J. Am. Chem. Soc. 1994, 116, 407–408

Tropothione S-Oxide: The First Example of a Sulfine Charge Reversion (Umpolung)[1]

Takahisa Machiguchi,* Toshio Hasegawa, and
Hiroyuki Otani

*Department of Chemistry, College of Liberal Arts and
Science, Saitama University, Urawa, Saitama 338, Japan*

Shinichi Yamabe

*Department of Chemistry, Nara University of Education
Nara, Nara 630, Japan*

Hiroshi Mizuno

*National Institute of Agrobiological Resources
Tsukuba, Ibaraki 305, Japan*

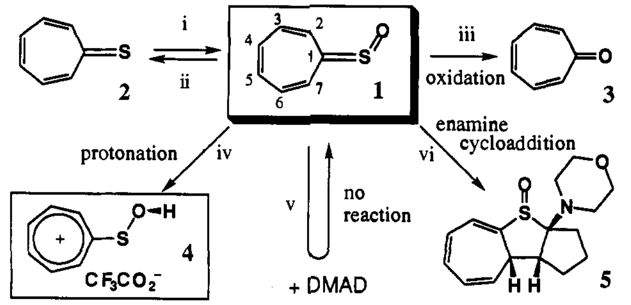
Received September 13, 1993

We report herein the synthesis and properties of tropothione (cycloheptatrienethione) *S*-oxide (**1**), providing the first examples both of a stable "annuleneheterocumulene" and sulfine charge reversion. In the annuleneheterocumulenes without benzene-ring fusion,[2] 8-oxoheptafulvene has been known as the only compound detected by chemical reactions owing to an extreme instability.[3] No representative of annuleneheterocumulenes has yet been isolated.

Peroxy acid oxidation of tropothione[4] (**2**) at room temperature afforded tropone (**3**). However, careful oxidation with the equimolar amount of *m*-chloroperbenzoic acid (*m*-CPBA) below −60 °C led to the isolation of **1**,[5] dark red needles, mp 67–68 °C (Scheme 1). This *S*-oxide is a surprisingly stable compound, in sharp contrast to a 2π aromatic system, diphenylcyclopropenethione *S*-oxide, which is unstable and cannot be isolated and characterized.[6]

The structure of the *S*-oxide **1** is fully consonant with the spectral data.[5] The X-ray structural analysis[7] of **1** indicates that the molecule has a planar and regular heptagonal structure with all the endocyclic bond angles ~128° (Figure 1) and an especially long C–S (1.681 Å) bond, whose double bond character is estimated to be 75%.[8] The length is the largest one in those of sulfines ever reported.[9] The ring C–C distances show the fairly nonalternant (aromatic) bond characters relative to those of **2**[4] and **3**.[10,11] The *S*-oxide **1** is found to have a larger dipole moment, μ = 4.57 D, than those of **2** (3.88 D)[4] and **3** (4.17 D).[12] The ^{17}O, ^{33}S, and ^{13}C NMR chemical shifts[5] in **1** show a large upfield shift for the oxygen and the sulfur and a downfield one for the sulfinyl carbon, respectively, compared with those[13] of a usual sulfine, fluorenethione *S*-oxide.[14] All these data demonstrate that **1** has a sulfine charge-reversion character through the power of the Hückel ($4n + 2$) rule; the remarkable stability of **1** may be attributed to optimal contribution of **1c** (ring aromatic sextet) in Scheme 2, viz. *sulfine charge reversion.*

Scheme 1. Synthesis and Selected Reactions of **1**[a]



[a] Conditions: (i) monoperphthalic acid or *m*-CPBA, 1.0 equiv, CH_2Cl_2, −60 °C, 2 h, 75% yield; (ii) tetraphosphorus decasulfide, CH_2Cl_2, −5 °C, 1.5 h, 91%; (iii) *m*-CPBA, 2.2 equiv, CH_2Cl_2, −50 °C, 3 h, 73%, or $Pb(OAc)_4$, 1.0 equiv, CH_3CO_2H, 20 °C, 2 h, 77%; (iv) CF_3CO_2H, CH_2Cl_2, 0 °C; (v) DMAD, $CHCl_3$, reflux, 2 days; (vi) 1-morpholinocyclopentene, CH_2Cl_2, room temperature, 4 h, 73%.

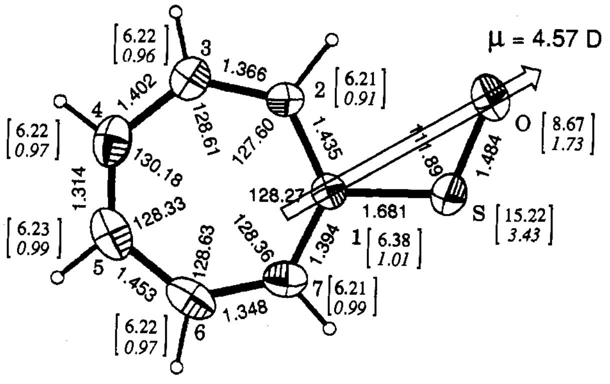


Figure 1. ORTEP drawing of the X-ray structure of tropothione *S*-oxide (**1**) illustrating selected bond lengths (Å) and angles (deg). Bracket values are 3-21G* total (upper) and π (lower) atomic densities.[18] The 3-21G* dipole moment vector arrow starting from C(1) is found to be just across the oxygen atom (anionic center).

Sulfines[15,16] are usually represented by combination of the neutral (>C=S=O), ylene ($>C=S^+-O^-$), and ylide ($>C^- -S^+=O$) resonance structures,[17] which are reproduced by the 3-21G*[18a] π electron distribution[18b] (C −0.110, S +0.746, O

---

(1) Dedicated to Professor Klaus Hafner on the occasion of his 66th birthday.

(2) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and their Valence Isomers*; CRC: Boca Raton, FL, 1987; 3 volumes. Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333–357.

(3) Asao, T.; Morita, N.; Kitahara, Y. *J. Am. Chem. Soc.* **1972**, *94*, 3655–3657.

(4) Machiguchi, T.; Hasegawa, T.; Itoh, S; Mizuno, H. *J. Am. Chem. Soc.* **1989**, *111*, 1920–1921. Machiguchi, T.; Hasegawa, T.; Ishii, Y.; Yamabe, S.; Minato, T. *J. Am. Chem. Soc.* **1993**, *115*, 11536–11541 and references therein.

(5) **1**: IR (KBr) ν_{max} 1089 (vs), 990 (vs) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.01 (ddd, H-6), 6.13 (dddt, H-4), 6.20 (ddd, H-3), 6.21 (ddddd, H-5), 6.57 (ddt, H-7), 7.29 (ddt, H-2); $J_{2,3}$ 11.6, $J_{2,4}$ 1.0, $J_{2,5}$ 2.2, $J_{2,6}$ < 1.0, $J_{2,7}$ 1.0, $J_{3,4}$ 7.6, $J_{3,5}$ 1.5, $J_{4,5}$ 11.0, $J_{4,6}$ 1.2, $J_{4,7}$ 1.0, $J_{5,6}$ 7.6, $J_{5,7}$ 2.1, $J_{6,7}$ 11.8 Hz; ^{13}C NMR (100.6 MHz) δ 189.46 (s, C-1), 137.26 (d, C-5), 133.67 (d, C-4), 132.91 (d, C-3), 132.44 (d, C-7), 130.93 (d, C-6), 130.83 (d, C-2); ^{17}O NMR (54.2 MHz, $CDCl_3$, external D_2O) δ 153; ^{33}S NMR [30.7 MHz, $CDCl_3$, external $(NH_4)_2SO_4$] δ −6.

(6) Lown, J. W.; Maloney, T. W. *J. Org. Chem.* **1970**, *35*, 1716–1718.

(7) Crystal data for **1**: monoclinic, space group $P2_1/a$, $a = 6.885(1)$, $b = 14.128(1)$, and $c = 6.840(1)$ Å, $\beta = 102.75(1)°$, $V = 648.9(1)$ Å^3, $Z = 4$, $D_c = 1.415$ g cm^{-3}; 1110 reflections measured, 836 observed $[F_o > 3\sigma(F_o)]$; $R = 0.051$, $R_w = 0.050$. The structure was solved by direct methods.

(8) Abrahams, S. C. *Q. Rev., Chem. Soc.* **1956**, *10*, 407–436.

(9) Bates, R. B.; Wolfe, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 6854–6855. Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 1264–1265. Britton, T. C.; Lobl, T. J.; Chidester, C. G. *J. Org. Chem.* **1984**, *49*, 4773–4780. Reference 15b and references therein.

(10) Barrow, M. J.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1973**, 66–67.

(11) Bertelli, D. J.; Andrews, T. G., Jr.; Crews, P. O. *J. Am. Chem. Soc.* **1969**, *91*, 5286–5296.

(12) Di Giacomo, A.; Smyth, C. P. *J. Am. Chem. Soc.* **1952**, *74*, 4411–4413. Kurita, Y.; Seto, S.; Nozoe, T.; Kubo, M. *Bull. Chem. Soc. Jpn.* **1953**, *26*, 272–275.

(13) NMR data of fluorenethione *S*-oxide: ^{13}C NMR ($CDCl_3$, Me_4Si) δ 179.21 (C-1); ^{17}O NMR ($CDCl_3$, external D_2O) δ 215; ^{33}S NMR [$CDCl_3$, external $(NH_4)_2SO_4$] δ 233, measured here for comparison with those of **1**. ^{17}O NMR data of sulfines have been recorded for propanethial *S*-oxide and ethanethial *S*-oxide at δ 196 and 199, respectively.[15c]

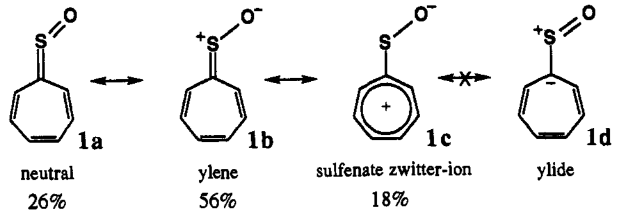
(14) Sheppard, W. A.; Diekmann, J. *J. Am. Chem. Soc.* **1964**, *86*, 1891–1892.

(15) For reviews of sulfines, see, e.g.: (a) Zwanenburg, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *43*, 1–24. (b) Zwanenburg, B. *Recl: J. R. Neth. Chem. Soc.* **1982**, *101*, 1–27. (c) Block, E. In *Org. Sulfur Chem., Invited Lect. Int. Symp., 9th*; Freidlina, R. Kh.; Skorova, A. E. Eds.; Pergamon: Oxford, 1981; pp 15–34.

(16) Recent reports on sulfines: e. g., Block, E.; Schwan, A.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 3492–3499. Gradel, J.; Sundermeyer, W. *Chem. Ber.* **1992**, *125*, 1889–1894.

0002-7863/94/1516-0407$04.50/0

Scheme 2. Resonance Contributions of **1**[a]



[a] The % weights are obtained by the use of π electron densities in Figure 1 (supplementary material).

–0.636) of the parent sulfine, $H_2C{=}S{=}O$.[19] This π electron distribution is in contrast to that (ring +0.160, S +0.572, O –0.732 in Figure 1) of **1**. This cationic nature of the ring arises from the effective three-body π MO mixing of the HOMO of hexatriene and the HOMO and LUMO of $H_2C{=}S{=}O$ (supplementary material). The second in-phase MO mixing leads to an accumulation of anomalously large π electronic charge on the oxygen and consequently to the large dipole moment. The contribution of **1c** is evidenced by the rigid planarity of the ring. With the RHF/3-21G* vibrational analysis, **1** is calculated to have the harmonic frequency (200 cm^{-1}) of the out-of-plane puckering mode which is larger than the 70 cm^{-1}of **2** and the 81 cm^{-1} frequency of **3**.[18]

Scheme 1 exhibits the selected reactions of **1**. The *S*-oxide **1** reacts with CF_3CO_2H to form a *stable* sulfenic acid **4** (dark orange prisms with the melting point between –25 and –24 °C),[20] with a tropylium cation system,[21] in solution through the out-of-plane protonation to the oxygen.[22] Reaction of **1** with dimethyl acetylenedicarboxylate (DMAD) does not occur, in contrast to [4 + 2][23] or [8 + 2][24] cycloaddition between DMAD and **3** or **2**, respectively. The nonoccurrence indicates that the α-carbons (C-2, C-7) lose their electron-donating strength due to the canonical structure, **1c**. In contrast, **1** reacted readily with an enamine to give an unprecedented sulfine–enamine cycloadduct, **5**,[25] whose orientation is opposite that of fluorenethione *S*-oxide.[14,26] Thus, the reaction behaviors also support the conclusion that the contribution of **1c** as well as **1b** is essentially important.

In conclusion, the three-body π MO mixing is effective enough to reverse the normal electron distribution of the parent sulfine ($H_2C{=}S{=}O$) and accordingly to give the first stable annulene-heterocumulene, **1**, and its protonated species **4**. The tropylium cation **4** is the first *stable* sulfenic acid (–S—O—H) without bulky groups[27] identified explicitly by NMR (^{13}C, ^1H, ^{17}O, and ^{33}S) spectroscopies. The stability of **4** is remarkable and is in agreement with earlier proposals that reducing the nucleophilicity of the sulfenic acid with electron-attracting groups will increase stability.[28]

Supplementary Material Available: Tables of atomic coordinates, thermal parameters for **1**, the way of computing % weights of **1a–c** in Scheme 2, further MO interpretation for the difference in the stability between **1** and diphenylcyclopropenethione *S*-oxide, the HOMO shape of **1** arising from the effective three-body π MO mixing, and NMR (^{13}C, ^1H, ^{17}O, and ^{33}S) charts of **1** and **4** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(17) Zwanenburg, B.; Thijs, L.; Strating, J. *Recl: J. R. Neth. Chem. Soc.* **1967**, *86*, 577–588. Duss, F. In *Thiocarbonyl Compounds*; Barton, D., Ollis, W. D., Jones, D. N., Eds.; Comprehensive Organic Chemistry, The Synthesis and Reactions of Organic Compounds; Pergamon: Oxford, U.K., 1979; Vol. 3, pp 409–415.

(18) (a) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048. (b) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A. GAUSSIAN 82 program package; Chemistry Publishing Unit: Carnegie-Mellon University, Pittsburgh, PA, 1982.

(19) Snyder, J. P. *J. Org. Chem.* **1973**, *38*, 3965–3967. Block, E.; Bock, H.; Mohmand, S.; Rosmus, P.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 383–384. Flood, E.; Boggs, J. E. *J. Mol. Struct.* **1976**, *34*, 147–151. Block, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135–1178 and references therein.

(20) **4** (in CF_3CO_2H): λ_{max} 382 nm (log ϵ 4.16); ^{13}C NMR (Me_4Si) δ 192.15 (s), 149.42 (d), 148.73 (d), 139.88 (d); ^1H NMR (Me_4Si) δ 8.53, 8.38, 8.30; ^{17}O NMR (external D_2O) δ 73; ^{33}S NMR [external $(NH_4)_2SO_4$] δ –85. Carefully degassed solution of **4** is stable in a sealed NMR tube at room temperature for more than several weeks. When exposed to moisture, it is converted gradually to form **2** ($t_{1/2}$ ca. 4 weeks). On warming of the solution to 60 °C, sulfenic acid **4** could not be recovered.

(21) Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361–6362. Stang, P. J.; Maas, G.; Smith, D. L; McCloskey, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4837–4845.

(22) Schwab, M.; Sundermeyer, W. *Chem. Ber.* **1986**, *119*, 2458–2465. Sundermeyer, W. *Synthesis* **1988**, 349–359.

(23) Kinstle, T. H.; Carpenter, P. D. *Tetrahedron Lett.* **1969**, 3943–3946.

(24) Machiguchi, T.; Hoshino, M.; Ebine, S.; Kitahara, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 196.

(25) **5**: bp 55 °C/0.01 mmHg; IR ν_{max} (CCl_4) 1160 (s) (>S=O), 724 (s) cm^{-1}; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 81.70 (s, C-13), 127.58 (s, C-2); ^1H NMR δ 5.01 (dd, 1 H, $J_{7,8}$ = 5.8 Hz, H-7).

(26) Majid Hamid, A.; Trippett, S. *J. Chem. Soc. C* **1968**, 1612–1615.

(27) Cf. Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205–216. Nakamura, N. *J. Am. Chem. Soc.* **1983**, *105*, 7172–7173. By microwave spectroscopy, the structure of methanesulfenic acid CH_3–S–O–H was determined: Penn, R. E.; Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 3622–3623.

(28) Davis, F. A.; Jenkins, L. A.; Billmers, R. L. *J. Org. Chem.* **1986**, *51*, 1033–1040.