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Synthesis and Isolation of Tropothione: A Comparative Study of Spectral Property with Tropone[1]

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Abstract: The synthesis, isolation, and spectral characterization of tropothione (**1**), the sulfur analogue of tropone (**2**), are described with comparison of those for **2**. Direct sulfurization of **2** with tetraphosphorous decasulfide using triethylamine as a catalyst yields the titled compound **1** in high yield. Although **1** is thermally unstable material [$t_{1/2}$ (crystalline state, 0 °C) 56 min], dilute solutions are found to be sufficiently stable enough for measuring spectral data [$t_{1/2}$ (0.01 mol/L, 25 °C) 10.4 days]. The compound **1** is isolated as a labile material of deep red crystals with the melting range of 20–21 °C. IR spectrum of **1** exhibits a very strong band of the νC=S stretching vibration at 1087 cm^{-1} in CCl_4. Raman spectrum supports the assignment. UV–visible spectra in six solvents show three transitions at around 225 (log ε ca. 4), 253 (ca. 4), and 380 nm (ca. 4.2), while **1** exhibits an additional weak absorption of n–π* transitions at 610 nm (log ε 1.62). ^{1}H NMR of **1** shows wide signals of symmetrical AA'BB'XX' pattern comprising with a large downfield part of α-protons in the ring due to the magnetic anisotropy of the C=S group greater than that of C=O one in **2**. ^{13}C NMR of **1** displays three doublet signals (δ 131.48, 138.36, and 153.80) accompanying with the singlet one at δ 213.83 (C=S). ^{33}S NMR of **1** exhibits δ –287 as the first measurement for thiocarbonyl compounds. These physical properties of **1** are in sharp contrast to those of **2**.

Although a great deal of efforts has been expended in studying the chemistry of both troponoid[2] and thiocarbonyl compounds,[3] little is known about their combined system ([7]annulenethione system), because of the potential instability of thioketone structure.[4] Replacement of the exocyclic heteroatom in [7]annulenone system to the sulfur forms a new family of tropothione[5] (cycloheptatrienethione) (**1**) having the same ring system and number of π-electrons. The effect of this atomic mutation has been the object of theoretical and experimental interest.[6,7] The titled compound **1**, the sulfur analogue of tropone (**2**), is one of the simplest possible novel (nonbenzenoid) aromatic compounds, therefore the compound is a substance of theoretical importance. Recently we have reported several substantial information acquired on the synthesis and chemical properties on some of substituted tropothione derivatives which can be handled at room temperature.[5] Owing to its instability, the parent tropothione **1** has been largely ignored despite the importance having the fundamental structure. The instability and low yield of **1** have long precluded the isolation, structural confirmation, and analysis of this compound.[8]

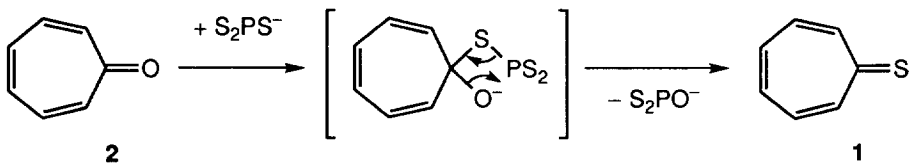
The fundamental structure of tropothione (**1**) encouraged us to attempt to synthesize by direct sulfurization of tropone under mild conditions using tetraphosphorous decasulfide,[9] although Nozoe et al. reported

that this reaction of tropone with tetraphosphorous decasulfide could not be achieved.[10] We have found that tropone can directly be sulfurized in the exocyclic position under mild conditions in high yield, when we used a catalyst.[6,9] The structural similarity between tropothione (**1**) and tropone (**2**) allows an intriguing comparison with respect to their spectral properties. This paper describes fully the synthesis, isolation as crystals, and fundamental spectral properties of **1** which are in remarkable contrast to those of **2**.

RESULTS AND DISCUSSION

Synthesis, Isolation as Crystals, and Instability.

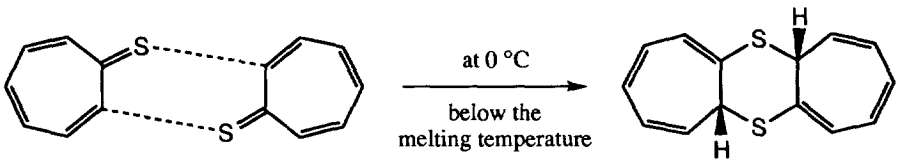
The synthesis of tropothione (**1**) has been accomplished by direct displacement of the oxygen in tropone (**2**) to the sulfur using tetraphosphorous decasulfide and an excess amount of triethylamine as a catalyst in anhydrous organic solvent (benzene, carbon tetrachloride, chloroform, or dichloromethane) in high yield.[6] Triethylamine is the indispensable catalyst for the efficient preparation. In the absence of the catalyst, the yield is significantly diminished.[8] We have found that molarity of the reagent and catalyst is important in this synthetic reaction. The combination of tetraphosphorous decasulfide and triethylamine[9] in the above synthetic conditions has been clarified that it is formed a transient and reactive species, trithiometaphosphate anion (S_2PS^-), which has been isolated as the tetraphenyl arsonium salt ($Ph_4As{\cdot}PS_3$).[11]



Scheme 1. Synthesis of Tropothione (**1**).

The isolation of tropothione as a pure crystalline material was successful only after a long series of failures and our finding of the above efficient preparation of solution of the compound. One of the efficient conditions for successful isolation seems to be that all operations should be carried out at low temperatures below 0 °C, rapidly and carefully and that the catalyst, triethylamine, is indispensable. Immediately after the preparation of tropothione in dichloromethane, the resultant deep red solution was chromatographed in a refrigerated room[12] at −20 °C. Solvent removal below −40 °C in vacuo isolated the desired compound **1** as crystalline material. Recrystallization from cold ether gave pure crystals of deep red needles with the melting point of 20–21 °C.[13] Sublimation at 10–20 °C (bath temperature) under reduced pressure (0.005 mmHg) yielded deep red slender needles. Surprisingly, we have noticed at a final stage during this work that the compound **1** *is not sensitive to air*. This stability of tropothione against oxygen is sharp contrast to the air-sensitivity of dithiotropolone[14] (2-mercaptotropothione) and thioketones reported so far.[3]

The crystals of tropothione thus obtained as deep red needles can be kept at −80 °C and remain unchanged at least over half an year at −40 °C. On standing at 0 °C below the melting temperature, however, the crystals of tropothione spontaneously change to an amorphous solid of dimeric substance (Scheme 2) yielding exclusively an [8 + 8]-type cycloadduct of **1**. The reaction completes within 2 days. This solid-state cyclodimerization of tropothione constitutes the first example of nontopochemical reaction.[4]



Scheme 2. Spontaneous Decomposition of Solid-State Tropothione (**1**).

Table 1 lists the half-life times of tropothione in the crystalline (0 °C) and molten (30 ° C) states as well as those in solutions (25 °C, in several concentrations), judging from Fourier-transform ^{1}H NMR monitoring and UV–visible detection. Thus, a dilute solution of tropothione (**1**) in chloroform has a relatively long half-life, but a concentrated solution of **1** deteriorates within several hours at room temperature. Tropothione affords mainly trimeric substances at the final stage in solutions similarly to the molten-state reaction of tropothione.[4]

Table 1. Half-life Times of Tropothione (**1**) in the Crystalline, Molten, and Solution States[a] Obtained in Several Conditions.

solid state	$t_{1/2}$ (0.0 °C)		56 min[b,c]
molten state	$t_{1/2}$ (30.0 °C)		3 min[b]
solution state	$t_{1/2}$ (25.0 °C)[d]	1.00 mol/L	9.1 h
		0.10	29.2 h
		0.010	10.4 days
		0.001	38.0 days

[a] $CHCl_3$ solution. [b] Determined by ^{1}H NMR monitoring at 400 MHz by intermittent dissolution of the crystals of **1**. Taken from reference 4. [c] The decomposition to cyclodimer (reference 4) occurs after an interval of the induction period (20–40 min). [d] Determined by UV–visible spectral monitoring in $CHCl_3$.

The compound **1** gave satisfactory combustion (C, H, and S) microanalysis data. These data alone might not be very informative owing to the dimeric nature of crystals of the compound. However, it is at present believed to be satisfactory since the crystalline-state dimerization occurs after an interval of induction period (20–40 min),[4] depends on the crystal purity and shape for the solid-state cyclodimerization (Scheme 2). Chemical-ionization mass spectrometry deduced the actual molecular weight. The isobutane chemical-ionization mass spectrum of tropothione exhibited $M^+ + 1$ molecular ion isotopic clusters that correlated with the simulated molecular ion patterns for the parent ions. The accurate mass measurement for the M^+ molecular ion peak is in accord with the calculated value. Similarly, the molecular weight of tropothione was further confirmed by mass spectrometry through direct inlet system by the introduction of a sample into the inlet system because of the instability of **1**. The accurate mass measurement revealed the molecular ion at *m/z* 122.0188 in accordance with the calculated value of *m/z* 122.0190 for C_7H_6S.

Immediately after the isolation of pure crystals of tropothione we have performed the ^1H NMR spectroscopic measurement *at room temperature*. Figure 1 shows the isolation to be successful. The second calibration of the sample appeared small abundant signals at around δ 6.0, 5.0, and 3.4 due to the contamination of the [8 + 8] cyclodimer[4] by its rapid formation. The low-temperature spectroscopic data (vide infra) entirely confirm the structure assignments.

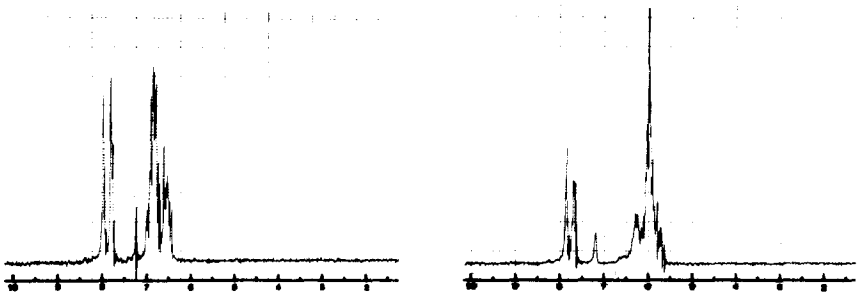


Fig. 1. 60-MHz ^1H NMR Spectra of Tropothione (**1**) in $CDCl_3$ (left) and Benzene-d_6 (right).

The charts were obtained immediately after dissolving **1** into the solvent and calibrated at ambient probe temperature (26 ± 1 °C). Owing to the instability of **1**, the second calibration of the sample at the temperature appeared small abundant signals at around δ 6.0, 5.0, and 3.4 due to the contamination of a cyclodimer of **1** by its rapid formation.

Spectroscopic Characterization.

IR Spectroscopy. We performed carefully the IR measurements of tropothione (**1**) at low temperatures. Tropothione displays the very strong absorption band at 1087 cm^{-1} in CCl_4 accompanied with strong ones at 1495 and 1463 cm^{-1}. The former is ascribed to the C=S stretching vibration whose assignment is supported by the strongest absorption in the Laser-Raman spectrum of **1** to be 1090 cm^{-1} in CCl_4. The latter may be ascribed to the stretching vibrations of C=C bonds similar to those of tropone (**2**). The strongest absorption at 1087 cm^{-1} of **1** can be compared with 1645 cm^{-1} for those C=O stretching vibration of **2**.[15] The value of the strongest frequency in **1** agrees closely with the theoretically estimated one (1070 cm^{-1}) as calculated using the method proposed by Spinner.[16] Furthermore, the ratio of the C=O stretching frequency of tropone to the C=S stretching one in **1**, $\nu_{C=O}/\nu_{C=S}$, reveals 1.51 in accordance with Mecke's rule.[17] These results indicate that the structure of **1** is consistent with the replacement of the carbonyl to thiocarbonyl in tropone structure, viz. cycloheptatrienethione.

It has been shown that for geometrically similarly disposed groups there is a good correlation between the frequency and the calculated bond order. Thus, we may infer that delocalization of electrons decreases (bond order of C=S increases) as we go from 2-aminotropothiones[5] (1040–1048 cm^{-1}) and 2-mercaptotropothione (dithiotropolone, 1058 cm^{-1})[14] to tropothione (1087 cm^{-1}). That is, the parent **1** is less polar than any other known tropothione derivatives bearing an electron-donating group.[5] By this criterion in the IR spectroscopy, tropothione has less delocalization than the others, but more polar than tropone.

UV–visible Spectroscopy. Table 2 lists the UV–visible spectrum of tropothione in six solvents consists of three absorption maxima of one n–σ* and two π–π* transitions around 225 (log ε ca. 4), 253 (ca.

4), and 380 nm (ca. 4.2), respectively. While, the longest wavelength absorption in tropone appears at 312 nm.[18] The color of tropothione assuming deep red differs from that of tropone being pale yellow. Its maximum of the longest wavelength absorption shifts about 70 nm towards the red in comparison with that of tropone.[19,20] It may be assigned that the longest wavelength band (380 nm) is due to the in-plane excitation to the molecular plane, whose transition is regard as intramolecular charge transfer type.[21] The large bathochromic shift in the longest absorption in **1** implies that the π polarization of tropothione is enhanced relative to that of tropone according to the Hückel $(4n + 2)\pi$ rule in cross-conjugated systems.

Table 2. Electronic Spectral Data for Tropothione (**1**) in Various Solvents.

solvent	λ_{max} nm (ε; log ε)			
cyclohexane	224 (8511; 3.93)	253 (9772; 3.99)	371 (15849; 4.20)	610 (42; 1.62)
hexane	224 (7762; 3.89)	253 (9333; 3.97)	371 (15136; 4.18)	610 (42; 1.62)
EtOH	225 (9514; 3.98)	253 (10336; 4.01)	381 (15795; 4.20)	
MeOH	225 (9772; 3.99)	253 (10471; 4.02)	381 (16218; 4.21)	
CH_3CN	225 (9332; 3.97)	253 (9998; 4.00)	383 (16596; 4.22)	
H_2O	225 (10233; 4.01)	257 (10229; 4.01)	390 (16215; 4.21)	

^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of tropothione (**1**) in five ordinary solvents (CCl_4, $CDCl_3$, benzene-d_6, Me_2SO-d_6, or acetone-d_6) has shown broad signals of a 32-line AA′BB′XX′ pattern for the six ring protons into two well-separated multiplets of the intensity ratio of 1:2 at around δ 7.8 and 7.0–6.5 even with a low resolution instrument (60 MHz) as Figure 1 shows. This is a noteworthy feature in comparison with that tropone shows a singlet signal[22] at δ 6.95[23] at 60-MHz ^{1}H NMR in CCl_4 or $CDCl_3$.

The most striking observation is the downfield shift of the α-protons (δ 7.8) of **1** at variance with ca. 1 ppm comparing with those in tropone. This is interpreted in terms of the strong anisotropic effect[24] of the thiocarbonyl bond in the exocyclic position of **1**. Thus, the 2- and 7-hydrogens (α-protons) may be assignable, however, the positions of the remaining hydrogens are not readily discerned from inspection of the spectra. It is uninterpretable without specific deuterium labeling. However, it may be assumed a relative assignment for chemical shifts of the hydrogens in **1** with considering the slopings by the coupling purterbation. Thus, the chemical shift assignments have been made tentatively in the order of downfield to upfield by α- (H-2,7), γ- (H-4,5), and β-protons (H-3,6), respectively. Strictly speaking, the true assignment must await a detailed analysis with an aid of deuterium labeling toward specific positions of tropothione. The remarkable downfield shift of the α-protons appears to be characteristic of this structural unit. This signal pattern is consistent with a symmetrical structure for tropothione.

^{13}C NMR Spectroscopy. The proton-noise-decoupled ^{13}C NMR spectrum (22.5 MHz) of tropothione (**1**) consists of only four signals, suggesting a symmetrical form of **1** in solution. The chemical shifts of **1** have appeared at δ 213.83 (s, C=S), 153.80 (d, C-2,7), 138.36 (d, C-4,5), and 131.48 (d, C-3,6), whereas, those of tropone (**2**) did at δ 187.65 (s, C=O), 141.90 (d, C-2,7), 134.64 (d, C-4,5), and 135.89 (d, C-3,6) in CCl_4. The assignments for both the compounds are based on the off-resonance and selective decoupling

experiments. The downfield-resonance position for C-1 in **1** relative to that in **2** is rationalized by the anisotropic effect of C=S bond[24] stronger than that of C=O group. We deduced the $^1J_{CH}$ coupling constants to be $^1J_{C(2)-H}$ = 162.9, $^1J_{C(3)-H}$ = 155.5, and $^1J_{C(4)-H}$ = 159.9 Hz for **1**, while those of **2** appeared to be $^1J_{C(2)-H}$ = 164.2, $^1J_{C(3)-H}$ = 161.8 , $^1J_{C(4)-H}$ = 160.8 Hz. From these values, s-characters of the ring carbons are estimated to be 0.326 (C-2,7), 0.311 (C-3,6), and 0.320 (C-4,5) for **1**, while those in **2** are deduced to be 0.328 (C-2,7), 0.324 (C-3,6), and 0.322 (C-4,5).

^{33}S NMR Spectroscopy. ^{33}S NMR can in principle have a chemical application as the identification of structure of sulfur-containing compounds, since NMR chemical shifts are intimately related to the electronic environment of a given nucleus.[25] Unfortunately, the experimental difficulties associated with ^{33}S NMR have discouraged organic chemists from exploring this interesting field. Only a limited number of organosulfur compounds are measured, and chemical shifts of thioketone compounds are still unknown.[26] We would like to show here the first measurement of ^{33}S NMR for thiocarbonyl compounds.

Figure 2 shows the ^{33}S NMR spectrum (30.7 MHz, $CDCl_3$) of tropothione (**1**). We obtained the spectrum as a broad signal at δ −287 downfield from an external standard, $(NH_4)_2SO_4$. The signal is observed at downfield relative to that of sulfides (ca. −360 ppm).[27] This tendency of chemical shifts between the thioketone **1** and sulfides is similar to those in ^{17}O NMR spectra between ketones and ethers.[28]

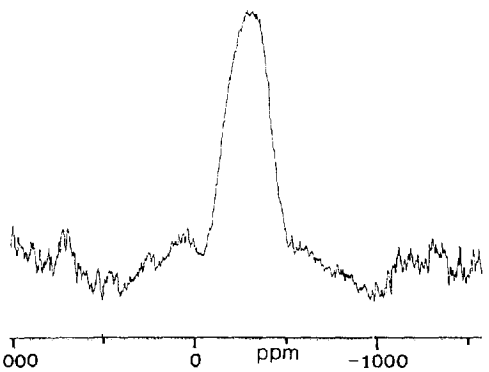


Fig. 2. ^{33}S NMR Spectrum of Tropothione (**1**) Taken at −40 °C.

The ^{33}S NMR spectrum ($CDCl_3$) was recorded for 0.4-mol/L solution calibrated in three parts measured at different spectral range in 1000 to −600, 500 to −1100, and 0 to −1600 ppm, separately.

SUMMARY AND CONCLUDING REMARKS

We have efficiently synthesized and isolated tropothione (**1**) as a pure crystalline material despite the thermal instability. Table 3 summarizes the difference between tropothione and tropone (**2**) in their physical constants as well as some of those prominent characters. According to this work it was realized that all of systematic spectroscopic data of tropothione were in sharp contrast to those of tropone.

Table 3. Summary of Physical Constants. A Comparison of Prominently Different Characters of Tropothione (**1**) and Tropone (**2**).

	Tropothione (**1**)[a]	Tropone (**2**)
Color, habit	Deep red needles	Pale yellow oil (almost colorless)[f]
Mp or bp	Mp 20–21 °C (dec)[b]	Bp 69.5 °C (10.5 mmHg)[g]
	Sublimative[c]	Volatile[h]
Half-life time at 0 °C	$t_{1/2}$ (crystalline) 58 min[d]	Stable at room temperature[i]
IR (CCl_4)	ν(C=S) 1087 (vs) cm^{-1}	ν(C=O) 1645 (s) cm^{-1}[j]
Raman (CCl_4)	ν(C=S) 1090 (vs) cm^{-1}	ν(C=O) 1637 (s) cm^{-1}[k]
UV–vis π–π*	λ_{max} (log ε) 224 (3.93), 253 (3.99), 371 nm (4.20)	λ_{max} (log ε) 225 (4.33), 297 (3.74), 310 nm (3.67)[l]
n–π*	λ_{max} 610 nm (log ε 1.62)	λ_{max} 384[m] nm (log ε 1.99)[n]
MS M^+	*m/z* 122 (C_7H_6S)	*m/z* 106 (C_7H_6O)[o]
^1H NMR (60 MHz, CCl_4)	wide pattern of 32-line signals (AA'BB'XX')	broad singlet[p]
	δ 8.08–7.64 (dm, 2 H, XX')	δ 6.95 (br s, 6 H)[q]
	δ 7.09–6.39 (m, 4 H, AA'BB')	
^{13}C NMR (22.5 MHz, CCl_4)	δ 131.48 (d, C-3,6)	δ 135.89 (d, C-3,6)[a,r]
	δ 138.36 (d, C-4,5)	δ 134.64 (d, C-4,5)
	δ 153.80 (d, C-2,7)	δ 141.90 (d, C-2,7)
	δ 213.83 (s, C=S)	δ 187.65 (s, C=O)
$^1J_{C-H}$ (s-character)	$^1J_{C(2)-H}$ = 162.9 (0.326)	$^1J_{C(2)-H}$ = 164.2 (0.328)[a]
	$^1J_{C(3)-H}$ = 155.5 (0.311)	$^1J_{C(3)-H}$ = 161.8 (0.324)
	$^1J_{C(4)-H}$ = 159.9 (0.320)	$^1J_{C(4)-H}$ = 160.8 (0.322)
^{17}O NMR (54.2 MHz, $CDCl_3$)	———	δ 484.56[a,s]
^{33}S NMR (30.7 MHz, $CDCl_3$)	δ −287[e]	———

[a] This study. [b] The decomposition of the molten-state reaction of tropothione leads to a mixture of its dimers and trimers (ref 4). [c] Sublimative at 10–20 °C (bath temperature/0.005 mmHg). [d] The decomposition of the solid-state reaction yields an [8 + 8] cyclodimer (see Scheme 2, ref 4). [e] $CDCl_3$, external standard $(NH_4)SO_4$. [f] Refs 29 and 30. [g] Taken from ref 29. See also ref 30a (bp 104–105.5 °C/10 mmHg) and ref 30b [bp 113 °C/15 mmHg; mp −8 to −5 °C (ether)]. [h] Benzaldehydelike odor. [i] Tropone can be kept at 0 °C for a long period when it is pure. However, contamination of hydrochloric acid often causes a formation of jellylike polymeric material at the temperature during a storage (see ref 29). [j] Ref 15. [k] Ref 15b. [l] Ref 18. [m] Ref 19. [n] Ref 20. [o] Ref 31. [p] Ref 22. [q] Ref 23. [r] Ref 32. [s] Cf. δ 502 (pure liquid) in Ref 33.

EXPERIMENTAL SECTION

Reagents and Starting Material. The starting material, tropone (**2**), was obtained according to a previously reported method.[29] Tetraphosphorous decasulfide was recrystallized from carbon disulfide after a trituration or an extraction with a Soxhlet extractor from a commercially available reagent. Triethylamine, used as a catalyst, was freshly distilled and degassed. All the solvents used for the preparation and isolation of tropothione (**1**) were freshly distilled under nitrogen from appropriate drying agents and were all degassed. For column chromatography, Merck Kieselgel 60 (0.063–0.200 mm) was employed. To prevent from the decomposition of tropothione in various solvents the spectroscopic data were obtained quickly and at low temperatures between −40 and −15 °C (except the 60-MHz ^{1}H NMR spectra taken at an ambient probe temperature) immediately after the isolation of the compound. All experimental procedures were carried out under nitrogen stream. Isolation experiments for tropothione were performed in a low-temperature-thermostatted room.

Instrumentation/Analytical Procedures. Melting point was determined on a Büchi 511 apparatus in a sealed (under nitrogen atmosphere) capillary tubes and is uncorrected. Elemental analyses were performed at the Chemical Analysis Center, Saitama University, as well as at the Microanalytical Laboratory, the National Institute of Physical and Chemical Research (Riken), Wako-shi, Saitama, Japan. IR and Neon Laser-Raman spectra were recorded on a Hitachi 260-50 spectrometer and a JASCO R-500 instrument, respectively. UV–visible spectra were taken with a Hitachi EPS-3T recording spectrometer using 1-cm quartz cells. Molecular weight data were obtained with a JEOL DX-303 double focusing mass spectrometer using a direct inlet and reported *m/z* values. ^{1}H NMR spectra were recorded on a Hitachi R-24B (60 MHz) as well as a JEOL FX-90Q (90 MHz) instrument. ^{13}C NMR spectra were recorded on a JEOL FX-90Q (22.5 MHz) spectrometer. For the ^{1}H and ^{13}C spectra, chemical shifts are given in ppm downfield from internal Me_4Si. Chemical shifts of the ^{17}O NMR spectrum for **2** and ^{33}S NMR for **1** are given in ppm from external D_2O and $(NH)_4SO_4$ in D_2O, respectively. The ^{17}O (54.2 MHz) and ^{33}S NMR (30.7 MHz) spectra were run with a Bruker AM-400 spectrometer.

Preparation of Solution of Tropothione (1). In a typical preparation, 15.0 g (33.7 mmol) of tetraphosphorous decasulfide and triethylamine (10.0 mL, 71.9 mmol) were added in 250 mL of chloroform (benzene, carbon tetrachloride, or dichloromethane) and cooled to 0 °C. To this solution, 3.00 g (28.3 mmol) of tropone (Rf = 0.07, silica gel, $CHCl_3$) in 10 mL of chloroform was added dropwise. After the vigorous stirring for 30 min, the displacement reaction is complete (tropothione: Rf = 0.47, silica gel, $CHCl_3$, −20 °C). The reaction mixture was washed with cold 5% sodium hydrogencarbonate solution and finally with an ice-water, then dried over magnesium sulfate and stored in a cool place at −20 °C for 30 min. Filtration of drying agent gave the deep red solution (280 mL) of tropothione (**1**). Ultraviolet analysis showed the presence of 28.1 mmol (99%) of **1**. The above dilute solutions (0.1 M) have a half-life of about 29 h at room temperature (see Table 1).

Isolation of crystals of 1. Immediately after the above preparation of tropothione (**1**) in dichloromethane, the resultant red solution was chromatographed over silica gel column eluted from dichloromethane at −20 °C. The solvent of the resulting red band was then removed in vacuo below −40 °C to give 3.05–3.43 g (88–99%) of red needles, mp 20–21 °C, whose melting point was measured in a capillary sealed under a nitrogen atmosphere. Elemental analysis was performed immediately after recrystallization from cold ether at −78 °C. Anal. Calcd for C_7H_6S: C, 68.81; H, 4.95; S, 26.24. Found: C, 68.73; H, 4.96; S, 26.28. The pure crystals thus obtained is fairly stable at low temperatures and can be kept at −80 °C for more than one year. A sublimation led to the slender red needles [15 °C (0.005 mmHg), bath temperature], mp 20.5–21.5 °C, which gave satisfactory combustion microanalysis and accurate mass spectrometry. Anal. Found: C, 68.52; H, 4.95; S, 26.39. **1**: IR (CCl_4, −15 °C) ν_{max} 3020 (m), 1495 (s), 1463 (m), 1433 (m), 1365 (w), 1262 (w), 1165 (w), 1087 (vs), 924 (w), 880 (w), 548 (s) cm^{-1}; Raman (CCl_4, −15 °C) ν_{max} 1090 (vs) cm^{-1}; UV–vis, see Table 2; ^{1}H NMR (90 MHz, $CDCl_3$, −40 °C) δ 8.06–7.97 (dm, 2 H, H-2,7), 7.08–7.00

(m, 2 H, H-4,5), 6.85–6.75 (m, 2 H, H-3,6); ^{13}C NMR (22.5 MHz, $CDCl_3$, −40 °C) δ 213.96 (s, C-1), 153.55 (d, C-2,7), 138.41 (d, C-4,5), 131.27 (d, C-3,6).

Mass Spectrometry. To prevent from the decomposition of **1** this spectrum was taken by direct inlet system at ionizing potential of 70 eV. The accurate mass measurement for the molecular ion: Calcd for C_7H_6S: 122.0190. Found: 122.0188. The $M^+ + 1$ and $M^+ + 2$ peaks with abundances relative to the parent peak (*m/z* 122) were 123 (7.8%) and 124 (4.7%). Calculated intensities based on natural isotopic abundances were 7.8 and 4.7%, respectively.

^{33}S NMR Spectrometry of 1. The spectrum was measured at a probe temperature of −40 °C. A high-power probe system equipped with a solenoid insert operating at 30.7 MHz and a 10-mm glass tube was used. All parameters were first optimized for neat CS_2. With the equipment the ringing decayed to approximately 200 ms, as measured with a sample of neat $CHCl_3$. Thus an equivalent time was allowed after the pulse before accumulation. The conditions were pulse width 90°, spectral width 50 kHz, and 8K data points. For tropothione the concentration was 0.4 and 0.8 mol/L, and the accumulation time required to obtaine a good signal-to-noise ratio was 12 and 24 h, respectively. The absolute frequency of the signal of 4 mol/L $(NH_4)_2SO_4$ in D_2O solution was measured, and the chemical shift of **1** was calculated with respect to this frequency. ^{33}S Resonance at downfield with respect to $(NH_4)_2SO_4$ was considered to have a positive chemical shift: δ −287 ($W_{1/2}$ 11500 Hz).

Spectroscopy for Tropone (2). The following spectra of **2** were measured at room temperature: ^1H NMR (90 MHz, $CDCl_3$) δ 6.98 (br s, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 187.98 (s, C-1), 141.77 (d, C-2,7), 135.84 (d, C-3,6), 134.49 (d, C-4,5); ^{17}O NMR (54.2 MHz, $CDCl_3$) δ 484.56 (s).

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REFERENCES AND NOTES

1. Dedicated to Professor Emeritus Tetsuo Nozoe on the occasion of his 93rd birthday and a life-long career in novel (nonbenzenoid) aromatic chemistry. He and his coworkers attempted the first synthetic try (see reference 10), as far as we know, for the titled compound, although it could not be achieved.

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