

partial melting, as a prelude to complete disappearance of a crystalline phase, throughout the accessible range of  $n$  within which pure compounds are available. This assertion is, of course, substantiated by evidence on the narrow melting ranges ( $\leq 1^\circ$  which is  $\ll \Delta T$ ) for the  $n$ -paraffin hydrocarbons.<sup>26</sup> For sufficiently large  $n$  the molecular crystals stable at low temperatures should, according to eq. 17, undergo partial premelting

(26) W. F. Seyer, R. F. Peterson, and J. L. Keays, *J. Am. Chem. Soc.*, **66**, 179 (1944).

to "crystallites" having a dimension  $\zeta < n$ , assuming of course that equilibrium prevails. The value of  $n$  required may, however, be very large (e.g.,  $> 10^4$ ). This predicted transformation in advance of final melting establishes an essential connection between the melting of pure chain homologs of finite  $n$  and the limiting case  $n = \infty$ .

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## Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of 1,2,5-Thiadiazole<sup>1a</sup>

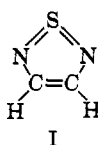
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The microwave spectra of four isotopic species of 1,2,5-thiadiazole have been assigned and analyzed. The value of the inertial defect indicates that the molecule is planar in the ground vibrational state. Moments of inertia obtained from the analyses of the spectra together with the center of mass condition give the following structural parameters: S-N =  $1.631 \pm 0.003$  Å., C-N =  $1.328 \pm 0.003$  Å., C-C =  $1.420 \pm 0.003$  Å., C-H =  $1.079 \pm 0.003$  Å.,  $\angle$ NSN =  $99^\circ 33' \pm 10'$ ,  $\angle$ CCN =  $113^\circ 46' \pm 10'$ ,  $\angle$ CCH =  $126^\circ 14' \pm 10'$ . The dipole moment is  $1.565 \pm 0.015$  D. Quadrupole coupling constants are  $|\chi_{AA}| < 1$  Mc. and  $\chi_{CC} - \chi_{BB} = 5.2 \pm 0.3$  Mc. These were obtained by a direct comparison of two corresponding transitions of thiadiazole and diazine, a molecule whose quadrupole coupling constants have previously been determined from microwave data. An analysis of the hyperfine structure for high  $J$   $Q$ -branch transitions using a limiting expression for the splittings confirmed the value and sign of  $\chi_{CC} - \chi_{BB}$ . Relative intensities of the components of the hyperfine multiplets are consistent with the assumption that the molecule is planar in the ground-vibrational state. Quadrupole energies for a molecule having two equivalent nuclei of spin 1 are tabulated.

### I. Introduction

1,2,5-Thiadiazole, a five-membered heterocyclic ring compound, was initially prepared and identified by Carmack, Weinstock, and Shew.<sup>2a,b</sup> These authors conducted an extensive study of the chemical and physical properties of this compound and its substituted derivatives, and on the basis of this study proposed the structure, I, as best representing the properties ob-



served. On considering the known isoelectronic relationship between thiophene and benzene and between quinoxaline and 2,1,3-benzothiadiazole, they predicted a close chemical relationship between 1,2,5-thiadiazole and pyrazine since these are also isoelectronic. Chemical evidence supported these predictions and indicated that the ring does not possess purely dienoid character. Similarity between aromatic compounds containing the -CH=CH- group and those in which the vinyl group has been replaced by -S- had been noted previously.<sup>3</sup> Assuming that sulfur can expand its valence shell to ten electrons,<sup>4</sup> all resonance forms of the vinyl group become possible for the sulfur atom. For this reason they investigated properties dependent on mobile electrons, comparing the ultraviolet spectra and polarographic behavior of 1,2,5-thiadiazole with that of pyrazine. On the basis of the experimental results, these authors proposed the structure already noted.

(1) (a) This research was supported by a grant from the National Science Foundation. (b) Recipient, du Pont Teaching Assistant Award 1961-1962. (c) Alfred P. Sloan Foundation Fellow.

(2) (a) M. Carmack, L. M. Weinstock, and D. Shew, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959, p. 37P. (b) L. M. Weinstock, *Dissertation Abstr.*, **19**, 3136 (1959).

(3) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(4) L. Pauling and V. Shomaker, *J. Am. Chem. Soc.*, **61**, 1773 (1939).

Preliminary electron diffraction results of Bonham and Momany<sup>5</sup> likewise suggested that the system is highly aromatic. Their work indicated that the C-C bond distance is nearly that of benzene and that the C-N bond distance is considerably shorter than the structure proposed by Carmack, Weinstock, and Shew would imply. It should be noted that the experimental uncertainties in the measurement of these two parameters were rather large. Their results indicate that the ring is planar to within 0.1 Å.

The present work is concerned with the determination of the structure, dipole moment, and quadrupole coupling constants of 1,2,5-thiadiazole from its microwave spectrum.

### II. Experimental

Samples of C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>S and C<sub>2</sub>D<sub>2</sub>N<sub>2</sub>S were kindly provided by M. Carmack. These were purified by gas chromatography. A proton nuclear magnetic resonance spectrum (60 Mc.) was run in tetramethylsilane, giving a chemical shift of 516.7 c.p.s. to low field with respect to the solvent and evidence of two equivalent protons.

### III. Microwave Spectrum and Dipole Moment

A Stark modulated spectrometer (100 kc.) was used for measuring the rotational transitions of five isotopic species of 1,2,5-thiadiazole in the region 8 to 30 kMc. The species C<sub>2</sub>H<sub>2</sub>N<sub>2</sub><sup>34</sup>S (4.22%), C<sup>13</sup>CH<sub>2</sub>N<sub>2</sub>S (2.22%), and C<sub>2</sub>H<sub>2</sub>N<sup>15</sup>NS (0.73%) were observed in natural abundance.

Hyperfine structure arising from quadrupole effects was partially resolvable for the C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>S and C<sub>2</sub>D<sub>2</sub>N<sub>2</sub>S species. The Hamiltonian for the interaction of several quadrupolar nuclei with the molecular field may be expressed as

$$H_Q = \sum_i \frac{eQ_i(\partial^2 V/\partial z^2)_i}{2J(2J-1)I_i(2I_i-1)} \left[ 3(I_i \cdot J)^2 + \frac{3}{2}(I \cdot J) - I_i^2 \cdot J^2 \right] \quad (1)$$

where  $(\partial^2 V/\partial z^2)_i$  represents the second derivative of the electrostatic potential with respect to a space-fixed

(5) R. A. Bonham and F. A. Momany, *ibid.*, **83**, 4475 (1961).

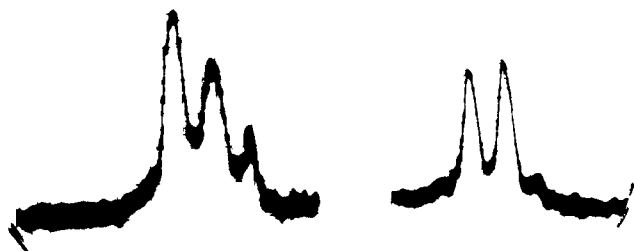


Fig. 1.—Oscilloscope traces of  $7_{43} \leftarrow 7_{44}$  and  $9_{54} \leftarrow 9_{55}$  transitions of  $C_2H_2N_2S$ . Theoretical intensity ratios arising from spin effects are 1:8:6 and 3:8:10, respectively.

$z$ -axis evaluated at the center of the  $i$ th nucleus. For molecules having two identical quadrupolar nuclei, the appropriate vector coupling scheme is  $I_1 + I_2 = I$ ;  $I + J = F$ . It has been shown<sup>6</sup> that if these two nuclei are furthermore symmetrically located in the molecule and  $I_1 = I_2 = 1$  (or  $3/2$ ), the resulting first-order secular equation may be solved explicitly. The exact expressions for the quadrupole energies are given in Table I. These solutions rapidly coalesce as  $J$  increases, and even for relatively low  $J$  the nine sublevels induced by the quadrupole perturbation reduce to three. The energies in this limit are also given in Table I. Since the  $\Delta F$

TABLE I  
QUADRUPOLE ENERGIES FOR A MOLECULE HAVING  
TWO EQUIVALENT NUCLEI OF SPIN 1; SPIN WEIGHTS OF  
ROTATIONAL STATES WITH TWO ADDITIONAL EQUIVALENT  
PROTONS OR DEUTERONS IN THE MOLECULE

F	I	$W_Q^a$	$W_Q^b(J \rightarrow \infty)$	Spin wt. for 2 equiv.			
				Pro- tons		Deu- terons	
				$+^c$	$-^c$	$+^c$	$-^c$
$J + 2$	2	$J(2J - 1)$	$1/2$	1	3	2	1
$J + 1$	2	$-1/2(2J - 1)(J + 6)$	$-1/4$	1	3	2	1
$J$	A(0, 2)	$1/4[-(2J - 3)(2J + 5) + 3(16J^4 + 32J^2 - 8J^2 - 24J + 25)^{1/2}]$	$1/2$	1	3	2	1
$J$	B(0, 2)	$1/4[-(2J - 3)(2J + 5) - 3(16J^4 + 32J^2 - 8J^2 - 24J + 25)^{1/2}]$	$-1$	1	3	2	1
$J - 1$	2	$-1/2(2J + 3)(J - 5)$	$-1/4$	1	3	2	1
$J - 2$	2	$(2J + 3)(J + 1)$	$1/2$	1	3	2	1
$J + 1$	1	$-1/2J(2J - 1)$	$-1/4$	3	1	1	2
$J$	1	$1/2(2J - 1)(2J + 3)$	$1/2$	3	1	1	2
$J - 1$	1	$-1/2(J + 1)(2J + 3)$	$-1/4$	3	1	1	2

<sup>a</sup> Apart from the factor:  $eQ(\partial^2 V/\partial z^2)[2J(2J - 1)]^{-1}$ . <sup>b</sup> Apart from the factor:  $eQ(\partial^2 V/\partial z^2)$ . <sup>c</sup> Symmetry of the rotational wave function.

$\neq \Delta J$  components rapidly become weaker as  $J$  increases, we need only consider the  $\Delta F = \Delta J$  components. The  $Q$ -branch transitions will then consist of three equally spaced components. As may be seen from Table I, these would have, were the Pauli exclusion principle inoperative, intensity ratios of 1:4:4. Labeling the components  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  consecutively, the zero-order frequency in this limit is

$$\nu = \nu_2 - 1/3(\nu_2 - \nu_3) \quad (2)$$

In  $C_2H_2N_2S$  we have, besides the nitrogen nuclei, two equivalent hydrogen nuclei. Since a rotation about the  $C_2$  axis interchanges both a pair of bosons (the nitrogen atoms) and a pair of fermions (the protons), the over-all wave function must be antisymmetric with respect to this operation. Thus for the first six entries in Table I (spin 0 and 2), the states having symmetric rotational wave functions (+ states are those for which  $K_{-1}$  is even) will combine with the antisymmetric spin states of hydrogen, and the states having antisymmetric rotational wave functions (- states are those for

which  $K_{-1}$  is odd) with the symmetric spin states of hydrogen. For the antisymmetric spin states of the nitrogen nuclei, the reverse is true. Statistical weights are tabulated for this species as well as for the case of two equivalent deuterons. Summing these for the three components of  $Q$ -branch transitions in the limit of high  $J$ , the intensity ratios of Table II are predicted

TABLE II  
INTENSITY RATIOS FOR  $Q$ -BRANCH ROTATIONAL TRANSITIONS OF  
1,2,5-THIADIAZOLE FOR THE LIMIT  $J \rightarrow \infty$

$K_{-1}$	Rotational state	$C_2H_2N_2S$	$C_2D_2N_2S$
Even	+	1:8:6	2:6:7
Odd	-	3:8:10	1:6:5

Thus the intensity ratios of the three components of transitions of  $C_2H_2N_2S$  involving odd values of  $K_{-1}$  are predicted to be 3:8:10; those for even  $K_{-1}$  are 1:8:6. For the species  $C_2D_2N_2S$  these ratios are 1:6:5 and 2:6:7, respectively. Experimentally, two components were observable for all  $Q$ -branch transitions in these two species. A third much weaker high frequency component was observed in some instances (see Table III).

TABLE III  
MICROWAVE SPECTRA OF  $C_2H_2N_2S$  AND  $C_2D_2N_2S$

Transition	Frequency, Mc. <sup>a</sup>			
	$C_2H_2N_2S$		$C_2D_2N_2S$	
	Obsd.	Zero order	Obsd.	Zero order
$1_{01} \leftarrow 0_{00}$	9967.02	9967.02 <sup>b</sup>	9057.79	9057.79 <sup>b</sup>
$2_{02} \leftarrow 1_{01}$	18534.61	.....	16997.21	.....
$2_{12} \leftarrow 1_{11}$	17234.92	.....	15737.67	.....
$2_{11} \leftarrow 1_{10}$	22632.80	.....	20493.13	.....
$3_{22} \leftarrow 3_{03}$	19752.09	.....	18608.80	.....
$3_{03} \leftarrow 2_{02}$	25767.56	.....	23733.86	.....
$3_{13} \leftarrow 2_{12}$	25119.20	.....	23014.67	.....
$3_{22} \leftarrow 2_{21}$	29900.98	29900.98 <sup>b</sup>	27173.18	27173.18 <sup>b</sup>
$4_{22} \leftarrow 4_{23}$	12411.33 <sup>c</sup>	12412.16 <sup>d</sup>	10478.99 <sup>c</sup>	10479.96 <sup>d</sup>
			10480.45	
			10481.38	
$4_{32} \leftarrow 4_{13}$	23110.03	.....	22662.34	.....
$5_{23} \leftarrow 5_{24}$	21117.92	21118.74	18255.79	18256.65
			18257.08	
			18258.15	
$6_{32} \leftarrow 6_{34}$	16776.06	16776.72	13624.90	13625.51
			13625.81	
			16777.05	
			16778.07	
$7_{34} \leftarrow 7_{35}$	26521.49	26522.10	22381.05	22381.74
			22382.08	
			26523.27	
$7_{42} \leftarrow 7_{44}$	11703.38	11703.92	8633.03	8633.56
			8633.82	
			8634.50	
$8_{44} \leftarrow 8_{45}$	21242.42	21243.02	16647.64	16648.20
			16648.48	
			16649.44	
$9_{54} \leftarrow 9_{55}$	15084.15	15084.68	10606.08	10606.46
			10606.65	
			15084.95	
			15085.69	

<sup>a</sup> Uncertainty:  $\pm 0.05$  Mc. <sup>b</sup> See section V for method of determination of zero-order frequency. <sup>c</sup> Two most intense components listed first; then the weak one if resolved. <sup>d</sup> Calculated from eq. 2 (for  $Q$ -branch transitions).

Figure 1 shows oscilloscope traces of two transitions of  $C_2H_2N_2S$  clearly exhibiting the dependence of intensities on spin effects.

Using the Stark effect as a guide, the assignment of the spectra of the four species  $C_2H_2N_2S$ ,  $C_2D_2N_2S$ ,  $C_2H_2N_2^{34}S$ , and  $C^{13}CH_2N_2S$  was made. Tables III and IV list transition frequencies for the ground vibrational state. Zero-order frequencies of  $Q$ -branch transitions (Table III) were calculated from eq. 2. The  $1_{01} \leftarrow 0_{00}$

(6) J. K. Bragg, Dissertation, Harvard University, 1948!

TABLE IV  
MICROWAVE SPECTRA OF C<sub>2</sub>H<sub>2</sub>N<sub>2</sub><sup>34</sup>S, C<sup>13</sup>CH<sub>2</sub>N<sub>2</sub>S, AND  
C<sub>2</sub>H<sub>2</sub>N<sup>16</sup>NS<sup>a</sup>

Transition	Frequency, Mc.			
	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> <sup>34</sup> S Obsd. <sup>b</sup>	C <sup>13</sup> CH <sub>2</sub> N <sub>2</sub> S Obsd. <sup>c</sup>	C <sub>2</sub> H <sub>2</sub> N <sup>16</sup> NS Obsd. <sup>c</sup> Calcd. <sup>d</sup>	
2 <sub>02</sub> ← 1 <sub>01</sub>	18229.10	18266.98	°	.....
2 <sub>12</sub> ← 1 <sub>11</sub>	16902.84	°	°	.....
2 <sub>11</sub> ← 1 <sub>10</sub>	22079.36	22229.73	°	.....
3 <sub>03</sub> ← 2 <sub>02</sub>	25411.10	25422.77	°	.....
3 <sub>13</sub> ← 2 <sub>12</sub>	24689.04	24748.81	24891.27	24890.79
3 <sub>22</sub> ← 2 <sub>21</sub>	29236.74	29396.32	°	.....
4 <sub>22</sub> ← 4 <sub>23</sub>	11593.80	11978.58	°	.....
5 <sub>23</sub> ← 5 <sub>24</sub>	20027.32	20510.28	°	.....
5 <sub>32</sub> ← 5 <sub>33</sub>	°	°	9279.90	9278.74
6 <sub>33</sub> ← 6 <sub>34</sub>	15305.08	16041.14	°	.....
7 <sub>34</sub> ← 7 <sub>35</sub>	24793.38	25616.88	°	.....
7 <sub>43</sub> ← 7 <sub>44</sub>	10061.53	10927.16	13078.21	13079.80
8 <sub>44</sub> ← 8 <sub>45</sub>	18968.99	20145.77	°	.....
8 <sub>53</sub> ← 8 <sub>54</sub>	°	°	8346.44	8348.46
9 <sub>54</sub> ← 9 <sub>55</sub>	12603.09	13929.28	°	.....
10 <sub>55</sub> ← 10 <sub>56</sub>	°	24319.06	°	.....
11 <sub>65</sub> ← 11 <sub>66</sub>	15198.67	17072.85	°	.....
12 <sub>75</sub> ← 12 <sub>76</sub>	8636.30	10296.73	14891.40	14897.54
14 <sub>86</sub> ← 14 <sub>87</sub>	10342.71	12567.64	°	.....
16 <sub>97</sub> ← 16 <sub>98</sub>	12126.59	14998.73	°	.....

<sup>a</sup> Observed in nature abundance. <sup>b</sup> Estimated uncertainty ≤ 0.1 Mc. <sup>c</sup> Estimated uncertainty ≤ 0.15 Mc. <sup>d</sup> See section III for method of calculation. <sup>e</sup> Not observed.

and 3<sub>22</sub> ← 2<sub>21</sub> transitions were not perceptibly perturbed by quadrupole effects (see section V). Zero-order frequencies were used in computing rotational constants of C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>S and C<sub>2</sub>D<sub>2</sub>N<sub>2</sub>S. Hyperfine structure could not be resolved for the <sup>34</sup>S and <sup>13</sup>C species, and for these species observed frequencies without correction were employed in analyzing for rotational constants. A least squares analysis of the same set of eight transitions ( $J \leq 9$ ) for each of the species gave the rotational constants listed in Table V. Deviations of the frequencies analyzed from those calculated are well within the limits of experimental uncertainty and the approximations used.

Using the rotational constants of Table V together with the center of mass condition and the *A* moment of inertia of the parent species, a complete structure (see section IV) was calculated. Rotational constants for the C<sub>2</sub>H<sub>2</sub>N<sup>16</sup>NS species were then obtained using differences in the moments predicted on the basis of the calculated structure. Although Stark patterns could not be resolved for this species, five lines of appropriate intensity were observed which correspond very closely to the spectrum predicted in this way (see Table IV). By the same method the spectra of the species C<sub>2</sub>D<sub>2</sub>N<sub>2</sub><sup>34</sup>S and C<sup>13</sup>CD<sub>2</sub>N<sub>2</sub>S were calculated, and three transitions were observed in each case (3<sub>03</sub> ← 2<sub>02</sub>, 3<sub>13</sub> ← 2<sub>12</sub>, and 9<sub>54</sub> ← 9<sub>55</sub>). The first two were clearly identified by Stark patterns. The average deviation from predictions obtained in this way was 0.72 and 1.03 Mc., respectively.

The dipole moment as obtained from Stark measurements of the 1<sub>01</sub> ← 0<sub>00</sub> and 2<sub>11</sub> ← 1<sub>10</sub> ( $M = 1$ ) transitions is 1.565 ± 0.015 D. The system was calibrated by measuring the displacement of the Stark lobe of the 1 ← 0 transition of OCS for which the dipole moment was taken to be 0.7124 D.<sup>7</sup> Stark coefficients were calculated by the method of Golden and Wilson.<sup>8</sup>

#### IV. Structure

The center of mass coordinates of the sulfur, carbon, and hydrogen atoms in C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>S were calculated from

(7) S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1957).

(8) S. Golden and E. B. Wilson, *J. Chem. Phys.*, **16**, 669 (1948).

Kraitchman's equations<sup>9</sup> using the ground state moments of inertia. The nitrogen atoms are very nearly on the *B*-axis. Their position was determined using the center of mass condition and the *A* moment of inertia of the parent species. Table VI lists bond distances and bond angles obtained from these calculations as well as those of the electron diffraction analysis of Bonham and Momany.<sup>5</sup> Since the system is planar (see below), the "r<sub>s</sub>" structural parameters<sup>10</sup> may be calculated using three possible combinations of differences in moments of inertia. This was used as an aid in assigning error limits.

The electron diffraction analysis indicates that the ring is planar to within 0.1 Å. The value of the quantum defect ( $\Delta = I_C - I_B - I_A$ ) obtained in this work (Table V) strongly supports a planar structure.

TABLE V  
GROUND-STATE ROTATIONAL CONSTANTS (Mc.), MOMENTS OF  
INERTIA (AMU-Å<sup>2</sup>), AND QUANTUM DEFECT OF  
1,2,5-THIA DIAZOLE<sup>a</sup>

	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> S	C <sub>2</sub> D <sub>2</sub> N <sub>2</sub> S	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> <sup>34</sup> S	C <sup>13</sup> CH <sub>2</sub> N <sub>2</sub> S
<i>A</i>	8538.55	8041.82	8538.72	8471.89
<i>B</i>	6333.03	5717.76	6166.89	6215.60
<i>C</i>	3633.97	3339.97	3578.69	3583.17
<i>I</i> <sub>A</sub>	59.2057	62.8628	59.2045	59.6716
<i>I</i> <sub>B</sub>	79.8245	88.4142	81.9750	81.3326
<i>I</i> <sub>C</sub>	139.1126	151.3579	141.2615	141.0848
Q.D. <sup>b</sup>	0.0824	0.0809	0.0820	0.0806

<sup>a</sup> Conversion factor:  $h/8\pi^2 = 505531$  Mc.-amu-Å<sup>2</sup>. <sup>b</sup> Q.D. =  $I_C - I_B - I_A$ .

TABLE VI  
MOLECULAR PARAMETERS OF 1,2,5-THIA DIAZOLE

	This work	Electron diffraction <sup>a</sup>
<i>d</i> <sub>SN</sub> , Å.	1.631 ± 0.003	1.628 ± 0.008
<i>d</i> <sub>CN</sub> , Å.	1.328 ± .003	1.329 ± .010
<i>d</i> <sub>CC</sub> , Å.	1.420 ± .003	1.400 ± .022
<i>d</i> <sub>CH</sub> , Å.	1.079 ± .003	
∠NSN	99° 33' ± 10'	99.4 ± 2°
∠CCN	113° 46' ± 10'	
∠CCH	126° 14' ± 10'	

|χ<sub>AA</sub>| < 1.0 Mc.

χ<sub>CC</sub> - χ<sub>BB</sub> = 5.2 ± 0.3 Mc.

μ = 1.565 ± 0.015 D.

<sup>a</sup> R. A. Bonham and F. A. Momany, *J. Am. Chem. Soc.*, **83**, 4475 (1961).

#### V. Quadrupole Coupling Constants

The determination of the quadrupole coupling constants of thiadiazole is made possible by a comparison of the hyperfine structure of the 1<sub>01</sub> ← 0<sub>00</sub> and 2<sub>11</sub> ← 2<sub>12</sub> transitions of the parent species with the corresponding transitions of diazine (CH<sub>2</sub>N<sub>2</sub>). Both molecules have C<sub>2v</sub> symmetry,<sup>11</sup> A-type transitions, and two equivalent nitrogen and hydrogen nuclei. The hyperfine structure of the 1<sub>01</sub> ← 0<sub>00</sub> transition is directly proportional to χ<sub>AA</sub>. The factor of proportionality is the same for both molecules as it depends only on nuclear and rotational quantum numbers and not in any way on the asymmetry parameter. Similarly, the hyperfine structure of the 2<sub>11</sub> ← 2<sub>12</sub> transitions will differ only through the factor χ<sub>CC</sub> - χ<sub>BB</sub>. Thus the quadrupole coupling constants may be obtained from a direct comparison of the hyperfine structure of these transitions.

Quadrupole coupling constants of diazine have previously been determined from its microwave spectrum.<sup>11</sup> No fine structure could be resolved for the 1<sub>01</sub> ← 0<sub>00</sub> transition, and from the observed line width of

(9) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

(10) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(11) L. Pierce and S. V. Dobyms, *J. Am. Chem. Soc.*, **84**, 2651 (1962).

0.5 Mc. at half power it was determined that  $|\chi_{AA}| < 1$  Mc. From an analysis of the  $Q$ -branch splittings of the  $\text{CH}_2\text{N}^{15}\text{N}$  species, it was found that  $\chi_{CC} - \chi_{BB} = 6.2 \pm 0.3$  Mc.

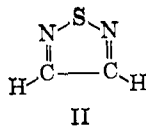
In the case of thiadiazole, it was again impossible to resolve any fine structure in the  $1_{01} \leftarrow 0_{00}$  transition. Here, a second transition having fine structure dependent only on  $\chi_{AA}$  falls within our frequency range, *viz.*,  $3_{22} \leftarrow 2_{21}$ . Since the half width of both is 0.8 Mc., it was concluded that  $|\chi_{AA}| < 1$  Mc. The hyperfine patterns of the  $2_{11} \leftarrow 2_{12}$  transitions were observed to be nearly identical for the two molecules. In both cases, five components were resolvable with the corresponding components having corresponding relative intensities. Thus the sign of  $\chi_{CC} - \chi_{BB}$  is the same for both molecules. The splittings of the components of thiadiazole were, within experimental error, smaller by a constant factor than those of diazirine. A least squares analysis of these splittings gives a value of  $5.2 \pm 0.3$  Mc. for  $\chi_{CC} - \chi_{BB}$ . As an independent check on this parameter, we have noted that in the limit of high  $J$ , the structure of the  $Q$ -branch transitions consists of three equally spaced components (see section III). Representing these as  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  in order of decreasing frequency, the frequency differences may be expressed as

$$\nu_1 - \nu_2 = \nu_2 - \nu_3 = \frac{\chi_{CC} - \chi_{BB}}{b_p(J+1)(2J+3)} \Delta[\langle P_A^2 \rangle - W(b_p)] \quad (3)$$

where  $b_p$  is Wang's asymmetry parameter<sup>12</sup> and  $W(b_p)$  the reduced energy. An analysis of the two most intense components (see section III) of five suitable transitions (splitting  $\geq 0.50$  Mc.) confirmed the value and sign of this coupling constant. Table VII lists experimental data pertinent to these calculations.

## VI. Discussion

The structural parameters obtained in this work, which agree within experimental error with the parameters obtained in the electron diffraction study of Bonham and Momany, are best represented by the structure



In particular, the C-C distance is, within the limits of error, the same as that found in 1,2,5-oxadiazole (1.421)<sup>13</sup> and is very nearly the same as that for the corresponding distance in thiophene ( $1.4234 \pm 0.0023$ ).<sup>14</sup> It is longer than in benzene ( $1.397 \pm 0.001$ —electron diffraction<sup>15</sup>;  $1.3974 \pm 0.001$ —Raman<sup>16</sup>) or in the ring positions of benzonitrile (1.391 to 1.400),<sup>17</sup> but

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TABLE VII  
DATA USED IN DETERMINATION OF  $\chi_{CC} - \chi_{BB}$

Transition	—Obsd. splitting, Mc.—		$\chi_{CC} - \chi_{BB}$ , Mc. C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> S
	CH <sub>2</sub> N <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> S	
$2_{1,1} \leftarrow 2_{1,2}$	0.83	0.67	5.2
	1.45	1.27	
	1.15	0.99	
	1.09	.91	
$11_{6,5} \leftarrow 11_{6,6}$	..	.74	5.2
$12_{7,5} \leftarrow 12_{7,6}$	..	.55	5.1
$14_{8,6} \leftarrow 14_{8,7}$	..	.55	5.0
$16_{9,7} \leftarrow 16_{9,8}$	..	.58	5.3
$18_{10,8} \leftarrow 18_{10,9}$	..	.56	5.1

shorter than the single bond distance of 1.549 in trimethylene oxide,<sup>18</sup> or 1.558 in cyclobutane (Raman).<sup>19</sup> These data indicate that the C-C bond in thiadiazole possesses more single than double bond character. Although cyclic molecules containing a C-N bond for which microwave data are available are limited in number, we conclude that the reverse is true for the C-N bond. In diazirine, this distance is  $1.483 \pm 0.003$ ,<sup>11</sup> for pyridine<sup>20</sup> it is 1.3402, and in 1,2,5-oxadiazole it is 1.300.<sup>13</sup> The thiadiazole C-N bond distance is then intermediate between that of pyridine and oxadiazole. Suitable data for comparison with the S-N bond in this molecule is, to our knowledge, not available. The parameters cited above, in particular those for oxadiazole, indicate that this bond does possess some double bond character.

Pauling<sup>21</sup> has estimated that the resonance structure of thiophene corresponding to II represents 72% of the total contribution. While no thermal studies of 1,2,5-thiadiazole are known to us, we would not expect a large variation in the relative contributions of the various resonance structures of these two molecules since they are isoelectronic and the structural parameters do not vary greatly. We conclude, therefore, that II more nearly represents the molecular parameters and the principal resonance structure of this molecule.<sup>22</sup>

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(22) NOTE ADDED IN PROOF.—It should be noted that the results obtained in this work are not necessarily incompatible with the conclusions of Carmack, Weinstock, and Shew (see section I). The structural parameters determined here pertain only to the ground electronic and vibrational states. Carmack, Weinstock, and Shew drew their conclusion from experiments in which the properties of excited electronic and vibrational states as well as the ground state play an important role.