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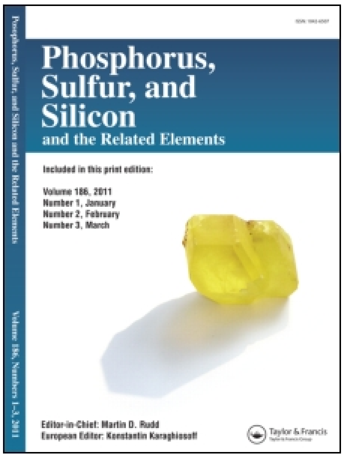

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MASS, NUCLEAR MAGNETIC RESONANCE, AND RAMAN SPECTROSCOPY OF OCTADECYL SULFIDE, DISULFIDE, AND TETRASULFIDE

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MASS, NUCLEAR MAGNETIC RESONANCE, AND RAMAN SPECTROSCOPY OF OCTADECYL SULFIDE, DISULFIDE, AND TETRASULFIDE

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Model compounds prepared for evaluation as extreme pressure lubricant additives were studied by mass, nuclear magnetic resonance, and Raman spectroscopy. Mass spectral studies showed strong molecular ions upon electron impact of octadecyl sulfide and disulfide. Both sulfur-sulfur and carbon-sulfur cleavages were noted for octadecyl disulfide and tetrasulfide. With octadecyl tetrasulfide the molecular ion appears to lose sulfur even at 15 eV; this sulfur loss was not observed with octadecyl sulfide and disulfide. From nuclear magnetic resonance measurements it was noted that a chemical shift downfield occurs for the α-methylene protons with increasing length of the sulfur moiety. Raman spectra showed strong peaks attributed to S-S stretching. For octadecyl disulfide these peaks occurred at 510 and 526 cm^{-1} (solid state) and for octadecyl tetrasulfide peaks were found at 432 and 488 cm^{-1} (solid state) and 437 and 488 cm^{-1} (liquid state, undiluted as a melt at 58°). All have weak peaks between 625 and 800 cm^{-1} which probably arise from C-S vibrations.

INTRODUCTION

Since passage of the Endangered Species Act protecting sperm whales, considerable attention has been concentrated on the development of extreme-pressure (EP) lubricant additives from other sources. Reasons for superiority of sulfurized sperm whale oil as an EP agent are not adequately known, and there is need for knowledge on the relationship of structure to extreme-pressure properties. To acquire information on this relationship, we prepared model compounds for evaluation. One series was octadecyl sulfide (19-thiaheptatriacontane), octadecyl disulfide (19,20-dithiaoctatriacontane), and octadecyl tetrasulfide (19,20,21,22-tetrathiatetracontane). The sulfide and disulfide are known, but the pure tetrasulfide is unreported. Patent literature[1–4] refers to octadecyl tetrasulfide in methods of producing mixtures of organic polysulfides but fails to show isolation or characterization of a crystalline tetrasulfide. Modern physical methods such as mass spectrometry, nuclear magnetic resonance (nmr), and laser Raman spectroscopy ease the identification and characterization of model compounds. Very little characterization data is reported on the octadecyl polysulfide series. Mass spectra are published for short chain dialkyl sulfides[5] and disulfides,[6] but there is a void in the literature on the mass spectra of tetrasulfides. Brown[7] has reviewed the nmr spectra of sulfur compounds in general and includes some polysulfides, but there are no references to the octadecyl series. Raman spectra are reported for S-S linkages,[8–11] and Raman spectroscopy has

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been used in elucidating conformations of disulfides.[12] This paper describes the use of mass spectroscopy, nmr, and laser Raman spectroscopy in identifying and characterizing octadecyl sulfide, disulfide, and tetrasulfide.

RESULTS AND DISCUSSION

Table I lists principal mass fragments of octadecyl sulfide, octodecyl disulfide, and octadecyl tetrasulfide. These spectra can be separated into hydrocarbon fragments and sulfur-containing fragments. The hydrocarbon fragments form clusters of ions at 29, 43, 57, 69, 83, 97, 101, and 125 and indicate that the molecule has a long hydrocarbon chain. Octadecyl sulfide yields a strong 285 peak, which is attributed to $CH_3(CH_2)_{17}S^+$ and is formed by the cleavage of a carbon-sulfur bond. Octadecyl disulfide and octadecyl tetrasulfide also have fragments at mass 285, but these are formed by cleavage of sulfur-sulfur bonds. All three compounds have a peak at mass 283, two hydrogens less than the 285 peak, forming an unsaturated aliphatic sulfur ion. The peak at 318 is a rearrangement fragment formed by the sulfur abstracting a hydrogen from the hydrocarbon moiety as follows: $CH_3(CH_2)_{17}SS(CH_2)_{17}CH_3 \rightarrow CH_3(CH_2)_{17}S^+SH + CH_2 = CH(CH_2)_{15}CH_3$. Cook and Foster[13] have noted in mass spectra of simple dithiaalkanes that the charge remained with the sulfur fragments and that sulfur through its polarity was responsible for abstracting atoms during rearrangements.

TABLE I

Mass spectra of octadecyl sulfide, disulfide, and tetrasulfide

Molecular weight	Sulfide 538	Disulfide 570	Tetrasulfide 634
m/e	Percentages of base peak		
634	—	—	2.9
602	—	—	31.8
570	—	100.0	60.2
542	0.5	10.2	—
538	33.3	0.2	0.7
318	0.2	5.7	18.0
285	70.2	8.2	20.5
283	3.1	6.8	5.5
256	0.2	0.3	1.4
252	3.7	1.9	11.1
224	0.4	0.3	5.2
192	0.1	0.3	12.8
165	0.2	0.3	25.9
160	0.2	—	17.5
128	0.2	0.3	13.5
125	3.2	2.0	9.7
111	7.1	5.0	18.7
103	1.4	1.0	2.2
101	3.9	10.1	14.6
97	19.4	13.9	39.2
96	3.7	3.1	9.2
85	16.2	24.1	36.3
83	29.6	20.9	48.8
71	31.0	38.5	56.4
69	37.7	30.5	52.7
64	0.2	0.1	29.7
57	78.7	69.3	100.0
55	51.9	42.3	69.8
43	100.0	64.9	82.1
41	39.7	26.0	47.7
32	0.2	0.8	7.4
29	16.7	10.9	16.3
27	5.2	2.8	5.3

Figure 1 is a mass spectrum of octadecyl tetrasulfide. The 318 fragment appears to result from symmetric cleavage with rearrangement and is identical to the 318 fragment discussed for octadecyl disulfide. Only a very small peak is observed at 350, $C_{18}H_{37}S_3H^+$, and none is found at 382 for $C_{18}H_{37}S_4H^+$. Fragmentation of octadecyl tetrasulfide shows a much less intense 285 peak due to sulfur-sulfur cleavage than was noted for octadecyl sulfide where the most intense sulfur fragment was 285. Octadecyl tetrasulfide was run at both 70 and 15 eV. The high-mass region for both was similar, indicating that sulfur was probably lost before electron impact. Work is in progress on this problem to determine reason for loss of sulfur. Scans were made up to 800, but nothing was detected above 634. Fragments at 256, 224, 192, 160, 128, 96, 64, and 32 are sulfur species with the peaks 128, 160, 192, and 256 identified by high resolution peak matching. Polysulfides have weak S-S bonds[14] and their bond lengths have been reviewed by Abrahams.[15] Twiss,[16] Jones and Reid,[17] and Bloomfield[18] conclude thermal decomposition of tetrasulfides as complex. Pryor[19] reports that tetrasulfides decompose upon heating to form a disulfide and sulfur.

Nuclear magnetic resonance data for octadecyl sulfide, disulfide, and tetrasulfide are shown and compared with data for butyl disulfide and tetrasulfide in Table II. A chemical shift downfield is noted for the α-methylene protons in progressing from sulfide to disulfide to tetrasulfide. This shift can be attributed to increasing electronegativity as the number of sulfur atoms increases in the series. The *d* orbitals of sulfur are used in explanations of the electron rich and polar characteristics of sulfur-sulfur bonds.[21] Wazer and Grant[22]

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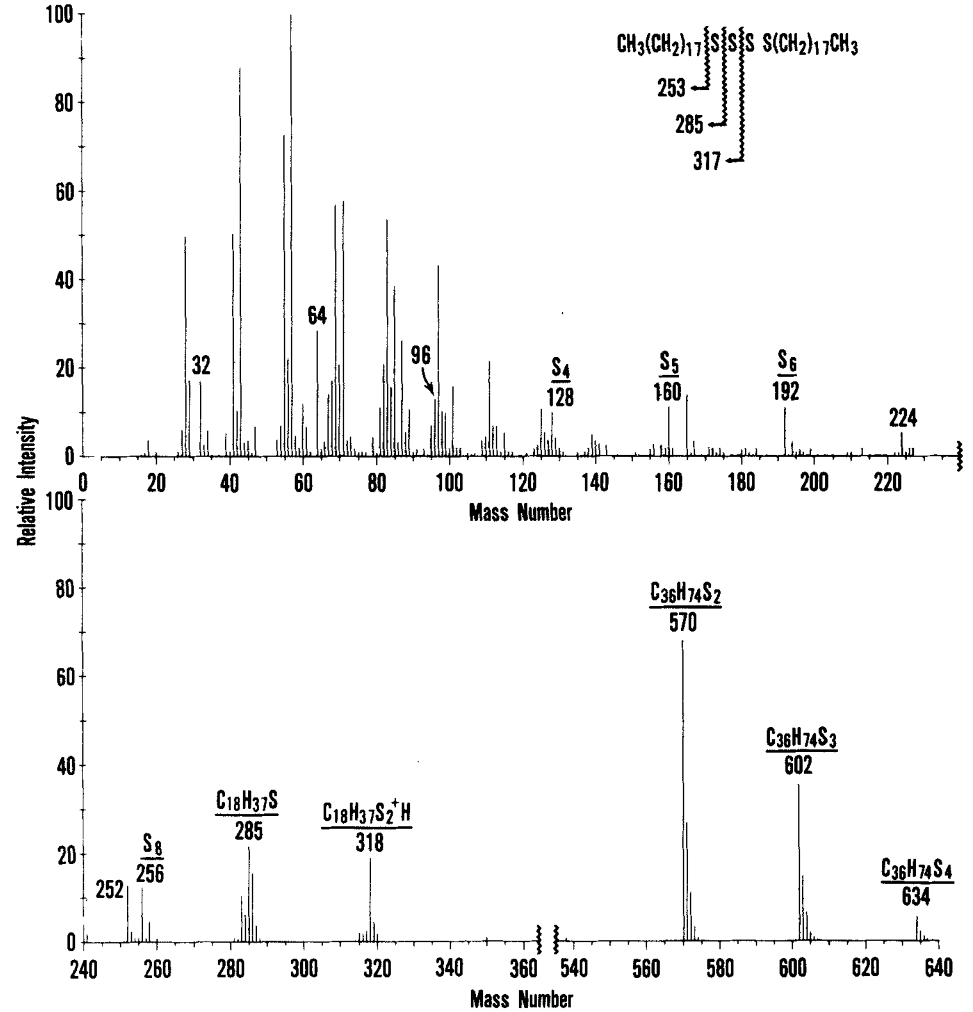

FIGURE 1 Mass spectrum of octadecyl tetrasulfide with underlined formulas obtained by high-resolution peak matching.

TABLE II

Chemical shifts[a] for α-methylene protons in butyl and octadecyl disulfides and tetrasulfides

	Butyl[b]	Octadecyl
Monosulfide	—	2.46
Disulfide	2.64	2.65
Tetrasulfide	2.95	2.91

[a] Relative to external $Si(CH_3)_4$.
[b] Reference 20 (Vineyard).

studied nmr shifts with various values of n in RS_nR with R = Me, t-Bu, or $PhCH_2$ and also found chemical shifts downfield with increasing length of the sulfur chain.

Infrared spectra on octadecyl disulfide and tetrasulfide showed weak absorption for S-S stretching and no pronounced absorption differences among members of the series. Raman spectroscopy is a more attractive method since each species gives its own characteristic vibration, which can be useful for identification.[23] Table III lists prominent Raman peaks of methyl, ethyl, and octadecyl sulfides, disulfides, and tetrasulfides. Methyl disulfide vibrational frequencies were measured at 694.0 cm^{-1} (ρ = 0.15) for C-S stretch, and at 509.1 (ρ = 0.06) for S-S stretch. Octadecyl disulfide showed two C-S stretching vibrations at 708 and 745 cm^{-1} and two S-S stretchings at 510 and 526 cm^{-1} (pair of rotameric peaks). Octadecyl tetrasulfide (Figure 2) has strong peaks at 432

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TABLE III

Raman shift wavenumbers for strong S-S stretch vibrations of solid octadecyl sulfides and some depolarization ratios[a] compared with data for the lower analogs

	Wave number (depolarization ratio[a])		
	Octadecyl	Methyl	Ethyl
Monosulfides	None from 700–300	None	None
Disulfides	510, 526[b]	509; (0.06)	507; (0.07[c])
Tetrasulfides,	488; (0.07)	487[c]	486[c]
2 peaks	432; (0.19)	441[c]	438[c]

[a] Obtained in benzene solutions.

[b] A pair of rotameric peaks; that at 526 cm^{-1} greatly predominated in the solid state, and that at 510 cm^{-1} moderately predominated in benzene solution.

[c] Reference 24 (Freeman), pages 229 and 239.

and 488 cm^{-1} (solid state) and at 437 and 488 cm^{-1} (liquid state) which suggest presence of rotamers. Tsurugi and Nakabayashi[25] report infrared absorption peaks at 487.8 and 491.4 cm^{-1} for dibenzhydryl tetrasulfide and claim these as rotational isomers. Wieser *et al.*[26] studied the vibrational spectrum of hydrogen tetrasulfide and give vibrational assignments for conformers. Daly and Brown[27] obtained Raman spectra of sodium tetrasulfide in water and in amines and conclude that S_4^{2-} is a tetratomic dianion with C_2 symmetry as suggested by Ward.[28] A similarity is noted between our Raman spectra of octadecyl tetrasulfide and that of sodium tetrasulfide.[27]

The identities claimed for the octadecyl sulfides are supported, not only by their synthetic history and NMR, mass, and infrared spectrometries, but further by conformance of their Raman S-S stretch patterns (Figure 2 and Table III) with those reported for the lower analogs. Correspondingly, the value of the Raman patterns of methyl and ethyl sulfides for identifying sulfide types in general is augmented by showing that the longer chain analogs gave similar patterns.

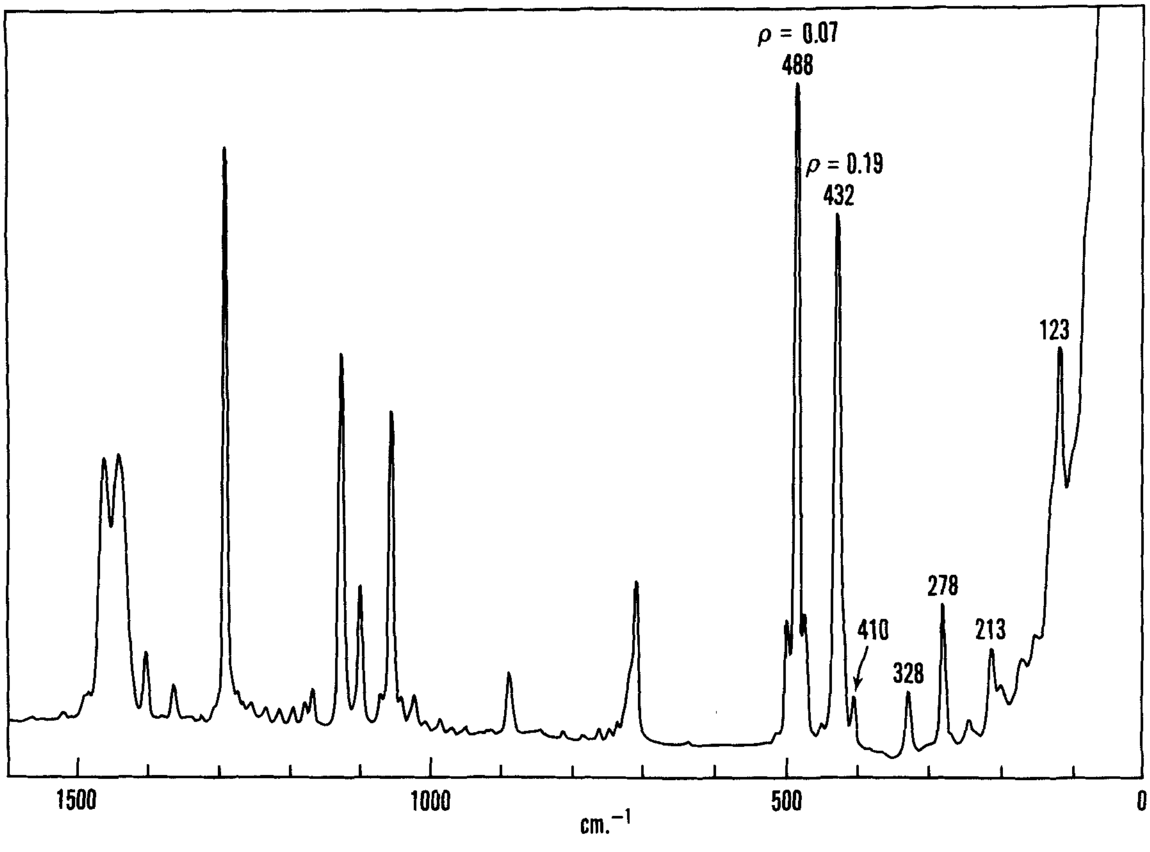

FIGURE 2 Raman spectrum of compacted crystals of octadecyl tetrasulfide with some depolarization ratios obtained with benzene solutions.

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EXPERIMENTAL

Reagents and chemicals. Octadecyl sulfide and disulfide obtained from the Wateree Chemical Co., Lugoff, S.C., were purified by recrystallization from ethanol. Products had respective melting points of 68–69° and 61–62°. Octadecyl mercaptan from the Aldrich Chemical Co., Milwaukee, Wisc., was recrystallized from ethanol to an mp of 31–32°. Sulfur monochloride obtained from Eastman Kodak Co. was vacuum distilled at 51°/43 mm. Methyl disulfide was commercial grade from Sigma Chemical Co.

Preparation of octadecyl tetrasulfide. With magnetic stirring 14.3 g (0.05 mole) octadecyl mercaptan was dissolved in 300 ml hexane. To this solution was added dropwise 3.37 g (0.025 mole) sulfur monochloride in 80 ml hexane. Hydrogen chloride evolved during addition. Solution was refluxed 1 h and then cooled to room temperature, admixed with 380 ml of dry acetone, and refrigerated at 5°. After filtration, crystals were vacuum dried at 25°. Yield: 15.1 g; mp 44–45°; Calcd for $C_{36}H_{74}S_4$: C, 68.07; H, 11.74; S, 20.19; Found: C, 67.86; H, 11.04; S, 19.31.

Mass spectra. These were obtained with a Nuclide 12-90 DF mass spectrometer by direct insertion probe. Accelerating potential was 8 KV, electron energy was 70 eV but was also run at 15 eV for octadecyl tetrasulfide to determine any pattern change in the molecular ion region. Ionization current was $20\,\mu$A and temperature of ion source was 110°. Data during determinations were collected by a PDP-8 mini-computer and were stored and processed on a Modcomp II computer.

Nuclear magnetic resonance (nmr). This analysis was performed in $CDCl_3$ solution with a Varian HA-100 research model.

Infrared (ir). Spectra were obtained either on a thin film or in carbon disulfide with a Beckman IR 8 spectrometer.

Raman spectra. These spectra were obtained either on compacted crystals or in benzene solution. For rho values, the tubes were examined with 90° angle illumination using a Spectra-Physics Model 165-8, 4 watt argon ion laser with a Spex 1401 Ramalog 4 double spectrometer. Laser excitation was at 514.5 nm. Frequencies were measured by their relationships to nearby neon lines. Spectra of the solid octadecyl derivatives were obtained by the 180° angle technique on crystals compacted in a small metal cavity in the end of an all-metal structure. The temperature was stabilized at 1° by circulation of ice water through the metal structure that held the cavity. For the spectrum of the melted tetrasulfide, the temperature was raised to 58° and the resulting liquid was retained in the cavity with a bacteriological cover glass held by a cap that was drilled for light passage. Measurements of commercial methyl disulfide and of depolarization ratios (P) of solutions of the tetrasulfide were made by 90° angle excitation in a cell spun by an nmr spinner assembly. The cell for this measurement was constructed by opening the end of a 5 mm nmr tube, flaring, and soldering on a cover glass as incident beam window by using 1 : 1 In-Sn solder that adheres to glasses.

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