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General Synthesis, Spectroscopic Properties, and Dipole Moments of 2-Substituted Tropothiones[1)]

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Several 2-substituted tropothiones (2,4,6-cycloheptatriene-1-thiones) having an electron-donating group (Me, Ph, NH_2, NHMe, OH, OMe, or SMe) were synthesized by direct sulfurization from the corresponding tropones in a one-pot reaction. In contrast to the instability of the parent tropothione (**1a**), most of these 2-substituted derivatives were insensitive to air and were thermally stable compounds which can be handled at room temperature. These tropothione derivatives were characterized by spectroscopic and dipole moment measurements. The IR spectra showed ν(C=S) vibrations at around 1100—1040 cm^{-1}. The UV-vis spectra displayed three π–π^* transitions accompanied by n–π^* transitions. The 400-MHz ^1H NMR spectra of the thiones showed that only protons at the 7 position resonate well-separated downfield from the other ring protons due to the strong C=S anisotropy. In the ^{13}C NMR (100.6 MHz) spectra, the C=S carbon signals appeared at $<\delta=183$ and the other ring carbons resonated at $\delta=154$—112. Variable-temperature ^{13}C as well as ^{14}N NMR spectroscopic studies clarified that 2-amino- and 2-(methylamino)tropothiones exist as an equilibrium mixture of the thione and enethiol structures in an approximate ratio of 64 : 36. This is different from the results of a previous investigation showing that the structures exist as the thione form exclusively. Dipole moments of some derivatives of **1a** were measured and compared with those of the corresponding tropones. These tropothione derivatives obtained were more ionic than both the parent compound **1a** and the corresponding tropones.

In recent years, we have reported the synthesis,[2)] isolation, physical properties[2,3)] involving X-ray structural analysis[4)] (performed at −40 °C), and unusual chemical reactivity[2,5—9)] of the parent tropothione (2,4,6-cycloheptatriene-1-thione, **1a**, R=H) as well as the novel reactivities[10—12)] of related compounds derived from **1a**. The substituent-free tropothione **1a** is obtained as a thermally unstable crystalline material with a very short half-life time [$t_{1/2}$ (0 °C, crystalline state) = 56 min],[8)] which cyclodimerizes spontaneously in an [8+8] manner even below the melting temperature (21 °C) (Chart 1). This solid-state cyclodimerization represents the first example of a nontopochemically-controlled reaction.[8)] This thermal instability of **1a** has long precluded its isolation as a pure crystalline material and limited detailed investigations. We need accordingly to prepare and treat thermally stable derivatives which can be handled at room temperature. The thermal instability of the substituent-free tropothione (**1a**) is due to less efficient overlap of the $2_{p_\pi}(C)$–$3_{p_\pi}(S)$ orbitals than that of the $2_{p_\pi}(C)$–$2_{p_\pi}(O)$ conjugation in the C=O linkage. Hence, the instability of **1a** seems to be depressed by the introduction of an electron-donating group at the terminal position, adjacent to the C=S group, of the seven-membered ring in conjugation resulting in appreciable resonance stabilization over the ring.

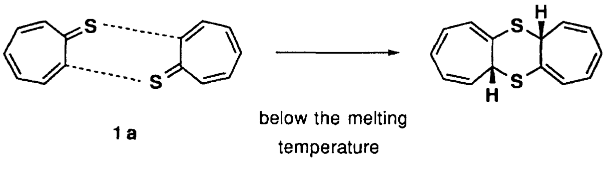

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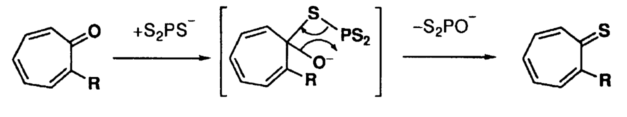
Chart 1.

Despite keen interest and developments in recent years in the chemistry of thiocarbonyl compounds,[13—15)] only a very limited number of tropothiones have been synthesized over the past 30 years. Brasen et al. prepared 2-amino- and 2-(methylamino)tropothiones,[16,17)] starting from 6,6,7,7-tetrafluorobicyclo[3.2.0]hept-2-ene via the mixture of tetrafluorocycloheptadienes in several steps. Nozoe et al. reported the preparation of 2-hydroxytropothione[18—20)] from tropolone via 2-chlorotropone. Forbes et al. synthesized 2-mercaptotropothione[21,22)] from 1,2-diethoxycycloheptatrienylium tetrafluoroborate in several steps and isolated it as a labile material.

We report herein a general and facile synthetic method to obtain a variety of 2-substituted tropothiones (**1b**—**h**), and describe in full their dipole moments and spectral characterization.

Results and Discussion

We accomplished the synthesis of the desired tropothiones, **1b**—**h**, in a one-pot reaction from the corresponding tropones (**2b**—**h**) using tetraphosphorus decasulfide in polar solvent (dichloromethane or acetonitrile) along with triethylamine as a catalyst (Scheme 1). For efficient synthesis, we have found that triethylamine is an indispensable catalyst.[2,23)] It seems that S_2PS^- anion formation[24,25)] is easy under these reaction conditions. ^{31}P NMR spectral inspection of this reaction mixture indicated that the anion signals appeared at around $\delta=+87$ (downfield from external H_3PO_4), while the reaction mixture without the catalyst or using it at less than two equivalents revealed the signals at $\delta=-7$ upfield to those under the above con-



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R: a, H; b, Me; c, Ph, d, NH_2; e, NHMe; f, OH; g, OMe; h, SMe

Scheme 1.

ditions. The former signal disappears gradually at low temperature with the process of the reaction. Hence, we presume that a transient anion species, S_2PS^-, is generated as a reactive intermediate and changes by the displacement reaction to another anion, S_2PO^-. 2-Substituted tropones were selected as starting material, and preparative conditions were sought for the thiocarbonylation to proceed smoothly.

We carried out the synthetic reactions of the substituted tropothiones by direct sulfurization of the corresponding tropones in a modification of the reported procedure for the substituent-free tropothione from tropone.[2)] Instead of nonpolar solvents (benzene or carbon tetrachloride) used in the latter synthetic scheme, we chose polar solvents. Application of the reaction conditions using the nonpolar solvents did not enable the reaction to proceed smoothly; the starting tropones were recovered unchanged or the yields of the desired tropothiones were diminished significantly. We have also found that not only is the choice of solvent polarity important, but also homogeneity and molarities of the reagent and catalyst affect the reaction. When the reaction was carried out using two equivalents of the sulfurization reagent with a four molar excess of the catalyst, the reaction proceeded smoothly under homogeneous conditions. Table 1 summarizes the experimental results. The yields of 2-substituted tropothiones **1b**—**h** were satisfactory. The present method enabled us to synthesize four new 2-substituted tropothiones, **1b**, **1c**, **1g**, and **1h**, in addition to known derivatives **1d**—**f**. Only attempts at direct sulfurization to 2-mercaptotropothione[21,22)] were unsuccessful; however, the formation of a minor amount of the compound could be found by ^{1}H NMR monitoring.

The thermal stabilities of thiones **1b**—**h** are generally high as they can be kept at room temperature without decomposition. However, the 2-methyl (**1b**) and 2-phenyl (**1c**) derivatives have slightly lower stabilities. They tend to decompose gradually at 10 °C.[26)] The 2-substituted tropothiones (**1b**—**h**) thus obtained are orange (**1d**—**f**), dark red (**1b**,**1c**), or brick red-colored (**1g**,**1h**).

The IR spectra of these tropothiones (**1b**—**h**) are characterized by the distinct broad absorptions at 1600—1554 and 1103—1042 cm^{-1} due to the C=C and C=S stretching vibrations, respectively. The latter strong absorptions are one of the most characteristic displays in the spectroscopies of **1**. The ratios of the C=O stretching frequency in tropones **2b**—**h** to the C=S one in tropothiones **1b**—**h**, $\nu(C=O)/\nu(C=S)$, are in the range of 1.52—1.55 in agreement with Mecke's rule.[27,28)] This result indicates that the direct conversion of the carbonyl group in the starting tropones to the thiocarbonyl group is successful. Figure 1 shows the IR spectrum of 2-methoxytropothione (**1g**) as a representative example of the titled compounds.

Three tropothione derivatives (**1d**—**f**) may form an intramolecular hydrogen bond closing a five-membered ring through the heteroatoms and chelate proton at the exocyclic position of the seven-membered carbon ring. The N–H or O–H stretching vibration in **1d**—**f** appears at around 3000 cm^{-1}. These absorptions shift to lower wavenumbers which appear at 2596 and 2368, 2300, and 2083 cm^{-1} for **1d**, **1e**, and **1f**, respectively, by deuterium exchange. The ratios [$\nu(X\text{–}H)/\nu(X\text{–}D)$; X=N or O] of the stretching vibration of the X–H bond to that of the newly-formed X–D linkage in each case are between 1.32 and 1.35.

Table 2 exhibits the UV-visible absorptions taken in both polar and nonpolar solvents. The UV-visible spectra of the tropothiones (**1b**—**h**) show three characteristic π–π^* transitions whose longest wavelength absorptions are at a high-wavelength position (more than 380 nm) with a strong intensity (more than the absorptivity of $\log \varepsilon = 4$). The longest-wavelength absorptions shift to the blue in the nonpolar solvent hexane. Figure 2 shows the UV-visible spectra of 2-methoxytropothione (**1g**) in both a polar solvent, methanol, and a nonpolar one, hexane. The absorptions of the n–π^* transitions of some red-colored derivatives appear at around 600 nm with a weak transition ($\log \varepsilon <$ ca. 2) in the solvent, in agreement with the color. However, such n–π^* absorptions did not explicitly appear for the three enethiolizable tropothione derivatives **1d**—**f**, which assume an orange color, even in a nonpolar solvent. It is thought that the π–π^* absorption maxima of the longest-wavelength shift near 500 nm and the strong absorption of the π–π^* transitions hide the n–π^* ones.

The ^{1}H NMR spectra of 2-substituted tropothione derivatives **1b**—**h** resonate in two well-separated signals in an integral ratio of 1 : 4 in the regions $\delta = 8.8$—8.1 and 7.7—6.5 in $CDCl_3$ or CCl_4 even in 60-MHz spectroscopy. The former signal is ascribed to the 7-H protons depending upon the nature of the strong C=S bond anisotropy.[29)] This is the most noteworthy feature in the ^{1}H NMR of the tropothiones, and is sharply different from those of the corresponding tropones (**2b**—**h**) whose spectra reveal narrower signals than those of **1** under similar conditions. Other ring proton signals of **1b**—**h** appear in the latter range as complex multiplets. Table 3 lists the results of the 400-MHz ^{1}H NMR spectroscopy of the tropothiones obtained. Table 3 shows that the complexity of the ring-proton signals in the tropothiones which appeared in low-resolution spectroscopies (60 and 90 MHz)[2)] is solved almost completely

Table 1. Reaction Conditions, Yields, C=S Stretching Vibrations, and Molecular Ion Peaks for Syhthesized 2-Substituted Tropothiones

Compd	R	Conditions			Yield	ν_{max}(C=S)a)	Mass (M^+)b)
		Solvent	Temp/°C	Time	%	cm^{-1}	m/z
1ac)	H	CCl_4	10	30 min	98	1087	122
1b	Me	CH_2Cl_2	0	1 h	94	1055	136
1c	Ph	CH_2Cl_2	0	1 h	62	1103	198
1dd)	NH_2	CH_3CN	20	3 h	63	1069	137
1ee)	NHMe	CH_2Cl_2	0	1 h	75	1042	151
1ff)	OH	CH_3CN	20	1 h	86	1095	138
1g	OMe	CH_2Cl_2	0	40 min	96	1049	152
1h	SMe	CH_3CN	0	30 min	82	1059	168

a) In CCl_4. b) Measured at an ionization potential of 75 eV. c) Taken from Ref. 2 for comparison. d) Lit,16,17) mp 137—138.5 °C (from methanol). e) Lit,17) mp 67—67.5 °C (from ethanol). f) Lit,18—20) mp 55 °C (from petroleum ether).

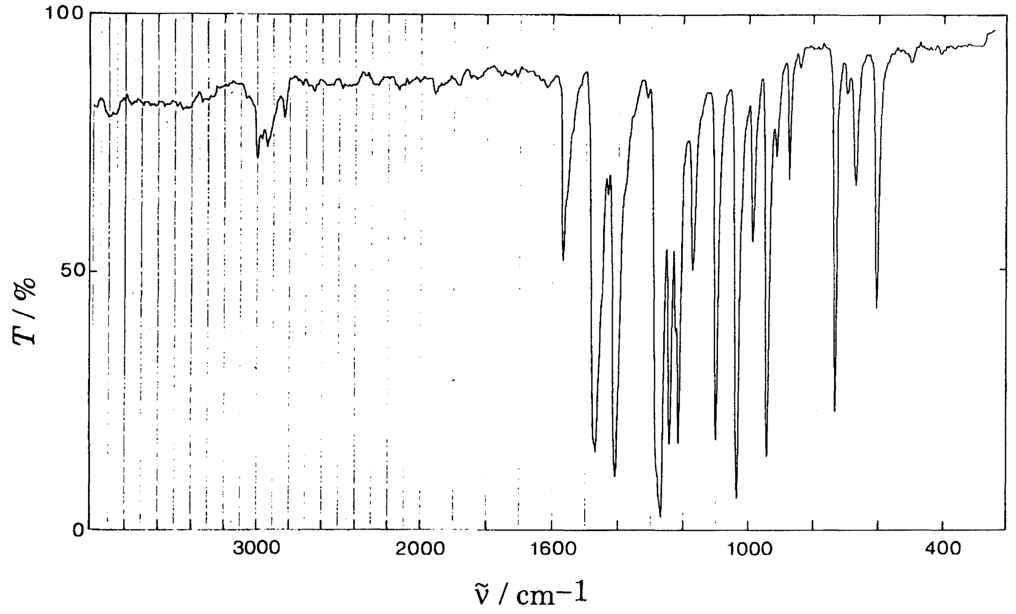


Fig. 1. IR spectrum of 2-methoxytropothione (**1g**) on a KBr pellet.

Table 2. UV and Visible Spectral Data for the 2-Substituted Tropothiones

Compd	R	MeOH λ_{max}/nm (log ε)			Hexane λ_{max}/nm (log ε)				
1aa)	H	225 (3.97)	253 (4.02)	381 (4.21)	224 (3.89)	253 (3.97)	371 (4.18)	610 (47)c)	
1b	Me	227 (4.02)	261 (4.10)	387 (4.18)	227 (3.99)	255 (4.10)	376 (4.18)	628 (42)c)	
1c	Ph	228 (4.44)b)	252 (4.30)	388 (4.01)	226 (4.44)b)	252 (4.32)b)	378 (4.01)	612 (45)c)	
1d	NH_2	236 (4.06)	276 (4.43)	444 (4.26)	239 (3.82)	281 (4.30)	442 (4.07)		
1e	NHMe	240 (4.03)	284 (4.40)	456 (4.16)	241 (3.92)	286 (4.41)	454 (4.12)		
1f	OH	234 (4.13)	266 (4.22)	418 (4.10)	236 (4.05)	267 (4.23)	416 (4.12)		
1g	OMe	238 (4.10)	271 (4.22)	412 (4.22)	246 (4.02)	268 (4.16)	396 (4.19)	544 (118)c)	620 (53)c)
1h	SMe	226 (4.04)	304 (4.35)	428 (4.05)	225 (4.16)	304 (4.45)	424 (4.09)	564 (106)c)	604 (39)c)

a) Taken from Ref. 2 for comparison. b) Shoulder. c) The values are represented in ε units.

in the 400-MHz spectroscopy to reveal the individual proton signals in contrast with tropone derivatives remaining still unresolved.

The vicinal coupling constants determined by ^{1}H NMR spectroscopy are an important measure of the degree of bond alternation to assess the aromaticity. The ^{1}H–^{1}H coupling constants are summarized in Table 3. The differences between the constants ($^3J_{H,H}$) connected to adjacent protons reveal that those between $J_{3,4}$ and $J_{4,5}$, $J_{4,5}$ and $J_{5,6}$, and $J_{5,6}$ and $J_{6,7}$ are 1.0,

Table 3. ^{1}H NMR Spectroscopic Data (400 MHz, $CDCl_3$, Me_4Si) for the 2-Substituted Tropothiones

		δ_H/ppm						J_{vic}[a]			
Compd	R	7-H	6-H	5-H	4-H	3-H	Substituent	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$
1b	Me	8.28	6.80	7.05	6.95	7.43	2.52 (Me)	9.1	10.1	8.5	11.7
1c	Ph	8.15	6.73	6.99	6.93	7.16	7.66—7.23 (Ph)	8.6	9.5	7.9	11.8
1d	NH_2	8.67	7.08—7.01[b]		7.25	7.14	8.6—7.4 and 7.4—6.3 (NH)	10.4	9.4[c]	9.2[c]	11.9
1e	NHMe	8.66	7.04	7.00	7.38	6.74	9.14 (NH), 3.24 (NMe)	10.5	9.2	9.5	11.7
1f	OH	8.51	7.19	7.24	7.36	7.44	9.93 (OH)	10.5	9.3	9.7	10.6
1g	OMe	8.50	6.91	7.05	7.13	6.75	4.04 (OMe)	9.9	10.1	8.2	11.7
1h	SMe	8.30	6.94	7.11	7.47	7.08	2.48 (SMe)	9.2	10.6	8.3	11.4

a) Units: Hz. b) Chemical shift values are not given for the 5-H and 6-H protons because their resonances were unresolved. In benzene-d_6 the resonances are well-separated: δ=8.70 (7-H), 8.57—7.51 (br s, hydrogen-bonded NH), 6.35 (4-H), 6.28 (6-H), 6.24 (5-H), 5.84 (3-H), and 5.66—4.48 (br s, NH). c) Determined by the spectrum obtained in benzene-d_6.

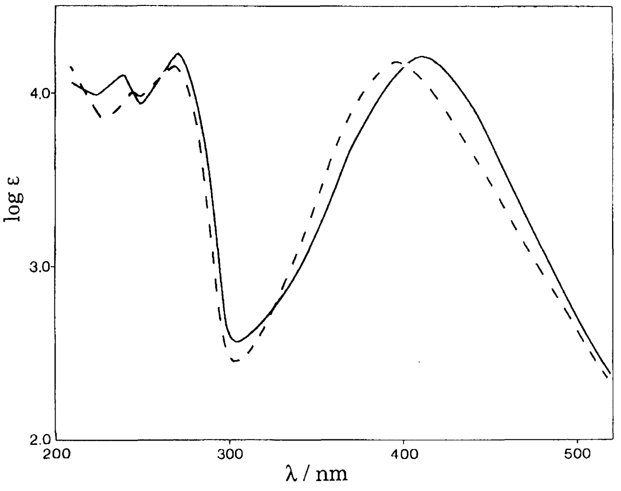
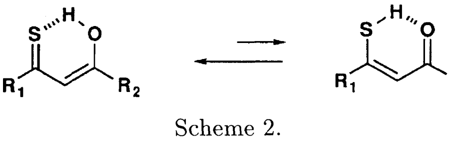


Fig. 2. UV-vis spectra of 2-methoxytropothione (**1g**) in methanol (——) and hexane (- - -).

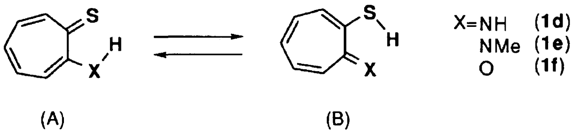
1.6, and 3.2 Hz for **1b** (R=Me), 0.9, 1.6, and 3.9 Hz for **1c** (R=Ph), 1.0, 0.2, and 2.7 Hz for **1d** (R=NH_2), 1.3, 0.3, and 2.2 Hz for **1e** (R=NHMe), 1.2, 0.4, and 0.9 Hz for **1f** (R=OH), 0.2, 1.9, and 3.5 Hz for **1g** (R=OMe), and 1.4, 2.3, and 3.1 Hz for **1h** (R=SMe), respectively. These values indicate an apparently smaller bond alternation in these 2-substituted tropothiones than those of the substituent-free compound, **1a**.[4]

It has been reported that the β-thioxo ketones exist preferentially as the enol (viz. thione) form.[30—32] Three compounds, **1d**, **1e**, and **1f**, are vinylogs of the above system and may accordingly have the possibility of thione–enethiol tautomerism with intramolecular hydrogen bonding (Scheme 2).

The ^{1}H NMR spectra of the 2-amino- and 2-(methylamino)tropothiones are deceptive. The chemical shift and integration values for these enethiolizable tropothiones suggest that the compounds may exist exclusively in the thione (A) structure in solution under these conditions. In fact, Brasen et al. reported that the structure of 2-(methylamino)tropothione (**1e**) existed as the thione form exclusively on the basis of the 60-MHz ^{1}H NMR spectroscopic data,[17] which indicated the 7-H proton shifted to isolate to downfield from the other ring protons and showed the *N*-methyl protons as a doublet signal. The IR and UV-vis spectra of these enethiolizable tropothiones (**1d**—**f**) resemble those of the other nonenethiolizable tropothiones (**1b**, **c**, **g**, and **h**). Contrary to the above fact, we have found a distinct difference in the NMR spectra between the enethiolizable and nonenethiolizalbe tropothiones.



Scheme 2.

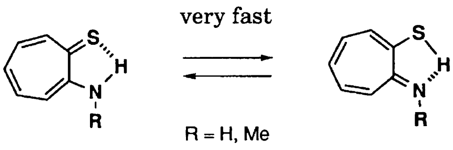


Scheme 3.

We have reinvesigated the structure of the 2-amino derivatives (**1d** and **e**) based on NMR spectroscopies and have found that these tropothiones exist as tautomeric mixtures of the thione (A) and enethiol (B) structures in solution (Scheme 3). As reference compounds for the fixed forms of the thione (A) and enethiol (B) structures, we chose 2-methoxytropothione (**1g**) and 2-methylthio-*N*-methyltroponimine (**3**), respectively. The latter compound was prepared form 2-(methylamino)tropothione (**1e**) and methyl iodide (see Experimental Section). The chemical shift values (δ=183) of 1-C of amino derivatives **1d** and **e** are between those (δ=200—213) of the nonenethiolizable tropothiones (**1b**, **1c**, **1g**, and **1h**) [thione (A) form] and that (δ=153) of 2-methylthio-*N*-methyltroponimine (**3**) [enethiol (B) form](Table 4). From the chemical shifts, we have found that the amino tropothiones (**1d** and **e**) exist as a rapid equilibrium mixture of the thione (A) (64%) and the enethiol structure (B) (36%). We estimated the ratio based on the chemical shift values of the thione form (δ=200) and that of the enethiol form (δ=153). We also performed variable-temperature ^{13}C NMR spectroscopies of the compounds in CD_2Cl_2

in the temperature range between 27 and -80 °C. However, significant differences in each chemical shift were not observed at all ($\Delta\delta<0.030$ ppm/K). This result strongly suggests the existence of a very fast equilibrium of the compounds (**1d** and **e**) between the thione (A) and enethiol (B) structures. The energy barrier is estimtated to be a small value less than 7.4 kcal mol^{-1}. The ^{14}N NMR sepctra of amino derivatives **1d** and **e** also support a fast equilibrium in this system. The chemical shifts (**1d**: $\delta=-273$; **1e**: $\delta=-266$) are intermediate between that ($\delta=-371$) of dimethylamine and that ($\delta=-93$) of the imino group of 2-methylthio-*N*-methyltroponimine (**3**). From the chemical shifts, the amino derivatives, **1d** and **e**, are estimated to exist in a rapid equilibrium mixture of the thione (A) and enethiol (B) forms in an approximate ratio of 64 : 36, which is the same result as that derived from the ^{13}C NMR spectroscopy.

Thus, the two amino derivatives (**1d** and **1e**) of tropothione exist as a very rapid equilibrium mixture in the solution state (Scheme 4). This result contrasts with that previously reported by Brasen et al.[17)]



Scheme 4.

The dipole moment of 2-(methylamino)tropothione (**1e**) in benzene at 20 °C was measured to be 4.73 D (1D$=3.3356\times10^{-30}$ C m), compared to that (3.36 D) for the corresponding tropone, 2-(methylamino)tropone (**2e**). This result gives an indication of the polarity of the molecules, in sharp contrast to the polarities of the parent tropothione (**1a**) (3.88 D)[2)] and tropone (4.17 D[33)] or 4.30 D[34)]). The compounds with an amino- (**1d** and **e**), methoxy- (**1g**), or methylthio- (**1h**) group were hydrolyzed with potassium hydroxide in ethanol to give 2-hydroxytropothione (**1f**) in high yields.

In conclusion, we have demonstrated that the 2-substituted tropothiones (**1b**—**h**) can be synthesized directly from the corresponding tropones (**2b**—**h**) in moderate yields and that the spectroscopic properties for the 2-substituted tropothiones **1** are characteristic compared with those of the corresponding tropones. These synthesized tropothione derivatives are more stable and aromatic than the parent tropothione (**1a**). In the approach shown here, several synthetic steps for three known compounds (**1d**—**f**) are no longer necessary.

Experimental

General. Melting points were determined in open capillary tubes on a Büchi 511 melting points determinator and are not corrected. Elemental analyses were performed at the Analytical Laboratory, Department of Chemistry, The University of Tokyo, Hongo, Tokyo for sulfur, and at the Microanalytical Laboratory, the Chemical Analysis Center, Saitama University for carbon and hydrogen. IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer; measurements were done on 1% KBr pellets or in 0.3 mol dm^{-3} CCl_4 solutions. UV-visible spectra were taken with a Hitachi EPS-3T spectrophotometer using 1-cm quartz cells. ^{13}C and ^{1}H NMR spectra were measured on a JEOL FX-90Q (90 MHz, 22.5 MHz) instrument as well as a Bruker AM-400 (400 MHz, 100.6 MHz) spectrometer. The assignments were aided by both off-resonance and selective decoupling spectra. ^{14}N NMR spectra were measured on a Bruker AM-400 (28.9 MHz) spectrometer. Nitromethane was used as an external standard. ^{31}P NMR spectra were measured on a JEOL FX-90Q (36.3 MHz) instrument. Mass spectra were obtained with a JEOL MS-01SG-2 spectrometer operating at an ionization potential of 75 eV.

Reagents and Starting Material. The starting material, tropone (**2**), was obtained by a disproportionation of bis(2,4,6-cycloheptatrienyl) ether, which was prepared from cycloheptatriene by treating with trifluoroacetic acid as a catalyst according to a previously reported method.[35)] The tropone thus obtained led to tropolone via 2-aminotropone.[36)] 2-Methyl-,[37)] 2-phenyl,[38,39)] 2-methylamino-,[40)] 2-hydroxy-,[41)] and 2-methoxytropone[42—44)] were prepared by literature methods starting from tropone or tropolone. 2-(Methylthio)tropone[45,46)] was prepared from 2-hydroxytropothione[18,19)] with diazomethane in anhydrous ether in a 91% yield. All starting tropones (**2a**—**h**) were used after purification by recrystallization or redistillation. Tetraphosphorus decasulfide was recrystallized from carbon disulfide after a trituration or an extraction with a Soxhlet extractor using carbon disulfide from a commercially available reagent. Triethylamine, used as a catalyst, was freshly distilled. The solvents used for the preparation of tropothiones (**1**) were all degassed. Light petroleum refers to the fraction boiling in the range 40—60 °C. For column chromatography, Merck Kieselgel 60 (0.063—0.200 mm) or Wako activated alumina (ca. 200 mesh) were employed.

General Procedure for 2-Substituted Tropothiones (1b—h). Under the presence of triethylamine (3.3 cm^3) as a catalyst, a solution of 817 mg (6.00 mmol) of 2-methoxytropone in 5 cm^3 of dichloromethane was added to a solution of tetraphosphorus decasulfide (2.7 g, 6.1 mmol) in 45 cm^3 of anhydrous dichloromethane at 0 °C. The reaction mixture was stirred vigorously over a period of 40 min under a nitrogen stream. The mixture was washed with aqueous 1 mol dm^{-3} hydrochloric acid to remove the catalyst, then with ice–water and dried over magnesium sulfate. Solvent removal under reduced pressure left the product as an oily crystalline material. Short column chromatrgraphy (silica gel) followed by recrystallization from ethanol gave 877 mg of product **1g** as red prisms.

2-Methoxytropothione (1g): Red prisms; mp 74—75 °C (crystallized from ethanol); IR (KBr) $\nu_{\max}$ 2990 (w), 2930 (w), 2825 (w), 1570 (m), 1470 (s), 1406 (m), 1265 (s), 1238 (s), 1210 (s), 1165 (m), 1100 (s), 1043 (s) (C=S), 995 (m), 944 (s), 915 (m), 875 (m), 733 (s), 669 (m), and 605 (m) cm^{-1}; IR (CCl_4) $\nu_{\max}$ 3008 (w), 2960 (w), 2935 (w), 2831 (w), 1481 (s), 1460 (m), 1420 (s), 1272 (s), 1233 (s), 1211 (s), 1169 (m), 1108 (s), 1049 (s) (C=S), 978 (w), 940 (s), 861 (w), 696 (w), 667 (w), and 615 (w) cm^{-1}. Found:

Table 4. ^{13}C NMR Spectral Data (δ_C/ppm) for 2-Substituted Tropothiones[a]

		Carbon atom δ_C							
Compd	R	1-C[b]	2-C[b]	3-C[c]	4-C[c]	5-C[c]	6-C[c]	7-C[c]	Substituent[d]
1a[e]	H	213.08	153.86	132.32	138.84	138.84	132.32	153.86	—
1b	Me	212.07	162.26	133.02	135.59	136.83	129.65	153.77	30.67 (Me)
1c	Ph	213.22	162.84	133.29	136.07	137.52	129.86	154.78	144.84,[b] 128.47,[c] 127.81,[c] 127.34[c] (Ph)
1d	NH_2	183.28	164.12	114.69	137.73	129.64	132.25	146.45	—
1e	NHMe	183.19	162.88	111.68	137.77	128.11	132.47	143.84	31.15 (N–Me)
1f	OH	183.42	173.89	120.48	138.02	133.05	134.01	143.63	—
1g	OMe	200.41	173.10	112.03	134.97	132.51	130.49	151.42	57.56 (O–Me)
1h	SMe	203.25	170.50	128.55	134.16	134.38	130.17	149.12	19.86 (S–Me)

a) Determined at 100.6 MHz in $CDCl_3$ with $SiMe_4$ as an internal standard. Assignments are based on the $^{13}C-^{1}H$ heteronuclear shift-correlated 2D NMR spectra (see Experimental section). b) Multiplicities, singlet. c) Multiplicities, doublet. d) Multiplicities, quartet except **1c**. e) Taken from Ref. 2 for comparison.

C, 63.06; H, 5.25; S, 20.80%. Calcd for C_8H_8OS: C, 63.13; H, 5.30; S, 21.06%.

Other tropothiones (**1b**—**f**, **h**) were prepared in similar ways as described in Table 1.

2-Methyltropothione (1b): Red needles; mp 38—39 °C (crystallized from cold ether); IR (KBr) ν_{max} 3010 (w), 2960 (w), 2910 (w), 1565 (w), 1500 (s), 1465 (m), 1445 (m), 1410 (m), 1388 (m), 1370 (m), 1290 (m), 1255 (w), 1238 (m), 1130 (m), 1105 (s), 1050 (s) (C=S), 1025 (w), 960 (w), 942 (w), 880 (w), 840 (w), 735 (m), 655 (w), 638 (w), 609 (w), and 590 (w) cm^{-1}; IR (CCl_4) ν_{max} 3021 (w), 2888 (w), 1496 (m), 1462 (m), 1441 (w), 1409 (m), 1390 (m), 1371 (m), 1286 (w), 1228 (w), 1112 (s), 1055 (s) (C=S), 960 (w), 939 (w), 881 (w), 667 (w), and 629 (w) cm^{-1}. Found: C, 70.41; H, 5.74; S, 23.16%. Calcd for C_8H_8S: C, 70.54; H, 5.92; S, 23.54%.

2-Phenyltropothione (1c): Red viscous oil; IR (neat) ν_{max} 3040 (m), 3010 (m), 1592 (m), 1482 (s), 1440 (s), 1360 (m), 1263 (s), 1120 (m), 1102 (m) (C=S), 1069 (m), 933 (m), 907 (m), 792 (m), 750 (s), 732 (s), 670 (m), 645 (m), and 548 (m) cm^{-1}; IR (CCl_4) ν_{max} 3050 (w), 3024 (w), 2952 (m), 2925 (m), 2855 (w), 1483 (m), 1410 (m), 1393 (m), 1284 (s), 1263 (s), 1134 (m), 1103 (s) (C=S), 1071 (m), 898 (w), 880 (w), 695 (s), and 649 (w) cm^{-1}. Found: C, 78.46; H, 4.99; S, 16.51%. Calcd for $C_{13}H_{10}S$: C, 78.75; H, 5.08; S, 16.17%.

2-Aminotropothione (1d): Orange needles; mp 137—138 °C (crystallized from ethanol) [lit,[16,17] 137—138.5 °C (from methanol)]; IR (KBr) ν_{max} 3270 (w), 3090 (w), 1600 (s), 1575 (s), 1555 (m), 1488 (m), 1455 (m), 1433 (s), 1386 (s), 1340 (m), 1276 (m), 1236 (m), 1143 (w), 1048 (s) (C=S), 990 (m), 940 (m), 878 (m), 855 (m), 736 (s), 699 (w), 570 (s), and 465 (w) cm^{-1}; IR (CCl_4) ν_{max} 3470 (m), 3198 (w), 2914 (w), 2850 (w), 1460 (m), 1433 (m), 1402 (s), 1342 (w), 1069 (s) (C=S), 968 (m), 695 (w), 648 (w), and 584 (w) cm^{-1}.

2-(Methylamino)tropothione (1e): Orange needles; mp 66—67 °C (crystallized from ethanol) [lit,[17] 67—67.5 °C (from ethanol)]; IR (KBr) ν_{max} 3070 (w), 3020 (w), 1590 (m), 1525 (s), 1495 (m), 1423 (m), 1406 (s), 1265 (s), 1230 (m), 1220 (m), 1080 (m), 1040 (s) (C=S), 985 (w), 952 (m), 905 (w), 880 (m), 740 (m), 708 (w), 635 (m), and 590 (m) cm^{-1}; IR (CCl_4) ν_{max} 3080 (w), 3033 (w), 2935 (w), 2910 (w), 2830 (w), 1487 (m), 1448 (s), 1431 (s), 1400 (s), 1378 (m), 1269 (s), 1208 (m), 1090 (s), 1042 (s) (C=S), 960 (m), 902 (w), 886 (m), 685 (w), 634 (m), 601 (m), and 508 (w) cm^{-1}.

2-Hydroxytropothione (1f): Orange plates; mp 54—55 °C (crystallized from low-boiling light petroleum ether) [lit,[18—20] 55 °C (petroleum ether)]; IR (KBr) ν_{max} 2970 (w), 1579 (w), 1545 (m), 1464 (s), 1440 (m), 1417 (s), 1402 (s), 1298 (s), 1252 (s), 1220 (s), 1204 (m), 1095 (s) (C=S), 1010 (m), 951 (m), 937 (w), 880 (m), 774 (w), 746 (w), 735 (m), 720 (m), 695 (m), 590 (m), and 489 (w) cm^{-1}; IR (CCl_4) ν_{max} 3053 (w), 2742 (w), 2670 (w), 2483 (w), 2449 (w), 1470 (s), 1428 (s), 1410 (s), 1300 (s), 1256 (s), 1220 (m), 1095 (s) (C=S), 1012 (m), 952 (m), 923 (w), 879 (m), 693 (m), and 590 (m) cm^{-1}.

2-(Methylthio)tropothione (1h): Red prisms; mp 75—76 °C (crystallized from hexane); IR (KBr) ν_{max} 3010 (w), 2970 (w), 2946 (w), 2890 (w), 1554 (w), 1455 (s), 1425 (w), 1410 (s), 1385 (s), 1310 (m), 1270 (s), 1240 (s), 1233 (s), 1095 (s), 1090 (s), 1060 (s) (C=S), 930 (m), 875 (m), 730 (s), 657 (w), 600 (w), and 560 (m) cm^{-1}; IR (CCl_4) ν_{max} 3038 (w), 2969 (w), 2914 (m), 2849 (w), 1456 (s), 1442 (m), 1413 (s), 1380 (s), 1273 (s), 1245 (m), 1218 (m), 1102 (s), 1059 (s) (C=S), 980 (m), 920 (m), 878 (m), 700 (m), 654 (m), and 560 (m) cm^{-1}. Found: C, 56.96; H, 4.81; S, 37.76%. Calcd for $C_8H_8S_2$: C, 57.10; H, 4.79; S, 38.11%.

Hydrolysis of 2-Substituted Tropothiones (1d, e, g, and h). Into a solution of 400 mg of potassium hydrox-

Table 5. Weight Fractions (w) of the Solutes (**1e**, **1g**, and **2e**) vs. Dielectric Constant (ε) and Density (d) Increments at 20 °C

Compd	R	$w\times10^5$	$\Delta\varepsilon\times10^3$	$\Delta d\times10^4$ g cm^{-3}
1e	NHMe	598	99	9
		1051	173	19
		2207	372	46
1g	OMe	1053	154	50
		1941	377	69
		2993	572	112
2e	NHMe	996	96	23
		1800	173	39
		2188	213	48
		2844	271	66

Table 6. Empirical Constants (ε_1, d_1, α, and β), Polarizations (P) of the Solutes, Molar Refractions (R_D) for the D Sodium Line, and Dipole Moments (μ) at 20 °C.

Compd	R	ε_1	d_1	α	β	P	R_D	μ
			g cm^{-3}		g cm^{-3}	cm^3	cm^3	D
1e	NHMe	2.2824	0.8780	16.867	0.2123	514.4	50.3	4.73±0.01
1g	OMe	2.2664	0.8786	19.597	0.3612	589.9	48.4	5.10±0.01
2e	NHMe	2.2846	0.8782	9.581	0.2276	275.2	41.3	3.36±0.01

ide in 10 cm^3 of ethanol was added 75.5 mg of 2-(methylamino)tropothione (**1e**) in 12 cm^3 of ethanol. The reaction mixture was refluxed with stirring for 5 h, and then was neutralized with aqueous 2 mol dm^{-3} hydrochloric acid. The mixture was then extracted with ether. The ether layer was washed with saturated NaCl solution several times and dried with magnesium sulfate. Solvent removal left 60.1 mg of the product, 2-hydroxytropothione (**1f**). Recrystalllization from pentane gave 53.8 mg of pure material of **1f** as red plates, mp 54—55 °C. The melting point of the product was undepressed on admixture with an authentic sample of **1f** which was prepared according to the literature method.[18] The IR spectrum of the product was superimposable with that of the authentic sample.

In similar ways, 2-amino- (**1d**), 2-methoxy- (**1g**), and 2-(methylthio)tropothione (**1h**) were hydrolyzed to give 2-hydroxytropothione (**1f**) in 70—78% yields.

Reaction of 2-(Methylamino)tropothione (1e) with Methyl Iodide. To crystals of 2-(methylamino)tropothione (**1e**) (65.0 mg, 0.430 mmol) was added methyl iodide (5.0 cm^3, 80 mmol) at 0 °C. The mixture was allowed to stand at 20 °C for 30 min and then the volatile material was removed under reduced pressure. The residue was recrystallized from methanol to give 2-methylthio-*N*-methyltroponiminium iodide (**4**) as yellow needles (124 mg, 0.423 mmol, 98%).

The salt (**4**) (89.8 mg, 0.306 mmol) was dissolved in water (5 cm^3). To the solution was added 3% potassium hydroxide aqueous solution slowly. The obtained yellow solution was extracted with dichloromethane, then dried with anhydrous magnesium sulfate. Solvent removal gave yellow crystals which were recrystallized from hexane to yield 2-methylthio-*N*-methyltroponimine (**3**) as yellow needles (45.5 mg, 0.276 mmol, 90%).

2-Methylthio-*N*-methyltroponiminium Iodide (4): Yellow needles; mp 188—189 °C; UV-vis (CH_3CN) 208 (log ε 4.37), 247 (4.28), 274 (4.10), 337 (sh, 3.64), 361 (3.76), and 389 nm (sh, 3.72); IR (KBr) ν_max 3440 (s), 3142 (s), 3015 (s), 1598 (m), 1529 (s), 1472 (s), 1419 (s), 1321 (w), 1288 (s), 1262 (m), 1031 (s), 991 (w), 934 (m), 752 (s), 636 (w), and 565 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.86 (3H, s, SCH_3), 3.29 (3H, s, NCH_3), 7.63 (1H, d, J=11.6 Hz, 7-H), 7.65 (1H, dd, J=10.1 and 8.5 Hz, 5-H), 7.73 (1H, ddd, J=10.1, 9.7, and 1.6 Hz, 4-H), 7.96 (1H, d, J=9.7 Hz, 3-H), and 8.04 (1H, ddd, J=11.6, 8.5, and 1.6 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ=16.24 (q, SCH_3), 32.61 (q, NCH_3), 123.71 (d, 7-C), 134.82 (d, 5-C), 136.26 (d, 3-C), 137.14 (d, 4-C), 143.44 (d, 6-C), 148.42 (s, 2-C), and 161.90 (s, 1-C). Found: C, 36.71; H, 4.30; N, 4.55; S, 10.86%. Calcd for $C_9H_{12}NSI$: C, 36.87; H, 4.12; N, 4.78; S, 10.94; I, 43.29%.

2-Methylthio-*N*-methyltroponimine (3): Yellow needles; mp 68—69 °C; UV-vis (MeOH) 212 (log ε 4.05), 242 (4.06), 277 (4.03), 337 (3.75), and 354 nm (3.75); UV-vis (hexane) 211 (log ε 4.03), 242 (4.03), 292 (4.00), 354 (3.60), and 372 nm (sh, 3.56); IR (KBr) ν_max 2945 (w), 2890 (w), 2840 (w), 1614 (m), 1573 (s), 1542 (s), 1493 (s), 1456 (m), 1433 (m), 1418 (m), 1378 (s), 1275 (m), 1229 (m), 1121 (w), 1068 (w), 1001 (s), 974 (m), 953 (m), 920 (m), 880 (m), 811 (m), 760 (s), 706 (w), 652 (m), 582 (w), 558 (m), and 517 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s, SCH_3), 3.29 (3H, s, NCH_3), 6.36 (1H, dd, J=11.5 and 7.5 Hz, 5-H), 6.37 (1H, d, J=7.4 Hz, 3-H), 6.46 (1H, d, J=11.7 Hz, 7-H), 6.56 (1H, ddd, J=11.5, 7.4, and 1.1 Hz, 4-H), and 6.60 (1H, ddd, J=11.7, 7.5, and 1.1 Hz, 6-H); ^{13}C NMR ($CDCl_3$) δ=16.28 (q, SCH_3), 37.53 (q, NCH_3), 121.75 (d, 3-C), 121.83 (d, 7-C), 126.29 (d, 5-C), 130.70 (d, 4-C), 131.20 (d, 6-C), 152.63 (s, 2-C), and 162.56 (s, 1-C); MS (75 eV) m/z (rel intensity) 166 (M^++1, 65%), 165 (M^+, 83), 151 (69), 150 (80), 149 (25), 136 (30), 135 (23), 133 (38), 132 (40), 124 (20), 122 (29), 121 (50), 120 (32), 119 (58), 118 (62), 117 (17), 110 (49), 109 (56), 106 (22), 105 (59), 104 (57), 103 (10), 91 (86), 90 (58), 89 (19), 78 (100), 77 (72), 76 (24), 70 (23), 69 (23), 66 (33), 65 (37), 64 (30), 54 (47), 53 (61), and 52 (23). Found: C, 65.35; H, 6.53; N, 8.54; S, 19.64%. Calcd for $C_9H_{11}NS$: C, 65.41; H, 6.71; N, 8.48; S, 19.40%.

Dipole Moment Measurements. The dipole moments of **1e**, **1g**, and **2e** were measured on an instrument (built in-house)[47] in purified benzene at 20.0±0.1°C. The dielectric constants (ε) of the solutions were observed by the heterodyne beat method. The densities (d) were measured with an Ostwald pycnometer. The results are shown in Tables 5 and 6. The molar polarizations of the solutes were calculated from the experimental data. The measured values of the dielectric constants (ε_{12}) and specific volumes (d_{12}) of the solutions were found to be linear functions of the weight fractions (w_2) of the solutes according to the equations $\varepsilon_{12}=\varepsilon_2+\alpha w_2$ and $d_{12}=d_{12}+\beta w_2$. The molar refractions for the D sodium line (R_D) were calculated from the values of the bond refractions in the literature.[48] The dipole moments were then obtained from the usual equation. The observed dipole moments include an inaccuracy of 0.01 D.

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