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Crystal and Molecular Structure of Tropothione at -40 °C

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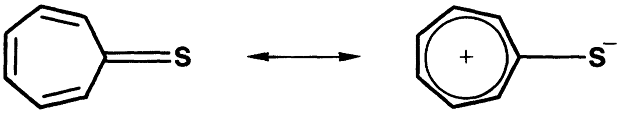
An X-ray analysis of thermally unstable tropothione (**1**) has revealed a conspicuous packing of anti-parallel arrangement in sheets quite different from that of the parent tropone, an approximate planar carbon ring, and an especially longer C=S bond than that in diphenylcyclopropenethione. The bond alternation of **1** is also confirmed by NMR simulation analysis.

Tropothione (**1**) (2,4,6-cycloheptatriene-1-thione), which is iso-π-electronic with tropone (**2**), is the parent molecule of a non-benzenoid aromatic seven-membered ring system$^{1)}$ containing sulfur, and therefore the molecule (**1**) has aroused theoretical interest. In recent years the chemistry of thiocarbonyl compounds has extensively been studied, but conjugated thioketones have little been explored because of their instability. We have recently reported the synthesis and isolation of **1** as a thermally unstable crystalline compound.$^{2)}$ The tropothione system has been cited as an example of non-benzenoid aromatic compounds which may be formally represented by the following resonance contribution forms.



1 **1a**

In view of the theoretical significance of the compound, it seems of interest and importance that the crystal structure by X-ray analysis and the NMR parameters are determined. In this paper, we would like to report the crystal and molecular structure of **1** as a fundamental geometrical data both for a conjugated thioketone and an annulenethione system, and the high resolution ^{1}H NMR spectroscopy with simulation analysis to evaluate the aromaticity of **1**.

Red needle-shaped crystals suitable for X-ray crystallographic study were obtained by recrystallization from ether at -80 °C.$^{2)}$ The crystals rapidly turn pale yellow at the mp (21.5 °C) and decompose gradually even below the mp. X-Ray intensity data of a crystal, 0.1 x 0.2 x 0.4 mm^3, were collected on an Enraf-Nonius CAD-4 diffractometer equipped with an FR558SH cryogenic device operated at -40 °C

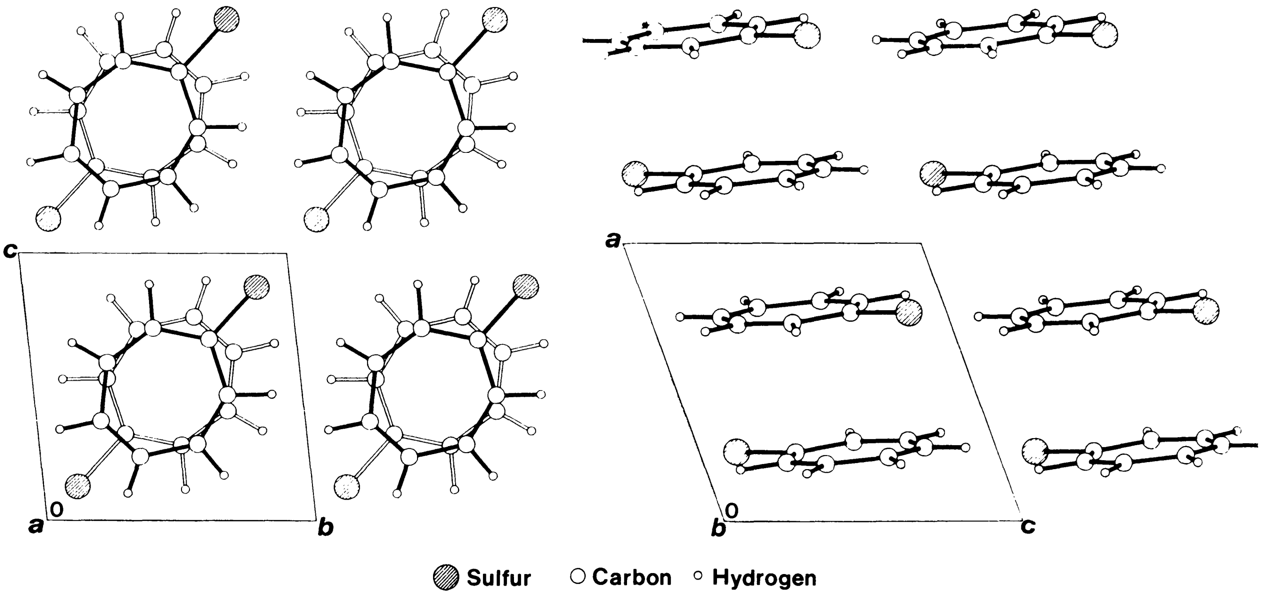


Fig. 1. Molecular packing diagram along the *a* axis (left) and the *b* axis (right).

(liquid nitrogen as the coolant),[3] employing the ω-2θ scan mode, and no appreciable decomposition was observed during the data measurements. During the data collection three reflections were monitored for crystal decay. The cell constants were determined from a least-squares refinement of the setting angles of 25 medium angle reflections. Of a total of 1862 reflections up to 2θ = 60°, 958 with intensities greater than $10\sigma(I)$ were used for the structure analysis. These were corrected for Lorentz and polarization factors but not for absorption. The crystal data are: C_7H_6S, M = 122.19, triclinic, space group $P\bar{1}$, a = 7.404(15), b =6.983(8), c = 7.022(7) Å, α = 105.31(8), β = 114.19(12), γ = 65.48(13)°, V = 299.4 Å^3, D_c = 1.356 g cm^{-3}, Z = 2; Mo-$K\alpha$ radiation with a graphite monochrometer, λ = 0.71069 Å, μ (Mo-$K\alpha$) = 4.01 cm^{-1}. The structure was solved by direct methods with the program MULTAN 82.[4] Positional and anisotropic thermal parameters for non-H atoms were refined by full-matrix least-squares. All H atoms were located on difference Fourier maps. Their positional parameters were included in the refinement with a fixed isotropic thermal parameter of 1.6 Å^2. Final refinement converged to R = 0.085 and R_w = 0.118.[5] Atomic scattering factors used were taken from International Tables for X-ray Crystallography.[6] Calculations were carried out on a VAX 750.

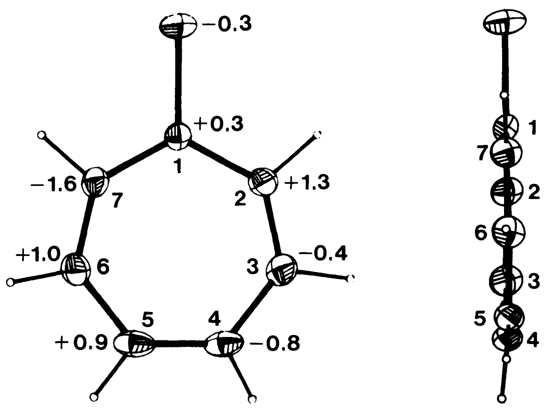


Fig. 2. ORTEP[7] drawings of tropothione (1): front (left) and side view (right).

The most characteristic feature in the crystal structure is the stacking interactions. Figure 1 shows that the molecules are arranged in pairs of anti-parallel packing over centers of symmetry, running along the *a* axis.

The distance between the planes is 3.45 Å. This arrangement contrasts sharply with a parallel packing observed in the crystal structure of **2**.[8] The molecule is approximately planar. Figure 2 illustrates the deviation of atoms in hundredths Å from the least-squares plane defined by atoms C(2)-C(7). Table 1 summarizes the bond lengths and angles. The lengths of the C=C double bonds and the C-C single bonds in **1** nearly approximate to those of **2**.[8] The exocyclic C=S bond length reveals an especially large distance (1.676 Å)[9] close to that in 1,3-dimethylimidazole-2(3*H*)-thione (1.696 Å)[10] which has been reported as indicating the major contribution of polar resonance structure, and in contrast to those in diphenylcyclopropenethione (1.630 Å)[11] and in 2,4,6-tri-*t*-butylthiobenzaldehyde (1.596 Å) whose C=S bond is not conjugated with the benzene ring.[12]

Table 1. Bond lengths (Å) and angles (°) of non-hydrogen atoms

C(1)-S	1.676(5)	C(1)-C(2)	1.431(7)	C(2)-C(3)	1.365(6)	C(3)-C(4)	1.437(7)
C(4)-C(5)	1.355(8)	C(5)-C(6)	1.418(7)	C(6)-C(7)	1.373(7)	C(7)-C(1)	1.461(7)

C(7)-C(1)-C(2)	122.8(4)	C(1)-C(2)-C(3)	131.1(5)	C(2)-C(3)-C(4)	129.7(5)
C(3)-C(4)-C(5)	128.2(4)	C(4)-C(5)-C(6)	127.7(5)	C(5)-C(6)-C(7)	130.3(5)
C(6)-C(7)-C(1)	130.3(5)	S-C(1)-C(2)	119.0(4)	C(7)-C(1)-S	118.3(3)

In addition to the above analysis in solid state, we examined high resolution ^1H NMR spectroscopies on **1** at 90, 200, and 400 MHz spectrometers to evaluate the bond alternation of **1** in solution state. In these spectra, the three types of protons resonated.[13] The NMR parameters for **1** are summarized in Table 2[14] with those of **2**[16] for comparison. The assignments were confirmed by its simulation analysis and ^1H-^1H and ^1H-^{13}C decoupling experiments, and further verified by the synthesis of tropothione-2,7-d_2 (**1**-d_2).[17] The difference between $J_{2,3}$ and $J_{3,4}$ and $J_{3,4}$ and $J_{4,5}$ in **1** are 5.0 and 4.0 Hz, respectively, which are significantly greater than those of **2** (3.8 and 2.8 Hz[16]). Furthermore, these vicinal coupling constants are very similar to those of cyclohepta-2,4-dienone ($J_{2,3}$ = 13.0, $J_{3,4}$ = 7.4, and $J_{4,5}$ = 11.4 Hz[16]).

Table 2. NMR parameters of tropothione (**1**)

	Solvent	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{2,4}$	$J_{2,7}$	$J_{3,5}$	$J_{2,5}$	$J_{2,6}$	$J_{3,6}$
1	$CDCl_3$	12.5	7.5	11.5	1.2	2.9	1.3	0.9	-0.4	0.1
2	Benzene-d_6	12.0	8.2	11.0	1.1	3.2	1.1	0.7	-0.3	0.1

Thus tropothione (**1**) has a conspicuous packing of anti-parallel arrangement and a fairly similar bond alternation in the ring to that of tropone (**2**) in crystalline state, but in solution **1** exhibits a somewhat greater bond alternation than **2**. The latter result is in agreement with the smaller dipole moment of **1** (3.88 D, benzene)[2] than that of **2** (4.30 D),[19] which suggests a less polar character of **1**.

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References

1) For a recent review: T. Asao and M. Oda, "Carbocyclische π-Elektronen-Systeme," in "Houben-Weyl, Methoden der organischen Chemie," ed by E. Müller and O. Bayer, Georg Thieme, Stuttgart (1986), Band 5, Teil 2c, pp. 49-780.

2) T. Machiguchi, H. Otani, Y. Ishii, and T. Hasegawa, Tetrahedron Lett., 1987, 203.

3) We thank Drs. Y. Kawakami and M. Nezu for their courtesy in kind permission for use of the X-ray diffractometer at the Laboratory of Eisai Co. Ltd.

4) P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. -P. Declercq, and M. M. Woolfson, "MULTAN 82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univ. of York, England, and Louvain, Belgium (1982).

5) The atomic coordinates and thermal parameters for **1** are available on request.

6) International Tables for X-Ray Crystallography, Kynoch Press, Birmingham (1974), Vol. 4, pp. 72-151.

7) C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Lab. (1976).

8) M. J. Barrow and O. S. Mills, J. Chem. Soc., Chem. Commun., 1973, 66.

9) It seems that the C=S bond length of **1** suggests a certain contribution of the polar resonance structure (**1a**).

10) G. B. Ansell, J. Chem. Soc., Perkin Trans. 2, 1972, 841.

11) L. L. Reed and J. P. Schaefer, J. Chem. Soc., Chem. Commun., 1972, 528.

12) R. Okazaki, Kagaku No Ryoiki, 37, 178 (1983); R. Okazaki, "Perspectives in the Organic Chemistry of Sulfur," ed by B. Zwanenburg and A. J. H. Klunder, Amsterdam (1987), pp. 41-56.

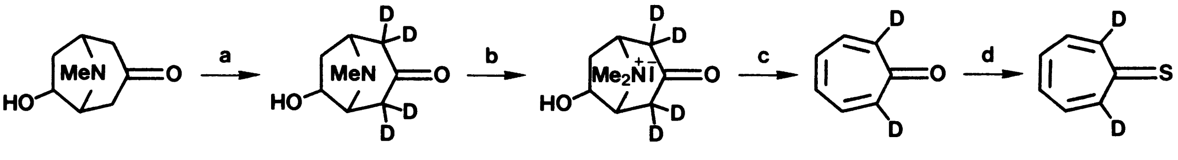
13) δ (400 MHz, $CDCl_3$, -40 °C) 8.02 (H-2,7), 7.04 (H-4,5), and 6.80 (H-3,6).

14) It is known that geminal coupling constants vary widely with solvent polarity. However, vicinal coupling constants in both vinyl and aromatic systems vary only 2-3% over wide range of solvent polarity.$^{15)}$ The change of vicinal coupling constants in **1** was 0.1 Hz or less in passing from CCl_4 to DMSO-d_6.

15) V. S. Watts and J. H. Goldstein, J. Chem. Phys., 42, 228 (1965); H. M. Hutton and T. Schaefer, Can. J. Chem., 43, 3116 (1965).

16) D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, J. Am. Chem. Soc., 91, 5286 (1969).

17) **1**-d_2 (isotopic purity: d_2, 97.3%; d_1, 2.7%; d_0, 0.0%, by mass spectrometry) was synthesized via tropone-2,7-d_2 (d_2, 97.8%; d_1, 2.2%) according to our previous paper$^{2)}$ starting from 6-hydroxytropinone$^{18)}$ as the following scheme.



(a) K_2CO_3/D_2O, 90 °C, 4 h; 95%. (b) MeI/EtOH, 5 °C, 10 h; 99%.
(c) Na_2CO_3/D_2O, 60 °C, 3 h; 76%. (d) P_2S_5-$Et_3N/CHCl_3$, 0 °C, 30 min; 95%.

18) E. E. van Tamelen, P. Barth, and F. Lornitzo, J. Am. Chem. Soc., 78, 5442 (1956).

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

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