The Complete Substitution Structure of 1,2,5-Thiadiazole

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Double Resonance Modulation (DRM) microwave spectroscopy has been used to determine the complete substitution structures of 1,2,5-thiadiazole and 3,4-d$_2$-1,2,5-thiadiazole. The ^{34}S-, ^{13}C- and ^{15}N-species of these two "parent" molecules were studied in natural abundance. The structure parameters of the two parent forms agree to within ±0.0005 Å and ±0.02° with the following averaged values:

Distances (in Å)	Angles (in degrees)
S–N = 1.6296	NSN = 99.44
C=N = 1.3270	SNC = 106.51
C–C = 1.4167	NCC = 113.77
C–H = 1.0805	CCH = 126.27

The new data confirm the earlier work on this substance, but the precision of the structure parameters is improved by a factor of ~ 10. The apparent C–C bond length in the normal species is found to differ by ~ 0.001 Å from that in the 3,4-d$_2$-species. Vibrational contributions (ΔI^{vib}) to the effective changes of the moments of inertia are determined for the sulphur atom and the near-axis nitrogen atoms as $\Delta I^{\text{vib}}(\text{S}) = -0.0017$ μÅ^2 and $\Delta I^{\text{vib}}(\text{N}) = -0.0035$ μÅ^2.

Energy transfer through collisions has been exploited to overcome traditional difficulties in the identification of high-J Q-branch transitions of rare isotopic forms.

I. Introduction

In conjunction with the structure determinations on some five- and six-membered heterocyclics [1, 2], and as a result of the work on 1,2,4- and 1,2,3-thiadiazole [1c, d] in particular, we were led to re-examine the substitution structure of the C_{2v} symmetrical molecule 1,2,5-thiadiazole, which has previously been studied by Dobyns and Pierce [3]. While one aim of these studies is to establish for the four thiadiazoles substitution structures which can be considered comparable not only with respect to the experimental method and the completeness of the data, but also with respect to the approach taken in the structure calculation and the precision of the results, the decision to re-investigate 1,2,5-thiadiazole was greatly influenced by our interest in the magnitude and signs of the vibrational contributions [1d] to the changes in the effective moments of intertia under isotopic substitutions. Moreover, in conjunction with recent quantum-chemical calculations [4] of molecular properties of 1,2,5-thiadiazole, some doubt had arisen concerning the large value of the NSN-angle in this compound. With experimental techniques sufficiently improved [5], we considered it straightforward to settle these three aspects through a re-investigation of the microwave spectrum of this substance.

II. Experimental

a) Samples. The sample of 1,2,5-thiadiazole was kindly provided by Dr. M. H. Palmer (Edinburgh) who prepared it by the standard method [6]. Dr. Patsy J. Thomas of this department prepared the perdeuterated form by direct exchange: The normal species was stirred for six days with 2 M NaOD in D$_2$O at 95 °C, with dioxan being used to aid solubility. 3,4-d$_2$-1,2,5-thiadiazole was then separated off by distillation, and the subsequent analysis by DRM indicated an enrichment of ~ 70%. All other isotopic forms were studied in their natural abundances.

b) Instrumental. Details of the DRM instrument and of our general mode of operation have been described in the literature [5, 7]. In the present study, pump frequencies were taken from 15 to 26 GHz, and signal frequencies varied from 22 to 40 GHz. All measurements were made at room temperature and at sample pressures of ~ 30 mTorr, and absorptions were observed on the oscilloscope.

Supplementary SEM measurements were made on a conventional Stark effect modulation (SEM) spectrometer [8].

III. Spectroscopic Results

a) Assignments. With rotational constants for the normal, the ^{34}S-, ^{13}C- and the 3,4-d$_2$-species available from the original study [3], the extension of the corresponding spectra did not meet with any difficulty, and about ten new transitions (DRM signals) were obtained for each of those isotopic species. For the ^{15}N-species only a few transitions had been tentatively identified before (Ref. [3], Table IV), and these were not sufficient for the derivation of rotational constants. The present DRM work on this species yielded 13 signal transitions, which together with one measurement by Dobyns and Pierce [3], permitted the determination of the constants to the same accuracy as for the other isotopic forms (see below). After the atomic coordinates in normal 1,2,5-thiadiazole had been deduced from the resulting complete set of isotopic data, the previously unobserved spectra due to the ^{34}S-, ^{13}C- and ^{15}N-species of the 3,4-d$_2$-form could be confidently predicted and were readily identified by the standard method [5].

b) Use of collision-induced signals. Due to the planarity and symmetry of 1,2,5-thiadiazole, and the resulting absence of *c*- and *b*-type transitions, its DRM spectrum is very scarce; even for the extended frequency area with pump frequencies down to 15 GHz (normal range: 18–26 GHz) there occurred only between 15 and 18 transitions for each isotopic form in the extended signal range from 22–40 GHz (normal range: 28–40 GHz). R-type signal transitions ($J < 5$) were predominant, and the few accessible Q-branch connections reached only to $J_{\max} = 8$ for the ^{34}S- and ^{13}C-species, and to $J_{\max} = 9$ in the DRM spectrum of the parent and the ^{15}N-species. In combination with the often noticeable broadening of transitions due to quadrupole finestructure, this restriction to low J-values at first resulted in rather poorly determined rotational parameters, and it was necessary, therefore, to seek extension of the Q-branch measurements to higher J-values in order to determine the rotational and distortion constants with the usual accuracy.

Without doubt, for the normal and the enriched 3,4-d$_2$-species this could have been achieved by recourse to single resonance techniques, since high-J Q-branch transitions would have been easily recognised by their intensity. For the rare isotopic forms, however, this approach was judged likely to lead to a familiar problem of SEM spectroscopy: though reasonably well predictable on the basis of the DRM work, transitions in the intermediate J-range from $J = 8-15$ had to be expected to be too weak for detection under SEM (partly due to hfs), whereas transitions in the high J-range ($J = 20-40$) with receding hyperfine splittings and with sufficient intensity for detection in a 3.5 meter Stark cell, could not be reliably enough predicted on the basis of least squares (LSQ) fits involving only low-J DRM transitions.

Fortunately, in checking the origin of some accidentally observed collisional "relaxation signals" [9] of the parent species, it was noticed that the Q-branch spectrum of 1,2,5-thiadiazole not only consisted of mostly just one transition for every J-value above $J = 15$, but also that the K_{-1} quantum number (n) was often repeated for successive J-values to lead to pairs of transitions of the type

$$J_{n,J-n+1} \rightarrow J_{n,J-n}\,,$$
$$J+1_{n,J-n+2} \rightarrow J+1_{n,J-n+1}\,.$$

In such pairs both the lower and the higher levels of the two transitions are interconnected by the prevailing a-type selection rule (see Figure 1), and the change in population produced by the pump radiation in each level of one transition ($J = 13$, in

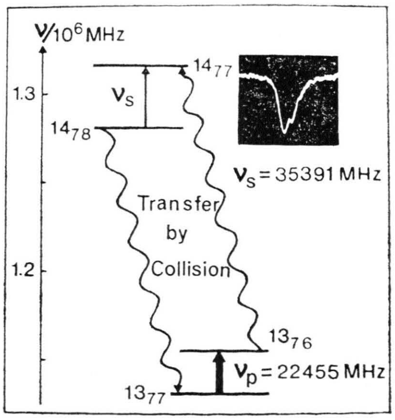

Fig. 1. Disposition of energy levels which gives rise to collision-induced DRM signals between Q-branch transitions of 1,2,5-thiadiazole. In the photograph of the signal the triplet structure due to quadrupole coupling should be noted (frequency increases from left to right).

Fig. 1) is therefore transmitted to both levels of the other transition of the pair ($J = 14$, in Figure 1). Due to the modulation of the pump radiation, the intensity of the normal absorption at ν_S (which is *not* observed under DRM) thus changes periodically and gives rise to a singal which represents this change of the intensity of the (unobserved) normal absorption at ν_S.

Encouraged by the strength of such signals in the parent species of 1,2,5-thiadiazole, we thought it worthwhile to attempt to use these relaxation lines for the unequivocal identification of high-J Q-branch transitions of the rare isotopic forms and, although their intensity was about a factor ten smaller than the intensity of signals produced by direct modulation, it turned out possible to identify at least a few such relaxation signals even for the ^{15}N-species through double-searches [5] in appropriate frequency areas. After the inclusion of these transitions in the LSQ fits, other Q-branch lines up to $J = 39$ could be predicted to ± 1 MHz for subsequent measurement by SEM spectroscopy.

c) Derivation of rotational parameters. The R-branch DRM signals of 1,2,5-thiadiazole carry only minute hyperfine splittings. We considered it legitimate, therefore, to take the observed frequencies as coincident with the hypothetical centres of these transitions. High-J Q-branches, on the other hand, mostly appeared as narrow triplets (see the trace of Fig. 1, for example), and in these cases we have used the approximation given by Dobyns and Pierce [3] to deduce hypothetical centre frequencies: $\nu_{\mathrm{hyp.\,cent.}} = \nu_2 - (1/3)(\nu_2 - \nu_1)$, where ν_2 refers to the middle component and ν_1 is the low-frequency component of the triplet. For the normal species, centre frequencies of transitions studied soon after the structure work (subsequent paper) were also included in the final fit of the spectrum.

As in previous studies on planar ring compounds [1, 2] the transitions of 1,2,5-thiadiazole were fitted to a Hamiltonian which included only quartic distortion terms [10]. Not unexpectedly, the measured transitions turned out unsuitable for a reliable determination of the distortion constants τ_{aabb} and τ_{abab}. It was noticed, however, that despite their rather large uncertainties, the values of τ_{aabb} were very similar (-6.3 ± 2.5 kHz and -9.1 ± 2.1 kHz) for the normal and the 3,4-d$_2$-species for which the largest number of transitions had been measured. We therefore considered it

Table 1. Rotational parameters of the parent and isotopic species of 1,2,5-Thiadiazole.

	Species		I Normal	II ^{34}S	III ^{13}C	IV ^{15}N	V 3,4-d$_2$	VI 3,4-d$_2$-^{34}S	VII 3,4-d$_2$-^{13}C	VIII 3,4-d$_2$-^{15}N
1	DRM signal transitions		7R & 3Q	9R & 5 Q	9R & 5Q	9R & 5Q	8R & 4Q	10R & 4Q	8R & 5Q	8R & 5Q
2	J-range		2–5 & 5–8	2–5 & 5–8	2–5 & 5–8	2–5 & 5–9	2–5 & 5–8	2–5 & 5–7	2–4 & 5–8	2–4 & 5–8
3	DRM relaxation signals		7	7	4	2	9	6	3	3
4	SEM measurements [a]		36 (8)	25 (3)	30 (5)	20 (1)	35 (13)	22	23	20
5	Transitions in fit ($J_{\max}$)		53 (38)	46 (39)	48 (39)	36 (39)	56 (39)	42 (39)	39 (39)	36 (39)
6	Standard deviation (MHz)		0.05	0.06	0.07	0.08	0.05	0.05	0.06	0.08
7	A	in MHz	8538.436 (13) [b]	8538.670 (12)	8472.029 (15)	8324.235 (17)	8041.747 (10)	8041.972 (13)	7981.850 (14)	7851.445 (16)
8	B		6333.038 (8)	6166.960 (9)	6215.713 (11)	6333.303 (14)	5717.785 (8)	5569.697 (9)	5629.614 (11)	5717.895 (13)
9	C		3633.926 (7)	3578.661 (8)	3583.153 (10)	3594.629 (10)	3339.958 (6)	3288.903 (8)	3299.474 (10)	3306.690 (12)
10	τ_{aaaa}	in kHz	−15.74 (30)	−15.54 (30)	−15.47 (37)	−15.43 (45)	−13.15 (27)	−13.21 (39)	−13.11 (54)	−13.31 (54)
11	τ_{bbbb}		− 9.65 (12)	− 9.34 (15)	− 9.22 (17)	− 9.62 (30)	− 7.72 (14)	− 7.43 (17)	− 7.57 (13)	− 7.72 (16)
12	τ_{abab} [c]		− 1.62 (36)	− 1.54 (30)	− 1.30 (30)	− 1.33 (49)	− 0.81 (25)	− 0.55 (42)	− 0.79 (33)	− 0.49 (42)
13	I_a	in μÅ^2	59.18836 (7)	59.18673 (8)	59.65230 (11)	60.71140 (12)	62.84405 (8)	62.84230 (10)	63.31564 (11)	64.36726 (13)
14	I_b		79.79993 (9)	81.94897 (12)	81.30620 (15)	79.79659 (22)	88.38668 (14)	90.73672 (15)	89.77098 (17)	88.38497 (20)
15	I_c		139.07163 (27)	141.21932 (30)	141.04226 (38)	140.59199 (39)	151.31210 (38)	153.66097 (36)	153.16866 (46)	152.83442 (54)
16	$\mathrm{I.D.} = I_c - I_a - I_b$		0.08334 (30)	0.08362 (33)	0.08376 (42)	0.08399 (45)	0.08137 (30)	0.08195 (41)	0.08204 (50)	0.08219 (60)
17	δ (I.D.) [d]		–	0.00028	0.00042	0.00065	–	0.00048	0.00067	0.00082

[a] The figures in brackets give the number of transitions taken over from the work of Dobyns and Pierce (3). For the normal and the 3,4-d_2 species they include the $J = 0 \to 1$ and $1 \to 2$ R-branch lines. [b] Three times standard deviation. [c] τ_{aabb} was taken as -7.7 kHz for all species. [d] Deviation of the inertia defect from that of the "parent" species.

justified to adopt the average of $\tau_{aabb} = -7.7$ kHz as a fixed parameter for all eight isotopic forms.

The results of the LSQ fits of the spectra to six rotational parameters are collected in Table 1. This table also contains information concerning the number of DRM and SEM transitions measured for each of the isotopic forms, the maximum J-value being $J_{\max} = 39$ for all but the normal species. Listings of line frequencies may be obtained from the author. They have also been deposited with the "Zentrum für Struktur-Dokumentation" of the University of Ulm (West-Germany).

IV. Structure Calculation

The isotopic data of Table 1 are sufficient for two independent determinations of the substitution structure [12] of 1,2,5-thiadiazole. From the moments of inertia in columns I—V, a complete set of substitution coordinates can be calculated with respect to the principal axes of the normal species, and from the data in columns I and V—VIII the coordinates can be derived with respect to the inertial axes of the 3,4-d$_2$-species. In the limit of a rigid structure and infinite accuracy in the rotational constants, the b-coordinates (see Fig. 2) in the two reference frames should coincide, whereas the a-coordinates should differ by a constant amount, equal to the shift of the centre of gravity under substitution of two deuteriums for the hydrogen atoms. As in previous similar situations [1 b—e] we have first determined the structure of 1,2,5-thiadiazole in each reference frame separately (Table 2, columns I and II), and we have then averaged the two independent sets of results to arrive at a "best" substitution structure (column IV).

For consistency with the approach taken in the previous studies [1, 2] we had intended to calculate every pair of substitution coordinates from the changes in the moments I_a and I_b, in I_a and I_c and, finally, from the changes in I_b and I_c, and the average of the three values thus obtained was to be taken as the best substitution coordinate. However, it turned out that this method could be applied for the carbon atoms only. Since ΔI_a for both ^{34}S-species and ΔI_b for both ^{15}N-species is negative (see Table 1), we have calculated the coordinates a_S and b_N once from the observed changes ΔI_b^{eff} and ΔI_a^{eff} alone, and then from the quantities $\Delta I_b^* = \Delta I_c^{\text{eff}} - \Delta I_a^{\text{eff}}$ (in the case of the sulphur atom) and from $\Delta I_a^* = \Delta I_c^{\text{eff}} - \Delta I_b^{\text{eff}}$ (in the case of the b_N-coordinate). A corresponding approach was used to locate the hydrogen atoms, and the two values obtained for each of the coordinates a_S, b_N, a_H and b_H were averaged. The deviations of individual values from these averages were taken as a measure of compatibility. They are given in square brackets in Table 2. While the C$_{2v}$ symmetry of 1,2,5-thiadiazole clearly requires $b_S = 0$ in both reference frames, the a-coordinate of the nitrogen atoms could not be determined from isotopic substitution as $\Delta I_b < 0$ in both axis systems. a_N was therefore calculated from the first moment condition after the other three atoms had been located.

The results of these coordinate calculations are collected in rows 1—4 of Table 2. From column III, rows 5 and 6, it is seen that although the nitrogens are "below" the b-axis of the normal species and "above" the b-axis in the 3,4-d$_2$-species, the differences in the four a-coordinates are not only very consistent, but also in good agreement with the shift of the centre of gravity, as calculated from the substitution coordinates of the hydrogen atoms.

Finally, in order to deduce a "best" set of substitution data, the a-coordinates determined for the 3,4-d$_2$-species were transformed to the normal reference frame through subtraction of the shift of the centre of gravity, and they were then averaged with their counterparts determined in the normal axis system directly. Of the resulting structure parameters (Table 2, column IV, rows 7—15) all angles and the bond distances S—N and N=C

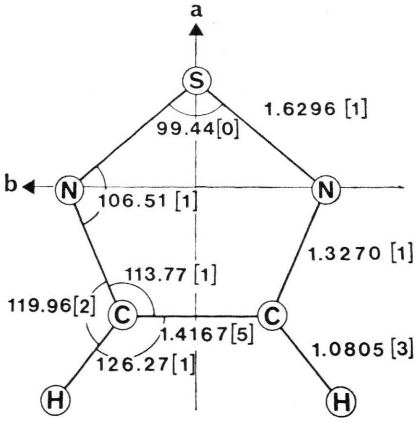

Fig. 2. Averaged substitution structure of 1,2,5-thiadiazole (for significance of square brackets see text or footnote of Table 2).

Table 2. Summary of structure calculations for 1,2,5-thiadiazole.

		I Normal axis system		II 3,4-d_2 axis system		III	IV Combined data (Normal axis system)	
	Coordinates (in Å)							
		a	$\|b\|$	a	$\|b\|$	$a^{D_2} - a^{H_2}$	a	$\|b\|$
1	S (1)	+ 1.04969 [03] [a]	0	+ 1.09743 [07]	0	0.04774	+ 1.04966 [03] [a]	0
2	N (2/5)	− 0.00377 [16] [b]	1.24323 [14]	+ 0.04382 [25] [b]	1.24316 [16]	0.04759	− 0.00387 [10]	1.24320 [04]
3	C (3/4)	− 1.21848 [12]	0.70861 [21]	− 1.17041 [19]	0.70808 [33]	0.04807	− 1.21834 [14]	0.70835 [27]
4	H (3/4)	− 2.08948 [12]	1.34757 [18]	− 2.04170 [12]	1.34757 [18]	0.04778	− 2.08948 [0]	1.34757 –
5					Average shift:	0.04779		
6					Calculated shift	0.04778		
	Bond lengths (in Å)					Difference		
7	S − N	1.62954 [23] [c]		1.62958 [33] [c]		0.00004	1.62956 [02] [a]	
8	N = C	1.32715 [40]		1.32690 [60]		− 0.00025	1.32702 [13]	
9	C − C	1.41722 [42]		1.41616 [66]		− 0.00106	1.41669 [53]	
10	C − H/D	1.08024 [42]		1.08078 [55]		0.00054	1.08051 [27]	
	Bond angles (in degrees)							
11	N S N	99.44 [03] [c]		99.44 [04] [c]		0.00	99.44 [00] [a]	
12	S N C	106.52 [04]		106.50 [05]		− 0.02	106.51 [01]	
13	N C C	113.76 [03]		113.78 [03]		+ 0.02	113.77 [01]	
14	N C H/D	119.98 [05]		119.94 [08]		− 0.04	119.96 [02]	
15	C C H/D	126.26 [04]		126.28 [06]		+ 0.02	126.27 [01]	
	Effective and calculated moments (in μÅ^2)							
16	$I_a^{\text{subst.}}$	58.99827		62.63006			58.98734	
17	$I_a^{\text{eff.}} - I_a^{\text{subst.}}$	0.19009 (0.32%)		0.21399 (0.34%)			0.20102 (0.34%)	
18	$I_b^{\text{subst.}}$	79.66163		88.22778			79.65145	
19	$I_b^{\text{eff.}} - I_b^{\text{subst.}}$	0.13830 (0.17%)		0.15890 (0.18%)			0.14848 (0.19%)	

[a] The square brackets in columns I and II indicate the compatibility of the averaged coordinates with the values obtained from different combinations of ΔI-values. Those in column IV refer to the compatibility of the combined data with values deduced in the normal and the 3,4-d_2 frame separately.
[b] Value derived from first moment condition. [c] These values are calculated from the most unfavourable "incompatibilities" in the coordinates.

appear to be very accurately determined, and the largest discrepancies occur for the C--C and C—H/D bond lengths. This "best" substitution structure is depicted in Figure 2.

V. Discussion

a) Comparison with earlier work. The results of the present structure determinations fall inside the error limits (± 0.003 Å for bond lengths and $\pm 0.2°$ for angles) quoted in the previous work [3] on 1,2,5-thiadiazole. The chemical conclusions drawn in the original study are therefore not affected by our present results.

A small alteration of the earlier data arises from the observation of the ^{15}N-spectra, since these new data allow the distance of the nitrogen atoms from the symmetry axis to be determined from substitution directly, rather than indirectly by matching this parameter to the effective moment I_a of the normal species. As has been found in many molecules by now, the effective moments of a "parent" species are normally a few tenths of a percent larger than those calculated from a complete set of substitution coordinates (Table 2, rows 16—19). In keeping with this general observation, we now find the S—N and C=N bonds ~ 0.001 Å shorter than indicated by Dobyns and Pierce [3]. The C—C bond length in the normal species (1.4172 Å) lies only just inside the error limits of the previous value (1.420 Å), and this difference is readily traceable to the refinement of the rotational constants of the ^{13}C-species. The bond angles in 1,2,5-thiadiazole are barely affected by these adjustments, and the very large NSN angle reported by Dobyns and Pierce is fully confirmed by the present work.

The chief distinction between the present and the earlier study thus consists in the improvement by about a factor ten in the precision of the structure parameters. This was brought about by the determination of the complete structure in two reference frames and by the unequivocal identification, up to high J-values, of comparable sets of transitions for all eight isotopic forms. Clearly, our success in establishing the required experimental data owes much to the use of DRM techniques [5].

b) Consistency of structure parameters. With the exception of the C—C bond length, and hence also the C—H bond length, the structure parameters in the two reference frames show a high degree of compatibility, and the remaining differences (Table 2, column III) are comparable in size with those remaining in related compounds [1 b—e]. From row 9 of Table 2 the "compatibility limits" (square brackets) which emerge from the calculation of coordinates from the three different combinations of ΔI-values, appear to be slightly too large to allow an identical C—C bond length in the normal and the 3,4-d$_2$ frame to be ruled out entirely. However, in view of the much better consistency between all other pairs of corresponding quantities, it seems improbable that the relatively large discrepancy of 0.0011 Å between the two values for the C—C length arises solely from an unidentifyable anomaly in the experimental data (compare the obviously parallel behaviour of the minute changes of the inertia defect for sulphur, carbon and nitrogen isotopes in the normal and the 3,4-d$_2$-species (row 17 of Table 1)). Moreover, it is seen from Table 3 that the incompatibilities of Table 2 are noticeably larger than the uncertainties which emanate from the 3σ-limits on the experimental data alone, and the calculation of the C—C bond lengths from corresponding combinations of ΔI-values in the two reference frames points to a reduction of this bond length for each of the three combinations.

On these grounds we feel compelled to accept the discrepancy between the two values for the C—C length as a true change in the r_S-value, caused by deuteration at both ends of this bond. Such an effect was first noted in methyl chloride and methyl bromide [11] (reduction of C—Cl bond by 0.0008 Å and of C—Br by 0.0011 Å under perdeuteration) and, more recently, in the study of maleic anhydride

Table 3. Calculation of the C—C bond length from different combinations of ΔI-values and with uncertainties arising from the 3σ-limits on the rotational constants of the parent and the ^{13}C species.

ΔI-values used in calculation	C—C bond length		Reduction
	I Normal frame	II 3,4-d$_2$ frame	II—I
ΔI_a & ΔI_b	1.41700(28)	1.41582(30)	−0.00118(58)
ΔI_a & ΔI_c	1.41701(28)	1.41584(32)	−0.00117(60)
ΔI_b & ΔI_c	1.41765(100)	1.41682(80)	−0.00083(180)
Average:	1.41722(31)^a	1.41615(47)^a	−0.00106(16)^a

^{a} Standard deviation of the three individual values.

[1e]. In the latter case we determined an apparent reduction of the C=C bond by 0.0008 Å in the 3,4-d_2-species. Clearly, these figures are in good agreement with the present result on 1,2,5-thiadiazole.

c) Vibrational contributions for near-axis atoms. The stated differences in the C—C and C—H/D bonds between the two parent species do not preclude the determination of the small vibrational contributions (ΔI^{vib}) to the changes of the moments of inertia under substitution. As the *b*-coordinate of the sulphur atom is zero by symmetry in both parent species, the value of ΔI^{vib} accompanying substitution by ^{34}S can be read off from Table 1, columns I and II (columns V and VI), row 13, as

$$\Delta I_a^{\text{vib}}(\text{S}) = \Delta I_a^{\text{eff}} = -0.00163\ (-0.00175)\ \mu\text{Å}^2\,,$$

with numbers in brackets referring to the 3,4-d_2-species.

The good consistency of *a*-coordinates in the two reference frames suggests that the small distance of the nitrogen atoms from the *b*-axis is also determined with good precision. If this is accepted, one finds that for a rigid structure the moment I_b should have remained unchanged under substitution of ^{15}N in normal 1,2,5-thiadiazole, where $\Delta I_b^{\text{calc}} = 0.00002\ \mu\text{Å}^2$, and that it should have increased by $\Delta I_b^{\text{calc}} = 0.00201\ \mu\text{Å}^2$ in the case of the 3,4-d_2-species. Comparison of these values with the observed changes $\Delta I_b^{\text{eff}} = -0.00334\ (-0.00171)\ \mu\text{Å}^2$ thus indicates

$$\begin{aligned}\Delta I_b^{\text{vib}}(\text{N}) &= \Delta I_b^{\text{eff}} - \Delta I_b^{\text{calc}} \\ &= -0.00336\ (-0.00372)\ \mu\text{Å}^2\,.\end{aligned}$$

In view of their smallness, the internal consistency of these quantities and their good agreement with corresponding data from other cyclic compounds [1d, e] should perhaps be noted.

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