The Structure of 1,2,4-Thiadiazole by DRM Microwave Spectroscopy

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(Z. Naturforsch. **31 a**, 1681—1689 [1976]; received October 20, 1976)

Rotation spectra of 1,2,4-thiadiazole have been studied for naturally occurring ^{34}S-, ^{13}C- and ^{15}N-species of the normal and the 5-d_1 form, and the 12 sets of moments of inertia have been used to determine the substitution structure in the two principal axes systems. Agreement within less than 0.0005 Å and 0.02° for distances and angles, respectively, between the two independent sets of structure parameters was obtained through the use of the rotation of axes under substitution in combination with the first and second moment conditions.

The averaged bond lengths (in Å) and angles (in degrees) are:

S(1) — N(2) : 1.6490	C(5) S(1) N(2) : 92.75
N(2) — C(3) : 1.3166	S(1) N(2) C(3) : 107.09
C(3) — N(4) : 1.3663	N(2) C(3) N(4) : 120.12
N(4) — C(5) : 1.3133	C(3) N(4) C(5) : 107.74
C(5) — S(1) : 1.7071	N(4) C(5) S(1) : 112.30
C(5) — H(5) : 1.0785	S(1) C(5) H(5) : 123.90
C(3) — H(3) : 1.078	N(2) C(3) H(3) : 119.94

The H(3) atom was assumed on the external bisector of N(2) C(3) N(4) at a distance of 1.078 Å from C(3).

Geometric features of the four thiadiazoles are compared, and the method used in the structure calculation is discussed.

I. Introduction

In recent studies[1] by double resonance modulation (DRM) microwave spectroscopy[2] we have determined the accurate geometries of four small molecules, including three heterocyclic compounds. While, from an experimental viewpoint, this work has clearly demonstrated the advantages of the DRM technique for structure determinations, its results have proven of value in conjunction with quantum chemical calculations[3] of the electron distribution and aromaticity of heterocyclic compounds[4]. In view of this, and since earlier work on the two C_{2v} symmetrical isomers 1,2,5-thiadiazole[5] and 1,3,4-thiadiazole[6], together with our study of 1,2,3-thiadiazole[1d], has left the structure of only one out of the four thiadiazoles undetermined, we considered it appropriate to complete this group of five-membered heterocyclics with a structure study on the remaining 1,2,4-thiadiazole.

The physical and chemical properties of this compound, as well as its physiological uses, have been thoroughly reviewed by Kurzer[7]. Its microwave spectrum was first observed by Sheridan and collaborators[8], who also determined the dipole moment and who studied the hyperfine structure of rotational transitions due to the two quadrupolar nitrogen nuclei.

II. Experimental

a) Instrumental

Measurements of rotational absorptions of 1,2,4-thiadiazole and its isotopic species were made solely by DRM spectroscopy. Details of the instrument and of our standard mode of operation have been given previously[2, 9]. OKI klystrons type 20V10 and 24V10A with output powers of ~200 mW respectively, were used to cover the pump region from 18 GHz to 26 GHz. Signal frequencies ranged from 28 GHz to 40 GHz. All measurements were made at room temperature and at sample pressures near 20 mTorr.

b) Samples

Some time ago, a sample of 1,2,4-thiadiazole had been kindly given to this laboratory by Professor J. Goerdeler (Universität Bonn), who first synthesised this compound[10]. A small portion (~0.5 ml) of this sample had been left over from the earlier work[8] and was used for the present study.

After completion of the isotopic species spectra arising from ^{34}S, ^{13}C and ^{15}N in their natural abundances, the sample was treated with a weakly alkaline (K_2CO_3) D_2O solution which yielded ~90% deuteration in the 5-position. As expected, there occurred no detectable (i. e. less than 0.2%)

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exchange at the 3-position in this solution, and attempts to exchange the H(3) hydrogen under more strongly alkaline conditions proved unsuccessful. In contrast to the behaviour of 1,2,3-thiadiazole[1d] where the supposedly[11] very stable H(4) proton could be exchanged by treatment with NaOD in D_2O over about two weeks, the 1,2,4-isomer was completely decomposed under such conditions. A small fraction ($\sim 5\%$) of the sample survived the alternative treatment with D_2SO_4, but again no detectable exchange at the 3-position was achieved. Three attempts to synthesise 1,2,4-thiadiazole or its 3-d_1 species according to the method[10] described in the literature were unsuccessful. As it was learned at that time that similar failures had also occurred in other laboratories[12], no further attempts were made at the synthesis.

III. Results

a) Method and Sequence of Isotopic Analysis

The identification and assignment of isotopic species spectra was accomplished through double-resonance double-searches[2b] in combination with the usual procedure of predicting such spectra from the moments of inertia (I) of the parent molecule and the estimated positions of atoms in the principal axis system of this species. The molecular model from which the estimates of atomic coordinates were derived was constructed from the bond distances and angles in thiazole[13] and the other three thiadiazoles. The unforeseeable deficiencies of this model (section V a) were more than compensated for by the efficiency of the double search technique, and all isotopic species spectra were readily identified.

The ^{34}S species was studied first because of its relatively high natural abundance (4.2%). The rotation spectra due to molecules with ^{13}C and ^{15}N (natural abundance: 1.1% and 0.36%, respectively) in the 5- and 2-position of the ring (see Fig. 2 for numbering of atoms) were studied next, since the small a-coordinates of these atoms allowed a fairly good prediction of the rotational constant B for these species. Despite poor predictions, the assignment of the two spectra due to ^{13}C and ^{15}N in the 3- and 4-position of the ring, respectively, followed readily, and the 5-d_1 species (90% enriched) was studied last. The period needed for the unsuccessful attempts to exchange the H(3) hydrogen was used for the analysis of naturally occurring ^{34}S-, ^{13}C- and ^{15}N-spectra associated with the 5-d_1 species as the parent molecule.

b) Derivation of Rotational Parameters

Rotational and distortion constants[14a] were derived by a least-squares fitting procedure[14b] for planar asymmetric rotors. To obtain optimal values of the distortion constants, special attention was paid to transitions with high values of J. As usual, the distortion constant τ_{aabb} could not be determined with good accuracy, and it was therefore held fixed to its value in the parent species for the rare isotopic forms.

The rotational parameters of the parent molecule and isotopic species of 1,2,4-thiadiazole are collected in Table 1. Rows 2 and 3 of this table give information on the number of observed Q- and R-branch signal transitions[2b] and the range of J-values studied for each isotopic form[15]. As may be verified from this table, all rotational constants are determined to within ± 0.05 MHz (three times standard deviations), and the distortion constants τ_{aaaa}, τ_{bbbb} and τ_{abab} appear to be fixed to $\pm 10\%$. From the last row of this table the inertia defects are seen to vary but little between isotopic species. This result not only indicates complete planarity of the molecular structure, but also provides conclusive evidence that no confusion between the spectra of isotopic species and those of excited vibration states had occurred in the analysis.

IV. Structure Calculation

In addition to the incompleteness of the isotopic data caused by chemical difficulties (section II b), the calculation of atomic coordinates (Table 2) with Kraitchman's equations[16] for planar molecules shows 1,2,4-thiadiazole to be a very unsuitable case for a structure determination by microwave spectroscopy: No less than four (see Fig. 1) out of the six atoms for which isotopic data were obtained are found to lie so close to a principal axis (within less than 0.2 Å) that their small coordinates can not be determined reliably by the substitution method[16, 17]. This manifests itself quite clearly in the large discrepancies between the values of these coordinates when calculated from ΔI_a and ΔI_b, ΔI_a and ΔI_c and from ΔI_b and ΔI_c, and in the inconsistencies between the bond lengths derived from these coordinates in the normal and the 5-d_1 reference frames (Table 2). Moreover, whereas it is often possible to overcome the difficulties arising with near-axis atoms through the use of the centre-of-

Table 1. Rotational parameters of the normal and isotopic species of 1,2,4-thidiazole.

Isotopic species		Normal [a]	^{34}S (1)	^{15}N (2)	^{13}C (3)	^{15}N (4)	^{13}C (5)
Transitions in fit		31R & 41Q	12R & 30Q	10R & 22Q	10R & 25Q	10R & 23Q	10R & 28Q
Range of J-values		0−20	2−17	3−18	3−16	3−16	8−18
A	in MHz	8811.08 (2) [b]	8809.75 (3)	8591.19 (3)	8731.40 (3)	8759.14 (4)	8598.97 (3)
B		5938.20 (1)	5774.93 (2)	5937.86 (1)	5848.03 (2)	5813.92 (2)	5936.25 (1)
C		3545.34 (1)	3486.27 (1)	3509.06 (1)	3500.25 (1)	3492.42 (1)	3509.80 (1)
τ_{aaaa}	in kHz	−15.2 (17)	−13.3 (27)	−13.8 (26)	−13.4 (30)	−15.0 (38)	−13.0 (25)
τ_{bbbb}		−7.87 (31)	−7.17 (50)	−7.84 (42)	−7.48 (50)	−7.30 (57)	−7.63 (40)
τ_{aabb}		−0.94 (50)	−0.94 [c]	−0.94 [c]	−0.94 [c]	−0.94 [c]	−0.94 [c]
τ_{abab}		−3.47 (20)	−3.34 (27)	−3.33 (15)	−3.48 (21)	−3.23 (26)	−3.43 (15)
I_a	in μÅ^2	57.3569 (1)	57.3655 (2)	58.8249 (2)	57.8803 (2)	57.6970 (2)	58.7717 (2)
I_b		85.1059 (2)	87.5120 (2)	85.1109 (2)	86.4181 (2)	86.9252 (2)	85.1339 (2)
I_c		142.5464 (3)	144.9618 (5)	144.0204 (3)	144.3827 (4)	144.7064 (4)	143.9902 (3)
I.D.		0.0836 (4)	0.0843 (6)	0.0846 (5)	0.0843 (5)	0.0842 (5)	0.0846 (4)

Isotopic species		^{2}D (5)	^{2}D (5) − ^{34}S (1)	^{2}D (5) − ^{15}N (2)	^{2}D (5) − ^{13}C (3)	^{2}D (5) − ^{15}N (4)	^{2}D (5) − ^{13}C (5)
Transitions in fit		12R & 40Q	8R & 11Q	5R & 9Q	8R & 12Q	6R & 9Q	8R & 12Q
Range of J-values		1−17	3−12	3−12	3−12	3−11	3−18
A	in MHz	8091.37 (1)	8090.91 (4)	7897.87 (5)	8019.29 (3)	8052.52 (6)	7920.20 (3)
B		5937.91 (1)	5774.57 (2)	5937.52 (2)	5847.74 (2)	5813.19 (3)	5935.86 (2)
C		3422.73 (1)	3367.73 (1)	3387.47 (1)	3379.82 (1)	3374.11 (1)	3391.03 (1)
τ_{aaaa}	in kHz	−11.6 (9)	−11.4 (30)	−13.0 (30)	−12.9 (23)	−13.5 (36)	−12.0 (15)
τ_{bbbb}		−7.76 (16)	−7.11 (50)	−8.14 (60)	−7.51 (60)	−7.20 (90)	−8.05 (40)
τ_{aabb}		−0.94 [c]	−0.94 [c]	−0.94 [c]	−0.94 [c]	−0.94 [c]	−0.94 [c]
τ_{abab}		−3.27 (12)	−2.74 (30)	−3.40 (55)	−2.79 (45)	−2.50 (70)	−3.13 (12)
I_a	in μÅ^2	62.4587 (1)	62.4622 (3)	63.9889 (4)	63.0201 (3)	62.7600 (4)	63.8085 (2)
I_b		85.1101 (1)	87.5176 (2)	85.1157 (3)	86.4225 (3)	86.9361 (4)	85.1395 (2)
I_c		147.6529 (3)	150.0642 (3)	149.1899 (5)	149.5274 (4)	149.7804 (5)	149.0331 (3)
I.D.		0.0841 (3)	0.0845 (5)	0.0853 (7)	0.0849 (6)	0.0843 (8)	0.0851 (4)

[a] From Ref. [8] with 30 additional transitions to improve the distortion constants.
[b] Uncertainties are three times the standard deviations and given in units of the last digit quoted.
[c] Assumed as in normal species.

gravity and product-of-inertia conditions, the present case is exceptional since four small coordinates (b_1, a_2, a_5, a_6) would need to be revised, while only three auxiliary conditions are available, i. e.

$$\sum m_i a_i = 0\,, \tag{1}$$

$$\sum m_i b_i = 0\,, \tag{2}$$

$$\sum m_i a_i b_i = 0\,. \tag{3}$$

This shows that even if a complete set of substitution data of 1,2,4-thiadiazole were available, it would still not suffice for the revision of all small coordinates, and that one more auxiliary condition must be found.

As the DRM method had readily yielded isotopic data for the ring atoms with respect to the principal axes of the normal *and* the 5-d_1 species, it was possible to obtain the required fourth condition as follows: The magnitude of the coordinates of C(3) and N(4), together with the good agreement between the two values for the bond length C(3) − N(4) (Table 2, rows 3, 4 and 9) in the normal and the 5-d_1 reference frame, suggests that the positions of these two atoms are well determined in each axis system. If this is accepted, one may calculate from these coordinates the angle between the bond C(3) − N(4) and the axes of each reference frame (see Figure 1). The angle (Θ) by which the axes of the normal species are rotated when deuterium is substituted for H(5) is, therefore, calculable from the changed orientation of the bond C(3) − N(4) with respect to the a-axis as $\Theta = 0.22 \pm 0.03°$. Analogous calculations (see Fig. 1 and column 1 of Table 3) for the bonds N(2) − C(3) and N(4) − C(5) are in substantial agreement with this value, although not the same weight can be attached to these two results

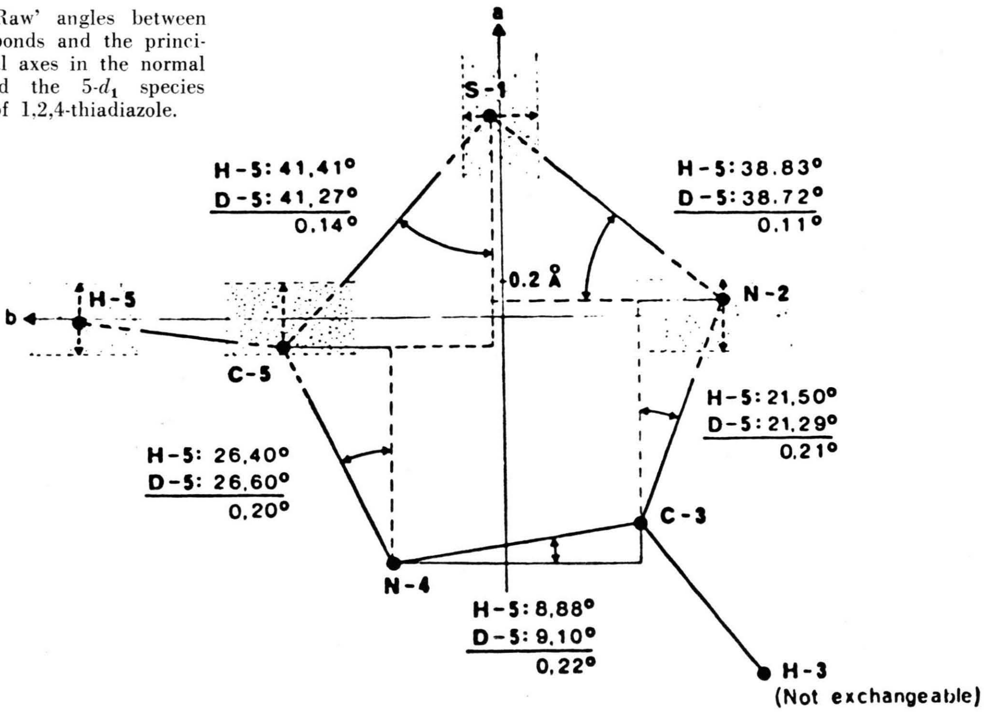

Fig. 1. 'Raw' angles between the ring bonds and the principal inertial axes in the normal (H-5) and the 5-d_1 species (D-5) of 1,2,4-thiadiazole.

Table 2. 'Raw' substitution coordinates and resulting structure parameters of 1,2,4-thiadiazole.

	Reference frame	Normal Species		5 – d_1 Species		
	Coordinates	$\lvert a \rvert$	$\lvert b \rvert$	$\lvert a \rvert$	$\lvert b \rvert$	
1	S(1)	1.11054(10) [a]	0.07027(200)	1.11078(6)	0.04529(160)	
2	N(2)	0.07145(500)	1.22068(30)	0.07532(500)	1.24626(30)	
3	C(3)	1.13945(20)	0.74359(30)	1.13605(20)	0.77410(30)	
4	N(4)	1.35036(15)	0.60657(34)	1.35199(5)	0.57477(13)	
5	C(5)	0.16458(200)	1.19513(30)	0.16792(200)	1.16762(30)	
6	H(5)	0.05992(300)	2.26500(7)	0.07258(300)	2.23842(8)	
	Bond lengths					Difference
7	S(1) – N(2)	1.65718		1.65538		0.00180
8	N(2) – C(3)	1.30150		1.30013		0.00137
9	C(3) – N(4)	1.36653		1.36605		0.00048
10	N(4) – C(5)	1.32381		1.32420		0.00039
11	C(5) – S(1)	1.70036		1.70138		0.00102
12	C(5) – H(5)	1.07498		1.07504		0.00006
	Angles					
13	C(5)S(1)N(2)	92.59		92.55		0.04
14	S(1)N(2)C(3)	107.33		107.43		0.10
15	N(2)C(3)N(4)	120.38		120.39		0.01
16	C(3)N(4)C(5)	107.52		107.50		0.02
17	N(4)C(5)S(1)	112.19		112.13		0.06
18	S(1)C(5)H(5)	125.83		126.18		0.35

[a] These quantities reflect the compatibility of substitution coordinates when calculated from the three possible combinations of ΔI-values.

because their calculation involves the small substitution coordinates a_2 and a_5. The bonds C(5) – S(1) and S(1) – N(2), in contrast, appear to be rotated by differing amounts, which again points to the incompatibility of the small coordinates in the two reference frames. Nevertheless, knowledge of the approximate angle of rotation and of the b-coordinate of the hydrogen H(5) seems to permit the equation

$$\tan 2\Theta = 2\mu a b\,\{(I_b + \mu a^2) - (I_a + \mu b^2)\}^{-1} \quad (4)$$

[which relates the rotation (Θ) of the axes with the moments (I) of the parent molecule and the position (a, b) of the substituted atom] to be invoked as a fourth condition for testing or revising a small coordinate. In the present case, the initial value $\Theta = 0.22 \pm 0.03^\circ$ yielded $a_6 = 0.039 \pm 0.004$ Å, which should be compared with the 'raw' substitution value of 0.0599 Å (0.047 Å as opposed to 0.0726 Å in the 5-d_1 frame).

With the H(5) hydrogen located in the described manner, the H(3) atom needed to be placed next before the remaining three small coordinates b_1, a_2 and a_5 could be revised through Eqs. (1) – (3). Since chemical difficulties had prevented this atom from being placed through substitution, it was *assumed*, firstly, that the H(3) atom would lie on the external bisector of the ring angle N(2)C(3)N(4) and, secondly, that its distance from C(3) could safely be taken as 1.078 ± 0.001 Å. This latter value is suggested by the corresponding C – H lengths in 1,2,3- and 1,2,5-thiadiazole [1d, 5], while the first assumption rests on the equality of the hetero atoms adjacent to the C(3) carbon. With coordinate values for H(3) derived from these assumptions and from the known positions of C(3) and N(4), the small b_1 coordinate of the sulphur atom was then refined through the auxiliary condition (2). This, in turn, allowed the revision of a_2 and a_5 through the simultaneous Eqs. (1) and (3).

As this first revision of a_2 entailed a small modification of the initial angle N(2)C(3)N(4) and its external bisector, the H(3) position was re-adjusted in accordance with the assumptions, and Eqs. (1) – (3) were applied again. Calculation of the rotation of bonds under the H(5)→D(5) substitution now not only showed better consistency than before (column 2 of Table 3), but also suggested $\Theta = 0.235^\circ$ (initial value: 0.22°). Hence, with this new value of Θ the entire revision of small coordinates was carried out once more with Eqs. (4), (2) and (1) and (3) being used to obtain 'final' values of a_6, b_1 and a_2 and a_5, respectively.

Table 3. Rotation Θ of ring bonds with repect to the principal axes unter substitution of H(5) by deuterium.

Bond Rotation calculated from:	Rotation Θ (in degrees) 'Raw' coordinates	Revised coordinates	'Final' coordinates
S(1) – N(2)	0.111	0.236	0.233
N(2) – C(3)	0.211	0.238	0.236
C(3) – N(4) [a]	0.219	0.219	0.219
N(4) – C(5)	0.200	0.229	0.232
C(5) – S(1)	0.143	0.259	0.248
Most probable value	0.219 [b]	0.235 [c]	0.234

[a] The rotation of this bond was not subjected to revision.
[b] Angle used for initial refinement of data.
[c] Angle used for second revision of coordinates.

The atomic coordinates and molecular structure parameters obtained by the described procedure are listed in Table 4. In contrast to the 'raw' data of Table 2, they show very good consistency between the results derived in the normal reference frame and those in the 5-d_1 frame: The two values for each bond length differ by less than 0.0005 Å, and the angles deviate from each other by 0.02° at the most (column 3 of Table 4). In view of the above mentioned unsuitability of 1,2,4-thiadiazole for a structure determination by the substitution method, this close coincidence is all the more remarkable. We therefore propose the averaged values as the 'best' structure parameters for this molecule (column 4 of Table 4 and Figure 2).

Not unexpectedly, the 'final' structure parameters of 1,2,4-thiadiazole differ considerably from the 'raw' data of Table 2. As may be verified by a comparison between Table 2 and 4, the largest change occurs in the bond length N(2) – C(3) which is increased by as much as 0.016 Å through the revision of the N(2) position with Eqs. (1) and (3). At the same time, the bond length N(4) – C(5) is reduced by 0.011 Å through the revision of the H(5) and C(5) positions. As a result, the N(4) – C(5) bond, which at first appears by 0.023 Å longer than the N(2) – C(3) bond, turns out to be 0.0033 Å shorter than the latter, and the two carbon-nitrogen double bonds become almost equal. A similar modification of lengths also occurs for the S(1) – N(2) and the S(1) – C(5) bonds which are corrected by approximately equal but opposite amounts (– 0.0072 Å and + 0.0062 Å, respectively), so that their difference is enlarged from 0.0446 Å to 0.0581 Å. The C(5) – H(5) bond, finally, is increased from 1.0750 Å to the more reasonable value of 1.0785 Å.

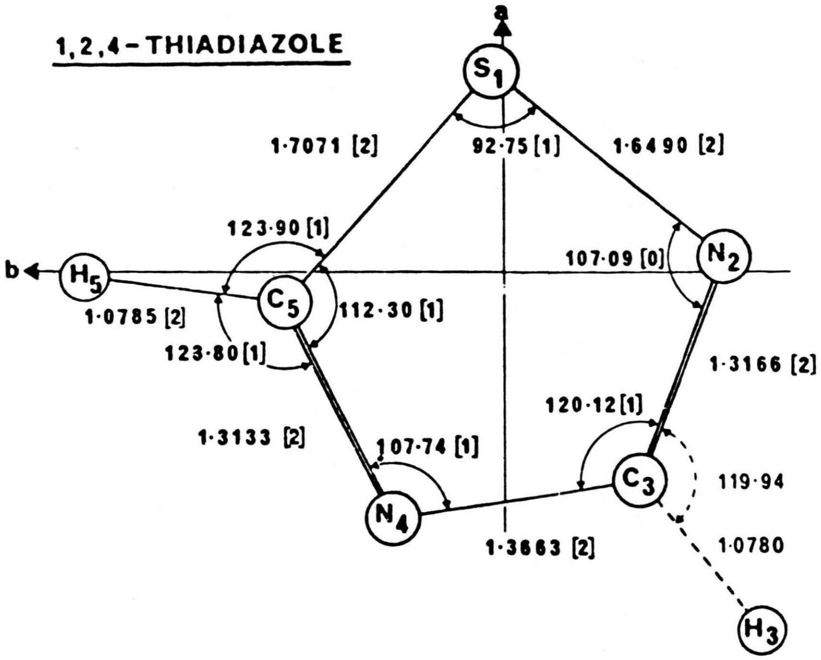

Fig. 2. The 'best' structure of 1,2,4 thiadiazole. — The quantities in square brackets reflect the compatibility of the averaged parameters with the values calculated independently in the normal and the 5-d_1 axis system. H(3) is *assumed* on the external bisector of N(2)C(3)N(4) at a distance of 1.078 Å from C(3).

Table 4. 'Final' values of atomic coordinates and deduced structure parameters of 1,2,4-thiadiazole.

	Reference frame	Normal Species		5 − d_1 Species				
	Coordinates [a]	*a*	*b*	*a*	*b*			
1	S(1)	1.11054	0.07284 [b]	1.11078	0.05119 [b]			
2	N(2)	0.08752 [c]	−1.22068	0.09319 [c]	−1.24626			
3	C(3)	−1.13945	−0.74359	−1.13605	−0.77410			
4	N(4)	−1.35036	0.60657	−1.35199	0.57477			
5	C(5)	−0.17611 [c]	1.19513	−0.18039 [c]	1.16762			
6	H(5)	−0.041 [d]	2.26500	−0.050 [d]	2.23842			
7	H(3) [e]	−1.97934	−1.41936	−1.97342	−1.45300			
	Bond lengths					Difference	Average	Compatibility
8	S(1)−N(2)	1.64917		1.64890		0.00027	1.64903	0.00014
9	N(2)−C(3)	1.31646		1.31680		0.00034	1.31663	0.00017
10	C(3)−N(4)	1.36653		1.36605		0.00048	1.36629	0.00024
11	N(4)−C(5)	1.31349		1.31306		0.00043	1.31328	0.00022
12	C(5)−S(1)	1.70734		1.70691		0.00043	1.70712	0.00022
13	C(5)−H(5)	1.07837		1.07871		0.00034	1.07854	0.00017
14	C(3)−H(3) [e]	1.0780		1.0780		—	1.0780	—
	Angles							
15	C(5)S(1)N(2)	92.76		92.74		0.02	92.75	0.01
16	S(1)N(2)C(3)	107.09		107.09		0.00	107.09	0.00
17	N(2)C(3)N(4)	120.13		120.11		0.02	120.12	0.01
18	C(3)N(4)C(5)	107.73		107.74		0.01	107.74	0.01
19	N(4)C(5)S(1)	112.30		112.31		0.01	112.30	0.01
20	S(1)C(5)H(5)	123.90		123.91		0.01	123.90	0.01
21	N(4)C(3)H(3) [e]	119.94		119.94		—	119.94	—
	Effective and calculated moments							
22	$I_a^{\text{subst.}}$	57.1630		62.2292				
23	$I_a^{\text{eff.}} - I_a^{\text{subst.}}$	0.1939 (0.34%)		0.2295 (0.37%)				
24	$I_b^{\text{subst.}}$	84.9751		84.9734				
25	$I_b^{\text{eff.}} - I_b^{\text{subst.}}$	0.1308 (0.15%)		0.1367 (0.16%)				

[a] For the choice of the positive direction of axes see Figure 1. [b] Coordinate derived from Eq. (2). [c] Coordinates derived from Eqs. (1) and (3). [d] Coordinate derived from Eq. (4) with $\Theta = 0.235°$. [e] Bond length and angle assumed (see text).

V. Discussion

a) Comparison of 1,2,4-Thiadiazole with Related Compounds

According to observations first made by Nygaard and collaborators in the case of thiazole[13], the structure of 1,2,4-thiadiazole would be expected to be that of a hybrid molecule composed of one half of 1,2,5-thiadiazole and one half of 1,3,4-thiadiazole[5, 6]. The parameters linking the two halves, i. e. the angle C(5)S(1)N(2) and the bond C(3) – N(4), should be close to the averages between corresponding quantities in the two 'component molecules'. From Fig. 3 it may be seen that the only parameter to fulfil these expectations is the angle C(5)S(1)N(2), while the bond length C(3) – N(4) is the same as in 1,2,3-thiadiazole and shorter than the average between the C(3) – C(4) and N(3) – N(4) lengths in 1,2,5- and 1,3,4-thiadiazole, respectively. The S(1) – C(5) bond lies about half way between that of 1,3,4- and 1,2,3-thiadiazole, and the S(1) – N(2) bond is longer than in 1,2,5-thiadiazole, but again close to the average between the S – N length of the 1,2,3- and 1,2,5-isomer. The two nearly equal C = N lengths in 1,2,4-thiadiazole differ by equal amounts from their counterparts in 1,3,4- and 1,2,5-thiadiazole, so that their average coincides with that of the C = N bonds in the two component molecules.

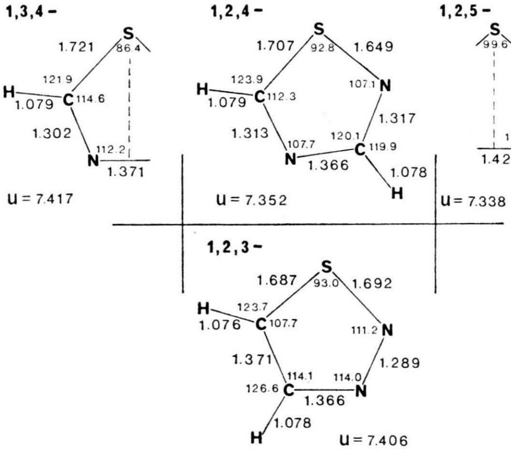

Fig. 3. The structures of the four thiadiazoles (from Ref. [5, 6, 1d] and the present work).

While the ring angles N(4)C(5)S(1) and C(3)N(2)S(1) of 1,2,4-thiadiazole agree at least approximately with corresponding angles in the symmetrical isomers, the remaining two angles show little resemblance with expected values. The most striking feature is the angle N(2)C(3)N(4) = 120.1° which suggests a high degree of localisation around the C(3) carbon atom[20]. This result should perhaps be linked with the extreme chemical stability of the 3-position in this molecule[7, 10].

From these comparisons and the circumference (U) of the four molecules, 1,2,4-thiadiazole is seen to be more akin to 1,2,5-thiadiazole, whereas 1,2,3-thiadiazole lies structurally closer to the 1,3,4-isomer. More specific trends within this quartet are not easily recognizable and a discussion of probable changes in the electronic configuration and aromaticity of these compounds is therefore deferred until the dipole moments and quadrupole coupling constants of all four thiadiazoles can be included in such considerations.

b) Structure Determination

The lack of substitution data for the hydrogen atom H(3) renders the structure determination of 1,2,4-thiadiazole incomplete. But this deficiency, which was caused by the combination of chemical difficulties and the lack of a sufficiently large sample to make the investigation of the 3-d_1 species in its natural abundance feasible, is largely counterbalanced by the wealth of isotopic data (normal species and 11 isotopic forms for the location of only seven atoms). It seems also reasonable to suppose that the assumed C(3) – H(3) bond length is one of the less interesting features of this molecule, and it is found, in addition, that the uncertainty in this parameter does not critically influence the location of the heavy atoms and, hence, the more important ring structure. Thus, on account of Eq. (2), the uncertainty introduced into the *b*-coordinate of the sulphur atom is 32 times smaller than the uncertainty in the assumed *b*-coordinate of H(3). Similarly, only about one tenth of the uncertainty in H(3) is transmitted to be *a*-coordinates of N(2) and C(5) as calculated from Eqs. (1) and (3). In Table 4 such estimated uncertainties have been omitted since the differences between pairs of independently calculated values for each structure parameter were judged a more objective indication of the uncertainties.

The application of Eq. (4) for the revision of a small coordinate from a minute rotation of the principal axes under substitution is undoubtedly the most questionable step in the structure calculation on 1,2,4-thiadiazole. While it can not be ruled out that its apparent success may be partly fortuitous, the following points should also be considered: By Kraitchman's equation, the small substitution coordinate of H(5) results from a small inertial change (ΔI_b) which is likely to contain a proportionately large contribution from vibrational effects. In contrast, the rotation of axes (Θ) is deduced from large changes in the moments of inertia. Hence, even if the vibrational changes accompanying $^{12}C \rightarrow {}^{13}C$ and $^{14}N \rightarrow {}^{15}N$ substitution within the ring are as large as those for H → D substitution outside the ring, they will still represent a proportionately small fraction of the large ΔI-values that are used in the calculation of Θ. The angle Θ should therefore be determinable with greater reliability than the small substitution coordinate of a near-axis atom. If this is accepted, it follows that the small coordinate in Eq. (4) must be determinable with the same reliability as Θ itself, since all other quantities entering this equation are large and therefore known to relatively high accuracy.

While this consideration assumes that only two atoms (i. e. *one* bond) have been placed reliably in two inertial axes systems (normal and 5-d_1 system in the present case), the availability of two nearly complete sets of isotopic data for 1,2,4-thiadiazole provides additional criteria concerning the rotation of axes, the applicability of Eqs. (1) – (4), and the choice of the 'best' structure. Thus, if either the small coordinate of H(5) were incorrect due to inapplicability of Eq. (4) or if the use of Eqs. (1) – (3) were inappropriate, one would neither obtain close coalescence between all pairs of bond lengths and angles calculated independently in different reference frames, nor would the 'final' orientation of each bond point to the same rotation of the axes under substitution of H(5). As none of these tests on the internal consistency of the final result can be applied when only singly substituted species of a molecule have been studied, one has to conclude that the wealth of isotopic data now emerging so readily through the use of DRM-methods, offers not only a chance for comparing the results obtained in different reference frames, but can also lead to an improvement in the accuracy and reliability of substitution structures.

If this optimistic interpretation of the present work should prove justified through future studies, it would also appear possible to quantify the 'vibrational effects' which, in the present example, falsify the small ΔI-values of S(1), N(2), C(5) and H(5). This would be done through a comparison of the observed changes in the moments ($\Delta I^{\text{eff.}}$) with those calculated from the 'final' coordinates. As may be seen from Table 5, while amounting to up to 100% of $\Delta I^{\text{eff.}}$, the vibrational contributions ($\Delta I^{\text{vib.}}$) calculated in this simple manner for the two 'parent' species of 1,2,4-thiadiazole turn out to be in very satisfactory agreement with each other, as should indeed be the case for the normal and a deuterated species of the same molecule. Moreover, the magnitude of the apparent vibrational contributions in 1,2,4-thiadiazole is found in good agreement with values estimated previously [18, 19].

Table 5. Vibrational contributions ($\Delta I^{\text{vib.}}$) to the four small ΔI-values in 1,2,4-thiadiazole (in μÅ^2).

Atom		Normal species	5 − d_1 Species
S(1)	$\Delta I_a^{\text{calc.}}$	0.0095	0.0046
	$\Delta I_a^{\text{eff.}}$	0.0086	0.0035
	$\Delta I_a^{\text{vib.}}$	−0.0009	−0.0011
N(2)	$\Delta I_b^{\text{calc.}}$	0.0092	0.0092
	$\Delta I_b^{\text{eff.}}$	0.0050	0.0056
	$\Delta I_b^{\text{vib.}}$	−0.0042	−0.0036
C(5)	$\Delta I_b^{\text{calc.}}$	0.0327	0.0343
	$\Delta I_b^{\text{eff.}}$	0.0280	0.0294
	$\Delta I_b^{\text{vib.}}$	−0.0047	−0.0049
H(5)	$\Delta I_b^{\text{calc.}}$	0.0020	0.0023
	$\Delta I_b^{\text{eff.}}$	0.0042	0.0042
	$\Delta I_b^{\text{vib.}}$	+0.0022	+0.0019

Acknowledgements

The author would like to thank Professor J. Goerdeler for helpful information and for provision of his last small sample of 1,2,4-thiadiazole during the final stages of this work. He also wishes to record his sincerest gratitude to Professor J. Sheridan.

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[20] Note added in proof: Recently, Dr. M. H. Palmer and collaborators have kindly pointed out to us that this conclusion can not be reconciled with the results of their work [3], and that the large NCN-angle is probably due to repulsion between the charge on the nitrogen atoms.