The Quadrupole Coupling Constants of 1,2,5-Thiadiazole

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The nitrogen quadrupole coupling constants along the inertial axes of 1,2,5-thiadiazole are determined as $\chi_{aa} = 0.90 \pm 0.01$ MHz, $\chi_{bb} = -3.13 \pm 0.06$ MHz, $\chi_{cc} = \chi(\perp) = 2.22 \pm 0.06$ MHz, and Dobyns and Pierce's value for the dipole moment is confirmed as $\mu = \mu_a = 1.58 \pm 0.02$ D. (The uncertainties are three standard deviations.)

Comparison of these data with their counterparts in related compounds leads to speculation that the direction of the main field gradient in the molecular plane deviates from the SNC bisector towards the sulphur atom by $\theta \sim 5° - 10°$. From this assumption the principal in-plane coupling constants are $\chi_{\text{radial}} = \chi_{zz} \sim -3.82$ MHz and $\chi_{\text{tangential}} = \chi_{xx} \sim 1.60$ MHz, with uncertainties of ± 0.20 MHz due to a probable error of $\pm 2°$ in the assumed direction ($\theta = 8°$) of the z-axis of the field gradient tensor.

I. Introduction

Along with dipole moments and structure parameters, nuclear quadrupole coupling constants represent a third, valuable piece of molecular information which is often obtained from gas-phase rotational spectra. As a measurable manifestation of the electron distribution inside a molecule, the coupling constants are usually invoked in the discussion of the chemical properties of compounds, and they are increasingly being used to test the success (or inadequacy) of the methods and approximations of quantum-chemical computations [1]. In view of this, and since the earlier work [2] on 1,2,5-thiadiazole has yielded only semi-quantitative values for the coupling constants of that compound ($|\chi_{aa}| < 1.0$ MHz, $\chi_{cc} - \chi_{bb} = 5.2 \pm 0.3$ MHz, and hence: $\chi_{bb} \sim -\chi_{cc} = -2.6 \pm 0.7$ MHz), we considered it appropriate to continue our re-investigation [3] of the microwave spectrum of 1,2,5-thiadiazole with an attempt to reduce the uncertainties in the coupling constants to limits small enough to allow comparisons with existing and future quadrupole data on other five-membered heterocyclics containing one or two nitrogen atoms [4—10].

II. Experimental

The sample of 1,2,5-thiadiazole had been kindly provided by Dr. M. H. Palmer (University of Edinburgh).

Measurements of hyperfine splittings (and Stark effects) were made at room temperature and at a sample pressure of ~1 mTorr on a conventional Stark Effect Modulation (SEM) spectrometer [11] with an X-band absorption cell. The modulation frequency was 95 kHz. All but one measurement were made with free-running, frequency-swept klystrons permitting a minimum sweep rate of ~1 MHz/sec. Signals were observed on the oscilloscope. The hyperfine splitting of the transition $2_{21} - 3_{22}$ was deduced from several slow-sweep recordings with a phase-stabilised klystron.

III. Results

a) Quadrupole coupling constants. First-order theory describing the interaction of two quadrupolar nuclei with the overall rotation of molecules is well established, and the numerical difficulties in the calculation of hyperfine patterns have been eliminated through the availability of computer programs [12, 13]. In the present work the program by G. L. Blackman [13] has been used (coupling scheme: $I_1 + I_2 = I_{12}$, $I_{12} + J = F$).

The determination of the coupling constants in 1,2,5-thiadiazole is simplified by the fact that the two quadrupolar ^{14}N nuclei ($I_1 = I_2 = 1$) are in equivalent positions in the molecule and the field gradients at the two sites are therefore equal. As a result of this and of the Laplace condition, the hyperfine splittings of rotational transitions depend on only two parameters. Following the original study [2], we have chosen χ_{aa} and $\chi_{cc} - \chi_{bb}$ as the independent parameters. The C_{2v} symmetry of the molecule also leads to variations of the relative intensities of hfs components within a given pattern, and the intensity distribution in transitions between even or odd rotational levels differs in a characteristic way (Ref. [2], Figure 1). As discussed by

Dobyns and Pierce [2], these intensity effects arise from spin statistics due to the presence of two equivalent protons.

Naturally, our attempts to refine the quadrupole data for 1,2,5-thiadiazole started out from the previous results and from the observation [2] that the splittings of high-J Q-branch transitions ($J > 15$) are insensitive to the value of χ_{aa}. Accordingly, attention was focussed on the transitions with $J < 10$, as these offered not only an increasing dependence of the splittings on χ_{aa}, but also, on account of their larger splittings, a more sensitive means for the determination of $\chi_{cc} - \chi_{bb}$, once χ_{aa} had been refined.

To improve the value of χ_{aa} the following approach was chosen: The hyperfine patterns of all transitions between 15—26 GHz with J-values below 10 were computed for χ_{aa}-values of -1.0 MHz, 0, and $+1.0$ MHz, with $\chi_{cc} - \chi_{bb}$ fixed at 5.20 MHz. The effects of spin statistics on the relative intensities were included in these calculations, and the overall pattern of each transition was modelled by summation over the (assumedly) Lorentzian line shapes of individual hfs components [13]. The total splitting of each computed transition was then examined for its sensitivity towards the stated variations in χ_{aa} and, not unexpectedly, the lowest accessible Q-branch transition (3_{03}—3_{22}) was found to be the most sensitive: The calculated overall splitting of this transition was obtained as 2.26 MHz for $\chi_{aa} = -1.0$ MHz, decreasing linearly towards 1.40 MHz for $\chi_{aa} = +1.0$ MHz. Although the relative weakness and the unfavourable intensity distribution of this transition prevented the measurement of the total splitting to better than ± 0.05 MHz, the experimental value of $\Delta\nu_{\text{total}} =$ 1.53 MHz strongly suggested that the correct χ_{aa}-value was to be found in the range 0.8 MHz $< \chi_{aa} <$ 1.0 MHz.

As the use of an instrument comparable with that employed in the original study (SEM at 100 kHz, X-band absorption cell) could not be expected to permit a further refinement of χ_{aa} on account of superior resolution, the computed hyperfine patterns were now re-examined for detailed features particularly sensitive to the value of χ_{aa}, and such a feature was noted first in the transition 1_{11}—2_{12}: From the model calculations, a resolvable peak ($F(I_{12}) = 1(0) - 2(2)$) would have had to occur at the low-frequency side of the strongest component if $\chi_{aa} \sim 0$ (Figure 1a). For $\chi_{aa} \geq 0.5$ MHz, on the other hand, this component would merge with the centre line while the second strongest component ($F(I_{12}) = 2(2) - 3(2)$) would resolve on the high-frequency side of the strongest component $F(I_{12}) = 3(2) - 4(2)$), with the group of five weak, low-frequency transitions becoming resolvable into a doublet (Figure 1d). Comparison of the observed pattern with these calculations (Fig. 1c) gave a preliminary value of $\chi_{aa} = 0.89 \pm 0.03$ MHz, in good agreement with the result deduced from the transition 3_{03}—3_{22}.

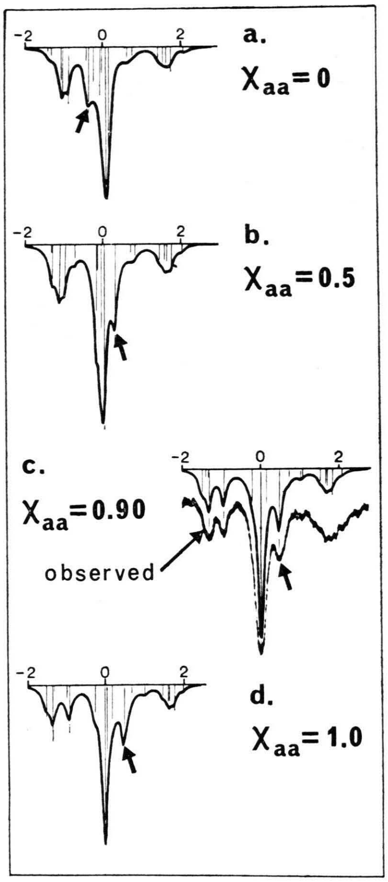

Fig. 1. Computed hyperfine pattern of the transition 1_{11}—2_{12} for different values of χ_{aa}. Pattern a), b) and d) are computed with χ_{cc}—χ_{bb} 5.20 MHz. Pattern c. is computed with the final values of the coupling constants and superimposed on a photograph of the observed transition (the frequency scale (in MHz) increases from left to right).

Encouraged by this consistency and by the observation that splittings as small as ~ 0.25 MHz could be detected in favourable circumstances, we next examined the transition $2_{21}-3_{22}$, the splitting of which depends solely on χ_{aa}. Our experiments on this transition, which had been reported unresolvable previously [2], yielded a splitting of 0.278 ± 0.01 MHz, which by comparison with computations for the range 0.5 MHz $< \chi_{aa} <$ 1.0 MHz, resulted in a value of $\chi_{aa} = 0.906 \pm 0.02$ MHz.

With χ_{aa} thus refined, the hyperfine patterns for low-*J* Q-branch transitions were computed for different values of $\chi_{cc}-\chi_{bb}$ (5.0 MHz—5.4 MHz) with the goal of reducing the uncertainty in this parameter through additional experiments. In these model calculations particular care was taken to adjust the half width of hyperfine components in such a way that the resolution obtained in the experiments was optimally matched by the computations. By this method a halfwidth of ~ 100 kHz and a value of $\chi_{cc}-\chi_{bb} = 5.35 \pm 0.03$ MHz was obtained from the transitions listed in Table 1. These two values were then used in the final evaluation of χ_{aa}-dependent splittings, which also included analyses of the transitions $2_{20}-3_{21}$ and $1_{10}-2_{12}$, with the latter showing a feature similar to that described above for the transition $1_{11}-2_{12}$.

Table 1. Summary of quadrupole analysis on 1,2,5-thiadiazole.

Rotational transition	Hyperfine components				Splitting	Coupling parameters	
	I $F(I_{12})$	$F'(I'_{12})$	II $F''(I''_{12})$	$F'''(I'''_{12})$	II − I (in MHz)	χ_{aa} (in MHz)	$\chi_{cc}-\chi_{bb}$ (in MHz)
$1_{11}-2_{12} = 17234.78$ [a]	3 (2)	4 (2)	2 (2)	3 (2)	0.439	0.900 (20) [b]	c)
	3 (2)	4 (2)	3 (2)	3 (2)	− 0.957	d)	5.35 (07)
$1_{10}-2_{11} = 22632.97$	3 (2)	4 (2)	2 (2) 2 (1)	3 (2) 3 (1) [e]	0.336	0.904 (20)	c)
	3 (2)	4 (2)	3 (2)	3 (2)	1.335	d)	5.32 (04)
	3 (2)	4 (2)	1 (0) 2 (2) 1 (0) 2 (1)	2 (0) 1 (2) 1 (2) 2 (1)	− 1.401	d)	5.36 (06)
$2_{21}-3_{22} = 29900.72$	1 (2) 1 (2) 2 (1) 2 (1)	1 (2) 2 (2) 2 (1) 3 (1)	3 (1) 3 (1) 3 (1)	2 (1) 3 (1) 4 (1)	0.278	0.906 (15)	–
$2_{20}-3_{21} = 34033.81$	2 (0) 2 (1)	3 (0) 3 (1)	3 (1)	4 (1)	0.725	0.906 (20)	c)
$3_{13}-3_{12} = 15663.16$	5 (2)	5 (2)	3 (2)	3 (2)	3.041	d)	5.37 (02)
	5 (2)	5 (2)	4 (2)	4 (2)	1.960	d)	5.30 (05)
	5 (2)	5 (2)	1 (2)	1 (2)	− 1.121	d)	5.39 (07)
$4_{14}-4_{13} = 23980.22$	6 (2)	6 (2)	5 (2)	5 (2)	1.496	d)	5.31 (04)
	6 (2)	6 (2)	4 (2)	4 (2)	2.449	d)	5.37 (04)
$8_{45}-8_{44} = 21249.99$	6 (2) 8 (0) 8 (1) 10 (2)	6 (2) 8 (0) 8 (1) 10 (2)	8 (2)	8 (2)	1.803	d)	5.32 (04)
$10_{56}-10_{55} = 25930.96$	12 (2) 10 (1) 10 (0) 8 (2)	12 (2) 10 (1) 10 (0) 8 (2)	10 (2)	10 (2)	1.628	d)	5.37 (04)
$13_{77}-13_{76} = 22455.61$	11 (2) 13 (0) 13 (1) 15 (2)	11 (2) 13 (0) 13 (1) 15 (2)	13 (2)	13 (2)	1.394	d)	5.36 (04)
					Average ± σ	0.904 ± 0.003	5.347 ± 0.03

[a] The quoted hypothetical centre frequencies are taken from the least squares fit of the entire spectrum.
[b] These error limits correspond to an estimated uncertainty of ±0.01 MHz in the splittings.
[c] $\chi_{cc}-\chi_{bb}$ taken as 5.35 MHz. [d] χ_{aa} was taken as 0.90 MHz. [e] Unresolved hyperfine components.

From these experiments, the quadrupole coupling constants along the principal inertial axes in 1,2,5-thiadiazole are (with 3σ-limits):

$$\chi_{aa} = 0.90 \pm 0.01 \text{ MHz},$$
$$\chi_{bb} = -3.13 \pm 0.06 \text{ MHz},$$
$$\chi_{cc} = 2.22 \pm 0.06 \text{ MHz}.$$

b) Dipole moment. As the SEM spectrometer used for the quadrupole analysis was needed during the same period for the "project work" of undergraduate students, we found it convenient to teach theoretical and practical aspects of "dipole determinations by microwave spectroscopy" using the example of 1,2,5 thiadiazole.

Low-J transitions with negligible hyperfine splitting were selected and, after calibration of the absorption cell with carbonoxysulphide ($J = 1 - 2$, $\mu_{\text{OCS}} = 0.71521$ D [14]), seven Stark lobes were studied. Stark coefficients, $\Delta\nu/E^2$, were calculated by the method of Golden and Wilson [15], and a moment of $\mu = \mu_a = 1.579 \pm 0.007$ D was obtained (Table 2). This agrees well with the previous value of Dobyns and Pierce [2] which, after correction for the difference in the reference moment in use at that time ($\mu_{\text{OCS}} = 0.7124$ D), is $\mu_a = 1.571 \pm 0.015$ D.

Table 2. Stark effect measurements of 1,2,5-thiadiazole.

Transition	M	Stark coefficient $\Delta\nu/E^2$		Dipole moment μ[b]
		Calculated[a]	Observed[a]	
$1_{01} - 2_{02}$	0	$-3.9793\ \mu^2$	-9.908	1.578
	1	$2.8978\ \mu^2$	7.128	1.568
$1_{10} - 2_{11}$	0	$2.7472\ \mu^2$	6.864	1.581
$2_{02} - 3_{03}$	0	$-0.4982\ \mu^2$	-1.258	1.589
	2	$1.5098\ \mu^2$	3.799	1.586
$2_{12} - 3_{13}$	1	$0.8762\ \mu^2$	2.162	1.571
	2	$4.1327\ \mu^2$	10.349	1.582
			Average $\pm\ \sigma$:	1.579 ± 0.007

[a] in 10^6 MHz$(\text{V/cm})^{-2}$. [b] in Debye units.

IV. Discussion

The quadrupole coupling constants deduced in the previous section are comparable in accuracy with the quadrupole data available for other five-membered heterocyclics [4—10]. They are, however, of only limited use because the in-plane values refer to the field gradients along the inertial axes, and not to the gradients along the principal axes of the field gradient tensor. For direct comparison with the results of *ab initio* calculations or with experimental data from NQR spectroscopy, or for the calculation of orbital populations [16] and ionicities around the nitrogen atoms, the above values of the coupling constants would first have to be transformed [17] to the principal axes of the coupling tensor. This, in turn, requires knowledge of the direction of the principal in-plane field gradients with respect to the molecular geometry and the orientation of the inertial axes. For oxazole [7], isoxazole [8] and 1,3,4-oxadiazole [10] such knowledge has been established from the study of the hyperfine structure in the spectra of isotopically substituted species with differing orientations of the inertial axes. In thiadiazoles, however, the required data are not easily obtained because the large weight of the sulphur atom, with respect to carbon and nitrogen, allows only small rotations of the inertial axes under substitution, and this entails correspondingly small changes in the hyperfine patterns and the coupling constants along the inertial axes.

In the present case of 1,2,5-thiadiazole it is easily calculated on the basis of the preceding structure work [3] that the largest rotation (6.8°) of the inertial axes would occur if one hydrogen were substituted by deuterium, and the determination of the two sets of in-plane coupling constants for that isotopic form would probably yield a reasonably accurate indication of the orientation and magnitude of the principal field gradients. For the ^{13}C-species, on the other hand, the orientation of the inertial axes with respect to the molecular skeleton would alter by only 2,3° and, within the resulting two sets of in-plane coupling constants, corresponding χ-values would differ by less than 0.35 MHz from each other, and by less than 0.20 MHz from those of the parent species. Although the transition frequencies for the ^{13}C-species are precisely known from the previous work, the study of such subtle changes in the coupling constants on weak transitions (natural abundance: 2.2%) on a conventional SEM spectrometer did not seem promising to us in view of the instrumental limitations in sensitivity and, in particular, in resolution. For the singly substituted ^{15}N-species, finally, no rotation of the inertial axes in 1,2,5-thiadiazole would occur.

In this situation one is confronted with the alternatives of either abruptly terminating the

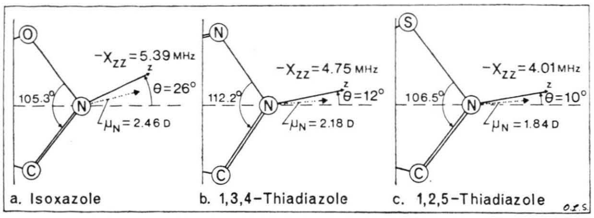

Fig. 2. Relative orientations of χ_{zz} (solid arrow), μ_N (dotted arrow) and the X−N=C-bisector (X=O,N,S (dashed line)) in isoxazole, and the likely directions of χ_{zz} and μ_N in 1,3,4- and 1,2,5-thiadiazole.

discussion or substituting *speculation* for the lack of experimental data.

If the latter approach is chosen, one may argue that the direction of the largest in plane field gradient (usually pictured to arise from the nitrogen lone pair orbital which, in cyclic compounds, would point in an approximately radial direction: $\chi_{\text{lone pair}} = \chi_{\text{radial}} = \chi_{zz}$) would either coincide with the external bisector of the SNC-angle (see Fig. 2) or, more probably, deviate from the bisector towards the sulphur atom due to the presence of an in-plane lone pair on the latter. This effect has been observed in several compounds [4, 10, 12] with adjacent nitrogen atoms and, most recently, in the case of isoxazole [8], where the direction of the "radial" gradient deviates by as much as 26° from the bisector towards the oxygen atom (Figure 2a). In the absence of similar, guiding data from isothiazole [6] it is of course difficult to estimate the magnitude of such a deviation for 1,2,5-thiadiazole, but it is probably reasonable to assume that the effect of the lone pair on the sulphur atom on the direction of the field gradients at the nitrogen atoms in 1,2,5-thiadiazole would be less than that of an adjacent oxygen or nitrogen atom. On that basis, and in order to emphasize the *speculative character* of these considerations, we have calculated (Table 3) the principal field gradients and the resulting orbital populations [16] and ionicities with the assumptions that the direction of $\chi_{\text{rad}} = \chi_{zz}$ coincides with the direction of the SNC-bisector ($\theta = 0°$, column Ia) or that it deviates from it by $\theta = 5°$ or $\theta = 10°$ towards the sulphur atom (columns Ib and Ic). The necessary geometrical information on the SNC angle

Table 3. Comparison of estimated principal quadrupole coupling constants (in MHz), orbital populations, ionicities (in e.u.) and dipole moments (in D) between 1,2,5- and 1,3,4-thiadiazole and their counterparts, deduced from observed data, on thiazole.

		Ia.	Ib.	Ic.	II.	III.
		1,2,5-Thiadiazole estimated in this study			1,3,4-Thiadiazole ref. 4	Thiazole ref. 5
1	Assumed deviation of tensor axis from bisector	$\theta = 0$	$\theta = 5°$	$\theta = 10°$	$\theta \sim 12°$	$\theta = 0.4°$
	Principal coupling constants					
2	$\chi_{zz} \equiv \chi_{\text{radial}}$	−3.35	−3.60	−4.01	−4.75	−4.41
3	$\chi_{xx} \equiv \chi_{\text{tangential}}$	1.13	1.38	1.79	2.64	1.83
4	$\chi_{yy} \equiv \chi_{\text{normal}} = \chi_{cc}$	2.22	2.22	2.22	2.11	2.58
5	$\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$	0.326	0.234	0.108	−0.112	0.170
	Orbital populations [a])					
6	a (π)	1.252	1.202	1.138	1.194	1.137
7	b_1 (σ)	1.352	1.222	1.090	1.031	1.183
8	b_2 (σ) (N = C bond)	1.352	1.299	1.267	1.329	1.191
9	*Ionicity* = $a + b_1 + b_2 - 3$	0.902	0.723	0.495	0.554	0.511
	Dipole moment					
10	$\mu_N = (\mu/\chi_{zz})_{\text{Pyr.}}^{*}\ \chi_{zz}$	1.54	1.65	1.84	2.18	2.02
11	$\mu_{\text{total}}^{\text{calc.}} = \Sigma\, \mu_N + \mu_{\text{resid.}}$ [b])	1.24	1.57	1.99	3.50	1.60
		1.24	1.43	1.69	3.30	1.60
12	$\mu_{\text{total}}^{\text{obs.}}$			1.58	3.28	1.61

[a] Calculated with $\chi_p = -10.0$ MHz.

[b] In calculating the upper row, μ_N was assumed to coincide with the direction of the z-axis. The values in the lower row are obtained if μ_N is assumed to lie about half-way between the bisector and the z-axis (compare Fig. 2). $\mu_{\text{resid.}}$ was taken as 0.55 D (thiophene).

and the direction of the bisector with respect to the inertial axes was, of course, known precisely from the previous structure work [3].

From row 9 of Table 3, the assumption $\theta = 0$ is seen to lead to an ionicity of the nitrogen atoms of 0.90 e, which is nearly twice as large as in thiazole [5] and 1,3,4-thiadiazole [4], and more than ten times larger than the ionicities of the nitrogen atoms in oxazole [7], isoxazole [8] and 1,3,4-oxadiazole [10] (Ref. [7], Table 3, row 8d). On this account, an angle of $\theta \sim 10°$ (column Ic) between the bisector and the z-axis must be favoured over $\theta = 0$, since the former leads to principal field gradients, orbital populations and an ionicity value which are much more in keeping with the data for the related compounds.

This speculative conclusion finds further support by a consideration of the dipole moment of 1,2,5-thiadiazole:

It has been previously suggested [5] that the electric dipole moment, μ_N, associated with the lone pair of the "pyridine-like" nitrogen atoms in heterocyclic compounds may be assumed proportional to the moment of pyridine, with the ratio of the radial field gradients as proportionality constant:

$$\mu_N = (\mu/\chi_{zz})_{\text{Pyrid.}} * \chi_{zz} \,. \tag{1}$$

While μ_N is not determinable directly by experiment, we have found [7] relation (1) in good agreement with the values of μ_N derived by vectorial addition of a residual ring moment μ_{resid} (taken from thiophene [18] or furan [19], as appropriate) to the observed dipole moment in several five-membered heterocyclics (Ref. [7], Table 3, rows 2 and 3a). In addition, among thiazole, 1,3,4-thiadiazole, oxazole, isoxazole and 1,3,4-oxadiazole, the smallest value of μ_N derived either by relation (1) or by vectorial composition is $\mu_N \sim 1.85$ D, and to reach this lower limit in 1,2,5-thiadiazole, one has to postulate a radial component of at least -4.0 MHz. This however again implies a deviation of the z-axis from the bisector by $\sim 10°$. On the other hand, vectorial addition of such μ_N moments (1.84 D oriented along the z-direction) to the residual moment of the ring (0.55 D) would lead to a total moment of 1.99 D, which is 0.4 D larger than the observed value. Thus, in attempting to reconcile all the presently available data for 1,2,5-thiadiazole one is forced to *speculate* that the tensor axis in this molecule may be rotated by $\sim 10°$ from the bisector towards the sulphur atom, while the moment μ_N is rotated by only about half that amount. If this were indeed the case, the situations in 1,2,5- and 1,3,4-thiadiazole would be replicas of the findings [7] on isoxazole, with corresponding angles scaled down by a factor of ~ 2.5 (see Figure 2).

In conclusion, we would suggest that the data of Table 3, column Ic, be used [20] for comparison with NQR values or with the results of *ab initio* calculations until experimental data on the monodeuterated species of 1,2,5-thiadiazole become available.

Acknowledgements

It is a great pleasure to thank Dr. M. H. Palmer (Edinburgh) and Dr. M. Redshaw (Salford) for helpful discussions and for the exchange of theoretical and experimental results on 1,2,5-thiadiazole and other five-membered heterocyclics. The self-explanatory terms: "radial" or "tangential" field gradient (in place of the often confused suffices xx, yy, zz) were suggested by Dr. Palmer. I am greatly indebted to Dr. G. O. Sørensen (Copenhagen) for his instant response to my enquiry about quadrupole programs. Finally, I would like to thank Mr. B. Issari (in the meanwhile: B. Sc., Bangor) for his diligence in the dipole moment measurements (Section IIIb).

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[20] If the observed dipole moment (1.58 D) were taken as the decisive criterion, the best fit would be obtained for $\sim 8°$. In this case, rows 2–11 of Table 3 would read: Principal coupling constants: −3.82, 1.60, 2.22, $0.162 = \eta$; Orbital populations: 1.165, 1.147, 1.280; Ionicity: 0.592; Dipole moment: 1.75, 1.80/1.57.