The Molecular Structures of Divinyl Sulfide and Divinyl Sulfoxide in the Gas Phase from Electron Diffraction†

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The molecular geometries and conformations of divinyl sulfide (DVS), $(CH_2{=}CH)_2S$, and divinyl sulfoxide (DVSO), $(CH_2{=}CH)_2SO$, have been determined by gas-phase electron diffraction and vibrational analysis. The C=C bonds tend to eclipse other bonds or a sulfur lone pair in the free molecules. The only conformer found in the vapours of DVS at room temperature has no symmetry and is characterized by dihedral angles C–S–C=C of 32(9)° and −148(7)°; both CH_2 groups lie on the same side of the C–S–C plane. This form is very similar to the prevailing form of divinyl ether.[8] DVSO is a mixture of conformers. The form present in 78(17)% at 82 °C has C–S–C=C of 121(4)° and −121(4)° and C_s symmetry; both C=C bonds eclipse the S=O bonds. Intramolecular O · · · H(C) interactions of about 2.5 Å seem to stabilize existing conformers of DVSO. Important parameters are (r_g with estimated total errors), for DVS: S–C 1.758(4), C=C 1.342(3), C–H 1.092(3), $(C{\cdot}H)_{mean}$ (within a $CH_2{=}CH$ group) 2.108(6) Å, C–S–C 101.8(21)°, S–C=C 123.7(6)°; for DVSO: S=O 1.477(3), S–C 1.785(4), C=C 1.330(3), C–H 1.091(5), $(C{\cdot}H)_{mean}$ 2.141(10) Å, C–S=O 107.5(14)°, C–S–C 99.2(18)°, S–C=C 118.5(8)°. Bond lengths do not indicate effects of conjugation in these molecules.

Conformational and electronic properties and the molecular geometries of vinyl ethers and vinyl sulfides have been widely studied by vibrational, electronic, NMR and rotational spectroscopy, electron diffraction, and by theoretical methods.[1] The problem of rotation about two axes, including the relaxation of bond lengths and bond angles during rotation and the relevant potential functions, have been treated by combinations of experimental and theoretical techniques for dimethyl ether,[2] methyl vinyl ether,[3–6] divinyl ether[7–9] and methyl vinyl sulfide.[10] While alkyl derivatives exist in staggered conformations,[2,11] vinyl derivatives prefer eclipsed forms.[12]

Gas-phase molecular structures of sulfur compounds, first of all sulfones, were systematically studied in this laboratory during the past years. Effects of substituents, changes of the geometry in the sulfone, sulfoxide, sulfide series, correlations with vibrational frequencies and substituent electronegativities were established.[12,13]

The joint electron diffraction, vibrational spectroscopic, and CNDO/2 semiempirical study of divinyl sulfone was published a long time ago.[14] We report here the results of the structure determination of divinyl sulfide (DVS) and divinyl sulfoxide (DVSO) by gas-phase electron diffraction, augmented by vibrational spectroscopic calculations. Both molecules have been studied by different methods.[15] It was concluded from the vibrational spectra that DVS is a mixture of two forms,[16–19] possibly of C_1 and C_2 symmetry,[18] in the pure liquid phase and in solution. DVSO also exists as a mixture of two conformers in these phases[16,17] and in the gas phase.[20] One conformer persists in the crystals of DVS[16,18] and DVSO.[16]

Results and Discussion

The final results of structure refinements, r_a and l(ED) from the electron diffraction analysis, and also amplitudes l(SP) from spectroscopic calculations, are listed in Tables 1 and 2. Important geometrical parameters of DVS and DVSO (r_g with estimated total errors) are given in the Summary. Total errors include least-squares standard deviations, effects of data correlation, and systematic (scale) errors.[21]

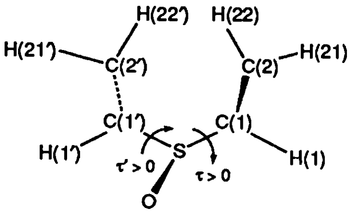

Fig. 1 The model of divinyl sulfoxide (DVSO) with the numbering of atoms and the definition of dihedral angles (τ,τ'); τ = τ' = 0° for the *syn*, *syn* C=C–S–C=C chain, τ = −τ' for conformers with C_s symmetry, and τ ≈ 120°, τ' ≈ −120° if both C=C bonds eclipse the S=O bond

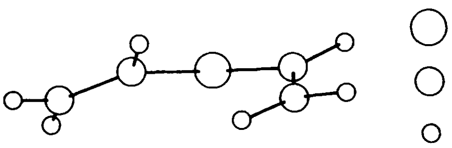

Fig. 2 The (32°, −148°) conformer found for DVS. Model projected down the bisector of the C–S–C angle.

Conformation.—The conformation of DVS and DVSO is given by the two C–S–C=C dihedral angles (τ,τ') (Fig. 1).

In the case of DVS, the only conformer that has been found to fit satisfactorily the electron diffraction intensities is a non-symmetric form characterized by torsional angles C–S–C=C of 32(9)° and −148(7)° (*i.e.*, both methylene groups are on the same side of the C–S–C plane, see Fig. 2). This effective structure is the result of torsional vibrations about the S–C bonds, and can be derived from more specific forms, *viz.*, from the form with torsional angles (τ,τ') of (0°, −120°), in which the C=C bonds eclipse an S–C bond and a lone electron pair of the sulfur atom, or from the *syn*, *anti* (0°, 180°) conformer with C_s symmetry. The large values of mean amplitudes of some rotation-dependent distances (Table 1) may indicate large-

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† Taken in part from the Diploma work by Z. E. Horváth, Eötvös University, Budapest, 1989.

Table 1 Refined parameters r_a and l(ED) and calculated mean amplitudes l(SP) of divinyl sulfide (DVS)[a]

	r_a/Å Angle/°	l(ED)/Å	l group no.	l(SP)/Å
Independent parameters[b]				
S–C	1.7566(4)	0.0497(5)	1	0.0495
C=C	1.3410(6)	0.0490(7)	2	0.0424
C–H	1.0868(14)	0.0741(13)	3	0.0773
$(C{\cdot}H)_{mean}$	2.1031(34)	0.0987(39)	4	0.0987
C–S–C	101.8(15)			
S–C=C	123.7(4)			
C=C–H[c]	119.7(3)			
τ	32.1(63)			
τ'	−147.9(48)			
Dependent distances				
C1···C1′	2.726(29)	0.079(1)	5	0.0764
S···C2	2.738(6)	0.070	5	0.0677
S···H1	2.445(5)	0.115(9)	6	0.1172
S···H21	3.732(3)	0.098(11)	7	0.0974
S···H22	2.900(8)	0.105(10)	8	0.1441
H1···H21	2.418(11)	0.170[d]		0.1703
H1···H22	3.068(5)	0.124[d]		0.1240
H21···H22	1.888(7)	0.125[d]		0.1245
C1′···C2	3.020(14)	0.149	8	0.1884
C1′···H1	3.674(53)	0.154	7	0.1539
C1′···H21	4.069(13)	0.247(43)	9	0.1798
C1′···H22	2.619(53)	0.365	6	0.3667
C1···C2′	3.953(10)	0.095(10)	10	0.1300
C1···H1′	2.800(69)	0.208	5	0.2055
C1···H21′	4.756(21)	0.322(108)	11	0.1510
C1···H22′	4.361(27)	0.389	11	0.2188
C2···C2′	4.148(31)	0.323	9	0.2558
C2···H1′	2.806(48)	0.424	5	0.4219
C2···H21′	4.738(23)	0.462	11	0.2917
C2···H22′	4.718(50)	0.525	11	0.3541
C2′···H1	4.923(24)	0.308	11	0.1378
C2′···H21	5.205(26)	0.440	11	0.2695
C2′···H22	3.521(61)	0.385	7	0.3849
R	0.049			

[a] Least-squares standard deviations in parentheses are given in units of the last digit of the parameter, and for a group of amplitudes l(ED) they are listed only with the first member of the group. R is the goodness-of-fit factor, $R^2 = \Sigma[sM^E(s) - sM^T(s)]^2/\Sigma[sM^E(s)]^2$. [b] $(C{\cdot}H)_{mean}$ is the mean C···H distance within a CH_2=CH moiety, τ, τ' are the dihedral angles C–S–C=C (Fig. 1). [c] Dependent parameter. [d] Fixed.

amplitude torsional vibrations. We cannot exclude the presence of small amounts of other conformers either.

Similar torsional angles, albeit with different mutual positions of the two methylene groups, were obtained by molecular mechanics (38°, 124°) and by 3-21G *ab initio* calculations (18°, 116°), and a second conformer (122°, 122°), with C_2 symmetry was found.[22] *Ab initio* calculations at the 3-21G* level with six sulfur d orbitals led to the (132°, 132°) C_2 conformer.[23] This energy minimum is flat, and the planar *anti*, *anti* (180°, 180°) C_{2v} conformer lies only 5.4 kJ mol^{-1} higher.[23]

Two conformers of divinyl ether have been detected at room temperature in an electron diffraction analysis combined with microwave data and *ab initio* calculations.[8] The form present in 80(6)% has 13(6)° and −145(4)° torsional angles, which are practically the same as we have found in DVS.

This electron diffraction study indicated, in accord with spectroscopic evidence,[16,17,20] that DVSO exists in the vapour as a mixture of conformers. The most abundant form at 82 °C possesses C_s symmetry and torsional angles of 121(4)° and −121(4)°, *i.e.*, the C=C bonds eclipse the S=O bond (Fig. 3). Other forms in the mixture can be the (0°, −120°) or (120°, 120°) or both, also having the C=C bonds eclipsing a bond or the lone electron pair of sulfur. The presence of further forms is also possible.

Table 2 Refined parameters r_a and l(ED) and calculated mean amplitudes l(SP) of divinyl sulfoxide (DVSO)[a]

	r_a/Å Angle/°	l(ED)/Å	l group no.	l(SP)/Å
Independent parameters[b]				
S=O	1.4758(8)	0.0375(14)	1	0.0392
S–C	1.7832(8)	0.0517(12)	2	0.0520
C=C	1.3281(12)	0.0409	1	0.0426
C–H	1.0858(28)	0.0801(26)	3	0.0772
$(C{\cdot}H)_{mean}$	2.1362(65)	0.1130(85)	4	0.0972
C–S=O	107.5(10)			
C–S–C	99.2(13)			
S–C=C	118.5(6)			
C=C–H[c]	124.2(7)			
τ_1	121.2(30)			
τ_1'[c]	−121.2(30)			
τ_2	0.0[d]			
τ_2'	−120.0[d]			
x_1	0.78(12)			
x_2[c]	0.22(12)			
Dependent distances				
O···C1	2.635(16)	0.073(4)	5	0.0793
C1···C1′	2.716(26)	0.077	5	0.0828
S···C2	2.684(8)	0.069	5	0.0747
S···H1	2.478(9)	0.122(22)	6	0.1150
S···H21	3.722(6)	0.089(8)	7	0.1019
S···H22	2.867(14)	0.155(6)	8	0.1559
H1···H21	2.548(21)	0.159[d]		0.1593
H1···H22	3.118(9)	0.120[d]		0.1202
H21···H22	1.796(17)	0.128[d]		0.1276
Conformer 1				
O···C2	2.878(14)	0.124	8	0.1250
O···H1	3.608(19)	0.084(25)	9	0.1129
O···H21	3.949(14)	0.435(165)	10	0.1490
O···H22	2.486(21)	0.217	6	0.2098
C1′···C2	3.728(19)	0.142	7	0.1554
C1′···H1	2.977(56)	0.203	8	0.2039
C1′···H21	4.622(21)	0.175(38)	11	0.1704
C1′···H22	4.049(35)	0.556	10	0.2702
C2···C2′	4.466(58)	0.263	11	0.2585
C2···H1′	4.146(38)	0.542	10	0.2561
C2···H21′	5.366(56)	0.288	11	0.2827
C2···H22′	4.541(90)	0.402	11	0.3972
Conformer 2				
O···C2	3.570(20)	0.117	9	0.1458
O···H1	3.055(16)	0.183	8	0.1840
O···H21	4.524(25)	0.168	11	0.1630
O···H22	3.785(24)	0.241	7	0.2539
C1′···C2	2.766(32)	0.128	5	0.1335
C1′···H1	3.744(24)	0.097	7	0.1105
C1′···H21	3.813(33)	0.149	7	0.1625
C1′···H22	2.234(36)	0.231	4	0.2154
O···C2′	2.876(12)	0.133	8	0.1338
O···H1′	3.610(18)	0.084	9	0.1123
O···H21′	3.947(13)	0.443	10	0.1572
O···H22′	2.482(16)	0.225	6	0.2183
C1···C2′	3.717(22)	0.144	7	0.1575
C1···H1′	2.988(35)	0.205	8	0.2061
C1···H21′	4.613(29)	0.183	11	0.1780
C1···H22′	4.031(18)	0.555	10	0.2688
C2···C2′	3.702(35)	0.236	7	0.2493
C2···H1′	2.714(42)	0.306	5	0.3115
C2···H21′	4.357(45)	0.282	11	0.2772
C2···H22′	4.239(27)	0.661	10	0.3748
C2′···H1	4.707(19)	0.184	11	0.1795
C2′···H21	4.685(38)	0.293	11	0.2882
C2′···H22	3.057(43)	0.349	8	0.3503
R	0.073			

[a] See footnote *a* to Table 1. [b] $(C{\cdot}H)_{mean}$ is the mean C···H distance within a CH_2=CH moiety, τ_1, τ_1' and τ_2, τ_2' are the dihedral angles C–S–C=C (Fig. 1), x_1 and x_2 are the mole fractions of conformer 1 and 2, respectively. [c] Dependent parameter. [d] Fixed.

Table 3 Correlation matrix elements 1000 ρ_{ij} ($|1000\,\rho_{ij}| > 500$) from the structure refinement of DVS[a]

	(C-H)$_{\text{mean}}$	C-S-C	S-C=C	τ	τ'	$l1$	$l5$	$l7$	$l9$
C-S-C	514								
S-C=C	−552	−974							
τ	553	931	−892						
τ'		915	−896	841					
$l5$		734	−679	747	668				
$l6$		−620	617	−599	−566				
$l8$		518		658			694		
$l10$								713	
$l11$									523
k_{19}						723			

[a] Factor k_{19} is included in $sM^{T}(s)$ to scale it to $sM^{E}(s)$ for the 19 cm camera range.

Table 4 Correlation matrix elements 1000ρ_{ij} ($|1000\,\rho_{ij}| > 500$) from the structure refinement of DVSO[a]

	C-S=O	C-S-C	S-C=C	τ_1	$l1$	$l2$	$l5$
S-C=C	−859	−546					
τ_1		−707					
$l2$					758		
$l5$	835		−580				
$l6$		−569	504	506			
$l7$	718		−587				637
$l9$	508						587
x_1	−596						−523
k_{19}					824	832	

[a] Factor k_{19} is included in $sM^{T}(s)$ to scale it to $sM^{E}(s)$ for the 19 cm camera range.

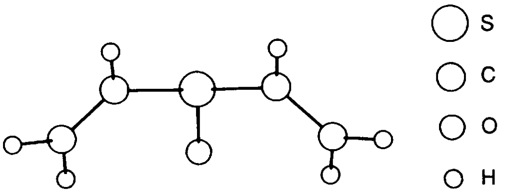
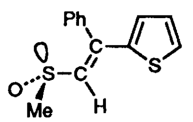


Fig. 3 The main conformer of DVSO (121°, −121°), with C_s symmetry. Projected down the bisector of the C-S-C angle.

Thus, the predominant conformers of DVS and DVSO have been identified by electron diffraction. Coexisting other forms could not be well determined because the outer parts of the radial distributions contain little information, which is blurred by large noise (see Figs. 6 and 7).

Our findings are in line with the observation that C=C bonds in vinyl derivatives tend to eclipse other bonds or a lone pair.[12,24–26] Different situations may occur in crystalline vinyl sulfoxides, *e.g.*, the C=C bond eclipses the sulfur lone pair in **1**[27] but staggers the S=O and S-Me bonds in **2**.[28] Eclipsed forms are preferred in sulfoxides of other π-bonded systems. *E.g.*, according to *ab initio* calculations and X-ray crystallographic studies, the S=O bond is often nearly coplanar with the aromatic ring in *ortho*-substituted methyl phenyl sulfoxides,[29] and also in methylsulfinyl derivatives of furan and thiophene,[30] but steric effects of substituents may lead to large deviations from coplanarity.



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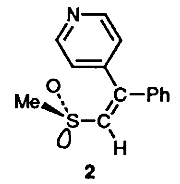

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There are short O···H distances of about 2.5 Å in the conformers of DVSO (Table 2). Somewhat shorter (2.4 and 2.3 Å) O···H distances have been found in free molecules of (*E*)-MeSO$_2$CH=CHX, X = Cl[25b] and X = CN.[26] This interaction might be related[26] to the smaller S-C=C angles in DVSO and in (*E*)-MeSO$_2$CH=CHX, compared to S-C=C in DVS and (*Z*)-MeSO$_2$CH=CHX.[25,26] Intramolecular O···H-C hydrogen bonds seem to be important factors in the conformational behaviour of vinyl sulfones,[25b] as well as of vinyl sulfoxides.

Bond Lengths and Bond Angles.—In the asymmetric forms and mixtures of conformers tested here, only the mean values of the parameters were obtained. Bond lengths of DVS and DVSO are well determined from electron diffraction. Bond angles have large uncertainties (see Summary), and are strongly correlated with other parameters (Tables 3 and 4). The determination of bond angles was somewhat influenced by the incomplete conclusion concerning the presence of minor conformers in the gas phase.

Some parameters of DVS are compared with those of related molecules in Table 5. The C=C bond lengths in vinyl derivatives are similar to that in ethylene,[38] 1.337(2) Å. The carbon bonds to O, S, Se are shorter than in the methyl derivatives. These bonds are shorter, the C=C bonds are longer in furan, thiophene and selenophene than in the corresponding divinyl derivatives (Table 5). The bond angle of the chalcogen atom closes from O to Se. Table 6 shows parameters of simple sulfides, sulfoxides, and sulfones with S-C(sp^3) and S-C(sp^2) bonds. Data from the present work fit in the series and are consistent with earlier observations:[12,13] sulfur bonds lengthen, bond angles get narrower from the sulfone to the sulfoxide, according to expectations from the VSEPR model, while the changes from the sulfoxides to the sulfides cannot be so simply predicted.[43] The S-C bond lengths in sulfones and sulfoxides are less sensitive to carbon hybridization than in sulfides[13] (Table 6). Bond lengths in DVS, DVSO and divinyl sulfone[14] do not indicate any appreciable electron delocalization in these molecules.

The S-C bond lengths in DVS and DVSO are close to mean values obtained from a statistical analysis[44] of crystallographic data in the Cambridge Structural Database: S-C(sp^2) 1.751(17) Å, $n = 61$, in sulfides with aliphatic carbon atoms, and (O=)S-C$_{\text{ar}}$ 1.790(10) Å, $n = 41$, in sulfoxides with an aromatic carbon (in samples of n observations; standard deviations given in parentheses). The S=O bond length in DVSO is smaller than the mean, S=O 1.497(13), $n = 90$, for crystalline sulfoxides.[44]

Table 5 Bond lengths and bond angles in ethers, sulfides and selenides

	r	C=C/Å	C(sp^2)–X/Å	C(sp^3)–X/Å	C–X–C/°	C=C–X/°	Ref.
X = O							
Me$_2$O	r_g			1.415(1)	111.8(2)		2
Et$_2$O	r_s			1.411(3)	112.1(3)		31
CH$_2$CHOMe	r_g	1.337(10)	1.359(15)	1.427(7)	116.8(18)	127.3(18)	3
(CH$_2$CH)$_2$O[a]	r_g	1.337(2)	1.389(2)		118.8(20)	118.5(20) 124.2(20)	8
C$_4$H$_4$O[b]	r_α^0	1.3640(9)	1.3641(7)		106.74(7)		32
X = S							
Me$_2$S	r_g			1.807(2)	99.05(4)		33
CH$_2$CHSMe	r_a	1.343(1)	1.759(8)	1.795(8)	102.1(5)	127.5(7)	10
(CH$_2$CH)$_2$S	r_g	1.342(3)	1.758(4)		101.8(21)	123.7(6)	*c*
C$_4$H$_4$S[b]	r_α	1.3783(15)	1.7136(11)		92.56(8)		34
X = Se							
Me$_2$Se	r_s			1.945(1)	96.33(1)		35
(CH$_2$CH)$_2$Se	r_a	1.333(3)	1.916(4)		100.3(10)	122.8(8)	36
C$_4$H$_4$Se[b]	r_s	1.3695(12)	1.8547(9)		87.77(7)	111.57(13)	37

[a] Parameters for the more abundant (*sp*, *ap*) conformer. The two values of angle C=C–O refer to the *sp* and the *ap* vinyl group, respectively. [b] Furan, thiophene and selenophene. [c] Present work.

Table 6 Comparison of the sulfur bond geometry in some sulfides, sulfoxides and sulfones

	r	S–C/Å	S=O/Å	C–S–C/°	C–S=O/°	Ref.
Me$_2$S	r_g	1.811(4)		99.2(6)		12
Me$_2$SO	r_z	1.808(4)	1.485(6)	96.6(2)	106.6(1)	13, 39
Me$_2$SO$_2$	r_a	1.771(4)	1.435(3)	102.6(9)	108.3[a]	40
Ph$_2$S	r_a	1.771(5)		103.7(13)		41
Ph$_2$SO	r_g	1.804(6)	1.489(5)	93.9[b]	107.6[b]	42
Ph$_2$SO$_2$	r_g	1.772(5)	1.440(5)	98.7(23)	109.2[a]	42
(CH$_2$CH)$_2$S	r_g	1.758(4)		101.8(21)		*c*
(CH$_2$CH)$_2$SO	r_g	1.785(4)	1.477(3)	99.2(18)	107.5(14)	*c*
(CH$_2$CH)$_2$SO$_2$	r_a	1.769(4)	1.438(3)	107.7(10)	107.3(2)	14

[a] Calculated from the original data. [b] For one of the possible conformers, error estimation not given. [c] Present work.

Table 7 Bond lengths and angles in vinyl sulfoxides **1** and **2**

	C=C/Å	S–C(sp^2)/Å	S=O/Å	C–S–C/°	C(sp^2)–S=O/°
1	1.332(8)	1.767(6)	1.509(4)	97.5(3)	104.7(3)
2	1.331(4)	1.765(2)	1.499(2)	96.4(1)	105.3(1)

The bond length r_g(S=O) = 1.477(3) Å in DVSO and the experimental stretching wavenumber[16,45] ν(S=O) = 1100 cm^{-1} fit perfectly the empirical relationship established for sulfoxides:[12,46] $\log \nu(\mathrm{S{=}O}) = -4.62 \log r(\mathrm{S{=}O}) + 3.824$.

Some vinyl sulfoxides show antianoxia activity and have been studied in the crystalline phase by X-ray diffraction. Molecules of **1**[27] and **2**[28] have very similar bond lengths and bond angles in the crystal, while S–C(sp^2) is shorter, S=O is longer, angle C(sp^2)–S=O is narrower than in the free DVSO molecule (Table 7).

Experimental

Electron Diffraction Experiment and Structure Analysis.—Samples of divinyl sulfide (DVS, purity 99.9%) and divinyl sulfoxide (DVSO, purity checked by IR spectra) were provided by Drs. Yu. L. Frolov and B. Nagel, respectively. Electron diffraction patterns were recorded in a modified EG-100A apparatus[47] with 60 kV electrons. The electron wavelength was determined from TlCl diffraction patterns.[48] Other experimental conditions and the ranges of experimental intensities from the two camera distances (50 and 19 cm) are as follows.

DVS: stainless steel evaporator, nozzle at 21 °C, Kodak electron image plates

50 cm, 6 plates, $2.000 \leqslant s \leqslant 14.000$, $\Delta s = 0.125$ Å^{-1}

19 cm, 4 plates, $9.250 \leqslant s \leqslant 34.750$, $\Delta s = 0.250$ Å^{-1}

DVSO: membrane nozzle system,[49] nozzle at 82 °C, Agfa Gevaert 23D56 plates

50 cm, 5 plates, $2.000 \leqslant s \leqslant 14.000$, $\Delta s = 0.125$ Å^{-1}

19 cm, 4 plates, $8.000 \leqslant s \leqslant 35.000$, $\Delta s = 0.250$ Å^{-1}

Total experimental intensities and final backgrounds have been deposited at the British Library as *Supplementary Publication*, No. 56944 (5 pages).*

Reduced experimental molecular intensities[21] (Figs. 4 and 5) were used with unit weights in the structure analysis. Molecular parameters were refined with a least-squares program,[50] modified and adapted to our IBM-compatible personal computers. Tabulated coherent and incoherent scattering factors[51] were interpolated to the electron energy used. Background corrections were performed graphically as the structure refinement proceeded.

Initial structural parameters were estimated from the experimental radial distributions (Figs. 6 and 7) and from parameters of related molecules. Starting values of mean vibrational amplitudes l(SP) were obtained from spectroscopic calculations. Force fields needed were compiled from those of DVSO[20,45] and propene,[52,53] then fitted by a least-squares

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* For details, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

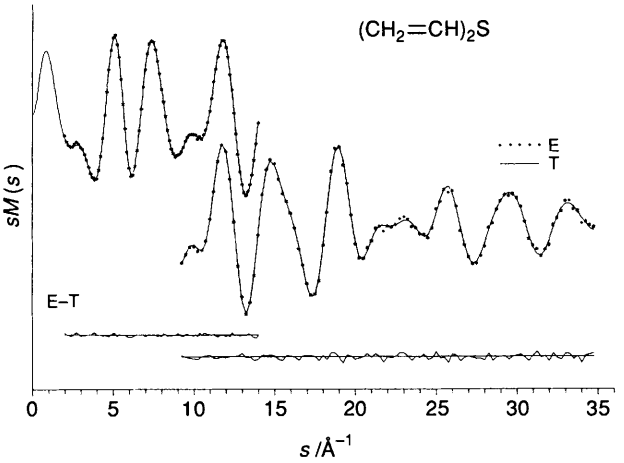

Fig. 4 Molecular intensities $sM(s)$ of DVS: E experimental, T calculated for the model in Table 1, E − T difference curves

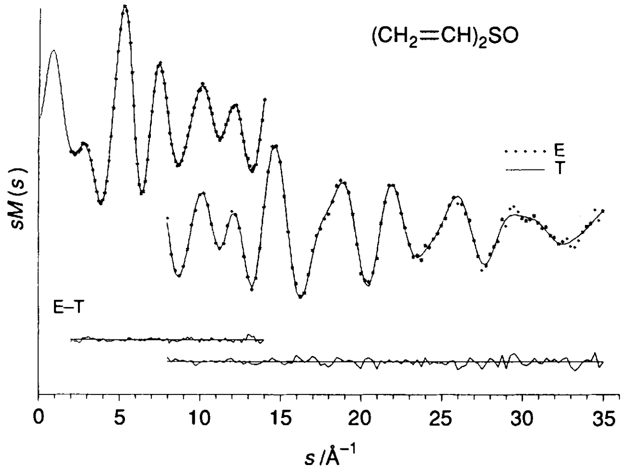

Fig. 5 Molecular intensities $sM(s)$ of DVSO: E experimental, T calculated for the mixture in Table 2, E − T difference curves

program[54] to experimental frequencies of DVS[18,55] and DVSO,[20,45] respectively. Normal coordinate analyses and calculation of amplitudes were repeated later with more reliable refined geometrical parameters. Since low frequencies of torsional vibrations were not available from the experimental spectra, calculated amplitudes of rotation-dependent distances should be treated with caution as preliminary guesses. Amplitudes were grouped according to ranges of the radial distributions, their differences within a group being fixed (*cf.* Tables 1 and 2).

The conformation of molecular models is characterized by the two angles of torsion C–S–C=C (τ, τ') about the S–C(1) and S–C(1′) bonds (Fig. 1). Thus, models of both molecules with $\tau = -\tau'$ have C_s symmetry. The two models of DVSO with (τ, τ') and ($-\tau'$, $-\tau$) are either identical (if $\tau = -\tau'$), or they are enantiomers, indistinguishable by electron diffraction. It is assumed that the S–CH=CH$_2$ moieties are planar and their geometries are identical in asymmetric models and in a mixture of conformers. We did not attempt to determine the individual bond lengths and bond angles of the two vinyl groups. *Ab initio* calculations have shown that the potential minimum in DVS is rather flat in terms of τ and τ', and bond lengths and bond angles are only slightly affected by the choice of different torsional angles.[23] The geometry of DVS models is thus defined by mean bond lengths S–C, C=C, C–H, and the mean non-bonded C···H distance within a vinyl group, bond angles C–S–C and S–C=C, and

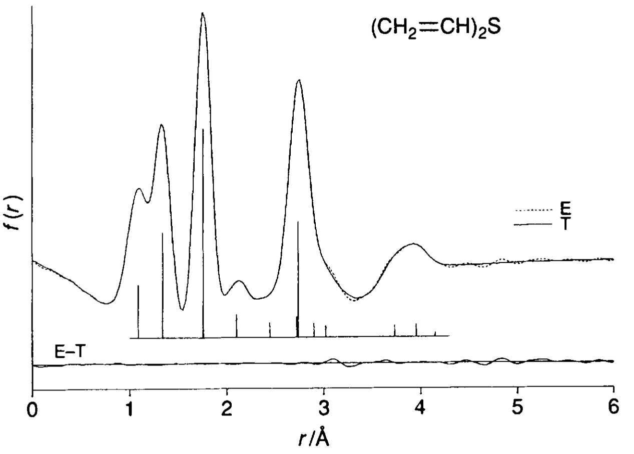

Fig. 6 Experimental (E) and calculated (T) radial distributions $f(r)$ of DVS and the difference curve (E − T). Damping constant a = 0.002 Å^2. Contributions from important internuclear distances are shown.

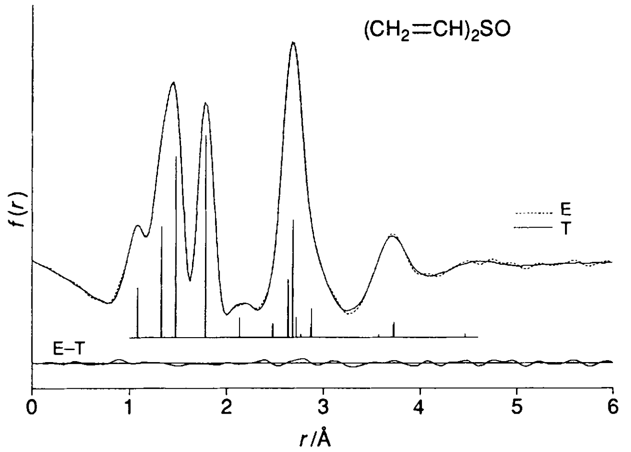

Fig. 7 Experimental (E) and calculated (T) radial distributions $f(r)$ of DVSO and the difference curve (E − T). Damping constant a = 0.002 Å^2. Contributions from important internuclear distances are shown.

torsional angles τ and τ' (Table 1). Bond length S=O and mean bond angle C–S=O are added for DVSO (Table 2). Single conformers and mixtures of two conformers were tested in this structure analysis.

The C–H and S–C bond distances and the independent non-bonded C···H distance are separated in the radial distributions, while contributions of the S=O and C=C bonds overlap in DVSO (Figs. 6 and 7). Bond lengths in both molecules could be well determined and were not affected by the conditions of refinements. The overlap of contributions from the 1,3 non-bonded distances and even some rotation-dependent distances about 2.6 to 3.1 Å, however, led to high parameter correlation (Tables 3 and 4), and made the determination of bond angles and the conformation more difficult. Therefore, refinements were carried out with a very large number of different initial parameter sets and refinement schemes, including mixtures of two conformers. One of the conformers in a mixture was confined to $\tau = \tau'$, or $\tau = -\tau'$. At the beginning, we fixed the torsional angles in the refinement, and changed them in steps of 30°. Models close to $\tau = \tau' = 0°$ have a too short intramolecular H···H contact and were excluded. All models where a C=C bond is in *gauche* position to an S–C or S=O bond, *i.e.* τ or τ' is about 60° or −60°, or, in DVSO only, about 180°, have a contribution about 3.1 Å which is not present in the experimental radial distribution.

The curious oscillations in the experimental radial distribution curves (Figs. 6 and 7) from about 4 Å could not be attributed to any interatomic distances, nor to an error in the background line, nor to flaws at some definite places in the intensity curves. Inverse Fourier transforms of the residual (E − T in Figs. 6 and 7) of the radial distributions indicated that this feature arose from the noise in the experimental molecular intensities (Figs. 4 and 5).

As to DVS, the best agreement with the experimental data was achieved for the (0°, 120°) C_1 conformer alone. Other least-squares minima, nearly as good, appeared for the (0°, 180°) C_s form mixed with about 10% of either (120°, 120°) C_2 or (120°, −120°) C_s. In later stages of the analysis, when backgrounds were better adjusted, the torsional angles of the main conformer were also refined, and both the (0°, 120°) and the (0°, 180°) forms converged to the same conformer (Table 1). The percentage of any other form in the mixture vanished within error limits. The largest variation occurred in the C–S–C angle, which refined to 101.8° now (Table 1), instead of 103.3° with fixed (τ, τ') of (0°, 120°). No other single form or mixture of two conformers could be fitted to the experimental data, unless some of the amplitudes became unrealistically large.

For DVSO, two types of mixtures were found to be consistent with the experimental data. The more abundant is the (120°, −120°) C_s form in both cases, mixed either with about 33% of (0°, −120°) C_1, or with about 17% of (120°, 120°) C_1. The former mixture fits the experimental data slightly better. Table 2 lists the results for this mixture with refined torsional angle of the more abundant symmetric conformer.

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