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Synthesis and Properties of *anti, anti*-8,17-Epithia-1,6;10,15-bismethano[18]annulene-7,18-dione and Its Dicationic Species

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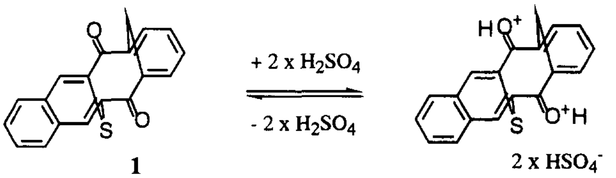
Abstract: The titled quinone compound has been synthesized, and the X-ray crystallographic analysis of this compound revealed that it has anti-anti-configuration for stereochemical relationship between two methylene and sulfur bridges. Its ^1H and ^{13}C NMR spectra in D_2SO_4 indicate that the cationic species formed by protonation has localized positive charges on the carbony carbons, mainly due to the unfavorable p-orbital overlap. © 1997 Elsevier Science Ltd.

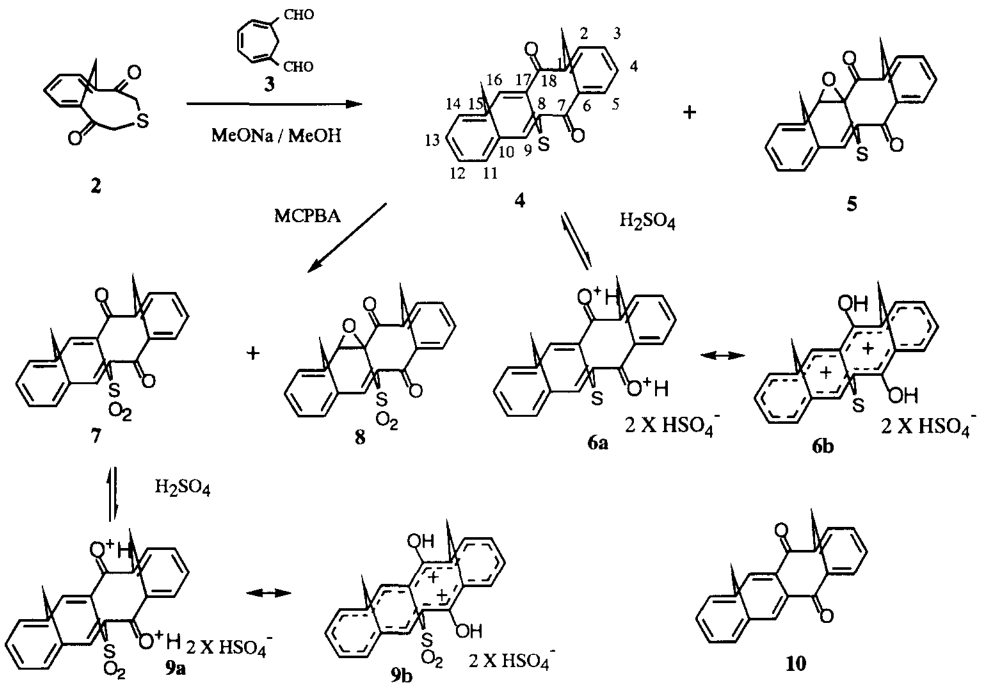
Although dependence of the dia- and paratropicity of the bridged annulenes upon the number of π electrons has been well documented,[1a~c)] little is known of the configurational effect of bridged annulenes,[2)] especially of heteroatom-bridged annulenes, on the tropicity.[3a~c)] Recently, we reported the first synthesis of *anti*-6,15-epithia-8,13-methano-benzo[d][14]annulene-7,14-dione **1** and generation of its dicationic species.[4)] In the study, however, we could not properly estimate the tropicity of its dicationic species; this difficulty may be attributed to the fact that the benzannelation substantially reduces the tropicity of the annulated π-electron system and it sometime interupts the peripheral conjugation. Therefore, we required an alternative ring system which has similar π-electron array without benzannelation to clarify the above question. Now we report here the stereoselective synthesis of *anti, anti*-8,17-epithia-1,6;10,15-bismethano[18]annulene-7,18-dione (**4**) and its sulfone derivative which have an isoelectronic structure to **1**, and generation of their dicationic species.



1

Scheme 1

Reaction of the bicyclic sulfide **2** with 1,6-diformyl-1,3,5-cycloheptatriene (**3**) in the presence of sodium methoxide in dry methanol at r. t. for 5 h[5)] gave **4** as fairly stable crystals in 20% yield, along with a small amount of the epoxide derivative **5** as pale yellow needles. The structures of **4** and **5** were confirmed by their spectral data and elemental analyses. The ^1H and ^{13}C NMR spectra of **4** showed a structure with planar symmetry which includes the sulfur atom and two methylene carbons, and the assignment of all protons was made by the ^1H-^1H and ^1H-^{13}C COSY spectra.[9)] The two bridged methylene protons resonated at δ3.57 and 2.19 for the C_{19} position, and δ2.78 and 1.97 for the C_{20} position with geminal coupling constants of 14.7 and



Scheme 2

11.9 Hz, respectively, clearly indicating that both cycloheptetriene parts have the open form rather than the norcaradiene form. The difference between the two coupling constant values suggests that the through-space distance between $C_1$and C_6 is longer than that of C_{10} and C_{15}. The latter phenomenon might be derived from the electronic repulsion of two carbonyl groups. The ring protons of **4** appear at slightly higher field than those of **1**.[4] The ^{13}C NMR spectra showed 11 peaks and the signals for all carbons are observed at lower field than those of **1** except one for the carbonyl carbons which resonated at δ194, being a little higher than that of **1** (δ197).[4] Configuration between three bridges in **4** was deduced by the ^1H chemical shifts of the inner protons on the methylene carbons observed at higher fields compared with those of 1-thia-4,9-methano[11]annulene.[6] Furthermore, the spectral data of **7**, prepared by the oxidation of **4** with 2.2 equiv. of MCPBA in 67% yield along with the epoxide **8**, supported this *anti*, *anti*-configuration, judging from the slight differences in the ^1H chemical shifts of the methylene protons between the sulfide **4** and sulfone **7**, since a large difference is expected in the case of *syn*-configuration. Definitive confirmation was made by the X-ray crystallographical analysis, and a perspective view of the molecular structure of **4** is shown in Figure 2.[10] It is seen that the configuration between three bridges is an *anti-anti*-one and through-space carbon-carbon distances of the bridging parts are 2.466 Å (C_{10}-C_{15}), 2.522 Å (C_1-C_6), and 2.943 Å (C_8-C_{17}) long shown as average values, which are in good agreement with the above ^1H NMR spectral elucidation. The stereoselective formation of products with *anti*, *anti*-configuration might be due to the larger atomic radius of the sulfur atom which prevents the approaching electrophilic substrate **3** from arranging the transition state with *syn-syn* type of configuration contrary to the case of the similar oxygen bridged annuleno-annulene.[3a] The ^1H NMR spectra of **4** and **7** in

D_2SO_4 showed signals of ring protons at lower field by about 0.6-1.5 ppm compared to those of the corresponding protons in $CDCl_3$, indicating formation of the dicationic species **6** and **9** by protonation.4) The chemical shifts of the methylene protons of dications **6** and **9** were also observed at lower field by 1.5 and 1.8 ppm compared to those in $CDCl_3$, respectively. All ^{13}C chemical shifts of **6** and **9** observed at lower fields also support the formation of the dicationic species and those of the carbonyl carbons similar to those of **1**.7) However, these spectral data showed that the distribution of positive charges in **6** and **9** is far less than those in the mono- and dicationic species of *syn,syn*-1,6:8,17:10,15- trismethano[18]annulene.8) Therefore, the structure of the dicationic species formed can be best regarded a resonance structure depicted in the forms of **6a** and **9a**.The main reason for this charge localization can be attributed to its stereochemistry; that is, in the crystal structure of **4** the peripheral conjugation is prevented by the unfavorable overlap of the p-orbitals through the zigzagged C_6-C_7-C_8-C_9-C_{10}-C_{11}-C_{12} chain due to the large torsion angles between them [especially that of C_9-C_{10}-C_{11}-C_{12} is 65.6° (av.)]. In the meantime, the dicationic species **6a** changed under the conditions of NMR measurament with a halflife time $\tau_{1/2}$=ca. 10 min at 36 °C, increasing new signals, the assignment of which had remained unclear.

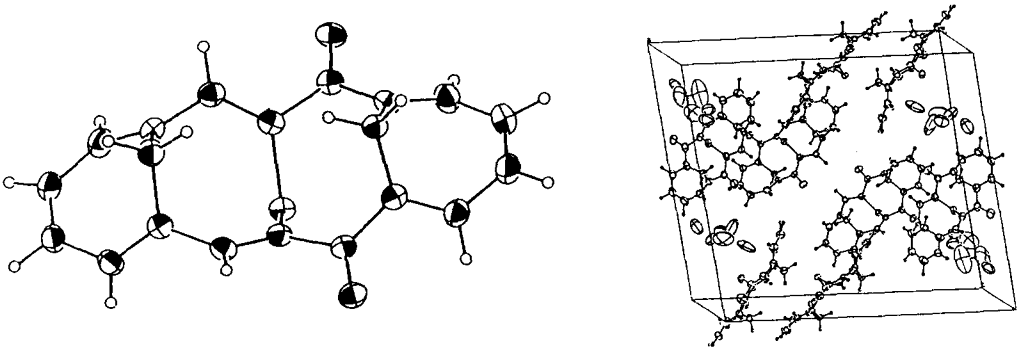


Fig. 2 The X-ray structure of **4**.

An attempt at thermal desulfurization of **4** to obtain a new annuleno-annulenedione **10** was unsuccessful; it did not show any change under its melting point4) and it decomposed above that point without formation of any identifiable product. The fact of the relatively longer distance between C_8 and C_{17} observed in the X-ray structure accounts for the resistance against thermal desulfurization. The cyclicvoltammograms of **4** in dimethyl sulfoxide (DMSO) showed two reversible half-wave reduction potentials ($^1E_{1/2}$= -0.97V, $^2E_{1/2}$= -1.36V) which are more negative than those of **1** ($^1E_{1/2}$= -0.81V, $^2E_{1/2}$=-1.17V). The reason for the instability of the dianionic species genarated from **4** compared to the case of **1** can be due to the less favorable p-orbital overlap mainly derived from the doubled *anti*-configuration.

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7) Addition of a large excess of water to this solution soon after the formation of the dicationic species resulted in recovery of the starting materials **4** and **7** quantitatively.

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9) Physical properties of **4** and **7**.

4: Yellow needles, mp 268-271°C; IR (KBr) 3020w, 3000w, 1655vs (C=O), 1600s, 1565s, 1430s, 743s, 1270m, 1190s, 855m, 830m, 740s, 720s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 2H, H-9, 16), 7.07 (m, 2H, H-2, 5), 6.90 (m, 2H, H-3, 4), 6.82 (m, 2H, H-12, 13), 6.32 (m, 2H, H-11, 14), 3.57 (d, *J*=14.0Hz, 1H,H-19b), 2.78 (d, *J*=11.9Hz, 1H,H-20a), 1.97 (d, *J*=11.9Hz, 1H, H-20b), 1.68 (d, *J*=14.0Hz, 1H, H-19a).: (D_2SO_4) δ 9.23 (s, 2H, H-9, 16), 7.70 (m, 2H, H-2, 5), 7.39 (m, 2H, H-3, 4), 7.18 (m, 2H, H-12, 13), 6.82 (m, 2H, H-11, 14), 4.49 (d, *J*= Hz, 1H,H-19b), 3.44 (d, *J*= Hz, 1H,H-20a), 3.27 (d, *J*= Hz, 1H, H-20b), 2.29 (d, *J*= Hz, 1H, H-19a). ; ^{13}C NMR ($CDCl_3$) δ194.1 (C=O), 150.9, 138.5, 133.6, 133.2, 129.7, 129.4, 128.5, 123.0, 43.8, 31.5; (D_2SO_4) δ208.8 (C=O), 171.4, 144.9, 141.8, 138.8, 132.6, 132.1, 131.7, 128.6, 47.1, 36.1.;UV-vis (CH_2Cl_2) λ_{max} 236.6 (logε=4.50), 255.6 (4.48), 364sh nm (2.66); MS m/z 318 (M$^+$, 100%), 257 (14%); HRMS M. Found: 318.0714. Calcd for $C_{20}H_{14}O_2S$: 318.0714.; CV (in Volts vs.SCE) $^1E_{1/2}$= -0.97V, $^2E_{1/2}$= -1.36V (in DMSO).

7: Yellow needles, mp>300°C; IR (KBr) 3020w, 2960w, 1665vs (C=O), 1583s, 1509m, 1439m, 1342m, 1272m, 1194m, 1063m, 742m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.94 (s, 2H, H-9, 16), 7.21 (m, 2H, H-2, 5), 6.99 (m, 2H, H-3, 4) 6.88 (m, 2H, H-12, 13), 6.50 (m, 2H, H-11, 14),4.02 (dt, *J*=1.70 & 14.4 Hz, 1H, H-19b), 2.58 (d, *J*=12.4Hz, 1H, H-20c), 2.15 (dt, *J*= 1.70 & 14.4Hz, 1H, H-19a), 1.85 (d, *J*=12.4 Hz, 1H, H-20d).: (D_2SO_4) δ 9.13 (s, 2H, H-9, 16), 7.73 (m, 2H, H-2, 5), 7.62 (m, 2H, H-3, 4), 7.41 (m, 2H, H-12, 13), 7.22 (m, 2H, H-11, 14), 4.04 (d, *J*= Hz, 1H,H-19b), 3.59 (d, *J*= Hz, 1H,H-20a), 3.05 (d, *J*=1 Hz, 1H, H-20b), 2.64 (d, *J*= Hz, 1H, H-19a). ^{13}C NMR ($CDCl_3$) δ189.7 (C=O), 152.2, 143.1, 133.7, 132.2, 130.3, 130.0, 124.7, 121.6, 40.8, 30.7; MS m/z 350 (M$^+$, 1%), 334 (100%); HRMS M. Found: 350.0623. Calcd for $C_{20}H_{14}O_4S$: 350.0612.

10) The X-ray crystal analysis established the exact structure of the dione **4**. The crystal containing hexane $[(C_{20}H_{14}O_2S)_{2n} \cdot (C_6H_{14})_n]$ has monoclinic space group P21/a with a=22.478(4) Å, b=6.488(4) Å, c=25.768(4) Å, and β=104.74(6)°, V=3634.16(6) Å, z=8, Dx=1.150 Mgm^{-3}, Dm=1.162 Mgm^{-3}. Intensity data were collected on a four-circle differactometer with graphite monochromated Mo/K-α radiation. Structure was refined to an R value of 0.0652.

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