Nuclear Quadrupole Coupling in 5-Membered Ring Oxygen and Sulphur Heterocyclic Compounds; Studies by Nuclear Quadrupole Resonance and Ab Initio Molecular Orbital Calculations

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The ^{14}N nuclear quadrupole resonance spectra for the compounds **2**a, b, **3**b, **4**b, **5**a, b, **6**b have been obtained at 77 K and the asymmetry parameter and coupling constants extracted. A comparison of these with microwave spectral results, shows that small but systematic differences occur between the solid and gaseous states. There is a high level of agreement for the observed coupling constants from NQR or MW spectra and the *ab initio* calculations in both magnitude and direction. This enables us to extract further principal axis data from the observed microwave spectra, and to predict with some confidence the axes and coupling magnitudes for other members of the series where incomplete determinations are available. Variations in coupling constants with structure are discussed.

I. Introduction

In our previous work we have separately investigated the electronic structure and distribution in some nitrogen compounds by either nuclear quadrupole resonance (NQR) spectroscopy [1, 2] or by a combination of photoelectron spectroscopy and ab initio calculations [3–5]. In the present joint study, we have been working on the aza-derivatives of furan (**1**a) and thiophen (**1**b), namely isoxazole (**2**a) and isothiazole (**2**b), oxazole (**3**a) and thiazole (**3**b), 1,2,5-oxadiazole (**5**a) and the 1,3,4- (**4**b), 1,2,5- (**5**b), 1,2,3- (**6**b) and 1,2,4-thiadiazoles (**7**b). There have been previous NQR studies of **2**a [6] and **4**a [7], and MW studies of **2**a [8], **3**a [9], **3**b [10], **4**a [11], **5**a [12] although in some instances (**5**a, b; **6**b) insufficient information was available for a determination of the nuclear quadrupole coupling constants (NQCC) and their directions.

A feature of the present work is a comparison of both NQR and available MW data with those calculated, by *ab initio* calculations, from the electric field gradient values in the principal axes. It will be shown that the excellent level of agreement between the 3 sets of data makes it possible to confidently predict the NQCC and directions for the other members of the series, where experimental

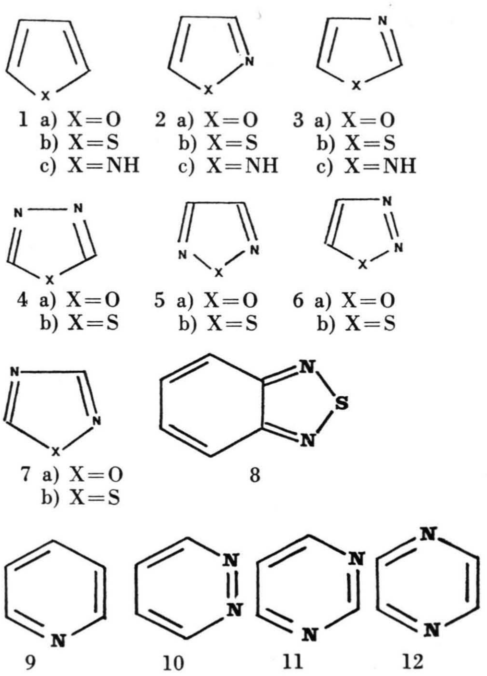

Fig. A

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data are lacking (e.g. 5a, b; 6b, 7b). Systematic trends were observed between the (calculated) principal axes of the electric field gradient and those of the quadrupole coupling tensor, and these are also discussed below.

II. Computational and Theoretical Methods

II(a) *Basis sets.* All of the present studies used either a double zeta (DZ, O/N heterocycles) or better than double zeta basis. The exponents for C, N, O are from Dunning [15] and are a 9s/5p set completely uncontracted in the valence shell. The basis set for S is a new one, although based upon the lowest energy choice of Veillard [16]; briefly, Dunning [15] has shown that an alternative contraction of the Veillard [16] basis for chlorine can lead to a much lower total energy; we have investigated similar procedures for the S atom and find that recontraction of the 12s/9p set to [5,1,2,1,1,1,1; 6,1,1,1] i.e. a (7s, 4p) set yields a lower (cf. Ref. [16]) total energy of − 397.49655 a.u., to be compared with the STO Hartree-Fock limit of − 397.50475 a.u. The exponents and contraction coefficients are given in Appendix 1. In the molecular calculations all the S compounds were studied both with the above (DZ + 4s) basis (sp) and also with a single set of $3d_S$ orbitals (DZ + 4s + $3d^6$, spd), using our previous exponent. The principal energy results are shown in Table 1.

II(b) *Electric field gradients and quadrupole moments.* These (q_{ij} and Q_{ij} respectively) were calculated directly from the wavefunctions for 2—7, using both basis sets (sp, spd) in most cases and the full operators in which Eqs. (1) and (2) give typical diagonal and off-diagonal examples of each type.

Electric field gradient operators

$$q_{xx} = (3x^2 - r^2)/r^5, \quad q_{xy} = 3xy/r^5 . \qquad (1)$$

Quadrupole moment operators

$$Q_{xx} = (3x^2 - r^2)/2, \quad Q_{xy} = (3/2)\,xy . \qquad (2)$$

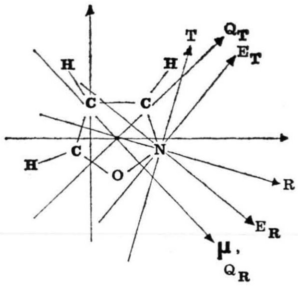
For both q_{ij} and Q_{ij} the values were obtained for the principal axes, and the values are shown numerically in Tables 2 and 3. The asymmetry parameter (η) was evaluated from $(q_{aa} - q_{bb})/q_{cc}$ where q_{aa}, q_{bb} and q_{cc} are the two smaller and largest values of the electric field gradients respectively.

II(c) *Nuclear quadrupole coupling constants (NQCC).* The traceless nature of the NQCC tensor clearly means that a change in one coupling parameter between two different molecules must imply a change in at least one other parameter in each molecule; thus there are difficulties in (say) discussion of the π-coupling throughout the series of compounds, without reference to the corresponding σ-term. Normally in NQR studies the convention is $\chi_{zz} > \chi_{yy} > \chi_{xx}$, while in MW studies, with inertial axes *a*, *b*, *c*, the out-of-plane coupling is χ_{cc}.

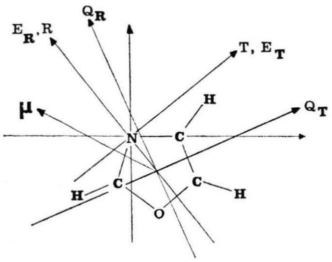
Table 1. Total Energies (a.u.)

Molecule	Total Energy E_T	Basis Set	Other lit. Values of E_T
Oxazole	−244.53087	DZ	−243.91324[a]
Isoxazole	−244.49121	DZ	−243.88971[a]
1,3,4-Oxadiazole	−260.48647	DZ	−259.81198[a]
1,2,5-Oxadiazole	−260.44074	DZ	−259.78809[a]
Thiazole	−567.19063 −567.24316	DZ + 4s DZ + $3d^6$ + 4s	−566.10215[b]
Isothiazole	−567.17096 −567.23473	DZ + 4s DZ + $3d^6$ + 4s	−566.09606[b]
1,2,3-Thiadiazole	−583.12635 −583.18978	DZ + 4s DZ + 4s + $3d^6$	−581.98747[b]
1,2,5-Thiadiazole	−583.13041 −583.21611	DZ + 4s DZ + 4s + $3d^6$	−582.01908[b]
1,3,4-Thiadiazole	−583.14449 −583.19713	DZ + 4s DZ + 4s + $3d^6$	−581.95671[b]
1,2,4-Thiadiazole	−583.22356	DZ + 4s + $3d^6$	−582.01855[b]

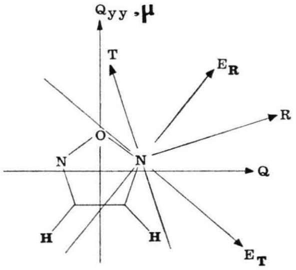
[a] Reference 3b. [b] Reference 3a.



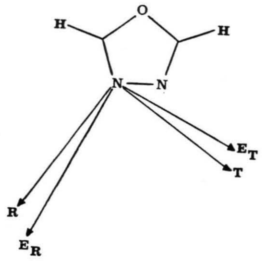
Isoxazole



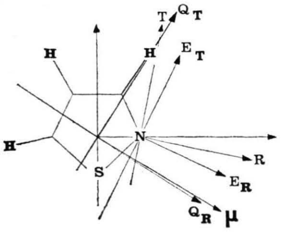
Oxazole



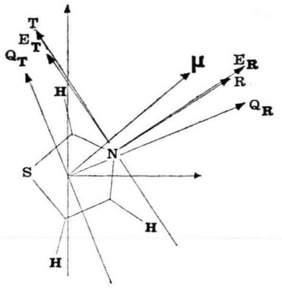
1,2,5-Oxadiazole



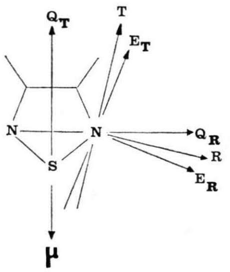
1,3,4-Oxadiazole



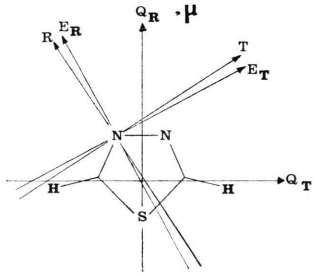
Isothiazole



Thiazole



1,2,5-Thiadiazole



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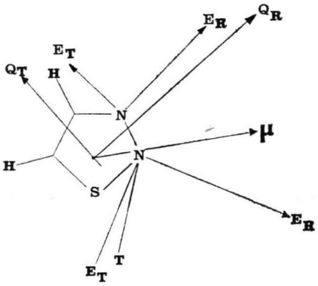
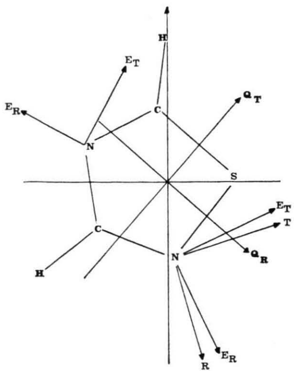


1,2,3-Thiadiazole



1,2,4-Thiadiazole

Fig. 1. Principal in-plane axes for Calculated Electric Field Gradients (*E*), Quadrupole Moment (*Q*), Dipole Moment (μ) and coordinate axes (x, y).

Table 2. Electric Field Gradients at Nitrogen (10^{16} e.s.u./cm^3).

Molecule	Principal Axis Angle to Radial Direction[a]	Electric Field Gradient (Principal Axis)			Asymmetry Parameter
		eq_R	eq_T	eq_π	
Isoxazole	22.0 (26.1)	0.4104	−0.4037	−0.0067	0.9674
Oxazole	−0.9 (5.7)	0.3442	−0.1683	−0.1759	0.0221
1,2,5-Oxadiazole	32.5 (−)	0.4350	−0.3260	−0.1090	0.4990
1,3,4-Oxadiazole	8.7 (16.0)	0.3932	−0.2414	−0.1518	0.2280
Isothiazole					
(sp)		0.3749	−0.2415	−0.1334	0.2884
(spd)	13.1 (16.5)	0.3640	−0.2245	−0.1397	0.2327
Thiazole					
(sp)	0.4 (0.4)	0.3646	−0.1574	−0.2072	0.1365
(spd)		0.3701	−0.1595	−0.2106	0.1383
1,3,4-Thiadiazole					
(sp)	5.5 (12.0)	0.3952	−0.2335	−0.1617	0.1818
(spd)		0.4018	−0.2340	−0.1678	0.1648
1,2,5-Thiadiazole					
(sp)	8.6 (10.0)	0.3499	−0.1786	−0.1713	0.0209
(spd)	7.0 (10.0)	0.3419	−0.1665	−0.1756	0.0266
1,2,3-Thiadiazole					
N-2 (sp)	6.7 (−)	0.3666	−0.2546	−0.1120	0.3889
(spd)	5.1 (−)	0.3643	−0.2443	−0.1202	0.3407
N-3 (sp)	10.9 (−)	0.4340	−0.1931	−0.2409	0.1101
(spd)	10.6 (−)	0.4416	−0.1970	−0.2445	0.1076
1,2,4-Thiadiazole					
N-2 (spd)	10.6 (−)	0.3110	−0.2218	−0.0894	0.4256
N-4 (spd)	2.0 (−)	0.3495	−0.1707	−0.1788	0.0230

[a] Literature values or estimates in parentheses.

In the present work we wish to compare the observed and calculated values for the group of molecules **2**—**7** and include the corresponding NH series (**1**—**3**, X = NH) and the azines **9**—**12** which have been reported elsewhere. Clearly, a unified system of axes and terminology is desirable in any comparisons between the molecules. In all of the MW studies [8—11] and calculations (Fig. 1), it is clear that one of the in-plane electric field gradient axes (q) lies close to the external bisector at the N atom; following our earlier [17] usage in relation to $2p_\sigma$ orbitals, it is convenient to refer to this axis as the *radial* axis (R) and the other σ-axis as the *tangential* axis (T). This close correlation between the calculated EFG axes (q_R/q_T) and R/T is shown in Fig. 1, and is especially so in oxazole (**3**a), thiazole (**3**b) and N-4 for 1,2,4-thiadiazole (**7**b) where E_R and R are effectively identical. In the compounds with adjacent lone pairs (either N/N, N/O or N/S) both MW and calculations show (see below) that one axis (q_R in Fig. 1) is rotated away from R by a considerable amount, and towards the adjacent lone pair (e.g. isoxazole **2**a). Even in these cases however, the *approximate* identity of say q_R and R still makes a meaningful comparison between the molecules (**1**—**12**) more simple if the EFG axes are referred to as q_R, q_T and q_π (for the out-of-plane value), and the NQCC as χ_R, χ_T and χ_π respectively.

In order to obtain calculated NQCC from the calculated electric field gradients, we require a value for the ^{14}N atomic quadrupole moment (Q_N) where $\chi_{ii} = eQ_N q_{ii}$. Various theoretical studies (for a review see [17]) have led to values for Q_N in the range 0.021 to 0.0150 barn. We chose a recommended value [13] of 0.015 barn and sought a scaling parameter a in aQ_N, such that the best fit with the experimental MW results was obtained (Figure 2). The value of a was 1.122 yielding an optimised value for Q_N (i.e. aQ_N) of 0.0167 barn, very close to the best value obtained (0.0164 barn) from extended basis set calculations [18, 19]. The data in Table 5 incorporate this value for Q_N, since it allows us to predict the numerical results for the

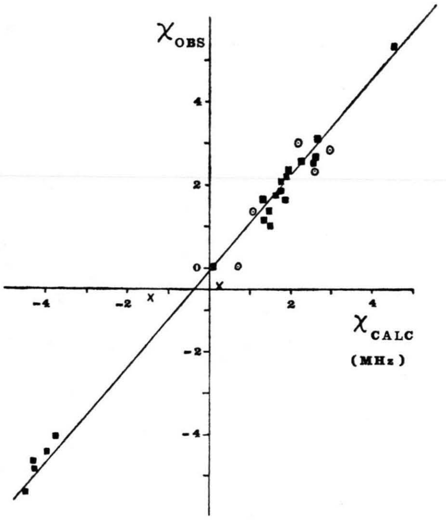


Fig. 2. Correlation of calculated and experimental nuclear quadrupole coupling constants.

two related compounds, 1,2,3-thiadiazole (**6**b) and 1,2,4-thiadiazole (**7**) where the relatively massive S atom has so far precluded direct measurement in the microwave spectra [20, 21].

Microwave spectra often *only* yield NQCC data in the *inertial axis* (*a*, *b*, *c*) system, and the off-diagonal element may not be readily extracted from the spectrum. None-the-less the trace of the three diagonal terms is zero, and hence these MW data are often called "principal axis" values; these values are quite distinct from the electric field gradient (EFG) principal axis value (χ_{ii}, where $i = x, y, z$), and we draw a clear distinction between the IA (*a*, *b*, *c*) and EFG (*x*, *y*, *z*) values. Interconversion between the two coordinate systems can be done via Eq. (3) if the requisite angle (θ_{ax}) is known:

Inertial $\chi_{(aa,\, bb)}$ to Principal Axes $\chi_{(xx,\, yy)}$

$$\begin{aligned} \chi_{xx} &= \frac{\chi_{aa}\sin^2\theta_{ax} - \chi_{bb}\cos^2\theta_{ax}}{\sin^2\theta_{ax} - \cos^2\theta_{ax}}\,, \\ \chi_{yy} &= \frac{\chi_{aa}\cos^2\theta_{ax} - \chi_{bb}\sin^2\theta_{ax}}{\cos^2\theta_{ax} - \sin^2\theta_{ax}}\,, \\ \chi_{zz}(\pi) &= \chi_{cc}(\pi)\,. \end{aligned} \tag{3}$$

In some instances θ_{ax} can be obtained directly from the MW spectra, but this has not been the case with most of the present series. Some empirical methods have been used [8, 9], and one of these is to find which angle (θ_{ax}) leads to optimal agreement with that obtained from the PA values from the NQR data or to use the calculated θ_{ax}.

Molecule	Principal Axis (X^2) (degrees)	Quadrupole Moment (Principal Axis)		
		X^2	Y^2	Z^2
Isoxazole	43.54	−4.7113	7.7598	−3.0484
Oxazole	23.89	11.5350	−9.2061	−2.3288
1,2,5-Oxadiazole	90.0	−3.9095	3.7132	0.1963
1,3,4-Oxadiazole	90.0	10.5620	−11.1424	0.5804
Isothiazole				
(sp)	57.28	−4.5984	8.5170	0.2884
Isothiazole				
(spd)	58.46	−4.2623	8.8621	−4.5998
Thiazole				
(sp)	−68.25	−8.1537	11.1660	−3.0123
(spd)	−66.62	−7.3597	10.9804	−3.6207
1,3,4-Thiadiazole				
(sp)	0.0	10.6912	−11.4834	0.7921
(spd)	0.0	10.1718	−10.2665	0.0947
1,2,5-Thiadiazole				
(sp)	90.0	−10.1566	10.5881	−0.4314
(spd)	90.0	−9.5637	10.8866	−1.3229
1,2,3-Thiadiazole				
(sp)	−48.92	3.6976	−3.3168	−0.3808
(spd)	52.71	4.2483	−3.1255	−1.1228

Table 3. Quadrupole Moments (at Centre of Mass) (10^{-26} e.s.u. cm^2 respectively).

Table 4. ^{14}N NQR frequencies (MHz) and derived data for the compounds studied at 77 K.

Compound	N-Site	ν^+	ν^-	ν_0	e^2Qq/h	η
Isoxazole	2	5.2982	2.67875	2.6195	5.3179	0.9850
(**2**a)		5.2930		2.61425	5.3145	0.9811
1,2,5-Oxadiazole	2/5	4.2223	2.7653	—	4.656	0.6274
(**5**a)			2.7582			
3,4-Dimethyl-1,2,5-Oxadiazole	2/5	4.2402	2.8416	—	4.721	0.592
1,3,4-Oxadiazole[a]	3/4	3.7834	2.8580	0.9254	4.427	0.418
(**4**a)		3.7648	2.8071	0.9577	4.381	0.437
Isothiazole	2	3.6639	2.8418	—	4.3371	0.3791
(**2**b)						
Thiazole	3	3.379	2.902	—	4.187	0.227
(**3**b)						
1,2,5-Thiadiazole	2/5	2.45365	2.3440		3.198	0.068
(**5**b)						
1,3,4-Thiadiazole	3/4	3.5837	3.03607	—	4.4131	0.2481
(**4**b)		3.56805	3.01720		4.3901	0.2506
2,5-Dimethyl-1,3,4-thiadiazole[b]	3/4	3.5018	2.7090	—	4.140	0.3829
2,1,3-Benzo-thiadiazole[b]	1/3	2.7000	2.4560	—	3.437	0.142
(8)		2.6750	2.4415		3.411	0.137
1,2,3-Thiadiazole	2	3.8907	2.8358	—	4.484	0.4704
(**6**b)	3	3.9755	3.1000	—	4.717	0.3712
Pyrazole[c]	2	3.6648	2.3653	—	3.9949	0.6570
(**2**c)	1	3.6396	2.3148			
			2.11818			
			2.07367			
Imidazole[c]	3	2.5586	2.3483		3.271	0.128
(**3**c)	1		1.41739			
Pyrrole (1c)[d]	1	1.685	1.408		2.0620	0.268

[a] Reference [7].

[b] L. Krause and M. Whitehead, J. Chem. Phys. **52**, 2787 (1970) (at 295 K).

[c] Reference [22].

[d] Reference [29].

III. Experimental Methods

(a) *Materials.* The compounds were prepared by standard methods described previously [6].

(b) *^{14}N NQR Measurements.* The spectra of the series of compounds **2**a, **2**b, **3**b, **4**a, **4**b, **5**a, **5**b, **6**b, were measured at 77 K using a Decca Radar NQR spectrometer. The observed frequencies ν_+ and ν_- (Table 4) were assigned, and the NQCC (e^2Q_q/h) and asymmetry parameter (η) extracted using Eqs. (4) and (5). The third resonance (ν_0) was usually too low or too weak to be observed. Only in the case of 1,2,3-thiadiazole (**6**b) did the failure to observe ν_0 lead to ambiguity. All possible combinations of the four possible resonances were considered and the NQCC evaluated (Table 5); the preferred set is based upon (a) consideration of the relationship to other molecules of the series, (b) the set which gives best agreement with the calculations.

$$3e^2 Q_q/h = 2(\nu_+ + \nu_-)\,, \tag{4}$$

$$\eta = 3(\nu_+ - \nu_-)/(\nu_+ + \nu_-)\,. \tag{5}$$

It is interesting to note that in several instances two pairs of resonances occur for ν_+ and ν_- (cf. [9, 13]); while in the case of 1,2,5-oxadiazole (**5**a) the lower frequency line (ν_-) is split, but the upper frequency is not observably split; a similar phenomenon has been reported for N-acetylpyrazole [22]. Both the phenomena are associated with two different crystalline sites in the unit cell of the compound concerned. The absence of the fourth resonance in the case of **5**a is then associated with accidental degeneracy, i.e. the two N atoms concerned do not have identical values for e^2Qq/h and for η. Whether these sites are on the same molecule or different molecules within the unit cell is unknown, but would be open to investigation by crystallographic analysis. In the following discussion, where pairs of frequencies were observed for a ^{14}N resonance, the average value was taken for subsequent calculations.

The principal axis quadrupole coupling constants (χ_{ii}, $i = x, y, z$) were evaluated from Eq. (6) where $q = q_{zz} > q_{yy} > q_{xx}$, and $\eta > 0$. In the absence of single crystal data, the NQR experiments yield the relative magnitudes, but not the directions. In view of the high degree of agreement (see below) between the NQR, MW and calculated data, the latter in both magnitudes and directions, the NQR axes were then transposed so as to be consistent with these, and signs were chosen to yield agreement. In some instances where two coupling constants are nearly equal (e.g. **2**a), it is clear that differences between the solid state and the gas phase could lead to a reversal of two axes; this does not have any effect upon the discussion where such small differences are unimportant.

Frequencies and energies

$$\begin{aligned} \nu_+ &= 0.5 e^2 Q\,|q_{zz} - q_{yy}|/h\,, \\ \nu_- &= 0.5 e^2 Q\,|q_{zz} - q_{xx}|/h\,, \\ \nu_0 &= 0.5 e^2 Q\,|q_{yy} - q_{xx}|/h\,, \\ E_0 &= -\,0.5 e^2 Q\, q_{zz}\,, \\ E_+ &= -\,0.5 e^2 Q\, q_{yy}\,, \\ E_- &= -\,0.5 e^2 Q\, q_{xx}\,. \end{aligned} \tag{6}$$

IV. Results and Discussion

(a) *Total Energy and Basis Sets.* In all ten cases (**2**a, b—**5**a, b; **6**b; **7**b) the present calculations yield lower energies than previous work (Table 1), and the difference is large, particularly in the S-compounds. The differences between the energies with the two basis sets (sp/spd) is very small, as expected, and this enables us to ignore basis set effects in the electric field gradient and quadrupole coupling data discussed below. Thus the $3d_S$ orbitals play no real part in the bonding of these molecules, and merely add variational flexibility to the calculations. There are some small systematic trends on the observed orbital energies and populations relative to our previous work and this is noted in Appendix 2.

(b) *Calculated Molecular Quadrupole Moments.* These (Table 3) are conventionally measured at the centre of mass, and in the case of the symmetric molecules the latter must lie along the symmetry axes (Figures 1—10). Of greater interest therefore are the unsymmetrical systems (**2**a, b; **3**a, b; **6**b; **7**b). In the mono-aza compounds (**2**, **3**), the principal QM axes lie remarkably close to or parallel to the EFG axes; furthermore the QM axes are also close to the internal and external bisectors of the C–H bond directions, regarding the molecules as approximate pentagons. Thus in oxazole (**3**a) Q_{xx} lies parallel to C_2–H_2 and bisects H_5C_5–C_4H_4. In the compounds with two unsymmetrical N-atoms (**6**b, **7**b) the orientation of the QM axes is still largely related to the CH internal and external bisectors, here close to one N atom, but is rotated slightly owing presumably to the unsymmetrical siting of the other N atom. These considerations of the C–H bonds also apply to the relative magnitude of the QM components Q_{xx}, Q_{yy}; thus in the unsymmetrical molecules (**2**a, b; **3**a, b), the principal *magnitude* of the QM lies on (or near to) the longest H,H distance (e.g. Q_{yy} in thiazole **3**b). In the symmetrical molecules (**4**a, b; **5**a, b) the components Q_{xx} and Q_{yy} are numerically nearly equal (and opposite), a contrast with the unsymmetrical compounds (**2**a, b; **3**a, b). There is no experimental data available for comparison.

(c) *The Transition Frequencies.* Strictly the EFG and NQCC are the most fundamental properties of the NQR experiment, but the difficulty of observing the very weak transitions makes a discussion of frequencies profitable. The data (Table 4), with the X = NH compounds (**1**c, **2**c, **3**c) included, show a number of trends for N2 and N3 with change in molecular structure. Thus while ν_- lies in a comparatively narrow range (2.7 ± 0.4 MHz), that for ν_+ is much larger (5.29 to 2.45 MHz). There appears to be a clear trend in ν_+ with electronegativity of the pair of adjacent ring atoms; thus for neighbours O and CH $5.30 < \nu_+ < 4.24$, for neighbours N and CH $4.0 < \nu_+ < 3.5$, for neighbours N and S (**6**b only) $\nu_+ = 3.89$, for neighbours CH and S or CH and CH $3.7 < \nu_+ < 2.4$ MHz. Put in another way, in the case of isomers, the 1,2-compounds (N-2) have higher values for ν_+ or for $(\nu_+ - \nu_-)$ than the corresponding 1,3-compounds (N-3). In contrast, comparison of pairs of compounds (**2**a, b; **5**a, b) where a 5-CH group is replaced by 5-N again shows that ν_+ is more markedly affected than ν_-, but that the additional aza-group leads to a reduction in ν_+ for N-2. Whilst ν_- is little affected in pairs **2**b and **6**b or **3**b and **6**b, in both cases ν_+ is raised in the thiadiazole (**6**b) over the mono-aza compounds (**2**b, **3**b).

Systematic studies of the variation of $\nu_\pm$ with temperature in 1,3,4-oxadiazole (**4**a) have shown [7] that both NQR frequencies drop by about 0.15 MHz on changing from 77 K to room temperature. Bearing this in mind, we can then use the MW values for the NQCC to obtain corresponding gas phase NQR $\nu_\pm$. As expected there is a good correlation between the two sets (not shown), and a least squares fit over all values available for the present series yields $\nu_{\mathrm{MW}} = 0.846\,\nu_{\mathrm{NQR}} + 0.743$ MHz, with a standard deviation of 0.196 MHz. It will be noted that the intercept is responsible for the paradox that the low temperature NQR frequencies (Table 4) are numerically smaller than the "gas phase" ones, and yet the correlation slope is less than unity. From the above it seems clear that temperature effects cannot offer an explanation for these differences and that differences in N atom environment between the two phases must be responsible.

(d) *The Asymmetry Parameters.* In almost all cases the value $\eta_{\mathrm{NQR}} > \eta_{\mathrm{MW}}$, and the difference is approximately 0.15 units. The sole exception is isoxazole (**2**a) where the value is effectively unity by both methods. For both NQR and MW studies the value of η is dependent upon the electronegativity of the atoms adjacent to N (cf. frequencies above). Thus in the 1,2-series (**2**a, b; **5**a, b) η varies in the order X = O > NH > S, and for the 1,3- and 1,3,4-series (**3**a, b; **4**a, b) where there is less data the order is O > S. The NQR result for imidazole (**3**c) is anomalous and this suggests that the well-known H-bonding tendencies of these NH compounds [23] in the condensed state is partially equalising the populations; microwave data for this compound is awaited.

(e) *Comparison of the NQCC from NQR, MW and Calculations.* The summary of principal axis directions from MW and calculations is shown in Table 3, while the magnitudes from all three methods [24—34] are shown in Table 5. As noted above, the NQR directions were assigned to be consistent with MW and/or calculated data; in fact since the level of agreement between the numerical values (Table 5) is so good this assignment is likely to be correct. Only in the case of oxazole (**3**a) have earlier calculated values been given [24]; the present results are in much better agreement with the MW values, both in magnitudes and in the ordering $|\chi_R| > |\chi_\pi| > |\chi_T|$. In the following discussion values quoted will normally be the experimental ones if available, with calculated in parentheses.

IV(e)(i) *Principal Axis Directions.* Only inertial axis data has so far been reported for **2**b, **5**a and **5**b (Table 5); thus whilst χ_π is unchanged, the PA values for χ_R and χ_T are required. However, in the C_{2v} symmetry molecules, the inertial axes correspond to the symmetry axes and we have calculated the EFG and χ_{ii} in these axes as well as the PA. For 1,2,5-thiadiazole (**5**b) the earlier IA results [12] have recently been extended [27] and the calculated values are in good agreement, namely χ_{bb} -3.13 (calc. -3.42), χ_{aa} $+0.90$ ($+1.28$), χ_{cc} $+2.22$ ($+2.14$) MHz; we obtain χ_{ab} 6.25 MHz, for the unmeasured in-plane component. For 1,2,5-oxadiazole the corresponding values are χ_{aa} -0.69 (-1.40), χ_{bb} -0.46 ($+0.22$), χ_{cc} $+1.15$ ($+1.33$) MHz, with χ_{ab} -4.06 MHz (calculated); the agreement is less satisfactory and further experimental work is being considered [27].

By use of Eq. (3), the IA was converted to PA data for various angles θ_{ax} for **2**b, **5**a and **5**b. For the oxadiazole, the angle (towards O) yielding good numerical agreement with the calculated and NQR value for χ_R and χ_T is near 43°; here Eq. (3) is particularly sensitive to small changes in θ_{ax}; the calculated angle between the IA and PA systems is 50.6° for **5**a. The corresponding study for 1,2,5-thiadiazole (**5**b) yields $\theta_{ax} \simeq 25°$ (towards S) in good agreement with the calculated value (22°). The situation for isothiazole (**2**b) is more complex since a complete structure has not yet been reported, and thus the *exact* direction of the IA is unknown. Stiefvater [27] obtained evidence for angles of 12.5° and ≃16.5° between inertial axis and radial (R), and E_R and R respectively. Use of the former with Eq. (3) suggests that rotation of the MW/IA data by 31° towards S is appropriate and this also gives good agreement with the NQR-PA values and the calculated data.

We now consider the PA directions as a function of molecular structure (Figure 1, Table 3). In general the PA directions lie comparatively close to R and T, but where O, N or S is adjacent to the N-centre, the axis is rotated towards the other heteroatom by about 25, 10 and 10 degrees respectively. The agreement between the calculated values and those obtained from or estimated from MW data is generally very satisfactory with the calculated values generally about 4° low.

These systematic trends can be utilised to give reliable information for the 1,2,3- and 1,2,4-thiadiazoles (**6**b, **7**b) (Figure 1) where no experimental information is available. In the 1,2,3- case (**6**b) it seems probable that E_R for N-3 is ~15° towards N-2 and this can be regarded as a normal value. However, N-2 is subject to LP interactions on either side, and the present calculations suggest that the S_{LP} has a stronger influence than N_{LP},

Table 5. ^{14}N Nuclear Quadrupole Coupling Constants (MHz) by various methods.

Compound	Method	Coupling Constants[a]			Asymmetry Parameter	Literature[b] Reference
		χ_R	χ_T	χ_π		
Isoxazole (**2**a)	a) Calc.	−5.00	4.93	0.082	0.9674	—
	b) NQR	−5.316	5.296	0.020	0.9811	—
	c) NQR	−5.43	5.02	0.41	0.8511	6
	d) MW	−5.39	5.37	0.02	0.9925	8
Oxazole (**3**a)	a) Calc.	−4.20	2.05	2.14	0.0221	—
	b) Calc.	−4.98	3.41	1.57	0.3695	24
	c) MW	4.04	1.66	2.38	0.178	9
1,2,5-Oxadiazole (**5**a)	a) Calc.	−5.31	3.97	1.33	0.4990	—
	b) NQR	−4.656	3.492	1.164	0.5000	—
	c) MW (IA)	−0.69[c]	−0.46[c]	1.15	—	25
1,3,4-Oxadiazole (**4**a)	a) Calc.	−4.80	2.94	1.85	0.2280	—
	b) NQR	−4.404	3.142	1.262	0.4271	7
	c) MW	−4.83	3.05	1.78	0.263	11
Isothiazole (**2**b)	a) Calc. — sp	−4.58	2.95	1.63	0.2884	—
	b) Calc. — spd	−4.44	2.74	1.71	0.2327	—
	c) NQR	−4.337	2.99	1.347	0.3791	—
	d) MW (IA)[c]	−2.42[c]	1.05[c]	1.37	—	26
	e) MW	−4.38	3.01	1.37	0.3740	27
Thiazole (**3**b)	a) Calc. — sp	−4.44	1.92	2.52	0.1365	—
	b) Calc. — spd	−4.57	1.94	2.57	0.1383	—
	c) NQR	−4.187	1.617	2.571	0.227	—
	d) MW	−4.41	1.83	2.59	0.1712	10
1,3,4-Thiadiazole (**4**b)	a) Calc. — sp	−4.82	2.85	1.97	0.1818	—
	b) Calc. — spd	−4.90	2.85	2.04	0.1648	—
	c) NQR	−4.401	2.750	1.651	0.2497	—
	d) MW	−4.64	2.53	2.11	0.0905	28
1,2,5-Thiadiazole (**5**b)	a) Calc. — sp	−4.26	2.18	2.09	0.0209	
	b) Calc. — spd	−4.18	2.03	2.14	0.0209	
	c) NQR	−3.198	1.498	1.708	0.0685	
	d) MW (IA)[c]	−3.13[c]	0.90[c]	2.22	—	12
	e) MW	−4.01	1.79	2.22	0.1072	27
	N-2					
1,2,3-Thiadiazole (**6**b)	a) Calc. — sp	−4.48	3.11	1.37	0.3889	—
	b) Calc. — spd	−4.44	2.98	1.47	0.3407	—
	c) NQR	−3.95	2.243	1.714	0.1337	—
	d) NQR[d]	−4.48	3.30	1.18	0.4732	—
	e) NQR[e]	−4.660	3.121	1.540	0.3393	—
	N-3					
	a) Calc. — sp	−5.29	2.36	2.94	0.1101	—
	b) Calc. — spd	−5.38	2.40	2.98	0.1076	—
	c) NQR	−5.244	2.707	2.537	0.0323	—
	d) NQR[d]	−4.715	3.234	1.481	0.3722	—
	e) NQR[e]	−4.541	3.403	1.124	0.5019	—
1,2,4-Thiadiazole (**7**b)	N-2					
	a) Calc. — spd	−3.79	2.71	1.09	0.4274	—
	b) MW (IA)[c]	−2.36[c]	1.05[c]	1.31	—	21, 17
	N-4					
	a) Calc. — spd	−4.26	2.08	2.18	0.0235	—
	b) MW (IA)[c]	−2.94[c]	−0.08[c]	3.02	—	21, 27
Pyrrole (**1**c)	a) NQR			−2.062	0.268	29
	b) MW	1.45	1.21	−2.66	0.090	14
	N-2					
Pyrazole (**2**c)	a) NQR	−3.99	3.31	0.69	0.657	29
	b) MW	−4.48	3.69	0.79	0.647	14
	N-1					
	a) MW	2.30	0.72	−3.02	0.523	14

Table 5. (continued)

Compound	Method	Coupling Constants[a]			Asymmetry Parameter	Literature[b] Reference
		χ_R	χ_T	χ_π		
Imidazole (**3**c)	N-3					
	a) NQR	−3.27	1.43	1.85	0.129	29
	b) MW	−4.08	1.79	2.29	0.123	14
	N-1					
	a) MW	1.49	1.1	−2.59	0.151	14
Pyridine (**9**)	a) NQR	−4.584	1.384	3.199	0.396	13
	b) MW	−4.88	1.43	3.45	0.414	30
Pyridazine (**10**)	a) NQR	−5.188	2.814	2.374	0.085	31
	b) MW	−5.65	2.38	3.268	0.157	32
Pyrimidine (**11**)	a) NQR	−4.436	1.362	3.074	0.386	31
	b) MW (IA)[c]	−3.107[c]	−0.223[c]	3.330	—	33
Pyrazine (**12**)	a) NQR	−4.857	1.127	3.730	0.536	34

[a] Using the optimal value of aQ_N (see text).

[b] Present work if no reference shown.

[c] Inertial axis (IA) data for in-plane components is not directly comparable with principal axis data; hence the asymmetry parameter is omitted.

[d] Alternative NQR assignments of the frequencies as in the following: 3.8907 and 2.8358 MHz to N-2, 3.9755 and 3.1000 to N-3.

[e] Alternative NQR assignment of the frequencies as in the following: 3.8907 and 3.1000 MHz to N-2, 3.9755 and 2.8358 MHz to N-3.

with a rotation of E_R towards S by 6.7°; this is only half of the value for isothiazole (**2**b), no doubt as a result of the adjacent N-3, but is about −20° relative to that for N–N in **4**b. The calculated PA directions for N-2 and N-4 in the 1,2,4-thiadiazole (**7**b) are similar to those in isothiazole (**2**b); E_R for N-4 is almost coincident with R, while that for N-2 is probably ~ 15° towards S if the analogy with **2**b holds experimentally. Thus the interaction of N-2 with N-4 is probably very small, and this is consistent with pyrimidine (**11**) where the angle between E_R and R is estimated at ~ 3° (towards the other N), with the value of χ_R largely as in pyridine [30, 31, 33].

Table 6. NQCC fom IA data and Equation (3).

Molecule	θ_{ax}	χ_{ii}	χ_{jj}
5a	0.0	−0.69	−0.46
	40.0	−1.23	+0.09
	42.0	−1.68	+0.53
	43.0	−2.22	+1.07
	44.0	−3.87	+2.72
	44.3	−5.28	+4.13
5b	0.0	0.90	−3.13
	12.0	1.09	−3.32
	20.0	1.52	−3.75
	23.0	1.79	−4.02
	25.0	2.02	−4.25
	28.0	2.49	−4.72
2b	0.0	1.05	−2.42
	20.0	1.57	−2.95
	25.0	2.01	−3.38
	30.0	2.78	−4.16
	33.0	3.58	−4.95

The recent determination [35] of the final ring geometric parameters for pyridazine (**10**), together with the earlier NQCC data [32], yields an angle (towards the other N) of +9.7° for the E_R/R separation. This can be compared with the values for **4**a, **4**b, **6**b. In the 1,3,4-cases (**4**a, **4**b) the MW values are 16.0° (calc. 8.7°) and 12.0° (calc. 5.5°) respectively; these suggests a slightly stronger interaction between N and N in the 5-membered ring heterocycles (**4**a, b); this can probably be ascribed to the lower (pentagonal) angle between the $\mathrm{LP_N}$.

IV(e)(ii) *Variation of Magnitude in NQCC with Structure.* In agreement with the concept of a largely localised lone pair at nitrogen, the values of the χ_R do not vary markedly (−5.4 to −4.0 MHz) across the series of compounds (**1**—**7**); none-the-less the absolute value is dependent upon the electronegativity of the adjacent centres, e.g. χ_R for **2**a > **2**c > **2**b, and **5**a > **5**b; in several instances the S atom relative to CH has a χ_R lowering effect e.g. in **6**b $|\chi_{\text{N-3}}| > |\chi_{\text{N-2}}|$ and **7**b $|\chi_{\text{N-4}}| > |\chi_{\text{N-2}}|$.

Comparison of these χ_R with pyridine [30] χ_R -4.88, χ_T 1.43, χ_C 3.45 MHz shows that in general the 5-membered ring values are numerically smaller and especially so when the N-atom concerned is in the group CH—N=CH. A direct comparison of values for various saturated ring sizes [36] suggests that χ_{LP} decreased in the compounds $(CH_2)_nNH$ as n goes from 6 to 2, provided the assumption $\chi_{LP} = e^2Qq_{zz}$ applies (as is reasonable). Thus increasing ring strain and $2p_N$ orbital bonding leads to a decrease in $|\chi_{LP}|$ and this is probably one of the factors in the higher value of $|\chi_R|$ for pyridine (**9**) relative to **1**—**7**, and **10** relative to **4**a, **4**b, **6**b.

The largest variation in NQCC for the series **1**—**7** occurs in χ_T (Table 5) with the highest value for isoxazole (5.37 MHz) and lowest for the 1,3-series of azoles where the nitrogen is flanked by CH (**3**a—c, all near 1.8 MHz). Thus all of the values are larger than that for pyridine (χ_T 1.43 MHz) which has similar neighbours. Direct comparison of the adjacent diaza compounds (**4**a, **4**b, **6**b) with pyridazine (χ_T 2.38 MHz) shows that the former groups are all numerically larger and with a fairly small variation in value, thus the decrease in ring size probably raises χ_T more than non-adjacent effects.

The wider range of χ_T than χ_R or χ_π can be directly correlated with the polarity of the σ-bonds to the N atom in question; there seems little doubt that most of the polarity in these molecules lies in the σ-rather than the π-system, for example from the bond population dipoles of Ref. [17] and the discussion above. Thus χ_T lies closer to the axes of these than χ_R or χ_π, and indeed in the N–O and N–S compounds (**2**a, b; **5**a, b) χ_T lies nearly along the N–O/N–S bonds.

The variation in the π-NQCC (χ_π) is quite large (Table 5) and is subject to the nature of the adjacent atoms; the trend is in the reverse direction to that for χ_R since adjacent atoms X lead to progressively larger coupling in the order $X = O < N < S < CH$; in isoxazole (**2**a) this leads to the extreme case of effectively zero π-coupling ($\chi_\pi = 0.02$ MHz); dilution of the effect of the oxygen atom as in 1,2,5-oxadiazole (**5**a) leads to a larger value for χ_π in **5**a; both adjacent N and NH lead to similar effects on χ_π, but less than O (**4**a, **4**b, **2**c). It is of interest to compare the 2,5-diaza-compounds (**5**a, b) with pyrazine (**12**) since in the 5-membered rings the N/N interaction through-space will be similar to **11**, while alternative through-bond routes involving 2 or 3 bonds are available. In both of **5**a, b, χ_π is markedly less than in pyrazine (χ_π 3.73 MHz, NQR value) which is particularly high in comparison with the other azines (**9**—**11**). Finally, it is interesting to note that all of the χ_π are positive in **1**—**7**, **9**—**12** and this contrasts with χ_π for the 1-position in the NH series (**1**c, **2**c, **3**c).

V. Conclusions

There is generally good agreement between the NQR, MW and *ab initio* values for the nuclear quadrupole coupling constants in both magnitude and direction; this allows the theoretical method to be used to predict values for compounds where either the NQR data is open to more than one assignment (e.g. 1,2,3-thiadiazole) or where the MW data does not readily yield values for the NQCC. In the case of nitrogen with an adjacent lone pair, the PA of the lone pair (χ_R) type is rotated towards the heteroatom in all cases, and this is expected to be true of all molecules. In the case of 1,2,3-thiadiazole where N-2 is flanked by S and N lone pairs, the former is the more dominant in its effect upon the EFG.

Appendix 1

Gaussian Basis for Sulphur

Contraction Coefficient	Exponent
s-Functions	
	1
0.0003	94181.1
0.0024	13921.8
0.01235	3168.04
0.04909	901.843
0.15099	296.954
	2
1.0	108.669
	3
0.40836	43.1579
0.18573	18.1168
	4
1.0	5.57096
	5
1.0	2.14387
	6
1.0	0.434389
	7
1.0	0.157093

Contraction Coefficient	Exponent
p-Functions	
	1
0.00313	494.274
0.02423	116.981
0.10600	37.496
0.28302	13.8938
0.43808	5.50267
0.31509	2.24291
	2
1.0	0.773628
	3
1.0	0.291781
	4
1.0	0.102867
d-Function	
	1
1.0	0.541

Appendix 2

Orbital Energies

We recently assigned [3] the photoelectron spectra of the present series of molecules (2—7), and it is clearly of interest to see whether any reassignments are indicated from the present results. Inspection of the wave-functions shows that the strict listing order of the orbital energies is correct between the earlier minimal basis and the present largest basis in 60 out of 69 IP's assigned, and in a further 4 the new order is irrelevant because more than one M.O. was assigned to an individual observed IP; thus only 5 re-assignments are to be considered. Nonetheless there are systematic differences in the orbital energies between the two basis sets; thus in the oxygen compounds the σ-levels are slightly stabilised (higher binding energy) in the DZ calculations, while the π-levels (in O and S compounds) are significantly destabilised (ca. 0.5 eV). These differences lead to a systematic shift of the inner-most π-level ($1b_1$ in the symmetric compounds), such that it is now at lower binding energy than another one of the σ-levels; however, these do not lead to frequent reassignments for the reasons given above. Also, the spectra were assigned by consideration of variations in structure versus IP as well as the Koopmans' theorem (KT) ordering, and thus we do not feel that the KT order should be strictly adhered to. For example the present calculations suggest IP space $\pi < \pi < LP_N$ for oxazole, whilst other considerations such as cross-section and comparison with other O/N heterocycles (as well as the MB calculations) all indicate $\pi < LP_N < \pi$ which we consider correct.

Atomic Populations

Comparison of the present largest basis set with our earlier largest basis set data [6] shows very high agreement in most molecules at most centres. There are trends, however, and in some where the effects are additive, there can be shifts of up to 0.2 e in extreme cases. Thus H is always more positive in the DZ than the MB cases, while (parallel) nitrogen is less negative, and C more negative respectively. Thus the C–H dipole is significantly larger in the DZ cases. The charge on oxygen is virtually unchanged between the two bases, while the effect on S is very variable. Owing to these, the net charge on the atoms changes in six atoms out of the total (S/O/N/C) of 40; in all these 6 cases a "positive" carbon (MB) becomes negative (DZ), and in each case there is at least one adjacent N atom, so that the effect is a result of increase in the $C^{\delta-}$–$H^{\delta+}$ dipole and reduction in the $C^{\delta+}$–$N^{\delta-}$ dipole.

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