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The Stereochemistry of Molecules Containing the C=C=N Group. II. The Crystal Structure of *N*-methyl-2-methylsulphonyl-2-phenylsulphonylvinylidineamine

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A three-dimensional analysis of a second compound containing the group C=C=N−*R* is described. Crystals of *N*-methyl-2-methylsulphonyl-2-phenylsulphonylvinylidineamine are monoclinic $P2_1/a$ with $a = 15{\cdot}248$, $b = 13{\cdot}030$, $c = 10{\cdot}660$ Å and $\beta = 144° 27'$. The results confirm that the vinylidineamine group is linear, and the abnormal bond lengths are corroborated. An attempt is made to account qualitatively for the linearity of this group, and it is suggested that two factors are operative. The presence of electronegative groups on the methylene carbon atom, which are essential for the stability of vinylidineamines, will tend to straighten the chain, and hyperconjugation between the group *R* and the multiply-linked chain will have the same effect. It is possible that the relative importance of these two factors may be investigated experimentally by changing *R*.

Introduction

In Part I (Wheatley, 1954) it was shown, by an X-ray analysis of the crystal structure of *N*-methyl-2:2-dimethylsulphonylvinylidineamine (DMV), that the single and double bonds to a nitrogen atom are not necessarily collinear. However, DMV is required by the space-group symmetry to have a twofold axis in the crystal, and there remained the possibility that the collinearity of the single and double bonds arose as a result of the more efficient packing that might be attained if the atoms were forced into collinearity. Furthermore, the bond lengths in the grouping C=C=N showed some unusual features, and confirmation of these lengths seemed desirable. For these reasons an X-ray analysis of the asymmetrical molecule *N*-methyl-2-methylsulphonyl-2-phenylsulphonylvinylidineamine (MPV) has been carried out.

Experimental

MPV (Dijkstra & Backer, 1952)

$$\begin{matrix} CH_3SO_2 \\ C_6H_5SO_2 \end{matrix}\!\!\diagdown\!\!\diagup C=C=N-CH_3$$

was recrystallized from toluene. The cell dimensions were determined by the Straumanis method with the following results:

$a = 9{\cdot}035 \pm 0{\cdot}005$, $b = 13{\cdot}030 \pm 0{\cdot}005$, $c = 10{\cdot}660 \pm 0{\cdot}005$ Å, $\beta = 101° 9'$.

The calculated density is 1·474 g.cm.$^{-3}$, if it is assumed that there are four molecules in the unit cell. This may be compared with the value of 1·479 g.cm.$^{-3}$ obtained by flotation. The systematic absences of $(0k0)$ for k odd and $(h0l)$ for $(h+l)$ odd show that the most probable space group is $P2_1/n$. For convenience the refinement of the structure was performed in the space group $P2_1/a$, and the cell constants are then:

$a = 15{\cdot}248$, $b = 13{\cdot}030$, $c = 10{\cdot}660$ Å, $\beta = 144° 27'$.

All the results are given in terms of these axes.

Cu $K\alpha$ radiation and the multiple-film technique were used to take photographs round the three principal axes. A total of 2052 independent reflexions were observed, and their relative intensities were estimated visually by comparison with a standard scale. The different sets of photographs were reduced to the same relative scale by the method described in Part I.

The X-ray structure analysis

Attempts to solve the structure from the three two-dimensional Patterson syntheses failed. A Harker section at $y = \frac{1}{2}$ was calculated with all the observed intensities but, although the sulphur atoms were correctly located, a full trial structure could not be obtained. Consequently, the full three-dimensional Patterson function was calculated on the electronic computer at Manchester University. In order to sharpen the Patterson peaks, each intensity was multiplied by a factor $\exp(4 \sin^2\theta)$ and for Cu $K\alpha$ radiation this factor is sufficient to reduce the net atomic temperature factors to about zero. The net temperature factor for the sulphur atoms was close to -1 Å^2, and the sharpening thus served to enhance the predominance of the S–S and S–X vectors, where X is C, N or O.

It proved possible to obtain the coordinates for all 17 atoms in MPV and to assign the 128 general and special vectors of the type S–S and S–X which appear in the asymmetric unit to some 96 peaks. The coordinates were confirmed by picking up several fourfold O–O and N–O vectors and the sixfold vector between two phenyl groups related by a centre of symmetry. The dimensions of the molecule afforded by DMV

served as a further check on the structure, but these dimensions were a convenience rather than a necessity. In particular, they served to restrict any set of atomic coordinates to a single molecule.

The atomic coordinates were refined as far as possible from the Patterson function by locating vector peaks more precisely and, where necessary, making some estimate of peak interactions. The coordinates of any X atom were determined, in general, by the coordinates of eight S–X vectors. If the coordinates of vector peaks are subject to purely random errors, the accuracy of the atomic coordinates derived from the several vector peaks will be greater than the accuracy of the coordinates of any one vector peak. There was in fact no evidence of systematic shifts, and the scatter of the vector coordinates suggested an error in the coordinates of the X atoms of about 0·07 Å. This was confirmed by the scatter of sulphur coordinates from individual sets of S–X vectors. The sulphur coordinates obtained from the S–S vectors were significantly more accurate than those from the S–X vectors: their estimated accuracy was 0·02 Å. These figures were confirmed by the shifts obtained from the subsequent refinement of the structure.

The thermal parameters for MPV were chosen to be similar to those for DMV and were shown to be consistent with the peak heights in the Patterson function. A set of three-dimensional structure factors was calculated with the initial coordinates and temperature factors. The scattering factors used were those due to Hoerni & Ibers (1954), with the exception of the sulphur atom for which the figures of Viervoll & Ögrim (1949) were employed. The initial R factor was 0·21.

The structure was refined in $P2_1/a$ by three successive cycles on the electronic computer. Programmes devised by Ahmed & Cruickshank (1953) and Miss D. E. Pilling were used. The maximum shifts in the x, y and z coordinates of any atom after the third cycle were 0·0099, 0·0125 and 0·0196 Å respectively, and the average shifts were 0·0052, 0·0038 and 0·0060 Å. The scale factor was chosen so as to make $\Sigma|F_o| = \Sigma|F_c|$, and the individual isotropic temperature factors were selected so as to make the differences between the three observed and calculated principal curvatures have at least one positive and one negative sign. The final values of the coordinates and the temperature factors are given in Table 1. The bond lengths

Table 2. *Bond angles*

S_1–C_2–S_2	122·4°	C_1–S_1–O_1	107·8°
		C_1–S_1–O_2	107·4
S_1–C_2–C_3	118·9	C_2–S_1–O_1	107·1
S_2–C_2–C_3	118·5	C_2–S_1–O_2	107·6
		C_5–S_2–O_3	107·5
C_2–C_3–N_1	177·0	C_5–S_2–O_4	107·1
		C_2–S_2–O_3	105·8
C_3–N_1–C_4	170·6	C_2–S_2–O_4	107·9
O_1–S_1–O_2	119·6	C_5–C_6–C_7	119·1
O_3–S_2–O_4	120·7	C_6–C_7–C_8	118·6
		C_7–C_8–C_9	120·4
C_1–S_1–C_2	106·8	C_8–C_9–C_{10}	119·9
C_5–S_2–C_2	107·2	C_9–C_{10}–C_5	118·3
		C_{10}–C_5–C_6	122·7
S_2–C_5–S_6	119·1		
S_2–C_5–S_{10}	118·2		

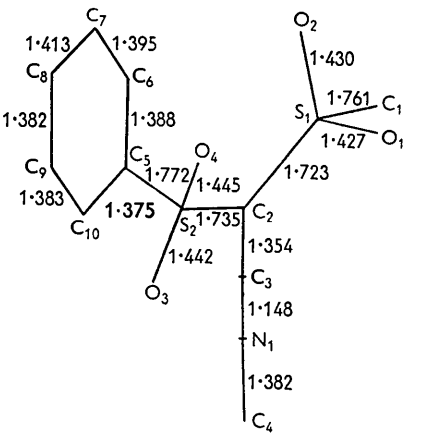

Fig. 1. Bond lengths and labelling of the atoms in MPV. The molecule is drawn as it appears when projected on to (100).

Table 1. *Final coordinates and temperature factors*

	x/a	y/b	z/c	B (Å²)
S_1	0·0159	0·0430	−0·2138	3·65
S_2	−0·2343	−0·1128	0·4602	3·80
O_1	0·0864	0·1180	−0·2097	5·30
O_2	0·1012	−0·0432	−0·0714	4·70
O_3	−0·3689	−0·1159	0·2277	5·30
O_4	−0·2439	−0·1120	−0·4156	5·30
N_1	−0·2276	0·0958	0·2351	5·50
C_1	−0·0552	0·1065	−0·1632	5·60
C_2	−0·1376	−0·0035	−0·4736	4·70
C_3	−0·1897	0·0500	0·3657	4·70
C_4	−0·2897	0·1586	0·0721	5·60
C_5	−0·1221	−0·2199	−0·4516	4·20
C_6	−0·0568	−0·2788	−0·2817	4·70
C_7	0·0263	−0·3656	−0·2180	5·60
C_8	0·0387	−0·3914	−0·3320	6·20
C_9	−0·0271	−0·3301	−0·4991	5·60
C_{10}	−0·1111	−0·2447	0·4362	4·70

Table 3. *Standard deviations of the atomic coordinates*

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	R.m.s. (Å)
S_1	0·0020	0·0019	0·0019	0·0019
S_2	0·0022	0·0020	0·0024	0·0022
O_1	0·0091	0·0088	0·0083	0·0088
O_2	0·0077	0·0071	0·0074	0·0074
O_3	0·0099	0·0078	0·0119	0·0100
O_4	0·0078	0·0075	0·0092	0·0082
N_1	0·0149	0·0111	0·0113	0·0126
C_1	0·0129	0·0101	0·0118	0·0117
C_2	0·0098	0·0085	0·0097	0·0094
C_3	0·0087	0·0079	0·0081	0·0082
C_4	0·0116	0·0120	0·0117	0·0118
C_5	0·0095	0·0080	0·0093	0·0091
C_6	0·0121	0·0087	0·0106	0·0106
C_7	0·0155	0·0112	0·0128	0·0133
C_8	0·0166	0·0110	0·0165	0·0149
C_9	0·0123	0·0120	0·0122	0·0121
C_{10}	0·0108	0·0104	0·0103	0·0105

obtained from these coordinates are shown in Fig. 1, which also shows the labelling of the atoms. The bond angles are given in Table 2.

The standard deviations of the atomic coordinates were calculated by the method suggested by Cruickshank (1949), and are shown in Table 3. These figures yield the standard deviations of the bond lengths shown in Table 4. The standard deviations of some

Table 4. *Standard deviations of the bond lengths*

S_1–C_2	0·0096 Å	C_5–C_6	0·0139 Å
S_2–C_2	0·0096	C_6–C_7	0·0170
		C_7–C_8	0·0173
S_1–C_1	0·0118	C_8–C_9	0·0160
S_2–C_5	0·0094	C_9–C_{10}	0·0192
		C_5–C_{10}	0·0139
S_1–O_1	0·0090		
S_1–O_2	0·0076	N_1–C_4	0·0172
S_2–O_3	0·0102	N_1–C_3	0·0150
S_2–O_4	0·0085		
		C_2–C_3	0·0124

of the angles, calculated from the formula of Cruickshank & Robertson (1953) are shown in Table 5.

Table 5. *Standard deviations of some of the angles*

C_3–N_1–C_4	1·3°	C_6–C_5–C_{10}	0·9°
N_1–C_3–C_2	1·0	C_7–C_8–C_9	1·3
S_1–C_2–S_2	0·5		

The final peak heights and curvatures are given in Table 6.

The standard deviation of the electron density is 0·25 e.Å^{-3} and of the curvatures is 0·54 e.Å^{-5}. A list of observed and calculated structure factors for the *h*0*l*, *hk*0 and 0*kl* reflexions is given in Table 7. The final R factor is 0·171. Since the eleven hydrogen atoms have not been included in the calculation of the structure factors, and no attempt has been made to allow for anisotropic thermal motion, of which there is some evidence, the value of R seems reasonable in a structure of this complexity. Figs. 2(*a*) and (*b*) show the arrangement of the molecules in the unit cell. The third projection is very heavily overlapped, but Fig. 1 shows the molecule as it appears when projected on to (100).

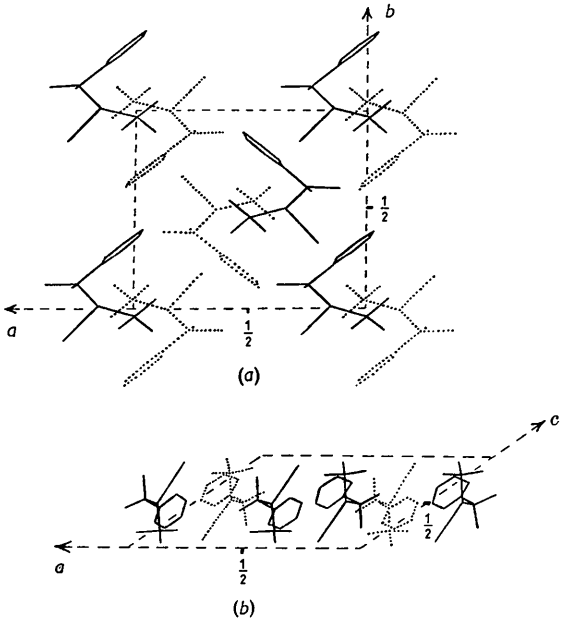

Fig. 2. Projections of the structure (*a*) on to (001), (*b*) on to (010). Some of the molecules are drawn with dotted lines in an effort to improve clarity, and no other significance should be attached to these lines.

Discussion of the structure

The similarity between the molecular dimensions found in MPV and DMV (Part I) is very striking. A comparison of analogous lengths and angles is made in Table 8. Most of the structural parameters which are common to both molecules have already been discussed in Part I. The asymmetry of MPV introduces some new

Table 6. *Final observed and calculated peak heights and curvatures*

	ϱ_o (e.Å^{-3})	ϱ_c (e.Å^{-3})	$-A^o_{hh}$ (e.Å^{-5})	$-A^o_{kk}$ (e.Å^{-5})	$-A^o_{ll}$ (e.Å^{-5})	$-A^c_{hh}$ (e.Å^{-5})	$-A^c_{kk}$ (e.Å^{-5})	$-A^c_{ll}$ (e.Å^{-5})
S_1	28·70	29·33	272·3	282·3	290·0	274·9	274·6	285·7
S_2	26·09	27·77	248·6	264·0	223·5	257·4	265·7	248·8
O_1	9·16	9·66	71·0	74·1	74·3	74·9	70·5	73·9
O_2	8·00	8·97	60·2	60·3	65·8	64·4	62·2	67·6
O_3	7·93	9·09	55·2	68·0	46·1	67·8	71·6	64·0
O_4	8·09	8·87	70·6	70·2	59·4	64·9	70·8	59·1
N_1	6·12	7·11	36·7	47·9	48·3	49·4	51·0	51·9
C_1	5·51	5·57	42·3	52·5	46·4	45·1	47·2	46·8
C_2	6·56	6·46	55·7	62·4	56·1	52·7	53·5	54·0
C_3	7·00	7·03	62·8	67·9	67·8	61·1	61·1	64·9
C_4	5·54	5·71	47·2	44·0	46·6	48·0	45·1	46·4
C_5	7·09	7·14	57·6	65·9	58·6	61·3	60·9	60·9
C_6	6·04	6·55	45·3	60·9	51·4	51·4	59·5	54·2
C_7	5·22	5·60	35·3	47·3	42·8	42·4	43·1	43·8
C_8	5·04	5·23	32·9	48·0	33·1	36·3	41·2	37·0
C_9	5·44	5·73	45·0	44·0	44·9	45·7	42·5	45·4
C_{10}	6·07	6·45	50·7	51·0	53·2	53·9	53·9	53·1

Table 7. *Observed and calculated structure factors*

Values are 10 times absolute scale

h	k	ℓ	F_o	F_c
0	1	1	100	117-
0	1	2	109	189+
0	1	3	107	106-
0	1	4	315	329-
0	1	5	51	62+
0	2	0	449	664+
0	2	1	298	336+
0	2	2	298	313-
0	2	3	153	140-
0	2	4	80	61+
0	2	5	143	136+
0	2	7	120	119-
0	3	1	339	341+
0	3	2	314	315+
0	3	3	334	363-
0	3	4	366	372-
0	3	5	150	160+
0	3	7	67	77+
0	4	0	672	907-
0	4	1	123	122+
0	4	2	165	202+
0	4	3	199	237+
0	4	4	120	88-
0	5	1	62	79+
0	5	2	154	113+
0	5	3	217	197-
0	5	4	158	143-
0	5	6	111	113+
0	6	0	424	473-
0	6	1	186	207+
0	6	2	224	175+
0	6	3	60	39+
0	6	5	78	73-
0	7	1	78	15+
0	7	2	44	35-
0	7	3	341	322-
0	7	5	65	77-
0	7	6	80	122+

h	k	ℓ	F_o	F_c
0	8	0	441	429+
0	8	1	336	343-
0	8	2	159	121+
0	8	3	178	172-
0	8	4	113	79+
0	9	1	185	157+
0	9	3	139	119-
0	9	4	121	126-
0	9	5	46	58+
0	10	0	50	25+
0	10	1	249	231-
0	10	2	163	125+
0	10	3	77	51-
0	10	4	31	26+
0	10	5	89	69-
0	11	1	121	95+
0	11	2	97	70+
0	11	4	88	79-
0	11	5	44	51+
0	12	0	339	283-
0	12	2	151	123+
0	12	3	74	71+
0	12	4	65	55-
0	12	5	69	67-
0	13	2	54	41-
0	13	3	70	56+
0	13	4	30	7-
0	14	0	215	207-
0	14	1	45	44+
0	14	3	71	76+
0	15	1	113	103-
0	15	3	26	29+
0	16	1	41	37-
0	16	2	24	33+

h	k	ℓ	F_o	F_c
0	0	1	714	1026-
0	0	2	218	178-
0	0	3	629	750-
0	0	4	434	464+
0	0	5	144	157+
0	0	6	110	92-
0	0	7	164	113-
2	0	0	219	212+
2	0	1	562	684+
2	0	2	567	620-
2	0	3	55	2+
2	0	4	106	72+
2	0	5	102	95+
2	0	6	67	60+
4	0	0	380	497+
4	0	1	79	99-
4	0	2	111	64+
4	0	3	158	158-
4	0	4	82	72+
4	0	5	51	55+
6	0	0	236	216-
6	0	1	312	302+
6	0	2	233	220-
6	0	3	39	26-
6	0	4	63	60-
8	0	0	309	259+
8	0	1	100	76-
8	0	2	67	69+
10	0	1	74	99+

h	k	ℓ	F_o	F_c
2	0	1	422	509+
2	0	2	363	1246-
2	0	3	363	379-
2	0	4	133	150+
2	0	5	210	165+
2	0	6	107	40-
2	0	7	126	151-
2	0	9	37	31+
4	0	1	489	526-
4	0	2	478	675-
4	0	3	290	257-
4	0	4	204	191-
4	0	5	27	29+
4	0	6	266	266-
4	0	7	152	70-
4	0	8	144	68+
4	0	9	168	160+
6	0	1	201	152-
6	0	2	152	136-
6	0	3	475	576+
6	0	4	547	699+
6	0	5	173	178-
6	0	6	175	127+
6	0	7	362	386-
6	0	8	475	503+
6	0	9	114	98-
6	0	11	51	110-
8	0	1	254	214-
8	0	2	126	111+
8	0	3	230	257-
8	0	4	290	317+
8	0	5	506	619+
8	0	6	570	665-
8	0	7	61	17+
8	0	8	205	182-
8	0	9	408	402+
8	0	10	166	135-
8	0	11	85	38-

h	k	ℓ	F_o	F_c
10	0	1	71	7+
10	0	2	113	93-
10	0	3	123	133+
10	0	4	161	141+
10	0	5	60	35-
10	0	6	162	115-
10	0	7	494	515-
10	0	8	145	138+
10	0	9	99	21+
10	0	10	50	15+
10	0	11	105	98-
12	0	1	70	79-
12	0	2	77	69-
12	0	3	87	60+
12	0	5	160	174+
12	0	6	405	390-
12	0	7	112	104+
12	0	8	33	14-
12	0	9	286	272+
12	0	11	110	49-
12	0	13	74	63+
14	0	4	191	186+
14	0	5	230	199-
14	0	6	53	3-
14	0	7	264	192-
14	0	8	344	386+
14	0	11	154	138-
14	0	12	37	59+
14	0	13	110	97+
16	0	5	74	61+
16	0	6	155	146-
16	0	7	176	162+
16	0	8	57	32-
16	0	9	146	121+
16	0	10	204	169-
16	0	11	42	25-
16	0	13	63	62+
18	0	8	65	60+
18	0	9	58	51-
18	0	10	51	56-
18	0	11	27	26-
18	0	12	41	41+
18	0	13	82	71+

h	k	ℓ	F_o	F_c
1	1	0	622	843+
2	1	0	372	386-
3	1	0	132	130-
4	1	0	56	66-
5	1	0	201	162+
6	1	0	133	83-
7	1	0	45	55-
8	1	0	116	89+
9	1	0	153	143+
10	1	0	73	65-
1	2	0	495	605-
2	2	0	55	5+
3	2	0	51	31+
4	2	0	232	253+
5	2	0	247	247-
6	2	0	166	127+
7	2	0	205	163+
8	2	0	111	90+
9	2	0	196	154-
10	2	0	30	33+
1	3	0	693	928+
2	3	0	599	689+
3	3	0	213	233+
4	3	0	164	132+
5	3	0	208	199+
6	3	0	220	168-
7	3	0	219	190+
8	3	0	29	21+
9	3	0	36	9+
10	3	0	53	53-
1	4	0	43	7+
2	4	0	453	560+
3	4	0	63	59+
4	4	0	478	508-
5	4	0	263	260-
6	4	0	306	298+
7	4	0	94	115-
8	4	0	44	32-
9	4	0	117	110-
10	4	0	60	75+

h	k	ℓ	F_o	F_c
1	5	0	137	77+
2	5	0	27	3+
3	5	0	99	39-
4	5	0	252	242-
5	5	0	158	146-
6	5	0	85	21+
7	5	0	290	277+
8	5	0	199	173-
9	5	0	44	27-
10	5	0	51	55-
1	6	0	517	635+
2	6	0	184	168+
3	6	0	118	89-
4	6	0	73	70-
5	6	0	194	151+
6	6	0	211	173+
7	6	0	262	184+
8	6	0	67	39-
9	6	0	32	25-
1	7	0	194	184-
2	7	0	122	89+
4	7	0	157	121-
5	7	0	109	91-
6	7	0	109	101-
7	7	0	84	56-
8	7	0	210	200-
9	7	0	37	41-
10	7	0	32	32-
1	8	0	305	311+
2	8	0	256	263-
3	8	0	119	93-
4	8	0	31	18-
5	8	0	81	43-
6	8	0	231	202-
7	8	0	203	165-
8	8	0	80	61+
10	8	0	28	57-

h	k	ℓ	F_o	F_c
1	9	0	166	111-
2	9	0	64	35-
3	9	0	230	206-
4	9	0	43	13-
5	9	0	69	35-
6	9	0	107	51-
7	9	0	132	115-
9	9	0	49	39+
1	10	0	315	289-
2	10	0	320	289-
3	10	0	62	64+
4	10	0	27	9-
5	10	0	127	101-
6	10	0	196	153-
7	10	0	54	48+
8	10	0	40	6+
9	10	0	55	64-
1	11	0	188	173-
2	11	0	31	13+
3	11	0	122	92-
4	11	0	70	42+
5	11	0	94	53+
6	11	0	60	43-
7	11	0	50	59-
8	11	0	51	38+
1	12	0	169	140-
2	12	0	107	81-
3	12	0	110	95+
4	12	0	166	117-
5	12	0	87	63-
7	12	0	43	35+
8	12	0	11	47-
1	13	0	148	131-
2	13	0	30	7-
3	13	0	102	82-
4	13	0	41	33+
5	13	0	121	107-
7	13	0	41	38+

h	k	ℓ	F_o	F_c
1	14	0	82	65+
2	14	0	123	117-
3	14	0	37	30-
4	14	0	133	116-
5	14	0	80	79+
6	14	0	30	22+
1	15	0	57	51-
2	15	0	35	16-
3	15	0	38	32-
5	15	0	6	25-
1	16	0	50	52+
2	16	0	40	35-
3	16	0	33	33-

features, and only those will be discussed here. The standard deviations of the bond lengths and angles given in Tables 3 and 4 allow the following conclusions to be drawn:

(1) The C–C distances in the phenyl group do not differ significantly from the mean value of 1·389 Å (maximum $\Delta/\sigma = 1{\cdot}0$), and this mean value is close to the values of 1·393 Å (Cox, Cruickshank & Smith, 1955) and 1·397 Å (Stoicheff, 1954) found in benzene. The fact that the mean distance is slightly, though not significantly, less than in benzene may well be due to the fact that no correction has been made for anisotropic thermal motion (Cruickshank, 1956). The benzene ring is essentially planar. The maximum distance of a carbon atom from the best plane through the six atoms is less than 0·02 Å.

(2) The mean value of the C–S–O angles, 107° 15′, is significantly less than the tetrahedral angle ($\Delta/\sigma = 6{\cdot}0$).

(3) The mean value of the six angles in the benzene ring is close to 120°, but C_6–C_5–C_{10} is probably significantly larger than 120° ($\Delta/\sigma = 3{\cdot}0$).

(4) The angle N_1–C_3–C_2 is probably significantly different from 180° ($\Delta/\sigma = 3{\cdot}0$).

Table 8. *Comparison of the analogous distances and angles in* DMV *and* MPV

	DMV	MPV*
$S–C_{1,5}$	1·770 Å	1·767 Å
S–O	1·433	1·436
$S–C_2$	1·726	1·729
$C_2–C_3$	1·342	1·354
$C_3–N_1$	1·154	1·148
$N_1–C_4$	1·426	1·382
O–S–O	118·4°	120·1°
C–S–O	107·8	107·3
S–C–S	122·6	122·4
$C_1–S–C_2$	106·8	107·0
S···S	3·03	3·03

* Mean values are taken where appropriate.

(5) The angle $C_3–N_1–C_4$ is significantly different from 180° ($\Delta/\sigma = 7{\cdot}2$).

From the molecular dimensions and the conclusions given above, it can be seen that the present investigation confirms the fact that the bond number of the carbon atom C_3 is very high. C_3 is joined to C_2 by a double bond, and to N_1 by a triple bond, as in DMV. Moreover, the chain of atoms C=C=N−C is again substantially linear. However, there is a significant departure from strict linearity, but this can be seen to arise from the packing in the crystal. The two non-bonded atoms in neighbouring molecules which are closest to C_4 are oxygen atoms, and C_4 moves so as to make the distances to both these oxygen atoms identical at 3·249 Å. It seems much more reasonable in the light of this and previous evidence to assume that the chain is linear with distortions away from linearity, rather than that the chain is non-linear with distortions towards linearity.

The linearity of the C=C=N−C chain must be explicable in terms of the electronic structures of these molecules. Normally a nitrogen atom forming a single and a double bond gives three non-linear atoms, and calculations have shown that this is to be expected (Wheland & Chen, 1956). Hence DMV and MPV must have some additional features which favour the linearity. There is little doubt that the unsubstituted parent molecule vinylidineamine, $CH_2=C=NH$, would be bent, by analogy with allene, with the N–H bond pointing out of the plane of the $CH_2=C=N$ group. The lone pair of electrons on the nitrogen atom would point out of this plane on the opposite side to the N–H bond, and it is primarily the repulsion between the lone pair and the electrons in the C–N and N–H bonds that causes the C–N–H angle to be less than 180°. In order to form stable vinylidineamines it has been observed (Dijkstra, 1952) that the methylene group must be substituted with electronegative groups. Provided the electronegative groups have the correct symmetry properties (Koch & Moffitt, 1951) they will attract electrons from the chain and the molecule will adopt more of the character $C-C\equiv\overset{+}{N}-H$. In doing this the nitrogen will tend to lose its lone pair, and the repulsion between the lone pair and the electrons in the C–N and N–H bonds will be reduced. This loss of repulsion will tend to allow the chain to straighten.

A further effect is operating which might also lead to linearity. From the length of the $N_1–C_4$ bond it can be seen that considerable hyperconjugation exists between the *N*-methyl group and the multiply-linked chain. This hyperconjugation will be at a maximum if the chain is linear. Thus *N*-methylvinylidineamine itself might possibly be linear, if it existed, even though the methylene group is not substituted with electronegative groups.

In conclusion, therefore, it appears that the linearity of the C=C=N−C group is brought about by the action of the electronegative groups and by hyperconjugation of the *N*-substituent. It seems unlikely that the first effect can be investigated experimentally, since the presence of electronegative groups is essential to the existence of this type of compound. However, the effect of hyperconjugation might be investigated by an appropriate choice of *N*-substituent.

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