Tropothione *S*-Sulfide. A New Class of Thiosulfine[1]

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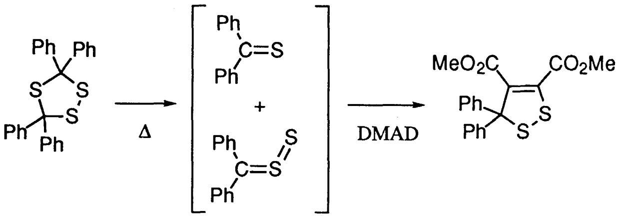
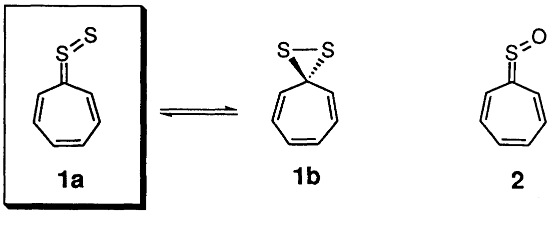
Tropothione *S*-sulfide is synthesized from tropone hydrazone with disulfur dichloride in deaerated chloroform at –78 °C. The *S*-sulfide is detected as an unprecedented $[10\pi + 2\pi]$-type cycloadduct with dimethyl acetylenedicarboxylate.

Recently, there has been a great deal of interest in the thiosulfine[2] (thione *S*-sulfide) of organosulfur compounds.[3] Okazaki et al. reported that the reaction of ketone hydrazones with disulfur dichloride produces thioketones in high yields.[4] The resulted thioketones are thought to be formed via thiosulfines[2,5] as extremely unstable and undetectable intermediates. Huisgen et al. demonstrated the first unequivocal evidence of the existence of thiosulfine bond.[2] The thermal decomposition of 3,3, 5,5-tetraphenyl-1,2,4-trithiolane, thiobenzophenone *S*-sulfide was trapped by dimethyl acetylenedicarboxylate (DMAD).



We report herein the synthesis of tropothione (cycloheptatrienethione) *S*-sulfide (**1a**) in connection with tropothione *S*-oxide (**2**).[6] The titled compound **1a** constitutes the first example of annulene thiosulfine and undergoes the first instance of $[10\pi + 2\pi]$-type cycloaddition. The possibility of a geometric isomer, dithiirane **1b**, is examined theoretically.

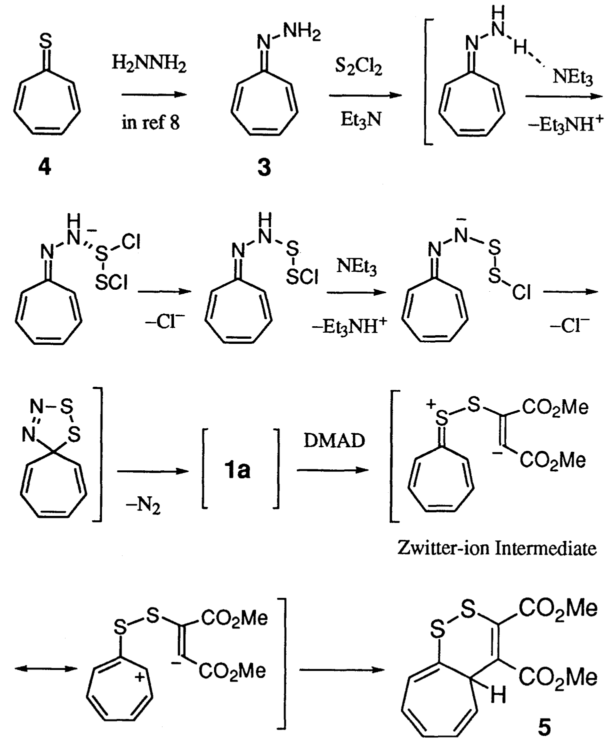


1a **1b** **2**

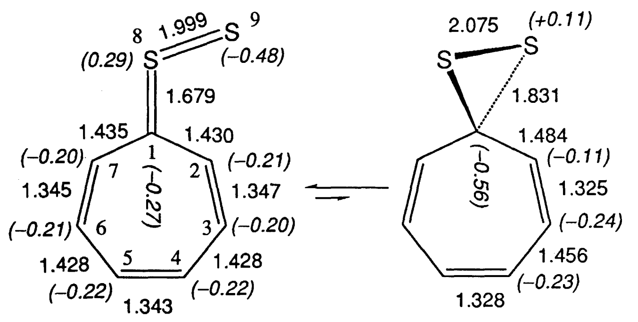
We previously reported the synthesis of tropone hydrazone[7] (**3**) from the reaction of tropothione[7–9] (**4**) and hydrazine. In contrast, tropone itself does not form its hydrazone by treatment with hydrazine but gives only 2-aminotropone exclusively.[10] Taking advantage of the formation of **3**, we have succeeded in the synthesis of **1a**, the first example of an annulenethione *S*-sulfide viz. unsaturated thiosulfine.

We have performed the generation of the *S*-sulfide **1a** in situ using the hydrazone (**3**) and disulfur dichloride (S_2Cl_2) in carefully deaerated solution of anhydrous chloroform at –78 °C under the presence of triethylamine. In contrast to the nonoccurrence of the reaction between the *S*-oxide **2** and DMAD,[6] the *S*-sulfide **1a** was trapped efficiently by an excess amount of DMAD to give cycloadduct **5**, pale yellow liquid,[11] as a predominant product. Column and repeated thin-layer chromatographic separation followed by bulb-to-bulb distillation [bp 32 °C (0.001 mmHg)] led to the isolation of the product in 23% yield (pure isolated). Elemental analysis and mass spectrometric data of the cycloadduct **5** indicate that **5** is a 1:1 adduct between the *S*-sulfide **1a** and DMAD. The ^{1}H NMR spectrum[11] shows a six-spin system indicating a cycloheptatrienethiol moiety. The ^{13}C NMR spectral data[11] demonstrate that the structure is of a novel $[10\pi + 2\pi]$-type cycloadduct. The structure of **5** shows unequivocal evidence of the formation of tropothione *S*-sulfide **1a**. Senning et al. reported an equilibrium between thiosulfines and dithiiranes.[3] It is theoretically examined whether the *S*-sulfide **1a** or the dithiirane **1b** intervenes predominantly in the present experiment.

Ab initio MO (RHF/3-21G*) calculations[12] demonstrate that **1a** is by 3.9 kcal/mol more stable than **1b**, which confirms that **1a** intervenes as a reactive species in Scheme 1. Net charges (positive, cationic in parentheses) are attached to optimized geometries of **1a** and **1b**. While two sulfur atoms of **1b** is



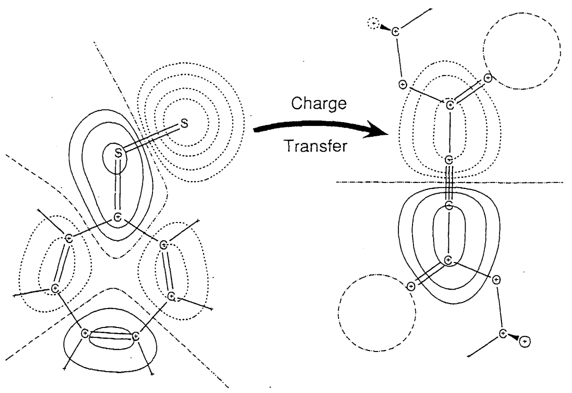
Scheme 1. Schematic interpretation of the formation and detection of tropothione *S*-sulfide (**1a**) and its $[10\pi + 2\pi]$ cycloadduct (**5**).



1a (C_3)
0 kcal/mol

1b (C_{2v})
+3.9 kcal/mol

Figure 1. Molecular and electronic structures of tropothione *S*-sulfide (**1a**) and dithiirane (**1b**) optimized with RHF/3-21G* method. **1a** is computed to be planar and **1b** is to be of C_{2v} symmetry. Numbers in parentheses denote net electronic charges (positive, cationic). The bond distances are presented in Å.



HOMO of **1a** LUMO of DMAD

Figure 2. A charge-transfer interaction between two frontier orbitals. The HOMO of **1a** and the LUMO of DMAD are both π orbitals. The shapes of the RHF/3-21G* frontier orbitals are drawn at the 1.5 Å-above the molecular plane. Interrupted lines denote borderlines of positive and negative contours.

slightly cationic (+0.11), the terminal one of **1a** is quite anionic (−0.48). This anionic nature may be related to the electrophilic attack by DMAD. In fact, Figure 2 indicates an effective charge donation for formation of the zwitter-ionic intermediates in Scheme 1. This one-site interaction is likely owing both to the [10π + 2π] symmetry forbiddeness and to the large size difference between the reaction-center distances, S(9)•••C(2) in **1a** and C≡C in DMAD. In contrast to the flexible C–S bond in the intermediate, the rigid C–O bond in the similar zwitter-ionic intermediate of the thione *S*-oxide (**2**) and DMAD[6] would interfere with the C–C bond completion for a [10π + 2π] cycloadduct.

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References and Notes

1 This paper is dedicated to Professor Emeritus Rolf Huisgen, Universität München, on the occasion of his visiting Japan. For his biography and research history, see: R. Huisgen, "The Adventure Playground of Mechanisms and Novel Reactions" ed by J. I. Seeman; Profiles, Pathways, and Dreams: Autobiographies of Eminent Chemists; American Chemical Society, Washington, DC, USA (1994).

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11 The product **5** has given a satisfactory elemental analysis. Selected spectral data for **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (d, 1H, *J*=5.7 Hz), 3.81 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.41 (dd, 1H, *J*=9.0, 5.7 Hz), 6.46 (dd, 1H, *J*=9.0, 5.8 Hz), 6.58 (d, 1H, *J*=6.3 Hz), 6.92 (dd, 1H, *J*=11.2, 6.3 Hz), and 7.13 (dd, 1H, *J*=11.2, 5.8 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 52.11 (q, OMe), 53.18 (q, OMe), 53.82 (d), 121.06 (d), 126.01 (d), 126.64 (d, 2C), 127.26 (s), 129.85 (s), 134.40 (s), 136.72 (d), 161.95 (s), and 163.47 (s); EI-MS (30 eV) *m*/*z* (relative intensity) 282 (M^+, 26), 218 (77), 154 (93), 122 (100), 121 (63), 78 (88), 64 (48).

12 RHF/3-21G* geometry optimizations were carried out, using the GAUSSIAN 92 program[13] installed both on a CONVEX C-220 computer in the Information Processing Center of Nara University of Education and on a CONVEX C-3420 computer in the Computer Center of Nara University.

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