

# The Stereochemistry of Molecules Containing the C=C=N Group: The Crystal Structure of *N*-methyl-2:2-dimethylsulphonylvinyldineamine

BY P. J. WHEATLEY

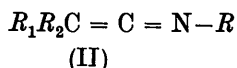
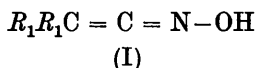
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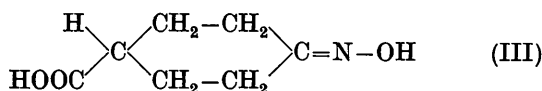
A three-dimensional structure analysis of a compound containing the group =C=C=N-R is described. All four atoms in this chain are shown, rather surprisingly, to be linear. The bond number of the central carbon atom in the multiply-linked chain is shown to be very high, being joined on the one side to a nitrogen atom by what appears, from the length of 1.154 Å, to be a triple bond, and on the other side to a carbon atom by what seems, from the length of 1.342 Å, to be a double bond. The occurrence of this 'pentavalent' carbon atom suggests that, in condensed systems of this type, bond length is not a satisfactory criterion of bond order.

## Introduction

The stereochemistry of a nitrogen atom forming one double and one single bond has been regarded as well established for some time (see e.g. Sidgwick, 1937; Wells, 1950), and X-ray investigations (e.g. Bierlein & Lingafelter, 1951) have confirmed the conclusion of classical stereochemistry that in oximes the single and double bonds to the nitrogen atom are not collinear. There is no direct evidence, however, regarding the configuration of compounds of the type (I) or more generally of



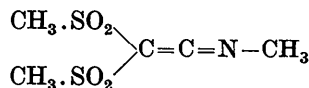
the type (II), although an investigation of (I) was contemplated by Mills & Bain (1910), but, because of experimental difficulties, rejected in favour of cyclohexanone-4-carboxylic acid (III).



These authors succeeded in resolving salts of this acid into enantiomorphs and thus demonstrated the non-linearity of the nitrogen bonds. This result has been taken to have more general validity on the assumption that the saturated ring in (III) is stereochemically equivalent to a double bond, but the results reported in the present paper suggest that this is not the case; a detailed X-ray crystal analysis of  $(CH_3SO_2)_2C=C=N-CH_3$  shows that the grouping  $C=C=N-C$  is strictly linear.

## Experimental

A specimen of *N*-methyl-2:2-dimethylsulphonylvinyldineamine (Dijkstra & Backer, 1952)



was recrystallized from ethyl acetate and formed excellent crystals. The unit-cell dimensions, measured from Straumanis photographs, are

$$\begin{aligned} a &= 12.082 \pm 0.005 \text{ \AA} \\ b &= 8.656 \pm 0.005 \text{ \AA} \\ c &= 8.627 \pm 0.005 \text{ \AA} \end{aligned}$$

The density, determined by flotation, is 1.58 g.cm.<sup>-3</sup>, which may be compared with a calculated value of 1.55 g.cm.<sup>-3</sup>, assuming four molecules in the unit cell. The systematic absences of  $(0kl)$  for  $k$  odd,  $(h0l)$  for  $l$  odd and  $(h+k0)$  for  $(h+k)$  odd show that the space group is *Pbcn*. The space group, together with the fact that there are only four molecules in the unit cell, demands that the molecule possesses either a centre of symmetry or a twofold axis. The latter is the only alternative possible, so that, unless a statistical distribution of less symmetrical molecules obtains, the linearity of  $C=C=N-C$  is immediately established.

In order to establish the lengths of the bonds in this unusual system, a three-dimensional analysis was performed. Cu  $K\alpha$  radiation and a multiple-film technique were employed in taking Weissenberg photographs about the three principal axes. The relative intensities of the reflexions were estimated visually. A total of 711 planes had non-zero structure amplitudes, and the present investigation is based on these values. The observed structure factors were placed on an absolute scale by a method which avoids direct correlation between different exposures, and which is very convenient to use when complete sets of calculated structure factors are readily available. Each layer line is treated quite independently, and values of the calculated structure factors obtained from the coordinates of a reliable trial structure are placed opposite each observed value. The observed structure factors (for

each layer line) are then multiplied by a constant so as to make  $\Sigma F_o = \Sigma F_c$ . This yields up to a maximum of three independent values of  $F_o$  for each plane, and an arithmetic mean is taken of these values. This method can be used as a successive approximation, repeating the whole process after each three-dimensional refinement, but in practice it has been found unnecessary to do this. The technique may have to be used with caution if a whole layer line, for reasons of symmetry, is systematically weak, when there may be a danger of obscuring the very features that are being sought; but in general it seems faster and more accurate than a method involving correlation through a small number of common planes.

### The X-ray structure analysis

The structure was first investigated using the ( $h0l$ ) projection. A Patterson synthesis readily gave the position of the single sulphur atom in the asymmetric unit, and a Fourier synthesis was performed with the signs given by the sulphur atom for the planes with  $h$  odd, and by the chain atoms for the planes with  $h$  even. The resulting electron-density map seemed satisfactory, but the model of the molecule was assumed to have a plane of symmetry and it was found that refinement would not occur, the lowest  $R$  factor obtained being 0.33. A model was then chosen in which the methylsulphonyl group was rotated round the bond joining the sulphur atom to the chain, which has the effect of moving the oxygen atoms in the two halves of the molecule as far apart as possible, and the  $R$  factor immediately dropped to 0.21. A difference synthesis was then carried out, the final  $R$  factor being 0.15.

The ( $hk0$ ) projection was next solved by means of a Patterson synthesis to obtain the  $y$  coordinate of the sulphur atom, the rest of the  $y$  coordinates being derived from the assumed model. A single Fourier synthesis, followed by a difference synthesis, sufficed to reduce  $R$  to 0.14. A temperature factor of  $B=3.4 \text{ \AA}^2$ , derived from a  $\log (F_o/F_c) v. \sin^2 \theta$  plot, was applied to the scattering-factor curves (Viervoll & Ögrim, 1949) for both projections. The projections yielded the coordinates given in Table 1 and the bond lengths in

Table 1. Atomic coordinates derived from projections

Atom	$x/a$	$y/b$	$z/c$
S	0.118	0.331	0.188
O <sub>1</sub>	0.083	0.210	0.098
O <sub>2</sub>	0.187	0.443	0.123
C <sub>1</sub>	0.180	0.252	0.360
C <sub>2</sub>	0	0.420	0.25
C <sub>3</sub>	0	0.575	0.25
C <sub>4</sub>	0	0.882	0.25
N <sub>1</sub>	0	0.714	0.25

Table 2. The labelling of the atoms will be found in Fig. 3.

Table 2. Bond lengths derived from projections

Bond Length (Å)		Bond Length (Å)	
SO <sub>1</sub>	1.371	C <sub>2</sub> C <sub>3</sub>	1.342
SO <sub>2</sub>	1.396	C <sub>3</sub> N <sub>1</sub>	1.203
SC <sub>1</sub>	1.798	N <sub>1</sub> C <sub>4</sub>	1.454
SC <sub>2</sub>	1.706		

Since it was proposed to perform the three-dimensional refinement on the electronic computer at Manchester University\* it was deemed unnecessary to carry these projections any further. Instead, a complete set of structure factors was calculated using the coordinates listed in Table 1 and the temperature factor of  $B=3.4 \text{ \AA}^2$ . The observed structure factors were placed on an absolute scale by the method described above, and an  $R$  factor of 0.146 was obtained for the 711 planes. A  $\log (F_o/F_c) v. \sin^2 \theta$  plot showed that a mean temperature factor of  $4.0 \text{ \AA}^2$  was more appropriate for the complete set of structure factors, and when this was applied, with a corresponding change in scale factor, the  $R$  factor rose to 0.159. A differential synthesis was now computed at all the atomic peaks, using both observed and calculated structure factors and a new set of coordinates, corrected for termination of the series effects (Booth, 1948), was obtained. The peak heights and curvatures suggested that an overall temperature factor was not a very good approximation in the present case, and it was decided to use different, but still isotropic, temperature factors for the different atoms. The new values of  $B$  were obtained partly by estimation and partly from the tables recently given by Higgs (1953), and are shown in Table 3. It is not

Table 3. Temperature factors used in the final refinement

Atom	$B (\text{Å}^2)$	Atom	$B (\text{Å}^2)$
S	3.7	C <sub>2</sub>	4.0
O <sub>1</sub>	5.0	C <sub>3</sub>	4.0
O <sub>2</sub>	5.0	C <sub>4</sub>	4.6
C <sub>1</sub>	4.6	N <sub>1</sub>	5.0

suggested that these  $B$  values are a true reflexion of the different amplitudes of vibration, but they are probably nearer the truth than a mean value of  $B$ . There can be no doubt that further changes in these values, in particular the introduction of anisotropic temperature factors, would produce better agreement between the observed and calculated densities and curvatures, and hence lower the  $R$  factor.

With the new scattering factors and the new coordinates, a further refinement was carried out. A set of structure factors, observed and calculated differential syntheses, and a final set of structure factors were calculated. Every calculation was repeated twice and checked within the machine, a third (and subsequent) calculation being performed if the check failed. This

\* The programmes used for these computations were modifications of those described by Ahmed & Cruickshank (1953).

whole operation, including solving the matrices required to obtain the final corrected coordinates, and including printing out the final set of structure factors, took 132 min.

These calculations resulted in the final coordinates given in Table 4 and the molecular dimensions given in Table 5 and shown in Fig. 3. The final peak heights and curvatures are given in Tables 6 and 7. The final *R* factor was 0.111. Figs. 1 and 2 show the arrangement of the molecules in the unit cell. The closest distances of approach between non-bonded molecules in the same molecule are: S...S, 3.03; O...O,

Table 4. Final atomic coordinates

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S	0.11748	0.33188	0.18891
O <sub>1</sub>	0.08402	0.20207	0.09675
O <sub>2</sub>	0.18934	0.44437	0.12071
C <sub>1</sub>	0.18192	0.25616	0.35678
C <sub>2</sub>	0	0.42763	0.25
C <sub>3</sub>	0	0.58266	0.25
C <sub>4</sub>	0	0.88066	0.25
N <sub>1</sub>	0	0.71597	0.25

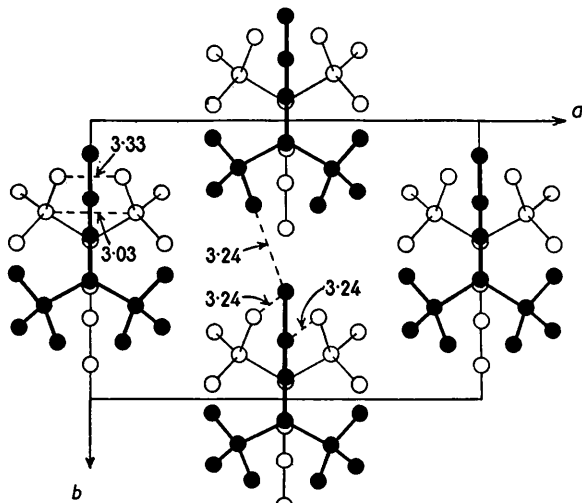


Fig. 1. Projection on (001). Open circles show the molecules with their chain atoms at  $z = \frac{1}{4}$ , and full circles those at  $z = \frac{3}{4}$ .

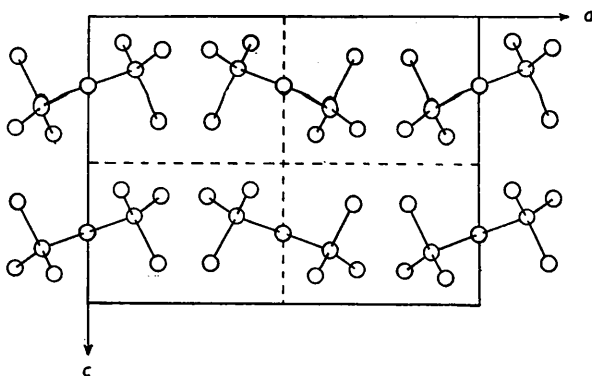


Fig. 2. Projection on (010).

Table 5. Final molecular dimensions

Bond	Length (Å)	Angle (°)	(°)
SO <sub>1</sub>	1.435	SC <sub>2</sub> S'	122.6
SO <sub>2</sub>	1.431	C <sub>1</sub> SC <sub>2</sub>	106.8
SC <sub>1</sub>	1.770	O <sub>1</sub> SO <sub>2</sub>	118.4
SC <sub>2</sub>	1.726	O <sub>1</sub> SC <sub>2</sub>	108.3
C <sub>2</sub> C <sub>3</sub>	1.342	O <sub>2</sub> SC <sub>1</sub>	108.7
C <sub>3</sub> N <sub>1</sub>	1.154	O <sub>1</sub> SC <sub>1</sub>	106.7
N <sub>1</sub> C <sub>4</sub>	1.426	O <sub>2</sub> SC <sub>2</sub>	107.3

Table 6. Final peak heights

Atom	$\rho_o$ (e.Å <sup>-3</sup> )	$\rho_c$ (e.Å <sup>-3</sup> )	$\rho_o/\rho_c$
S	28.18	29.05	0.970
O <sub>1</sub>	9.16	9.17	0.999
O <sub>2</sub>	8.53	9.22	0.925
C <sub>1</sub>	5.83	6.05	0.964
C <sub>2</sub>	6.95	6.93	1.003
C <sub>3</sub>	7.53	7.62	0.988
C <sub>4</sub>	5.50	6.20	0.887
N <sub>1</sub>	7.17	7.69	0.932

Table 7. Final mean curvatures

Atom	$-A_o$ (e.Å <sup>-5</sup> )	$-A_c$ (e.Å <sup>-5</sup> )	$A_o/A_c$
S	264.1	268.9	0.982
O <sub>1</sub>	67.5	66.1	1.021
O <sub>2</sub>	61.1	66.7	0.916
C <sub>1</sub>	42.6	48.1	0.885
C <sub>2</sub>	56.5	56.5	1.000
C <sub>3</sub>	67.3	68.1	0.989
C <sub>4</sub>	42.3	50.4	0.839
N <sub>1</sub>	56.9	60.3	0.943

3.33 Å, and between non-bonded atoms in adjacent molecules: C...O, 3.24; N...O, 3.24 Å.

### The accuracy of the analysis

An estimation of the accuracy of the analysis was made in the manner described by Cruickshank (1949), due allowance being made for the atoms in special positions (Cruickshank & Rollett, 1953). The positional deviations of the atoms are shown in Table 8, together with the r.m.s. values, the latter yielding the standard deviations of the bonds shown in Table 9. Using the

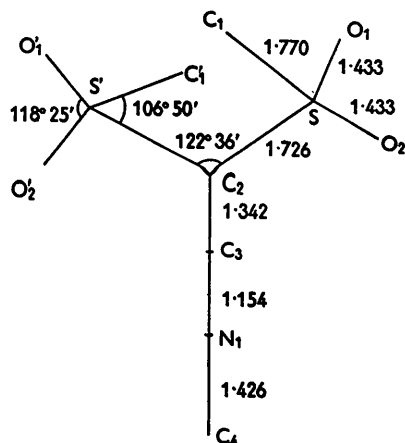


Fig. 3. Final dimensions of the molecule.

Table 8. *Positional deviations of the atoms*

Atom	(x) (Å)	(y) (Å)	(z) (Å)	R.m.s.
S	0.0014	0.0013	0.0015	0.0014
O <sub>1</sub>	0.0053	0.0054	0.0055	0.0054
O <sub>2</sub>	0.0056	0.0061	0.0063	0.0060
C <sub>1</sub>	0.0089	0.0077	0.0091	0.0086
C <sub>2</sub>	—	0.0066	—	0.0066
C <sub>3</sub>	—	0.0051	—	0.0051
C <sub>4</sub>	—	0.0067	—	0.0067
N <sub>1</sub>	—	0.0056	—	0.0056

Table 9. *Standard deviation of the bonds*

Bond	Deviation (Å)	Bond	Deviation (Å)
SC <sub>1</sub>	0.0087	C <sub>2</sub> C <sub>3</sub>	0.0083
SO <sub>1</sub>	0.0056	C <sub>3</sub> N <sub>1</sub>	0.0076
SO <sub>2</sub>	0.0062	C <sub>4</sub> N <sub>1</sub>	0.0087
SC <sub>2</sub>	0.0067		

customary significance levels, and adopting the notation used previously (Wheatley, 1953), it may be concluded from Table 9 that:

- (1) the bond SC<sub>1</sub> is shorter than a normal single bond of 1.80 Å ( $\Delta/\sigma = 3.4$ );
- (2) the bond SC<sub>2</sub> is considerably shorter than a normal single bond ( $\Delta/\sigma = 11.0$ );
- (3) the SO bonds may be considered equal with a length of 1.433 Å, and do not differ from a normal value (Jeffrey, 1951) of 1.44 Å ( $\Delta/\sigma = 1.2$ );
- (4) the bond C<sub>2</sub>C<sub>3</sub> does not differ from the double-bond distance of 1.34 Å ( $\Delta/\sigma = 0.2$ );
- (5) the bond C<sub>3</sub>N<sub>1</sub> does not differ from the CN distance of 1.157 Å (Herzberg, 1945; Gordy, 1948) found in HCN ( $\Delta/\sigma = 0.4$ ), and hence has the length of a CN triple bond;
- (6) the N<sub>1</sub>C<sub>4</sub> distance is shorter than the normal single-bond distance (Cox & Jeffrey, 1951) of 1.43 Å ( $\Delta/\sigma = 6.2$ ).

The standard deviation of the angles in the methylsulphonyl group, calculated from the formula of Cruickshank & Robertson (1953), are small, since all the angles involve at least one S atom, and vary from 0.33° to 0.37°. The standard deviation of the angles will be taken as 0.4°, and it may be concluded from this figure that:

- (1) the angle SC<sub>2</sub>S' is larger than 120° ( $\Delta/\sigma = 6.5$ );
- (2) the angle C<sub>1</sub>SC<sub>2</sub> is less than the tetrahedral angle ( $\Delta/\sigma = 6.6$ );
- (3) the angle O<sub>1</sub>SO<sub>2</sub> is considerably greater than the tetrahedral angle ( $\Delta/\sigma = 22.4$ );
- (4) the four OSC angles are not all equal. The pair of angles O<sub>1</sub>SC<sub>2</sub> and O<sub>2</sub>SC<sub>1</sub> do not differ from each other significantly, nor from the tetrahedral angle, but they are greater than the pair O<sub>1</sub>SC<sub>1</sub> and O<sub>2</sub>SC<sub>2</sub>, which are also significantly less than the tetrahedral angle.

The standard deviation of the electron density has the value 0.159 e.Å<sup>-3</sup> for general positions, and 0.174 e.Å<sup>-3</sup> for positions on the twofold axis.

## Discussion of the structure

The bond lengths in the methylsulphonyl group are in good agreement with predicted and with previous experimental values. There is a slight shortening of the SC<sub>1</sub> bond, presumably due to hyperconjugation of the methyl with the sulphone group. The two SO bonds agree well with each other and with the expected value. The bond SC<sub>2</sub> is considerably shorter than a single bond, principally owing to resonance of the sulphone group with the multiply-linked chain. The angles differ quite considerably from those of a regular tetrahedron, the most noticeable feature being the large value of the O<sub>1</sub>SO<sub>2</sub> angle. The angle between the methylsulphonyl group, SC<sub>2</sub>S', is greater than 120°, and this may be due to repulsion between the S atom, or to hybridisation changes in the atom C<sub>2</sub>.

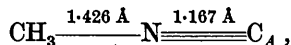
When we consider the chain atoms, the position is by no means so well-defined. There can be no doubt that the chain is strictly linear. Space-group considerations might perhaps be satisfied by a statistical distribution of bent chains, or by molecules in which the end methyl group is precessing. However, there is no significant difference between the peak heights of the two methyl carbon atoms, which is strong evidence that the atom C<sub>4</sub> remains in the chain. Furthermore it is doubtful whether an *R* value as low as 0.11 could be obtained if the space group demands were not rigorously observed.

It is difficult to select any molecules which can be compared with the present case, the only ones that occur being C<sub>3</sub>H<sub>4</sub> (allene) (Eyster, 1938), HNCO (Jones, Schoolery, Schulman & Yost, 1950), HNCS (Jones & Badger, 1950; Reid, 1950), CH<sub>3</sub>N<sub>3</sub> (Pauling & Brockway, 1937) and HN<sub>3</sub> (Schomaker & Spurr, 1942). Allene has the correct number of electrons to satisfy the normal valencies of the atoms, all the electrons being shared, and consequently the central carbon atom forms two double bonds of normal length. The other four molecules, which each have a chain of atoms joined by multiple links, are all non-linear, in marked contradistinction to the present case. To keep the atom C<sub>4</sub> in the chain we would expect the bond C<sub>3</sub>N<sub>1</sub> to be short, and accordingly we find that N<sub>1</sub> and C<sub>3</sub> are only 1.154 Å apart, and hence are joined by a bond as short as the normal triple bond. However, we also find that C<sub>2</sub> and C<sub>3</sub> are joined by what appears from its length to be a pure double bond, and it must be concluded that, if customary bond-order/bond-length relations are observed, the atom C<sub>3</sub> is penta-valent.

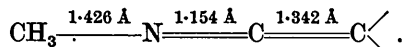
A rather similar state of affairs occurs in chains of atoms having adjacent single and triple bonds (e.g. Jeffrey & Rollett, 1952; Hannan & Collin, 1953), when the triple bonds adopt the standard values, whereas the single bonds are considerably shortened. However, the bond number of the carbon atoms does not rise above 4.6 on the Pauling (1940) scale. It is well-known that order/length relations become less

certain for bonds of high order, as small changes in length are associated with considerable changes in order. It is also agreed that order-length relations hold better for aromatic than for aliphatic compounds. The present example provides a most convincing case that these effects are incompletely understood.

To emphasise the present peculiarity, this compound demands that in methyl isocyanide (Gordy, 1948), which has the following bond lengths



the atom  $\text{C}_A$  can form yet a further double bond, the only effect being, if anything, a slight shortening of the bond  $\text{NC}_A$ :



It seems unwise to speculate on the nature of the bonding within the chain of this molecule until comparable results are available for other molecules, or until a theoretical study has been made of similar systems. The present set of results seems to be unique, one of the more noticeable features being the compactness of the whole molecule.

Further work is being carried out on similar compounds, in particular on molecules which possess no symmetry elements. It is hoped to present a more detailed discussion of the bonding when these investigations are completed.

I would like to offer my thanks to Prof. E. G. Cox, who suggested this problem and who has taken a keen interest in the progress of this work; to Dr R. Dijkstra and Prof. H. J. Backer for preparing and donating the sample; and to the Manchester Computing Laboratory staff for the use of the computer.

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