

# A Microwave and *Ab Initio* Study of the Conformational Properties of Ethyl Vinyl Sulfide

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The microwave spectrum of ethyl vinyl sulfide has been investigated in the 18.0–38.0 GHz spectral region at  $-55^{\circ}\text{C}$ . Two conformers, denoted *anti* and *gauche*, were assigned. The *anti* form was found to be the more stable by  $1.2(5)$  kJ mol $^{-1}$ . Further conformers are at least 3 kJ mol $^{-1}$  less stable than *anti*. *Ab initio* calculations at the 3–21  $G^*$  level were made for four selected conformations. The results obtained for *anti* and *gauche* are in good agreement with the experimental findings.

Ethyl vinyl sulfide (EVS) is an example of a compound containing several axes of internal rotation, and consequently there are many possible conformations. In Fig. 1 four selected conformations are shown. An earlier IR solution study<sup>1</sup> indicated that EVS exists in more than one conformation. Similar findings were made in more recent IR and solution dipole-moment studies.<sup>2–4</sup> No definite conclusions regarding the geometries of the conformations observed in these studies<sup>1–4</sup> could be made, but it was alleged<sup>1–4</sup> that one of them was likely to be the *anti* conformation shown in Fig. 1. This microwave (MW) and *ab initio* study was carried out to establish the correct low-energy conformations of EVS. It was found that the *anti* and *gauche* conformers are the two low-energy forms of the molecule, with *anti*  $1.2(5)$  kJ mol $^{-1}$  more stable.

## Experimental

The sample used in this work was purchased from Tokyo Kasei, Tokyo, Japan. It was purified by gas chromatography before use. The spectrum was studied extensively in the 18.0–33.0 GHz spectral region. Many measurements were also made in the 33.0–38.0 GHz spectral range. The temperature was approximately  $-55^{\circ}\text{C}$  during the spectral measurements and the pressure was about 1 Pa. The spectrometer is an improved version of the one described briefly in Ref. 5 employing klystrons as radiation sources.

## Results

*Ab initio calculations.* The *Ab initio* calculations were performed using the Gaussian 88 program package.<sup>6</sup> The 3–21  $G^*$  basis set<sup>7,8</sup> with d-polarization functions on sulfur<sup>9</sup> was utilized. The computations were made for the four conformations sketched in Fig. 1 with full geometry optimization.

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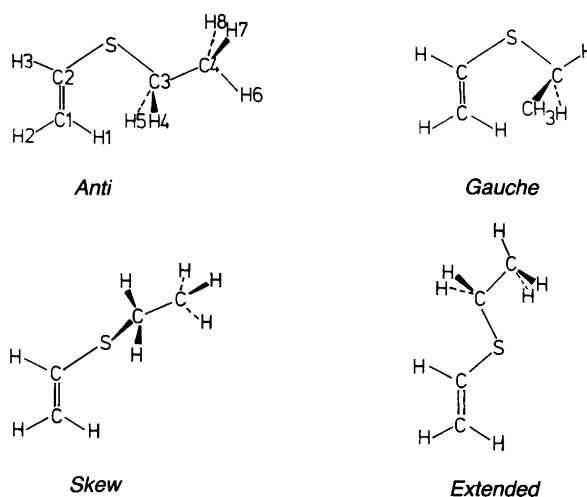


Fig. 1. Four possible conformations of ethyl vinyl sulfide. *Anti* and *gauche* were assigned. *Anti* is  $1.2(5)$  kJ mol $^{-1}$  more stable than *gauche*.

The reason for selecting these four conformations for study by the theoretical calculations are as follows. The closely related compound methyl vinyl sulfide has been investigated thoroughly by MW,<sup>10,11</sup> electron diffraction<sup>11</sup> and quantum-mechanical calculations.<sup>11</sup> The stable form of methyl vinyl sulfide<sup>10,11</sup> was found to be similar to the *anti* conformation of Fig. 1. Rotation around the S–C3 bond by about  $120^{\circ}$  produces the *gauche* conformation (Figs. 1 and 2) which is known to be rather prevalent in other sulfides such as, e.g., ethyl methyl sulfide,<sup>12</sup> where the *gauche* conformer is the more stable, and in ethylthioethyne,<sup>13</sup> where the *gauche* conformer was the only one assigned by MW spectroscopy.<sup>13</sup>

The other notable finding in the case of the methyl vinyl sulfide<sup>11</sup> was the rather strong indication that a *skew* conformer coexists at higher energy (in the order of 4–8 kJ mol $^{-1}$ ), with the more stable heavy-atom planar form (simi-

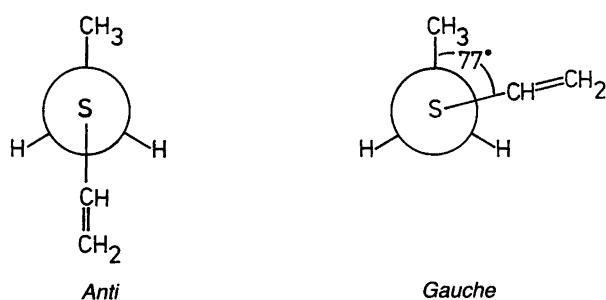


Fig. 2. *Anti* and *gauche* viewed along the S-C3 bond. The C2-S-C3-C4 dihedral angle was found to be 77(2)° from *syn*.

lar to *anti* of Figs. 1 and 2). This was the reason for carrying out *ab initio* computations for the *skew* conformation.

It has been discussed<sup>1-4</sup> whether a conformation similar

Table 1. Optimized structures<sup>a</sup> calculated using the 3-21 G\* basis set.

	<i>Anti</i>	<i>Gauche</i>	<i>Skew</i>
Bond distances/pm			
S-C2	175.6	175.2	176.7
S-C3	181.5	181.6	182.5
C1-C2	131.8	131.8	131.6
C3-C4	154.2	154.0	154.0
C1-H1	107.1	107.1	107.3
C1-H2	107.3	107.3	107.3
C2-H3	107.5	107.5	107.5
C3-H4	108.2	108.2	108.2
C3-H5	108.5	108.3	108.1
C4-H6	108.4	108.5	108.4
C4-H7	108.3	108.2	108.3
C4-H8	108.3	108.2	108.3
Bond angles/°			
C1-C2-S	128.9	129.6	123.4
C2-S-C3	103.2	104.0	100.3
S-C3-C4	109.2	113.6	109.5
H1-C1-C2	123.4	123.4	121.2
H2-C1-C2	120.3	120.3	121.1
H3-C2-C1	120.0	119.8	120.7
H4-C3-S	109.3	109.4	109.1
H5-C3-S	109.3	104.8	109.1
H6-C4-C3	109.7	110.5	109.9
H7-C4-C3	110.8	110.1	110.7
H8-C4-C3	110.8	111.1	110.7
Dihedral angles <sup>b</sup> /°			
C2-S-C3-H4	59.4	-48.9	55.6
C2-S-C3-H5	-59.4	-163.6	-63.0
S-C3-C4-H6	180.0	180.4	180.0
S-C3-C4-H7	60.3	60.6	60.3
S-C3-C4-H8	-60.3	-59.3	-60.2
S-C2-C1-H1	0.0	-0.8	-4.0
S-C2-C1-H2	180.0	179.1	175.5
H3-C2-C1-H2	0.0	0.0	-0.9
C1-C2-S-C3	0.0	6.2	133.4
C2-S-C3-C4	180.0	76.3	176.0

<sup>a</sup>Atom numbering given in Fig. 1. <sup>b</sup>From *syn*.

Table 2. Selected molecular parameter obtained in the *ab initio* calculations with the 3-21 G\* basis set.

	<i>Anti</i>	<i>Gauche</i>	<i>Skew</i>
Energy relative to <i>anti</i> <sup>a</sup> /kJ mol <sup>-1</sup>	0.0	2.1	1.7
Rotational constants/MHz			
A	9017.65	5454.73	14190.86
B	2325.32	3139.03	1880.73
C	1891.80	2242.13	1762.64
Dipole moments <sup>b</sup> /10 <sup>-30</sup> C m			
$\mu_a$	0.62	1.56	0.71
$\mu_b$	4.72	4.48	5.31
$\mu_c$	0.0	1.19	0.71

<sup>a</sup>The total energy of *anti* was calculated to be -550.907649 hartree. <sup>b</sup>Components of the total dipole moment along the principal inertial axes calculated using the theoretical structures shown in Table 1.

to the *extended* form of Fig. 1 might be stable. Computations were thus made for this conformation as well.

Selected results of the computations are shown in Tables 1 and 2. It is seen in Table 2 that the *anti* conformer is predicted to be the more stable, with the *gauche* and *skew* forms approximately 2 kJ mol<sup>-1</sup> less stable. The *extended* conformation (not included in Table 2) was predicted to be a saddle point with an energy 4.6 kJ mol<sup>-1</sup> above that of the *anti* conformer. The *extended* conformation is thus not predicted to be a stable form of EVS.

*Microwave spectrum and assignment of the anti conformer.* The MW spectrum of EVS is very dense, with absorption lines occurring every few MHz throughout the entire MW spectral range. The intensities of the strongest transitions, which turned out to be high-*J* *b*-type *Q*-branch lines of both *anti* and *gauche*, are roughly 4 × 10<sup>-7</sup> cm<sup>-1</sup> at -55 °C.

Searches were first made for the *anti* conformer's high-*J* *b*-type *Q*-lines owing to the fact that both the theoretical calculations reported above (Table 2) as well as the bond-moment calculations,<sup>14</sup> which were made subsequently and not reported in detail herein, predict a large  $\mu_b$ . Moreover, in the case of the closely related molecule methyl vinyl sulfide<sup>11</sup> the similar conformation was found to predominate.

The trial spectrum was predicted using the plausible, experimentally based structure reported below in Table 7. The *b*-type *Q*-branch lines in question were soon found as were the low-*J* *b*-type *R*-branch transitions. The assignments were then gradually extended to high-*J* *P*- and *R*-branch lines of the *b*-type variety. The assignments of these transitions were greatly facilitated by their rapid Stark effects produced by a small component of the dipole moment along the *a*-inertial axis. The maximum value of *J* was 79 (Table 3). Higher-*J* transitions were searched for, but they could not be identified, presumably because of insufficient intensities. Finally, the much weaker low-*J* *a*-type *R*-branch

Table 3. Selected transitions of the ground-state MW spectrum of the *anti* conformer of ethyl vinyl sulfide.

Transition	Observed frequency/ MHz	Obs. - calc. frequency/ MHz	Centrifugal distortion/MHz	
			Total	Sextic
2 <sub>2,1</sub> ← 1 <sub>1,0</sub>	28 462.28	0.00	-0.31	
5 <sub>1,5</sub> ← 4 <sub>0,4</sub>	24 905.37	0.02	-0.06	
5 <sub>2,3</sub> ← 4 <sub>2,2</sub>	21 816.29	-0.01	-0.19	
6 <sub>1,6</sub> ← 5 <sub>1,5</sub>	24 174.43	-0.01	-0.23	
6 <sub>3,3</sub> ← 5 <sub>3,2</sub>	25 854.59	-0.02	-0.22	
7 <sub>1,7</sub> ← 6 <sub>0,6</sub>	31 286.28	0.03	-0.18	
7 <sub>3,4</sub> ← 7 <sub>2,5</sub>	31 751.20	0.11	-0.70	
9 <sub>1,8</sub> ← 8 <sub>2,7</sub>	27 189.48	-0.02	-2.05	
9 <sub>1,8</sub> ← 9 <sub>0,9</sub>	21 158.09	0.06	-1.67	
9 <sub>2,8</sub> ← 9 <sub>1,9</sub>	30 795.34	0.00	-0.97	
11 <sub>1,10</sub> ← 11 <sub>0,11</sub>	28 703.60	0.03	-3.36	
12 <sub>3,9</sub> ← 12 <sub>2,10</sub>	26 468.62	-0.05	0.96	
13 <sub>2,11</sub> ← 13 <sub>1,12</sub>	24 011.86	0.04	-4.02	
14 <sub>2,12</sub> ← 14 <sub>1,13</sub>	27 058.30	0.03	-5.96	
15 <sub>2,13</sub> ← 15 <sub>1,14</sub>	30 591.14	0.04	-8.30	
16 <sub>3,13</sub> ← 16 <sub>2,14</sub>	26 413.61	-0.06	-2.52	
17 <sub>3,14</sub> ← 17 <sub>3,14</sub>	27 764.62	-0.01	-5.11	
18 <sub>4,15</sub> ← 17 <sub>5,12</sub>	18 388.28	0.05	-6.43	
19 <sub>3,16</sub> ← 19 <sub>2,17</sub>	32 375.49	0.08	-13.05	
21 <sub>4,18</sub> ← 20 <sub>5,15</sub>	29 703.41	0.01	-9.07	
24 <sub>6,18</sub> ← 23 <sub>7,17</sub>	20 173.20	0.01	-19.58	0.01
25 <sub>6,19</sub> ← 24 <sub>7,18</sub>	25 391.82	0.00	-27.12	0.01
28 <sub>7,21</sub> ← 27 <sub>8,20</sub>	24 470.44	-0.03	-31.22	0.02
31 <sub>8,24</sub> ← 30 <sub>9,21</sub>	23 728.61	-0.08	-34.88	0.04
32 <sub>8,25</sub> ← 31 <sub>9,22</sub>	28 601.99	0.03	-44.54	0.05
35 <sub>9,26</sub> ← 34 <sub>10,25</sub>	28 313.41	0.07	-54.40	0.07
39 <sub>10,28</sub> ← 38 <sub>11,27</sub>	27 876.30	-0.03	-62.62	0.11
39 <sub>10,29</sub> ← 38 <sub>11,28</sub>	32 766.10	0.03	-77.13	0.12
Coalescing <i>P</i> -branch transitions <sup>b</sup>				
18 <sub>9</sub> ← 18 <sub>9</sub>	31 654.41	-0.08	-35.27	
23 <sub>10</sub> ← 24 <sub>9</sub>	23 040.33	0.03	-36.79	-0.01
26 <sub>11</sub> ← 27 <sub>10</sub>	23 335.50	-0.02	-46.67	-0.02
30 <sub>13</sub> ← 31 <sub>12</sub>	32 895.17	-0.04	-88.67	-0.04
34 <sub>14</sub> ← 35 <sub>13</sub>	28 697.55	0.02	-96.04	-0.07
37 <sub>15</sub> ← 38 <sub>14</sub>	28 978.83	-0.11	-113.87	-0.11
41 <sub>16</sub> ← 42 <sub>15</sub>	24 743.77	-0.11	-118.35	-0.18
46 <sub>18</sub> ← 47 <sub>17</sub>	29 799.04	0.01	-178.60	-0.31
51 <sub>19</sub> ← 52 <sub>18</sub>	21 017.97	-0.04	-158.13	-0.52
55 <sub>21</sub> ← 56 <sub>20</sub>	30 587.95	-0.03	-261.62	-0.75
59 <sub>22</sub> ← 60 <sub>21</sub>	26 327.09	0.08	-262.40	-1.06
71 <sub>26</sub> ← 72 <sub>25</sub>	27 327.02	0.00	-400.70	-2.65
Coalescing <i>R</i> -branch transitions <sup>b</sup>				
49 <sub>14</sub> ← 48 <sub>15</sub>	21 680.70	0.01	-76.46	0.39
53 <sub>15</sub> ← 52 <sub>16</sub>	26 092.67	0.04	-109.61	0.57
57 <sub>16</sub> ← 56 <sub>17</sub>	30 506.33	-0.07	-149.85	0.82
62 <sub>18</sub> ← 61 <sub>19</sub>	25 127.48	-0.08	-138.88	1.25
65 <sub>19</sub> ← 64 <sub>20</sub>	24 813.93	0.08	-148.35	1.59
69 <sub>20</sub> ← 68 <sub>21</sub>	29 193.98	0.08	-201.53	2.14
79 <sub>23</sub> ← 78 <sub>24</sub>	32 923.25	-0.01	-296.18	4.21

<sup>a</sup>±0.10 MHz. <sup>b</sup>The  $K_{-1}$  doublets coalesce for high values of  $J$  and  $K_{-1}$ . Subscripts on the  $J$  quantum number refer to  $K_{-1}$ .

Table 4. Spectroscopic constants<sup>a,b</sup> of the *anti* conformer of ethyl vinyl sulfide in the ground and first excited state of the lowest torsional vibration.

Vibrational state	Ground	First excited torsion
No. of transitions	218	114
R.m.s. deviation/MHz	0.052	0.069
<hr/>		
$A_e$ /MHz	8 849.352 9(21)	8 780.234 1(43)
$B_e$ /MHz	2 369.860 91(56)	2 367.828 6(12)
$C_e$ /MHz	1 914.526 22(72)	1 916.095 6(14)
$\delta_J$ /kHz	0.460 8(26)	0.448 9(38)
$\Delta_{JK}$ /kHz	-1.875(16)	-2.248(26)
$\Delta_K$ /kHz	22.319(11)	20.005(20)
$\delta_J$ /kHz	0.126 20(78)	0.107 4(14)
$\delta_K$ /kHz	0.878(41)	1.476(73)
$\Phi_J$ /Hz	0.000 228 2(66)	0.001 019(36)
$I_a + I_b - I_c$ / <sup>c</sup> 10 <sup>-20</sup> u m <sup>2</sup>	6.390 919(62)	7.239 72(11)

<sup>a</sup>A-reduction,  $I'$ -representation.<sup>15</sup> <sup>b</sup>Uncertainties represent one standard deviation. <sup>c</sup>Further sextic centrifugal distortion constants preset at zero. <sup>d</sup>Conversion factor 505 379 × 10<sup>-25</sup> u m<sup>2</sup>.

transitions were identified owing to the fact that their spectral positions could now be very accurately predicted. A portion of the spectrum is listed in Table 3.\* A total of about 240 transitions were measured in the 18.0–33.0 GHz spectral region, 218 of which were used to determine the spectroscopic constants reported in Table 4. Only one of the sextic centrifugal distortion constants was allowed to be varied in the least-squares fit. This was sufficient in order to get a fit with a root mean-square deviation of the same order of magnitude as the experimental uncertainty of ±0.10 MHz.

It is seen in Table 4 that  $I_a + I_b - I_c = 6.390919(62) \times 10^{-20}$  u m<sup>2</sup>. This value is typical for a molecule that possesses a symmetry plane and four sp<sup>3</sup>-hybridized out-of-plane hydrogens.<sup>16</sup> For example, ethyl vinyl ether has been investigated thoroughly by MW spectroscopy<sup>17</sup> and found to prefer a conformation identical with the *anti* conformer of Fig. 1. The value of  $I_a + I_b - I_c$  is  $6.46 \times 10^{-20}$  u m<sup>2</sup> for this molecule,<sup>17</sup> a value very close to that seen for the *anti* conformer of the title molecule.

Many attempts were made to resolve the Stark effect of low- and intermediate- $J$  transitions in order to determine the dipole moment of the *anti* conformer of EVS, but we were not able to find lines suitable for quantitative studies owing to either weakness of the transitions in question or crowdedness of the spectrum.

*Vibrationally excited state of anti.* According to the *ab initio* calculations reported above, the two lowest vibrations are torsional vibrations predicted at 93 and 153 cm<sup>-1</sup>,

\*The complete spectra are available from the authors upon request, or from The Microwave Data Center, National Institute of Standards and Technology, Molecular Spectroscopy Division, Rm. B268/Bldg. 221, Gaithersburg, MD 20899, U.S.A.

respectively. (These values are not included in Table 1 or 2.) Relatively strong spectra were thus expected for the first excited states of these two modes. As seen in Table 4, the first excited state of one such low-frequency vibration was assigned. Relative intensity measurements<sup>18</sup> yielded  $108(20) \text{ cm}^{-1}$  for this vibration, in good agreement with the theoretical value of  $93 \text{ cm}^{-1}$ . This fundamental is presumed to be the lowest torsional vibration. This is supported by the fact that  $I_a + I_b - I_c$  increases upon substitution (Table 4), which is characteristic for out-of-plane vibrations.<sup>19</sup> The second excited state of this mode was searched for next, but no definite assignments could be made.

The first excited state of the second lowest torsional vibration predicted by the theoretical calculations to have a fundamental frequency of  $153 \text{ cm}^{-1}$  was then searched for. It is believed that its strong *b*-type *Q*-branch transitions were assigned, but they could not be well fitted to a centrifugally distorted rigid rotor using Watson's Hamiltonian,<sup>15</sup> presumably because of higher-order rotation-vibration interactions. Twelve tentatively assigned transitions yielded  $A - C = 6995.3(5) \text{ MHz}$  and  $\kappa = -0.86879$  with a root mean-square deviation as large as  $4.49 \text{ MHz}$ . None of the much less intense low-*J* *b*-type *R*-branch lines could be assigned for this vibrationally excited state.

The third lowest fundamental vibration is predicted to have a frequency of  $186 \text{ cm}^{-1}$  according to the *ab initio* computations discussed above. This should be the lowest in-plane vibration. Searches were made for the first excited state of this mode, but it was not found.

*Assignment of the ground vibrational state of the gauche conformer.* After the assignment of *anti* was completed a very large number of lines which were too strong to be ascribed to vibrationally excited states of *anti* remained unassigned in the spectrum. According to the theoretical predictions shown in Table 2 as well as to bond-moment computations,<sup>14</sup>  $\mu_b$  for *gauche* was predicted to be about as large as  $\mu_b$  for the *anti* conformer. The theoretical computations also predict (Table 1) the C2-S-C3-C4 dihedral angle to be approximately  $16^\circ$  larger than the ordinary  $60^\circ$  from *syn* angle. With this in mind, trial rotational constants were predicted using the structural data in Table 7 below. The strongest *b*-type *Q*-branch transitions of the *gauche* form were then searched for and identified after some trials. The *b*-type *R*-branch transitions were harder to find, because they were much weaker than the *Q*-branch lines. Only *R*-branch transitions with  $J \leq 8$  were assigned because *b*-type *R*-branch transitions involving higher *J* are very weak and could not be identified. Some weak <sup>a</sup>*R*-transitions were finally assigned. A total of about 160 transitions were ultimately assigned for the ground vibrational state of the *gauche* conformer in the 18.0–38.0 GHz spectral region with a maximum *J* of 32. A portion of the spectrum is listed in Table 5, and the spectroscopic constants calculated from 149 selected transitions are shown in Table 6.

Attempts to measure the dipole moment for this con-

Table 5. Selected ground-state transitions of the *gauche* conformer of ethyl vinyl sulfide.

Transition	Observed frequency/ MHz	Obs. - calc. frequency/ MHz	Centrifugal distortion/ MHz
3 <sub>3,1</sub> ← 2 <sub>2,0</sub>	29 668.45	0.08	-0.35
4 <sub>2,3</sub> ← 3 <sub>1,2</sub>	27 030.61	0.03	-0.09
5 <sub>0,5</sub> ← 4 <sub>0,4</sub>	24 430.30	0.08	-0.37
5 <sub>0,5</sub> ← 4 <sub>1,4</sub>	24 034.83	0.05	-0.49
6 <sub>1,5</sub> ← 5 <sub>1,4</sub>	32 828.47	-0.09	-1.16
6 <sub>3,3</sub> ← 5 <sub>2,3</sub>	34 872.94	0.10	-2.13
7 <sub>0,7</sub> ← 6 <sub>1,6</sub>	33 296.03	-0.05	-1.00
6 <sub>5,1</sub> ← 6 <sub>4,2</sub>	23 246.28	0.11	-0.96
7 <sub>3,5</sub> ← 7 <sub>2,6</sub>	18 827.53	0.00	-0.84
7 <sub>6,1</sub> ← 7 <sub>5,2</sub>	28 672.34	0.01	-2.52
8 <sub>5,4</sub> ← 8 <sub>4,5</sub>	23 338.80	-0.06	0.68
9 <sub>2,8</sub> ← 9 <sub>1,9</sub>	28 489.42	-0.02	-2.96
10 <sub>3,8</sub> ← 10 <sub>4,7</sub>	24 253.63	-0.01	-2.85
11 <sub>3,9</sub> ← 11 <sub>2,10</sub>	30 936.75	-0.03	-6.43
12 <sub>7,5</sub> ← 12 <sub>6,6</sub>	31 754.54	-0.02	8.46
14 <sub>5,9</sub> ← 14 <sub>4,10</sub>	20 046.68	0.04	-19.77
15 <sub>5,11</sub> ← 15 <sub>4,12</sub>	35 372.21	0.04	-16.95
16 <sub>8,8</sub> ← 16 <sub>7,9</sub>	33 498.54	-0.02	36.17
18 <sub>7,11</sub> ← 18 <sub>6,12</sub>	22 275.65	-0.03	-5.88
20 <sub>7,13</sub> ← 20 <sub>6,14</sub>	28 466.33	-0.06	-80.89
22 <sub>9,13</sub> ← 22 <sub>8,14</sub>	28 098.75	-0.01	70.73
24 <sub>10,14</sub> ← 24 <sub>9,15</sub>	32 571.12	-0.05	136.63
26 <sub>9,17</sub> ← 26 <sub>8,18</sub>	37 447.70	0.02	-221.94
27 <sub>11,16</sub> ← 27 <sub>10,17</sub>	34 738.53	-0.04	184.40
29 <sub>11,18</sub> ← 29 <sub>10,19</sub>	33 385.23	-0.01	-43.96
31 <sub>12,19</sub> ← 31 <sub>11,20</sub>	35 571.45	0.10	86.63
32 <sub>12,20</sub> ← 32 <sub>11,21</sub>	36 564.07	0.01	-118.51

<sup>a</sup>±0.10 MHz.

former met with the same obstacles encountered for the *anti* form.

*Vibrationally excited states of gauche.* As seen in Table 6, two vibrationally excited states have been assigned for the *gauche* conformer. Relative intensity measurements<sup>18</sup> yielded  $128(15)$  and  $154(20) \text{ cm}^{-1}$ , respectively, for these two fundamental vibrational frequencies. According to the *ab initio* computations referred to above, the two lowest vibrational modes largely associated with the torsions around the two C-S bonds were calculated to be  $121$  and  $155 \text{ cm}^{-1}$ , respectively. There is thus good agreement between the theoretical and experimental values. The third and fourth lowest vibrational frequencies occur at  $206$  and  $293 \text{ cm}^{-1}$  according to the *ab initio* calculations. Searches for excited states of these vibrations were unsuccessful, as were those made for the second excited states of the two vibrations reported in Table 6.

*Energy difference between anti and gauche.* The internal energy difference between the *anti* and *gauche* forms was determined by relative intensity measurements, observing the precautions of Ref. 18. Strong lines apparently not perturbed by neighbouring transitions were selected. The statistical weight of *gauche* was taken to be 2, while a weight

Table 6. Spectroscopic constants<sup>a,b</sup> for the *gauche* conformer of ethyl vinyl sulfide.

Vibrational state	Ground	First excited lowest torsional vibration	First excited second torsional vibration
No. of transitions	149	108	87
R.m.s. deviation/MHz	0.049	0.067	0.055
$A_v$ /MHz	5 409.198 2(26)	5 445.122 3(55)	5 442.187 5(40)
$B_v$ /MHz	3 201.021 1(24)	3 175.162 8(52)	3 170.723 4(37)
$C_v$ /MHz	2 257.910 3(24)	2 249.876 7(51)	2 252.600 7(37)
$\Delta_J$ /kHz	2.145(27)	2.457(55)	1.998(38)
$\Delta_{JK}$ /kHz	-7.104(11)	-8.105(18)	-6.973(18)
$\Delta_K$ /kHz	10.931(27)	12.946(47)	11.173(48)
$\delta_J$ /kHz	0.791 7(10)	0.859 6(17)	0.775 7(16)
$\delta_K$ /kHz	0.801(10)	0.710(17)	0.766(16)

<sup>a,b</sup>Comments as for Table 4.

of 1 was assumed for *anti*. The  $\mu_b$  dipole moment components shown in Table 2 were used. In this manner, an internal energy difference of 1.2(5) kJ mol<sup>-1</sup> was determined. *Anti* is the more stable conformer. The uncertainty represents one standard deviation. The uncertainties of the dipole moment components have been taken into account in assessing the uncertainty of the energy difference.

*Searches for further conformations.* The assignments reported above include all the strongest lines of the spectrum, as well as a majority of intermediate intensity lines and many weak transitions too. The theoretical computations (Table 2) indicate that the *skew* conformation of Fig. 1 should be stable and have an energy close to those of *anti* and *gauche*. The  $\mu_b$  dipole moment predicted for the hypothetical *skew* conformation (Table 2) is large. The statistical weight is 2 for *skew* with respect to *anti*. If *skew* were present in high concentrations, it should thus have a strong MW spectrum. If the energy difference were as small as about 1.7 kJ mol<sup>-1</sup> (Table 2), its spectrum should be as strong as that of *anti*. This was clearly not observed. Extensive searches were next made for the hypothetical *skew* conformation amongst the unassigned intermediate-intensity lines, with, however, a negative result. The fact that none of the strongest transitions was unassigned leads us to conclude that the *skew* conformer is considerably less stable than the *anti*. Thus, intensity considerations strongly indicate that the *skew* form is at least 3 kJ mol<sup>-1</sup> less stable than the *anti*. This estimate is conservative and should be taken as a lower limit. This finding parallels the one made for methyl vinyl sulfide,<sup>11</sup> where a *skew* form was estimated to be 4–8 kJ mol<sup>-1</sup> less stable than the conformer that is similar to the *anti* form.

Our explanation for the remaining unassigned intermediate intensity and weak lines is that most, or perhaps all, of them belong to vibrationally excited states of the *anti* or *gauche* conformer.

*Structure.* The three rotational constants determined for each *anti* or *gauche* form furnish insufficient information

for a full structure determination of the two rotamers. Assumptions have to be made. In the case of the *anti* conformer, the C2–S–C3 angle was fitted in steps of 0.5°, while the remaining structural parameters shown in Table 7 were kept fixed. These fixed parameters were taken from recent, accurate structural studies,<sup>20</sup> and are perhaps slightly more accurate than the *ab initio* values of Table 1. It

Table 7. Plausible molecular structure<sup>a</sup> of the *anti* and *gauche* conformers of ethyl vinyl sulfide.

Structural parameters kept fixed for both rotamers <sup>b</sup>					
Bond	distances/pm	Angles/°	Dihedral angles/°		
S–C2	174.7	C1–C2–S	127.5	C2–S–C3–H	60.0°
S–C3	180.7	H–C1–C2	121.1	S–C3–C4–H6	180.0°
C1–C2	133.9	S–C3–H	109.47	S–C3–C4–H7,8	60.0°
H–C=	108.5	C3–C4–H	109.47		
Structural parameters different for <i>anti</i> and <i>gauche</i>					
Angles/°	Dihedral angles/°				
S–C3–C4	110.0 ( <i>anti</i> )	C1–C2–S–C3	0.0° ( <i>anti</i> )		
S–C3–C4	114.5 ( <i>gauche</i> )	C1–C2–S–C3	6.0° ( <i>gauche</i> )		
Fitted structural parameters					
C2–S–C3	103.0 ( <i>anti</i> ) <sup>d</sup>	C1–C2–S–C3	77° ( <i>gauche</i> )		
Rotational constants for <i>anti</i> /MHz					
	Observed	Calculated <sup>e</sup>	Difference (%)		
A	8849.35	8829.17	0.22		
B	2369.86	2368.76	0.05		
C	1914.53	1913.08	0.04		
Rotational constants for <i>gauche</i> /MHz					
	Observed	Calculated <sup>e</sup>	Difference (%)		
A	5409.20	5415.19	0.11		
B	3201.02	3235.89	1.09		
C	2257.91	2279.19	0.94		

<sup>a</sup>See text. <sup>b</sup>The vinyl group was assumed to be planar for both conformers. <sup>c</sup>From *syn*. <sup>d</sup>This value was used for both rotamers. <sup>e</sup>Calculated using the structural parameters of this table.

is seen in Table 7 that the C2-S-C3 angle is found to be 13.0(5)° (the uncertainty represents one standard deviation), a value close both to the *ab initio* value (Table 1) and the electron diffraction value of 104.5(5)° for methyl vinyl sulfide.<sup>11</sup> The rotational constants are very well reproduced, as can be seen in Table 7.

The C2-S-C3-C4 dihedral angle was fitted for the *gauche* conformer. The C2-S-C3 angle was assumed to be 103.0° for this rotamer. Results from the *ab initio* calculations of Table 1 were utilized. It is seen in this table that the S-C3-C4 angle increases by about 4.5° in the *gauche* form as compared with the *anti* form. Moreover, the C1-C2-S-C3 dihedral angle is seen to be about 6° from planarity in the *gauche* form. With these two structural changes incorporated, the fit of the C2-S-C3-C4 dihedral angle was carried out in steps of 1°. The best agreement was found with C2-S-C3-C4 = 77° from *syn* as indicated in Table 7 and Fig. 2. The uncertainty limit (three standard deviations) of this angle is judiciously estimated to be 2°. This value of 77(2)° compares very well with 76.3° found in the theoretical computations reported in Table 1. The agreement between the observed and calculated rotational constants (Table 7) is slightly worse in this case than in the case of *anti*. It is also noted that the rotational constants obtained by *ab initio* computations (Table 2), based on the structures of Table 1, are not in such good agreement with the experimental constants as the rotational constants calculated (Table 7) using the structure of Table 7.

## Discussion

The fact that EVS takes *anti* and *gauche* conformers as the most stable rotamers of the molecule is similar to what was found for ethyl methyl sulfide,<sup>12</sup> but at variance with ethylthioethyne, where only the *gauche* conformer was identified.<sup>13</sup> Both ethyl methyl sulfide<sup>12</sup> and ethylthioethyne<sup>13</sup> prefer *gauche* conformers as their most stable forms, while the *anti* form is more stable in the case of the title compound. Perhaps the reason why the *anti* form is preferred to *gauche* in EVS is steric repulsion between the methyl and vinyl groups. The unusually large C2-S-C3-C4 dihedral angle of 77(2)° instead of the normal 60° separates the methyl and vinyl groups from each other. However, this 17° increase of the dihedral angle presumably costs energy, resulting in the fact that the *anti* form becomes more stable than *gauche* by 1.2(5) kJ mol<sup>-1</sup>.

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