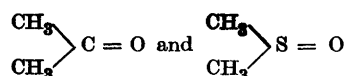# A Comparison between the Structures of Acetone and Methyl Sulphoxide

O. BASTIANSEN and H. VIERVOLL
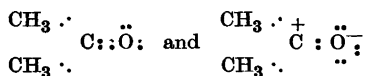
Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

Accoding to the classical theory of valency the two compounds acetone and methyl sulphoxide should have similar formulae

$$\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!\!\!> C = O \quad \text{and} \quad \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!\!\!> S = O$$

and a similar atomic arrangement might be expected in the two cases. The modern theory of valency, however, leads to a decisive difference between the two structures.

In order to explain the great dipole moment of the acetone molecule, Pauling has introduced the assumption of resonance between the two structures [1],

$$\begin{array}{c} CH_3 \cdot \\ CH_3 \cdot \end{array}\!\!\!\! C \!:\! \ddot{O}\!: \quad \text{and} \quad \begin{array}{c} CH_3 \cdot \cdot + \\ CH_3 \cdot \end{array}\!\!\!\! C : \ddot{O}\bar{\cdot}$$

the contribution of each of them to the normal state of the molecule being about 50 %. Considering the general rules for estimating the relative stabilities of different structures which occur in a resonating molecule *, the 50 % contribution seems rather surprising. The first structure for acetone has the adventage of 1) having the octet arrangement for the central carbon atom maintained, 2) having the largest number of bonds, and 3) having no formal charges. For both these structures, however, a plane arrangement of the bonds originating from the central carbon atom must be expected. In both cases the electron configuration of the central carbon atom is assumed to contain one »promoted» electron, leading to an sp^2-configuration. In the first structure

---

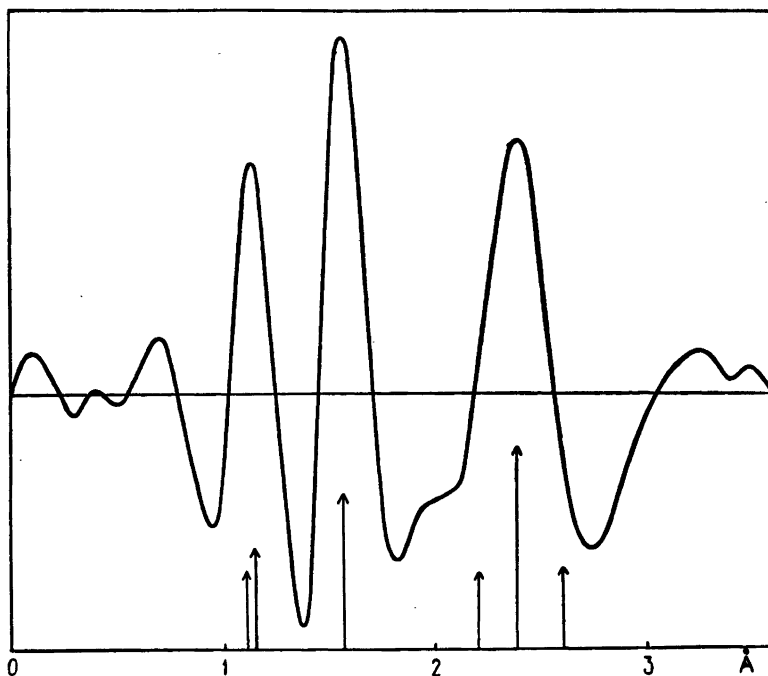* See for instance: Wheland, G. W., *The theory of resonance* (1944) pp. 15—17.

Fig. 1. Experimental $\dfrac{\sigma(r)}{r}$-curve for acetone.

the fourth electron of the central carbon atom is responsible for the additional π-bond, and in the second structure the fourth electron is given to the oxygen atom to complete its shell.

The most probable configuration for methyl sulphoxide by the light of modern theories is indicated by the formula:

$$CH_3$$
$$:\ddot{S}^+ : \ddot{O} :^-$$
$$CH_3$$
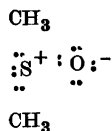
The bond between the sulphur atom and the oxygen atom is a dative covalent bond, *i. e.* both the electrons forming the bond originate from one atom, here the sulphur atom. The sulphur atom has a lone pair, *i. e.* it has in its valency shell an electron pair which does not take part in the formation of any bond.

The electron configuration of the sulphur atom in its ground state, omitting the closed shells, is s^2p^4. Here no promotion of an s-electron to a p-orbital is

to be expected. The two s-electrons can therefore not take part in the forma-
tion of bonds, but will form the lone pair. — We can now imagine that the
dative covalent sulphur-oxygen bond is formed in the following two steps:
1) The sulphur atom gives one of its electrons to the oxygen atom, resulting in
a positive charge on the sulphur atom and a negative charge on the oxygen
atom. 2) The formation of a usual two-electron bond takes place. From that
point of view the electron configuration of the sulphur atom responsible for
the bonds is p^3, i. e. the symmetry of the bonds should be trigonal pyramidal.
Such a pyramidal structure has been observed in the thionyl halides [2].

To demonstrate the difference between the structures of acetone and methyl
sulphoxide, these compounds have been studied by means of the electron
diffraction sector method [3]. Fig. 1 gives the experimental $\frac{\sigma(r)}{r}$-curve for acetone.
The line diagram indicates the position of the distances occuring in the acetone
molecule. Because of the uncertainty in the position of the hydrogen atoms
the O—H and the greatest C—H-distances are omitted. The contri-
bution of these distances to the $\frac{\sigma(r)}{r}$-curve is, however, small compared with the
contribution of the C—C and C—O distances. The experimental $\frac{\sigma(r)}{r}$-curve
leads to a plane structure. The atomic distances and the CCO angle are
given in Table 1.

Table 1. *Distances and angle occuring in the acetone molecule.*

C — H	1.09 Å	CCO	123° ± 3°
C — C	1.56 »		
C — O	1.14 »		

The value for the C—C distance is in good agreement with that calculated by
the visual method [4].

In Fig. 2 the upper curve, Exp., — is the experimental curve for methyl
sulphoxide. The curves A—F are theoretical curves for various structures of
the molecule, the S—H-distance and the greatest C—H-distances having been
omitted. The observed distances are listed in Table 2.

Table 2. *Distances occuring in the methyl sulphoxide molecule.*

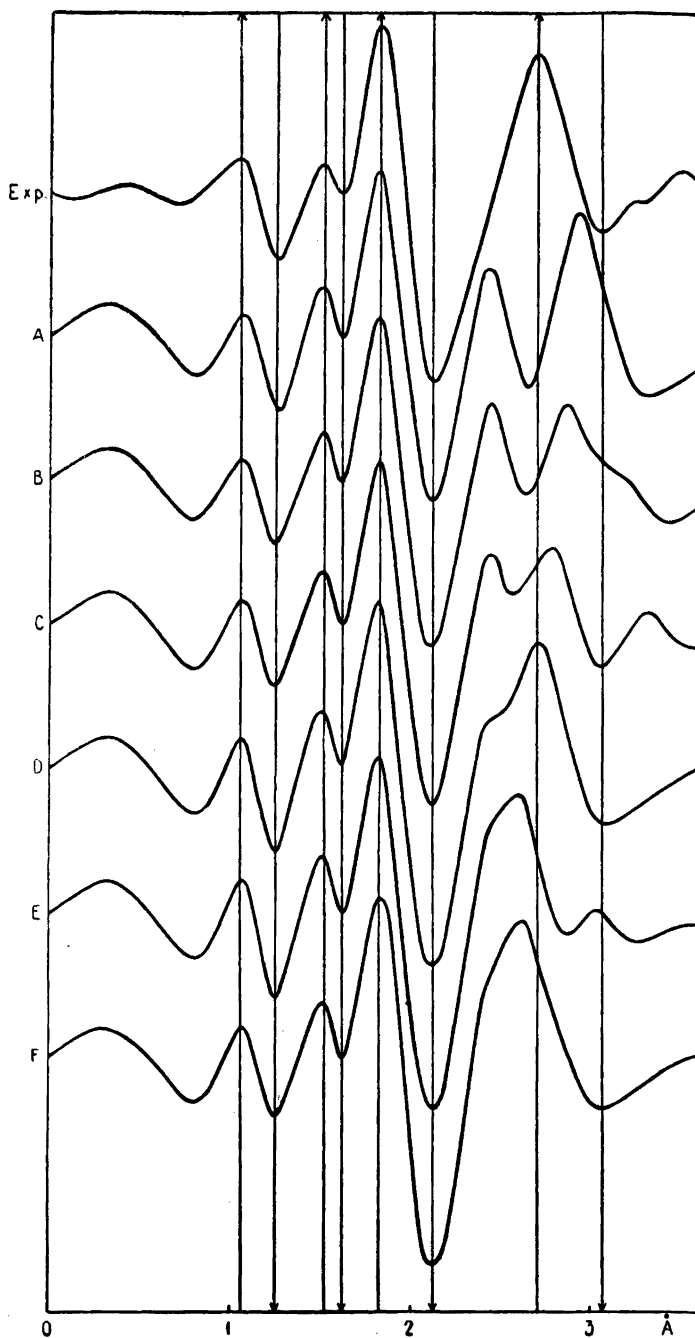|	
C — H	1.08 Å
C — S	1.82 »
S — O	1.47 »

Fig. 2. The upper curve is the experimental $\frac{\sigma(r)}{r}$-curve for methyl sulphoxide. The curves A—F are theoretical $\frac{\sigma(r)}{r}$-curves for methyl sulphoxide based on various values for the CSC- and CSO-angles.

These distances are used in all the theoretical curves. The angles for the different models are listed in Table 3.

Table 3. CSC- and CSO-angles corresponding to the curves A—F in Fig. 2. The values in the last column correspond to the model of methyl sulphoxide which gives the best agreement with the experiments.

	A	B	C	D	E	F	
CSC	110°	120°	130°	100°	110°	100°	100° ± 5°
CSO	125°	120°	115°	110°	105°	105°	107° ± 5°

A comparison of the theoretical $\frac{\sigma(r)}{r}$-curves and the experimental one leads to exclusion of the plane structures A, B and C. The structures D and F seem to give the best agreement with the experimental $\frac{\sigma(r)}{r}$-curve. A more accurate determination of the angles is not possible in this case; the values tabulated in the last column of Table 3 will, however, within the limits indicated give the correct magnitude.

SUMMARY

A comparison of the structures of acetone and methyl sulphoxide has been carried out by the aid of the electron diffraction sector method. The investigation leads to a plane structure for the acetone molecule and a pyramidal structure for the methyl sulphoxide molecule.

LITERATURE

1. Pauling, L. *The nature of the chemical bond* (1939) p. 75.
2. Palmer, K. J. *J. Am. Chem. Soc.* **60** (1938) 2360.
3. Viervoll, H. *Acta Chem. Scand.* **1** (1947) 120; Hassel, O., and Viervoll, H. *Acta Chem. Scand.* **1** (1947) 149.
4. Hengstenberg, J., and Bru, L. *Anales soc. espan. quim.* **30** (1932) 341.