Pergamon

Tetrahedron Letters 40 (1999) 4375–4378

TETRAHEDRON
LETTERS

The First Isolation of the Hexafluoroantimonate Salt of a 1,4-Dithiin Radical Cation Stabilized by Bicyclo[2.2.2]octene Annelation

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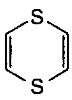
Received 12 March 1999; revised 7 April 1999; accepted 9 April 1999

Abstract: One-electron oxidation of 1,4-dithiin annelated with bicyclo[2.2.2]octene units (**3**) by $\mathrm{SbF_5}$ afforded stable radical cation salt $\mathbf{3}^{\cdot+}\mathrm{SbF_6}^-$. The X-ray crystallography indicated that the dithiin ring of $\mathbf{3}^{\cdot+}$ is planar in agreement with the theoretical prediction. The ESR coupling constant (a_S) due to ^{33}S in $\mathbf{3}^{\cdot+}\mathrm{SbF_6}^-$ was found to be 0.86 mT, which was smaller than that for thianthrene radical cation $\mathbf{2}^{\cdot+}$. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfur heterocycles; X-Ray crystal structures; Electron spin resonance; Theoretical studies

1,4-Dithiin (**1**) and its dibenzo-homologue, thianthrene (**2**), are characterized by a notably low first oxidation potential[1] due to the π-donor ability of the sulfur atom. However, the radical cation salt of 1,4-dithiin has not yet been isolated except for the case of benzo-annelated derivatives, particularly thianthrenes with electron-donating substituents.[2] On the other hand, we have shown that the annelation with bicyclo[2.2.2]octene units is quite effective for stabilization of the radical cation of cyclooctatetraene[3] which is isoelectronic to **1**, as well as the radical cations of several benzenoid compounds.[4,5] Here we report the first isolation and X-ray structural analysis of the radical cation salt of 1,4-dithiin derivative **3** annelated with bicyclo[2.2.2]octene units,[6] together with some of its spectral properties.



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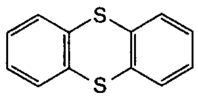

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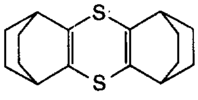

3

The cyclic voltammetry of **3** in $\mathrm{CH_2Cl_2}$ with 0.1 M $\mathrm{Bu_4NClO_4}$ as an electrolyte showed a reversible first oxidation wave at a remarkably low potential of $E_{1/2} = +0.00$ V vs Fc / Fc$^+$ and an irreversible second oxidation wave at $E_{pa} = +0.84$ V, indicating that radical cation $\mathbf{3}^{\cdot+}$ is stable while dication $\mathbf{3}^{2+}$ is labile. The reaction of **3** with 3 molar equivalents of $\mathrm{SbF_5}$ in $\mathrm{CH_2Cl_2}$ at room temperature gave an orange solution, to which was slowly diffused hexane to give brown crystals in 67% yield. The X-ray crystallography revealed that this product was

PII: S0040-4039(99)00752-2

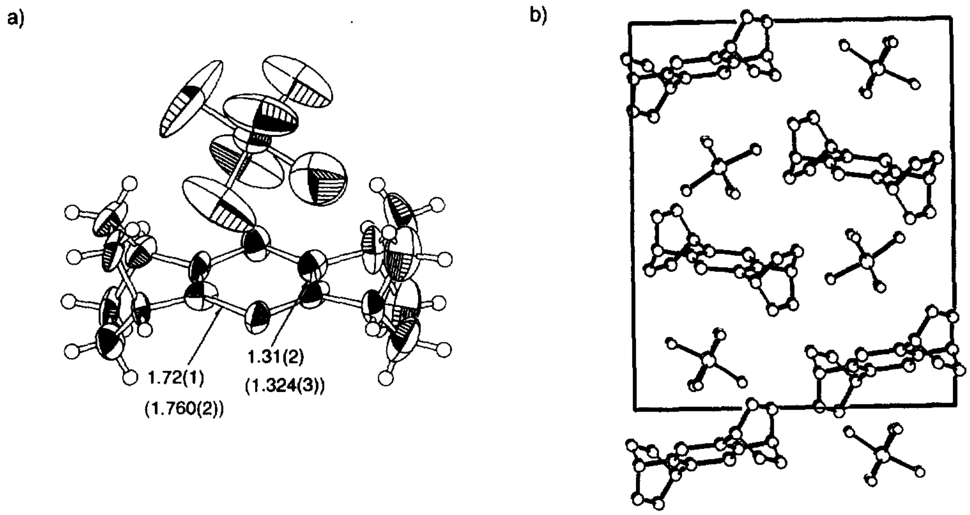

Fig. 1 a) ORTEP (50% probability) and b) crystal packing drawings showing the X-ray structure of $3^{\cdot+}SbF_6^-$. The averaged C–S and C=C bond lengths are included. The values for the X-ray structure of **3** are given in parentheses.

the SbF_6^- salt of radical cation $\mathbf{3}^{\cdot+}$,[7] which was so stable that no decomposition was observed upon standing in air for several days.

For the structure of $\mathbf{3}^{\cdot+}$ (Fig. 1a), the dithiin ring was found to be planar in agreement with the optimized structure[8] at the B3LYP/6-31G* level (Fig. 2c). As shown in Fig. 1a, the observed C–S bond length in the 1,4-dithiin ring is markedly shortened in radical cation $\mathbf{3}^{\cdot+}$ as compared with that of neutral **3**.[9] The theoretical calculations indicated the C–S and C=C bond lengths to be 1.781 and 1.341 Å for **3**, and 1.739 and 1.368 Å for $\mathbf{3}^{\cdot+}$, respectively. Similar results had been obtained also in the calculations of **1** and $\mathbf{1}^{\cdot+}$ [10] and are interpreted in such a way that the character of HOMO of **3**, with the symmetry for the C–S and C=C bonds being out-of-phase and in-phase, respectively, is weakened by the removal of one electron. As shown in the crystal packing of $\mathbf{3}^{\cdot+}SbF_6^-$ (Fig. 1b), no intermolecular S···S contact is possible due to the steric effect of the bicyclic frameworks. Instead, the SbF_6^- anion is located above the dithiin ring, and the cation and anion are arranged alternately along the *b*-axis.

The visible spectrum of $\mathbf{3}^{\cdot+}SbF_6^-$ in CH_2Cl_2 exhibited absorption maxima at 464 and 385 nm (2.67 and 3.22 eV, respectively; Table 1). The calculated transition energy[8] for $\mathbf{3}^{\cdot+}$ with some oscillator strength at the CIS/3-21G* level indicated that the lowest-energy and the second lowest-energy transitions correspond to the HOMO→SOMO and HOMO–1→SOMO transitions, respectively, in fairly good agreement with the observed energies.

A CH_2Cl_2 solution of $\mathbf{3}^{\cdot+}SbF_6^-$ in a lower concentration (~10^{-5} M) showed a nine-line ESR signal due to eight equivalent anti-protons ($a_H = 0.08$ mT, g = 2.0083) as shown in Fig. 2a. The B3LYP/6-31G* calculations indicated that the spin density at the anti-protons of the methylene bridge is 0.0013 while that at the syn-protons and at the bridgehead protons is –0.0004 and –0.0003, respectively. The calculated a_H value for the anti-proton

Table 1. Observed and Calculated Transition Energy for $3^{\cdot+}$

	Transition energy /eV	
	Transition 1	Transition 2
obs.	2.67 (6460)[a]	3.22 (1850)[a]
CIS/3-21G* //B3LYP/6-31G*	3.17 (0.171)[b] {0.98(HOMO→SOMO)}[c]	3.40 (0.066)[b] {0.74(HOMO-1→SOMO)}[c]

[a] ε. [b] Oscillator strength. [c] Main CI coefficients.

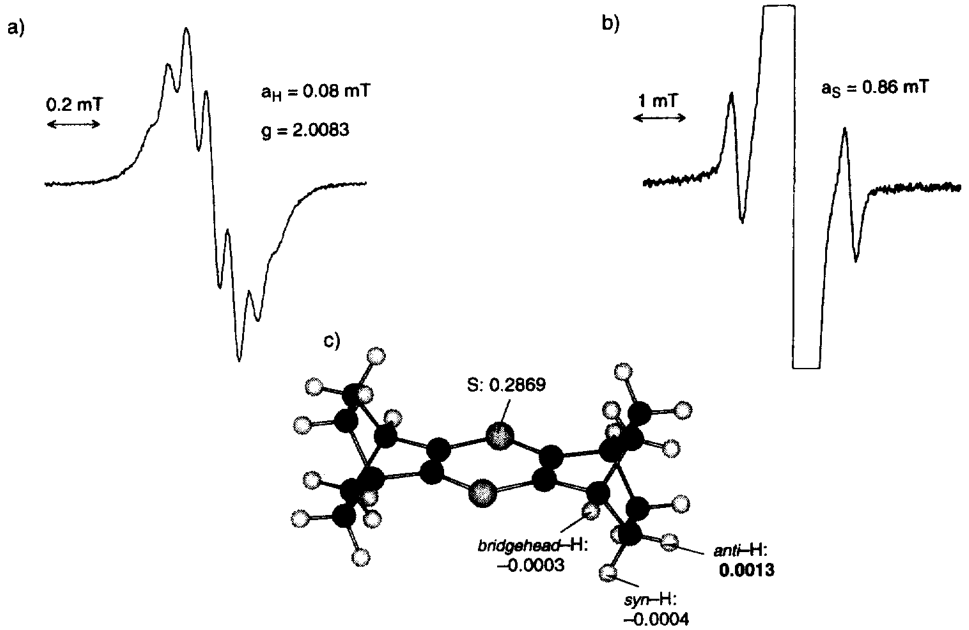

Fig. 2 ESR spectrum of $3^{\cdot+}SbF_6^-$ in CH_2Cl_2 at the concentration of a) ca. 10^{-5} M and b) ca. 10^{-3} M with c) the calculated structure and spin density of $3^{\cdot+}$ at the B3LYP/6-31G* level.

by Fermi contact analysis on Gaussian program was 0.069 mT in fair agreement with the observed value. In a higher concentration (~10^{-3} M), the hyperfine splitting by protons was lost but the signal caused by $M_S = \pm 3/2$ of ^{33}S (isotopic abundance, 0.75%) was observed (Fig 2b). The observed coupling constant was a_S = 0.86 mT, which was smaller than that for $2^{\cdot+}$ (0.92 mT) generated by the reaction with $AlCl_3$,[11] indicating that the spin density on the sulfur atom of $3^{\cdot+}$ is lower than that of $2^{\cdot+}$. The calculated spin density on the sulfur atom of $3^{\cdot+}$ (0.2869 at B3LYP/6-31G*) was also slightly lower than that of $2^{\cdot+}$ (0.2874).

In conclusion, we have succeeded in the first isolation of the radical cation salt of a 1,4-dithiin derivative without benzoannelation. This radical cation was highly stable owing to the annelation with bicyclo[2.2.2]octene units.[4] The decrease in spin density on the sulfur atom for $\mathbf{3}^{\cdot+}$ in comparison with $\mathbf{2}^{\cdot+}$ would indicate the significance of the σ-π conjugation for spin delocalization in 1,4-dithiin radical cation $\mathbf{3}^{\cdot+}$.

Acknowledgement: The present work is supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 10146101) and a Grant-in-Aid for Scientific Research (A) (No. 09304060) 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.

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