

On the Structure of Gaseous Methyl Vinyl Sulphide

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Methyl vinyl ether has recently been shown by electron diffraction to exist as a mixture of two conformers; the most stable being the *syn* (or *cis*) form with the heavy atoms coplanar; in the less stable form the carbon atom in the methyl group lies outside the plane through the vinyl group.¹ Only a *syn* form has been found for methyl vinyl sulphide by microwave spectroscopy.² This investigation was initiated to determine whether this compound exists as a mixture of conformers similar to those found for methyl vinyl ether.

The electron-diffraction data were recorded at the Oslo apparatus;³ the nozzle temperature was 190–200°C. A modified molecular intensity curve ranging from $s = 1.75 \text{ \AA}^{-1}$ to $s = 44.0 \text{ \AA}^{-1}$ was obtained in the usual way.⁴

The experimental radial distribution (RD) curve⁴ is given in Fig. 1. The $C_1 \cdots C_4$ distance in a planar *syn* form should contribute slightly above 3.0 Å. Comparison with theoretical curves showed that a considerable amount of a conformer with a non-planar heavy atom skeleton must be present. The ratio between the conformers could not be determined very accurately because of high correlation between this ratio and other parameters, in particular the mean amplitudes of vibration for the $C_1 \cdots C_4$ distances in the two forms. Various refinement schemes gave somewhat different results, all being fairly close to the 33 % of the *syn* form expected for zero energy difference. The standard deviation is about 6 %.

The experimental and theoretical RD curves are compared in Fig. 1. It was assumed that the bond distances and bond angles were the same in the two conformations, and that there is no tilt of the methyl group.

The molecular parameters were refined by least-squares refinement on the intensity data. The results for the bond distances and the most important non-bonded distances, the corresponding mean amplitudes of vibration (u), and the bond angles are given in Table 1. The standard

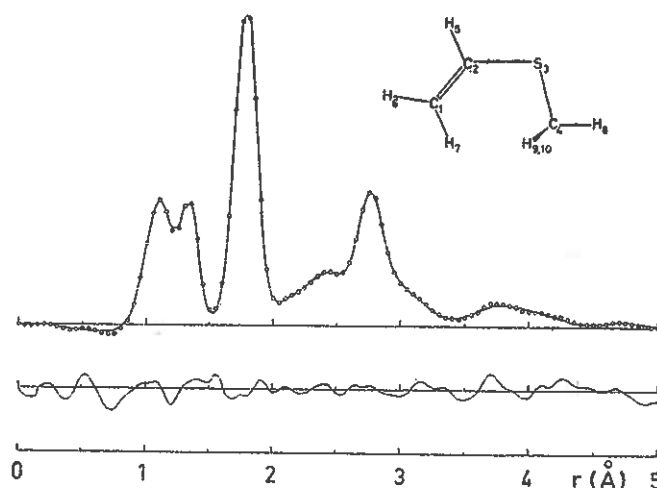


Fig. 1. Experimental (circles) and theoretical RD curves for methyl vinyl sulphide. (Artificial damping constant⁴ $k = 0.002 \text{ \AA}^2$.) The differences between experimental and theoretical curves multiplied by 5 are also shown.

Table 1. Distances, mean amplitudes of vibration, and bond angles in methyl vinyl sulphide. The standard deviations are given in parentheses.

	r (Å)	u (Å)
S—C ₂	1.748 (6)	0.046
S—C ₄	1.806 (6)	0.048
C=C	1.341 (2)	0.034 (2)
C ₁ —H, C ₂ —H	1.084 ^a	0.073
C ₄ —H	1.105 ^a	0.074
S...C	2.758 (5)	0.065 (2)
C ₂ ...C ₄	2.810 (13)	0.129 (17)
C ₁ ...C ₄ ^c	3.058 (16)	0.140 (48)
C ₁ ...C ₄ ^d	3.778 (29)	0.258 (37)
H ₁ ...H ₉ ^c	2.40	
degrees		
∠CSC	104.5 (0.7)	
∠CCS	125.9 (0.5)	
∠C ₂ C ₁ H	124.6 (2.3)	
∠C ₁ C ₂ H	117.7 (4.2)	
∠CSH	111.2 (1.5)	
∠(C ₂ —S) ^d	106.6 (3.2)	

^a The parameter was not refined at the same time as the other parameters in the table.

^b The difference between the u values was assumed.

^c Values for the *syn* conformer.

^d Values for the conformer with non-planar skeleton.

deviations are probably somewhat small since a diagonal weight matrix was used in the refinement.⁵ The uncertainty in the electron wave length is, however, included.

The structural parameters deviate somewhat from the values proposed by Penn and Curl.² The S—C₄ bond length is normal for an C(sp³)—S bond, 1.802 Å having been reported for dimethyl sulphide.⁶ As expected, the S—C₂ bond is somewhat shorter. The CSC angle is 5.6° larger than that in dimethyl sulphide. The torsional angle about the C₂—S bond in the conformer with a non-planar skeleton is slightly larger than that found in methyl vinyl ether.¹ However, the uncertainties are large in both cases, and the difference cannot be regarded as significant.

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