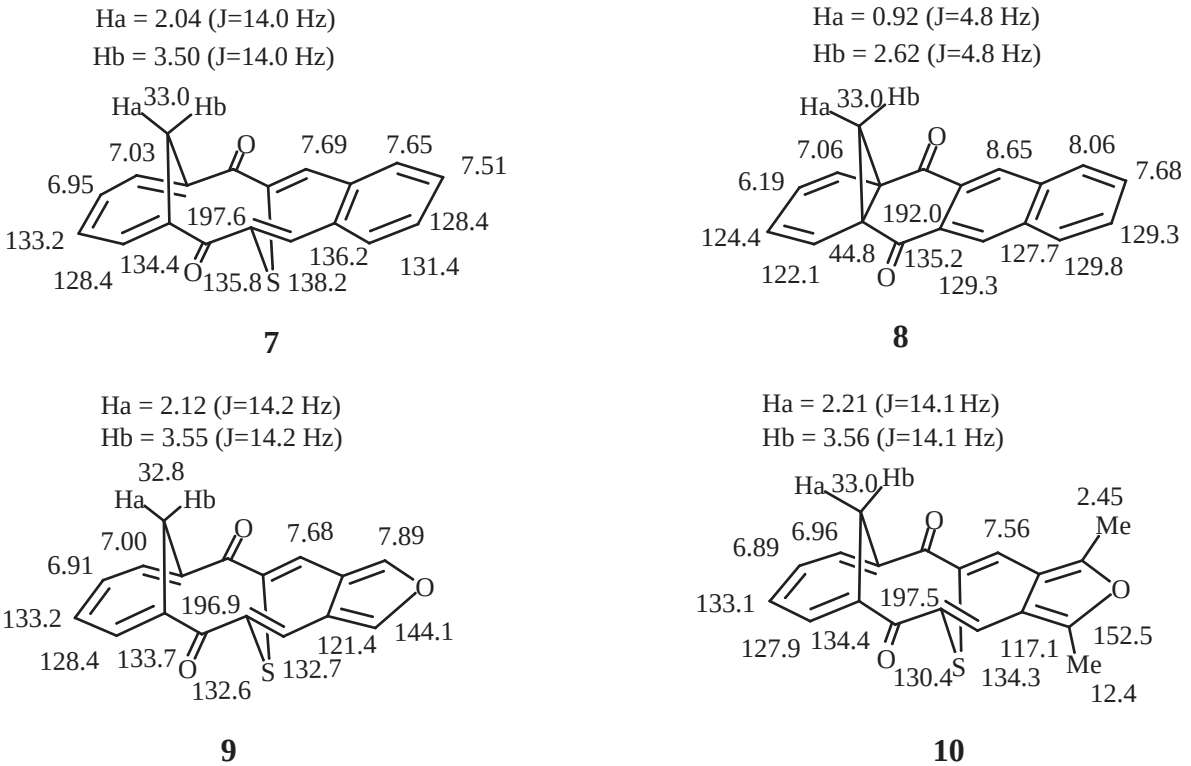
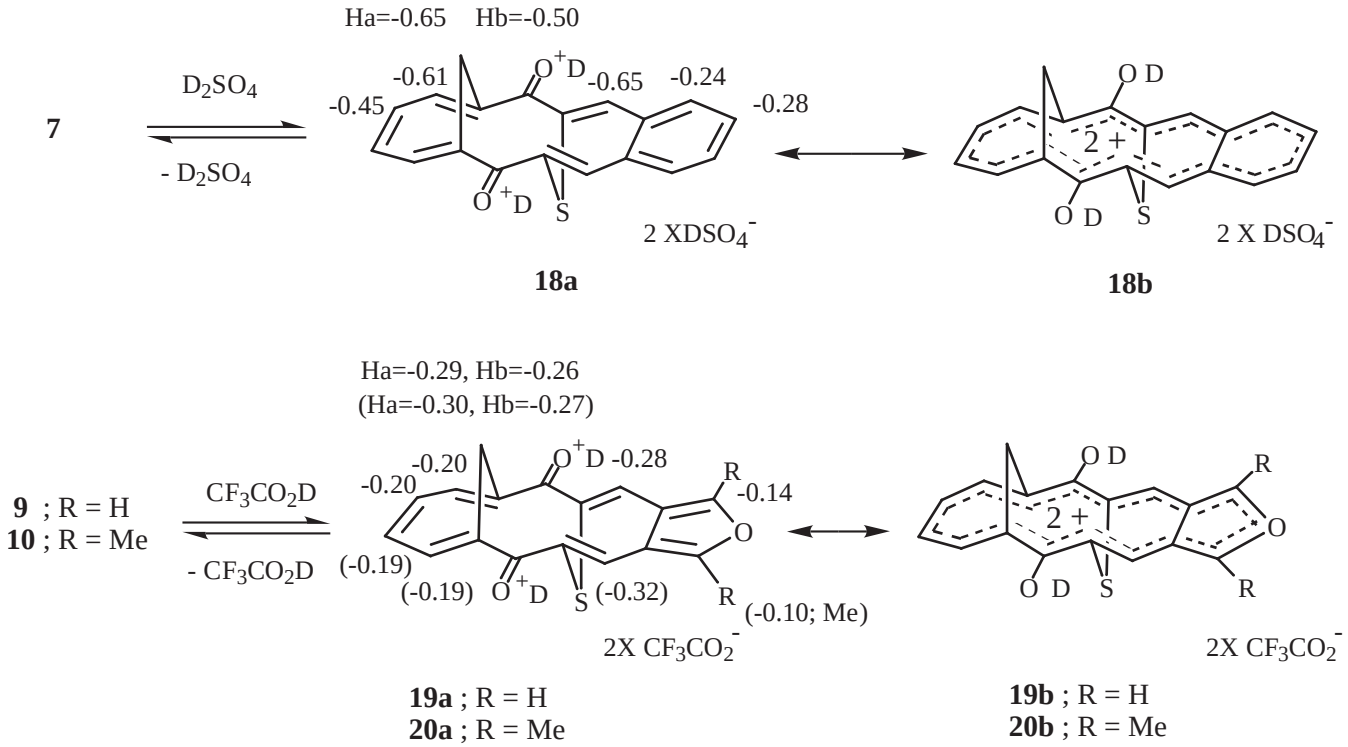


Figure 5. The assignments of the ^{1}H and ^{13}C NMR chemical shifts of **7**, **8**, **9**, and **10**

assigned for 14- and 15-positions, respectively. And the signals at δ 7.89 could be assigned for the ring protons on 2- and 4-positions by the comparison with those of 2,4-dimethyl derivative (**10**); the signal corresponding to the resonance at δ 7.89 observed in **9** is absent in **10**. The ^{13}C NMR spectra showed 9 peaks at slightly lower field than those of **9** except for the carbonyl carbons resonated at δ197 which is almost the same to that of **7** (δ 198). The assignments of the ^{1}H and ^{13}C NMR chemical shifts are illustrated in Figure 5.

THE FORMATION OF DICATIONIC SPECIES (18a, 19a, AND 20a) BY PROTONATION OF 7, 9, AND 10 IN D_2SO_4 AND CF_3COOD

7, **9** , and **10** were expected to form dicationic species by protonation in strong acid media and it is interested to know whether the positive charge delocalizes on a periphery of p-orbital array to form a 16 π electron system or localize at carbonyl carbons. The ^{1}H NMR spectrum of **7** in D_2SO_4 showed the formation of dicationic species **18a** by deuterionation as shown in Scheme 3. The addition of large excess of water to this solution gave a quantitative recovery of the starting material (**7**) indicating the stability of dicationic species. Both olefinic and methylene protons of **18a** were observed at slightly lower field in about 0.5-0.7 ppm compared to those of **7** in $CDCl_3$. It suggests a little contribution of 16 π electron peripheral conjugation having a paratropicity. In the ^{13}C NMR spectrum of **7** in H_2SO_4 the signal for carbonyl carbons resonated at δ 212.6 ppm which was clearly lower than that in $CDCl_3$ strongly indicates the localization of positive charges at carbonyl carbons, since the ^{13}C chemical shifts of carbonyl carbons of localized dicationic species formed by protonation of condensed quinones in H_2SO_4 were reported to be rather higher than those of $CDCl_3$.[12] The localization of charge in this cationic species might be attributedto



Scheme 3

the unfavorable conjugation through the distorted p-orbitals resulted from the *anti* configuration between methylene and sulfur bridges as seen in the case of the anti bismethylene bridged [14]annulene,[13] and additionally due to the formation of unstable paratoropic system by 16 π electron periphery. Thus, the structure of diacationic species formed can be best regarded as the form (**18a**) but not **18b**. Although dissolving **9** and **10** in D_2SO_4 resulted in quick decomposition of these compounds, those gave dicationic species (**19a**) and (**20a**) in CF_3CO_2D, their ^1H NMR spectrum indicates the little down field shift of the proton signals compared with those in $CDCl_3$, indicating week deuterionation on the carbonyl oxygene in **9** and **10**. The less magnitude of these shift compared with those of **7** in D_2SO_4 might be attributed to less acidity of CF_3CO_2D. The ^{1}HNMR-chemical shifts differences of down field from neutral species to dicationic species are indicated by minus values as shown in Scheme 3. In the case of **20a**, the values are shown in parenthesis. The ^1H NMR spectra of **7** , **8**, **9**, **10**, and their dicationic species except for **19a** formed in strong acidic media are shown in Figure 6.

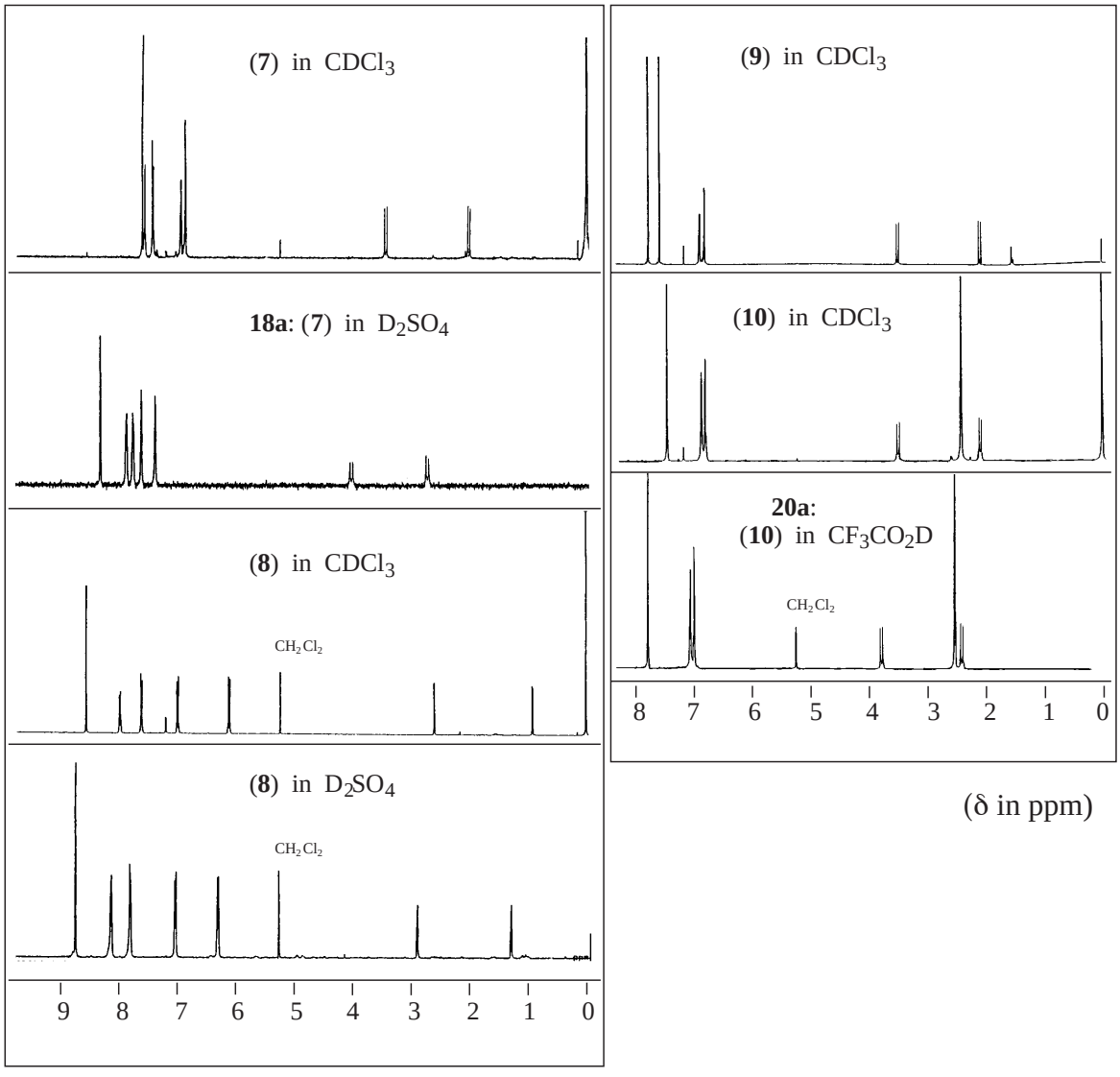
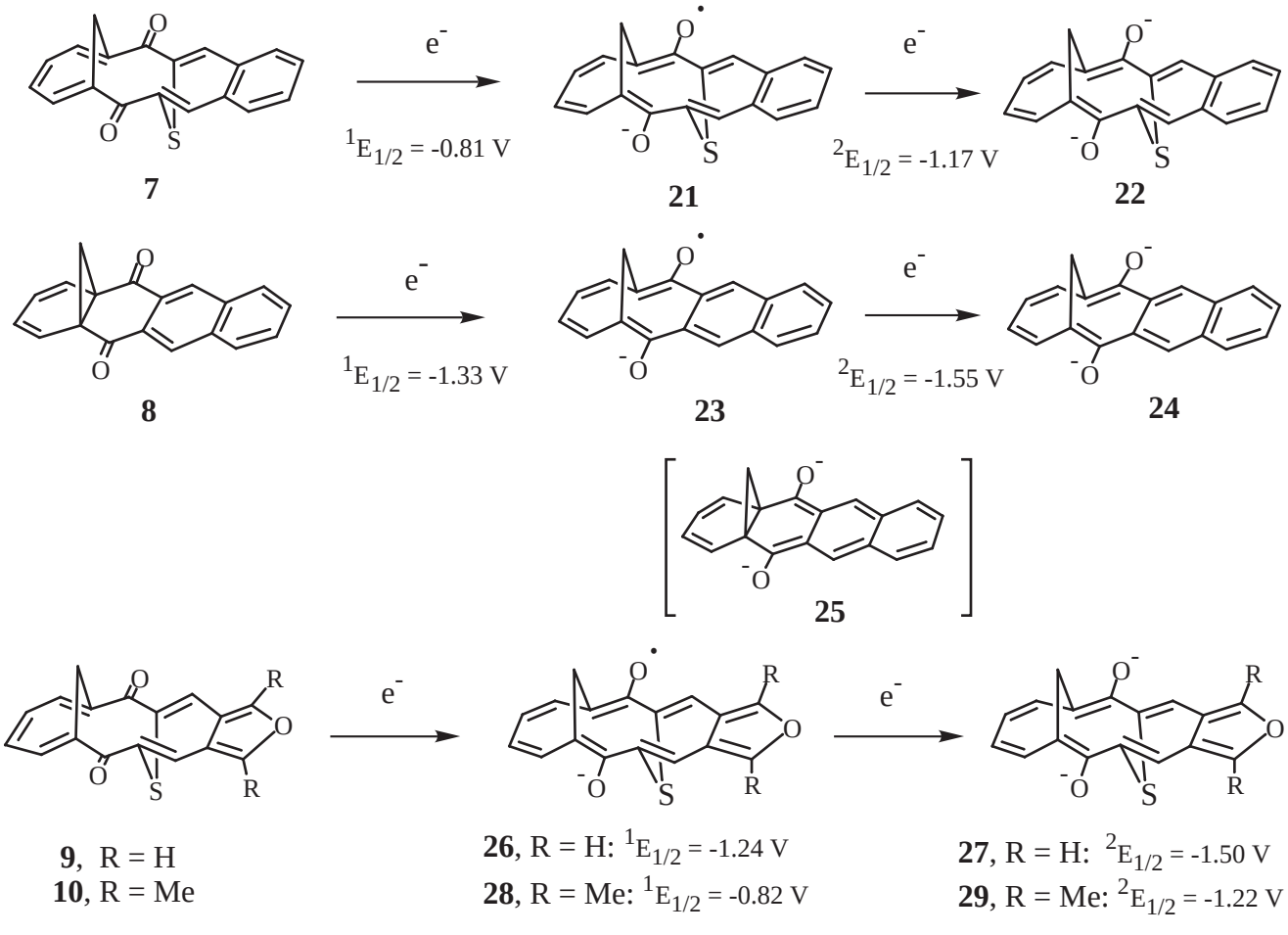


Figure 6. The ^{1}HNMR spectra of **7**, **8**, **9**, **10** and their cationic species in strong acids which are shown in the chart

THE FORMATION OF THE DIANIONIC SPECIES (22, 24, 27, AND 29) BY ELECTRICAL REDUCTION

The cyclic voltammograms (CV) of **7** in dimethyl sulfoxide (DMSO) showed two reversible half-wave reduction potentials ($^1E_{1/2}$= -0.81V, $^2E_{1/2}$= -1.17V) and a little difference between two potentials compared with those of anthraquinone ($^1E_{1/2}$= -0.78 V, $^2E_{1/2}$= -1.45 V)[14] was observed, indicating greater stability of the radical anions and dianions, as **21** and **22** than corresponding species of anthraquinone. And those of **8** were observed at more negative than those of **7**, indicating the instability of **8** ($^1E_{1/2}$= -1.33 V, $^2E_{1/2}$= -1.50 V) compared to **7**. Since formation of the dianion (**25**) should be less favorable because of its high-energy *o*-quinodimethane structure, it is suggested that **25** requires the extra energy for opening of the cyclopropane ring in the process of electron reduction to form **24** as shown in Scheme 4.Similarly the half-wave reduction potentials of **9** and **10** in DMSO were also obtained by the CV method. Althoguh the first reduction potential of **9** appeared at -0.89 V having no corresponding oxidation potential, the CV values of **9** ($^2E_{1/2}$ = -1.24 V) and **10** ($^1E_{1/2}$= -0.82 V, $^2E_{1/2}$= -1.22 V) are almost similar to those of **7**. The half-wave reduction potentials of these new quinone compounds indicate the formation of 18 π electron dianionic species (**27**) and (**29**) and the stablilty corresponding to that of anthraquinone. Though the exact extend of the delocalization of negative charges on carbonyl groups could not be determined by this method, and therefore the diamagnetism of these dianiones were also left unknown.



Scheme 4

ACKNOWLEDGEMENT

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EXPERIMENTAL

All the melting points were uncorrected. The IR spectra were taken on a JASCO IR-810 spectrometer, the UV-VIS spectra were recorded on a Shimazu UV-265FS. The ^{1}H NMR spectra were taken on Hitachi R-24 (60 MHz) on JEOL-FX90 (90 MHz), and JEOLα400 (400 MHz) spectrometers, and ^{13}C NMR spectra were taken on JEOL-FX90 (23 MHz) and JEOLα400 (100 MHz), in chloroform-*d* (TMS as internal standard) and DMSO-d_6 (CH_2Cl_2 as internal standard). The MS spectra were taken on a JEOL-OISG-2 mass spectrometer. The Cyclic voltammetric measuraments were done on a Yanco p-1100 and were carried out in a one-compartment cell consisting of a glassy carbon working electrode a platinum wire auxiliary electrode, and Ag/Ag^{+} reference electrode. Dimethylsulfoxide (DMSO) used as solvent was deoxygenated by passing a stream of nitrogen gas into the solution prior to recording the data. All potentials are quoted by volt *vs*. SCE electrode. And the i_{pa}/i_{pc} values are shown in parenthesis after the $E_{1/2}$ values.

1,6-Bis(bromoacetyl)cyclohepta-1,3,5-triene (5).

The reaction of 1,6-diacetylcyclohepta-1,3,5-triene (**4**) (5.00 g, 28.4 mmol) with cupric bromide ($CuBr_2$) (12.7 g, 56.8 mmol) in the presence of catalytic amount of ethyl acetate (*ca.* 0.5 mL) in 300 mL of $CHCl_3$ at refluxing for 2 h, and then the same amount of $CuBr_2$ (12.7 g, 56.8 mmol) was added and refluxed again for 2 h. The reaction mixture was filtered and the solids was washed three times with $CHCl_3$. The filterate was combined and the solvent was evaporated. The residue was chromatographed on silica gel. From 20% of AcOEt-hexane elution, 7.86 g (83%) of pale yellow solid of **5** was obtained as first fraction. **5**: pale yellow needles, mp 94-97 ˚C (hexane-CH_2Cl_2), IR (KBr) ν_{max} 3004w, 2949w, 1681s, 1600w, 1529w, 1428m, 1387m, 1276m, 1191s, 1144m, 1071m, 1021m, 981m, 852w, 749s, 700w, 641m cm^{-1}: ^{1}H NMR ($CDCl_3$-TMS) δ=7.28 (m, 2H), 7.04 (m, 2H), 4.30 (s, 4H), 3.04 (s, 2H): ^{13}C NMR ($CDCl_3$-TMS) δ=190.4 (C=O), 134.6, 133.9, 130.9, 30.7, 25.2: MS m/z (70 eV) 336, 334, 332 (M^{+}, 0.5, 0.7, 0.7%), 255, 253 (M^{+}-Br, 100, 90%), 213 (8%), 211 (8%), 175, (17%): *Anal*. Calcd for $C_{11}H_{10}O_2Br_2$: C, 39.56; H, 3.02. Found: C, 39.79; H, 3.00.

4-Thia-1,7-methano[11]annulene-2,6-dione (6).

The dibromide (**5**) (6.87 g, 20.6 mmol) was dissolved in 400 mL of acetone, and a solution of 4.94 g (20.6 mmol) of $Na_2S \cdot 9H_2O$ dissolved in a minimum volume of water was added to this solution dropwise for 30 min and stirred at r t for 2 h. The reaction mixture was filtered and the filterate was extracted with $CHCl_3$ (50 mL X3). The extracts were combined and washed with brine three times and dried over anhydrous $MgSO_4$. The solution was concentrated and chromatographed on silica gel. From 20% of AcOEt-hexane elution, 1.44 g (34%) of pale yellow solid of **6** was obtained as first fraction. **6**: pale yellow needles, mp 147-148 ˚C (hexane-CH_2Cl_2), IR (KBr) ν_{max} 3039w, 2995w, 1678s, 1657s, 1590s, 1513m, 1397s, 1286s, 1202s, 1146m, 1096m, 989s, 925m, 878m, 841w, 806w, 750s, 687s, 531s cm^{-1}: ^{1}H NMR

($CDCl_3$-TMS) δ=7.33 (m, 2H), 7.09 (m, 2H), 3.99 (d, *J*= 15.2 Hz, 2H), 3.60 (dt, *J*=14.4 and 1.6 Hz, 1H), 3.57 (d, *J*= 15.2 Hz, 2H), 1.71 (d, *J*= 14.4 Hz, 1H): ^{13}C NMR ($CDCl_3$-TMS) δ=196.8(C=O), 134.5, 131.1, 125.9, 43.7, 29.3 : MS m/z (70 eV) 207 (M^++1, 14%), 206 (M^+, 100%), 133 (13%), 132 (86%), 131, (17%) 118 (48%), 116 (17%), 90 (30%), 78 (14%) : HRMS for $C_{11}H_{10}O_2S$: 206.0368; Found: 206.0399 : *Anal*. Calcd for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89. Found: C, 63.78; H, 5.06.

***anti*-6,15-Epithia-8,13-methanobenzo[*e*][14]annulene-7,14-dione (7)**.

The benzene solution (60 mL) of **7** (3.40 g, 1.65 mmol) and *o*-phthalaldehyde (2.20 g, 1.65 mmol) in the presence of sodium methoxide (0.56 g, 5.00 mmol) was stirred at r t for 45 min. The reaction mixture was poured onto 50 mL of 3M HClaq. and then extracted with benzene (50 mL x 2). The combined organic layer was washed with brine two times and then dried over anhydrous $MgSO_4$. Evaporation of solvent left solids which was chromatographed on silica gel. From benzene elution, 1.00 g (20%) of pale yellow solid of **7** was obtained as first fraction. And from the second fraction, 0.23 g (10%) of **8** was obtained. **7**: Pale yellow needles, mp 116-118 ˚C (hexane-CH_2Cl_2) and then 212-217 ˚C, IR (KBr) ν_{max} 3045w, 1657vs, 1600s, 1173m, 751s cm^{-1}: ^{1}H NMR ($CDCl_3$-TMS) δ=7.69 (s, 2H, H-5, 16), 7.65 (m, 2H, H-1, 4), 7.51 (m, 2H, H-2, 3), 7.03 (m, 2H, H-9, 12), 6.95 (m, 2H, H-10, 11), 3.50 (d, *J*=14.0 Hz, 1H, H-18b), 2.04 (d, *J*=14.0 Hz, 1H, H-18a): ^{13}C NMR ($CDCl_3$-TMS) δ=197.6 (C=O), 138.2 (C-5, 16), 135.8, 133.4, 133.2, 131.4 (C-1, 4), 128.44 (C-2,3 or 9, 12), 128.39 (C-9, 12 or 2, 3), 32.8 (C-18): UV-VIS (CH_2Cl_2) λ_{max} 236.6 (log ε=4.50), 255.6 (4.48), 364sh nm (2.66). CV (DMSO) $^1E_{1/2}$= -0.81 V (5.94), $^2E_{1/2}$= -1.17 V (4.33); MS m/z 304 (M^+, 0.12%), 272 (51%), 244 (27%), 215 (100%); HRMS Calcd for $C_{19}H_{12}O_2S$; 304.0556; Found: 304.0537: *Anal*. Calcd for $C_{19}H_{12}O_2S$: C, 75.00; H, 3.95. Found: C, 74.92; H, 3.70.

18a: ^{1}H NMR (D_2SO_4-CH_2Cl_2) δ=8.34 (s, 2H, H-9,14), 7.89 (m, 2H, H-10,13), 7.79 (m, 2H, H-11,12), 7.64 (m, 2H, H-2,5), 7.40 (m, 2H, H-3,4), 4.00 (d, J=13.9 Hz, 1H, H-18b), 2.69 (d, J=13.9 Hz, 1H, H-18a); UV-VIS (D_2SO_4) λ_{max} 238.4 (log ε=4.38), 294.0 (4.35), 312.2 (4.33), 467.8 nm (3.66).

8: Pale yellow needles, mp 215-218 ˚C (hexane-CH_2Cl_2), IR(KBr) ν_{max} 3040w, 1675vs (C=O), 1617s, 1584m, 1293vs, 999s, 753s, 734m, 703s cm^{-1}: ^{1}H NMR ($CDCl_3$-TMS) δ=8.65 (s, 2H, H-5, 14), 8.06 (m, 2H, H-1, 4), 7.68 (m, 2H, H-2, 3), 7.06 (m, 2H, H-8, 11), 6.19 (m, 2H, H-9, 10), 2.62 (d, *J*=4.8 Hz, 1H, H-15b), 0.92 (d, *J*=4.8 Hz, 1H, H-15a): ^{13}C NMR ($CDCl_3$-TMS) δ=192.0 (C=O), 135.2, 129.8 (C-1, 4), 129.3 (C-2, 3, 4, 14), 127.7, 122.1 (C-8, 11), 121.4 (C-9, 10), 44.8 (C-7, 12), 24.5 (C-15): UV-VIS (CH_2Cl_2) λ_{max} 236.6 (log ε=4.50), 255.6 (4.48), 364sh nm (2.66). CV (DMSO) $^1E_{1/2}$= -1.33 V (4.45), $^2E_{1/2}$= -1.50 V (3.35); MS m/z 272 (M^+, 67%), 215 (100%); HRMS Calcd for $C_{19}H_{12}O_2$; 272.0835; Found: 272.0835: *Anal*. Calcd for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 83.65; H, 4.62.

***anti*-5,14-Epithia-1,13-methanofuro[3,4-*e*][14]annulene-5,13-dione (9)**.

To a solution (100 mL) of **7** (1.35 g, 6.57 mmol) and 3,4-diformylfuran (0.85 g, 6.57 mmol) in dry

methanol was added a solution of sodium methoxide (0.55 g, 10 mmol) in dry methanol (50 mL) at r t for 12 h and stirred further 12 h and then heated at 50 ˚C for 3h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (30 mL). The organic layer was washed with 10 mL of 3M HClaq. twice, and with brine twice and then dried over anhydrous $MgSO_4$. Evaporation of the solvent left solids which was chromatographed on silica gel. From benzene elution, 0.75 g (39%) of pale yellow needles of **9** was obtained. **9**: mp 230-290 ˚C (hexane-CH_2Cl_2), IR(KBr) ν_{max} 3100vw, 1655vs, 1595s, 1250m, 1185s, 1060s, 610w cm^{-1}: ^{1}H NMR ($CDCl_3$-TMS) δ=7.89 (s, 2H), 7.68 (s, 2H), 7.00 (m, 2H), 6.91 (m, 2H), 3.55 (dt, *J*=14.2 and 1.5 Hz, 1H, H-17b), 2.12 (d, *J*=14.2 Hz, 1H, H-17a): ^{13}C NMR ($CDCl_3$-TMS) δ=196.9, 144.1, 133.7, 133.2, 132.7, 132.6, 128.4, 121.4, 32.8: MS m/z 294 (M^+, 12.4%), 266 (11.9%), 237 (15.5%), UV-VIS (CH_2Cl_2) λ max 238sh (log ε=3.41), 256 (4.28), 231 nm (4.29). CV (DMSO) The first reduction potential= -0.89 V, $^2E_{1/2}$ = -1.50 V (9.48). HRMS Calcd for $C_{17}H_{10}O_3S$; 294.0248; Found: 294.0326: *Anal*. Calcd for $C_{17}H_{10}O_3S$: C, 69.39; H, 3.40. Found: C, 69.56; H, 3.20.

19a: ^{1}H NMR (CF_3CO_2D-TMS) δ=8.03 (s, 2H), 7.96 (s, 2H), 7.20 (m, 2H), 7.16 (m, 2H), 3.81 (dt, *J*=14.8 Hz, 1H, H-17b), 2.40 (d, *J*=14.8 Hz, 1H, H-17a).

1,3-Dimethyl *anti*-3,11-epithia-7,12-methanofuro[3,4-*e*][14]annulene-5,13-dione (10). The same treatment of **7** with 3,4-diformyl-2,5-dimethylfuran as in the case of **9** gave **10** in 34% yield. **10**: Pale yellow needles, mp 194 ˚C (hexane-CH_2Cl_2), IR(KBr) ν_{max} 2950w, 2849m, 1655vs, 1600s, 1280m, 1260s, 1190m, 1090m, 800m, 730w cm^{-1}: ^{1}H NMR ($CDCl_3$-TMS) δ=7.56 (s, 2H), 6.96 (m, 2H), 6.85 (m, 2H), 3.56 (dt, *J*=14.1 and 1.5 Hz, 1H, H-17b), 2.15 (d, *J*=14.1 Hz, 1H, H-17a): ^{13}C NMR ($CDCl_3$-TMS) δ=197.5, 152.5, 134.4, 133.1, 130.4, 127.9, 117.1, 33.0, 12.4: MS m/z 322(M+, 19.8%), 307 (8.1%), 290 (10.0%), UV-VIS (CH_2Cl_2) λ $_{max}$ 408sh (log ε=1.70), 332sh (3.30), 257 (4.12), 233 (4.04), 205 nm (3.56). CV (DMSO) $^1E_{1/2}$ = -0.82 V (10.10), $^2E_{1/2}$ = -1.22 V (4.49). HRMS Calcd for $C_{19}H_{14}O_3S$; 322.0661; Found: 322.0660: *Anal*. Calcd for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38. Found: C, 70.71; H, 4.39.

20a: ^{1}H NMR (CF_3CO_2D-TMS) δ=7.87 (s, 2H), 7.14 (s, 2H), 7.09 (m, 2H), 3.83 (dd, *J*=14.4 and 1.2 Hz, 1H, H-17b), 2.42 (d, *J*=14.8 Hz, 1H, H-17a).

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