

of 40–60%. IV, R = 4- and 5-thiazolyl,⁵ 2-phenyl-4-thiazolyl,* 2-chloro-4-thiazolyl,** 3-pyridyl, 3-quinolyl.⁸ All products had a strong IR absorption band in the region 1755–1770 cm^{-1} corresponding to the β -lactam system.

Paper chromatograms of all the penicillins were run in a butanol-ethanol-water (4:1:5) top layer system and were developed microbiologically.⁹ In all cases, only one zone corresponding to the penicillin was observed.

1. Bamberg, P., Ekström, B. and Sjöberg, B. *Acta Chem. Scand.* **21** (1967) 2210.
2. Frankel, M., Gertner, D., Wagner, D. and Zilkha, A. *J. Org. Chem.* **30** (1965) 1596.
3. U.S. Pat. 2,423,709.
4. Patterson, S. J. and Emery, W. B. *Analyst* **73** (1948) 207.
5. Mory, R. and Sohenkel, H. *Helv. Chim. Acta* **33** (1950) 405; Erlenmeyer, H. and Morel, Ch. J. *Ibid.* **28** (1945) 362.
6. Burger, A. and Ulliyot, G. E. *J. Org. Chem.* **12** (1947) 342.
7. Ganapathi, K. and Venkataraman, A. *Proc. Indian Acad. Sci.* **22** (1945) 362.
8. Jones, R. G., Soper, Q. F., Behrens, O. K. and Corse, J. W. *J. Am. Chem. Soc.* **70** (1948) 2343.
9. Batchelor, F. R., Doyle, F. P., Nayler, J. H. C. and Rolinson, G. N. *Nature* **183** (1959) 257.

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* 2-Phenylthiazolyl-4-acetic acid was prepared from ethyl γ -bromoacetoacetate⁶ and thiobenzamide according to a method given by Burger and Ulliyot.⁶

** 2-Chlorothiazolyl-4-acetic acid was prepared from ethyl 2-aminothiazolyl-5-acetate following a method of Ganapathi and Venkataraman.⁷

The Vibrational Spectra of Tetramethylene Sulphoxide

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We have recently studied the vibrational spectra of two 5-membered cyclic molecules, ethylene trithiocarbonate and ethylene thiourea, and concluded that these molecules were not planar.¹ Since we have previously been interested in the sulphoxides as electron donors to iodine,² it seemed natural to extend these studies to tetramethylene sulphoxide (TMSO). This molecule represents another 5-membered aliphatic ring with an heteroatom, and the structurally related molecule tetramethylene sulphone has previously been reported by Katon and Fearheller.³ A detailed vibrational analysis of dimethyl sulphoxide and the fully deuterated molecule has been carried out.⁴ Since TMSO consists of 14 atoms and therefore has 36 normal vibrations, no complete interpretation of the spectra is possible, but a tentative assignment of most of the fundamentals will be proposed.

Experimental. TMSO from Aldrich was shaken with PCl_5 and fractionated three times over barium oxide in a Vigreux column under reduced pressure. No impurity peaks (including water) could be detected in a gas chromatogram.

The infrared spectra were recorded with Beckman models IR-9 and IR-12 in the region 4000–240 cm^{-1} as a capillary and in sealed cells. No vapour spectrum could be obtained even with a 10 m path cell, but a spectrum of the solid was recorded at -78°C .

The Raman spectrum was recorded with a Cary model 81 spectrometer, using the 7 mm tube and the 4358 Å radiation. Semiquantitative polarization measurements were obtained by the standard method.

Results. The infrared and the Raman spectra of TMSO are shown in Fig. 1 and the observed frequencies are listed in Table 1. It appears that there are no obvious cases of Raman bands without infrared counterparts. Therefore, the planar model with C_{2v} symmetry can be excluded, since the 7 fundamentals of species A_2 should be Raman active (and depolarized)

Table 1. Infrared and Raman spectral data and tentative assignments of tetramethylene sulphoxide.

Infrared		Raman	Interpretation
Liquid	Solid -78°C		
3820 vw			
3320 w			
3284 vw		2974 m D	} CH stretch
2950 vs	2983 m	2955 vs P	
	2966 s	2923 vs P	
	2940 s	2906 w	
2913 m		2873 s	
2875 s	2876 m	2809 w	
2820 m	2820 w		
2610 w	2633 w		
2338 w			
2045 m	2010 w		
1904 m			} CH ₂ scissor
1512 s		1465 w	
1465 m	1462 m	1449 vs D	
1450 vs	1448 vs		
1425 w	1428 s	1416 vs D	
1414 vs	1410 s		
	1312 m		
1307 vs	1309 s	ca. 1320 w	
1275 s	1280 s		
1264 m	1261 m	1258 s P?	
1198 w	1195 w	1202 m D?	
	1155 m	1155 vw	CH ₂ wag
1151 s	1148 s	1139 m	CH ₂ twist
	1130 m		CH ₂ twist
1098 vs	1110 vs	1098 m P	CH ₂ twist
	1090 m		
ca. 1023 vvs.	ca. 1020 vvs	1030 vs P?	S=O stretch
992 m	990 s	996 w	CH ₂ rock
957 s	948 s	963 s D	CH ₂ rock
910 w	900 m	896 m P	CH ₂ rock
881 s	879 m	881 s P	ring stretch
781 m		786 w	ring stretch
737 m	743 m		
659 m	693 m	667 vs P	ring stretch
632 s	634 s	636 vs P	ring stretch
572 s	571 m		
542 vs	548 vs	536 m P	ring breath
	533 s		
443 s	442 m	446 w D?	ring bend
385 m	408 w		ring bend
344 vs	350 s	346 m D?	ring bend
324 vs	317 s	330 s D	S=O bend
ca. 240 s	ca. 238 s	250 w	ring bend

Abbreviations: s, strong; m, medium; w, weak; v, very; P, polarized and D, depolarized.

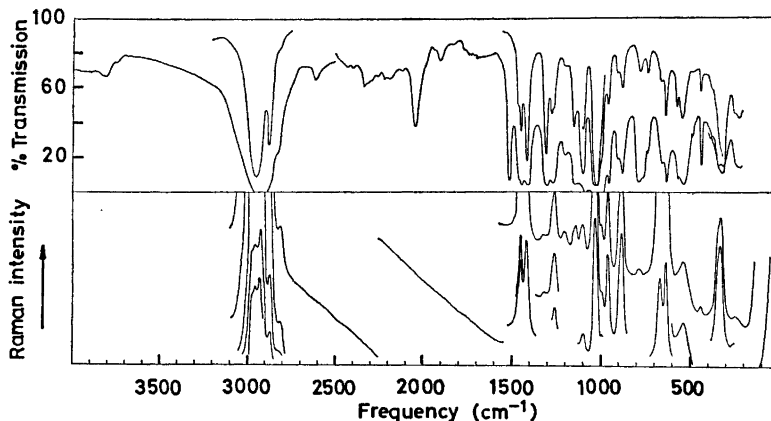


Fig. 1. The infrared (upper curve) and Raman (lower curve) spectra of liquid tetramethylene sulphoxide.

but infrared inactive. Other possibilities are a plane of symmetry (C_s), a two-fold axis (C_2) or no symmetry element (C_1). In the latter case all Raman bands should be polarized, with C_s or C_2 symmetry roughly half of the fundamentals should be polarized and the other half depolarized. Although various Raman bands appear depolarized, the C_1 symmetry cannot be ruled out, since depolarized Raman lines cannot be measured with certainty. However, it seems quite probable that TMSO might be a puckered ring with C_2 symmetry and the spectra can easily be interpreted on this basis.

The tentatively assigned fundamentals are listed in Table 1 and the descriptions should be considered as very approximate. No real distinction between the ring stretching and bending modes can be made and many of the skeletal frequencies are undoubtedly strongly coupled. Of the 36 fundamentals, the 8 CH stretching modes are expected around 3000 cm^{-1} and the remaining 28 modes below 1500 cm^{-1} . We have observed 22 Raman bands below 1500 cm^{-1} which all are believed to be fundamentals. Some of the Raman bands may be doublets, in other cases the fundamentals may only be observed in the infrared spectrum.

The infrared spectrum of the solid TMSO consisted in part by very sharp

peaks in which the liquid bands were split, probably caused by interactions with the lattice modes. The S=O stretching frequency around 1023 cm^{-1} is very intense in infrared and Raman, it is solvent sensitive⁵ and is "red shifted" on complex formation to iodine.³ In agreement with the data reported for the corresponding sulphone,³ no Raman bands were observed below 250 cm^{-1} although the far infrared spectra were not recorded. In the other 5-membered rings ethylene trithiocarbonate and ethylene thiourea, considerably lower bands were observed,¹ in agreement with the low bending modes expected for the heavy sulphur in these molecules.

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1. Klæboe, P. *Acta Chem. Scand.* **22** (1968). *In press.*
2. Grundnes, J. and Klæboe, P. *Trans. Faraday Soc.* **60** (1964) 1991; and earlier papers.
3. Katon, J. E. and Fairheller, W. R. *Spectrochim. Acta* **21** (1965) 199.
4. Horrocks, W. D. and Cotton, F. A. *Spectrochim. Acta* **17** (1961) 134.
5. Cairns, T., Eglinton, G. and Gibson, D. T. *Spectrochim. Acta* **20** (1964) 31.

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