

and C-N linkages. It clearly corresponds to the frequency near 1650, found in the N-alkyl amides.¹² The upward shift in this frequency of 50 cm.⁻¹ in glycylglycine is presumably due to the polar character of the neighboring amino and carboxyl groups. It cannot be explained by the fact that the measurements on glycylglycine were made in aqueous solution, while the N-alkyl amides were studied as pure anhydrous liquids; since we have found that the corresponding frequency near 1660 in acetamide is the same in aqueous solution as the values reported by other authors¹³ for acetamide as a pure liquid or in the crystalline state. In addition to the intense frequency at 1700 there is also a weak frequency at 1637 in the cation, which becomes weaker and broader and is shifted to 1618 in the dipolar ion. Probably this frequency is not related to the peptide linkage, since frequencies of almost the same value appear in the spectra of many carboxyl and amino acids and their salts, even when there is no peptide group in the molecule.⁴

Other Amino Acids Studied and Their Salts.—

The β -, γ - and ϵ -amino acids studied, as dipolar ions and as cations, show all the features previously discussed^{4a,4c} in relation to the ionization of the carboxyl group, and further discussion of this point is not required here. It should be noted, however, that the C=O frequency for the un-ionized carboxyl group lies near 1740 or 1745 for α -amino acids, while it lies between 1720 and 1730 for the β -, γ - and ϵ -amino acids. For the unsubstituted fatty acids in water, the corresponding value is almost exactly 1720. Thus, the presence of an adjoining charged ammonium group in the α -position increases the frequency by

(12) K. W. F. Kohlrausch and R. Seka, *Z. physik. Chem.*, **B43**, 355 (1939).

(13) Ref. 7, p. 275.

15–20 cm.⁻¹, but the effect becomes very small or negligible when the charged group is farther away. The lysine cation containing charged ammonium groups in both the α - and the ϵ -position shows the value of 1740 for this frequency, which is found in the other α -amino acids.

Some of the stretching frequencies of the molecular chain, between 800 and 1100 cm.⁻¹, are noticeably different in the dipolar ion and cation forms of some of the amino acids studied. However, there is no such striking change as that found in glycylglycine, and it seems premature at this time to attempt to interpret the data.

The reported spectrum for histidine represents only one state of the molecule—namely, the state of maximum total charge, with positive charges on the imidazole and the ammonium group and a negative charge on the carboxyl group. This spectrum invites comparison with that of imidazole itself and some of the substituted imidazoles,¹⁴ but the available data indicate that the relations are complex and that it will be more profitable to defer discussion until other related compounds have been studied.

Summary

1. Raman spectra are reported for the cationic forms of cysteine and cystine, for glycylglycine, lysine, histidine and some β -, δ - and ϵ -amino acids. Most of the substances have been studied both as dipolar ions and as cations in aqueous solution.

2. The characteristic S-H, C-S and S-S vibrations have been identified in cysteine and cystine.

3. A brief discussion is given of certain features in the spectra of glycylglycine and the other amino acids studied.

(14) K. W. F. Kohlrausch and R. Seka, *Ber.*, **71**, 985 (1938).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments and Structures of Some Alkyl Disulfides and of Methyl Trisulfide

BY LAWRENCE M. KUSHNER,¹ GEORGE GORIN² AND CHARLES P. SMYTH*

The chemical behavior and properties of organic trisulfides have been variously interpreted as indicating a straight (I) or a branched (II) chain structure. Recent evidence has almost uni-



formly favored the first formulation. From an electron diffraction study of methyl trisulfide

Donohue and Schomaker³ have, in fact, concluded that the molecule has structure I, and have given interatomic distances and angles. As a number of measurements had already been made in this Laboratory upon the dipole moments of di- and trisulfides,⁴ it seemed of interest to correlate this conclusion with the results of these measurements. Since structure II might be expected to give rise to a comparatively high dipole moment because of the coordinate linkage, a study of the dipole moment of methyl trisulfide was undertaken as a means of distinguishing between the two struc-

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(3) Donohue and Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).

(4) Westlake, Laquer and Smyth, *THIS JOURNAL*, **72**, 436 (1950).

tural possibilities. The dipole moments of methyl, ethyl and propyl disulfides were also measured for comparative purposes.

Experimental

Method.—The apparatus and method of measurement have been described previously.⁵ All measurements were made at 30°. Refractive indices were measured with a Valentine refractometer, which had been calibrated with several Eastman Kodak Co. refractometric standards.

Materials.—The disulfides, originally Eastman Kodak Co. "white label" products, were distilled twice, the second distillation effecting a change of no more than 0.0003 in the refractive indices. Methyl trisulfide was prepared by the reaction of one mole of sodium sulfide and two moles of sulfur with two moles of dimethyl sulfate⁶ and purified by three distillations. The third distillation changed the refractive index by 0.0001; the dipole moments of the substance before and after distillation were identical within the experimental error. The benzene used as solvent was a thiophene-free product of The Barrett Company. It was dried over sodium wire and distilled; the fraction collected for use boiled at 80.0° at 761 mm. Its dielectric constant, extrapolated from solution measurements, was 2.268 as compared to the literature value of 2.267.

TABLE I
PHYSICAL PROPERTIES OF THE SULFIDES

	$^{\circ}\text{C.}$	B. p., Mm.	d_{20}^{20}	n_{D}^{20}
Methyl disulfide	107.2		1.051	1.5208
Ethyl disulfide	152		0.9794	1.5021
Propyl disulfide	69-70	10	0.9498	1.4942
Methyl trisulfide	58.4-59	15	1.196	1.5972

Results

The values of the dielectric constant, ϵ_{12} , and the specific volume, v_{12} , of the benzene solutions containing mole fraction, c_2 , of the polar solute are given in Table II. The dipole moments, μ , were calculated by the method of Halverstadt and Kumler,⁷ employing the empirical equations

$$\epsilon_{12} = \epsilon_1 + \alpha'c_2$$

$$v_{12} = v_1 + \beta'c_2$$

The dipole moment values, the empirical constants of the equations, and the calculated values of the molar refraction, R_D , and of the molar polarization at infinite dilution, P_{∞} , are given in Table III.

Discussion

The values of the dipole moments are in satisfactory agreement with the earlier measurements⁴ which gave 1.99 for ethyl disulfide and 1.64 for ethyl trisulfide. The values found for the various disulfides are, of course, in excellent agreement among themselves.

A model of structure I built with Fisher-Hirschfelder-Taylor "atoms" indicates that steric interference between the methyl groups would prevent their occupying a *cis* position, but there is relatively little such interference in methyl disulfide. On the assumption that free rotation exists

TABLE II
DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES AT 30°

c_2	ϵ_{12}	v_{12}
Methyl disulfide		
0.001230	2.2747	1.15303
.002049	2.2796	1.15291
.002570	2.2821	1.15280
.003916	2.2886	1.15249
.006382	2.3019	1.15189
Ethyl disulfide		
0.000632	2.2704	1.15311
.001280	2.2736	1.15290
.001735	2.2755	1.15292
.002538	2.2804	1.15284
.003990	2.2878	1.15250
Propyl disulfide		
0.000926	2.2726	1.15324
.001546	2.2758	1.15306
.003213	2.2845	1.15282
.004499	2.2913	1.15247
.006119	2.3008	1.15221
Methyl trisulfide		
0.000949	2.2723	1.15292
.001660	2.2742	1.15255
.003113	2.2810	1.15178
.004725	2.2872	1.15093
.005506	2.2889	1.15075
Methyl trisulfide (redistilled)		
0.001180	2.2731	1.15274
.001683	2.2747	1.15255
.002910	2.2802	1.15186
.003669	2.2829	1.15148
.005941	2.2940	1.15027

TABLE III
EMPIRICAL CONSTANTS AND POLARIZATIONS AT 30°, REFRACTIONS AND DIPOLE MOMENTS

ϵ_1	α'	v_1	β'	P_{∞}	R_D	μ ($\times 10^{18}$)
Methyl disulfide						
2.2682	5.23	1.15337	-0.232	104.91	27.28	1.95 \pm 0.02
Ethyl disulfide						
2.2670	5.22	1.15323	-0.183	115.10	36.83	1.96 \pm 0.03
Propyl disulfide						
2.2677	5.24	1.15340	-0.195	124.72	46.08	1.96 \pm 0.01
Methyl trisulfide						
2.2681	4.10	1.15341	-0.527	91.86	35.96	1.65 \pm 0.03
Methyl trisulfide (redistilled)						
2.2678	4.20	1.15341	-0.529	93.33	35.96	1.67 \pm 0.02

in methyl disulfide, a moment of 1.44 is calculated for the $\text{CH}_3\text{-S}$ group by the use of Williams' formula⁸ and the value of 107° for the SSC angle indicated by the electron diffraction data of Stevenson and Beach.⁹ Such a value would lead to a calculated moment of 2.01 for the trisulfide on the basis of free rotation.¹⁰ Steric hindrance lowers

(5) Kushner and Smyth, *THIS JOURNAL*, **71**, 1401 (1949).

(6) Strecker, *Ber.*, **41**, 1106 (1908).

(7) Halverstadt and Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

(8) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, N. Y., 1931, p. 80.

(9) Stevenson and Beach, *THIS JOURNAL*, **60**, 2872 (1938).

(10) Smyth and Walls, *ibid.*, **54**, 2262 (1932).

the moment, since those configurations prevented by hindrance would have large moments.

It must be remarked that the observed low moment for methyl trisulfide does not exclude structure II as decisively as a high moment would have favored it. Whereas it is possible, in fact, to fix 2×10^{-18} as the upper limit for the moment of structure I if freedom of rotation exists, one can not determine the lower limit for structure II with equal certainty, since the actual polarity of the coordinate sulfur-sulfur bond involved in the latter formulation is not known, at least a certain amount of double bond character being possible in this bond.

The foregoing treatment has assumed the freedom of rotation around the S-S bonds normally associated with a single bond. If, as suggested by the electron diffraction results,³ the C-S bonds oscillate about mean positions approximately 106° out of the plane of the three sulfur atoms, a *cis* form with the two alkyl groups on the same side of the plane and a *trans* form with the alkyl groups on opposite sides of the plane should exist. The *cis* form would have a moment larger than the mean value calculated for the case of free rotation,

while the *trans* form would have a moment close to zero. A reasonable distribution of the molecules between the two configurations would give the observed moment. The observed dipole moment, therefore, does not rule out the existence of the molecules of the trisulfide in these two more or less fixed configurations. The dipole moment values do not decide unequivocally the structures of these polysulfides, but may be regarded as in accord with the other lines of evidence favoring an unbranched chain formulation.

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Summary

The dipole moments of methyl, ethyl and propyl disulfides, and of methyl trisulfide have been measured at 30° and found to be 1.95, 1.96, 1.96 and 1.66×10^{-18} respectively. The value for the trisulfide is consistent with an unbranched chain structure for that molecule.

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Absorption Spectra. VIII. The Infrared Spectra of Some Purines and Pyrimidines^{1,2}

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The purine and pyrimidine bases are organic compounds of considerable interest because they are components of nucleic acids and various enzymes, because they exert powerful physiological actions, and because they pose some interesting problems of structure. In connection with our work on infrared spectroscopy of compounds of biological systems,^{2,3,4} we have determined the spectra of a group of related pyrimidines and purines over the wave length region 2 to 15μ (670 to 5000 cm.^{-1}). The differences in the infrared spectra of such compounds are so marked that infrared absorption techniques should become important in the identification of this class of compounds, especially since many of their other physical properties such as melting point, solubility and ultraviolet absorption may fail to differentiate among various members of the class or between mixtures.

Drastic acid hydrolysis of yeast ribonucleic acid yields cytosine, uracil, adenine and guanine; and similar treatment of thymus deoxyribonucleic acid gives the same bases, except that thy-

mine is obtained in place of uracil.⁵ The products of such hydrolyses are soluble in aqueous solutions, but insoluble in organic solvents. This situation is satisfactory for ultraviolet absorption spectroscopy, but makes infrared work very difficult except by the use of the materials in the solid state. We have found that the high vacuum sublimation of purines and pyrimidines onto rock salt disks yields films which are generally suitable for infrared spectroscopic work.^{3,6,6a}

Pyrimidines from Nucleic Acids

The infrared spectra of cytosine (4-amino-2-

(5) Cf. Levene and Bass, "Nucleic Acids," Am. Chem. Soc. Monograph Series, New York, N. Y., 1931; Vischer and Chargaff, *J. Biol. Chem.*, **176**, 715 (1948); Chargaff, Vischer, Doniger, Green and Misani, *ibid.*, **177**, 405 (1949), for a summary of previous references.

(6) As a check against decomposition during sublimation, samples of the compounds before and after sublimation were submitted to spectral measurements in aqueous solution in the vicinity of their ultraviolet absorption maxima. The results of these measurements are shown in Table II. In general, with fairly pure compounds the position of the maximum ultraviolet absorption was unchanged by this treatment, although in some cases an increase in the extinction coefficient was noted in the sublimed material. This increased ultraviolet absorption of some of the sublimed samples is probably indicative of higher purity obtained through the sublimation procedure.

(6a) Since samples prepared in this manner may show molecular orientation (personal communication from Dr. C. D. West), it is conceivable possible that certain frequencies would be diminished in intensity or not be observed at all when viewed only along one direction with collimated unpolarized normally incident light.

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(1) Supported in part by funds from the Office of Naval Research.

(2) For the last paper in this series see Blout and Fields, *J. Biol. Chem.*, **178**, 335 (1949).

(3) Blout and Fields, *Science*, **107**, 252 (1948).

(4) Blout and Mellors, *ibid.*, **110**, 137 (1949).