



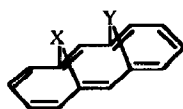
0040-4039(94)01525-2

**Synthesis and Properties of
anti-6,15-Epithia-8,13-methano-benzo[*d*][14]annulene-7,14-dione
and Its Dicationic and Dianionic Species**

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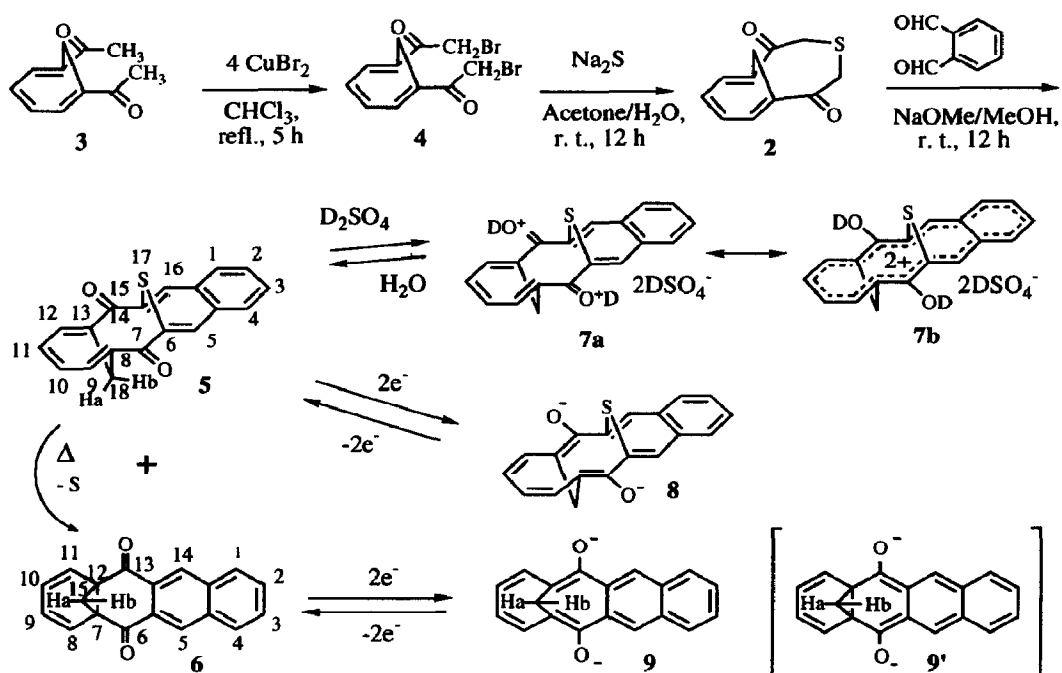
Abstract: The titled compound has been synthesized, and its ^1H and ^{13}C NMR spectra in D_2SO_4 indicate that the cationic species formed by protonation has localized positive charges at carbonyl carbons due to the unfavorable conjugation because of the *anti* configuration between methylene and sulfur bridges.

Although many kinds of bridged annulenes including heteroatom bridged annulenes **1a-e** have been investigated,^{1a-d)} none of sulfur bridged annulene has been reported yet. One of the reasons for this may be due to the lability of the sulfur-carbon linkage incorporated in π -conjugated systems, as having been known in thiepinines and 1-thia-4,9-methano[11]annulenes.²⁾ Since sulfur atom belongs to third-row elements in the periodic table having a larger atomic radius than those of second-row ones such as carbon, oxygen, and nitrogen atoms, 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)} This paper describes the first synthesis of *anti*-6,15-epithia-8,13-methano-benzo[*d*]-[14]annulene-7,14-dione (**5**) and generation of its dicationic and dianionic species.



1a : X = CH₂, Y = O
1b : X = O, Y = O
1c : X = CH₂, Y = NH
1d : X = NH, Y = NH
1e : X = NH, Y = O

The bicyclic sulfide **2** [mp 147-148° C, $\nu_{\text{C=O}}$ 1663 cm^{-1}] was prepared from 1,6-diacetyl-1,3,5-cycloheptatriene (**3**)³⁾ in two steps; bromination of **3** with cupric bromide⁴⁾ and subsequent treatment with aqueous sodium sulfide gave **2** as shown in Scheme 1. The reaction of **2** with *o*-phthalaldehyde in the presence of sodium methoxide in dry methanol at r. t.⁵⁾ gave exclusively one of the possible stereoisomers **5** as a fairly stable compound even in air and **6** as pale yellow needles, in 20% and 10% yields, respectively. The structures of **5** and **6** were determined by the spectral data and elemental analyses. The ^1H NMR spectrum of **5** recorded at 500 MHz showed the symmetrical structure shown in Fig. 1, and the assignment of all protons were made by the ^1H - ^1H and ^1H - ^{13}C COSY spectra.⁶⁾ The bridged methylene protons resonated rises at δ 3.50 and 2.04 with a large geminal coupling constant ($J=14\text{Hz}$), clearly indicating that the cycloheptatriene moiety has the open form. The benzene ring protons resonated at δ 7.65 and 7.51, the protons at 5 and 16 positions resonated at δ 7.69, similarly to those of 2,7-bis(methoxycarbonyl)benzothiepine.⁷⁾



The ^{13}C NMR spectrum showed 10 peaks and the carbonyl carbons resonated at $\delta 197.6$ which is lower than that of anthraquinone and is similar to those of normal enones.⁸⁾ Although the mass spectrum of **5** showed a small molecular ion peak, the analytical values satisfactorily agreed with those of calculated for **5**. The anti configuration between two bridges of **5** was elucidated by the fact that the chemical shift of the inner proton (Hb) on the methylene carbon in **5** was observed at higher field ($\delta 3.50$) than that of 1-thia-4,9-methano[11]annulene ($\delta 6.28$).²⁾ This stereochemical relationship was also supported by the

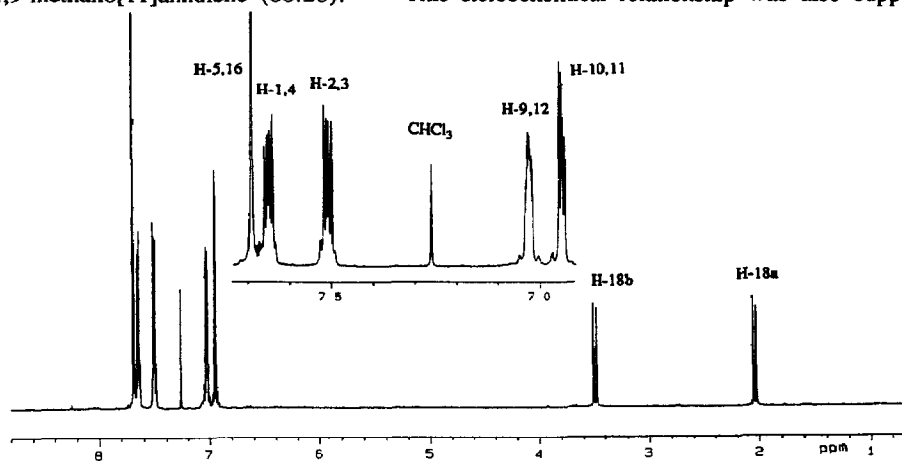


Fig. 1 ^1H NMR spectrum of **5** at 500 MHz in CDCl_3

examination of ^1H NMR measurements in the presence of an europium shift reagent. The magnitude of downfield shifts of both methylene protons of **5** by addition of $\text{Eu}(\text{fod})_3$ is smaller than those of **6**, indicating less influence of the shift reagent on the methylene protons of **5** than on those of **6**. These differential anisotropic effects on **5** and **6** are reasonably explained as follows; a paramagnetic europium complex places between the carbonyl oxygen and sulfur atom of the anti configuration in **5** and, however, just on the carbonyl oxygen in **6**. Desulfurization of **5** was confirmed by heating **5** in refluxing benzene to give **6** in quantitative yield. Its half life ($\tau=39.6\text{min}/60\text{ }^\circ\text{C}$) determined by the ^1H NMR spectral measurement of decreasing methylene protons of **5** is comparable to that of benzothiepinines,⁷⁾ therefore this desulfurization is suggested the operation of the similar mechanism in which **5** transforms to the thianorcaradiene intermediate and then elimination of sulfur atom proceeds to aromatization. The structure of **6** having the norcaradiene form, like 1,6-methano[10]annulene-2,5-dione,⁹⁾ was elucidated by the ^1H and ^{13}C NMR spectra as shown in reference.⁶⁾

The ^1H NMR spectrum of **5** in a strong acid, D_2SO_4 , showed the formation of the dicationic species **7** by protonation.¹⁰⁾ Both olefinic and methylene protons of **7** were observed at slightly down field, just by about 0.5-0.7ppm, compared to those of **5** in CDCl_3 .⁶⁾ In ^{13}C NMR spectrum of **5** in D_2SO_4 , the signal for carbonyl carbons resonated at $\delta 12.6$ which was clearly lower than that in CDCl_3 . It strongly suggests the localization of positive charges at carbonyl carbons, inasmuch as the ^{13}C chemical shifts of carbonyl carbons of delocalized dicationic species formed by protonation of condensed quinones in D_2SO_4 were reported to be rather higher than those in CDCl_3 .¹¹⁾ The localization of charges in the dicationic species might be attributed to the unfavorable conjugation through the distorted p-orbitals resulted from the anti configuration between the methylene and sulfur bridges as seen in the case of the anti bismethylene bridged [14]annulene.¹²⁾ Thus, the structure of the dicationic species formed can be best regarded as the form of **7a** but not **7b**.

The cyclic voltammograms of **5** and **6** in dimethyl sulfoxide (DMSO) showed two reversible half-wave reduction potentials and a little difference, compared with those of anthraquinone,¹³⁾ between two potentials in both compounds was observed, indicating the stability of the radical anions and dianions, as **8** and **9**. Meanwhile, the first reduction potential ($^1E_{1/2} = -0.81\text{eV}$) of **5** is more positive than that of **6** ($^1E_{1/2} = -1.33\text{eV}$). Since formation of the dianion **9'** should be less favorable because of its high-energy *o*-quinodimethane structure, it is suggested that **6** requires the extra energy for opening of the cyclopropane ring in the process of electron reduction to form **9**.

Acknowledgement. We are grateful to Nihondenshi (JOEL) Co. Ltd. for the measurement of NMR spectra of **5** and **6**.

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- 6) Physical properties of **5**, **6**, and **7**.
- 5: Pale yellow needles, mp 116-118°C and then 212-217°C; IR (KBr) 3045w, 1657vs (C=O), 1600s, 1173s, 751s cm⁻¹; ¹H NMR (CDCl₃) 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*=14.0Hz, 1H, H-18b), 2.04 (d, *J*=14.0Hz, 1H, H-18a); ¹³C NMR (CDCl₃) δ 197.6 (C=O), 138.2 (C-5,16), 136.2, 135.8, 133.4, 133.2 (C-10,11), 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 (CH₂Cl₂) λ_{max} 236.6 (logε=4.50), 255.6 (4.48), 364sh nm (2.66); MS *m/z* 304 (M⁺, 0.12%), 272 (51%), 244 (27%), 215 (100%); HRMS M. Found: 304.0555. Calcd for C₁₉H₁₂O₂S: 304.0537; Found: C, 74.92; H, 3.70%. Calcd for C₁₉H₁₂O₂S: C, 75.00; H, 3.95%; CV (in Volts vs. SCE) ¹E_{1/2}= -0.81eV, ²E_{1/2}= -1.17eV (in DMSO).
- 6: Pale yellow needles, mp 215-218°C; IR (KBr) 3040w, 1675vs (C=O), 1617s, 1584m, 1293vs, 999s, 753m, 734m, 703s cm⁻¹; ¹H NMR (CDCl₃) 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*=4.8Hz, 1H, H-15b), 0.92 (d, *J*=4.8Hz, 1H, H-15a); ¹³C NMR (CDCl₃) δ 192.0 (C=O), 135.2, 129.8 (C-1,4), 129.3 (C-2,3,5,14), 127.7, 122.1 (C-8,11), 121.4 (C-9,10), 44.8 (C-7,12), 24.5 (C-15); MS *m/z* 272 (M⁺, 67%), 215 (100%); HRMS M. Found: 272.0835, Calcd for C₁₉H₁₂O₂: 272.0835. CV (in Volts vs. SCE) ¹E_{1/2}= -1.33eV, ²E_{1/2}= -1.50eV (in DMSO).
- 7: ¹H NMR (D₂SO₄) δ 8.34 (s, 2H, H-5, 11), 7.89 (m, 2H, H-1, 4), 7.79 (m, 2H, H-2, 3), 7.64 (m, 13C NMR (CDCl₃) δ 212.6 (C=O), 150.7, 140.7, 139.3, 135.7, 133.9, 132.4, 130.7, 125.0, 37.2, (C-18); UV-Vis (D₂SO₄) λ_{max} 238.4 (logε=4.38), 294.0 (4.35), 312.2 (4.33), 467.8nm (3.66).
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(Received in Japan 27 May 1994)