

# 1,4-Dithiin annelated with bicyclo[2.2.2]octene units: experimental and theoretical evidence for the aromaticity in 1,4-dithiin dication

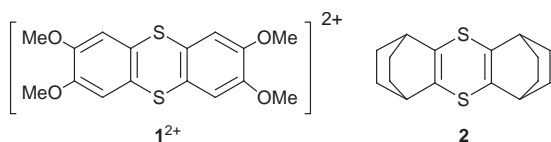
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Received (in Cambridge, UK) 15th February 1999, Accepted 16th March 1999

1,4-Dithiin dication annelated with bicyclo[2.2.2]octene units was generated by the two-electron oxidation of the neutral dithiin and found to be aromatic based on the results of NMR measurements and theoretical calculations.

Although there have been a considerable number of studies on cationic  $\pi$ -conjugated systems containing sulfur atom(s), surprisingly little is known on the dicationic species of 1,4-dithiin,<sup>1</sup> and the spectroscopically characterized derivative is limited only to the expanded  $\pi$ -system of 2,3,7,8-tetramethoxythianthrene dication ( $1^{2+}$ ). The <sup>1</sup>H NMR spectra of this dication showed broad signals at room temperature<sup>2</sup> while the  $\Delta m = 2$  transition was observed by EPR at low temperature.<sup>3</sup> From the EPR experiments, it was concluded that this dication is ground state triplet and the energy gap between the singlet and triplet states is  $< 1$  kcal mol<sup>-1</sup>.<sup>3</sup> These results are consistent with the X-ray structure of  $1^{2+}(\text{SbCl}_6^-)_2$ , in which it was interpreted that this dication is divided into two cyanine subunits with each  $\pi$ -delocalization more favored than the cyclic  $\pi$ -conjugation as a whole.<sup>4</sup>



Is the triplet state of non-expanded 1,4-dithiin dication itself also more stable than the singlet state which might have an aromatic stabilization? Here, is given the first experimental and theoretical evidence for the presence of aromaticity in a derivative of 1,4-dithiin dication, *i.e.* 1,4-dithiin dication  $2^{2+}$  annelated with bicyclo[2.2.2]octene units. The annelation of this bicyclic unit has been shown to be quite effective for the stabilization of the radical cation<sup>5</sup> and dication<sup>6</sup> of cyclooctatetraene, which is isoelectronic to 1,4-dithiin. Also the electronic structures of the singlet and triplet states are compared between the dications of parent 1,4-dithiin **3** and thianthrene **4** for better understanding of the electronic properties of these species.

For the synthesis of 1,4-dithiin derivative **2**,<sup>†</sup> the method of Nakayama *et al.*<sup>7</sup> was employed. Thus, 3-bromobicyclo[2.2.2]octan-2-one, synthesized from 2-bromobicyclo[2.2.2]octene by the same method for the chloro derivative,<sup>8</sup> was allowed to react with Na<sub>2</sub>S to give bis(3-oxobicyclo[2.2.2]oct-2-yl) sulfide (63%). The reaction of this sulfide with Lawesson's reagent<sup>9</sup> afforded **2** in 63% yield.

Cyclic voltammetry of **2** in CH<sub>2</sub>Cl<sub>2</sub> at  $-78$  °C under vacuum using a Pt wire as a pseudo-reference electrode showed two reversible oxidation waves at  $+0.00$ ‡ and  $+0.82$  V‡ *vs.* Fc/Fc<sup>+</sup> (Fig. 1), indicating that both the radical cation and dication of **2** are stable under these conditions. In comparison with the oxidation potential of tetramethoxythianthrene **1** ( $E^1 = +0.58$ ,  $E^2 = +0.83$  V *vs.* Fc/Fc<sup>+</sup>, calibrated from the potential *vs.* Ag/Ag<sup>+</sup> in acetonitrile),<sup>2¶</sup> the first oxidation potential of **2** is remarkably lowered owing to the inductive and  $\sigma$ - $\pi$  conjugative effects of bicyclo[2.2.2]octene units. On the other hand, the difference between the first and second oxidation potentials of

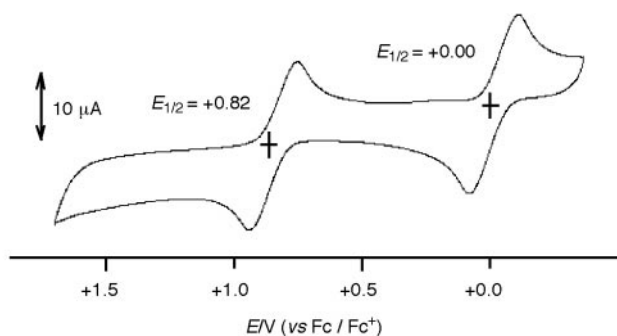


Fig. 1 Cyclic voltammogram of **2** in CH<sub>2</sub>Cl<sub>2</sub> containing NBu<sub>4</sub>ClO<sub>4</sub> (0.1 M) at  $-78$  °C under vacuum; scan rate, 0.1 V s<sup>-1</sup>.

**2** is larger than that of **1**, suggesting that there is a larger Coulombic repulsion in dication  $2^{2+}$  than in  $1^{2+}$ .

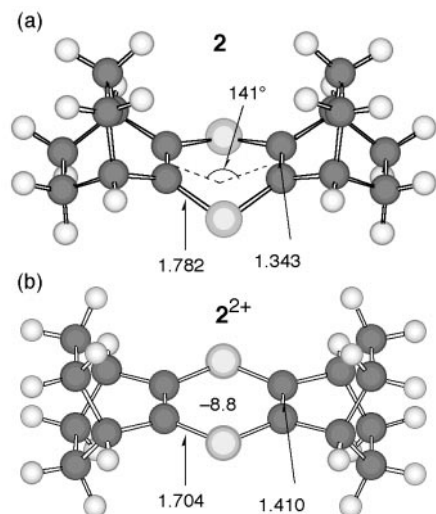
The reaction of **2** with an excess of SbF<sub>5</sub> in CD<sub>2</sub>Cl<sub>2</sub> at ambient temperature gave an orange solution, which exhibited <sup>1</sup>H and <sup>13</sup>C NMR signals at considerably low field compared with the neutral dithiin (Table 1). The observed chemical shifts for this orange solution were in fair agreement with the calculated values for  $2^{2+}$  (GIAO/HF/6-31+G\*/B3LYP/6-31G\*), giving a strong support to the formation of dication  $2^{2+}$ . The signal of bridgehead protons which are located in the plane of the dithiin's  $\pi$ -system exhibited a marked downfield shift of 2 ppm as compared with that of neutral **2**. This clearly indicates the presence of a diamagnetic ring current in the dicationic dithiin ring and the aromatic character in this  $6\pi$ -electronic system. The value of nucleus independent chemical shift (NICS)<sup>10</sup> of  $2^{2+}$  was calculated to be  $-8.8$  (GIAO/HF/6-31+G\*/B3LYP/6-31G\*), which also supports the aromaticity in this dication.

The optimized structures obtained theoretically at the B3LYP/6-31G\* level for neutral and dicationic species **2** and  $2^{2+}$  are shown in Fig. 2. As two electrons are removed from **2**, the C-S single bonds in the dithiin ring are shortened and the C=C double bonds elongated, with the conformational change from boat to planar structures. Such changes in the bond length and conformation can be rationalized by the enhanced cyclic  $\pi$  delocalization for  $2^{2+}$  again supporting the presence of the aromaticity in the 1,4-dithiin dication.

Table 1 <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts for **2** and  $2^{2+}$

Compound	$\delta_{\text{H}}$		$\delta_{\text{C}}$			
	CH	CH <sub>2</sub>	C=C	CH	CH <sub>2</sub>	
<b>2</b>	Obs. <sup>a</sup>	2.46	1.53 (8H) 1.33 (8H)	128.4	38.1	26.2
$2^{2+}$	Obs. <sup>a</sup>	4.48	2.47 (8H) 1.86 (8H)	180.0	43.0	25.1
	Calc. <sup>b</sup>	4.18	2.84 ( <i>anti</i> ) 1.66 ( <i>syn</i> )	197.0	38.7	22.2

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> GIAO/HF/6-31+G\*/B3LYP/6-31G\*.



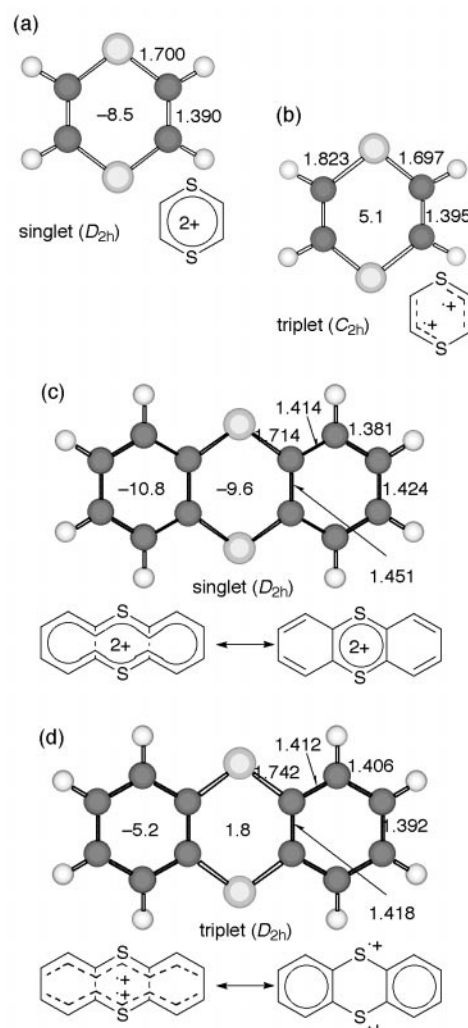
**Fig. 2** Calculated structures of (a) **2** and (b) **2<sup>2+</sup>** at the B3LYP/6-31G\* level. Selected bond lengths (Å), a bending angle of **2**, and a NICS value (ppm) of **2<sup>2+</sup>** are included.

The <sup>1</sup>H NMR spectrum of dication **2<sup>2+</sup>** showed no line broadening and the triplet state did not seem to mix to the singlet state in contrast to the case of **1<sup>2+</sup>**. In order to gain further insight with regard to these results, the difference in energy between the singlet (s) and triplet (t) states for the parent 1,4-dithiin dication **3<sup>2+</sup>** and for the thianthrene dication **4<sup>2+</sup>** were calculated (B3LYP/6-31G\*), together with their NICS values (GIAO/HF/6-31+G\*/B3LYP/6-31G\*). The calculated results are shown in Fig. 3, together with the resonance formulae for **4<sup>2+</sup>**. As to the dication **3<sup>2+</sup>**, the singlet state **3<sup>2+</sup>(s)** was shown to be more stable than the triplet state **3<sup>2+</sup>(t)** by 54.1 kcal mol<sup>-1</sup>, with a significant difference in the NICS value, *i.e.* -8.5 for **3<sup>2+</sup>(s)** and 5.1 for **3<sup>2+</sup>(t)**. Similarly the singlet state **4<sup>2+</sup>(s)** was found to be more stable than the triplet state **4<sup>2+</sup>(t)**, with the NICS value in the dithiin ring calculated to be -9.6 for **4<sup>2+</sup>(s)** and 1.8 for **4<sup>2+</sup>(t)**, but the energy gap between the singlet and triplet states was smaller (11.2 kcal mol<sup>-1</sup>). In the resonance structures, the canonical formulae of **4<sup>2+</sup>(t)** involve the extended π-conjugation for each of the radical cation parts as compared with **3<sup>2+</sup>(t)** and the retention of some aromaticity in the benzene ring (NICS value, -5.2). Thus it is concluded that, owing to further substitution with methoxy groups at appropriate positions, the triplet ground state has been attained for **1<sup>2+</sup>** while **2<sup>2+</sup>** with electron-donating σ-frameworks is exhibiting the singlet-state aromaticity.

The present work is supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 10146101) from the Ministry of Education, Science, Sports and Culture, Japan. Computation time was provided by the Super Computer Laboratory, Institute for Chemical Research, Kyoto University.

## Notes and references

† *Synthesis of 2*: An ethanol solution (10 ml) of 3-bromobicyclo[2.2.2]octan-2-one (1.31 g) and Na<sub>2</sub>S·9H<sub>2</sub>O (0.83 g) was refluxed for 50 min. After usual work-up and separation using GPC, bis(3-oxobicyclo[2.2.2]oct-2-yl) sulfide (0.57 g) was obtained as a colorless solid. This sulfide (0.48 g) was allowed to react with Lawesson's reagent (1.46 g) in toluene (18 ml) at reflux temperature for 3 h to give **2** as a crude product. Flash chromatography over alumina eluted with hexane–benzene (10 : 1) afforded **2** (0.30 g, 63%) as yellow crystals. **2**: mp 190 °C (decomp.). Anal. Calc. for C<sub>16</sub>H<sub>20</sub>S<sub>2</sub>: C, 69.51; H, 7.29. Found: C, 69.35; H, 7.20%.



**Fig. 3** Calculated structures of (a) **3<sup>2+</sup>(s)**, (b) **3<sup>2+</sup>(t)**, (c) **4<sup>2+</sup>(s)** and (d) **4<sup>2+</sup>(t)** at the B3LYP/6-31G\* level and their resonance formulae. Selected bond lengths (Å) and NICS values (ppm) are included.

‡  $E_{pa} + 0.09$ ,  $E_{pc} - 0.09$  V.

§  $E_{pa} + 0.91$ ,  $E_{pc} + 0.73$  V.

¶ For the results of electrochemical studies on 1,4-dithiins, see ref. 1 and references cited therein.

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Communication 9/01216H