deviations from additivity explains the regularly rising temperature of minimum heat capacity as the proportion of potassium to sodium decreases, these observed temperatures being, respectively, 504, 514, 560, 577 and 628° for 100, 78, 54, 45 and 0% potassium. It is noteworthy that these temperatures (in °K.) are 75 and 78% of the normal b.p.'s in the cases of pure potassium and sodium, respectively. This last correspondence is perhaps not particularly unexpected for two elements that are so similar in other properties.

Though these deviations of the heat capacities of the alloys from additivity are almost within the assigned uncertainties, there is a strong indication that they tend to be positive. It is worth mentioning that whereas for pure liquid potassium and sodium there were found cubic equations ((4) and (9)) that represent the observed enthalpy without apparent trend over the investigated temperature range, this seemed not to be the case for the one alloy (78% potassium) measured with maximum precision. The introduction of an exponential term into the enthalpy equation for this alloy (equation (5)) eliminated the trend otherwise present. This provides some evidence that the true heat-capacity, temperature curve of this alloy possesses a greater curvature at the lower temperatures and a smaller curvature at the higher temperatures than the corresponding additively calculated curve. This may have some theoretical significance.

Acknowledgments.—The authors wish to express their appreciation to J. L. Hague, R. A. Paulson and H. A. Bright, of the National Bureau of Standards, who developed and tested unusual techniques of analysis of the alloys and showed an active interest in verifying the accuracy of the compositions of the alloys by applying several independent methods. B. F. Scribner and associates, also of the Bureau, performed spectrochemical analyses of two of the samples. J. E. Noonan, of the Knolls Atomic Power Laboratory, assisted in the preparation of the samples.

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[CONTRIBUTION NO. 27 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

3,4-Dithiahexane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, and Thermodynamic Functions[1]

BY D. W. SCOTT, H. L. FINKE, J. P. MCCULLOUGH, M. E. GROSS, R. E. PENNINGTON AND
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The following thermodynamic properties of 3,4-dithiahexane were determined experimentally: heat capacity of the solid and liquid between 12 and 300°K., triple point (171.64°K.), heat of fusion (2248 cal. mole^{-1}), vapor pressure ($\log_{10} p = 6.97507 - 1485.970/(t + 208.958)$), heat of vaporization (9780 and 9380 cal. mole^{-1} at 373.73 and 400.04°K., respectively), entropy of the vapor ($S^0 = 107.31$ and 109.96 cal. deg.$^{-1}$ mole^{-1} at 373.73 and 400.04°*K*., respectively), and heat capacity of the vapor ($C_p^0 = 41.41$ and 42.71 cal. deg.$^{-1}$ mole^{-1} at 408.20 and 428.25°K., respectively). The functions $-(F^0 - H_0^0)/T$, $H^0 - H_0^0$, S^0, and C_p^0 were calculated from spectroscopic and molecular-structure data for selected temperatures up to 1000°K. In these calculations, a two-constant potential function for internal rotation of the ethyl groups was selected to fit the calorimetric values of the heat capacity and entropy of the vapor. Interpretation of the spectroscopic data for 3,4-dithiahexane led to the conclusion that the stable form of the molecule has both ethyl groups in the *trans*-configuration.

The investigation of the thermodynamic properties of organic sulfur compounds which is in progress in this Laboratory consists of detailed experimental and computational studies of selected members of homologous series which may be present in petroleum or be produced in refining processes. A previous paper[2] presented the results of a study of the first member of the symmetrical alkane disulfide series, 2,3-dithiabutane (dimethyl disulfide). This paper presents the results of a similar but somewhat more comprehensive study of the next higher homolog of the series, 3,4-dithiahexane (diethyl disulfide).

Experimental values were obtained for the entropy and heat capacity of the compound in the vapor state. Thermodynamic functions were then computed from spectroscopic and molecular structure data, using the experimental values of the entropy and heat capacity to evaluate certain necessary structural parameters. The results of previous studies in this Laboratory of simpler, structurally related compounds, particularly 2,3-dithiabutane and ethanethiol, were utilized in interpreting the spectra of the relatively complex 3,4-dithiahexane molecule and in treating its several internal rotations.

Experimental

The Material.—The 3,4-dithiahexane used for the experimental measurements consisted of two samples, which were prepared and purified at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A. One of these samples was used for low temperature studies and vapor pressure measurements. Its purity was determined during the course of the low temperature studies by measuring the melting point as a function of the fraction melted. The value of the purity so obtained was 99.92 mole per cent. The other sample was used for heat of vaporization and vapor heat capacity measurements. The purity of this second sample, determined at the Laramie Station by the time–temperature freezing point method, was reported to be 99.91 mole per cent. Both samples, when they were not being used for measurements, were stored in the dark as a precaution against photochemical decomposition.

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(1) This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950).

Low-Temperature Studies.—Measurements of the heat capacity of 3,4-dithiahexane in the solid and liquid states, and its triple point and heat of fusion were made in an apparatus similar to that described by Ruehrwein and Huffman.[3] The calorimeter used to contain the sample was constructed of platinum and had internal disks of gold to promote more rapid attainment of thermal equilibrium.

The results of the heat capacity measurements are given in Table I. $C_{\text{sat.}}$ is the heat capacity of the condensed phase under its own vapor pressure, which, for the temperature range of this table, does not differ significantly from C_p, the heat capacity at constant pressure. The temperatures listed in Table I are the mean temperatures of the individual measurements. The temperature increments employed (less than 10% of the absolute temperature below 50°, 5–6° from 50 to 100°, 6–10° above 100°K.) were small enough that no correction was necessary for non-linear variation of $C_{\text{sat.}}$ with temperature. The energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833. The precision of the measurements was, in general, better than 0.1%; above 30°K., the accuracy uncertainty of the heat capacity data probably does not exceed 0.2%. The heat capacity of the saturated liquid as a function of temperature may be represented by the equation

$$C_{\text{sat.}} = 56.792 - 0.13638\,T + 4.9906 \times 10^{-4}\,T^2 - 4.427 \times 10^{-7}\,T^3 \quad (1)$$

a plot which deviates less than 0.05% from a visually smoothed curve through the experimental points.

TABLE I

MOLAL HEAT CAPACITY OF 3,4-DITHIAHEXANE

0°C. = 273.16°K.; mol. wt. = 122.252

T, °K.	$C_{\text{sat.}}$, cal. deg.$^{-1}$	T, °K.	$C_{\text{sat.}}$, cal. deg.$^{-1}$	T, °K.	$C_{\text{sat.}}$, cal. deg.$^{-1}$
Solid		50.45	12.541	162.31	30.440
12.63	1.397	53.31	13.170	Liquid	
13.00	1.501	54.92	13.509	168.17	45.844
13.72	1.711	57.39	14.033	171.87	45.834
14.03	1.800	62.08	14.985	175.65	45.815
15.02	2.109	67.15	15.947	180.35	45.834
15.25	2.183	69.72	16.386	180.37	45.832
16.40	2.535	72.29	16.833	184.19	45.836
17.06	2.741	75.38	17.355	187.82	45.842
18.09	3.091	77.16	17.679	193.75	45.887
19.18	3.453	81.22	18.353	203.27	45.963
20.00	3.748	82.11	18.508	213.27	46.126
21.56	4.282	83.64	18.754	223.73	46.304
21.99	4.424	86.76	19.273	224.24	46.311
24.27	5.204	87.78	19.426	234.05	46.508
24.60	5.312	89.09	19.608	244.29	46.796
26.94	6.090	92.49	20.089	254.44	47.112
28.02	6.448	96.87	20.685	264.50	47.432
29.78	7.010	98.83	20.969	269.76	47.625
31.47	7.540	105.89	21.931	274.47	47.786
34.92	8.591	115.31	23.218	279.69	48.000
38.39	9.547	124.82	24.481	284.35	48.170
42.08	10.520	134.39	25.740	289.54	48.401
46.13	11.523	143.54	26.974	299.30	48.819
		152.34	28.238		

Equilibrium melting temperatures, as a function of the fraction melted, were determined by the method described in an earlier publication.[4] The results are summarized in Table II. The value obtained for the triple point is 171.64°K. Duplicate determinations of the heat of fusion gave the values 2247.6 and 2247.7 cal. mole^{-1}. The cryoscopic constant ($\Delta H_{\text{fusion}}/RT^2_{\text{T.P.}}$) calculated from these data is 0.0384 deg.$^{-1}$.

TABLE II

3,4-DITHIAHEXANE, MELTING POINT SUMMARY

0°C. = 273.16°K.; $T_{\text{T.P.}}$, 171.64 ± 0.05°K.; impurity, 0.08 ± 0.02 mole per cent. This value is obtained from the equation $N_2/F = 0.0384\,\Delta T$, where N_2 is the mole fraction of impurity in the whole sample, F is the fraction of the sample in the liquid state, and ΔT is $T_{\text{T.P.}} - T_{\text{obsd.}}$

Melted, %	$1/F$	T, °K. Obsd.	T, °K. Graph[b]
9.9	10.1	171.453	171.436
25.6	3.91	171.562	171.562
49.5	2.02	171.600[a]	171.600
70.8	1.41	171.614	171.612
90.6	1.10	171.618[a]	171.618
100.0	1.00		171.620
Pure	0.00		171.640

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point ($T_{\text{T.P.}}$). [b] These are values of T on the straight line of footnote a.

Vapor Pressure Measurements.—The vapor pressure of 3,4-dithiahexane was studied over suitable temperature ranges by a static method and by an ebulliometric method, both of which have been described previously.[5] To minimize reaction of the compound with mercury when using the static method, the sample was maintained at the temperature of solid carbon dioxide at all times except when measurements were actually in progress. Two series of measurements were made by the static method: Series I, after distilling material out of the sample container until about four-fifths of the original sample remained, and Series II, after distilling out additional material until only about one-fifth of the original sample remained. The satisfactory agreement of the two series, and their consistency with the results of the ebulliometric studies, are evidence that adequate precautions were taken to minimize reaction with mercury.

The measurements by the ebulliometric method were made with an ebulliometer similar to that described in ref. 5, but modified by enclosing the heating element in a re-entrant well so that the sample came into contact with nothing but glass. The measurements were made in order of increasing temperature. At temperatures up to and slightly above the normal boiling point the compound was stable, but at higher temperatures some decomposition occurred, as was evident from an increase in the difference between the boiling and condensation temperatures. All data obtained after this difference exceeded 0.010° were rejected.

The results obtained by both methods are presented in Table III. These data were correlated by means of the following Antoine equation

$$\log_{10} p = 6.97507 - 1485.970/(t + 208.958) \quad (2)$$

the constants of which were obtained by a least-squares adjustment.[6] In this equation, p is the vapor pressure in mm. and t is the temperature in °C. Values of the vapor pressure calculated by means of equation (2) are included in Table III for comparison with the experimental values. The normal boiling point, as given by equation (2), is 153.98°.

3,4-Dithiahexane is included in the extensive list of sulfur compounds whose vapor pressures have been studied ebulliometrically by White, Barnard-Smith and Fidler.[7] Over the pressure range covered by these investigators (100 to 1000 mm.) the boiling points which they report for 3,4-dithiahexane differ by less than 0.03° from those calculated by means of equation (2) of this paper.

Heat of Vaporization and Vapor Heat Capacity.—Vapor heat capacity data for 3,4-dithiahexane were essential for the treatment of its thermodynamic functions by the detailed methods of statistical mechanics. These data and the

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(3) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

(4) S. S. Todd, G. D. Oliver and H. M. Huffman, *ibid.*, **69**, 1519 (1947).

(5) Guy Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 797 (1949).

(6) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(7) P. T. White, D. G. Barnard-Smith and F. A. Fidler, paper presented at the Cleveland Meeting of the American Chemical Society, April, 1951.

TABLE III

VAPOR PRESSURE OF 3,4-DITHIAHEXANE

Static method

T, °C.		0.00	15.00	20.00	25.00	30.00	35.00	40.00	45.00
p(obsd.),	I	0.73	2.24	3.11	4.24	5.75	7.67	10.16	13.32
mm.	II	.78	2.20	3.08	4.21	5.73	7.65	10.11	13.32
p(calcd.), mm.		.73	2.19	3.05	4.20	5.71	7.66	10.15	13.30

T, °C.		50.00	55.00	60.00	65.00	70.00	75.00	80.00
p(obsd.),	I	17.32	22.23	28.26	35.59	44.55	55.23	68.02
mm.	II	17.23	22.13	28.13	35.52	44.39	55.08	67.89
p(calcd.), mm.		17.25	22.16	28.19	35.56	44.49	55.21	68.01

Ebullionietric method

Boiling point,	Water	60.000	65.000	70.000	75.000	80.000
°C.	$C_4H_{10}S_2$	100.567	107.079	113.627	120.230	126.884
Vapor pressure, mm.	Obsd.	149.41	187.57	233.72	289.13	355.22
	Calcd.	149.37	187.58	233.68	289.08	355.19

Boiling point,	Water	85.000	90.000	95.000	100.000	105.000
°C.	$C_4H_{10}S_2$	133.579	140.336	147.136	153.986	160.884
Vapor pressure, mm.	Obsd.	433.56	525.86	633.99	760.00	906.06
	Calcd.	433.45	525.85	634.02	760.08	906.19

associated heat of vaporization data could be obtained only after incorporating two important modifications in the cycling-vaporizer and flow-calorimeter assembly described previously[8] to adapt it to the study of such a high boiling and relatively unstable substance. These modifications were: (a) The heater in the vaporizer was enclosed in a glass spiral in order that the boiling liquid would be in contact with nothing but glass. (b) The glass stopcock used to divert the flow of vapor to the sample-collecting bulb was replaced with a solenoid-actuated valve made of stainless steel and having valve seats of gold and polytetrafluoroethylene. The solenoid valve is an improvement over the stopcock because it operates much more rapidly and particularly because it eliminates the use of stopcock grease. When a stopcock was used, the apparatus was limited by the softening points of available stopcock lubricants to the study of compounds with normal boiling points below about 100°. Installation of the solenoid valve removed this limitation and permitted the study of higher boiling compounds, such as 3,4-dithiahexane (153.98°).

The results of the heat of vaporization and vapor heat capacity measurements are summarized in Table IV. These calorimetric measurements were of necessity confined to a relatively small temperature interval, the lower limit of which was determined by the vapor pressure of the compound and the upper limit of which was determined by the instability of the compound at higher temperatures. The heat of vaporization was measured at 373.73 and 400.04°K., and the vapor heat capacity was measured at 408.20 and 428.25°K. at each of the two pressures, 149 and 355 mm. Tests for thermal decomposition in the calorimeter were carried out at both temperatures with negative results. These tests, which were made by measuring the heat capacity with different increments of temperature rise in the calorimeter (ΔT = 4, 8 and 12°), depended on the fact that the rate of a decomposition reaction is an exponential function of temperature while the heat capacity is nearly a linear function of temperature. If the flowing vapor were being warmed by heat from a decomposition reaction in addition to that supplied by the heater, the apparent heat capacity would be lower for a larger ΔT. Actually no change in apparent heat capacity was observed for a threefold change in ΔT.

TABLE IV

Heat of vaporization, cal. mole⁻¹		Vapor heat capacity, cal. deg.⁻¹ mole⁻¹			
T, °K.	$\Delta H_{vap.}$	T, °K.	C_p (355 mm.)	C_p (149 mm.)	C_p^0
373.73	9780 ± 3[a]	408.20	41.99	41.65	41.41 ± 0.17
400.04	9380 ± 4[a]	428.25	43.13	42.89	42.71 ± 0.17

[a] Maximum deviation from the mean of triplicate determinations.

Values of C_p^0, the heat capacity in the ideal gas state, were obtained by linear extrapolation of the experimental heat-capacity values to zero pressure. The limited range of pressure covered by the experimental measurements introduced some uncertainty into this extrapolation; the values of C_p^0 in Table IV have therefore been assigned an uncertainty of 0.4% instead of the usual 0.2%.

Entropy.—The calorimetric and vapor pressure data were utilized to calculate the entropy of 3,4-dithiahexane in both the liquid and vapor states. The calculations are summarized in Table V. For extrapolating the heat capacity of the solid below 12°K., a Debye function for five degrees of freedom with θ = 100.3° was used. For extrapolating the heat capacity of the liquid from 298.16°K. to the temperatures at which the heat of vaporization was measured, equation (1) was used; the integrals $\int_{298.16}^{T} C_{sat.}\, d \ln T$ were evaluated analytically. For computing the corrections for gas imperfection, an equation for the second virial coefficient, B, in the equation of state $PV = RT + BP$ was obtained from the calorimetric and vapor pressure data in the manner described previously.[9] This equation, $B = -880 - 12.66 \exp(1700/T)$ cc. mole⁻¹, is based on a meager amount of experimental data and may be of limited accuracy. However, it is adequate for computing the small correction for gas imperfection, $P(dB/dT)$. The uncertainty assigned to the experimental values of the entropy of the vapor includes the uncertainty in the rather long extrapolation of the heat capacity of the liquid outside the range of experimental measurement.

TABLE V

ENTROPY OF 3,4-DITHIAHEXANE, CAL. DEG.⁻¹ MOLE⁻¹

0–12°K.	Debye extrapolation	0.431
12–171.64°	Solid, graphical $\int C_{sat.}\, d \ln T$	33.602
171.64°	Fusion 2247.7/171.64	13.095
171.64–298.16°	Liquid, graphical $\int C_{sat.}\, d \ln T$	25.772
Entropy (±0.15) of liquid at 298.16°K.		72.90

T, °K.	373.73	400.04
Entropy of liquid at 298.16°K.	72.90	72.90
Liquid, $\int_{298.16}^{T} C_{sat.}\, d \ln T$	11.40	15.01
Vaporization, $\Delta H_{vap.}/T$	26.17	23.45
Compression, $R \ln (p/760)$	−3.23	−1.51
Gas imperfection	0.07	0.11
Entropy (±0.30) of ideal gas at 1 atm.	107.31	109.96

Thermodynamic Functions

Vibrational Assignment.—The molecular structure parameters that were required for computing the thermodynamic functions of 3,4-dithiahexane were (a) the complete set of fundamental vibrational frequencies of the molecule, (b) the moments of inertia for over-all and internal rotation, and (c) the shape and magnitude of the potential barriers hindering internal rotation. These will be discussed in that order in this and the following two sections.

The vibrational assignment that was made for 3,4-dithiahexane utilized Raman and infrared data from a number of sources.[10] All of these data

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[8] (a) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

[9] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[10] (a) S. Venkateswaren, *Indian J. Phys.*, **6**, 51 (1931) (Raman); (b) P. Donzelot and M. Chaix, *Compt. rend.*, **202**, 851 (1936) (Raman); (c) C. S. Venkateswaren and N. S. Pandya, *Proc. Indian Acad. Sci.*, **15A**, 396 (1942) (Raman with polarizations); (d) R. Vogel-Högler, *Acta Phys. Austriaca*, **1**, 311 (1948) (Raman with polarizations); (e) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 481 (1946) (infrared of liquid, 6–20μ); (f) American Petroleum Institute Research Project 44 at Carnegie Institute of Technology, Catalog of Infrared Spectrograms. Serial No. 1113 (infrared of liquid, 2–15μ); (g) unpublished measurements by J. K. Brown and N. Sheppard, University of Cambridge, Cambridge, England (infrared of liquid and solid, 6–22μ). Communicated by Dr. Norman Sheppard.

that are pertinent to the vibrational assignment are compiled in Table VI. Since the 3,4-dithiahexane molecule has rotational isomers, the frequencies of more than one of which may appear in the spectra, it is well to consider these rotational isomers before discussing the spectra in detail. By analogy with structurally related molecules, the dihedral angle of the two S–S–C planes of 3,4-dithiahexane must be close to 90°[11]; the existence of two equilibrium positions with respect to rotation about the S–S bond requires that there be optical isomers, but these optical isomers are not distinguishable spectroscopically. Rotational isomers that are distinguishable spectroscopically can result only from different configurations of the ethyl groups with respect to rotation about the S–C bonds. The bonds on either side of the S–C bonds probably have a staggered orientation. (The subsequent discussion will show that the assumption of a staggered orientation leads to a consistent interpretation of the spectroscopic and calorimetric data.) For a staggered orientation, there are three different configurations of an ethyl group, a *trans*-configuration (designated *t*) and two non-equivalent *skew* configurations (designated *s* and *s'*). Combinations of these for the two ethyl groups can result in six different, spectroscopically distinct, rotational isomers, as illustrated in Fig. 1. The three of these rotational isomers that have one or both ethyl groups in the *s'* configuration have non-bonded carbon–carbon distances significantly less than 4 Å. and therefore less than twice the van der Waals radius of a methyl or methylene group.[12] Because of steric repulsion, these would be expected to have higher energy than any of the other three isomers and hence would not be expected to exist in high enough concentrations at ordinary temperatures to be observed spectroscopically. Therefore only the three isomers not involving the *s'* configuration (*t–t*, *t–s* and *s–s*) need be considered in interpreting the spectra.

TABLE VI

SPECTRA OF 3,4-DITHIAHEXANE BELOW 1500 CM.$^{-1}$

Abbreviations used: $\bar{\nu}$, Raman displacement in cm.$^{-1}$; I, intensity; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; ρ, depolarization factor; p, polarized; d, depolarized; ν, frequency in cm.$^{-1}$.

Raman (liq.)			Infrared (liq.)[c]		Infrared (solid)[d]		
$\bar{\nu}$[a]	I	ρ[b]	ν	I	ν	I	Assignment
115	m	d					Torsion about S–S
180	s	0.71					S–S–C bend., sym.
198	m	0.80					S–S–C bend., unsym.
259	w	d					759 − 507 = 252
295	w	p					115 + 180 = 295
323	m	0.60					S–C–C bend., sym.
360	m	d					S–C–C bend., unsym.
400	w						2 × 198 = 396
458	w	p					642 − 180 = 462
507	s	0.32	507	m	507	m	S–S str.
522	m	0.25	525	w			S–S str. (less stable isomer)
578	w						759 − 180 = 579
644	s	0.57	640	s	640	s	S–S str.
668	m	0.48	667	w			S–C str. (less stable isomer)
758	m	p	760	s	763	s	CH_2 rock.
			779	m			CH_2 rock. (less stable isomer)
968	m	0.79	967	s	966	s	C–C str.
			ca. 1004	vw	998	w	360 + 642 = 1002
1032	m	d	1027	m	1027	m	CH_3 rock.
1052	m	0.45	1049	s	1050	m	CH_3 rock.
1125	w	p					360 + 759 = 1119
			1148	w	1151	vvw	507 + 642 = 1149
1238	w				*ca.* 1236	m	1418 − 180 = 1238
1258	m	0.57	1251	s	1248	s	CH_2 wag.
					1260	m	507 + 759 = 1266
			1278	s	1280	m	2 × 642 = 1284
1294	w						323 + 967 = 1290
			ca. 1309	vw			CH_2 twist.
					ca. 1322	vw	360 + 967 = 1327
			1337	vw			1447 − 115 = 1332
			1374	s	1369	s	CH_3 bend., sym.
			1403	w			642 + 759 = 1401
1418	m	0.84	1418	s	1420	m	CH_2 bend.
1446	m	0.86	1446	s	1450	s	CH_3 bend., unsym.

[a] Average of values reported by Venkateswaren and Pandya (ref. 10c) and by Vogel-Högler (ref. 10d) when observed in both investigations. [b] Data of Venkateswaren and Pandya. [c] Average of values reported in references 10e, 10f and 10g. [d] Data of Brown and Sheppard (ref. 10g).

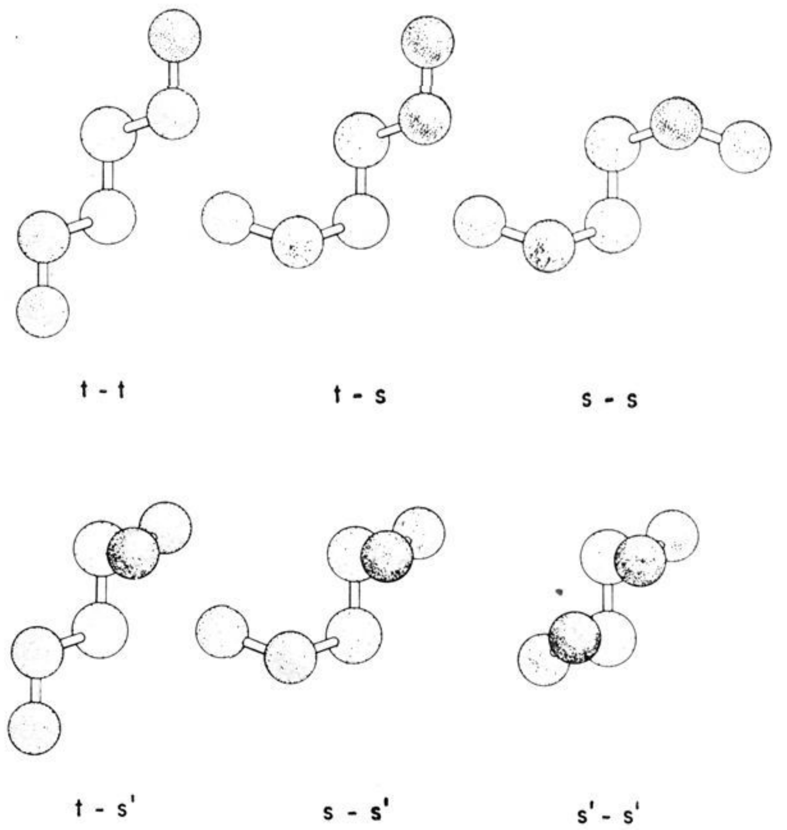

Fig. 1.—Rotational isomers of 3,4-dithiahexane. The larger spheres represent the sulfur atoms and the smaller spheres the carbon atoms. The hydrogen atoms are not shown. Only one enantiomorph of each pair of spectroscopically indistinguishable optical isomers is depicted.

As shown in the last column of Table VI, all but three of the observed frequencies of 3,4-dithiahexane can be satisfactorily interpreted as fundamentals, overtones or combinations of a single isomer. This fact shows that, at ordinary temperatures, only one rotational isomer is present in high concentration. However, the 507 and 642 cm.$^{-1}$ frequencies have weaker satellites at 524 and 668 cm.$^{-1}$ in both spectra, and the 760 cm.$^{-1}$ frequency

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(11) The corresponding dihedral angle is 92 ± 12° in S_2Cl_2 (G. Guthrie, Thesis, California Institute of Technology, 1949), 82° in 1,7-diiodo-3,4,5-trithiaheptane (J. Donohue, THIS JOURNAL, **72**, 2701 (1950)), 93° in 2,3,4-trithiapentane (*ibid.*, footnote 3), and 102° in S_8 (L. Pauling, *Proc. Nat. Acad. Sci.* U. S., **35**, 495 (1949)).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 176.

has a weaker satellite at 779 cm.$^{-1}$ in the infrared spectrum. Brown and Sheppard[10g] have observed that these three satellites in the infrared spectrum of the liquid disappear abruptly upon crystallization. The three frequencies 524, 668 and 779 cm.$^{-1}$ must therefore be attributed to a second rotational isomer present in small concentration at ordinary temperatures, and therefore having higher energy than the preponderant form.

It was necessary to decide which of the rotational isomers is the one that is present in high concentration at ordinary temperatures. Depending on whether the *t*- or the *s*-configuration of an ethyl group is of lower energy, this could be either the *t–t* or *s–s* form. The decision between these two forms was made by comparing the lower skeletal frequencies actually observed with those calculated for both *t–t* and *s–s* forms by a normal coördinate treatment. In this normal coördinate treatment, a six-atom chain approximation was used; that is, point masses of 14 and 15 atomic weight units were substituted for the methylene and methyl groups, respectively. Wilson's G–F matrix method[13] was employed and the C–C and S–C stretching frequencies were factored out. Force constants (2.4 × 10^5 dynes/cm. for S–S stretching and 0.92 × 10^{-11} erg/radian^2 for both S–S–C and S–C–C bending) were transferred from 2,3-dithiabutane and ethanethiol. The observed and calculated frequencies and their corresponding polarizations are compared below:

	Obsd.	Calcd. *t–t*	Calcd. *s–s*
S–S–C bend., sym.	180 ?	190 p	183 p
S–S–C bend., unsym.	198 ?	204 d	255 d
S–C–C bend., sym.	323 p	277 p	361 p
S–C–C bend., unsym.	360 d	361 d	352 d
S–S str.	507 p	552 p	520 p

It will be observed that the calculated frequencies and corresponding polarizations for the *t–t* form are in satisfactory accord with the observed data but that those for the *s–s* form are inconsistent in having the polarized S–C–C bending frequency higher than the depolarized one and in having a much greater separation of the two S–S–C bending frequencies than is actually observed. From these results (which are necessarily only qualitative because of the approximate nature of the normal coördinate treatment) it was concluded that the *t–t* form is the rotational isomer that is present in high concentration at ordinary temperatures. This is the result one would have expected *a priori* by analogy with other linear molecules (for example, the normal paraffin hydrocarbons) in which, almost without exception, the *trans*-configuration about a single bond is found to be more stable than a *skew* configuration.

A few details of the vibrational assignment that are not evident from the last column of Table VI remain to be discussed. The symmetrical and unsymmetrical S–C stretching frequencies are not resolved in the observed spectra, a fact that is not surprising since the analogous frequencies in 2,3-dithiabutane (685.8 and 692.2 cm.$^{-1}$) and S_2Cl_2 (437 and 451 cm.$^{-1}$) are nearly coincident and have been resolved only in the most recent investigation of the Raman spectra of these substances.[10d] The pairs of internal ethyl-group frequencies of 3,4-dithiahexane are likewise unresolved in the obobserved spectra. These frequencies correspond closely to the internal ethyl-group frequencies of ethanethiol and 2-thiabutane,[14] and were readily assigned by comparison with the other two compounds. The assignment of the CH_2 twisting frequency to a very weak infrared band was somewhat schematic. No detailed assignment was attempted for the ten C–H stretching frequencies, which make a relatively insignificant contribution to the thermodynamic functions. An average value of 2950 cm.$^{-1}$ was used for these.

The following complete set of vibrational frequencies (of the *t–t* form) was used for thermodynamic calculations: 180, 198, 323, 360, 507, 642 (2), 759, (2), 967 (2), 1029 (2), 1050 (2), 1254 (2), 1309 (2), 1374 (2), 1418 (2), 1447 (4), and 2950 (10) cm.$^{-1}$.

Moments and Reduced Moments of Inertia.—The methods of Kilpatrick and Pitzer[15] for molecules with compound internal rotation were used to compute the moments and reduced moments of inertia of the 3,4-dithiahexane molecule. These calculations were made for the *t–t* form, since in treating molecules with unsymmetrical internal rotations, the moments of inertia and vibrational frequencies must apply to the same equilibrium configuration.[16] The bond distances and angles were taken to be the same as those in structurally related substances, namely: S–S distance, 2.04 Å.; S–C distance, 1.78 Å.; C–C distance, 1.54 Å.; C–H distance, 1.09 Å.; S–S–C angle, 107°; all other bond angles, 109° 28′; and C–S–S–C dihedral angle, 90°. The value obtained for the product of the three principal moments of inertia was 1.048 × 10^{-112} g.^{3} cm.^{6}. The off-diagonal elements of the internal-rotational kinetic-energy matrix were neglected, and the diagonal elements were taken as the reduced moments of inertia. These were 5.106 × 10^{-40} g. cm.^{2} for methyl rotation, 38.70 × 10^{-40} g. cm.^{2} for ethyl rotation, and 38.52 × 10^{-40} g. cm.^{2} for rotation about the S–S bond. Neglect of the off-diagonal elements in this case is a rather poor approximation, as the square root of the determinant of the matrix differs by 13% from the square root of the product of the diagonal elements. However, error from this source is effectively canceled in the calculated thermodynamic functions by using potential barriers selected to give agreement with the calorimetric value of the entropy.

Barriers to Internal Rotation.—The potential barriers for rotation of the methyl groups and for rotation about the S–S bond were estimated without recourse to the calorimetric data. Threefold cosine-type barriers were assumed for the methyl rotations, and the barrier heights were taken to be

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(13) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); *ibid.*, **9**, 76 (1941).

(14) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington and H. M. Huffman, THIS JOURNAL, **73**, 261 (1951).

(15) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

(16) K. S. Pitzer, *ibid.*, **14**, 239 (1946).

the same as in ethanethiol, 3310 cal. mole^{-1}.[17] The torsional frequency associated with rotation about the S–S bond appears in the Raman spectrum at 115 cm.$^{-1}$. Torsion about the S–S bond could have been included with the other vibrations of the molecule and treated as a harmonic oscillation without serious loss of accuracy. However, the method that was used, namely, treating it as a hindered internal rotation with a twofold cosine-type barrier, included an approximate correction for anharmonicity. The barrier height was taken to be 13,200 cal. mole^{-1}, this being the value which, with the value of the reduced moment of inertia given previously, corresponds to a torsional frequency of 115 cm.$^{-1}$. No quantitative significance should be attached to this value of the barrier height; essentially it is an empirical parameter by the use of which nearly correct values are obtained for the important energy levels associated with the torsional motion.

The calorimetric values of the heat capacity and entropy were used to evaluate the parameters of the unsymmetrical potential barriers hindering the rotation of the ethyl groups. It seems well to point out here that the contributions of an internal rotation to the thermodynamic functions are quite insensitive to the detailed shape of the potential barrier.[18] This is an advantage from the standpoint of calculating thermodynamic functions, since only a crude approximation to the actual shape of the potential barrier is required for results of adequate accuracy. Conversely, it is a disadvantage from the standpoint of obtaining molecular structure information, since calorimetric data can yield little information about the detailed shape of potential barriers to internal rotation.

Any reasonable potential function for the rotation of an ethyl group in 3,4-dithiahexane must possess the following qualitative features: (a) a minimum at $\phi \approx 180°$ (where ϕ is the angle of internal rotation measured from the *cis*-configuration) corresponding to the stable *t*-configuration, (b) a higher minimum at $\phi \approx 60°$ corresponding to the less stable *s*-configuration, and (c) relatively high energy for about 60° on either side of $\phi = 325°$, this being the range in which a non-bonded carbon–carbon distance is less than 4.0 Å. The following function has these qualitative features

$$
\begin{aligned}
V &= \tfrac{1}{2}V_1(1 + \cos\phi) + \tfrac{1}{2}V_2(1 + \cos 3\phi) \quad 0 < \phi < \pi \\
&= \tfrac{1}{2}(V_1 + V_2)(1 + \cos 3\phi) \quad \pi < \phi < 2\pi \qquad (3)
\end{aligned}
$$

This potential function with $V_1 = 825$ cal. mole^{-1} and $V_2 = 1650$ cal. mole^{-1} was found to give satisfactory agreement with the experimental values of heat capacity and entropy and was adopted for computing the thermodynamic functions.

This potential function implies an energy difference between the *t*- and *s*-configurations of an ethyl group of 0.6 kcal. mole^{-1}. Because of the arbitrary form of equation (3) and the insensitivity of the thermodynamic functions to the barrier shape, as mentioned previously, this must be regarded as an order of magnitude value only. A direct measure of the energy difference could be obtained by studying the relative intensity of the Raman lines 507 cm.$^{-1}$ (*t–t* form) and 522 cm.$^{-1}$ (*t–s* form) as a function of temperature.

Thermodynamic Functions.—The functions $-(F^0 - H_0^0)/T$, $H^0 - H_0^0$, S^0 and C_p^0 for 3,4-dithiahexane were computed for selected temperatures up to 1000°K. by the usual statistical-mechanical formulas. The symmetry number is 2. The existence of *d*- and *l*-isomers corresponding to the two equilibrium positions with respect to rotation about the S–S bond contributes a mixing term $R \ln 2$ to $-(F^0 - H_0^0)/T$ and S^0. The internal rotations of the ethyl groups were treated classically, the reduced moment of inertia for an ethyl rotation being large enough to make such a treatment valid. The integrals necessary for evaluating the partition function and its first and second derivatives with respect to temperature were obtained by numerical integration between $\phi = 0$ and $\phi = \pi$ and by use of Bessel functions between $\phi = \pi$ and $\phi = 2\pi$. Simpson's rule with 10° intervals of ϕ was used for the numerical integration.

The calculated thermodynamic functions are tabulated in Table VII. For reasons of internal consistency, the tabulated values are given to four digits, although in some places in the table the retention of the last digit is not justified by the accuracy of the molecular structure parameters used in the calculations or by the reliability of the approximations employed.

TABLE VII

THERMODYNAMIC FUNCTIONS OF 3,4-DITHIAHEXANE

T, °K.	$-(F^0 - H_0^0)/T$, cal. deg.$^{-1}$ mole^{-1}	$H^0 - H_0^0$, kcal. mole^{-1}	S^0, cal. deg.$^{-1}$ mole^{-1}	C_p^0, cal. deg.$^{-1}$ mole^{-1}
298.16	75.90	6.887	98.99	34.24
300	76.04	6.951	99.20	34.37
400	83.19	10.72	110.0	40.94
500	89.55	15.12	119.8	46.74
600	95.35	20.04	128.8	51.66
700	100.7	25.43	137.0	55.89
800	105.7	31.20	144.7	59.54
900	110.5	37.31	151.9	62.73
1000	115.0	43.72	158.7	65.52

The values calculated for the entropy at 373.73 and 400.04°K., 107.27 and 110.00 cal. deg.$^{-1}$ mole^{-1}, may be compared with the calorimetric values at the same two temperatures, 107.31 and 109.96 cal. deg.$^{-1}$ mole^{-1}. Similarly the values calculated for the vapor heat capacity at 408.20 and 428.25°K., 41.46 and 42.68 cal. deg.$^{-1}$ mole^{-1}, may be compared with the calorimetric values at these two temperatures, 41.41 and 42.71 cal. deg.$^{-1}$ mole^{-1}, respectively.

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[17] J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, G. Waddington and H. M. Huffman, "Ethanethiol (Ethyl Mercaptan): Thermodynamic Properties in the Solid, Liquid and Vapor States. Thermodynamic Functions to 1000° K.," to be published.

[18] K. S. Pitzer and W. D. Gwinn have treated this matter quantitatively for symmetrical barriers (*J. Chem. Phys.*, **10**, 428 (1942)).