The Triply Determined Substitution Structure of 1,3,4-Thiadiazole by DRM Microwave Spectroscopy

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Double **R**esonance **M**odulation (DRM) microwave spectroscopy has allowed the determination of the complete substitution structure of normal, mono-deuterated and perdeuterated 1,3,4-thiadiazole ($N_2C_2H_2S$). The shift of the centre of gravity between the normal and the d_2-form and the swing of inertial axes relative to the C_{2v} symmetrical forms in the 2-d_1-species have been used to revise the small coordinates of hydrogen and deuterium atoms.

Bond lengths (in Å) and bond angles (in degrees), with uncertainties covering all three molecular forms, are found as follows:

S–C = 1.7200 [3] ∢ CSC = 86.38 [2]
C–N = 1.3031 [5] ∢ SCN = 114.64 [3]
N–N = 1.3711 [5] ∢ CNN = 112.17 [1]
C–H/D = 1.0771 [4] ∢ SCH/D = 122.49 [2]

The results suggest that the shift and the swing of inertial axes between different 'parent' forms, which can both be determined from the moments of multiply substituted molecular isotopes, may be used with advantage to refine the position of near-axis atoms.

I. Introduction

Since its inception in 1965 the Double Resonance Modulation (DRM) technique [1] has become recognised in most microwave laboratories as a powerful tool for the disentanglement of complex spectroscopic situations, and its applications in different branches of rotational spectroscopy have resulted in an improved efficiency and in a widened scope of microwave spectroscopy in general. In the specific field of of molecular structure determinations by the isotopic substitution method [2], the DRM technique has been particularly beneficial because its extreme molecular selectivity together with an enhanced sensitivity has greatly reduced the need for the usually expensive, and often difficult-to-prepare enriched isotopic forms.

The relative ease of identifying by DRM techniques the spectra of rare molecular isotopes containing ^{34}S, ^{13}C, ^{15}N or ^{18}O in their natural abundances has led almost inescapably to the study of multiply substituted species, particularly when a relatively cheap deuterated form had been enriched to ~ 50% or more. Thus, the substitution structures of 2,6-difluoropyridine [3a], maleic anhydride [3b], 1,2,3-, 1,2,4- and 1,2,5-thiadiazole [3c, d, e], of ortho- and meta-difluorobenzene [3f], and of furazan [3g] have all been determined not only with the normal form as the 'parent' molecule, but also with a mono-, di- or trideuterated form as the parent molecular species.

While we were initially content to look upon the values of doubly determined structure parameters as merely providing a check on the consistency and accuracy that seemed to be obtainable by the substitution method, it soon became apparent that multiple substitution data may also help to overcome the chief disadvantage of that method, which is its failure to provide reliable coordinate values for atoms near a principal inertial plane. For example, in the structure calculation on 1,2,4- and 1,2,3-thiadiazole the small coordinate of a near-axis hydrogen atom was revised from knowledge, deduced from multiply substituted forms, of the *swing of inertial axes* which results from substitution of that hydrogen atom by deuterium. In the separate structure calculations on the normal and a symmetrically deuterated form of 2,6-difluoropyridine, of maleic anhydride, of 1,2,5-thiadiazole, of difluorobenzenes and of furazan a high degree of consistency was noted between the *shift of the centre of gravity* as calculated directly from the known coordinates of the substituted hydrogen atoms, on the one hand, and as deduced, on the other hand, from the

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differences between coordinates of atoms in the two inertial reference frames. These latter findings seemed to imply that the small coordinate of an otherwise unplaceable near-axis atom may be determinable from the shift of the centre of gravity as apparent from the different coordinates of atoms in the two reference frames.

Of course, it cannot be denied that the apparent success of the 'swing method' and the good consistency of the 'shift data' in the aforementioned cases may have been partly fortuitous. This is why we thought it desirable to study a structure which would allow each of these two schemes to be applied separately for the determination of the small coordinate of the same near-axis atom.

With three previous structure studies on thiadiazoles, the selection of 1,3,4-thiadiazole [4] as the test-case was almost inevitable. Although this compound has two pairs of equivalent near-axis atoms, its C_{2v} symmetry offered the possibility of examining the 'shift scheme' for the location of the near-axis hydrogens from multiple substitution data relating to the normal and the d_2-form, while the 'swing scheme' for locating the same two hydrogens could be tested with the experimental data on the 2-d_1-species in combination with either C_{2v}-symmetrical form.

II. Experimental

a) Samples

The three samples (normal, mono- and perdeuterated) of 1,3,4-thiadiazole, which were needed for the present study, were kindly prepared by Dr. P. J. Thomas of this department. The normal form was obtained by the method of Foehlisch, Braun and Schultze [5], and the 2-d_1-species was prepared by a method based on the work of Bak and collaborators [4b]. The 2,5-d_2-form was obtained by direct exchange with D_2O [3e].

The degree of deuteration achieved in these preparations was assessed by the relative intensity of absorptions under DRM and gave the following approximate compositions: sample I: normal form ~18%, 2-d_1-species ~ 37%, 2,5-d_2-form ~ 45%; sample II: normal form ~ 45%, 2-d_1-species ~ 43%, and d_2-form ~12%. The molecular isotopes associated with ^{34}S, ^{13}C and ^{15}N were all studied in their natural abundances. The approximate concentration of these rarer isotopic forms relative to the normal species in a pure sample are given in row 3 of Table 1.

b) Instrumental

The essential part of the spectroscopic work was carried out by DRM spectroscopy, but additional measurements were made under Stark effect modulation (SEM) [6]. The DRM spectrometer, which has been described in detail previoulsy [7], has an 'empty' *K*-band absorption cell of 20 m in length, and employs frequency modulation of the pump radiation. In this respect it differs from all DRM spectrometers built later. DRM signal transitions were observed on the oscilloscope. For the present study the range of pump frequencies was taken from 15–30 GHz, with signal frequencies ranging from 22–42 GHz. The SEM spectrometer, with a *J*-band absorption cell of 3.5 m length, was operated in the same fashion as the DRM instrument. All measurements were made at room temperature and with sample pressures between 10–50 mTorr.

III. Spectroscopic Results

The rotation spectrum of 1,3,4-thiadiazole (TDA) has been the subject of previous investigations [4], in which rotational constants have been reported for the ^{34}S-species (natural abundance), the 2-d_1-species (75% enriched), the ^{13}C-form (52% enriched) and the ^{15}N-species (33% enriched) of normal 1,3,4-TDA. On the basis of these data the rotational constants of the nine additional isotopic forms of this study were closely predictable and their spectra were readily identified and assigned by standard DRM methods [7].

a) Sequence of Isotopic Analysis

Naturally, we chose to identify the nine new spectra in the order of decreasing spectral intensity. The perdeuterated form was studied first, followed by its ^{34}S-, ^{13}C- and ^{15}N-forms. In the 2-d_1-species which followed, the C_{2v} symmetry of the molecular mass distribution is destroyed, and the occurrence of a ^{13}C-atom in the 2- or 5-position of the ring leads to slightly different spectra. Similarly, there occur two distinct ^{15}N-forms so that five, rather than just three, molecular isotopes had to be studied for a complete determination of the ring structure. Fortunately, the sepa-

Table 1. Rotational constants and moments of inertia of 1,3,4-thiadiazole and its molecular isotopes.

1 Spectrum [a]		I	II	III	IV	V	VI	VII	VIII
2 Species		Normal (n)	n-^{34}S	n-^{13}C	n-^{15}N	2,5-d$_2$	2,5-d$_2$-^{34}S	2,5-d$_2$-^{13}C	2,5-d$_2$-^{15}N
3 Abundance [b]		100	4.2	2.2	0.7	45	2.0	1.0	0.3
4 R- & Q-branch lines		18 R & 49 Q	11 R & 31 Q	10 R & 30 Q	10 R & 39 Q	13 R & 46 Q	9 R & 36 Q	11 R & 32 Q	9 R & 25 Q
5 Range of J-values		1–20 & 3–50	1–5 & 4–39	1–5 & 4–39	1–5 & 4–38	1–16 & 3–38	1–5 & 4–38	1–5 & 5–37	2–5 & 6–37
6 Relaxation signals		11	8	6	7	8	9	8	3
7 St'd deviation (in MHz)		0.094	0.062	0.069	0.100	0.071	0.062	0.093	0.071
8 A	in MHz	8907.376 (17)[c]	8907.484 (24)	8696.617 (19)	8838.554 (26)	7565.918 (11)	7566.044 (11)	7413.475 (16)	7517.216 (15)
9 B		5569.321 (10)	5408.526 (9)	5569.263 (10)	5469.994 (14)	5567.338 (7)	5407.324 (9)	5567.237 (13)	5467.128 (11)
10 C		3424.779 (8)	3363.296 (8)	3393.119 (9)	3376.938 (13)	3205.561 (6)	3151.862 (8)	3177.816 (11)	3163.478 (9)
11 τ_{aaaa}	in kHz	−15.46 (40)	−13.89 (95)	−13.38 (75)	−12.00 (160)	−9.93 (28)	−9.67 (39)	−9.66 (56)	−11.85 (57)
12 τ_{bbbb}		−7.51 (7)	−6.97 (15)	−7.31 (17)	−7.51 (24)	−7.37 (10)	−6.77 (11)	−7.26 (18)	−7.05 (18)
13 τ_{abab} [d]		−3.93 (16)	−3.84 (57)	−3.88 (50)	−5.71 (90)	−3.18 (18)	−2.71 (10)	−2.89 (44)	−2.22 (43)
14 I_a	in μÅ^2	56.73686 (11)	56.73611 (15)	58.11179 (12)	57.17858 (16)	66.79639 (10)	66.79527 (9)	68.16992 (15)	67.22915 (12)
15 I_b		90.74284 (16)	93.44062 (15)	90.74379 (12)	92.39060 (24)	90.77516 (12)	93.46139 (15)	90.77680 (22)	92.43904 (18)
16 I_c		147.56455 (33)	150.26213 (35)	148.94143 (39)	149.65509 (56)	157.65604 (29)	160.34202 (40)	159.03251 (56)	157.75327 (45)
17 $I.D.$		0.08485 (39)	0.08539 (41)	0.08585 (45)	0.08591 (63)	0.08448 (33)	0.08536 (44)	0.08579 (61)	0.08508 (51)

1 Spectrum [a]		IX	X	XI	XII	XIII	XIV
2 Species		2-d$_1$	2-d$_1$-^{34}S	2-d$_1$-2-^{13}C	2-d$_1$-5-^{13}C	2-d$_1$-3-^{15}N	2-d$_1$-4-^{15}N
3 Abundance [b]		45	1.9	0.5	0.5	<0.2	<0.2
4 R- & Q-branch lines		14 R & 46 Q	10 R & 40 Q	9 R & 30 Q	9 R & 31 Q	9 R & 27 Q	9 R & 28 Q
5 Range of J-values		1–17 & 3–39	1–12 & 5–39	2–5 & 5–39	2–5 & 5–39	2–5 & 5–39	2–5 & 5–37
6 Relaxation lines		14	14	7	8	–	–
7 St'd deviation (in MHz)		0.060	0.077	0.090	0.087	0.080	0.093
8 A	in MHz	8190.071 (11)	8189.876 (16)	8019.104 (20)	8004.030 (19)	8134.555 (15)	8130.079 (18)
9 B		5568.156 (6)	5407.830 (9)	5568.179 (14)	5567.949 (13)	5469.463 (12)	5467.331 (14)
10 C		3312.800 (6)	3255.322 (7)	3284.460 (12)	3281.849 (11)	3268.673 (10)	3267.174 (12)
11 τ_{aaaa}	in kHz	−11.51 (34)	−11.78 (60)	−10.32 (71)	−11.03 (72)	−13.03 (72)	−10.67 (81)
12 τ_{bbbb}		−7.25 (8)	−6.87 (14)	−7.63 (25)	−7.11 (30)	−7.13 (19)	−7.35 (24)
13 τ_{abab} [d]		−3.47 (16)	−3.17 (42)	−4.47 (66)	−3.09 (63)	−3.10 (42)	−4.55 (52)
14 I_a	in μÅ^2	61.70594 (8)	61.70740 (12)	63.02150 (15)	63.14019 (15)	62.12706 (12)	62.16126 (14)
15 I_b		90.76183 (16)	93.45265 (16)	90.76146 (22)	90.76520 (21)	92.39956 (20)	92.43559 (23)
16 I_c		152.55251 (25)	155.24608 (34)	153.86881 (54)	153.99125 (53)	154.61196 (48)	154.68293 (56)
17 $I.D.$		0.08475 (29)	0.08604 (40)	0.08585 (60)	0.08587 (60)	0.08533 (53)	0.08608 (63)

[a] Spectra I–IV and IX have been investigated previously [4], and 21 transitions were taken over without remeasurement.

[b] Approximate percentage abundance

[c] 3σ uncertainties, given in units of the last quoted digit

[d] τ_{aabb} was taken as −0.5 kHz throughout.

ration between corresponding transitions of the two ^{13}C-forms, and the separations between the transitions of the pair of ^{15}N-forms, were generally large enough to allow the unequivocal assignment of transitions to one or the other component of each pair. The differences between the deduced constants turned out sufficiently pronounced to allow a definite correlation of the spectra with ^{13}C-substitution in the 2- or 5-position and with ^{15}N-substitution in the 3- or 4-position of the ring. Due to the absence of symmetry, the natural abundance of ^{13}C and ^{15}N was cut back to 1.1% and 0.36% of the parent 2-d$_1$-species. In view of the composition of sample I, this amounted to only ~ 0.5% and ~ 0.2% with respect to the normal species in a pure sample. For this reason, the two ^{15}N-forms of the 2-d$_1$-species were studied last.

b) Method of Assignment

Despite the fact that signals from all 14 isotopic forms were detectable in each of the deuterated samples, little difficulty was encountered in identifying the spectra of the nine new isotopic forms. In each case double resonance connections between the $J = 2 \rightarrow 3$ (pump) and $J = 3 \rightarrow 4$ (signal) transitions were located first through double searches [7], and the assignments were then completed through the identification of connected low-J ($J < 5$) Q-branch transitions. Such transitions with $6 < J < 10$ were located next by double searches involving only small ranges of pump and signal frequencies.

c) Hyperfine Splittings

The quadrupole fine structure of the $J = 2 \rightarrow 3$, $3 \rightarrow 4$ and $4 \rightarrow 5$ transitions, which were used in the DRM experiments, is very small (compare [4d], Table 1), and the observed frequencies could therefore be taken as identical with the hypothetical centre frequencies. For some Q-branch transitions, however, broadening or small splittings were noticeable. In such cases either the peak absorption frequency or the centre of resolved hyperfine components was taken as the unperturbed frequency of the transition. The uncertainties resulting from these approximations are estimated not to exceed ± 0.3 MHz and, while they may be responsible for the slightly larger than usual standard deviations of the fits (row 7 of Table 1), their influence on the accuracy of the rotational constants is considered neglibible.

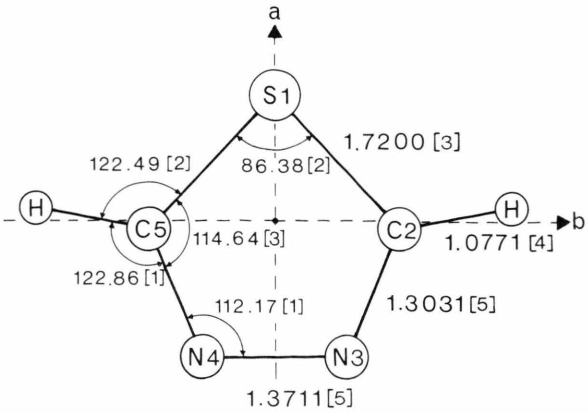

Fig. 1. Averaged structure of 1,3,4-Thiadiazole.

d) High-J Q-branch Transitions

As in the case of the closely related 1,2,5-thiadiazole [3e], the moments of 1,3,4-TDA, together with the molecular symmetry and the resulting ***a***-type selection rule, lead to a comparatively sparse DRM spectrum with the disadvantage that only few Q-branch transitions with low J-values are accessible. Since some of these transitions are broadened by hfs, we found it impossible to derive rotational parameters accurate enough for our purposes from the low-J DRM transitions alone. In particular, the rotational constant A could not be determined to better than ± 0.1 MHz, and there arose the need for the identification of high-J Q-branch transitions which would allow the refinement of the constants. Such transitions had previously been measured [4d] for the normal species of 1,3,4-TDA and, undoubtedly, they could have been identified in the present study by SEM spectroscopy for the enriched forms as well. For the rare isotopic forms, on the other hand, the identification of such transitions by SEM techniques appeared cumbersome since predictions based on transitions with $J < 10$ were unlikely to be of much help at J-values above 20. We considered it more promising to try and identify the high-J Q-branch transitions by the technique of DRM intensity modulation via collisional energy transfer (for a more detailed explanation see [3e], Figure 1). Although such 'collisional relaxation signals' were, typically, about ten times weaker than DRM signals produced by direct modulation, it was possible to identify at least a few such high-J Q-branch signals for all but the least abundant isotopic forms. After their incorporation in the fits, other high-J transitions could be accurately predicted and readily measured by SEM spectroscopy.

Unfortunately, for the crucial ^{15}N-forms of the 2-d$_1$-species we were prevented from applying the described technique by the deplorable lack of suitably powerful pump oscillators for the *J*-band (12 – 18 GHz) range. As a result, we were reduced to SEM spectroscopy alone, and it turned out that the identification of high-*J* Q-branch transitions of the two ^{15}N-forms of 2-d$_1$-TDA accounted for more than 90% of the total experimental effort required in the present study. Although apparently successful in the end (columns XIII and XIV of Table 1), the identification of these transitions could scarcely have been achieved without the precise knowledge of all transitions up to $J = 40$ of the other twelve isotopic forms, as deduced so easily by DRM techniques.

e) Derivation of Rotational Parameters

As in previous studies on planar heterocyclics [3], and in keeping with the earlier work [4] on the normal form of 1,3,4-TDA, the 14 spectra were fitted by least squares to a Hamiltonian with four quartic distortion constants [8]. Through the addition of 22 transitions, including 12 DRM identified R-branch lines with $2 < J < 21$, to the 45 transitions observed previously [4d], six of the seven parameters of the normal species were determinable with good accuracy. However, the distortion constant $\tau_{aabb} = (-0.49 \pm 0.18)$ kHz carries an uncertainty of ~ 30%. LSQ-fits of the 2-d$_1$ and 2,5-d$_2$ spectra, which were both studied to an extent comparable with the normal species, gave analogous results with $\tau_{aabb} = (-27 \pm 0.15)$ kHz and $\tau_{aabb} = (-0.73 \pm 0.18)$ kHz, respectively. In view of this, and since the identification of DRM connections involving the very weak, high-*J* R-branch transitions was not feasible for the rare isotopic forms, we considered it legitimate for our purposes to fit all 14 spectra to six parameters, with τ_{aabb} held constant at the average value of -0.50 kHz.

The results of these fits are collected in Table 1, where the uncertainty (3σ errors) of all rotational constants is seen to be smaller than ± 0.03 MHz, and the distortion constants are in qualitative agreement with each other throughout.

Since we can see no scientific advantage in the publication of 631 transition frequencies, we have collected general information on each of the 14 spectra in the upper half of Table 1, with the relevant parameters given in the lower half. Listings of the fitted transitions may, of course, be obtained from the author. They have also been deposited with the 'Sektion für Spektren und Strukturdokumentation' of the University of Ulm (FRG).

IV. Structure Calculations

In principle, the 14 sets of moments of molecular isotopes of 1,3,4-TDA allow three independent determinations of the structure of this simple molecule. The data of columns I – V and IX allow a structure calculation on the normal form, and those of V – IX together with I permit an analogous calculation for the d$_2$-form. The data in columns IX – XIV together with I and V allow the determination of the structure of 2-d$_1$-TDA. Unfortunately, however, none of these calculations can be completed satisfactorily because the proximity of the hydrogen (or deuterium) atoms to the ***b***-axis (see Fig. 1) prevents the placement, – via the first moment condition –, of the two carbon atoms which are still closer to the ***b***-axis than the hydrogens. These uncertainties, which arise from the failure of Kraitchman's equations (K.E.s) in the case of near-axis atoms, seem removable however if the multiple substitution data are utilised in combination with each other, rather than separately, because two additional criteria will then arise which seem to allow erroneous small coordinate values to be diagnosed and rectified. As mentioned above, these criteria are, firstly, the 'shift of the centre of gravity (C.o.G.)' between the normal and the 2,5-d$_2$-form and, secondly, the 'swing of the inertial axes' in the 2-d$_1$-species from their orientation in the C$_{2v}$ symmetrical forms.

In the calculations to be reported, atomic coordinates were obtained from K.E.s for planar molecules [2]. Since the planarity condition

$$\Delta(\text{I.D.}) = \Delta I_c - \Delta I_a - \Delta I_b = 0 \tag{1}$$

is rarely fulfilled strictly, the coordinates of every atom were calculated (– as in our previous studies –) from ΔI_a and ΔI_b, from ΔI_a and $\Delta I_b^* = \Delta I_c - \Delta I_a$, and from $\Delta I_a^* = \Delta I_c - \Delta I_b$ and ΔI_b, and the three coordinate values thus obtained were then averaged. In (1) the symbol Δ refers to changes under isotopic substitution, and I.D. is the inertia defect. The largest deviation of an individual coordinate value from the quoted average is given in square brackets in the following tables.

Table A-1. 'Raw' substitution coordinates (in Å) in C_{2v}-symmetrical forms of 1,3,4-TDA.

	Atom	Method of calculation	I Normal species		II 2,5-d_2-species		III shift s of C. o. G.
			a_i	$\|b_i\|$	a_i	$\|b_i\|$	$\|a_i^{H_2} - a_i^{D_2}\|$
1	S(1)	K.E.s.	+1.17608 [10]	–	+1.17328 [15]	–	0.00280
2 a	C(2/5)	K.E.s.	−0.03469 [875]	1.17759 [28]	−0.04394 [892]	1.17690 [36]	0.00925
2 b		$\sum m_i a_i = 0$ [a]	−0.07832 (47)		−0.08171 (50)		0.00339
3	N(3/4)	K.E.s.	−1.28470 [28]	0.68576 [55]	−1.28742 [16]	0.68530 [31]	0.00272
4 a	H/D	K.E.s. (H ↔ D)	+0.12756 [25]	2.23576 [2]	+0.12560 [79]	2.23562 [4]	0.00196
4 b		K.E.s. ($H_2 \leftrightarrow D_2$)	+0.12784 [36]	2.23569 [2]	+0.12492 [35]	2.23569 [2]	0.00292

[a] Averaged values of $a_H = 0.12770$ (30) and $a_D = 0.12526$ (60) were used for the derivation of a_C from the first moment condition.

Table A-2. Refined coordinates (in Å) of normal and d_2-1,3,4-TDA.

	Atom	Method of calculation	I Normal species		II 2,5-d_2-species		III shift s of C. o. G.
			a_i	$\|b_i\|$	a_i	$\|b_i\|$	$\|a_i^{H_2} - a_i^{D_2}\|$
1	S(1)	K.E.s.	+1.17608 [10]	–	+1.17328 [15]	–	0.00280
2 a	C(2/5)	$\sum m_i a_i = 0$ (shift)	−0.07788 (92)	1.17759 [28]	−0.08077 (111)	1.17690 [36]	0.00289
2 b		$\sum m_i a_i = 0$ (swing)	−0.07784 (56)		−0.08070 (59)		0.00286
3	N(3/4)	K.E.s.	−1.28470 [28]	0.68576 [55]	−1.28742 [16]	0.68530 [31]	0.00272
4 a	H/D	shift of C. o. G.	+0.12244 (430)	2.23572 [4]	+0.11964 (430)	2.23566 [4]	0.00280
4 b		swing of axes	+0.12205 (120)		+0.11923 (120)		0.00282

Comparison of effective and calculated moments (in $\mu Å^2$)

		I	II
5	I_a (observed)	56.73686	66.79639
6	I_a (calculated)	56.52671	66.52862
7	I_a (obs.) − I_a (calc.)	0.21015 = 0.37%	0.26777 = 0.40%
8	I_b (observed)	90.74284	90.77516
9	I_b (calculated)	90.62093	90.64467
10	I_b (obs.) − I_b (calc.)	0.12191 = 0.13%	0.13049 = 0.14%

IV-A. Structures of C_{2v} Symmetrical Forms

A-1. Separate Structure Calculation on Normal and 2,5-d_2 Form

Atomic coordinates, deduced in the manner outlined above from K.E.s, are collected for the two symmetrical forms of 1,3,4-TDA in Table A-1. The ***b***-coordinates are all determinable with good accuracy, and corresponding values in the two reference systems are in fair agreement with each other. From the large and well-determined ***a***-coordinates of sulphur and nitrogen atoms, the shift of the C.o.G. under deuteration is indicated as $s = 0.0028 \pm 0.0001$ Å. While a very similar shift (0.0029 Å) results from the small hydrogen and deuterium coordinates if these are calculated from symmetrical forms (row 4b), a discrepancy occurs when these ***a***-coordinates are determined from the 2-d_1-species in conjunction with either the normal or the d_2-form (row 4a). The complete breakdown of K.E.s in the case of the very small ***a***-coordinates of the carbon atoms (row 2a) is indicated not only by very large uncertainties (~ 0.009 Å), but also by the erroneous value of 0.0092 Å for the shift of the C.o.G. that results from these a_C-values. Revision of a_C with the first moment condition, $\Sigma m_i a_i = 0$, increases these coordinates by a factor 2, but leaves $s_C = 0.0034$ Å still noticeably larger than expected from the sulphur and nitrogen atoms.

A-2. Structures of Normal and d_2-Form from Combined Data on Both Forms

A-2.1 Shift of C.o.G. The results in columns I and II of Table A-1 may well give rise to the suspicion that the hydrogen and deuterium coordinates are in error, because their magnitudes fall under the Costain limit [9] of 0.15 Å. Further evidence for the unreliability of these coordinates cannot be extracted however from either set *alone*, and arises only from a comparison of both sets: If the small values of a_H and a_D were correct, they should, via the first moment condition, lead to a_C-coordinates which between the normal and d_2-form differ by the same amount as the $\boldsymbol{a}$-coordinates of the other atoms. Since this is not the case (row 2b, column III), it has to be inferred that a_H and a_D are indeed erroneous.

If confidence is placed on the large, and therefore well-determined $\boldsymbol{a}$-values of sulphur and nitrogen in each axis system, the shift of the C.o.G. under deuteration has to be accepted as $s = 0.0028 \pm 0.0001$ Å. However, s depends on the positions of hydrogen or deuterium atoms according to

$$s_{H_2 \to D_2} = \{2(m_D - m_H)/M(D_2)\}\, a_H \qquad (2\text{a})$$

and

$$s_{D_2 \to H_2} = -\, s_{H_2 \to D_2} = \{2(m_H - m_D)/M(H_2)\}\, a_D, \qquad (2\text{b})$$

where m_H, m_D are the masses of hydrogen and deuterium atoms, $M(H_2)$ and $M(D_2)$ those of the normal and 2,5-d_2 molecule. One may therefore consider revising, or at least checking, the values of a_H and a_D from (2) by use of the apparent value of s. – This yields in the present case

$$a_H = 0.1224 \pm 0.0043\,\text{Å} \quad \text{and} \quad a_D = 0.1196 \pm 0.0043\,\text{Å}.$$

The magnitude of these values may be confirmed, and their large error margins may be slightly reduced, by taking into consideration that acceptable a_H and a_D values should not only differ from each other by 0.0028 Å, but they should also lead to the same difference between the a_C-values which follow from them via the first moment condition in either reference frame. From this constraint one arrives at

$$a_H = 0.1215 \pm 0.0030\,\text{Å} \quad \text{and} \quad a_D = 0.1187 \pm 0.0030\,\text{Å}.$$

(Complete consistency of all $\boldsymbol{s}$-values at 0.00276 Å $= (s_S + s_N)/2 = s_{H/D} = s_C$ would occur for $a_H =$ 0.12069 Å and $a_D = 0.11793$ Å).

A-2.2. Swing of inertial axes. The second criterion for a check on, and the revision of the hydrogen and deuterium coordinates in the symmetrical forms with the help of multiple substitution data arises from the fact that the swing (θ) of inertial axes, which results from the replacement of one hydrogen atom by deuterium or of one deuterium atom of the d_2-form by hydrogen, can be determined experimentally from the sulphur and nitrogen positions which emerge from the study of the 2-d_1-species (IV-B, below). In particular, since $|\theta|$ is the same for the transition from the normal to the 2-d_1-species as from the 2,5-d_2-form to the latter, it follows that both a_H and a_D in the symmetrical forms should be determinable from Eq. (5) below, provided that $|\theta|$ and $b_H = b_D$ are known to good accuracy. This latter requirement however seems to be met by the large substitution values for $b_H = b_D$ in rows 4 of Table A-1, and the swing θ emerges in IV-B-2 as

$$0.53^\circ < \theta < 0.54^\circ.$$

Insertion of this 'multiple substitution information' into (5) yields

$$a_H = 0.1220 \pm 0.0012\,\text{Å} \quad \text{and} \quad a_D = 0.1192 \pm 0.0012\,\text{Å}.$$

These results are not only inside the error ranges of the values deduced independently from the shift of the C.o.G. between normal and d_2-form (above), but their difference coincides very closely with the difference between sulphur and nitrogen coordinates in the two reference frames. Naturally, the values of a_C in the two axis systems and the shift of the C.o.G. which follows from them agrees satisfactorily with the expectation $s = 0.0028 \pm 0.0001$ Å.

A-2.3 Refined coordinates of C_{2v}-symmetrical forms. The results of the preceding two subsections indicate that the refinement of the small coordinates a_H and a_D by consideration of the 'shift of the C.o.G.' leads to values which correlate remarkably well with those that are obtained by consideration of the 'swing of inertial axes'. The mutual agreement between the coordinate values refined by two different and independent methods is much closer than is expected on account of the necessarily large error margins associated with either method. Both results indicate that the hydrogen and deuterium coordinates in 1,3,4-TDA are ~ 0.005 Å *smaller* than the 'raw' values calculated from K.E.s. Via the first moment condition they lead to consistent refined values for the otherwise undeterminably small carbon coordinates a_C, which themselves are noticeably *larger* than the 'raw' substitution values.

The refined coordinates for the two symmetrical forms of 1,3,4-TDA are given in Table A-2, which also includes a comparison between the moments calculated with these coordinates and the observed moments of each form. The structure parameters which follow from Table A-2 are given in Table C.

IV-B. Structure of the 2-d_1 Species

B-1. 'Raw' Substitution Coordinates and Method of Refinement

Atomic coordinates in 2-d_1-1,3,4-TDA, calculated as outlined at the beginning of this section, are presented in Table B-1. Five of the 14 coordinates given in this table are seen to fall below the Costain limit and must hence be considered unreliable. The small ***b***-coordinate of the sulphur atom, however, is readily revisable from the first moment condition. There remain thus four different small ***a***-coordinates with, seemingly, only two 'rigid molecule conditions' for their refinement, namely the first moment condition

$$\sum m_i a_i = 0 \tag{3}$$

and the product of inertia condition

$$\sum m_i a_i b_i = 0 . \tag{4}$$

Table B-1. 'Raw' substitution coordinates in 2-d_1-1,3,4-TDA.

Atom	Method of calculation	Coordinates (in Å)	
		a_i	b_i
1 S(1)	K.E.s	+1.17444 [20]	−0.03214 [710]
1a	$\Sigma m_i b_i = 0$		−0.03671 (84)
2 C(2)	K.E.s.	−0.0089 [178]	+1.15177 [20]
3 N(3)	K.E.s.	−1.27966 [16]	+0.67195 [32]
4 N(4)	K.E.s.	−1.29298 [35]	−0.69929 [68]
5 C(5)	K.E.s.	−0.05975 [585]	−1.20271 [31]
6 D(2)	K.E.s.	+0.14765 [29]	+2.20856 [2]
7 H(5)	K.E.s.	+0.10480 [66]	−2.26262 [4]

As long as multiple substitution data remained difficult to obtain experimentally, one was forced in such situations to invoke 'reasonable assumptions' in order to match the number of ill-determined coordinates against an equal number of conditions for their refinement. The hazards inherent in that approach seem avoidable in the present case through use of information contained in the multiple substitution data of Table 1.

In the 2-d_1-species the inertial axes are rotated from their orientation in the symmetrical forms by an angle θ, which in terms of the coordinates a_k, b_k of H(2/5) or D(2/5) in the C_{2v}-forms is given by

$$\tan 2\theta = 2\mu a_k b_k / (I_b^0 - I_a^0 - \mu b_k^2 + \mu a_k^2) . \tag{5}$$

Here, I_a^0, I_b^0 are the moments of the normal (or 2,5-d_2) form, and μ is the reduced mass for substitution of H(2) by deuterium (or of D(5) by hydrogen). The same equation also describes the identical swing θ of axes from their orientation in the 2-d_1-species to that in symmetrical forms when D(2) is substituted by hydrogen (or when H(5) is replaced by deuterium). In that application of (5) I_a^0 and I_b^0 are the moments of the

Table B-2. The triangle N(3) S(1) N(4) and the orientation of its sides in the three inertial reference systems.

	Normal form	*D*	2-d_1-species	*D*	2,5-d_2-form
a) Dimensions of triangle N(3) S(1) N(4)					
S(1)...A	2.46078 Å	09	2.46087 Å	17	2.46070 Å
S(1)...N(3)	2.54455 Å	18	2.55437 Å	02	2.55435 Å
S(1)...N(4)		28	2.55483 Å	48	
N(3)...N(4)	1.37152 Å	22	1.37130 Å	70	1.37060 Å
∠N(3) S(1) N(4)	31.144°	06	31.138°	14	31.124°
b) Swing $\|\theta\|$ under substitution					
∠S(1)...A, *a*-axis	0		0.536°		0
∠S(1) N(3), *a*-axis	15.572°	0.535°	16.107°	0.545°	15.562°
∠S(1) N(4), *a*-axis	15.572°	0.541°	15.031°	0.531°	15.562°
Average $\|\theta\|$		0.538°		0.538°	

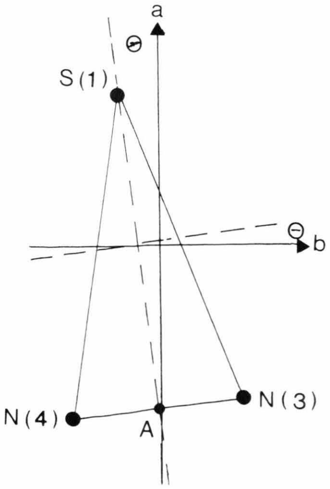

Table B-3. Refined coordinates in the 2-d$_1$-species of 1,3,4-TDA.

	Atom	Method of calculation	Coordinates (in Å)	
			a_i	b_i
1 a	S(1)	K.E.s.	+1.17444 [20]	
1 b		$\sum m_i b_i = 0$		−0.03671 (64)
2 a	C(2)	K.E.s.		+1.15177 [20]
2 b		$\sum m_i a_i = \sum m_i a_i b_i = 0$	−0.06864 (50)[a]	
3	N(3)	K.E.s.	−1.27966 [16]	+0.67195 [32]
4	N(4)	K.E.s.	−1.29298 [35]	−0.69929 [68]
5 a	C(5)	K.E.s.		−1.20271 [31]
5 b		$\sum m_i a_i = \sum m_i a_i b_i = 0$	−0.09045 (50)[a]	
6 a	D(2)	K.E.s.		+2.20856 [2]
6 b		swing of axes	+0.14122 (260)[a]	
7 a	H(5)	K.E.s.		−2.26262 [4]
7 b		swing of axes	+0.09945 (150)[a]	

Comparison of effective and calculated moments (in $\mu\text{Å}^2$)

8	I_a (observed)	61.70594
9	I_a (calculated)	61.47410
10	I_a (obs.) − I_a (calc.)	0.23184 = 0.38%
11	I_b (observed)	90.76183
12	I_b (calculated)	90.64498
13	I_b (obs.) − I_b (calc.)	0.11685 = 0.13%

[a] These uncertainties correspond to an error in θ of ± 0.01°.

2-d$_1$-species and μ is the reduced mass for the transition from the 2-d$_1$-species (now: parent) to the normal form (or to the d$_2$-form). Customarily, (5) is used to calculate the swing θ when an atom of known coordinates a_k, b_k is substituted.

Conversely, if the swing θ were determined experimentally and if either coordinate (here: b_k) were known accurately, the above relation could be considered as a 'rigid molecule condition' for the determination of the other coordinate (here: a_k).

For an arbitrary planar molecule of course only one small coordinate is revisable with the help of (5). In the present case, however, both $a_{D(2)}$ *and* $a_{H(5)}$ can be revised, since substitution of either D(2) by hydrogen or of H(5) by deuterium leads to a symmetrical form with inertial axes rotated by the same angle $|\theta|$ against the axes in the 2-d$_1$-species. Equation (5) therefore represents not just one, but two conditions which, together with (3) and (4), provide the required number for the revision of all *four* small ***a***-coordinates in the 2-d$_1$-species of 1,3,4-TDA.

From rows 6 and 7 of Table B-1 the large ***b***-coordinates of D(2) and H(5) can be considered accurate enough for use in (5), which we propose to reverse into a condition for the revision of the small values of $a_{D(2)}$ and $a_{H(5)}$. The determination of the swing θ on the basis of information from multiple substitution data is examined next.

B-2. Rigidity of the Triangle N(3)S(1)N(4) and Determination of the Swing θ

Atoms with a small and hence uncertain substitution coordinate are necessarily excluded from considerations aiming at the determination of the swing θ. This leaves, in the first instance, only the direction of the bond N(3)–N(4) relative to the axes of the 2-d$_1$-species as an indication of $|\theta|$. However, after revision of its small ***b***-coordinate with the first moment condition (row 1 a of Table B-1), the position of S(1) is also known to good precision. Accordingly, we have used the orientation of the triangle N(3) S(1) N(4) with respect to the axes of the 2-d$_1$-species to assess the value of θ.

Since variations under substitution in the geometry of this triangle would, naturally, reduce the accuracy of the θ-value to be determined, the dimensions of this triangle, as obtained independently in the normal form, in the 2-d$_1$-species and in the d$_2$-form, are examined first. The results are given in Table B-2, which indicates that the lengths of the sides are consistent to better than

Table C. Structures of 1,3,4-TDA as obtained in the three axis systems.

	Structure parameter	Normal form	D[a]	2-d_1-species	D	2,5-d_2-form	Averaged parameter
	Bond distances (in Å)						
1a	S(1)–C(2)			1.7198 (2)	0	1.7198 (2)	1.7200 [3][b]
1b	S(1)–C(5)	1.7202 (1)	+1	1.7203 (1)			
2a	C(2)–N(3)			1.3026 (3)	+4	1.3030 (2)	1.3031 [5]
2b	C(5)–N(4)	1.3032 (1)	+4	1.3036 (1)			
3	N(3)–N(4)	1.3715 (11)	−2	1.3713 (10)	−7	1.3706 (6)	1.3711 [5]
4a	C(2)–D(2)			1.0774 (3)	+1	1.0775 (3)	1.0771 [4]
4b	C(5)–H(5)	1.0769 (3)	−1	1.0768 (3)			
	Bond angles (in degrees)						
5	C(5)S(1)C(2)	86.40 (1)	−2	86.38 (1)	−2	86.36 (1)	86.38 [2]
6a	S(1)C(2)N(3)			114.67 (1)	−2	114.65 (1)	114.64 [3]
6b	S(1)C(5)N(4)	114.63 (1)	−2	114.61 (1)			
7a	C(2)N(3)N(4)			112.17 (1)	0	112.17 (1)	112.17 [1]
7b	C(5)N(4)N(3)	112.17 (1)	−1	112.16 (1)			
8a	S(1)C(2)D(2)			122.48 (9)	+1	122.49 (7)	122.49 [2]
8b	S(1)C(5)H(5)	122.50 (7)	+1	122.51 (5)			
9a	N(3)C(2)D(2)			122.85 (9)	+1	122.87 (7)	122.86 [1]
9b	N(4)C(5)H(5)	122.87 (7)	0	122.87 (5)			
	Non-bonded distances (in Å)						
10	H/D...H/D	4.4714 (1)	0	4.4714 (1)	−1	4.4713 (1)	4.4714 [1]
11	C(2)...C(5)	2.3552 (1)	−6	2.3546 (1)	−8	2.3538 (1)	2.3545 [7]
12a	S(1)...D(2)			2.4716 (6)	+1	2.4717 (5)	2.4717 [2]
12b	S(1)...H(5)	2.4717 (5)	+2	2.4719 (4)			
13a	N(3)...D(2)			2.0929 (9)	+5	2.0934 (8)	2.0932 [3]
13b	N(4)...H(5)	2.0932 (8)	+3	2.0935 (6)			

[a] Differences between corresponding parameters (in units of 10^{-4} Å and 10^{-2} degrees).
[b] Compatibility of averages with the three separate determinations.

0.001 Å between the three determinations. The angle NSN differs by 0.02° between the normal and the d_2-form, and this indicates the error margin which has to be expected for θ.

By comparison of the angles between the ***a***-axis and the directions of S...A, S...N(3) and S...N(4) in the 2-d_1-species with their counterparts in the symmetrical forms (see figure with Table B-2), one arrives at an average value of $\theta = 0.538°$ for the swing of inertial axes in the 2-d_1-species, with none of the three compared directions deviating from this average by more than 0.01°.

B-3. Refined Coordinates in 2-d_1-1,3,4-TDA

From the swing θ of inertial axes, as apparent from Table B-2, the small ***a***-coordinates of D(2) and H(5) in the 2-d_1-frame were revised according to condition (5). For these calculations the swing was taken as $\theta = 0.535°$, and an uncertainty of $\pm 0.01°$ was considered to obtain the error margins of Table B-3 on the resulting values of a_D and a_H. These revised values were subsequently utilised together with the large substitution coordinates to refine the small carbon coordinates $a_{C(2)}$ and $a_{C(5)}$ with conditions (3) and (4). The results of the entire procedure are collected in Table B-3.

While the described 'swing scheme' for the positioning of the D(2) and H(5) atom of 2-d_1-TDA automatically leads to the result that the non-bonded distance H(5)...D(2) deviates from the direction of the ***b***-axis of the 2-d_1-species by the same angle as the latter deviates from the ***b***-direction in symmetrical forms, the positions of the carbon atoms are, clearly, not involved in considerations of the swing of axes. Consequently, their final values provide an internal check on the consistency of the entire method of refinement, since the non-bonded C...C direction, which results after application of (5), (3) and (4), should, ideally, be parallel to the direction H(5)...D(2), and should therefore deviate by θ from the ***b***-axis of the 2-d$_1$-species. This additional criterion is met exactly for $\theta = 0.533°$, and lends support to the value of the swing adopted above.

IV-C. Combined Structure Results

The degree of compatibility – or inconsistency – of atomic coordinates in 1,3,4-TDA, as obtained in the three different inertial systems with the help of K.E.s and the revision of small coordinates on the basis of the 'shift of the C.o.G.' and the 'swing of inertial axes' can be judged after the transformation of the 2-d$_1$- and 2,5-d$_2$-data into the axis frame of the normal form. An equivalent assessment of the methods for refinement of small coordinates may be derived from a comparison of the bond lengths, bond angles and non-bonded distances which follow from the three coordinate sets of Tables A-2 and B-3. These structure parameters are presented in the following Table C.

Inspection of this table shows that the values of corresponding distances deduced in three separate axis systems do not differ by more than 0.001 Å from each other, and bond angles deviate from each other by 0.06° at the most. These findings differ from the data deduced with 'raw' hydrogen or deuterium ***a***-coordinates primarily through a smaller discrepancy between the two lengths C(2)–N(3) and C(5)–N(4) and between C–H and C–D in the 2-d$_1$-species. The adjustment of hydrogen or deuterium ***a***-coordinates to larger than the 'raw' substitution values increases such discrepancies considerably.

The averaged structure of 1,3,4-TDA which results from the present work is shown in Fig. 1, where square brackets indicate consistency margins between the three determinations.

V. Discussion

The mutually comaptible values for the small coordinates of hydrogen or deuterium atoms in 1,3,4-TDA, and the close agreement of structure parameters obtained in three different inertial axis systems, seem to confirm the view that both the 'shift of the C.o.G.' and the 'swing of inertial axes' may be used profitably as additional conditions for the refinement of atomic coordinates which are too small for reliable determination by K.E.s directly. The rigidity of small ring compounds may have contributed to the apparent success of the present study, and the thiadiazoles may be considered as satisfying Kraitchman's fundamental assumption of isotopic invariance of molecular structures particularly well. Larger open-chain molecules may perhaps not be equally amenable to the approach illustrated here.

The application of either 'shift' or 'swing' condition for the refinement of small coordinates requires, of course, that multiple substitution data be available, and hence necessitates the experimental study of more than one complete set of molecular isotopes. In view of the molecular selectivity and sensitivity of DRM spectroscopy, this requirement can hardly be considered prohibitively involved or expensive any longer, particularly since many of the rarer isotopic forms have been shown [3, 10] to be detectable in their natural abundances for many compounds.

An interesting by-product of the present study is the conclusion that the vibrational contribution $\Delta I^{\text{vib.}} = \Delta I^{\text{obs.}} - \Delta I^{\text{calc.}}$ to the small observed change $\Delta I^{\text{obs.}}$ for H → D substitution turns our positive ($\Delta I_b^{\text{vib.}} = + 0.0030(9)\,\mu\text{Å}^2 = 2 \times 0.0015(5)\,\mu\text{Å}^2$ for $H_2 \to D_2$, $+ 0.0016(6)\,\mu\text{Å}^2$ for $H_2 \to HD$, and $+ 0.0014(6)\,\mu\text{Å}^2$ for $HD \to D_2$ substitution). This follows from the result that the $a_{H/D}$-coordinates deduced from the 'shift' and 'swing' are ~ 0.005 Å *smaller* in all three reference frames than those calculated from $\Delta I^{\text{obs.}}$ with K.E.s. While such contributions are usually found *negative* (revised coordinate *larger* than 'raw' Kraitchman value) for near- or on-axis S-, C-, N- and O-atoms [3 a, b, d, e, g, 13], *both* signs occur for H → D substitution (compare, for example, the appropriate data in [3 a, d, g]). It would therefore appear advisable not to apply estimated vibrational corrections $\Delta I^{\text{vib.}}$ for the positioning of near-axis hydrogen atoms unless the sign of such corrections can be ascertained reliably. – In the earlier work [4 a, c] on 1,3,4-TDA the value of $\Delta I^{\text{vib.}}$ (H → D) had been assumed negative and, accordingly, an estimated positive correction was applied which, in turn, led to an a_H-value larger than indicated by $\Delta I_b^{\text{obs.}}$ Due to the small mass of hydrogen atoms in comparison with C, N and S, the resulting differences in structure parameters between the earlier and the present work on 1,3,4-TDA are minimal, however.

The hand-calculated results of this work represent an interesting test-case for the capabilities of the various computer schemes which have been devised for the extraction of structure parameters from the spectroscopic data on molecular isotopes of a compound. However, since inclusion of the results from such schemes, as regularly incorporated in our previous structure studies (e.g. [3]), would render the present paper unpalatably long, we prefer to give the results obtained with the help of the earliest such program (GEOM, [11]) and those from the most recent structure program by Rudolph [12] in a separate note. This will allow a comparison of the results from these programs with each other and with the results of the present study.

We are not aware of calculations of the structures of thiadiazoles by modern quantum chemistry. In view of identical experimental techniques, consistent procedures for the evaluation of structures, and comparable limits in the accuracy of deduced parameters, the present work together with the three previous studies [3c, d, e] on the four thiadiazoles may perhaps be considered as an ideal basis against which to gauge the success of future theoretical work on these four compounds.

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[13] By comparison of $\Delta I^{\text{obs.}}$ (Table 1) with ΔI-values calculated from the refined small coordinates of Table A-2 and B-3, the following values (in $\mu\text{Å}^2$) are obtained for $\Delta I^{\text{vib.}}$ for substitution of sulphur and carbon atoms in 1,3,4-TDA: $\Delta I_a^{\text{vib.}}$ (S): $-0.0007(3)$ in the normal, $-0.0009(3)$ in the 2-d$_1$-species, and $-0.0011(2)$ for the d$_2$-form; $\Delta I_b^{\text{vib.}}$ (C): $-0.0053(4)$ in the normal form, $-0.0053(4)$ for C(2) and $-0.0052(4)$ for C(5) in the 2-d$_1$-species, and $-0.0052(4)$ in the d$_2$-form.